7th International Conference on *f* Elements

7 IC*f*E

incorporating

XXII. Tage der Seltenen Erden
Terrae Rarae 2009

Cologne, Germany

August 23-27, 2009

Programme and Abstracts

Gerd Meyer, Ingo Pantenburg (editors)

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Gerd Meyer, Ingo Pantenburg (Hrsg.),
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7 ICfE 2009
Cologne

7th International Conference on f Elements

August 23-27, 2009
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Dear Conference Participants:

After Leuven, Helsinki, Paris, Madrid, Geneva, and Wroclaw, the International Conference on f Elements (ICfE) has now arrived in the Rhine River valley, at Cologne to be precise. ICfE is one of the three major Conferences on f element science now held successively in the United States (Rare Earth Research Conference), Australasia and Europe. The University of Cologne is proud and pleased to host ICfE 7. The XXII. Tage der Seltenen Erden, a primarily Germany-centered Conference, is incorporated in ICfE 7.

You, the participants of the Conference, have helped with your contributions and advise to put together an exciting program covering all areas of rare-earth and actinide chemistry and physics, some more than others. We, the organizers, mostly Ingo Pantenburg and Ingrid Müller and a sizeable number of graduate students and other helping hands and, alas, myself, are grateful for your help and advise and we hope that we can meet your expectations of a Conference that is devoted primarily to science, but also to a memorable number of side effects, meeting people and having fun.

We have also tried to keep the Conference both broad in science and lean in expenses, in times where sponsoring is almost non-existing. Nevertheless, we are grateful to the University of Cologne for making this event possible on campus, to the Fonds der Chemischen Industrie (Frankfurt am Main) and the companies MBraun (Garching) and Stoe (Darmstadt) for providing funds. We have organized this Conference with the aid of the Gesellschaft Deutscher Chemiker (GDCh) and under the auspices of the European Rare Earth and Actinide Society (ERES).

Thank you all for coming and participating actively in ICfE 7 at Cologne, Germany.

Gerd Meyer

CONFERENCE CONTRIBUTIONS

Plenary Sessions

PS Plenary Speakers

Oral Presentations

O01 Organometallics
O02 Organometallics
O03 Spectroscopy
O04 Spectroscopy
O05 Lanthanide Biological Chemistry
O06 Lanthanide Biological Chemistry
O07 Solid State Chemistry and Theory
O08 Actinides
O09 Solid State Physics
O10 Materials
O11 Materials and Spectroscopy
O12 Materials

Poster Contributions

P01 Actinides
P02 Organometallics
P03 Theory
P04 Materials and Applications
P05 Spectroscopy
P06 Coordination Chemistry
P07 Solid State Chemistry and Physics
P08 Lanthanide Biological Chemistry

SCIENTIFIC PROGRAMME

ORAL PRESENTATIONS

Sunday, 08/23			
14:00		Begin Registration	
16:00		Opening Ceremony	**Kurt Alder-Hörsaal**
Plenary Session 1			**Kurt Alder-Hörsaal**
Chair: Gerd Meyer			
16:30 – 17:15	William J. Evans	PS01	The Utility of the f Elements in Isolating New Types of Radicals and Metalated Cyclopentadienyl Ligands
17:15 – 18:00	Hans U. Güdel	PS02	Chemistry and physics of new lanthanide upconversion materials and processes
18:00 – 20:30		Opening Reception	

Monday, 08/24			
Plenary Session 2			**Kurt Alder-Hörsaal**
Chair: Anja-Verena Mudring			
9:00 – 9:40	Michael F. Reid	PS03	Spectroscopy of High-Energy States – Where to From Here?
9:40 – 10:20	Rhett Kempe	PS04	Rare Earth Transition Metal Bonding
Plenary Session 3			**Kurt Alder-Hörsaal**
Chair: Peter W. Roesky			
14:00 – 14:40	Peter C. Junk	PS05	Metal-Organic Rare Earth Chemistry Continues to Excite
14:40 – 15:20	Reiner Anwander	PS06	Synthesis and reactivity of homoleptic rare-earth metal methyl complexes

Monday, 08/24

Parallel Session O1	Organometallics		**Hörsaal II**
Chair: Rhett Kempe			
10:30 – 11:00	Peter W. Roesky	O01-1	Low Valent Main Group Compounds as Ligands in Lanthanide Chemistry
11:00 – 11:20	Kuburat O. Saliu	O01-2	Synthesis, Characterization and Structural Variation of Scorpionate Supported Lanthanide bis-Alkynide Complexes, "$(Tp^{R,R`})Ln(C{\equiv}CR``)_2$"
11:20 – 11:40	Jun Okuda	O01-3	Molecular Alkyl and Hydride Complexes of the Lanthanides
11:40 – 12:00	Norbert W. Mitzel	O01-4	Cyclic (poly)aminals as neutral or ionic ligands in rare-earth metal chemistry
12:00 – 12:20	H. Martin Dietrich	O01-5	Controlling alkyl/halo and amido/halo ligand combinations in organolanthanide complexes
Lunch Break			

Parallel Session O2	Organometallics		**Hörsaal II**
Chair: Peter W. Roesky			
15:30 – 16:00	Glen B. Deacon	O02-1	Lanthanoid Containing Bimetallics Prepared from the Elements
16:00 – 16:20	Kornelia Zeckert	O02-2	Lanthanide chemistry with dual functional ligand systems containing low valent Group 14 elements
16:20 – 16:40	Elise Abinet	O02-3	Highly Active Hydrosilylation Catalysts Based on Early Rare-Earth Metals Complexes
16:40 – 17:00	Christian Döring	O02-4	Aminopyridinato Ligand Stabilized Lanthanide Alkyl Complexes and Their Use in Polymerization of Ethylene and Isoprene
17:00 – 17:20	Matthias Tamm	O02-5	Imidazolin-2-iminato Complexes of Rare Earth Metals with Very Short Metal-Nitrogen Bonds – Experimental and Theoretical Studies
17:20 – 17:50	Sjoerd Harder	O02-6	Lanthanide Chemistry with Unusual Ligands
19:00 – 21:00			**Poster Session**

Monday, 08/24

Parallel Session O3	Spectroscopy		**Hörsaal III**
Chair: Hans-U. Güdel			
10:30 – 11:00	Anne-Sophie Chauvin	O03-1	Efficiency of ligands fitted with phosphoester or phosphonate *vs* carboxylate groups in the sensitization of lanthanide-centred luminescence
11:00 – 11:20	Nail M. Shavaleev	O03-2	Highly Luminescent Europium Complexes
11:20 – 11:40	Lada Puntus	O03-3	Can weak noncovalent interactions affect the energy transfer processes in lanthanide compounds with heterocyclic diimines?
11:40 – 12:00	Stefan Lis	O03-4	Chemiluminescence and Electrochemiluminescence of fluorochinolone systems containing Tb(III) ions
12:00 – 12:20	Markus Albrecht	O03-5	Approaches towards f-d and f-p heterodinuclear helicates
Lunch Break			

Parallel Session O4	Spectroscopy		**Hörsaal III**
Chair: Michael F. Reid			
15:30 – 16:00	Kohei Soga	O04-1	Application of f-Element Photonic Materials for NIR Biophotonics
16:00 – 16:20	Philippe Goldner	O04-2	A Highly Spin Concentrated Solid for Quantum Memories
16:20 – 16:40	Claudia Wickleder	O04-3	Luminescence of Dy^{2+} and Nd^{2+} Ions
16:40 – 17:00	Yehoshua Kalisky	O04-4	The Role of Spectroscopic Properties and Physical Processes in Solid State Lasers Based on f-Element ions
17:00 – 17:20	A. G. Macedo	O04-5	Luminescence and magnetic features from nanosized europium doped gadolinium oxide
17:20 – 17:50	Henning A. Höppe	O04-6	Surprising Luminescent Properties of the Polyphosphates $Ln(PO_3)_3$:Eu (Ln = Y, Gd, Lu)
19:00 – 21:00			**Poster Session**

Tuesday, 08/25			
Plenary Session 4			**Kurt Alder-Hörsaal**
Chair: Lester R. Morss			
14:00 – 14:40	Sergey V. Krivovichev	PS07	Actinyl compounds with VIth-group elements: the world of amazing structural diversity and complexity
14:40 – 15:20	Thomas Schleid	PS08	Geo-Inspired Phosphors Based on Rare-Earth Metal(III) Fluorides with Complex Oxoanions

Tuesday, 08/25			
Parallel Session O5	Lanthanide Biological Chemistry		**Hörsaal II**
Chair: Jean-Claude G. Bünzli			
9:00 – 9:30	Harri Härmä	O05-1	Solid-phase nonspecific binding sensors
9:30 – 9:50	Clémence Allain	O05-2	Changing the local coordination environment in mono- and bi-metallic lanthanide complexes through “click” chemistry
9:50 – 10:10	Stéphane Petoud	O05-3	Luminescent Lanthanide Dendrimer Complexes for Biologic Imaging in vivo
10:10 – 10:30	Vanesa Fernández-Moreira	O05-4	Bioconjugation of Luminescent Lanthanide Helicates and its Applications.
10:30 – 10:50	Loic Charbonnière	O05-5	A polyvalent approach to luminescent lanthanide biomarkers
Coffee Break			
11:20 – 11:40	David Parker	O05-6	Emissive Lanthanide Complexes: In Vitro and In Cellulo Applications
Flash presentation of selected posters			
11:40 – 11:45	Ilkka Hemmilä	P08-01-193	Europium-based assays to monitor GPCR activation
11:45 – 11:50	Geert Dehaen	P08-03-177	Self-assembled heteropolymetallic complexes as MRI contrast agents
Lunch Break			

Parallel Session O6	Lanthanide Biological Chemistry		**Hörsaal II**
Chair: David Parker			
15:30 – 15:50	Peter Caravan	O06-1	Design and in vivo application of multimodal imaging probes
15:50 – 16:10	Steve Comby	O06-2	Sensing of Biologically Important Molecules using Functional Lanthanide Luminescent Gold Nanoparticles
16:10 – 16:30	Goran Angelovski	O06-3	Unusual Calcium Sensitivity of Aminobis(methylenephosphonate)-Containing MRI Contrast Agents
16:30 – 16:50	Graeme Stasiuk	O06-4	Incorporation of 'Click' Chemistry into Lanthanide Chelates
Coffee Break			
17:10 – 17:30	Josef Hamacek	O06-5	Self-Assembly of Polynuclear Arrays for Sensing Purposes
17:30 – 17:50	Sara Figueiredo	O06-6	Paramagnetic liposomes as Enzyme-responsive Relaxometric agents
Flash presentation of selected posters			
17:50 – 17:55	Badr El Aroussi	P08-04-093	Insights into The Self-Assembly of a New Family of Dissymmetric Tripodal Ligands with Lanthanides
17:55 – 18:00	Elena De Luca	P08-05-047	Fluorinated Responsive Lanthanide Complexes for 19-F MRS/MRI
19:00 – 21:00			**Poster Session**

Tuesday, 08/25

Parallel Session O7	Solid State Chemistry and Theory		**Hörsaal III**
Chair: Sanjay Mathur			
10:30 – 11:00	Frank R. Wagner	O07-1	Position-Space Analysis of *TM*–*RE* Bonding Situations in Simple Molecules and Complex Solids
11:00 – 11:20	Nicolay A. Kulagin	O07-2	Electronic Structure of Clusters with RE or AC-Ions and Collaps of nf – Shell
11:20 – 11:40	Konstantin A. Lyssenko	O07-3	Chemical bonding pattern in lanthanide-containing systems via topological analysis of experimental charge density function
11:40 – 12:00	Ingo Hartenbach	O07-4	Rare-Earth Metal(III) Chloride *Ortho*-Oxomolybdates(VI): One Formula *RE*Cl[MoO_4] (*RE* = Y, La – Nd, Sm – Lu), but Four Structure Types
12:00 – 12:20	Holger Kohlmann	O07-5	Crystal structures and properties of europium and samarium hydrides
Lunch Break			

Parallel Session O8	Actinides		**Hörsaal III**
Chair: Peter C. Junk			
15:30 – 16:00	Daniel B. Rego	O08-1	New Routes to Actinide Nitrides *via* Low Temperature Syntheses
16:00 – 16:20	Gregory Nocton	O08-2	Coordination Chemistry of Pentavalent Uranyl: Structure and Magnetism
16:20 – 16:40	Pascale Delangle	O08-3	Impact of the softness of the heterocyclic N-donors Pyridine and Pyrazine on the selectivity for Am(III) over Eu(III)
16:40 – 17:00	G. Meinrath	O08-4	Direct Speciation of Uranyl(VI) Interaction with Carboxylic Acid N-oxides in Solution and Solid State
17:00 – 17:30	Michael Dolg	O08-5	Efficient quantum chemical valence-only treatments of actinide systems
19:00 – 21:00			**Poster Session**

Wednesday, 08/26			
Plenary Session 5			**Kurt Alder-Hörsaal**
Chair: Karl A. Gschneidner, Jr.			
9:00 – 9:40	Walter Temmermann	PS09	Electronic and Magnetic Phase Diagrams of the Rare Earths
9:40 – 10:20	John D. Corbett	PS10	Condensed Polymetal Salts That are Unique to the Rare-Earth Elements

Wednesday, 08/26			
Parallel Session O9	Solid State Physics		**Hörsaal II**
Chair: Walter Temmermann			
10:30 – 11:00	V. K. Pecharsky	O09-1	Controlling physics using precise chemical and microstructural tools
11:00 – 11:20	Karl A. Gschneidner, Jr.	O09-2	The Unprecedented Magnetic Behavior of GdNi
11:20 – 11:40	Hellmut Eckert	O09-3	High-resolution ^{45}Sc NMR Spectroscopy: A New Technique for the Structural Characterization of Intermetallic Compounds
11:40 – 12:00	Regino Sáez-Puche	O09-4	Pressure effects on the structural and magnetic properties of the $RCrO_4$ oxides (R= rare earths)
13:00			**Departure to Boat Ride**

Wednesday, 08/26			
Parallel Session O10	Materials I		**Hörsaal III**
Chair: Jorma Hölsä			
10:30 – 11:00	Luis Humberto da Cunha Andrade	O10-1	Combination of Ce^{3+}-doped glass phosphor and blue/UV LED for color balance to generate smart white light
11:00 – 11:20	Melissa A. Harrison	O10-2	Synthesis and Room Temperature Ultraviolet Luminescence in EuS Nanotubes
11:20 – 11:40	N. Kuzmina	O10-3	Lanthanide carboxylates as precursors of oxide thin film materials
11:40 – 12:00	A. Braud	O10-4	Down-conversion in rare-earth nano-clusters for silicon solar cell efficienty enhancement
12:00 – 12:20	Clemens K. Weiss	O10-5	Lanthanide-polymer hybrid nanoparticles prepared in miniemulsion – from nanoonions to luminescing films
13:00			**Departure to Boat Ride**

Thursday, 08/27			
Plenary Session 6			**Kurt Alder-Hörsaal**
Chair: Frank T. Edelmann			
9:00 – 9:40	Sanjay Mathur	PS11	Chemical Approaches to Functional Nanostructures: Growth, Applications and Devices
9:40 – 10:20	Robin D. Rogers	PS12	Aspects of the Application of Ionic Liquids in the Separations of f-Elements: Coordination and Solvation
Plenary Session 7			**Kurt Alder-Hörsaal**
Chair: Thomas Schleid			
14:00 – 14:40	Claude Piguet	PS13	A Short Trip Trough Lanthanide Self-Assemblies
14:40 – 15:20	Frank T. Edelmann	PS14	Organolanthanide Chemistry in Three Oxidation States: 20 Years of Fascination
15:20			**Closing Ceremony**

Thursday, 08/27			
Parallel Session O11	Materials and Spectroscopy		**Hörsaal II**
Chair: Nicolay A. Kulagin			
10:30 – 11:00	Jorma Hölsä	O11-1	Synchrotron Radiation Studies of Rare Earth Persistent Luminescence Materials
11:00 – 11:20	Petra Becker	O11-2	Non-centrosymmetric ammonium rare-earth nitrates $(NH_4)_2RE(NO_3)_5 \cdot 4\ H_2O$: Crystal growth and optical properties
11:20 – 11:40	M. Chavoutier	O11-3	Yb-LGOB single crystal, a new promising laser material
11:40 – 12:00	Andrea Simone Stucchi de Camargo	O11-4	Structural and Optical Characterization of Rare-Earth Doped Yttrium Aluminoborate Laser Glasses and Glass Ceramics
12:00 – 12:20	N. Rajmuhon Singh	O11-5	Synthesis and optical characterization of re-dispersible Tb^{3+}– doped $GdPO_4$ crystalline nanoparticles
Lunch Break			

Thursday, 08/27			
Parallel Session O12	Materials II		**Hörsaal III**
Chair: Glen B. Deacon			
10:30 – 11:00	Peter Nockemann	O12-1	Lanthanide and Actinide Chemistry in Ionic Liquids
11:00 – 11:20	Anna Mondry	O12-2	Crystal Structures and Photophysical Properties of Ln(III) Complexes with Ethylenediaminetetrakis(methylen ephosphonic acid) H8EDTMP
11:20 – 11:40	Ulrich Kynast	O12-3	Rare Earth Activated Nano Clays: Particles With Multifunctional Properties
11:40 – 12:00	Eva Hemmer	O12-4	Cytotoxicity of $Gd_2O_3:Ln^{3+}$ Nanostructures and their Potential as Biomarkers
12:00 – 12:20	Anja-Verena Mudring	O12-5	Luminescent lanthanide nanoparticles via metal vapour synthesis in ionic liquids
Lunch Break			

POSTER CONTRIBUTIONS

P01-01-090	Vladislav V. Gurzhiy, Sergey V. Krivovichev, Ivan G. Tananaev	Crown-ether-templated uranyl selenates: principles of structure formation
P01-02-068	Oleg I. Siidra, Sergey V. Krivovichev, Wulf Depmeier	Influence of the alkaline cations on the crystal structure of new uranyl molybdates $CsNa_3[(UO_2)_4O_4(Mo_2O_8)]$ and $Cs_2Na_8[(UO_2)_8O_8(Mo_5O_{20})]$
P02-01-159	T. Bauer, C. Döring, W. P. Kretschmer, B. Hessen, R. Kempe	Highly efficient NCN-ligand stabilized organolanthanide catalysts for the coordinative chain transfer ethylene polymerization
P02-02-144	Benjamin J. Hellmann, Norbert W. Mitzel	Interaction of Hydroxylaminato Rare-Earth Metal Complexes with $AlMe_3$, $GaMe_3$ and $InMe_3$
P02-03-143	Benjamin J. Hellmann, Norbert W. Mitzel	Hemilabile Hydroxylaminato Complexes of Rare-Earth Metals
P02-04-139	Daniel Bojer, Ajay Venugopal, Ina Kamps, Norbert W. Mitzel	C-H activation in Rare-Earth Metal Tetramethylaluminates Induced by a Neutral Ligand
P02-05-138	Noa K. Hangaly, Alexander R. Petrov, Michael Elfferding, Jörg Sundermeyer	Cyclopentadienylphosphazene Constrained Geometry Complexes of Rare-Earth Metals and their application in Hydroamination Reactions
P02-06-137	Nina S. Hillesheim, Michael Elfferding, Jörg Sundermeyer	New Cyclopentadienyl-*N*-silylphosphazene and Cyclopentadienyliden-phosphorane complexes of Rare-Earth Metals
P02-07-136	Oliver Thomas, Alexander R. Petrov, Thomas Linder, Jörg Sundermeyer	Homoleptic *Tris*-Aryl Complexes of the Rare Earth Metals
P02-08-135	Christoph Schädle, Christian Meermann, Karl W. Törnroos, Reiner Anwander	Rare-earth metal complexes bearing bulky phenyl(trimethylsilyl)amide ligands
P02-09-071	Glen B. Deacon, Peter C. Junk, Josh P. Townley	Synthesis and structures of some pseudo-lanthanoid(II) aryloxides by retralex reactions with alkaline earth metals, and the effect of solvent variation
P02-10-070	Glen B. Deacon, Peter C. Junk, Josh P. Townley	Low coordinate lanthanoid aryloxides by retralex reactions

P02-11-067	Daisy P. Pathmarajan, Glen B. Deacon, Craig M. Forsyth, Florian Jaroschik, Peter C. Junk	Synthesis and characterisation of bis(diphenylphosphinocyclopentadienyl)- rare earth and -alkaline earth mono- and bi- metallic complexes
P02-12-065	Alexandra Trambitas, Tarun K. Panda, Matthias Tamm	Rare Earth Metal Alkyl Complexes Supported by Imidazolin-2-Iminato Ligands: Synthesis, Structural Characterisation and Catalytic Application
P02-13-055	Sven Range, Jan Spielmann, Dirk F.-J. Piesik, Sjoerd Harder	Investigations of a Novel Bora-Amidinate Ligand in Lanthanide Chemistry
P02-14-053	David P. Mills, Ashley J. Wooles, Oliver J. Cooper, Stephen T. Liddle	Synthesis and Reactivity of Phosphorus-Stabilised Lanthanide Carbene Complexes
P03-01-173	Andrzej Kedziorski, Lidia Smentek	Theoretical description of the energy transfer in the lanthanide materials
P03-02-130	Viktor Bezugly, Frank R. Wagner	Quantum Mechanical *TM–RE* Bonding Analysis in Position Space: Methodology and Application
P03-03-107	Rafał Janicki, Mirosław Karbowiak, Anna Mondry	Crystal Field Analysis of Nd^{3+} Electronic Levels in $[Nd_4(EDTMP)_4]$ Anion
P03-04-100	Jorma Hölsä, Taneli Laamanen, Mika Lastusaari, Pavel Novák	Structure Optimization and Electronic Structure of the $SrAl_2O_4:Eu^{2+}$ Persistent Luminescence Material by DFT Calculations
P03-05-306	J. Wiebke, A. Weigand, M. Glorius, M. Dolg	Modeling Biological U(VI) Coordination from First Principles
P03-06-307	M. Hülsen, M. Dolg, U. Ruschewitz	Investigation of Electronic Structure and Properties of Solid EuC_2 and YbC_2
P03-07-309	Xiaoyan Cao, Michael Dolg	A MCDHF/DCB-Adjusted Energy-Consistent Pseudopotential for U and its Application to U^{4+}, U^{5+} and UH
P04-01-185	M. Rico, F. Esteban-Betegón, C. Cascales	Hydrothermal synthesis and 2.04 μm emission of Ho^{3+}-doped $NaGd(WO_4)_2$
P04-02-180	J. Sokolnicki, M. Bettinelli, M. Daldosso, J. Legendziewicz	VUV, UV and Vis Spectroscopic Behaviour of $Lu_2O_3:Pr^{3+}/Pr^{4+}$ Nanosize Phosphors

P04-03-148	L. A. Nurtdinova, Y. Guyot, S. L. Korableva, A. S. Nizamutdinov, V. V. Semashko, M.-F. Joubert	Photoionisation investigation in Ce^{3+} doped $LiY_{1-x}Lu_xF_4$ laser crystals
P04-04-147	Lucyna Macalik, Paweł Tomaszewski, Aleksandra Matraszek, Irena Szczygieł, Radosław Lisiecki, Jerzy Hanuza	Size effect on the phase transitions, structure and optical characterization of pure and Pr^{3+} doped $CePO_4$ nanocrystals
P04-05-141	Tomasz Grzyb, Mariusz Weclawiak, Stefan Lis	Synthesis and photophysical properties of nanomaterials based on lanthanides oxyfluorides
P04-06-132	F. Pedrochi, A. Steimacher, M. J. Barboza, A. N. Medina, M. L. Baesso, L. H. C. Andrade, Y. Guyot, G. Boulon	The temperature effect of Ce^{3+} doped CAS and LSCAS glasses luminescence
P04-07-126	Iko Hyppänen, Jorma Hölsä, Jouko Kankare, Mika Lastusaari, Laura Pihlgren, Tero Soukka	Preparation and Up-Conversion Luminescence Properties of $NaYF_4:Yb^{3+},Er^{3+}$ Nanomaterials
P04-08-122	Chantal Lorbeer, Joanna Cybinska, Anja-Verena Mudring	Rhombic YbF_3 and $GdF_3:Yb^{3+}$ nanoparticles synthesized in ionic liquids
P04-09-120	Nina von Prondzinski, Anja-Verena Mudring	Luminescent lanthanide nanoparticles via metal vapour synthesis in ionic liquids
P04-10-119	Mei Kappels, Anja-Verena Mudring	Lanthanide-containing Ionic Liquid Crystals
P04-11-110	Thomas B. Jensen, Emmanuel Terazzi, Bertrand Donnio, Daniel Guillon, Claude Piguet	Toward Rationally Designed Lanthanidomesogens
P04-12-085	Bruna Ganzeli Mantovani, Luis Humberto da Cunha Andrade, Sandro Marcio Lima	Broad and intense near infrared luminescence induced by structural changes in Pr^{3+}:Tellurite glasses
P04-13-076	F. Esteban-Betegón, C. Zaldo, C. Cascales	Control of the morphology in hydrothermal synthesis processes and emission near 2 μm of Tm^{3+}- doped Lu_2O_3 nanostructures

P04-14-074	Yvonne Kohl, Eva Hemmer, Kohei Soga, Sanjay Mathur, Hagen Thielecke	Biocompatibility of Eu^{3+}-doped Gadolinium Hydroxide and Oxide Nanorods
P04-15-069	Gaylord Tallec, Daniel Imbert, Marinella Mazzanti, Pascal H. Fries	Lanthanide complexes of tripodal ligands derived from hydroxoyquinolinate with potential application in magnetic resonance imaging
P04-16-044	Amir Zaim, Homayoun Nozary, Claude Piguet	Synthesis and Characterization of Novel Tridentate Receptors for the Preparation of Luminescent Lanthanide-Containing Materials
P04-17-028	Christoph Hauser, Clemens K. Weiss, Jeannine Heller, Dariush Hinderberger, Katharina Landfester	Lanthanide-polymer hybrid nanoparticles prepared by the miniemulsion technique - Design, characterization and application
P04-18-019	L. Moriggi, C. Cannizzo, A. Ulianov, E. Dumas, C. R. Mayer, L. Helm	Gold Nanoparticles Functionalized with Gadolinium Chelates as High Relaxivity MRI Contrast Agents
P04-19-115	Daniel Imbert, Marinella Mazzanti, Olivier Raccurt, Peter Cherns	Lanthanide complexes encapsulated in silica nanoparticles
P04-20-163	Thiago B. de Queiroz, Daniel Mohr, Hellmut Eckert, Andrea S. S. de Camargo	Structural and spectroscopy characterization of rare-earth ion doped PLZT ferroelectric ceramics
P04-21-063	Georgii Malashkevich, Galina Semkova, Tatiana Khottchenkova, Vladimir Sigaev	Optical Materials on the Basis of the CeO_2:Ln Nanoparticles
P04-22-223	Yee Hwa Sehlleier, Lisong Xiao, Sanjay Mathur	Lanthanide Containing Nanostructures: Microwave-assisted Synthesis
P04-23-189	Masakuni Ozawa, Yoshitoyo Nishio	Formation and microstructure of thermal stable La-containing complex oxide nanoparticles in catalytic alumina support
P04-24-190	Masakuni Ozawa	Development of environmental conscious ceramics using some rare earth doped compouds
P04-25-191	Masakuni Ozawa, Yukari Kaneko	Surface Modification and Oxygen Storage Capacity of CeO_2-containing Nanoparticlate Composite Prepared by Precipitaion Process

P04-26-192	Masakuni Ozawa, Tetsu Kuwahara	Internal friction and oxygen relaxation of some rare earth doped zirconia ceramics
P05-01-188	Elżbieta Tomaszewicz, Małgorzata Guzik, Joanna Cybińska, Janina Legendziewicz	Spectroscopic proprieties of new class tungstates; the role of co-doping d-electron ions
P05-02-187	M. Guzik, J. Cybińska, J. Legendziewicz	The photoluminescence properties of Eu^{3+} and Gd^{3+}- doped sodium doubles phosphates under VUV/UV excitation
P05-03-186	Joanna Cybinska, Gerd Meyer, Janina Legendziewicz	A spectroscopic study of potassium lanthanide ternary chlorides doped by Pr^{3+} and Yb^{3+} ions
P05-04-179	Paula Gawryszewska, Olesia V. Moroz, Victor A. Trush, Dagmara Kulesza, Vladimir M. Amirkhanov	Sensitised near-infrared luminescence of Ln(III) complexes
P05-05-176	Paula Gawryszewska, Olesia V. Moroz, Vladimir M. Amirkhanov	Effective LMCT of Eu(III) and Tb(III) complexes with sulfonylamide derivatives
P05-06-157	M. Guzik, B. Moine, L. Martinez	Thermosensible photoluminescent coating with Cr^{3+} and Eu^{3+} dopand ions
P05-07-152	Jerzy Sokolnicki	Influence of Ce^{3+} to Tb^{3+} energy transfer on Tb^{3+} emission in nanocrystalline Lu_2SiO_5 and $Lu_2Si_2O_7$ host lattices
P05-08-142	Flavie Lavoie-Cardinal, Matthias Adlung, Jennifer Kramer, Christoph Hennig, Claudia Wickleder	Photoluminescence Properties of Eu^{2+} doped in $CsMgCl_3$ and $CsCaCl_3$
P05-09-123	D. Kasprowicz, M. G. Brik, A. Majchrowski, E. Michalski, A. Lapinski	Spectroscopy of $KGd(WO_4)_2$ single crystals doped with Eu^{3+} and Ho^{3+} ions
P05-10-121	Sifu Tang, Anja-Verena Mudring	A Sweet Luminescent Ionic Liquid
P05-11-114	Matthias Adlung, Claudia Wickleder	Photoluminescence of Tm^{2+} Ions in Several Chloride Host Lattices
P05-12-111	Jorma Hölsä, Högne Jungner, Mika Lastusaari, Marja Malkamäki, Janne Niittykoski	Effect of Grinding on the Persistent Luminescence of $SrAl_2O_4:Eu^{2+},Dy^{3+}$
P05-13-083	KimNgan T. Hua, Jamie L. Lunkley, Gilles Muller	Importance of Using Circularly Polarized Luminescence Spectroscopy for the Chiroptical Characterization of Lanthanide(III) Complexes

P05-14-073	Konstantin Zhuravlev, Vera Tsaryuk, Valentina Kudryashova, Irina Pekareva, Jerzy Sokolnicki	Excitation energy transfer in europium 1- and 2- naphthylcarboxylates
P05-15-072	Gülay Bozoklu, Claire Marchal, Daniel Imbert, Marinella Mazzanti	NIR emitting hydroxyquinoline-based complexes
P05-16-066	Valter Kiisk, Triin Kangur, Tanel Tätte, Ilmo Sildos	Spectroscopic properties of europium-doped $Ti_xSn_{1-x}O_2$
P05-17-064	L. Nodari, F. Piccinelli, M. Giarola, G. Mariotto, S. Polizzi, M. Bettinelli, A. Speghini	Single crystal and nanocrystalline Pr^{3+} doped lutetium phosphate: a comparative analysis of the *f-f* luminescence properties
P05-18-061	A. Kamińska, A. Dużyńska, A. Suchocki, M. Bettinelli	High-pressure luminescence studies of f-f radiative transitions of Yb^{3+} ions in $GdPO_4$
P05-19-060	A. Kamińska, A. Dużyńska, A. Suchocki, M. Bettinelli	High-pressure spectroscopy of ytterbium doped YPO_4
P05-20-054	Peter A. Tanner, Chang-Kui Duan, Vladimir N. Makhov, Marco Kirm, Nicolas M. Khaidukov	Vacuum ultraviolet excitation spectra of lanthanide doped hexafluoroelpasolites
P05-21-052	Wang Jiwei, Peter A. Tanner	Valence transformation upconversion for oxides in vacuum
P05-22-046	Daniela Imperio, David Parker, Giovanni Battista Giovenzana	Luminescent Ln(III) complexes based on alternative ligands
P05-23-041	Vera Tsaryuk, Konstantin Zhuravlev, Konstantin Lyssenko, Anna Vologzhanina, Valentina Kudryashova, Vladislav Zolin	Structural regularities and luminescence properties of dimeric europium and terbium carboxylates with 1,10-phenanthroline (C.N. = 9)
P05-24-034	Julien Andres, Anne-Sophie Chauvin	Diethoxy, monoethoxy and dihydroxy 6-phosphoryl picolinic acid as luminescent lanthanide sensitizers

P05-25-033	S. Pagano, G. Montana, C. Wickleder, W. Schnick	Urea Route to Homoleptic Cyanates - Characterization and Luminescence Properties of $[M(OCN)_2(urea)]$ and $M(OCN)_2$ with M = Sr, Eu
P05-26-023	Prodipta Pal, Hans Hagemann	Luminescence of Sm^{2+} doped in BaFBr
P05-27-017	Emmanuel Deiters, Jean-Claude G. Bünzli	New acridone-benzimidazole fused ligands: towards the sensitization of Eu luminescence with excitation wavelength in the visible range
P05-28-014	Nail M. Shavaleev, Frédéric Gumy, Rosario Scopelliti, Jean-Claude G. Bünzli	Surprisingly Efficient Near-Infrared Luminescence of Ytterbium Complexes with Benzoxazole-Substituted 8-Hydroxyquinolines
P05-29-194	Chantal Lorbeer, Joanna Cybinska, Anja-Verena Mudring	Spectroscopic properties of $GdF_3:Eu^{3+}$ nanocrystals synthesized via microwave synthesis in ionic liquids
P05-30-197	Joanna Cybinska, Anja-Verena Mudring, Gerd Meyer	IR and Vis emission of K_2LnCl_5 (Ln=Gd, La) crystals doped by Tb^{3+} and Yb^{3+} ions
P05-31-202	Sascha Eidner, Katlen Brennenstuhl, Michael U. Kumke	Using Lanthanide Ion Probe Spectroscopy (LIPS) to Monitor Polyelectrolyte Conformation
P05-32-200	Simas Sakirzanovas, Holger Winkler, Aivaras Kareiva, Thomas Jüstel	Luminescence Properties of Divalent Samarium-Doped Strontium Tetraborate
P05-33-201	Arturas Katelnikovas, Holger Winkler, Aivaras Kareiva, Thomas Jüstel	Synthesis and Optical Properties of $CaY_2Al_4SiO_{12}:Ce^{3+}$
P05-34-011	Olga Snurnikova, Svetlana Kost, Natalya Rusakova, Stanislav Miroshnichenko, Olena Alyeksyeyeva, Vitaly Kalchenko, Yuriy Korovin	Luminescence of Lanthanides in Complexes with Phosphorus- and Carboxycalix[4]arenes
P05-35-057	Satoshi Shinoda, Hiroshi Tsukube	Intramolecular Energy Transfer of *d-f* Heterodinuclear Complexes
P05-36-098	C. Tiseanu, M. Kumke, V. A. Lorenz-Fonfria, A. Gessner, V. L. Parvulescu	Structure-photoluminescence relationships in europium doped microporous and mesoporous materials
P05-37-155	M. Lezhnina, E. Kopylov, M. Vorsthove, P. Klauth, U. Kynast	Luminescent Properties of Modified Eu^{3+} / Tb^{3+} Picolinates and Dipicolinates

P05-38-168	C. K. Jayasankar, K. Venkata Krishnaiah, Ch. Srinivasa Rao, N. Hemakumar	Luminescence characteristics of Dy^{3+}-doped Zn-Al-K-Na phosphate glasses
P05-39-198	Aneta Marcinkowska, Marcin Wójtowicz, Eugeniusz Zych, Leszek Kępiński	Eu and (Eu,Li)-Activated HfO_2 Phosphors – Phase Purity and Spectroscopic Properties
P05-40-104	K. Van den Eeckhout, P. F. Smet, D. Poelman	Persistent luminescence in rare-earth codoped $Ca_2Si_5N_8:Eu^{2+}$
P05-41-311	Bert Mallick, Joanna Cybinska, Anja-Verena Mudring	Luminescent and structural behaviour of copper(I)-doped rare earth containing ionic liquids
P06-01-171	Eike T. Spielberg, Juliane Bauer, Adrian E. Ion, Winfried Plass	Magnetic Interactions in Lanthanide containing Systems: From Synthesis to Characterization
P06-02-151	Przemysław Starynowicz	A europium(II) complex with dibenzo-30-crown-10
P06-03-134	Guillaume Calvez, Carole Daiguebonne, Olivier Guillou	Polymorphism of octahedral hexanuclear compounds
P06-04-133	Olivier Guillou, Carole Daiguebonne, Doddy Kustaryono, Nicolas Kerbellec	A new familly of porous lanthanide-containing coordination polymers : $Ln_2(C_2O_4)_3(H_2O)_6$ with Ln = Eu – Yb or Y
P06-05-131	Carole Daiguebonne, Nicolas Kerbellec, Victor Haquin, Olivier Guillou	The lanthanide terephthalate coordination polymers : A family with highly tuneable luminescent properties
P06-06-129	Victor Haquin, Elisabeth Guinard, Carole Daiguebonne, Olivier Guillou	Structural study of hetero-poly-nuclear coordination polymers
P06-07-128	Lilit Aboshya Sorgho, Annina Aebischer, Céline Besnard, Jean-Claude G. Bünzli, Claude Piguet	Non-covalent d-block containing cryptates for encapsulation of labile trivalent lanthanides
P06-08-105	Rafał Janicki, Anna Mondry	Some Insight into Physicochemical Properties of Lanthanide Carbonate Complexes

P06-09-094	Teresa Rodríguez-Blas, Adrián Roca-Sabio, Marta Mato-Iglesias, David Esteban-Gómez, Zoltan Palinkas, Eva Toth, Andrés de Blas, Carlos Platas-Iglesias	Selective Separation of Lanthanides: Receptors based on Azacrowns with Picolinate Pendants
P06-10-087	E. Terazzi, L. Guénée, B. Bocquet, J.-F. Lemonnier, N. Dalla-Favera, C. Piguet	Exploiting the consequences of effective concentration for designing novel neutral binuclear lanthanide triple-helices
P06-11-084	Mahboubeh A. Sharif, Masoumeh Tabatabaee, Fatemeh Vakili	A Ten-Coordinated La^{III} Complex obtained from benzene-1,2,4,5-tetracarboxylic Acid and 4,4'-bipyridine; Hydrothermal Synthesis and Crystal Structure
P06-12-059	Masoumeh Tabatabaee, Fatemeh Vakili	Hydrothermal Synthesis and Structural Studies of a new Co-crystal of a Cerium(III) complex and 2,2′-bipyridine
P06-13-039	Thomas Abel, Julie Ruff, Markus Albrecht	Helicates: Triple-stranded Dinuclear Complexes of Rare Earth Metals
P06-14-012	Grażyna Oczko	Investigation of lanthanide (III) coordination compounds with 4-pentenoic and 3-butenoic acids
P06-15-025	Oxana Kotova, Steve Comby, Konstantin Lyssenko, Svetlana Eliseeva, Jean-Claude G. Bünzli, Natalia Kuzmina	Heterobimetallic $[Zn(\mu–MO1)(\mu_2–CF_3COO)Ln(hfa)_2]$ (Ln = La^{III}, Nd^{III}, Sm^{III}–Dy^{III}) complexes: synthesis, structure and photophysical properties
P06-16-051	Anthony S. R. Chesman, David R. Turner, Glen B. Deacon, Stuart R. Batten	3d/4f Heterometallic and polycarbonatolanthanoid complexes
P06-17-077	Ulrich Baisch, Dario Braga, A. Guy Orpen	Molecular Solid State Synthesis of Ionic Coordination Polymers by Synthetic Rare Earth Crystal Engineering
P06-18-089	Federico Cisnetti, Christelle Gateau, Colette Lebrun, Pascale Delangle	Engineering of peptides for the complexation of Ln(III) ions
P06-19-170	Alexander Zurawski, Klaus Müller-Buschbaum	The Solvent Free Melt Synthesis – A Way to Generate Highly Aggregated Systems with Promising Properties
P06-20-300	Caroline Link, Gerd Meyer	New isotypic rare earth–silver 2D coordination polymers $Ag_2SE(Aba)_4(NO_3)_5$

P06-21-305	Thomas Bierke, Gerd Meyer	A new anhydrous lanthanide carboxylate: $Tb_2(OPr)_6(HOPr)$
P06-22-310	Christine Walbaum, Ingo Pantenburg, Gerd Meyer, Glen B. Deacon	Four different polyiodide anions in the crystal structure of $[Lu(db18c6)(H_2O)_3(thf)_6]_4(I_3)_2(I_5)_6(I_8)(I_{12})$
P06-23-224	Mathias S. Wickleder, Svetlana Schander	Chloride-oxo-arsenates(III) of the lanthanides with zinc and iron
P06-24-225	Natalia Dalla Favera, Laura Guenee, Gerald Bernadinelli, Claude Piguet	In search for tuneable intramolecular intermetallic interactions in polynuclear lanthanide complexes
P07-01-184	Partha Pratim Das, Lukas Palatinus, Anthony Linden, Hans-Beat Bürgi, Daniel Biner, Karl W. Krämer	Towards the Microscopic Structure of $Na_5Lu_9F_{32}$, a'cubic $NaLuF_4$'
P07-02-183	Henning A. Höppe, J. Michel U. Panzer	Crystal Structure, Vibrational Spectra and Activation of $BaCa(P_4O_{12})$ with Eu^{2+} Compared with β-$Sr(PO_3)_2$:Eu
P07-03-182	Henning A. Höppe	Phase transitions of the Polyphosphates $Ln(PO_3)_3$ (Ln = Y, Tb...Yb)
P07-04-181	Karolina Kazmierczak, Henning A. Höppe	Some new lanthanide sulphate hydrates
P07-05-169	Marta Demchyna, Bohdana Belan, Mykola Manyako, Lev Akselrud, Yaroslav Kalychak	Crystal structure of the $TbMn_{1.76}In_{0.23}$ compound
P07-06-164	F. Fernández, J. L.Montero, C. Cascales, J. Romero, R. Sáez Puche	Structural and magnetic characterization of ordered Sr_2LnSbO_6 (Ln=rare earth) perosvkites
P07-07-158	Frederick Casper, Shafagh Dastjani, Claudia Felser	Magnetoresistance in rare earth half-Heusler compounds
P07-08-150	K. Wiśniewski, W. Jadwisieńczak, A. Anders	High Pressure Luminescence Studies of GaN Epilayer Implanted with Praseodymium Ions
P07-09-116	Holger Kohlmann, Christian Reichert	The Laves phases $Eu_{1-x}M_xMg_2$ (M = La, Ce, Sm) and their hydrides: synthesis, structures and properties
P07-10-109	Marion C. Schäfer, Sabine Zitzer, Thomas Schleid	Two Modifications of the Novel Oxosilicate $NaTbSi_2O_6$ in Comparison

P07-11-108	Oliver Janka, Thomas Schleid	The New Modification of a Well-Known Compound: *C-Type* $LaTaO_4$
P07-12-058	Takeshi Hirai, Taketoshi Kawai, Shiro Sakuragi, Nobuhito Ohno	Formation of Gd^{3+} trap states in $NaGdF_4$
P07-13-037	Manuel C. Schaloske, Lorenz Kienle, Constantin Hoch, Hansjürgen Mattausch, Arndt Simon	Isolated Tetrahedra and capped trigonal Prisms: Pr_5CCl_{10}
P07-14-031	Yukio Hinatsu, Keiichi Hirose, Yoshihiro Doi	Magnetic Properties of $EuLn_2O_4$ (Ln = Lanthanides)
P07-15-009	H. Imamura, N. Yamada, T. Kanekiyo, K. Ooshima, Y. Sakata	Preparation of Cerium Nitride by Taking Advantage of the Reaction of Cerium Hydride with Ammonia
P07-16-010	D. Kasprowicz, A. Majchrowski, T. Runka, E. Michalski, M. Drozdowski	Temperature study of Ho^{3+}, Yb^{3+} and Tm^{3+} tridoped $KGd(WO_4)_2$ crystals by Raman spectroscopy
P07-17-088	M. Chavoutier, V. Jubera, P. Veber, M. Velázquez, F. Guillen, A. Fargues, A. Garcia	Study of $Li_6Ln(BO_3)_3$: Yb (Ln= Gd, Y) crystals : crystal growth, thermal, mechanical and optical characterizations
P07-18-162	Amal Ismail, Michael Dickman, Ulrich Kortz	22-Isopolytungstate Fragment $[H_2W_{22}O_{74}]^{14-}$ Coordinated to Lanthanide Ions
P07-19-301	Christian Rustige, Gerd Meyer	Structural relationships between the rare-earth halide cluster phases $\{ZRE_6\}X_{12}RE$ and $\{ZRE_6\}X_{10}$
P07-20-302	Matthias Brühmann, Gerd Meyer	$\{Ir_3Gd_{11}\}Br_{15}$ – a novel structure type in rare-earth halide chemistry
P07-21-303	Kathrin Daub, Gerd Meyer	$R\{R_6Z\}I_{12}$ with R = Dy, Ho
P07-22-304	Nina Herzmann, Anja-Verena Mudring, Gerd Meyer	Seven-Coordinate Ruthenium in the New Praseodymium Cluster Chloride $\{RuPr_3\}Cl_3$
P07-23-308	P. Link, U. Ruschewitz	Influence of crystal structure on valence states of Ytterbium and Europium in dicarbide solid solutions

P08-01-193	H. Härmä, A. Rozwandowicz-Jansen, E. Martikkala, P. Hänninen, H. Frang, I. Hemmilä	Europium-based assays to monitor GPCR activation.
P08-02-175	E. Torres, E. Terreno, R. Cavalli, S. Aime	Paramagnetic pH-sensitive liposomes with improved MRI properties
P08-03-177	G. Dehaen, T. N. Parac-Vogt, K. Binnemans	Self-assembled heteropolymetallic complexes as MRI contrast agents
P08-04-093	Badr El Aroussi, Gérald Bernardinelli, Josef Hamacek	Insights into The Self-Assembly of a New Family of Dissymmetric Tripodal Ligands with Lanthanides
P08-05-047	Elena De Luca, David Parker	Fluorinated Responsive Lanthanide Complexes for 19-F MRS/MRI
P08-06-013	Bo Song, Venkataragavalu Sivagnanam, Caroline D. B. Vandevyver, Ilkka Hemmilä, Hans-Anton Lehr, Martin A. M. Gijs, Jean-Claude G. Bünzli	On-chip Multiplexed Immunohistochemical Assays based on Lanthanide Luminescence bioprobes
P08-07-024	Jingpeng Sa, Laure Guénée, Josef Hamacek	Investigations of Lanthanides Complexes with Short Symmetrical Tripodal Ligands
P08-08-029	Svetlana V. Eliseeva, Gerald Auböck, Virendra Kumar Parashar, Frank Van Mourik, Andrea Cannizzo, Majed Chergui, Anne-Sophie Chauvin, Emmanuel Deiters, Caroline D.B. Vandevyver, Jean-Claude G. Bünzli	Enlarging the capability of lanthanide helicates as bioprobes: nanoparticles and multi-photon excitation
P08-09-045	Ga-lai Law, David Parker	Lanthanide Complexes as Bioprobes
P08-10-092	Soumaïla Zebret, Nathalie Dupont, Gérald Bernardinelli, Laure Guénée, Josef Hamacek	Self-Assembly of Tridimentional Tetranuclear Helicates with Lanthanides

P08-11-166	Eliana Gianolio, Roberta Napolitano, Franco Fedeli, Francesca Arena, Silvio Aime	Poly-β-Cycldextrin based Platform for pH mapping via a ratiometric $^{19}F/^{1}H$ MRI method

The Utility of the f Elements in Isolating New Types of Radicals and Metalated Cyclopentadienyl Ligands

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Keywords: Lanthanides, Actinides, Coordination Chemistry, Organometallic Chemistry

One of the exciting aspects of lanthanide and actinide chemistry is that the special properties of these metals can provide a basis to make advances in a variety of different areas of chemistry. This will be exemplified in this lecture by showing how recent studies of the reductive chemistry of the f elements have led to an expansion of the types of ligand systems that can be isolated in metal complexes. Specifically, new examples of radical ligands and metalated cyclopentadienyl ligands will be presented.

The first example of the isolation of the $(N_2)^{3-}$ radical formed by reduction of the $(N_2)^{2-}$ ligands in complexes of general formula $[Z_2(THF)_xLn]_2(\mu\text{-}h^2{:}h^2\text{-}N_2)$ (Z = aryloxide and amide) will be described as well as the extension of this approach to other systems. The isolation of the first crystallographically characterized example of an f element “tuck-in” moiety, i.e. a metalated pentamethylcyclopentadienyl ligand of general formula $(C_5Me_4CH_2)^{2-}$, will be discussed as well as three additional examples obtained by manipulation of organometallic coordination environments. Formation of other types of metalated cyclopentadienyl ligands will be described as well as their utility in creating a diverse set of new tethered "ansa" ligand environments for the f elements.

Chemistry and physics of new lanthanide upconversion materials and processes

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Keywords: Upconversion,upconversion materials, upconversion processes

The phenomenon of photon upconversion in lanthanide compounds has been known for more than 40 years. Excitation in the near infrared leads to light emission in the visible part of the spectrum. Examples from our own work in the past 20 years will be presented. New types of upconversion materials and processes as well as possible new applications have been found: transition metal ion systems, mixed transition metal/lanthanide compounds with novel upconversion mechanisms, upconversion involving f-d transitions in lanthanides, dispersible upconverting nanoparticles with potential applications in bio-labelling and bio-imaging. The Figure shows transparently dispersed nanocrystals of Yb3+/Er3+ and Yb3+/Tm3+ doped NaYF4 excited at 980 nm.

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Spectroscopy of High-Energy States – Where to From Here?

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Keywords: Lanthanides; Actinides; Spectroscopy; Theory;

A good understanding of energy levels, transition intensities, and dynamical processes within the $4f^N$ and $5f^N$ configurations of lanthanide and actinide compounds was achieved in the 1960s, and developed further in subsequent decades. The higher-energy $4f^{N-1}5d$, charge-transfer, and conduction-band states have also been studied since the 1960s but interest in these states became more intense over the last decade or so. This was, in part, due to the increased availability of high-resolution VUV spectra from synchrotron measurement, which made it possible to perform analyses across the lanthanide series in a number of compounds.

The data from these experiments has been analysed in a variety of ways. We have used phenomenological models that extend the well-established approach for the $4f^N$ and $5f^N$ configurations [1-2]. Simple (but highly effective) models for relating the energy levels of different ions in different hosts have also been developed [3]. In addition, a variety of ab-initio calculations have appeared [4-6].

Detailed comparisons between theory and experiment are still difficult because the available experimental data mainly consist of broad bands. Designing experiments to test the predictions of ab-initio calculations of excited-state bond lengths and potential-energy surfaces also provides interesting challenges.

This presentation will review recent developments in experimental and theoretical spectroscopy, and how they have contributed to our current understanding of the high-energy states. The relationship between ab-initio calculations and phenomenological models [7] and some speculative ideas on possible experimental and theoretical developments will also be discussed.

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Rare Earth Transition Metal Bonding

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Keywords: metal-metal bonding; core shell compounds

Chemical bonding and in particular the nature of a chemical bond, the electronic structure and its reactivity, is of fundamental interest. Reactivity expresses the significance of reaction pathways - it is a "projection" of reaction rates and the electronic structure allows us understanding why some of the reaction pathways a bond can undergo are relevant and some aren't. Chemical bonding is the heart of chemistry, the science of synthesis. Metal-metal bonding has received a lot of attention recently and during the lecture it is focussed on polar metal-metal bonds namely unsupported bonds between rare earths (RE) and transition metals (TM).

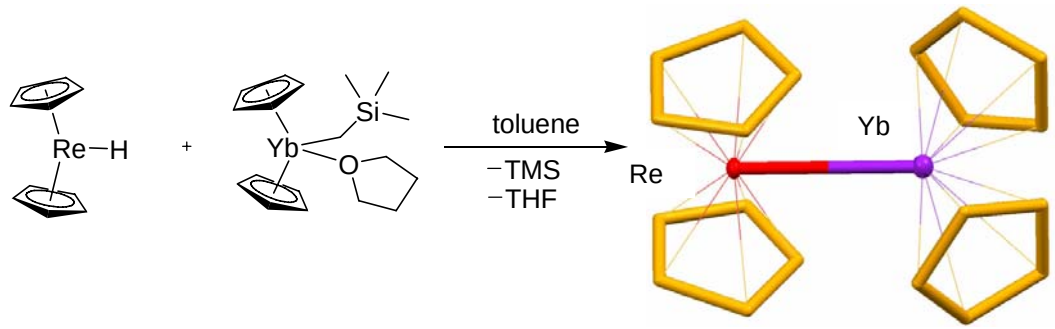

Figure 1. Unsupported RE-TM bonds via alkane elimination

Recently, we succeeded in synthesizing Re-RE bonds via alkane elimination.[1] The problems and consequences of this type of metal-metal bond formation reaction are discussed. A special focus is given towards bond formation methodologies to generate highly reactive albeit in solution stable mono-dispers RE-TM core-shell compounds.

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Metal-Organic Rare Earth Chemistry Continues to Excite

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Keywords:

Metal-organic chemistry of the rare earths has enjoyed remarkable success in recent years, and the isolation of exciting complexes involving low coordinate species, unusual oxidation states, exceptional reactivity including catalysis, and new synthetic approaches has ensured that this chemistry has stayed at the forefront of inorganic research.

In this presentation, new results involving low oxidation state chemistry (Ln(II), see our new Nd^{2+} in Fig. 1), C-F activation, sterically induced reactivity and near naked cationic species involving lanthanoids will be presented.

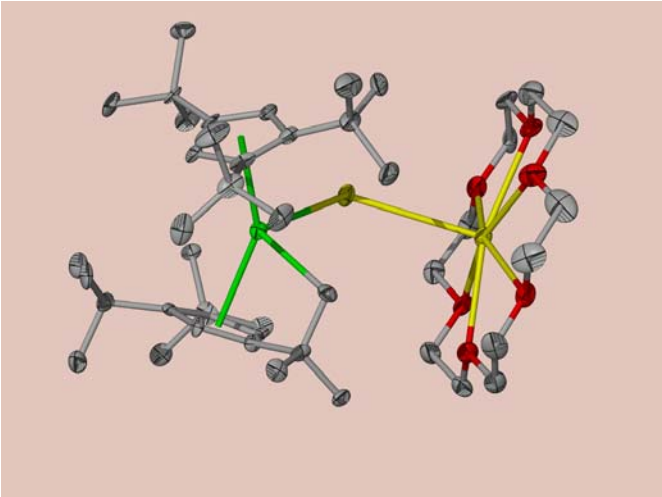

Figure 1: X-ray crystal structure of the low valent Nd^{2+} species $[Cp^{ttt}_2NdIK(18C6)]$

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Synthesis and reactivity of homoleptic rare-earth metal methyl complexes

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Keywords: lanthanides; organometallics; synthesis

Homoleptic tetramethylaluminate complexes $Ln(AlMe_4)_3$ display masked rare-earth metal methyl complexes "$LnMe_3(AlMe_3)_3$" as documented by their intrinsic reactivity.[1,2] The aluminum-free unmasked compounds of smaller-sized Ln metal centers such as yttrium and lutetium, which are accesible by cleavage reactions with donor molecules like diethylether, THF or trimethylphosphine, feature a polymeric composition $[LnMe_3]_n$.[2] Derivatives of the larger Ln metal centers (e.g., La, Sm) engage in multiple hydrogen abstraction reactions leading to $[Ln–CH_2]$, [Ln–CH], and [Ln–C] moieties.[3] In order to avoid such extensive methyl group degradation we developed new synthesis approaches toward $[LnMe_3]_n$. We also describe new reactivity features of $[LnMe_3]_n$ according to protonolysis reaction protocols.

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Actinyl compounds with VIth-group elements: the world of amazing structural diversity and complexity

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Keywords: Actinyl compounds; Topology; Nanotubules; Frameworks

Actinide and, especially, uranium oxysalts with hexavalent cations of the elements of the VIth group of the Periodic Table are important phases from mineralogical, environmental and technological points of view. These compounds are common constituents of the oxidized zones of uranium mineral deposits, form as a result of the alteration of spent nuclear fuel (SNF), form during burnup of nuclear fuels in reactors, represent insoluble reisudes undesirable for the recovery of plutonium from the SNF solutions, impact upon the transport of actinides in contaminated soils, and the mobility of radionuclides in a geological repository for nuclear waste, etc. Knowledge of the structures of these compounds is essential for understanding their behaviour in a wide range of environmental and technological processes. In our contribution, we concentrate on actinyl compounds, i.e. actinide compounds, containing linear actinyl ions ($[An^{m+}O_2]^{(m-4)+}$; m = 5, 6) and hexavalent cations of the VIth group elements (S, Cr, Se, Mo, and W). These compounds are subdivided on the basis of the principles of their structural architecture into: (i) structures described on the basis of the concept of anion-topology; (ii) structures containing structural units with corner-sharing actinyl polyhedra and TO_4 tetrahedra (T = S, Cr, Se, and Mo); (iii) structures containing structural units with edge-sharing actinyl polyhedra and TO_4 tetrahedra (T = S, Cr, Se, and Mo); (iv) structures with corner sharing between actinyl polyhedra. The group (ii) is analysed in more details in order to estimate flexibility of structural units on the basis of statistical analysis of bond lengths and angles. From the topological viewpoint, this group is extremely diverse and, in order to rationalize this diversity, we employ a graph theory that reflects polyhedral connectivity. To construct a structural hierarchy, the structures of the compounds under consideration are considered as based upon structural units with general formula $[(AnO_2)_p(TO_4)_q(H_2O)_r]$. According to their dimensionality, these units can be subdivided into 0- (finite clusters), 1- (chains), 2- (sheets) and 3- (frameworks) dimensional units. It is of interest that, except one example, topologies of all 2-dimensional $[(AnO_2)_p(TO_4)_q(H_2O)_r]$ sheets are derivatives of the highly symmetrical (3.6.3.6) graph [1]. The derivative graphs can be obtained from it by removing certain vertices and/or links. The p:q (= An:T) ratio may take values 1:1, 1:2, 2:3, 3:5, 5:8, etc., and, within each group, a number of topological variations and stereoismers is possible. From 1-dimensional units, uranyl selenate nanotubules are the most remarkable [2-4]; it seems that K^+ cations play some important role in controlling their topology and self-assembly. Among framework structures, chiral uranyl molybdate frameworks and their displacive phase transitions deserve special attention [5-8], as well as crown-ether-templated uranyl sulfate with the lowest framework density reported for actinide oxide framework so far [4].

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Geo-Inspired Phosphors Based on Rare-Earth Metal(III) Fluorides with Complex Oxoanions

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Keywords: Lanthanides; Chemistry; Solid-State; Structure

Bulk and M^{3+}-doped *bastnaesite*-type $LaF[CO_3]$ (hexagonal, $P\bar{6}2c$) can be prepared from aqueous solutions, containing La^{3+}, F^- and $[HCO_3]^-$ ions along with up to 3% M^{3+} dopant (M = Eu or Tb) if desired. Its thermal decomposition at 450°C yields volatile CO_2 and single-phase LaOF (trigonal, $R\bar{3}m$) as solid residue, which shows brilliant red (Eu^{3+}) or green (Tb^{3+}) luminescence [1]. Fluoride-derivatized rare-earth metal oxosilicates are available from appropriate M_2O_3:MF_3:SiO_2 mixtures at high temperatures. For *bastnaesite*-related $LaF(SiO_3)$ (≡ $La_3F_3[Si_3O_9]$; hexagonal, $P\bar{6}2c$) UV-luminescence has already been proven with Ce^{3+}-doped samples [2]. *Thalenite*-type $Y_3F[Si_3O_{10}]$ (monoclinic, $P2_1/n$) [3] can be doped with medium-size lanthanoids (M = Sm – Er) and exhibits not only the expected visible, but also IR-luminescence [4]. In contrast, $Er_4F_2(Si_3O_{11})$ (≡ $Er_4F_2[Si_2O_7][SiO_4]$; triclinic, $P\bar{1}$) [5] has no analogous yttrium counterpart as host for lanthanoid dopants so far. A very promising *apatite*-type candidate contains di- and trivalent europium simultaneously: $Eu_5F(Si_3O_{12})$ (≡ $(Eu^{II})_2(Eu^{III})_3F[SiO_4]_3$; hexagonal, $P6_3/m$) [6]. Therefore it should be possible to dope isotypic samples of *i.e.* $Ba_2La_3F[SiO_4]_3$ [7] with both suitable di- and trivalent lanthanoid cations. From the structural point of view more or less planar $[FM_3]^{8+}$ triangles and regular $[SiO_4]^{4-}$ tetrahedra are present in all four examples, which occur either isolated or condensed. The cations $[FM_3]^{8+}$ share vertices to form layers ($^{2}_{\infty}\{[FLa_{3/3}]^{2+}\}$ like in *tysonite*-type LaF_3) or edges to build up dimers ($^{0}_{\infty}\{([FEr_{2/1}Er_{2/2}]^{5+})_2\}$) if necessary, while the anions $[SiO_4]^{4-}$ use common corners, whenever they need to condense at all. Fluoride oxoselenates(IV) with the composition $MF[SeO_3]$ (M = La, Ce [8]; Ho – Yb, Y [9]: monoclinic, $P2_1/c$; M = Lu: triclinic, $P\bar{1}$ [10]) no longer exhibit a planar oxoanion such as $[CO_3]^{2-}$, but a ψ^1-tetrahedral $[SeO_3]^{2-}$ unit. This pyramidal $[SeO_3]^{2-}$ anion with a stereochemically active lone pair of electrons can serve as an extra energy reservoir due to possible s–p transitions, which may synergetically influence the f–f or f–d transitions of the lanthanoid M^{3+} cations doped into the different $LaF[SeO_3]$, $YF[SeO_3]$ and $LuF[SeO_3]$ host lattices. Even $Gd_3F[SeO_3]_4$ (hexagonal, $P6_3mc$) [11] might serve as a suitable host for Eu^{3+} or Tb^{3+} dopants. A similar effect could be achieved in the case of rare-earth metal(III) fluoride oxomolybdates(VI) with the composition $MF[MoO_4]$ (M = Sm – Tm; monoclinic, $P2_1/c$ [12]), since charge-transfer excitation within their isolated $[MoO_4]^{2-}$ should also work as synergetic assist for the f–f or f–d transitions of the doping lanthanoid M^{3+} cations in their optically innocent $YF[MoO_4]$ host [13]. The potential of new compounds such as $La_3F[MoO_4]_4$ (triclinic, $P\bar{1}$) and $YF[Mo_2O_7]$ (monoclinic, $P2/c$) still needs to be explored.

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Electronic and Magnetic Phase Diagrams of the Rare Earths

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Keywords: Lanthanides; Theory; Solid State; Modelling

An introduction is given to the Self-Interaction-Corrected Local-Spin-Density (SIC-LSD) method and its application to the rare earths in order to determine, without adjustable parameters, the valence of the rare earth in the elemental rare earths and their compounds.[1] The results of calculations of the rare earth's valence in 140 rare earth pnictides and chalcogenides are presented.
In addition, it is shown that the finite temperature SIC-LSD generalization allows to study phase diagrams. The charge and magnetic fluctuations are treated with the Coherent Potential Approximation (CPA) and the Disordered Local Moment (DLM) formalisms respectively. This has allowed to determine the critical point in Cerium [2] and the Curie temperatures, as well as the incommensurate Q-vectors, of all the late rare earths, from Gd onwards. This has resulted in a phase diagram of finite temperature magnetism of the heavy rare earths.[3]

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Condensed Polymetal Salts That are Unique to the Rare-Earth Elements

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Keywords: Clusters, Metal-metal bonding, Cluster stabilities

The rare-earth elements, which commonly afford three valence electrons per atom, form a sizable and singular group of polymetal cations when oxidized by limited amounts of simple non-metals: Cl, Br, I, Te especially. The large collection of binary and, principally, ternary mixed-metal condensed structures exhibit (average) R oxidation states around 1.0 ± 0.4. The structures contain fairly regular types of building blocks, principally octahedra or trigonal prisms of R, that are commonly centered by a single interstitial atoms, often a late transition metal (Z). The relatively small numbers of the isolated counter-anions present in these cases result in substantial condensation of the metal clusters, mainly to oligomers, chains and sheets with halide, but to sheets and some complex 3D networks with roughly half as many telluride anions per cluster. Only a few examples are presently known in R–(Z)–pnictide systems, principally with Sb. In contrast, cluster products of transition metal hosts after Y, e.g. Zr, Nb, Mo, with roughly the same cluster electron populations have higher charges and are increasingly isolated because of the increasing number of anions in those instances. In the other direction, alkaline-earth-metal examples with corresponding electron concentrations in very low (±) oxidation states have evidently not yet been achieved. Examples among particularly the ternary halides and tellurides will illustrate the nature and variety of metal-rich compounds so formed ($Y_3(Ru)I_3$, $Sc_{16}Fe_4Br_{28}$, Gd_2Cl_3, Sc_2Te, Dy_6IrTe_2, $Sc_{12}Ru_3Te_8$, $Er_7Au_2Te_2$, Lu_8Te). Some general principles will also be presented: (1) Valence d orbitals on R are dominant in the metal–metal bonding and (2) Striking stability differences for many such compound types clearly depend on the nature/location of R. These more unusual products are commonly found only among Sc, Y, and the heavier lanthanides Gd–Tm and Lu. These may be judged to be the less active metals among R with more tightly bound valence electrons, such as reflected in higher values of their ionization energies I1 + I2 (Figure 1) [1]. This trend should generate stronger binding between R and the d levels of the usual centered Z members [2].

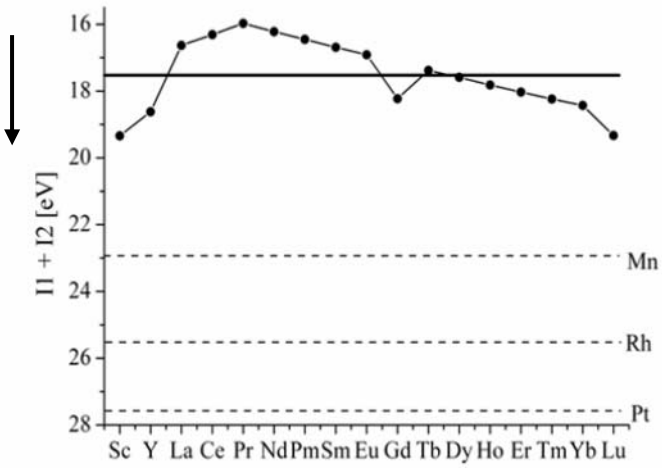

Figure1. The sum of the first two ionization energies of the rare-earth elements, increasing downward. Representative values for three transition metal interstitials are also shown. Those R elements below the (arbitrary) line form the more unusual compounds.

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Chemical Approaches to Functional Nanostructures: Growth, Applications and Devices

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Keywords:

Chemical design of inorganic materials deals with the transfer of short range chemical order, present in the molecular precursor state, to infinite correlation lengths in three dimensions. A generic chemical strategy based on the transformation of molecular precursors into functional inorganic nanostructures allows producing nanomaterials of different dimensions and morphologies with precisely controlled chemical composition and phase purity. The successful synthesis, modification and assembly of nanobuilding units such as nanocrystals, -wires and –tubes of different materials have demonstrated the importance of chemical influence in materials synthesis, and have generated great expectations for the future. Inorganic nanostructures inherit promises for substantial improvements in materials engineering mainly due to improved physical and mechanical properties resulting from the reduction of microstructural features by two to three orders of magnitude, when compared to current engineering materials. The chosen examples will include nanostructured functional films for hydrophobic, hydrophilic and barrier properties, application of superparamagnetic iron oxide nanoparticles for drug delivery applications, molecule-based synthesis of nanowires and development of single-nanowire based devices.

This talk will focus how chemically processed nanostructures open up new vistas of material properties, which can be transformed into advanced material technologies. It will also address the several steps involved in the transformation of laboratory scale research into nanotechnology-based products and devices.

Aspects of the Application of Ionic Liquids in the Separations of f-Elements: Coordination and Solvation

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Keywords:

Ionic liquids (ILs, salts that have a melting point less than 100 °C) have been investigated as potential replacement solvents for liquid/liquid separations, and the complex results have been highly dependent on the specific ILs, ligands, and systems studied.

Nonetheless, ILs provide the opportunity to explore solvation in totally ionic media at relatively low temperatures, compared with the dissolution in high-temperature molten salts or in molecular solvents. In addition, because solutes are dissolved in ionic melts at lower temperatures, the effects of molecular solvents (including water) and organic or inorganic coordinating ligands can be studied. (Such solvents or ligands would not survive the harsh conditions often used to generate high- temperature molten salts.)

This presentation will discuss our investigations of the fundamental interactions of solutes with and in IL solvents focusing primarily on the coordination and solvation of metal ions and ligands.

A Short Trip Trough Lanthanide Self-Assemblies

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Keywords: Lanthanide, Chemistry, Coordination, Thermodynamics

Deviations from statistical binding, ie. cooperativity, in self-assembled polynuclear lanthanide complexes partly result from intermetallic interactions $\Delta E^{M,M}$, whose magnitudes in solution depend on a balance between electrostatic repulsion and solvation energies. These two factors have been reconciled in a simple point-charge model, which suggests severe and counter-intuitive deviations from predictions based solely on the Coulomb law when considering the variation of $\Delta E^{M,M}$ with metallic charge and intermetallic separation in linear polynuclear triple-stranded helicates. In order to demonstrate this intriguing behaviour, the ten microscopic interactions which define the thermodynamic formation constants of some thirty homometallic and heterometallic polynuclear triple-stranded helicates obtained from the coordination of segmental multi-tridentate ligands with Zn^{2+} (a spherical d-block cation) and Lu^{3+} (a spherical 4f-block cation), have been extracted using the site binding model [1].

Since interligand interactions, intermetallic interactions and effective molarity for macrocyclization all produce unfavorable contributions to the complexation process, the driving force of the assemblies entirely relies on the intermolecular metal-ligand connections. However, the alarmingly small magnitude of the intermetallic interactions operating between triply charged cations held at 9Å is eventually responsible for the global stability of these highly charged polynuclear complexes in solution (Figure 1).

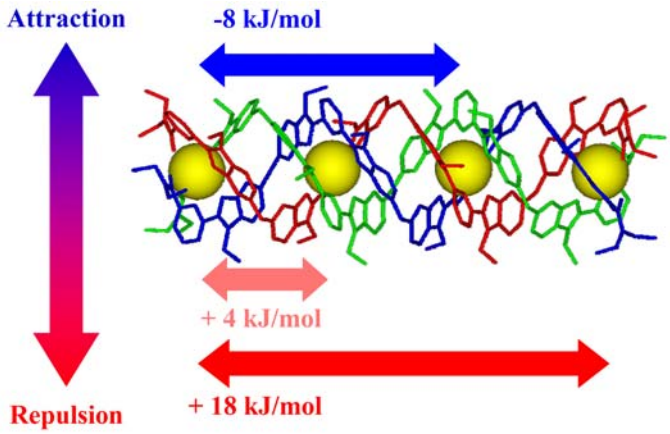

Figure 1. Microscopic intramolecular intermetallic interactions operating within the tetranuclear triple-stranded helicate $[Ln_4L_3]^{12+}$.

As predicted, but in contrast with the simplistic coulombic approach, the apparent intramolecular intermetallic interactions in solution are found to be (i) more repulsive at long distance ($Lu^{3+}\cdots Lu^{3+}$ repulsion at 27Å (18 kJ/mol) > $Lu^{3+}\cdots Lu^{3+}$ repulsion at 9Å (4 kJ/mol)), (ii) of larger magnitude when Zn^{2+} replaces Lu^{3+} ($Zn^{2+}\cdots Lu^{3+}$ repulsion at 9Å (18 kJ/mol) > $Lu^{3+}\cdots Lu^{3+}$ repulsion at 9Å (4 kJ/mol)) and (iii) attractive between two triply charged cations held at some specific distance ($Lu^{3+}\cdots Lu^{3+}$ attraction at 18Å = -8 kJ/mol). The physical origins and the consequences of these trends are discussed for the design of polynuclear complexes in solution.

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Organolanthanide Chemistry in Three Oxidation States: 20 Years of Fascination

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Keywords: Non-Cyclopentadienyl Organolanthanide Chemistry; Lanthanide Amidinates; Cyclooctatetraenyl Complexes; Cerocenes

This lecture is intended to give a personal review of the highlights of our organolanthanide research at Göttingen and Magdeburg during the past 20 years. We started out in this exciting area of organometallic chemistry by exploring new reactions of Evans' $Cp^*_2Sm(THF)_2$, leading *e.g.* to unprecedented dimerization of a phosphaalkine and formation of diazadiene complexes of the type $Cp^*_2Sm(DAD)$.

The dominating theme of most of our efforts in this field, however, was the search for non-cyclopentadienyl coordination environments for the lanthanide elements. It was first realized in our group almost 20 years ago that amidinate anions, $[RC(NR')_2]^-$, can be viewed as "steric cyclopentadienyl equivalents". Synthetic routes leading to lanthanide amidinates in all three readily available oxidation states (+2, +3, and +4) have been developed, the latest addition being a straightforward access to cerium(IV) derivatives. Since then, lanthanide complexes containing amidinate and the closely related guanidinate ligands have turned out to be efficient polymerization catalysts as well as ALD precursors for the production of lanthanide oxide thin layers [1]. Related lanthanide chemistry was developed for other heteroallylic ligands such as $[RS(NR')_2]^-$, $[R_2P(NR')_2]^-$, and $[Me_2Si(O^tBu)(N^tBu)]^-$. Heterometallic lanthanide disiloxanediolates form yet another class of lanthanide complexes which have been investigated in our lab. Such compounds can be described as either metallacrown complexes or "inorganic metallocenes", depending on the ionic radius of the rare earth metal. More complex metallasilsesquioxanes containing lanthanides can be regarded as "realistic" models for silica-supported lanthanide catalysts.

Organolanthanide complexes containing bulky COT ligands comprise another field where interesting achievements have been made. A notable highlight of our earlier work was the synthesis of crystalline and highly soluble 1,1',3,3',6,6'-hexakis(trimethylsilyl)cerocene. Use of the newly developed "super-bulky" 1,4-bis(triphenylsilyl)cyclooctatetraenyl ligand (= COT^{big}-1,4) resulted in novel coordination modes and reaction pathways, *e.g.* η^4-coordination to scandium or formation of the neutral cerocene $Ce(COT^{big}\text{-}1,3)_2$ through $SiPh_3$ group migration. Reactions of $LnCl_3$ with $Li_2(COT'')$ (COT'' = 1,4-bis(trimethylsilyl)cyclooctatetraenyl) gave rise to very different products such as the anionic sandwich complexes $[Ln(COT'')_2]^-$, the chloro-bridged dimers $[(COT'')Ln(THF)(\mu\text{-}Cl)]_2$ or the unprecedented cluster molecules $[Ln(COT'')]_2[Ln_2(COT'')_2]_2Li_2(THF)_2Cl_8$. Structural verification of the neutral tripledecker sandwich complexes $Ln_2(COT'')_3$, although first reported 10 years ago, remained elusive until very recently a newly discovered synthetic route enabled us to determine the molecular structure of $Nd_2(COT'')_3$. Finally, our synthetic efforts in this area culminated in the synthesis and structural characterization of the first linear lanthanide tetradecker sandwich complex $Cp^*Yb(\mu\text{-}\eta^8,\eta^8\text{-}COT''')Yb(\mu\text{-}\eta^8,\eta^8\text{-}COT''')YbCp^*$ (COT''' = 1,3,6-tris(trimethylsilyl)cyclooctatetraenyl).

Reference

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Low Valent Main Group Compounds as Ligands in Lanthanide Chemistry

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Keywords: Lanthanides, Chemistry, Coordination Compounds, Synthesis

Metal-to-metal bonds in clusters are of fundamental interest in many areas of natural science. In coordination chemistry of the transition metals, single and multiple metal-to-metal bonds are well established since the pioneering work in the mid 60^{ies}. In contrast to the rapid development in main group and transition metal chemistry, metal-to-metal bonds in rare earth complexes are almost unknown because the 4f valence shell is embedded into the interior of the ion, well shielded by the $5s^2$ and $5p^6$ orbitals. To the best of our knowledge, only one example of a non-supported metal-to-metal bond exists ([(THF)(η^5-C_5H_5)$_2$Lu-Ru(CO)$_2$(η^5-C_5H_5)]).[1] Herein, we now present the coordination of [(η^5-C_5Me_5)E] (E = Al, Ga)[2] on the sandwich complexes of the divalent lanthanides [(η^5-C_5Me_5)$_2$Ln] (Ln = Sm, Eu, Yb)[3,4] (Figure 1) and on the heavy alkaline earth metals [(η^5-C_5Me_5)$_2$M] (M = Ca, Sr, Ba)[5] resulting in donor-acceptor complexes with E-Ln and E-M bonds, respectively.

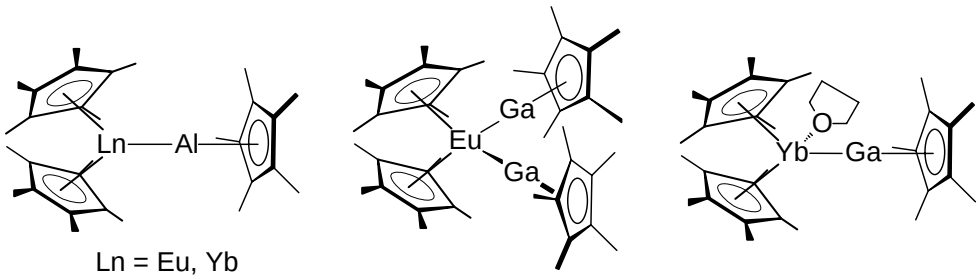

Figure 1. Compounds with aluminium-lanthanide and gallium-lanthanide metal-to-metal bonds

Moreover, the synthesis of the first lanthanide polyphosphide by a one-electron redox reaction of divalent samarocene and white phosphorus is reported. Diffusion of P_4 vapor into a toluene solution of solvate-free samarocene, [(η^5-C_5Me_5)$_2$Sm], over a period of several days resulted in the formation of [{(η^5-C_5Me_5)$_2$Sm}$_4$P$_8$]. In the center of the molecule a P_8 unit is located, which possesses a realgar-type homoatomic structure.

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Synthesis, Characterization and Structural Variation of Scorpionate Supported Lanthanide bis-Alkynide Complexes, "$(Tp^{R,R})Ln(C{\equiv}CR``)_2$"

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Keywords: Lanthanide; Scorpionate; Alkynide; Terminal

Protonolysis of the scorpionate supported lanthanide dialkyl complexes[1], $(Tp^{R,Me})Ln(CH_2SiMe_3)_2(THF)_n$ (Ln = Y, Lu; R = Me, n = 1; R = ^{t}Bu, n = 0) with terminal alkynes gave the bis-alkynide complexes "$(Tp^{R,Me})Ln(C{\equiv}CR``)_2$" (R = Ph, $SiMe_3$, ^{t}Bu, adamantyl, tris(3,5-di-tert-butylphenyl)methyl).

$$(Tp^{R,Me})Ln(CH_2SiMe_3)_2(THF)_n + 2\ R``CCH \xrightarrow{-SiMe_4} "(Tp^{R,Me})Ln(CCR``)_2" \qquad (1)$$

Ln = Y, Lu
R = Me, n = 1; **1**
R = ^{t}Bu, n = 0; **2**

The structure of the complexes depends on both the size of the substituent on the 3 position of the pyrazolyl group of the scorpionate ligand and the alkyne substituent.

With the Tp^{Me2} ligand and R´´ = Ph, $SiMe_3$, ^{t}Bu and adamantyl, dimeric complexes of the form $[(Tp^{Me2})Ln(\mu\text{-}C{\equiv}CR'')]_2(\mu\text{-}R''CCCCR'')$, **3**, were obtained. In these complexes, each metal centre is coordinated to two different alkynide moieties; a bridging and a coupled alkynide unit. The bonding within each alkynide moiety shows subtle differences depending on the steric size of the alkyne substituents. When R´´ = tris(3,5-di-tert-butylphenyl)methyl) however, the obtained complexes, $(Tp^{Me2})Ln(CCR'')_2(THF)$, **4**, have both alkynide moieties in terminal disposition.

With the $Tp^{tBu,Me}$ ligand on the other hand, the complexes obtained have terminal alkynide ligands $(Tp^{tBu,Me})Ln(CCR'')_2$, **5**, with no additional solvent coordination.

The dimeric complexes are catalysts for the dimerization of terminal alkynes, the stereo-selectivity of the product depending on the alkyne substituent.

The synthesis, characterization and structural variation of these complexes will be presented.

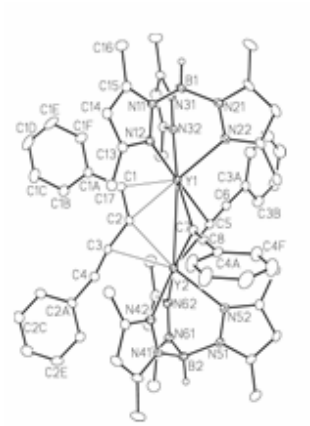

Figure 1. An ORTEP View of $[(Tp^{Me2})Y(\mu\text{-}C{\equiv}CPh)]_2(\mu\text{-}PhCCCCPh)$.

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Molecular Alkyl and Hydride Complexes of the Lanthanides

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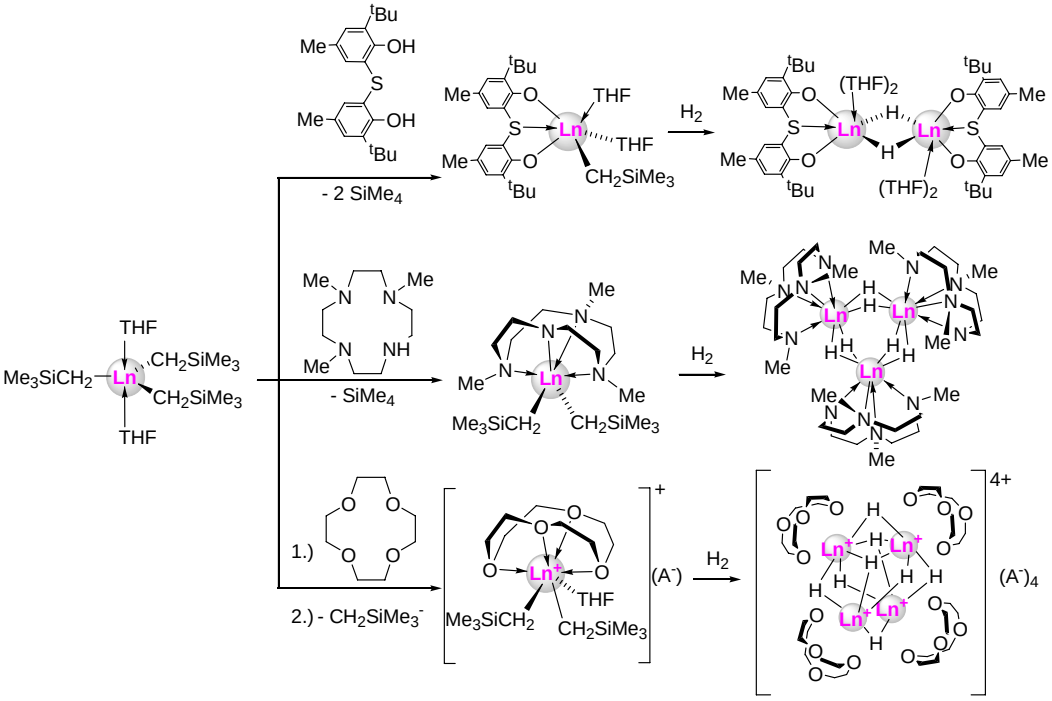
Keywords: Lanthanides; Chemistry; Organometallics; Synthesis

In the absence of a shielding metallocene scaffold, the design of the coordination sphere for large Lewis-acidic/electrophilic lanthanides centers becomes challenging. This is particular the case for complexes with highly nucleophilic alkyl and hydride functions which are of considerable interest in homogeneous catalysis. A selection of neutral, mono- and dianionic ligand sets have been introduced as inert ancillary ligands that allow access to reactive alkyl and hydride complexes. Neutral and cationic alkyl complexes of the lanthanide metals have recently been shown to play an important role as active species in the rare earth metal catalyzed homogeneous ethylene, 1-hexene, and 1,3-diene polymerization.[1] In the presence of neutral donors such as THF and crown ethers, robust cationic alkyl, σ-aryl, and π-allyl complexes can be isolated and structurally characterized. Methyl cations such as $[Ln(CH_3)_n(THF)_{7-n}]^{(3-n)+}$ (n = 1,2) have become also available through the use of synthons for the elusive trimethyl $[Ln(CH_3)_3]$.



Molecular lanthanide metal hydrides can be prepared by σ-bond metathesis.[2] Complexes containing a dianionic (OSSO)-type bis(phenolate) ligand or a monoanionic cyclen-derived (NNNN) macrocycle are aggregated in solution and in the solid state, yet active, e.g. in olefin hydrosilylation. Highly ionic metal-hydrogen bonds can be found in cationic clusters.

Acknowledgment: Financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and Alexander-von-Humboldt Foundation is gratefully acknowledged.

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Cyclic (poly)aminals as neutral or ionic ligands in rare-earth metal chemistry

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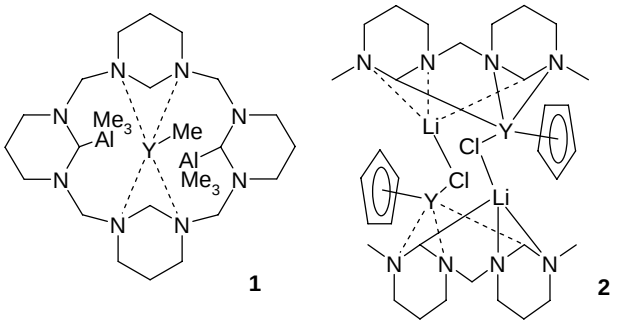
Keywords: Lanthanides, C-H-Activation, Carbenes, Carbides

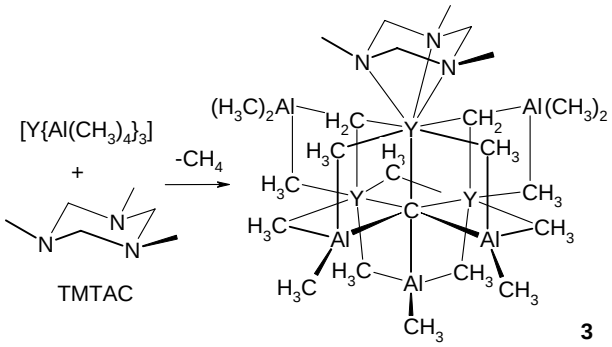
In the search for heterobimetallic reagents for selective deprotonation reactions we found that the rare-earth tetramethylaluminates $[M(AlMe_4)_3]$ can lead to direct and selective deprotonation of aminal functions embedded in macrocyclic arrangements (compound **1**). Such hetero-organometallic reagents can also be synthesised by reactions of lithiated aminals (which are surprisingly easy accessible by direct deprotonation, despite the double destabilisation of a N-bound carbanion)[1] with organo rare-earth metal halides like $CpYCl_2$ (compound **2**).

However, such saturated heterocycles can also act as neutral ligands in the chemistry of rare-earth tetramethylaluminates and initiate multiple C–H activation reactions.[2] The reaction of TMTAC with $[La(AlMe_4)_3]$ leads to a condensation of two anionic $[AlMe_4]^-$ units into a $[Me_3AlCH_2AlMe_3]^{2-}$ ion resulting in the complex $[(TMTAC)La(AlMe_4)(Me_3AlCH_2AlMe_3)]$.[3]



Scheme 1.

The reagent $[Sm(AlMe_4)_3]$ with the smaller samarium ion leads to further condensation of three anionic $[AlMe_4]^-$ units into a $[Me_3AlCH_2AlMe_2\text{-}CH_2\text{-}AlMe_3]^{3-}$ ion resulting in the complex $[(TMTAC)\text{-}Sm(Me_3AlCH_2AlMe_2CH_2AlMe_3)]$.[3] This points to ion size effects and a new type of mechanism. It is underlined by the fact that $[Sm(AlMe_4)_3]$ undergoes an additional reaction type, which is exclusively observed for $[Y(AlMe_4)_3]$. This reaction involves a complicated further methyl group degradation leading to complexes with three rare-earth metal atoms as depicted in Scheme 2 (compound **3**).



Scheme 2.

Further types of reactivity are found by application of triazacyclohexanes with more bulky ligands R at nitrogen. These include dismutation reactions to give cationic complexes $[L_2M(CH_3)_2]^+$ (L = $(RNCH_2)_3$, related to known Y-Me cations)[4] and sterically induced reduction[5] reactions affording $[LSm(AlMe_4)_2]$.

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Controlling alkyl/halo and amido/halo ligand combinations in organolanthanide complexes

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Keywords: alkyl, amide; cyclopentadienyl, halide

Rare-earth metal halides and activated variants such as $LnX_3(THF)_n$ feature the prevailing synthesis precursors in organolanthanide chemistry. Unfortunately, these pretty convenient salt metathesis routes often lead to ate complexation, ligand scrambling, and hard to separate byproducts, ruling out the isolation of well-defined heteroleptic complexes. Herein, we present the synthesis of halfsandwich halide complexes via amido/halo and alkyl/halo ligand exchange[1]. For example, $(C_5Me_5)Y(N\mathit{i}Pr_2)_2(THF)$ can be straightforwardly transferred into dimeric complex $[(C_5Me_5)Y(N\mathit{i}Pr_2)(\mu\text{-}I)]_2$ by reaction with $ISiMe_3$. The formation of Ln halfsandwich cluster compounds via partial alkyl/halo (chloro, bromo, iodo) ligand exchange in $(C_5Me_5)Ln(AlMe_4)_2$ contributes to a better understanding of multicomponent Ziegler catalysts. On the basis of X-ray structural data, it will be shown that cluster nuclearity is predominantly affected by the metal ion size[2]. Utilization of such mild alkyl/halo ligand exchange reactions for the generation of Ziegler Mischkatalysatoren and investigations into the inherent "chloride effect" in 1,3-diene coordination polymerization will be also addressed[3].

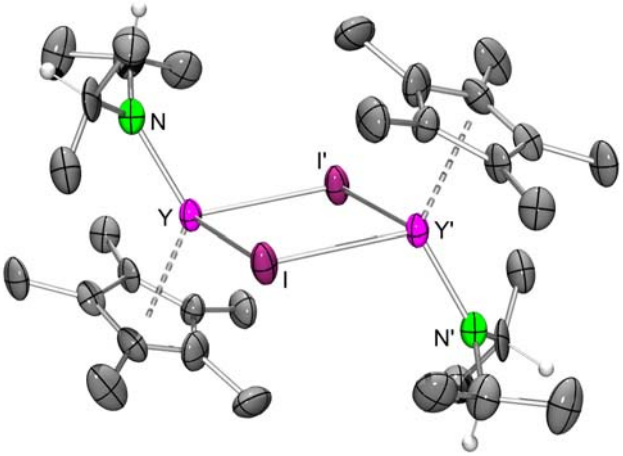

Figure 1. Molecular structure of $[(C_5Me_5)Y(N\mathit{i}Pr_2)(\mu\text{-}I)]_2$ (atomic displacement parameters set at the 50% level).

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Lanthanoid Containing Bimetallics Prepared from the Elements

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Keywords: Lanthanides, Chemistry, Organometallics, Synthesis

Treatment of a rare earth metal and a potentially divalent rare earth metal or an alkaline earth metal with 2,6-dipheylphenol (HOdpp) at elevated temperature (200 – 250°C) afforded heterobimetallic aryloxo complexes, either a charge separated species $[(Ln' \text{ or } Ae)_2(Odpp)_3][Ln(Odpp)_4]$ or a neutral bimetallic $[AeEu(Odpp)_4]$.[1]

$$2(Ln' \text{ or } Ae) + Ln + 7\ HOdpp \longrightarrow [(Ln' \text{ or } Ae)_2(Odpp)_3][Ln(Odpp)_4] + 3.5\ H_2$$

Ln' = Yb, Eu; Ae = Ca, Sr, Ba
Ln = Nd, Sm, Ho, Tm, Yb, Y

$$M + Ae + 4\ HOdpp \longrightarrow [AeM(Odpp)_4] + 2\ H_2$$

M = Eu, (Sr)
Ae = Ca, Sr, Ba (Ba)

The products were structurally characterized. The $[(Ln' \text{ or } Ae)_2(Odpp)_3]^+$ cation in the ionic heterobimetallic compounds is unusual in that it consists solely of bridging aryloxide ligands (e.g. Fig. 1).

As a result of the absence of additional donor ligands, the crystal structures of the heterobimetallic complexes feature extensive π-Ph-metal interactions involving the pendant phenyl groups of the Odpp ligands, enabling the large electropositive metal atoms to attain coordination saturation. A novel feature was the purification of many charge separated heterobimetallic species by extraction with toluene under pressure above the boiling point of the solvent. In donor solvents, the heterobimetallic complexes other than those containing barium were found to fragment into homometallics species. From analogous syntheses $[MEu(Odpp)_3]$ (M = Na, K) bimetallics have been prepared and structurally characterized.

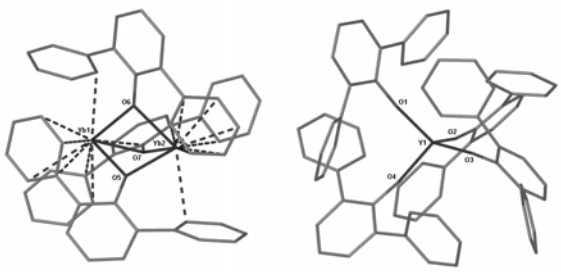

Figure 1. Structure of $[Yb_2(Odpp)_3][Y(Odpp)_4]\cdot 2PhMe$

References

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Lanthanide chemistry with dual functional ligand systems containing low valent Group 14 elements

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Keywords: Lanthanides; Chemistry; Organometallics; Synthesis

Since the last decades neutral tris(pyridyl) ligands have received considerable interest in coordination as well as organometallic chemistry. While most of these ligands reported to date consist of nonmetallic Main Group elements in the bridgehead position, only some examples are known containing Main Group metals.[1,2] Moreover, in studies of tris(pyridyl) ligands of Group 14 elements the anionic tris(organo)plumbate in $[LiPb(2\text{-py})_3(thf)]$[2b] is the only example of a low oxidation state Group 14 tris(pyridyl) ligand so far. In principle, besides a κ^3*N*-coordination by the pyridine rings the lone pair of electrons on the bridgehead metal centre of such a functionalised anionic ligand system $[E(2\text{-py})_3]^-$ (E = Sn or Pb) could be used for subsequent metal coordination, making this ligand system interesting, particularly in view of its potential dual functionality.

Herein we report on the reactivity of such anionic tris(pyridyl) derivatives like $[E(2\text{-}C_5H_3N\text{-}5\text{-}Me)_3]^-$ (E = Sn, Pb) towards selected lanthanide metal organic compounds.

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Highly Active Hydrosilylation Catalysts Based on Early Rare-Earth Metals Complexes

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Keywords: Lanthanides; Chemistry; Organometallics; Synthesis

Hydrosilylation catalysis is currently relying on platinum metals which are problematic due to toxicity and expense. Most of the precatalysts based on early lanthanides were not accessible until now because of the instability of the tri(alkyl). The thermal stability of the tri(allyl) [Ln(η^3-C_3H_5)(dioxane)$_m$] of lanthanum, cerium, praseodymium, neodymium and samarium offers new possibilities for precatalysts.[1,2]

A new class of non-metallocene catalyst precursors, containing a 1,ω-dithiaalkanediyl-bridged bisphenolate ligands (OSSO) with early rare-earth metals could be obtained.[3] The allyl-bisphenolato complexes [Ln(η^3-C_3H_5)(OSSO)(thf)$_n$])] (Ln = La, Ce, Nd, Sm) are obtained by reaction of the tri(allyl) [Ln(η^3-C_3H_5)$_3$(dioxane)$_m$] with the diprotonated ligand *via* elimination of propene.

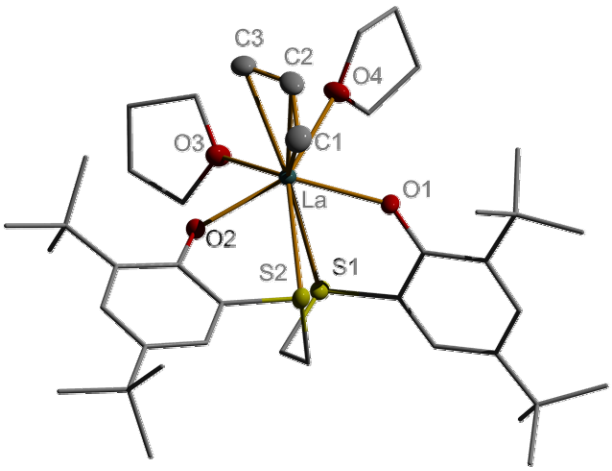

Figure 1. Diamond-picture of [La(η^3-C_3H_5)(OSSO)(thf)$_2$], hydrogen were omitted for clarity.

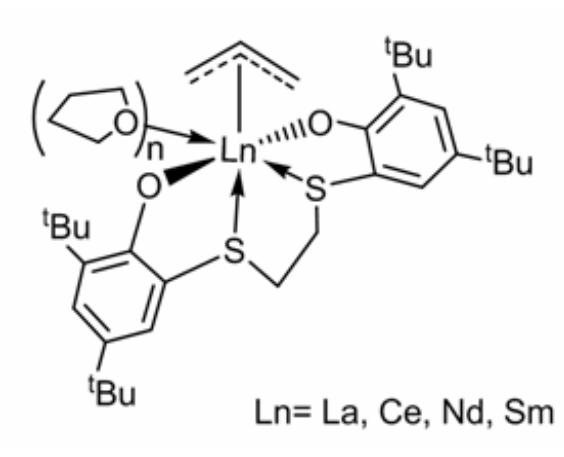

Figure 2. [Ln(η^3- C_3H_5)(OSSO)(thf)$_n$])] (Ln = La, Ce, Nd, Sm)

Allyl-bisphenolato complexes of the early lanthanides show high activities as precatalysts in the hydrosilylation of styrene.

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Aminopyridinato Ligand Stabilized Lanthanide Alkyl Complexes and Their Use in Polymerization of Ethylene and Isoprene

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Keywords: Lanthanides, Organometallics, Polymerization

The aminopyridinato ligands used thus far for the stabilization of lanthanides have exhibited a relatively low steric demand.[1] This restricted the ability of corresponding metal complexes to form stable bis(alkyl) complexes. To overcome this, bulkier aminopyridinato-ligands can be used, for example, by the introduction of 2,6-isopropylphenyl substitutents at the amido nitrogen and the 6-position of the pyridine ring.[2]

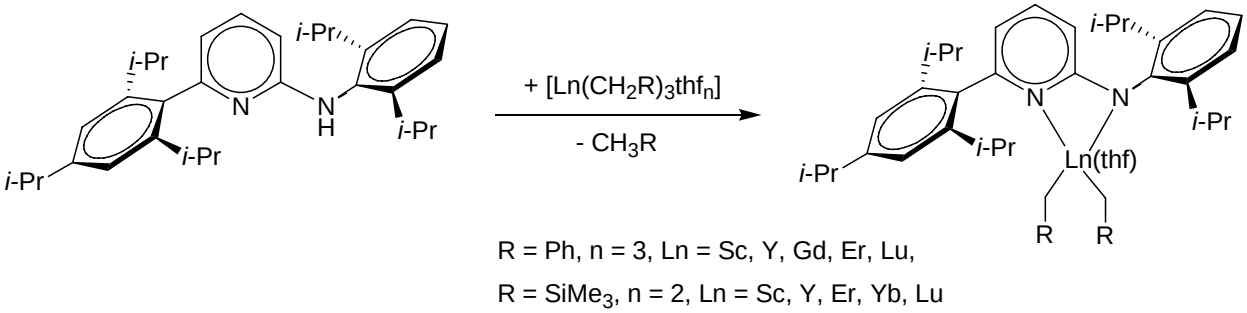

Figure 1. Synthesis of aminopyridinato stabilized lanthanide complexes.

Aminopyridinato stabilized lanthanide alkyl complexes can be obtained by reacting $[Ln(CH_2SiMe_3)_3(thf)_2]$[3] (Ln = Sc, Y, Er, Yb, Lu) or $[Ln(CH_2Ph)_3(thf)_3]$[4] (Ln = Sc, Y, Gd, Er, Lu) with one equivalent of the aminopyridine ligand (Figure 1). These lanthanide alkyl complexes are active precatalysts for the polymerization of ethylene[5] in the presence of perfluorinated borate ($[R_2NMeH][B(C_6F_5)_4]$, R = $C_{16}H_{31}$-$C_{18}H_{35}$) and aluminum alkyls (aluminoxanes). Under similar conditions these complexes polymerize isoprene in a 3,4-selective fashion.

Herein, we present our investigations to control the selectivity and activity of the polymerization reactions through variation of both the aminopyridinato ligand and the metal center.

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Imidazolin-2-iminato Complexes of Rare Earth Metals with Very Short Metal-Nitrogen Bonds – Experimental and Theoretical Studies

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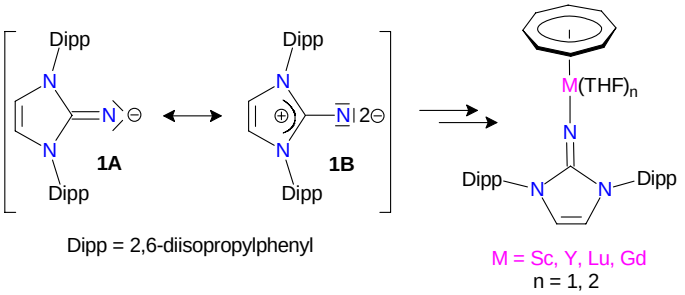
Keywords: Lanthanides; Theory; Organometallics; Synthesis

Organoimido complexes of the transition metals have been extensively studied in the past because of their important role in a number of biological, industrial and catalytic processes.[1] In stark contrast to the large number of imido complexes containing d-block elements, the imido chemistry of the f-elements is much less developed, and reports on well-defined lanthanide imido complexes are scarce. More specifically, structurally characterized lanthanide complexes containing terminal imido groups are unknown to date, since the imido group is generally found to bind in a capping or bridging fashion. The situation is similar in organogroup 3 metal chemistry despite several efforts to isolate terminal scandium imido complexes.[2]



Scheme 1. Mesomeric structures for the imidazolin-2-imide **1**; imidazolin-2-iminato rare earth metal complexes.

Coordination of the formally dianionic imido ligand $(NR)^{2-}$ as a terminal ligand involves a metal-nitrogen multiple bond consisting of one σ and either one or two π interactions.[3] This resembles the bonding in transition metal complexes containing monoanionic imidazolin-2-iminato ligands such as $Im^{Dipp}N$ (**1**), which can be described by the two limiting resonance structures **1A** and **1B** (Scheme 1), indicating that the ability of the imidazolium ring to stabilize a positive charge leads to highly basic ligands with a strong electron donating capacity towards early transition metals.[4] Because of their ability to act as 2σ,4π-electron donors, these ligands can be regarded as monodentate analogues of cyclopentadienyls, C_5R_5, and also as monoanionic imido ligands in a similar fashion to that described for related phosphoraneiminato ligands.[5] Therefore, lanthanide complexes with terminal imidazolin-2-iminato ligands, as presented in this contribution, might serve as models for elusive mononuclear lanthanide imido complexes, and their structural investigation could lead to a better understanding of lanthanide-nitrogen multiple bonding.[4,5]

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Lanthanide Chemistry with Unusual Ligands

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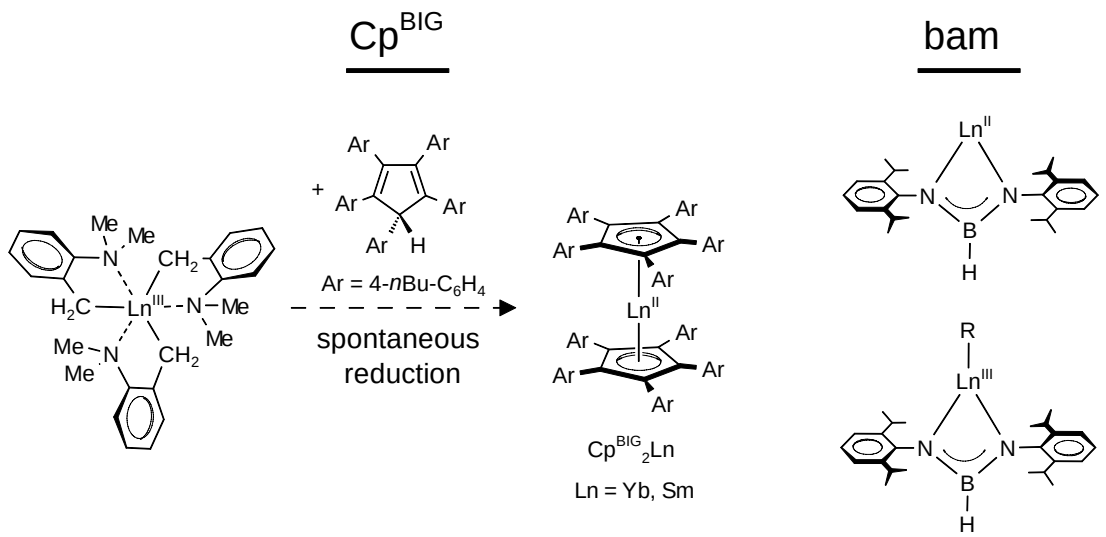
Keywords: Lanthanides, Organometallics

Despite the easy accessibility of pentaphenylcyclopentadiene (Ph_5CpH), the organometallic chemistry of this ligand has been hardly explored. This is mainly due to the extreme insolubility of its complexes which also hinders crystallization of its complexes. These problems can be circumvented by slight modification of the ligand (substituents in the aryl ring greatly increase the solubility) [1-4] or by modification of the synthetic procedure [5]. We recently reported on a new superbulky cyclopentadienyl ligand, $(4\text{-}n\text{Bu-}C_6H_4)_5Cp$, which we abbreviated as Cp^{BIG} [4] and forms complexes that are highly soluble even in hexane [4, 6, 7]. The lanthanide(III) chemistry of this particular ligand turned out to be surprising: spontaneous reduction from the +3 towards the +2 state was observed not only for Yb but also for Sm. Syntheses and properties of the metallocene complexes $(Cp^{BIG})_2Ln^{II}$ (Eu, Yb, Sm) are discussed.



We recently discovered a very convenient route to the unprecedented bora-aminidate ligand (*bam* [8]) (DIPP)NH-BH-HN(DIPP) which in its doubly deprotonated form acts as a dianionic ligand that is isolobal to the well-investigated amidinate ligands [9]. Whereas the Cp^{BIG} ligand protects the metal center to a very high extent and enables the stabilization of the +2 oxidation state, coordination of a dianionic *bam* ligand would lead to very poor metal protection. We here discuss lanthanide(II) and lanthanide(III) complexes with this particular ligand system.

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Efficiency of ligands fitted with phosphoester or phosphonate *vs* carboxylate groups in the sensitization of lanthanide-centred luminescence

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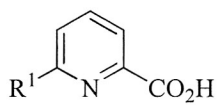
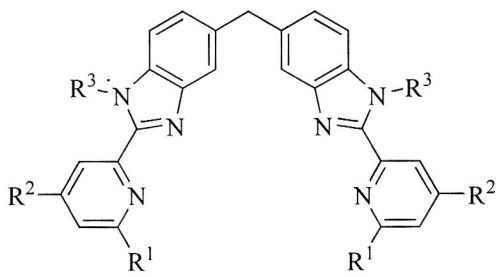
Keywords: Lanthanides; Chemistry; Coordination (incl. Supramolecular); Synthesis, Spectroscopy

The coordination ability of ligands fitted with phosphonate groups is well documented for d elements, and to a lesser extend for Ln ions. For the latter, carboxylates are often used as coordinating units in water solutions. Replacing a carboxylic acid by a phosphonate or phosphoester group can have dramatic effects regarding the coordination ability of the ligand, as well as the photoluminescence properties of its Ln complexes.
Two series of ligands were then developed, one of them being derived from picolinic acid, the second one from hexadentate ditopic receptors incorporating benzimidazole moieties [1-2]. For the second series, polyoxyethylene arms were introduced on the benzimidazole backbone for two of the ligands, in order to increase their solubility. 6-Substituted picolinic acid ligands yield stable 1:3 Ln:L complexes, while ditopic ligands form triple- stranded homobimetallic helicates, as ascertained by mass spectrometry and UV-visible titrations. The helicates display large thermodynamic stability with $\log\beta_{23} \approx 21$-24 for the Eu^{III} complexes. Photophysical measurements reveal adequate sensitization of the metal-centred luminescence in the europium and terbium complexes, which is modulated by the nature of the ligand. The lifetimes of the metal-centred excited states are long and reach values up to 4.5 ms, with hydration numbers equal to zero and with quantum yields as high as 25 % in water for europium complexes. The synthesis of the different ligands and their complexes, as well as their photophysical properties are detailed and compared to those of carboxylic acid-containing ligands [1-3].





$R^1 = CO_2H$	**DPA**	$R^2 = H, R^3 = Me$	$R^1 = PO(OH)(OEt)$	$\mathbf{L^{POEt}}$
$R^1 = PO(OEt)_2$	**DEPPA**		$R^1 = PO(OH)_2$	$\mathbf{L^{P}}$
$R^1 = PO(OH)(OEt)$	**MEPPA**	$R^2 = H,$		
$R^1 = PO(OH)_2$	**DHPPA**	$R^3 =$	$R^1 = CO_2H$	$\mathbf{L^{C3}}$
			$R^1 = PO(OH)(OEt)$	$\mathbf{L^{P3OEt}}$
			$R^1 = PO(OH)_2$	$\mathbf{L^{P3}}$

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Highly Luminescent Europium Complexes

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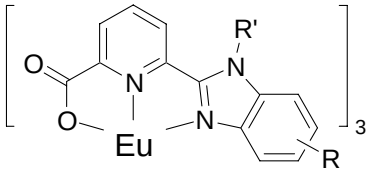
Keywords: Europium; Chemistry; 9-Coordination; Luminescence

A facile synthesis of benzimidazole-substituted pyridine-2-carboxylic acids has been developed. These tridentate ligands efficiently sensitize europium luminescence in homoleptic neutral nine-coordinate complexes with overall quantum yields and lifetimes reaching 73% and 3.0 ms, respectively, in solid state at ambient conditions [1]. The simple modification of the ligands opens the way for incorporation of their complexes in electro-/luminescent materials.



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Can weak noncovalent interactions affect the energy transfer processes in lanthanide compounds with heterocyclic diimines?

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Keywords: Lanthanides; Physics; Coordination; Spectroscopy

Weak noncovalent forces (hydrogen bonding, aromatic π–stacking interactions, charge-transfer attractions, etc.) are a subject of intensive study as a new approach of developing materials science. 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) as well as their complexes with transition and 4f metals are able to form various supramolecular architectures by these interactions [1]. Moreover these interactions can noticeably influence the photophysical properties of the resulting edifices by creating additional excited states.

A series of lanthanide complexes with different numbers of hererocyclic diimines, namely bpy or phen, chloride ions, and water molecules in the inner coordination sphere were investigated with the aim of relating their molecular geometry and crystal packing to the efficiency of ligand-to-metal energy transfer. Deciphering the luminescence properties of the Eu and Tb complexes needs to take into account both the composition of the inner coordination sphere and the peculiarities of the crystal packing. For instance, in addition to the classical ligand→Eu charge-transfer state (LMCT), another charge-transfer state induced by π-stacking interactions (SICT) was identified. These two states, located between the singlet and triplet states of the bpy ligands, provide relays facilitating the energy migration from the singlet to the triplet states and eventually to the excited Eu states, improving the overall ligand-to-Eu energy transfer. Another point is the involvement of the inner-sphere water molecules in H-bonding with chloride ions, which considerably lowers their luminescence quenching ability, so that the adducts remain highly luminescent. For instance, the terbium chloride with 2 bpy ligands is an efficient near-UV-to-green light converter, with an overall quantum yield equal to 37% despite the coordinated water molecules. The interpretations given are substantiated by topological analysis of the electron density distribution derived from the high-resolution X-ray diffraction data and by TD-DFT theoretical calculations of the complexes and ligand assemblies [2].

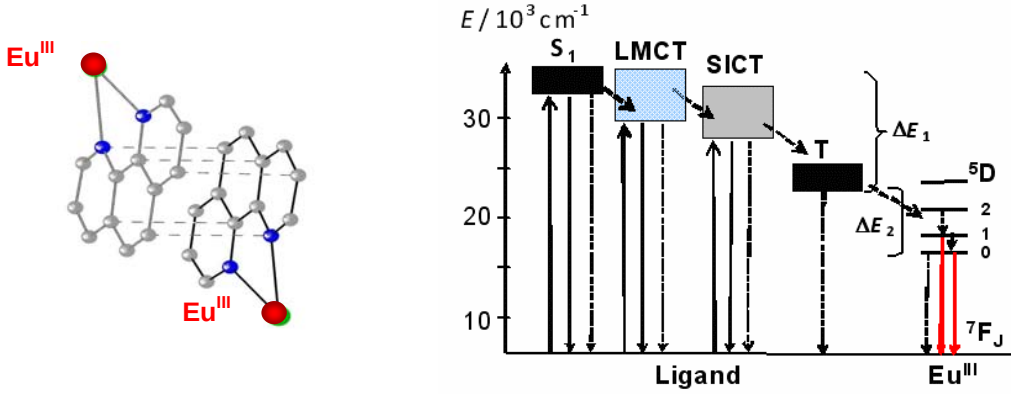

Figure 1. -stacking interaction between 1,10-phenantroline ligands in Eu chloride (left) and simplified diagram of energy migration processes in this complex (rigth)

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Chemiluminescence and Electrochemiluminescence of fluorochinolone systems containing Tb(III) ions

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Keywords: Lanthanides; Spectroscopy; Chemiluminescence; Energy Transfer

Fluoroquinolones (FQ) are synthetic chemotherapeutic agents used to treat severe and life threatening bacterial infections.

This paper concerns the use of chemiluminescence, CL, and electrochemiluminescence, ECL, methods in studies of fluorochinolones, such as ciprofloxacin, norfloxacin and ofloxacin. Spectral and kinetics studies of CL and ECL were performed using the home made system for ultraweak emission measurements based on single photon counting, as descried earlier [1]. Recently we have shown that the chemiluminescent method based on Eu(III) emission in the reaction system containing antibiotics (tetracycline) and Eu(III) ions can be successfully used for the determination of derivatives of tetracycline in various media [2].

Chemiluminescence studies of fluoroquinolones were carried out with the use of the following reaction systems in acidic solution: FQ-$KBrO_3$-H_2SO_4; FQ-KNO_2-H_2O_2-H_2SO_4; FQ-Fe(II)/(III)-H_2O_2-HCl, in the absence and presence of Tb(III) ions. In the ECL method the reagents were electrochemically generated on the Al/Al_2O_3 cathode. As the coreactants the aqueous solutions of $K_2S_2O_8$, K_2SO_4 and H_2O_2 were used. The systems of: KNO_2-H_2O_2-H_2SO_4 and Fe(II)/(III)-H_2O_2 (Fenton system) are the source of reactive forms of oxygen, such as peroxynitrous acid, hydroxyl radicals and singlet oxygen. Introduction of Tb(III) ions into the systems: FQ-$KBrO_3$-H_2SO_4 and FQ-Fe(II)/(III)-H_2O_2-HCl caused a strong increase in chemiluminescence intensity.

ECL observed in FQ solutions in the presence of Tb(III) ions has shown significant influence of coreactant on the emission intensity. In the system containing hydrogen peroxide the observed ECL intensity was 1,5 order of magnitude higher than that with other coreactants.
The results of spectral analysis from CL and ECL have shown that main emitters in the reaction mixtures are the Tb(III) ions, with the emission maximum at λ~545 nm, corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition.

However, it has been observed only an insignificant influence of pH on the spectrum and effectiveness of the ECL process. In strong acidic solutions fluoroquinolones do not form complexes with the Ln(III) ions. A lack of emission of Tb(III) in the systems: Tb(III)-$KBrO_3$-H_2SO_4; Tb(III)-KNO_2-H_2O_2-H_2SO_4 and Tb(III)-Fe(II)/(III)-H_2O_2-HCl, as well as results obtained from conventional spectrofluorimetry have shown that the excitation of Tb(III) in the analysed reaction systems: Tb(III)-FQ-$KBrO_3$-H_2SO_4; Tb(III)-FQ-KNO_2-H_2O_2-H_2SO_4 and Tb(III)-FQ-Fe(II)/(III)-H_2O_2-HCl as well as in the ECL systems, is a result of energy transfer from the oxidation products of fluoroquinolones to the uncomplexed Tb(III) ions.

In the Fenton system containing ciprofloxacin as a fluoroquinolone (Tb(III)-ciprofloxacin-Fe(II)/(III)-H_2O_2-HCl) the measured integrated CL intensity is linearly dependent on the concentration of ciprofloxacin. This observation can be applied for analytical purposes.

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Approaches towards f-d and f-p heterodinuclear helicates

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Keywords: Lanthanides, Chemistry, Coordination, Spectroscopy

Lanthanide coordination chemistry is important in order to obtain well defined compounds in which the properties of the metal center can be influenced by the complexed ligand. In this respect dinuclear (and especially heterodinuclear) compounds allow the investigation of cooperative effects between different metal centers.

Piguet and Bünzli [1] investigated a highly interesting ligand system which enables the formation of heterodinuclear d-f and f-f' helicates in which three ligand strands are wrapping around the metals. Following a related approach, we could obtain heterodinuclear d-f and p-f helicates in which discrimination between the metal centers occurs by different denticity of two connected metal binding sites. For this purpose, ligands were used which are based on 8-hydroxyquinoline and catechol binding sites. The complexes are fomed in self-assembly processes and were structurally as well as spectroscopically investigated.[2,3]

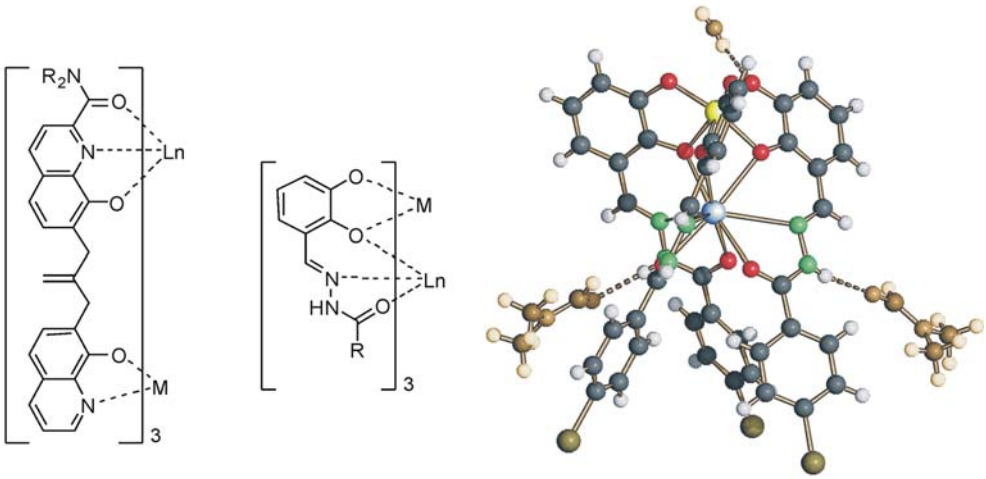

Figure 1. Heterodinuclear lanthanide containing triple stranded helicates based on 8-hydroxyquinoline and catechol binding sites at the ligands.

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Application of f-Element Photonic Materials for NIR Biophotonics

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Keywords: Rare Earth; Near Infrared; Bioimaging; Nano Phosphor; Ceramics

Fluorescence bioimaging (FBI) is one of the most important method for biological researches and medical diagnosis to visualize spacial distribution and transient movement of substances in biological systems as multi color images. Major problems of the current FBI are shallow observation depth due to scattering, color fading of the organic phosphors, auto-fluorescence to give background and damage to biological objects, which are mostly caused by the irradiation of short-wavelength excitation light such as UV or blue light to give visible fluorescence. On the other hand, the fluorescence may not be "visible" since most of the bioimaging are carried out by using CCD camera. Therefore, the near infrared (NIR) FBI is attracting interests in the fields of biological and medical research.

Rare-earth doped ceramics have been applied as laser or optical amplifier media for decades. 1064-nm emission under 800-nm excitation from Nd:YAG is used for one of the most popular solid state lasers. 1550-nm emission under 980-nm excitation from Er^{3+} doped in silicate glass fiber is used for optical amplifier in optical communication. Those applications are originated from the characteristic electronic states of 4f electrons, narrow energy bands and weak electron-phonon coupling, as a fruits of the shielding effects by the outer-lying filled 5s and 5p shells.

The author's group has applied rare-earth doped ceramic nano-phosphors (RED-CNP) for the NIR-FBI. We have focused to use the 1550-nm emission under 980-nm excitation of Er^{3+} ions doped in Y_2O_3 or YPO_4, though the use of f-elements are not limited to them. The whole project started from the fluorescence scheme design in atomic scale, RED-CNP fabrication and their surface modification with bio-functional polymers in nano-scale, development of cellular imaging (Figure 1) in micron-scale and that of *in vivo* imaging in millimeter to meter scales (Figure 2). As for the academic knowledge, it has been carried out all of the physics, chemistry and biology combined with various engineering studies [1].

The author will present whole of the project works including some demonstrative works, such as digestive tube imaging of both nematodes in micron-scale and mouse in millimeter scale.

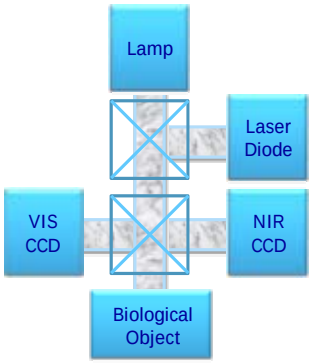

Figure 1. micron-scale NIR FBI system.

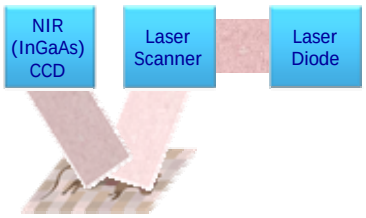

Figure 2. *in vivo* NIR FBI system.

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A Highly Spin Concentrated Solid for Quantum Memories

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Keywords: Spectroscopy; Materials; Applications

Quantum memories (QM) are able to store and retrieve faithfully quantum states of light. They are especially interesting for extending the range of communications using quantum cryptography by allowing long distance entanglement. To adapt to existing quantum cryptography schemes, especially those using conventional optical fibers, a strong interest has raised in solid state QM. Rare earth doped crystals are promising candidates for this purpose since these ions can exhibit hyperfine coherence lifetimes up to 30 s as well as long optical coherence lifetimes. However, up to now, most experiments on QM protocols in rare earth doped crystals have been performed in Pr^{3+}:Y_2SiO_5, a host with a very low magnetic moment density, which favors long coherence lifetimes.

In this paper, we will present results obtained in Pr^{3+}:$La_2(WO_4)_3$, which exhibits a high magnetic-moment density. Although the latter could seriously affect Pr^{3+} coherence lifetimes, a long nuclear-spin coherence lifetime of 250 µs has been observed, as well as electromagnetically induced transparency (EIT), which is a QM protocol [1]. This suggests that a broad range of materials could be considered for quantum memories for light. Absorption and dispersion curves are independently in very good agreement with EIT theory. Fano-like profiles have also been observed.

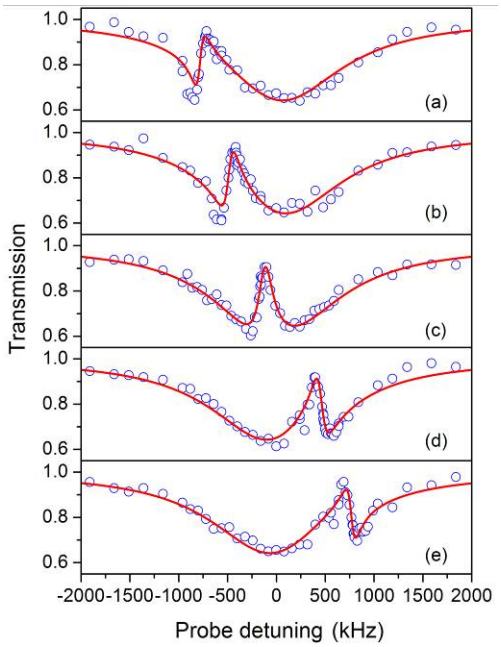

Figure 1. Electromagnetically induced transparency in Pr^{3+}:$La_2W_3O_{12}$ for various detunings of the coupling field. Open circles: experimental data, solid line: fitted model.

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Luminescence of Dy^{2+} and Nd^{2+} Ions

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Keywords: Lanthanides; Spectroscopy; Dy^{2+}; Nd^{2+}

While the luminescence properties of relatively stable divalent lanthanides, like Eu^{2+} and Yb^{2+}, are investigated for several times, spectra of more unstable divalent ions are only available in a very bad quality[1,2] and thus not suitable to get any information about the position and nature of the electronic states, especially 5d levels. The reason for this is the rather difficult preparation and handling of these compounds. While former works describe the preparation of the samples by irradiation with X-rays or simply heating of the trivalent ions our preparation route is different. First we synthesized the binary compounds, e.g. $NdCl_2$ and $DyCl_2$, which can be directly added to the starting materials of the host lattice, which are melt to get the doped compounds. The samples obtained with this procedure are at very high quality, in most cases without any amount of trivalent lanthanide ions.

In this work we present several host lattices doped with Dy^{2+} and Nd^{2+}. For Dy^{2+} 4f → 4f ($^5I_{5,6} \rightarrow {}^5I_8$) emission bands are observed for most of the host lattices (MX_2, M = Sr, Ba, X = Cl, Br; MFCl, M = Ca, Sr, Ba, $SrZnCl_4$), in some cases in high resolution. This can be explained by the fact that the 5d levels are positioned slightly above 4f states. For $KMgF_3:Dy^{2+}$, however, the 5d levels are shifted in this way that high and low spin 5d → 4f emission bands could be detected in a surprisingly high number and diversity (Fig. 1).

In the case of Nd^{2+} 4f → 4f ($^5F_1 \rightarrow {}^5I_{4,5,6}$) emission bands are observed exclusively due to the high density of 4f states, but excitation and reflection spectra showed intense 4f → 5d transitions. With these results we were able to estimate the position of the 5d states relative to 4f ground states at higher energies than expected by theoretical calculations.[3]

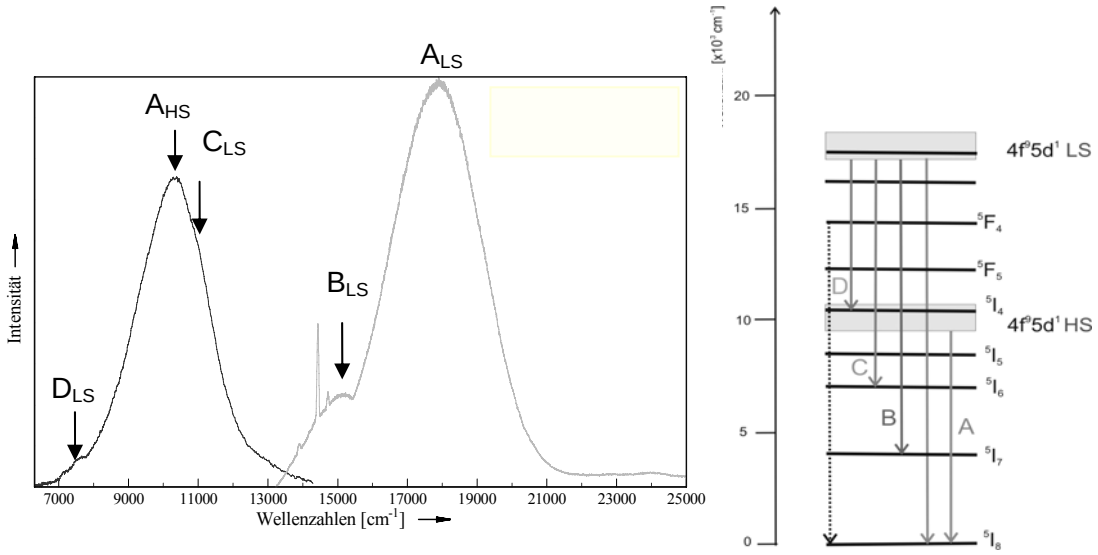

Figure 1. Emission spectrum of $KMgF_3:Dy^{2+}$ at 10 K.

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The Role of Spectroscopic Properties and Physical Processes in Solid State Lasers Based on f-Element ions

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Keywords: Physics; Materials; Spectroscopy ; Solid State Lasers

This paper and the lecture deals with the unique spectroscopic properties and the photo-physical process occurring within the well-shielded 4f-levels of rare earth ions. The various quantum-mechanical interactions among the f-levels (including crystal field effects) generate new energy sublevels capable of emitting spontaneous photons in a myriad number of wavelengths, with a spontaneous lifetime ranging from ms to μs time regime.[1] This lifetime scale is appropriate for efficient laser emission as well as energy storage and Q-switching operation, leading to high peak power laser performance. The crystal field effects and the phonon energies of the lasing host have crucial role in energy distribution within the f levels and the emission wavelength.

Energy transfer processes and excitation migration contribute to the laser performance and will be discussed with that context.[2]

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Luminescence and magnetic features from nanosized europium doped gadolinium oxide

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Keywords: lanthanides, materials, solid state, spectroscopy

Lanthanide (Ln)-containing compounds have been extensively used as high-performance phosphors, devices, catalysis, and other functional materials based on the electronic, optical, and chemical characteristics arising from their 4f electrons.[1,2] The processing of Ln-based materials in the form of nanotubes, as e.g. $Ln(OH)_3$ (Ln=Ce, Tb, Dy), LnO_3 (Ln=Ce, Tb), and $M_2O_3:Eu^{3+}$ (M=Y, Gd) affords highly functionalized materials as a result of both shape-specific and quantum size effects.[3-5] There is a growing interest in understanding how size-dependent quantum confinement affects the photoluminescence efficiency, excited state dynamics (including radiative and non-radiative lifetimes), energy-transfer and thermalization phenomena in nanophosphors.[3] Here, we wish to describe and discuss the photoluminescence features of $Gd_2O_3:Eu^{3+}$ nanotubes (0.16, 1.00, 3.30 and 6.65% Eu^{3+} concentration) and nanorods (3.30%) synthesised using different annealing conditions. These materials exhibit a remarkable anomalous thermalization effect, one order of magnitude larger than that previously reported for similar $Gd_2O_3:Eu^{3+}$ (3.96%) nanotubes.[3] This anomalous thermalisation effect is discussed on the basis of phonon confinement in nanocrystals. Excitation and emission spectra (recorded between 10 K and room temperature) show that the Eu^{3+} ions in the Gd_2O_3 host occupy two distinct crystallographic sites, with C_2 or S_6 symmetry. In the excitation spectra a broad band localized at 255 nm and ascribed to Eu^{3+} charge transfer states (CTS) is discerned. Selective site excitation spectra monitored at 580.4 nm (C_2) and 582.4 nm (S_6) show that the CTS of Eu^{3+} ions in S_6 site symmetry occurs at shorter wavelengths than that of ions locate in the C_2 site symmetry, an effect attributed to a shorter Eu-O bond in the S_6 symmetry. An unusual energy transfer from to $Eu^{3+}(C_2)$ to $Eu^{3+}(S_6)$ was detected in the nanotubes (3.30%-6.65%). For values up to 0.15 ms, the $^5D_0$ (C_2) decay curves of the nanotubes (0.16 and 1.00%, 394.4 nm excitation) are characterized by a risetime, associated with the contribution from the $^5D_1$ level (decay time around 100 μs). The maximum emission quantum yield (QY) of the nanotubes is 0.59, 30% lower than the value measured for the microcrystals. This is attributed to the increase of the non-radiactive decay channels due to a higher surface-to-volume ratio. Average magnetic susceptibility, arising from Gd^{3+} ions in both C_2 and S_6 local symmetries, was also monitored in the nanomaterials as a function of the temperature and magnetic field strength.

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Surprising Luminescent Properties of the Polyphosphates $Ln(PO_3)_3$:Eu (Ln = Y, Gd, Lu)

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Keywords: Lanthanides; Chemistry; Solid State; Spectroscopy

Crystalline compounds of rare-earth metals with condensed anions are of broad interest as possible host lattices useful for optical applications like white LEDs or with xenon plasma driven tubes and displays [1].

In recent contributions we shed light on the crystal chemistry of the polyphosphates $Ln(PO_3)_3$ with Ln = Sc, Y, Gd…Lu [2,3]. While $Lu(PO_3)_3$ and $Gd(PO_3)_3$ adopt normally ordered acentric and centrosymmetric crystal structures, respectively, the structures of the phosphates $Ln(PO_3)_3$ with Ln = Y, Tb…Yb are incommensurately modulated at room temperature, i. e. acentric β-$Ln(PO_3)_3$. Therefore these polyphosphates allow a comparison of the fluorescence in very similar host lattices which are only different in the size of the crystallographic site and the crystal symmetry.

Hence we investigated the optical emission properties of the polyphosphates $Ln(PO_3)_3$ (Ln=Y, Gd, Lu) doped with europium. The incommensurately modulated β-$Y(PO_3)_3$:Eu (super space group Cc(0|0.364|0)0) and $Gd(PO_3)_3$:Eu (space group $I2/a$) show basically the usual emission characteristics of Eu^{3+}. In $Gd(PO_3)_3$:Eu only a single significant emission at 622 nm appointed to the hypersensitive emission $^5D_0 \rightarrow {}^7F_2$ is found which gives a very pure red emission. In $Lu(PO_3)_3$:Eu (space group Cc) the europium is unprecedentedly reduced to the divalent state and gives a broad emission band at 406 nm excited at 279 nm. An explanation for the emission behaviour of the three different host lattices is given.

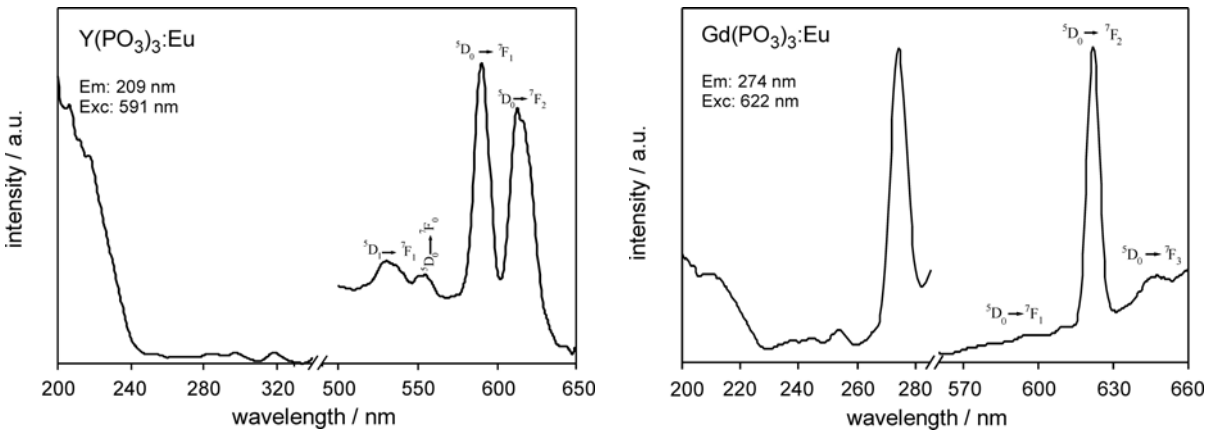

Figure 1. Excitation and emission spectra of $Y(PO_3)_3$:Eu (left) and $Gd(PO_3)_3$:Eu (right).

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Solid-phase nonspecific binding sensors

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Keywords: Nonspecific binding, Lanthanides, Applications, Sensors

Specific binding to a particular molecule is always accompanied with nonspecific binding. This nonspecific binding may severely limit the applicability and sensitivity of a specific assay and is usually considered as an undesired property. The nature of nonspecific binding is broad and varies based on the conditions of a particular assay. The magnitude of the nonspecific binding is dependent on the molecule of interest and the assay configuration. The binding strength (affinity) of such nonspecific binding can even exceed that of specific interactions and e.g. surface-based adsorption phenomena are practically irreversible leading to infinitely high affinities. Here we show how this undesired binding phenomena can be put into use and utilized in developing novel high sensitivity assays.

We have constructed sensors based on nonspecific interactions and competitive adsorption of sample molecules and labeled proteins on solid-phases [1,2]. These sensors rely on the use of lanthanide(III) chemistry and time-resolved fluorescence detection. A variety of particles have been utilized as solid support in bioaffinity assays - the ability to modify the particle properties makes them a versatile tool in assay development. In separation-free fluorescence resonance energy transfer (FRET) assays, Eu(III) chelate incorporated particles have been used as donors due to their high binding capacity and high specific activity. The orientation of individual donors and acceptors is not a limiting factor since the availability of multiple acceptor fluorophores within the FRET range enables efficient sensitization. Eu(III) nanoparticle based sensor have been applied to the determination of protein total concentration and cell counting as well as to size analysis of proteins and non-polypeptidic compounds.

Specific detection suffers from the conceptual problem of specificity – only known and selected species can be detected. We have investigated an array-like detection of multiple species of molecules by nonspecific means in order to fingerprint samples of different origin. This versatile detection relies on lanthanide(III) chemistry and is applied to the detection of water and wine samples. Different red wines and vintages were efficiently separated by the technique as well as drinking water from different raw water sources.

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Changing the local coordination environment in mono- and bi- metallic lanthanide complexes through "click" chemistry

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Keywords: lanthanides; chemistry; molecular; spectroscopy

Lanthanide complexes have considerable potential as *in vivo* imaging agents, as their properties permit them to be used in Magnetic Resonance Imaging (Gd)[1] and luminescent assays.[2] We are interested in the syntheses of polymetallic complexes under kinetic control, using kinetically stable building blocks.[3] We investigated the scope of the "click" (copper catalysed [3+2] cycloaddition between alkynes and organic azides) reaction for the obtention of such polymetallic lanthanide complexes. The synthesis of alkyne appended lanthanide complexes will be described as well as their use in "click" reactions with organic azides to give mono- and bimetallic complexes. The spectroscopic properties of the resulting complexes will be presented.

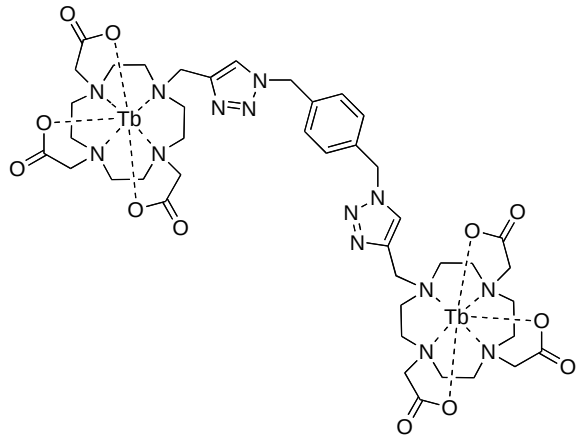

Figure 1. bimetallic triazole appended terbium complex

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Luminescent Lanthanide Dendrimer Complexes for Biologic Imaging in vivo

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Keywords: Lanthanide; Luminescence; Coordination; Imaging

Fluorescence and luminescence are detection techniques that possess important advantages for bioanalytical applications and biologic imaging: high sensitivity, versatility and low costs of instrumentation.

A common characteristic of biologic analytes is their presence in small quantities among complex matrices such as blood, cells, tissue and organs. These matrices emit significant background fluorescence (autofluorescence), limiting detection sensitivity. The luminescence of lanthanide cations has several complementary advantages over the fluorescence of organic fluorophores and semiconductor nanocrystals, such as sharp emission bands for spectral discrimination from background emission and long luminescence lifetimes for temporal discrimination. In addition, several lanthanides emit near-infrared (NIR) photons that can cross deeply into tissues for non-invasive investigations and that result in improved detection sensitivity due to the absence of native NIR luminescence from tissues and cells. The main requirement to obtain lanthanide emission is to sensitize them with an appropriate chromophore.

An innovative concept for such sensitization of lanthanide cations is proposed herein; the current limitation of low quantum yields experienced by most mononuclear lanthanide complexes is compensated for by using larger numbers of lanthanide cations and by maximizing the absorption of each discrete molecule, thereby increasing the number of emitted photons per unit of volume and the overall sensitivity of the measurement. To apply this concept, we are developing a family of dendrimer-naphthalimide ligands that are able to incorporate several lanthanide cations. Polyamidoamine (PAMAM) dendrimers have been chosen as a basis for these complexes because the oxygen atoms of the amido groups located along their branches can bind and protect the lanthanide cations inside the dendrimer core.[1] Derivatives of naphthalimide groups, required for the sensitization of the lanthanide cations, are located at the branch termini. Our synthetic approach allows facile modification of the dendrimer complex for control over photophysical properties and solubility. It also provides for the attachment of different types of targeting agents such as peptides, oligonucleotides or proteins, as well as other sensing agents, to provide functionality to these compounds in a broad range of applications.

In this paper, we will present several examples of luminescent polymetallic lanthanide complexes based on a generation-3 PAMAM dendrimer. This polymetallic lanthanide complex has been successfully tested as a luminescent reporter in living cells and small animals.

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Bioconjugation of Luminescent Lanthanide Helicates and its Applications.

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Keywords: Lanthanides; Bioinorganic chemistry; Bio-conjugation, Bio-imaging

Luminescent lanthanide bioprobes (LLB) are generating a great interest as diagnostic tools in medicine and for the follow-up of therapy [1]. Their long lifetimes, long excitation wavelengths and line-shape emission, among others features, allow to overcome problems intrinsic to commercially available organic fluorophores, such as autofluorescence or photobleaching. Moreover, the development of LLBs opens the door to using new available technologies such as time-resolved detection and multi-photon excitation.

Directing a luminescent tag towards a specific targets such as cancerous cells can be performed by its covalent conjugation to the corresponding biomolecule. Here avidin is coupled to the LLB and the bioconjugate is then attached to a biotinylated antibody taking advantage of the strong avidin-biotin interaction. Alternatively, properties such as membrane permeability, extremely important in intracellular delivery of many therapeutic and diagnostic agents, can also be modified by the same strategy, for example using cell permeable peptide (CPPs) [2] such as Tat-peptide bioconjugated to the luminescent tag.

Herein we present a highly thermodynamically and kinetically stable lanthanide helicate [3] modified to covalently link biomolecules such as proteins or peptides. Synthesis and applications of the luminescent europium bioprobes will be presented and its potentiality discussed.

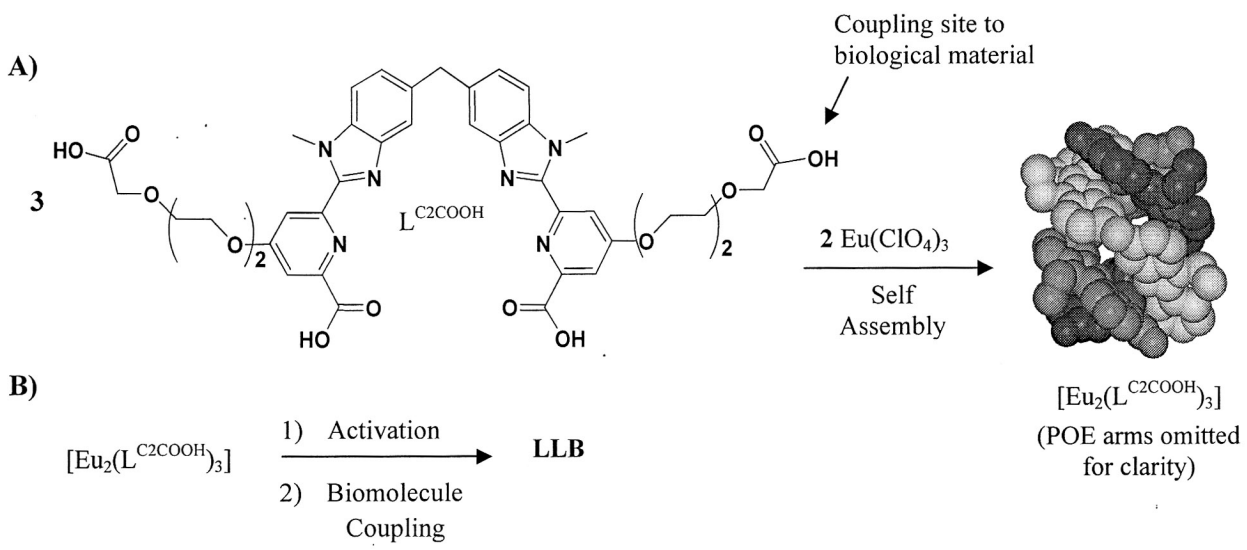

Figure. A) Chemical structure of L^{C2COOH} and self assembly process, B) Synthesis of the bioconjugated lanthanide helicates, LLB.

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A polyvalent approach to luminescent lanthanide biomarkers

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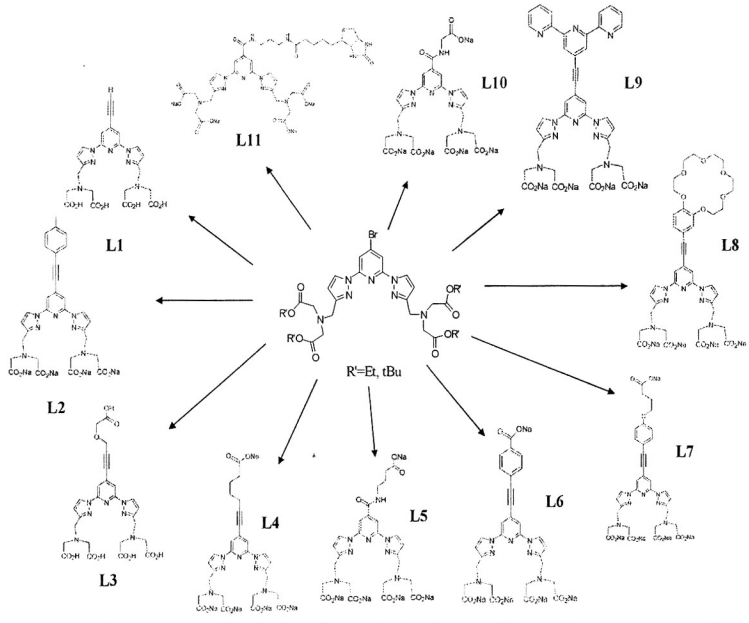
Keywords:

The ever growing interest in luminescent lanthanide biomarkers for applications as bioprobes,[1] for biphotonic applications[2] or for highly sensitive time-resolved fluoro-immunoassays[2] still rely on the development of new probes and complexes each reaching specific requirements.

The choice of the ligand acting as antenna must then be governed by the matching of the intermediate ligand centered excited states with that of the targeted emitting lanthanide cation. This generally requires the synthesis of the proper ligand for each specific lanthanide. Furthermore, an efficient luminescence can only be obtained by an optimal protection of the cation from solvent molecules including water. Finally, a targeted use of luminescent lanthanide complexes will also require the synthetic input of a specific function to integrate the complex into a functional molecular device, *e.g.* a grafting function, for biolabeling applications, or a recognition site, for sensing and detection. Up to now, the fulfillment of all these requirements is only achieved by a specific synthetic design of the ligand fitted to the selected lanthanide cation.



In our recently developed synthetic approach,4 the ligand design offers diverging pathways providing first an efficient complexation site, which can then be functionalized at will to tune the required electronic properties and/or to introduce specific functions.

Using this new methodology, we'll show that a broad scope of highly luminescent lanthanide complexes with visible and Near InfraRed emission can be obtained, and used for various applications such as biolabelling for luminescence microscopy or time-resolved fluoro-immunoassays.

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Emissive Lanthanide Complexes: In Vitro and In Cellulo Applications

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Keywords: Lanthanides; Chemistry; Coordination; Spectroscopy

Summary A series of over 75 emissive lanthanide(III) complexes has been prepared designed to report on the local environment by modulation of spectral form, lifetime or circular polarisation. These responsive complexes have been used for the *in vitro* analysis of key bioactive species (pH, pO_2, pX) in various biological fluids and for real time microscopy applications in viable living cells. A key aspect has been the application of ratiometric methods, analysing the relative intensity of two emission spectral bands for europium complexes, or examining both Eu and Tb complexes of a common ligand [1,2].

The emission spectral form of Eu(III) complexes is sensitive to changes in the local coordination environment, arising from reversible coordination of certain anions to the metal centre in aqueous media. The affinity of the anion for the metal centre can be modulated in several ways including variation of overall complex charge, variation of the steric demand at the metal centre and the introduction of reversibly bound donors into the ligand structure. Complexes have been defined that can signal changes in bicarbonate, lactate and citrate based on this approach, Fig. 1 [3,4]. For example, citrate analyses in less than 1μL samples of prostate fluid samples have been made and results correlated with enzymatic measurements, seeking to correlate the reduction of citrate with progression of prostate adenocarcinoma.

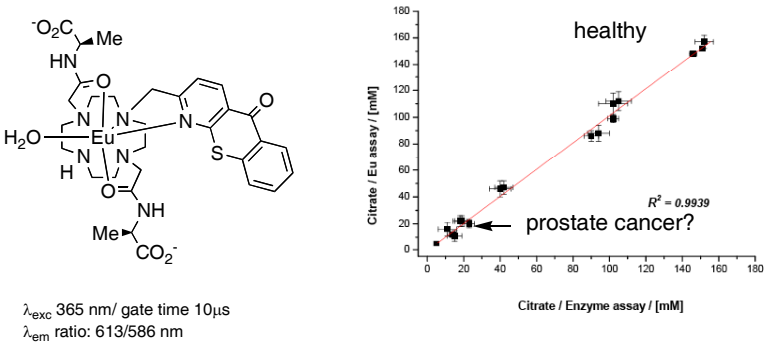

Figure 1 Structure of the Eu(III) complex used to selectively bind citrate in prostate fluid samples

Following our inital reports of the use of lanthanide probes as stains for cells in 2002/3, these emissive complexes may also be used as cellular probes. The complexes have been shown by inhibition, promotion and co-staining experiments to enter the cell by macropinocytosis [5]; the probes are trafficked to different cell compartments following protein recognition. It is the constitution and linkage mode of the sensitising moiety that determines the cell uptake profile [1,6]. Use of a pH or bicarbonate responsive probe allows changes in local pH or p[HCO_3] to be followed, in real time, within the mitochondrial compartment of the living cell by confocal microscopy.

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Design and in vivo application of multimodal imaging probes

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Keywords: magnetic resonance imaging – positron emission tomography – multiple probe – dual imaging

The value of multimodal approaches to medical imaging is becoming increasingly apparent. The success of hybrid positron emission tomography – computed tomography (PET-CT) in clinical oncology is such that vendors no longer sell stand alone clinical PET scanners. Other modalities such as fluorescence tomography, magnetic resonance imaging, and single photon emission computed tomography have been combined with each other or with PET or CT. Hybrid instrumentation overcomes limitations of the single modality. For instance the low spatial resolution of PET is compensated by the higher resolution and anatomical contrast of MRI, while PET offers the sensitivity to image receptor binding and metabolic pathways inaccessible with MRI alone. Imaging probes can also combine multiple image reporters (Gd(III), positron emitter, gamma emitter, near IR fluorophore, etc) and provide an imaging readout in multiple modalities. In this presentation we will discuss potential applications of multimodal probes, challenges in their design and synthesis, and recent in vivo data using a hybrid PET-MRI system that allows for simultaneous image acquisition.

Sensing of Biologically Important Molecules using Functional Lanthanide Luminescent Gold Nanoparticles

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Keywords: Lanthanides; Coordination chemistry; Gold Nanoparticles, Sensing

Gold nanoparticles (**AuNPs**) have attracted much attention in the development of novel devices, due to their biocompatibility, unique size- and shape-dependence and optoelectronic properties.[1] Furthermore, **AuNPs** can be surface modified to achieve the introduction of a variety of recognition moieties, functional groups, etc. The purpose of this project is to combine the **Ln** unique luminescent properties and **AuNPs** to achieve luminescent sensing of biological substrates, a topic not much explored to date.[2]

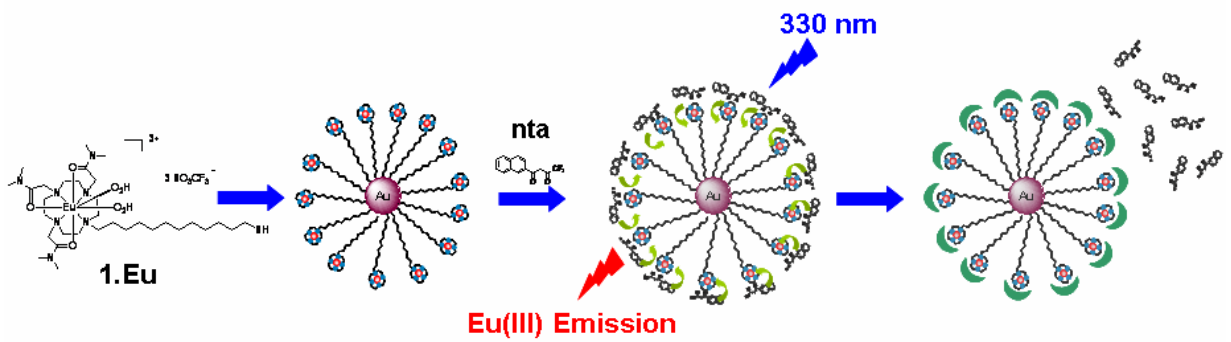

Figure 1. Displacement assay using **Ln**-based **AuNPs**.

In order to enable the incorporation of **Ln**-based cyclen complexes onto the surface of **AuNPs** and the formation of functional hybrid nanomaterials, functionalised alkyl thiol cyclen-based ligands have been synthesized, such as **1**. In complex **1.Eu**, the metal-centred emission is switched on through the formation of a ternary complex with naphthoyltrifluoroacetylacetonate (**nta**). Such complexes have been incorporated onto **AuNPs** and the resulting **AuNP-1·Eu-nta** demonstrated successful sensing of flavin monophosphate, the displacement of the antenna resulting in a significant quenching of the Eu^{III} emission.[3] The **AuNP-1·Eu-nta** system has also been tested for the sensing of larger biomolecules such as proteins. It has been observed that in presence of bovine serum albumin (BSA), the Eu^{III} emission is switched off as for flavin. These initial results open up the avenue for developing highly versatile Ln-AuNP-based sensors for targeting single molecules, as well as more challenging targets such as larger biomolecular structures where the **Ln** emission is modulated upon recognition and binding of such targets. Moreover, by simply changing the antenna, sensing using near-infrared (NIR) **Ln**-centred emission can be achieved. These NIR-emitting systems are currently being investigated in our laboratory as well as the sensing of other relevant biological molecules.
This work is supported by the Irish Research Council for Science, Engineering and Technology (IRCSET).

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Unusual Calcium Sensitivity of Aminobis(methylenephosphonate)-Containing MRI Contrast Agents

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Keywords: 1. Lanthanides; 2. Chemistry; 3. Coordination; 4. Magnetic resonance imaging.

Magnetic resonance imaging (MRI) is currently one of the most powerful tools in medical diagnosis and is strongly related to the development of paramagnetic contrast agents. These are commonly based on trivalent gadolinium which has the strong influence on the relaxation of surrounding water protons.

The objective of our study is to develop a MRI-detectable molecule for tracking the modulation in calcium, which is an excellent marker tightly linked to brain activation. Recently, our group synthesized and investigated the properties of several Ca-sensitive, smart contrast agents (SCA) [1,2]. Using a different approach than previously reported, we prepared a new series of potential DO3A-based SCAs, having alkylaminobis(methylenephosphonate) side chains. Four different ligands with propyl, butyl, pentyl or hexyl linkers between the aminobis(methylenephosphonates) and DO3A were prepared and the physico-chemical properties of their Gd(III) and Eu(III) complexes were studied.

Significant differences were observed in the longitudinal relaxivity (r_1) response of studied Gd(III)-complexes towards Ca(II) being dependant on the aliphatic side chain length. No changes in r_1 of the propyl analogue were found over the whole span of Ca(II) concentration whereas the decrease to 61% of the initial r_1 value was observed for the complex bearing hexyl linker.

Additional studies, including various NMR and luminescence spectroscopy methods, were performed on these systems in order to understand their unusual behavior. The results indicate very unique coordination properties of these complexes leading to a specific triggering mechanism responsible for the r_1 changes. These findings will be helpful for future design of novel SCA classes, as well as for their application in MRI.

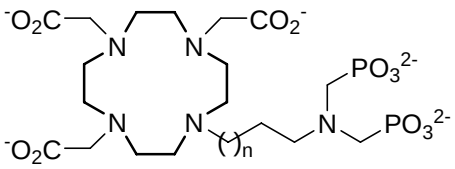

Figure 1. Structures of investigated alkylaminobis(methylenphosphonates), n=1–4.

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Incorporation of 'Click' Chemistry into Lanthanide Chelates

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Keywords:

Click chemistry using the atom efficient Cu(I) azide-alkyne cycloaddition to form 1,2,3- triazoles,[1] has been used with great effect to link many compounds of interest, such as biological molecules, glucose and nucleosides to metal chelates.[2]

Reaction of lanthanide complexes bearing pendant propargyl moieties (the alkyne) with *in-situ* generated azides (via alkyl/aryl bromides in the presence of sodium azide) was thought to be a clean, facile reaction. In our hands, this was not the case, and contrary to conventional wisdom, two products formed: the desired alkyl-triazole (Ln.1) and (Ln.2). The unsubstituted 1,2,3-triazole is readily synthesised at room temperature in the presence of sodium azide using Cu(I)-catalysed cycloaddition, conditions under which, reaction is not supposed to occur. Luminescence and ^{1}H NMR studies on the products of these reactions will be presented, and their pH-responsive behaviour will be discussed, (Ln = Eu, Gd, Tb).

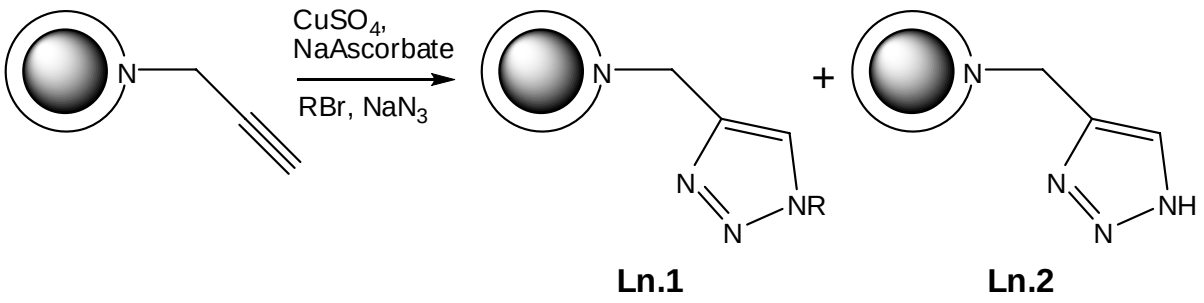

Figure 1. click reaction forming Ln.1 and Ln.2

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Self-Assembly of Polynuclear Arrays for Sensing Purposes

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Keywords: Lanthanides; Coordination; Self-Assembly; Polynuclear Complexes

A number of analytical and biomedical applications are based on exploiting luminescent and paramagnetic properties of lanthanide-containing complexes. Despite significant advances in this field, there is still an unexplored space for the response improvement.
We are interested in a controlled preparation of discrete polynuclear arrays, which would provide a significant enhancement of measured signals by adding up contributions from all cations within a discrete supramolecular complex. Advantageously, different cations may be also combined in heterometallic systems allowing the development of multimodal probes and devices with boosted near-infrared emission.
Herein, we present the self-assembly of three-dimensional tetrametallic helicates, where lanthanide cations adopt a tetrahedral arrangement.[1] These nanometric systems may be potentially used as luminescent markers. The second part deals with new trinuclear triangular complexes with a peculiar coordination mode, which stimulates a strong luminescence despite two water molecules coordinated to each Eu(III) cation.[2] X-ray crystal structures, thermodynamic, paramagnetic and luminescent properties of these remarkable supramolecular systems will be discussed in details.

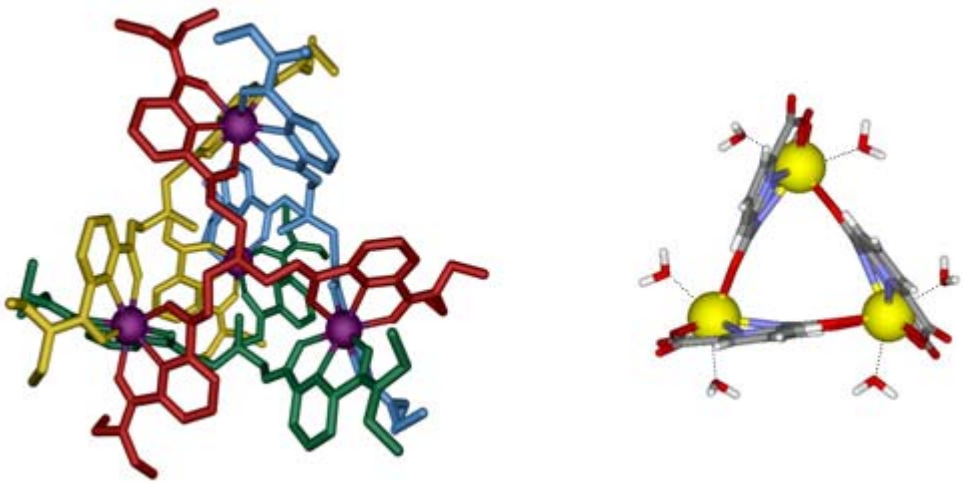

Figure 1. Crystal structures of polynuclear complexes.

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Paramagnetic liposomes as Enzyme-responsive Relaxometric agents

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Keywords: Lanthanides; MRI; Liposome; Triggered Release

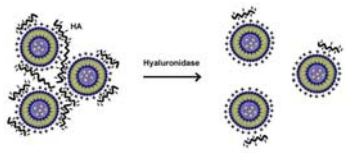
Assessment of a given enzymatic activity is an important task in Molecular Imaging investigations. When Magnetic Resonance is the imaging modality of choice it is necessary to design highly sensitive systems in order to overcome the relatively low sensitivity of this technique. Therefore we have envisaged an approach to enzyme-responsive agents based on the use of liposomes loaded with a high number of paramagnetic metal complexes. Liposomes are self-assembled vesicles formed by saturated and unsaturated phospholipids after used in drug delivery procedures. The contrast agent units (GdHPDO3A) have been loaded in the inner aqueous cavity of the liposome. The overall relaxation enhancement of solvent water protons depends upon the permeability of the liposome membrane to water molecules. The full release of the paramagnetic payload occurs with the disruption of the liposomial vesicle. Our work has addressed the objective of i) modifying the permeability of liposome membrane thus pursuing an enhancement of the observed proton relaxation rate upon the enzymatic cleavage of peptides covalently bounded to the phospholipid moieties or ii) promoting the disruption of low relaxivity aggregates formed by the binding capabilities of a macromolecular substrate that is selectively cleaved by the enzyme of interest.

As representative example of class i) systems a liposome containing a lipopeptide in its membrane will be reported. The peptide is cleaved by a specific MMP activity[1]. In class ii) the activity of Hyaluronidase is assessed by using paramagnetic cationic liposomes covered by negatively charged, high molecular weight Hyaluronic Acid (HA).

Low permeability
Low relaxivity

High permeability
High relaxivity

Figure 1. Liposomes containing a substrate for a matrix metalloproteinase have the property to release their content upon enzymatic activation, increasing the permeability of the liposomial membrane and therefore the relaxivity.



Aggregated
Low relaxivity

Disaggregated
High relaxivity

Figure 2. The activity of Hyaluronidase is assessed by promoting the disruption of low relaxivity aggregates formed by the binding capabilities of a macromolecular substrate.

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Position-Space Analysis of *TM–RE* Bonding Situations in Simple Molecules and Complex Solids

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Keywords: Theory; Electron Localizability; ELI; QTAIM

The quantum mechanical characterization of chemical bonding situations on the basis of physical descriptors based on the 1- and 2-particle density matrices in position space represents an active field of research, both, on the development and on the application side. While the topological analysis of the electron density in position space yields electron density basins serving for the quantum definition of an atom in a molecule (the QTAIM atoms) [1], the topological analysis of the electron localizability indicator (ELI-D) [2] leads to a space-partitioning into regions to be ascribed to bonds, lone pairs and inner atomic shells. In the framework of QTAIM the Laplacian of the electron density plays a special role as a local descriptor for interatomic interactions. Historically it has been considered as the physical basis for the VSEPR model [3]. Recently, this quantity has been put into a more general framework in the course of position-space decomposition analysis of ELI-D and the Laplacian of ELI-D[2g]. The specific topology of ELI-D has been shown to be a result of a competitive interplay between its two constituent functions, the electron density and the pair-volume function.

Experimentally, the number of structurally characterized stable molecular compounds with a short unsupported transition metal (*TM*)–rare earth metal (*RE*) contact is rather small. Besides the classical bimetallic complex $[(CO)_2CpRu–Lu(thf)Cp_2]$ [4] only one further example $[Cp_2Re–RECp_2]$, (*RE* = Y, Yb) [5] has been published until now. Understanding of the basic chemical bonding features of these prototype compounds not only opens the door for experimental variations of the bonding motif [6], but it also allows for deeper understanding of the more complex bonding situations *TM–RE* occurring in rare earth carbometalates $RE_nTM_mC_k$, as will be shown for $La_7Os_4C_9$ [7] and $Dy_{15}Fe_8C_{26}$ [8].

The overall bonding features can be discussed in terms of

- transition metal "lone pairs", created by the specific ligand types and arrangements, or
- transition metal–transition metal bonds

acting as e^- donor towards the rare earth atom(s) to form rather polar 2-center or polycentric donor–acceptor bonds.

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Electronic Structure of Clusters with RE or AC-Ions and Collaps of nf – Shell

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Keywords: Electronic structure; Level scheme; X ray spectra; nf-collapse

The review presents results of study of the electronic structure of solids and clusters doped with rare earths, RE and actinides, AC ions. Theoretical description based on original ab initio SCF approach for clusters and computation programs [1-2]. Experimental description focuses to study of the energy level schemes, spectra of f ↔ f, f ↔ d optical transitions and X ray spectra, too [3]. Hartree-Fock - Pauli and Dirac - Hartree-Fock systems of equations for one electron wave functions including full interactions of electrons and ions and correlation effects were developed and studied for RE: $[L]_k$ clusters. Numerical results and experimental data for optical and X ray spectra are closely correspond to each other. Study of electronic structure of nf ions in solids and clusters under pressure or diminishing RE (AC) – ligand distance reveals possibility for collapse of nf-shell and related change of the main configuration and electronic structure of the clusters [3].

It is well known that energy of X ray lines of RE and AC and other ions depends on their electronic state (valence) and environment of the ions. Powerful theoretical approach for study and calculation of the valence shift of X ray lines upon change of electronic state of nf - ions in oxides, fluoride and other compounds before and after of irradiation or thermal treatment was developed on bases of original SCF theory for clusters and solids [1-2]. Relative error for energy of X ray lines for ions in solids or clusters is less 10^{-4} % and for energy shift is order to 01.eV. For experimental study we have used X ray microanalysor as source of fluorescent irradiation and original two-crystal spectrometer tested the shape of X ray lines with accuracy 2 - 20 meV. Minimum concentration value of the doped ions which is necessary for study of the change of their electronic state upon irradiation or thermal treatment is of about 10^{-2} wt %.

In the framework of the approach we studied stability and change of electronic state of the RE and AC ions included radioactive ones, energy level schemes and spectral properties of separate bulk and clusters oxides such as A_2O_3, ABO_3 and $A_3B_2C_3O_{12}$ consist of the nf ions as host as impurity ones

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Chemical bonding pattern in lanthanide-containing systems via topological analysis of experimental charge density function

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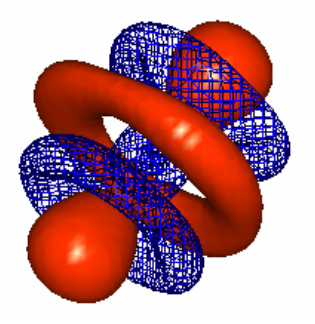
Keywords: Lanthanides, theory, structure, charge density analysis, solid state

One of the most successful approaches for investigation of interatomic interactions in crystals is topological analysis of the electron density distribution function ρ(**r**) derived from the high-resolution X-ray diffraction (XRD) data by means of Bader's "Atoms in Molecule" (AIM) theory [1]. The AIM formalism in conjunction with accurate XRD experiment allows distinguishing the binding interatomic interactions from all other contacts, directly estimating covalent contribution, charges, charge trasfer, and etc. An additional advantage of this approach is the unique opportunity to estimate the energy of the interatomic contacts on the basis of the potential energy density function v(**r**) value [2] in the corresponding bond critical point CP (3,-1). The accuracy of this approach for analysis of inter- or intramolecular interactions was tested on various classes of compounds including carboranes, high-energetic compounds, polyhydrates, metallocenes, amino acids, heterocycles, ionic liquids etc. [3].

The applicability capabilities of modern XRD technique for analysis of lanthanide-ligand bonding has been illustrated in such complexes as of Eu and Gd chlorides and nitrates with 1,10-phenantraline [4], 2,2-bipyridyl and 2-pyridineketon, as well as hydrates of triflates and nitrates of Eu, Tb and Nd (Fig. 1). The special attention was paid to the investigation of supramolecular organization (H-bonding, stecking, Cl…π and NO_3…π) affecting the charge distribution in these complexes and its manifestations in the luminescent properties.



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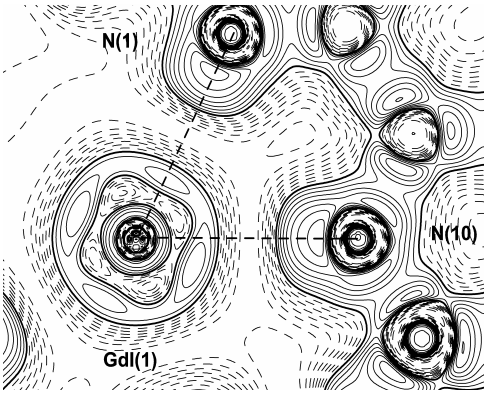

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Figure 1. Deformation electron density in vicinity of Eu atom in $[Eu(H_2O)_9](SO_3CF_3)_3$ (**A**) and ELF in $[GdCl(phen)_2(H_2O)_3]Cl_2$ obtained from X-ray diffraction data

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Rare-Earth Metal(III) Chloride *Ortho*-Oxomolybdates(VI): One Formula *RE*Cl[MoO_4] (*RE* = Y, La – Nd, Sm – Lu), but Four Structure Types

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Keywords: Lanthanides; Chemistry; Solid-State; Structure

While searching effective host materials for luminescence applications, tungstates and molybdates work their way into the focus, since doped and even undoped compounds with *scheelite*-type structures have already proven to be luminescent materials [1]. If trivalent lanthanoid cations are used as dopants, an appropriate position in the crystal structure has to be offered, and therefore, the title compounds can be considered as suitable hosts. The reaction of MoO_3 with the respective RE_2O_3 and $RECl_3$ binaries (molar ratio: 3:1:1) in evacuated silica ampoules for seven days at 850 – 900°C leads to single crystals of the respective rare-earth metal(III) chloride molybdate *RE*Cl[MoO_4], which emerges phase pure according to X-ray powder diffraction data. LaCl[MoO_4], CeCl[MoO_4], and PrCl[MoO_4] [2] crystallize isotypically with CN = 9+*1* for RE^{3+} and a distorted tetrahedral chloride environment (CN = 3+*1*). In these compounds chains of apically vertex-shared trigonal bipyramids according to ${}^{1}_{\infty}\{[MoO^{v}_{2/2}O^{t}_{3/1}]^{2-}\}$ are found as molybdate entities, rather than the expected isolated tetrahedral *ortho*-anions $[MoO_4]^{2-}$. This is no longer true for the coordination of the Mo^{6+} cations in neodymium chloride oxomolybdate [3], since there $[MoO_4]^{2-}$ tetrahedra operate as the common building blocks. But not only the molybdenum cations show smaller coordination numbers in NdCl[MoO_4], the Nd^{3+} cations with CN = 8 (slightly distorted trigonal dodecahedra) do so as well. Eventually, even the Cl^- anions reduce their coordination environment to two Nd^{3+} cations, exhibiting two different structural features. The first one is a *zigzag*-chain according to ${}^{1}_{\infty}\{[ClNd_{2/2}]^{2+}\}$, the second is an isolated planar unit of the formula ${}^{0}_{\infty}\{[Cl_2Nd_2]^{4+}\}$ as seen in figure 1. This very peculiar rhombus-shaped entity can also be observed in the chloride molybdates with the smaller lanthanides *RE*Cl[MoO_4] (*RE* = Sm – Yb) (*RE* = Sm – Lu [4]). While the typically to YCl[MoO_4] [5] in the representatives crystallize isomonoclinic system, the lutetium compound undergoes a symmetry reduction to triclinic. Although the fundamental structural setup remains rather comparable, since it also contains the aforementioned isolated rhombus-shaped cations $[Cl_2RE_2]^{4+}$ (*RE* = Sm – Lu) and tetrahedral $[MoO_4]^{2-}$ oxoanions. Although the coordination number of the lanthanoid cation in the *RE*Cl[MoO_4] series shrinks from eight for *RE* = Sm – Yb to seven in LuCl[MoO_4]. Besides their interesting structural characteristics, these rare-earth metal(III) chloride *ortho*-oxomolybdates(VI) appear to be suitable materials for luminescence applications, which can be proven by the observation of bulk luminescence for EuCl[MoO_4] (red) and TbCl[MoO_4] (green). Magnetic measurements of the representatives with lanthanoid cations bearing a large magnetic moment (*e. g.* Gd^{3+}, Tb^{3+}, and Dy^{3+}) show *Curie-Weiss* behaviour, since the metal centres are too far apart from each other for constructive magnetic interactions, although the polyhedra around the rare-earth metal trications display edge-connectivity to layers, in which the central atoms are arranged just like the As atoms in grey arsenic [6].

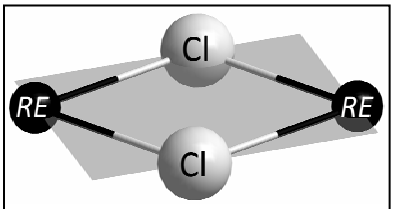

Figure 1: Planar ${}^{0}_{\infty}\{[Cl_2RE_2]^{4+}\}$ rhombus in the crystal structure of *RE*Cl[MoO_4] (*RE* = Nd – Lu)

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Crystal structures and properties of europium and samarium hydrides

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Keywords:

Rare earth hydrides such as $LaNi_5H_x$ are of use as hydrogen storage materials [1]. In general the structural characterization requires neutron diffraction in order to locate the hydrogen (deuterium) positions. In case of europium and samarium these experiments are hampered by the enormous absorption for thermal neutrons (σ_a: 5922 barn (Sm), 4530 barn (Eu) at λ = 179,8 pm [2]). By optimizing the neutron diffraction experiment, i. e. exploiting the wavelength dependence of σ_a and using annular samples on high intensity diffractometers (D4 and D20 at ILL, Grenoble), we could provide the first complete refined crystal structures of europium and samarium hydrides (deuterides) including hydrogen (deuterium) positions [3-6 and references therein].

While the hexagonal Laves phase $EuMg_2$ forms a salt-like hydride $EuMg_2H_6$ [3], its cubic congener $SmMg_2$ takes up even more hydrogen to form $SmMg_2H_7$ [4]. A gradual transition in bonding type is found in the Eu-Pd-H system, starting from ionic in binary EuH_2 via mixed ionic-covalent in Eu_2PdH_4 with homoleptical 18 electron hydridometallate complexes $[PdH_4]^{4-}$ to metallic in the perovskite type $EuPdH_3$ and finally typical interstitial in $EuPd_2H_x$ ($x \leq 2.1$) [5]. 18 electron complexes are also found in Eu_2IrH_5, in which at room temperature a K_2PtCl_6 type structure is found with five hydrogen atoms distributed statistically over the six positions of an octahedron around iridium and an order-disorder transition at low temperature [6]. Europium hydrides are ferromagnetic with Curie temperatures below 35 K, while samarium hydrides show a complex magnetic behaviour. Potential use of europium and samarium hydrides as hydrogen storage materials or phosphors will be discussed.

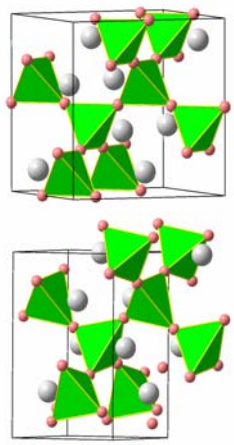

Fig. 1: Crystal structure of the cubic Laves phase $SmMg_2$ (top) and of its hydride $SmMg_2H_7$ (bottom, hydrogen atoms omitted for clarity)

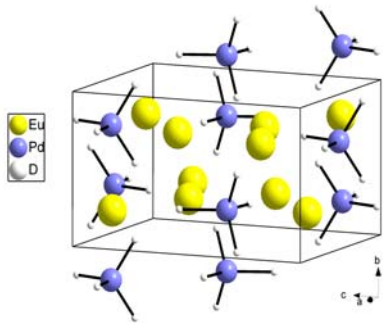

Fig. 2: Crystal structure of Eu_2PdD_4

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New Routes to Actinide Nitrides *via* Low Temperature Syntheses

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Keywords: Uranium, Nitrides, Nuclear, Neptunium

Actinide nitrides are of great interest for use in nuclear reactors due to their neutronic properties and thermal and physical stability at high temperature. Temperatures as high as 2200 °C are typically necessary to prepare high phase pure actinide nitrides using carbothermic reduction. Our recent studies of actinide nitride synthesis have lead us to examine several routes to actinide nitrides of high purity in high yields using various low temperature routes from halide and oxide starting mateials *via* amides, ammonia and trilithium nitride. The formation of thorium, uranium, and neptunium nitrides from their respective ammonium floride salts and ammonia with temperatures over 1000 °C lower than previous methods has been achieved. Metathesis of both actinide oxides and halide salts with trilithium nitride have given thorium and uranium nitrides in high yields. The utility of sodium as a concomitant *in situ* "getter" of advantageous oxygen as well as, in part, a molten solvent, facilitates the formation of uranium and thorium nitrides. Uranium nitride has also been obtained in high yield from reactions with amides in *liq.* ammonia at temperature as low as –60 °C in the initial reaction steps with subsequent formation of the nitride by heating under vacuum. The morphology of the reactant products explored by transmission electron microscope (TEM) and scanning electron microscope (SEM) will also be presented.

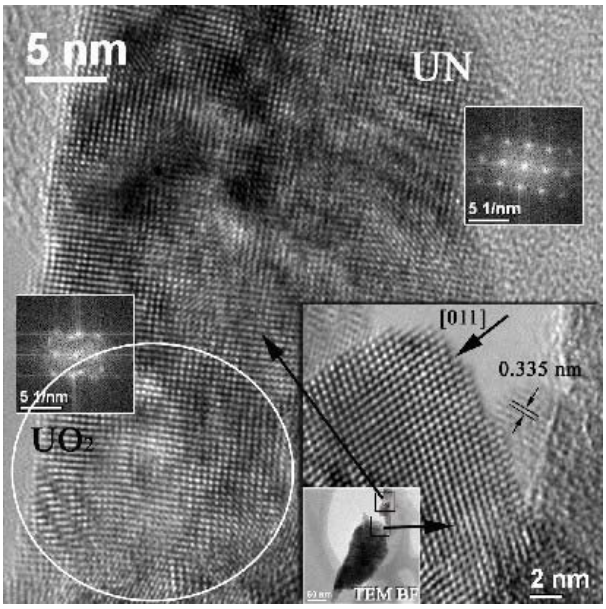

Figure 1. HRTEM (High Resolution Transmission Electron Microscope) images of two thin areas of a 25 nm thick UN nano particle (cross-sectional TEM BF image is shown) prepared using the microtome cutting method. In HRTEM images, bulk areas represent reflections due to (200) UN planes. Lattice fringe spacing (0.335 nm) due to UO_2 phase was found at one edge of the particle as indicated. Some UN areas are disrupted by UO_2 inclusions (circled), mainly at particle edges.

Coordination Chemistry of Pentavalent Uranyl: Structure and Magnetism

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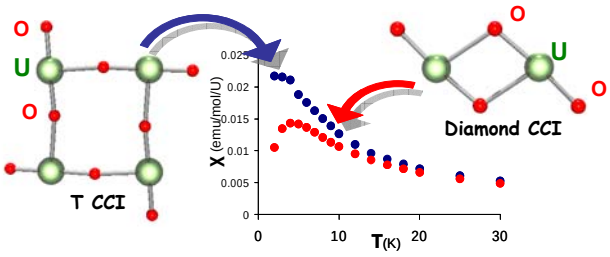
Keywords: Uranium, Cation-cation, pentavalent uranyl, assemblies, magnetism

Besides its high fundamental interest, the chemistry of actinyl cations ($AnO_2^{+/2+}$) plays a crucial role both in nuclear technology and in the environmental mobility of actinides.[1] Moreover, stable UO_2^+ complexes are ideal candidates for the development of photocatalysts and for active materials for efficient electric power storage due to the reversibility of the electron-transfer reaction $UO_2^{2+}\ldots UO_2^+$.[2] However, UO_2^+ is highly unstable in solution and, except in low pH or concentrated aqueous carbonate solutions, it readily disproportionates to form U(IV) and UO_2^{2+}.[3] Recently, in our laboratory, the controlled oxidation of trivalent uranium by a mixture of water and pyridine N-oxide allowed the easy isolation of a stable iodine complex of $U(V)O_2^+$.[4] The use of this iodide complex of U(V), $\{[UO_2Py_5][KI_2Py_2]\}_n$ as a starting material provides a very convenient route to the preparation of UO_2^+ complexes. The reaction of this complex with simple ligands such diketonate ligands or tetradentate salan type ligands allowed the formation of several UO_2^+ complexes[5] including polymetallic assemblies in which one actinyl oxo atom is coordinated as an equatorial ligand to the actinide center of an adjacent group.[6] We will present how the formation of such assemblies impacts the stability and the properties, in particular the magnetic properties, of the UO_2^+ cation.



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Impact of the softness of the heterocyclic N-donors Pyridine and Pyrazine on the selectivity for Am(III) over Eu(III)

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Keywords: Lanthanides; Actinides; Chemistry; Coordination

The separation of trivalent actinides (An(III)) from trivalent lanthanides (Ln(III)) is a key step in the partitioning and transmutation strategy, which is one of the scenarios being seriously considered for the future management of nuclear waste. It is one of the most challenging issues owing to the very similar physicochemical properties of these two series of cations. Indeed, lanthanides and transplutonium actinides both exist predominantly in their trivalent oxidation state in solution. They are hard acids in the Pearson classification with close ionic radii. Nevertheless, the higher spatial expansion of the 5f actinide orbitals with respect to the 4f lanthanide orbitals opens possibilities to discriminate them through their relative hardness, with ligands containing soft nitrogen or sulfur functionalities.[1,2]

We present here two novel tetrapodal hexadentate ligands, which bear two hard acetate groups to provide stability to the An(III) and Ln(III) complexes and two N-heterocyclic soft groups to provide Am(III) *vs* Eu(III) selectivity. The two N-heterocycles pyridine and pyrazine were chosen because their soft characters are significantly different. The two ligands L^{py} and L^{pz} only differ in their N-donor moieties and allowed us to quantify the impact of the N-donor softness onto the coordination of f-elements in aqueous solution, and in particular on the selectivity for Am(III) over Eu(III) (Figure 1).[3]

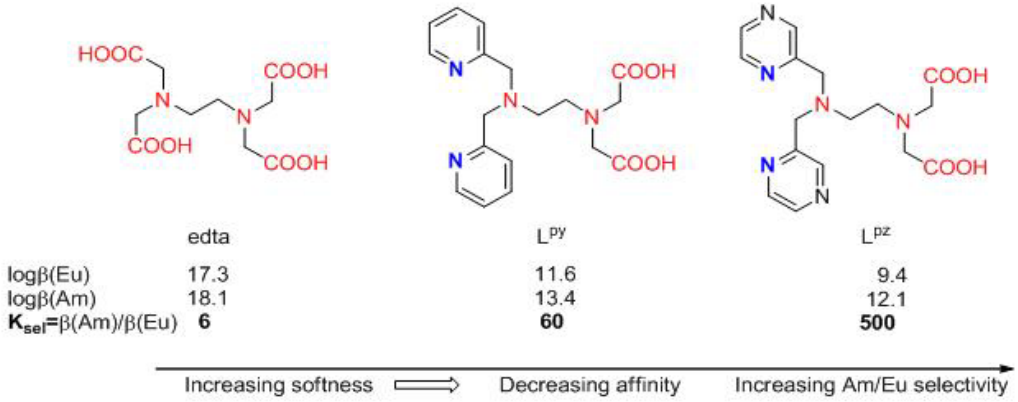

Figure 1. Complexation properties of tetrapodal ligands of trivalent f-elements

These novel tetrapodal N,O ligands present attractive selectivities that make them good candidates for the back extraction of Am(III) from organic solutions containing 4f and 5f elements. In particular L^{pz} combines a high selectivity, a low basicity and is still an efficient ligand in the conditions of back-extraction, *i.e.* at acidic pH (pH ~ 3).

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Direct Speciation of Uranyl(VI) Interaction with Carboxylic Acid N-oxides in Solution and Solid State

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Keywords: Actinides; Chemistry; Speciation; Chemometrics

Besides its nuclear properties, the hexavalent state of uranium, governed by the structural entity UO_2^{2+}, comprises a unique subject for chemical investigation [1]. The weak absorption of U(VI) at 413.8 nm and the early onset of hydrolysis are a reason for the lasting discrepancies within U(VI) aqueous chemistry [2]. The applications of multivariate chemometric techniques for direct spectroscopic speciation in combination with fluorescence and absorption spectroscopy is able to forward evidence underscored by statistical figures of merit [3]. The application of these procedures is demonstrated in the quantitative resolution of the U(VI)-isonicotinic acid N-oxide system in aqueous solution. Competitive omplexation of U(VI) by the weak acid isocicotinic acid N-oxide (isonic NO; $pK_s = 2.9$) in hydrolysed solutions resulted in a single component spectrum of the U(VI)-isonic NO species and its thermodynamic formation constant $\lg K_{11} = 2.1$. The complete measurement uncertainty ($k = 2$) is $u = 0.2$.

In the 1970s, Görrler-Walrand has forwarded an interpretation of U(VI) single component spectra in terms of the coordination geometry in the equatorial plane of the UO_2^{2+} entity [4]. This correlation was found helpful in previous work for the derivation of a single component spectrum if the dicarbonato species $UO_2(CO_3)_2^{2-}$ [5]. In order to get independent information on the coordination geometry of the bifunctional ligand isonic NO, ab initio molecular modeling using density functional theory were performed and the crystal structure of $[UO_2Cl(HisonicNO)(isonicNO)]_n$ an hitherto unknown U(VI)-isonic NO compound, was determined. Thus, the correlation proposed by Görrler-Walrand et al. can be tested using more reliable data than available in the 1970s.

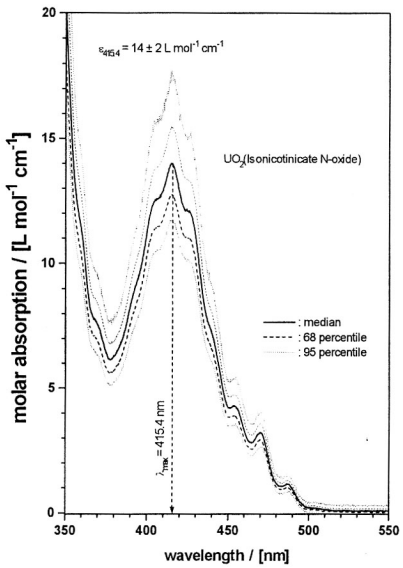

Figure 1. Single component spectrum of the U(VI) Isonicotinic acid N-oxide species

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Efficient quantum chemical valence-only treatments of actinide systems

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Keywords: Actinides; Theory

The accurate description of the electronic structure of lanthanide and actinide systems requires an inclusion of relativistic and electron correlation effects [1]. Effective core potential methods restrict the explicit quantum chemical treatment to the valence space, thus lead to computational savings compared to all-electron methods and allow a straightforward implicit inclusion of relativistic contributions [2]. Therefore effective core potentials, especially pseudopotentials, are frequently used tools in heavy element quantum chemistry.
The presentation will focus on two types of actinide effective core potentials, i.e. 5f-in-valence small core pseudopotentials as well as 5f-in-core large-core pseudopotentials, and will discuss their advantages and shortcomings in quantum chemical calculations.

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Controlling physics using precise chemical and microstructural tools

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Keywords: Lanthanides; Materials; Intermetallics; Structure and Magnetism

Intermetallic compounds of the rare earth metals (*R*) with group 14 elements (*T*) at the R_5T_4 stoichiometry provide numerous opportunities to clarify structure-property relationships, and, in the future, to exploit this knowledge [1]. The uniqueness of these compounds lies in well-defined, self-assembled layers composed of *R* and *T* atoms coupled with the flexibility to modify their arrangements in closely related structures using a variety of triggers, i.e. temperature, magnetic field, and/or presure. In this presentation we will be concerned with some recently discovered, extraordinarily interesting magnetic and electronic transport phenomena that are related to targeted structural and microstructural modifications that facilitate an unprecedented level of control over the physical behaviors of these compounds.

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The Unprecedented Magnetic Behavior of GdNi

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http://mse.iastate.edu/people/gschneidner.html

Keywords: Lanthanides; Materials; Intermetallics; Structure; Magnetism

GdNi, which has the orthorhombic CrB type structure undergoes a paramagnetic (PM) to ferromagnetic (FM) second order transition at 72K. The GdNi basically does not exhibit a volume change at PM-FM transition, but a large magnetostriction along the *c* axis. This is unique since materials with small volumes change only exhibit small magnetostrictions, e.g. Gd metal; while those with large volume changes generally exhibit large (giant) magnetostrictions, e.g. $Gd_5(Si,Ge)_4$. In this paper we describe the results of measuring the lattice parameters as a function of temperature (T) (10-300 K) and of magnetic (H) field (0 to 40 kOe). In addition the magnetic properties and heat capacity have also been studied as a function of T and H. First principle total energy calculations show that the exotic behavior of GdNi is due to an unusual interplay between magnetism and the crystal structure and accounts for the remarkable magnetostriction in this compound.

High-resolution ^{45}Sc NMR Spectroscopy: A New Technique for the Structural Characterization of Intermetallic Compounds

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Keywords: intermetallic compounds, scandium NMR, electric field gradients

To date, the NMR spectroscopy of the rare-earth elements in the solid state has been rather poorly developed. Although numerous potentially suitable NMR nuclides exist, the detection of the NMR signal is obviated by atomic paramagnetism. For those elements that are diamagnetic (scandium, yttrium, lanthanum and lutetium) the detection of NMR signals is often rendered difficult by small magnetic moments and long spin-lattice relaxation times. Recent studies in our laboratory have shown that the new class of intermetallic compounds ($RE_x\ T_yX_z$) (RE = Sc); T = late transition element; X = Si, Ge, Sn) present a host of interesting structural questions that can be successfully studied by high-resolution solid state NMR experiments. Utilizing high magnetic field strengths (11.7 T), fast magic-angle-spinning (30 kHz spin rate), and multiple-quantum excitation in conjunction with lineshape simulation procedures and quantum mechanical electric field gradient calculations, we have developed a state-of-the art solid state NMR strategy for the structural characterization of scandium containing intermetallic compounds. Our studies have resulted in the first comprehensive ^{45}Sc NMR data base on $RE_x\ T_yX_z$ materials and reveal the unique ability of scandium single and double resonance solid state NMR to resolve and quantify crystallographically distinct sites, to characterize their local bonding symmetries and to provide information about electronic properties via Knight shift measurements. In particular, the comparison of electric field gradient information extracted from the NMR spectra with theoretically calculated values using the WIEN2k code serves for the validation of proposed crystal structures and for NMR peak assignments in compounds having multiple scandium sites. These and analogous results obtained for the other rare-earth isotopes suggest that NMR has become a powerful new technique for addressing structural issues relating to positional or occupational disorder, local distortions, and superstructure formation in crystalline intermetallics, with possible extension to amorphous materials.

Pressure effects on the structural and magnetic properties of the $RCrO_4$ oxides (R= rare earths)

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Keywords: Lanthanides; Synthesis; Crystal structure; Magnetism; Magnetic structure

RXO_4 compounds, where R stands for a rare earth element and X= P, As, V and Cr; crystallize in two structural types depending on the size of the R and X elements. In the case of the lighter rare earths, they present the monazite-type structure, space group $P2_1/n$, while the remaining oxides of these families of compounds crystallize with the zircon-type structure, space group $I4_1/amd$. Although arsenates, phosphates and vanadates have been extensively studied because of their very interesting properties, however the studies concerning the analogous $RCrO_4$ oxides are scarce. Recently, $RCrO_4$ oxides have received renewed interest and the structural and magnetic properties have been reported [1,2].

In this work, the structural zircon-scheelite phase transition induced by pressure in this family of oxides is reported. In this sense, when the zircon-type $RCrO_4$ oxides are treated under high pressure and temperature conditions, i.e., 40 Kbar and about 770 K they transform into scheelite-type structure, space group $I4_1/a$. These new scheelite polymorphs show a very different magnetic behaviour when are compared with the ferromagnetic zircon forms. In the case of scheelite-type $RCrO_4$ (R= Tm, Er, Ho and Tb) the bulk magnetic measurements indicate that they behave as antiferromagnetic with Néel temperatures about 27, 23, 24 and 29 K, respectively. Besides, a metamagnetic transition induced by the magnetic field (2.6 T) has been observed for the scheelite-type $TbCrO_4$ oxide. The change of the sing of the magnetic interaction has been explained taking into account the different pathways R-O-Cr through which the magnetic interactions take place in these two structural types. Finally, the analyses of neutron powder diffraction data at low temperature, Figure 1, corresponding to the scheelite forms have allowed us to determine the magnetic structures. These can be described on the basis of wave vector **k**= (0,0,0) with both the magnetic moments of R^{3+} and Cr^{5+} antiferromagnetic aligned along the *a*-axis (Tm, Er and Ho) or *c*-axis (Tb) of the structure.

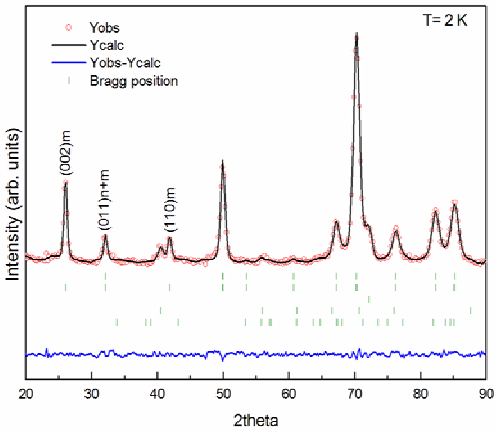

Figure 1. Observed (open circles), calculated (full line) and difference (lower full line) neutron powder profiles for scheelite-type $TmCrO_4$ at 2 K. The rows of tick marks correspond to the position of allowed nuclear reflections (first row) and magnetic reflections for the scheelite polymorph (second row), and the remaining rows denote the nuclear reflections for the minor Cr_2O_3 and $TmCrO_3$ impurities.

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Combination of Ce^{3+}-doped glass phosphor and blue/UV LED for color balance to generate smart white light

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Keywords: Lanthanides, White light; LED; Glass; Ce^{3+}

The search for efficient and tunable white light sources remains a scientific and technological challenge in our modern society [1] and WL sources based on LEDs have been proposed as promising candidates to replace the traditional fluorescent mercury lamps. One material that has been extensively studied for this propose is the phosphor Ce^{3+}:YAG, which presents a broad yellow luminescence band under blue excitation between 410 and 480nm [2]. This system is very interesting because the own radiation of the GaN-based UV-blue LEDs used for excitation, added to the yellow emission of the Ce^{3+}:YAG, with appropriate intensity, makes possible to obtain WL [3, 4]. There are few Ce^{3+}-doped crystals emitting in the yellow region, and those ones which are reported, show a broad emission band within limited visible spectral range, such as $Ce^{3+}/Li^{+}:Sr_3SiO_5$ or garnet structure materials like $Ce^{3+}:Y_3Al_5O_{12}$ (Ce^{3+}:YAG), $Ce^{3+}:Tb_3Al_5O_{12}$, (Ce^{3+}:TAG), Ce3+:$Lu_3Al_5O_{12}$ (Ce^{3+}:LuAG), $Ce^{3+}:Y_3Al_2Ga_3O_{12}$ and also $Ce^{3+}:SrY_2O_4$ [5-7].

Figure 1 (a) Emission vs. Excitation spectra of LSCAS+2.0 mol % CeO_2. (b) White light spectrum of LSCAS+2.0 mol% CeO_2 excited under 405nm blue LED.

We present the first glass-doped with Ce^{3+} able to produce yellow light when excited in the blue region with high emission efficiency. Because of this special property, this glass has a high potential to produce white light combining a glass phosphor with light-emitting diodes. The analysis of the combined emissions of the OH^- free CeO_2-doped low silica calcium aluminosilicate glass and the 405nm blue LED using the CIE 1931 x-y chromatic diagram showed that this system presents emission close to the ideal white light and allows tenability, as shown in the Figure 1. In addition, this glass presents also important advantages over the most used crystals like easier synthesis and lower production cost. The blue emission range of the Ce^{3+}:LSCAS glass which can be easily obtained by a commercial UV LED, is also interesting for the control of circadian rhythms of humans. In conclusion, the developed glass combined with LED emission is promising for smart white lighting and therefore may contribute to improve environmental lighting and human well being [3].

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Synthesis and Room Temperature Ultraviolet Luminescence in EuS Nanotubes

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Keywords: Lanthanides; Materials; Synthesis; Structure

We report the observation of room temperature, ultraviolet (UV) absorption and photoluminescence spectra in europium sulfide (EuS) nanotubes. Nanotubes were synthesized by thermolysis of a single source precursor[1], infused into porous alumina membranes. We confirmed the formation of EuS nanotubes by high resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) analyses. The crystallinity of the as-synthesized EuS nanotubes was probed via x-ray diffraction and selected area electron diffraction analysis. Optical spectroscopy identified energy band blue shifts in the absorption and photoluminescence spectra into the UV, compared to bulk EuS. We attribute these changes to quantum confinement effects within the nanotubes' walls and strain-induced lattice deformations. [2,3]

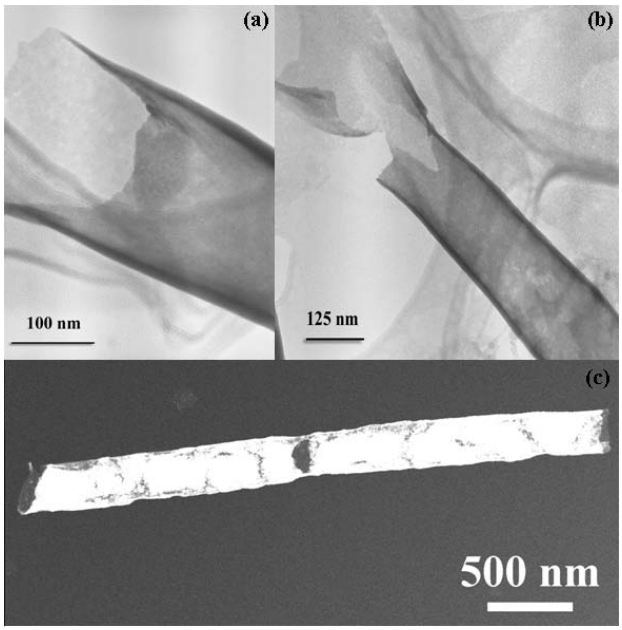

Figure 1: (a) and (b) HR-TEM images of EuS nanotubes. (c) STEM image of a EuS nanotube.

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Lanthanide carboxylates as precursors of oxide thin film materials

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Keywords: Lanthanides; Materials; Coordination; Synthesis, Structure; Oxide Thin Film Precursors

The preparation of lanthanide-containing thin film materials is a major branch of modern material engineering. Recently lanthanide coordination compounds with organic ligands find a lot of applications in this field. As an example, the films of lanthanide oxides result from the decomposition of lanthanide organic complexes (precursors) in the vapor or solution onto the surface of the substrate. Much attention has been given to design and synthesis of volatile lanthanide precursors for MOCVD applications. In the last two decades solution-based deposition routes for lanthanide oxide thin films have been developed due to their ease of incorporating multiple elements, good control of local stoichiometry, and feasibility for large area deposition. Metal-Organic Chemical Solution Deposition (MOCSD) method have been already used for preparation of lanthanide oxide thin films, however, in our opinion the design and detail characterization of soluble metal-organic precursors (MOP) have received little attention. In MOCSD method the formation of oxide film occurs according to schematic equation:
MOP(solution) $\rightarrow$ MOP(film) $\rightarrow$ oxide thin film + by-products.

To establish correlations between precursor molecule(s) composition structure, interaction mechanisms with substrate surface and composition and functional of resulting films, the composition of precursors in solution, on substrate surface and features of their thermal decomposition should be studied. Here we demonstrate some advantages of this approach to tailoring of MOCSD precursors on example of lanthanide carboxylates.

Mixed ligand and/or heterometallic lanthanide carboxylates are the most promising candidates for MOCSD precursors. Solubility and thermal stability of such compound can be varied within the requisite limits by purposeful change their ligand composition taking into consideration the features of lanthanide ions capability for coordination compound formation. The composition of new precursors in solutions and in thin films on substrate surfaces were studied by mass spectrometry. Electrospray mass spectrometry (ESMS) technique allows the direct analysis of species present in solution and reaction solutions and this method is particularly effective for studies of labile systems like lanthanide carboxylate solutions. The MALDI-TOF MS method was used for of analysis of the composition of lanthanide carboxylate thin films on substrates .

This approach has been sampled by syntheses of CeO2 buffer layers and $LnNiO_3$ (Ln = Nd, Sm) thin films. New precursors were found among mixed ligand complexes of cerium(III) carboxylates with polyglymes and aminoalcoholes, heterometallic complexes [Ni(SB)], in which nickel Schiff base complexes, Ni(SB), act as neutral donor ligands saturating the coordination sphere of the lanthanide ions in their carboxylates, $Ln(Carb)_3$. The composition features of these complexes in solutions and in the solid state are discussed, based on the data of mass spectrometry and X-ray structure analysis, and correlated with their thermal stability. The advantages of new precursors have been demonstrated in thin film deposition experiments by spin- and drain-coating techniques.

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Down-conversion in rare-earth nano-clusters for silicon solar cell efficienty enhancement

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Keywords:

One of the well-known loss mechanisms of Si solar cells is the thermalization of charge carriers generated by the absorption of high-energy photons. These losses could be reduced by using a rare-earth based luminescence converter to realize multiple electron–hole pair generation per incident photon. Incident photons with energies larger than twice the bandgap of the Si solar cell are absorbed within converter, which transforms them into two or more lower energy photons by means of energy transfer between rare-earth ions. We present here results obtained in (Pr^{3+}, Yb^{3+}) and (Er^{3+}, Yb^{3+}) codoped CaF_2 crystals showing absorption of blue light by Pr^{3+} or Er^{3+} ions followed by an efficient energy transfer towards Yb^{3+} ions which subsequently emit around 1.2eV. When trivalent rare-earth ions are incorporated in CaF_2, charge compensation is required to maintain the electrical neutrality of the system. The consequence is the unique formation of rare-earth nano-clusters in the form of pairs (or dimers) of adjacent rare-earth ions, trimers, tetramers depending on the concentration and nature of the rare-earth. The reduced distance between ions within these rare-earth clusters in CaF_2 leads to an increase of energy transfer rates by two orders of magnitude in comparison to other rare-earth doped glasses or crystals. We show that such a drastic increase in the energy transfer rates leads to a significant enhancement of the down-conversion efficiency.

Lanthanide-polymer hybrid nanoparticles prepared in miniemulsion – from nanoonions to luminescing films

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Keywords: Lanthanides; Nanomaterials; Polymer-inorganic hybrid; Miniemulsion

Lanthanide compounds as complexes, clusters or sold state materials have unique optical or magnetic properties. Some of them are difficult to process or sensitive towards the environment, thus their high potential cannot be easily exploited for any application. Incorporation of such compounds in polymeric nanoparticles can shield and protect them from environmental influence and, in the form of aqueous dispersions the hybrid nanoparticles can be very easily processed and handled.

The miniemulsion technique is a very convenient method for the preparation of polymeric nanoparticles and simultaneous encapsulation of various compounds. Taking advantage of this method it was possible to prepare hybrid particles from several hydrophobic lanthanide complexes (e.g. $Ln(tmhd)_3$), multinuclear clusters (e.g. $[H_5[M_5O_5(Ph_2acac)_{10}]$) and even micro- and nanocrystalline solid state materials (Ce:YAG). Basically, the sizes of the particles can be adjusted from 70 – 250 nm. The polymeric matrix can be prepared from a wide variety of monomers or monomer mixtures (e.g. styrene, acrylates or copolymers) suitable for the desired application.

The nature of the incorporated material and the polymer determine the internal structure of the particles and their properties. With several β-diketonato-lanthanide complexes, internal onionlike or pillarlike layered structures of the inorganic component and the polymeric matrix could be observed. Without the possibility for further coordination, the complex will be dispersed throughout the polymeric matrix. Here, detailed studies were performed on the encapsulation of several hydrophobic multinuclear rare earth clusters. Up to 10 wt% of the complexes could be embedded in polystyrene or poly(butylacrylate-*co*-methylmethacrylate) (PBA-*co*-PMMA). Aqueous dispersions of polystyrene based hybrid nanoparticles as well as dispersions and films prepared from PBA-*co*-PMMA based nanoparticles exhibited similar optical properties as the pure complexes.

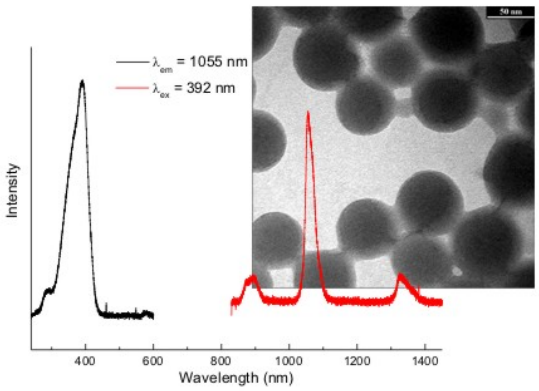

Figure 1. Luminescence spectrum and TEM micrograph of $[H_5[M_5O_5(Ph_2acac)_{10}]]$/polystyrene hybrid nanoparticles

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Synchrotron Radiation Studies of Rare Earth Persistent Luminescence Materials

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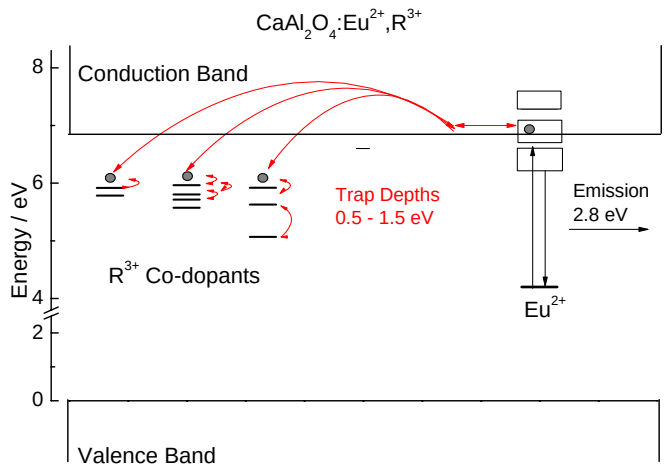
Keywords: Persistent Luminescence; Calcium Aluminate; Europium, Synchrotron Radiation

The persistent luminescence materials have been known and exploited for hundreds of years since the beginning of the 17th century – or even earlier - thus presenting the oldest documented form of luminescence [1]. Despite the long history of the materials, the understanding of even the mere basics of the phenomenon itself has not achieved the same level. Practically no progress occurred earlier than the mid 1990s prior to the advent of the commercial exploitation of the modern and efficient aluminate based persistent luminescence materials [2].

In preventing the deeper understanding of the persistent luminescence mechanism(s), there seem to be several critical issues which can possibly be cleared with the Synchrotron Radiation (SR) studies. For instance, the relationships between the energy levels of the $R^{2+/3+/IV}$ ions, the lattice defects and the electronic band structure of the host lattice are not well-known. Neither are identified the possible changes in the valence state of the dopants (e.g. Eu^{2+}, Ce^{3+}, Eu^{3+} or Tb^{3+}) during the different persistent luminescence processes.

In the present work, these problems are addressed to with the SR study of the Eu^{2+} doped and R^{3+} co-doped calcium aluminate ($CaAl_2O_4$:Eu^{2+},R^{3+}) persistent luminescence materials. The UV-VUV excited luminescence yields the relationships between the energy levels of the (co-)dopants and the electronic host band structure and gives strong evidence of the existence of lattice defects in the materials.



Further, the presence of the $Eu^{2+/3+}$ and $R^{2+/3+/IV}$ ions are probed by the SR X-ray absorption methods (XANES and EXAFS) at different temperatures. In addition to the experimental determination of the hosts' electronic band structure, a simultaneous theoretical study has been carried out with the density functional theory (DFT) calculations. Eventually, a self-consistent persistent luminescence mechanism (Fig.) is suggested based on these experimental and theoretical results in agreement with previous results [3].

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Non-centrosymmetric ammonium rare-earth nitrates $(NH_4)_2RE(NO_3)_5 \cdot 4\ H_2O$: Crystal growth and optical properties

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Keywords: Lanthanides; Materials; Solid State; Other (Optical Properties)

In the group of alkali metal rare-earth nitrates the potassium compounds $K_2RE(NO_3)_5 \cdot 2\ H_2O$ (*RE* = La, Ce), that crystallize with non-centrosymmetric space group symmetry *Fdd*2 [1,2] possess remarkable nonlinear optical properties [3,4]. Our recent analysis of the optical properties of the rubidium rare-earth nitrates tetrahydrates, $Rb_2RE(NO_3)_5 \cdot 4\ H_2O$, that are known to crystallize in the space group *Cc* [5-7], proves the attractivity of these crystals for optical frequency conversion as well. In spite of the centrosymmetric space group *C*2/*c* given in literature (e.g. [8,9]) for the corresponding ammonium compounds $(NH_4)_2RE(NO_3)_5 \cdot 4\ H_2O$ a first study on small crystals of the La and Ce compounds revealed unambiguously the occurrence of the piezoelectric and the pyroelectric effect, thus giving strong evidence for non-centrosymmetry of the crystals.

Encouraged by these results large single crystals of the colorless compounds $(NH_4)_2La(NO_3)_5 \cdot 4\ H_2O$ and $(NH_4)_2Ce(NO_3)_5 \cdot 4\ H_2O$, that serve as the basis for crystal physical investigations, were grown from diluted nitric acid at 38°C by controlled evaporation of the solvent. During a growth period of 14 weeks crystals of dimensions up to 2.5 x 2.5 x 2.0 cm^3 were obtained. In Fig. 1 an example of a grown crystal of the Ce compound is given.

Figure 1. Example of a grown crystal of $(NH_4)_2Ce(NO_3)_5 \cdot 4\ H_2O$. The region of the initial seed crystal is clearly visible in the center of the crystal, outer parts of the crystal are of optical quality.

Using the prism method precise refractive indices and their dispersion were measured in the wavelength range from 365 nm to 1083 nm. These data were used for a detailed analysis of phase matching possibilities for optical frequency conversion processes, such as second harmonic generation (SHG) and sum frequency mixing (SFM).

Additionally to these investigations, our ongoing study of the alkali metal rare-earth nitrates signals that all compounds $A_2RE(NO_3)_5 \cdot 4\ H_2O$ with *A* = NH_4, Rb, Tl and *RE* = La, Ce, Pr, Nd are non-centrosymmetric and isotypic.

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Yb-LGOB single crystal, a new promising laser material

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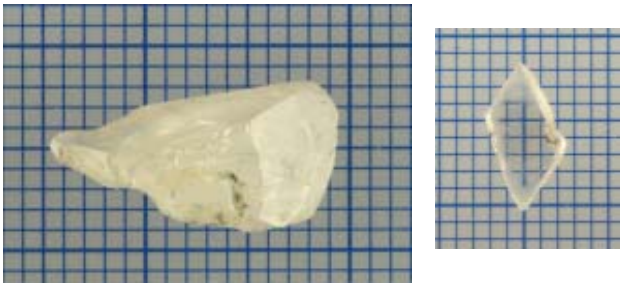
Keywords: Lanthanides; Solid State; Crystal Growth; Spectroscopy

The diversity of borate compounds provides a large accessibility to numerous materials which can be used for different applications (lighting, displays, scintillators or laser applications). In borate matrices, oxygen atoms from rare earth polyhedra can be bridging or non-bridging with Boron from $(BO_3)^{3-}$ oxoanions. In the latter case, the materials are called oxyborate [1] and provide interesting luminescent properties [2] due to chemically different Re-O bonds.
The crystallographic structure of the oxyborate $LiGd_6O_5(BO_3)_3$ (LGOB) has been solved in 1999 [1]. The cell is monoclinic (space group $P2_1/c$, Z=4) with a=8.489(4)Å, b=15.706(3)Å, c=12.117(6)Å, β=132.27(2)° (ρ= 6.706 g/cm^3). Rare earths are located in six different crystallographic positions in eightfold coordination or sevenfold coordination polyhedra.
Ytterbium ions doped materials are more and more used for laser applications, thanks to the recent development of high performance InGaAs laser diode. Ytterbium ion shows suitable properties for laser effect, like a long lifetime transition and a very simple energy level scheme (implying no parasitic effects such as excited state absorption).
To our knowledge, no LGOB centimetre-sized crystals have ever been grown.
LGOB decomposes at 1080°C with a peritectic transformation. So, we used a high temperature solution growth method. The flux was sought in the pseudo-ternary diagram Li_2O-B_2O_3-Gd_2O_3. For the first time, a satisfying size of Yb^{3+}: LGOB was grown by this method. (Figure 1 a).

a)



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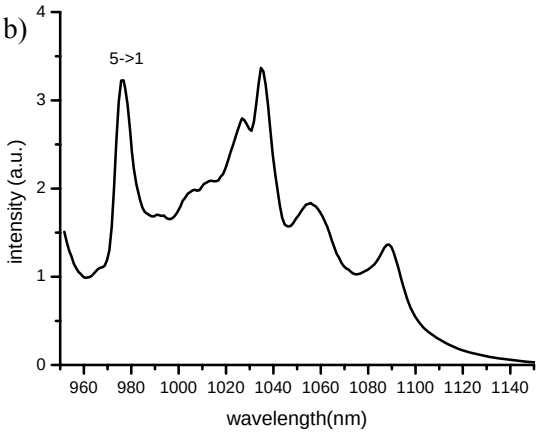

Figure 1. a) Single crystals of LGOB; b) emission spectrum of LGOB crystal excited at 932 nm at room temperature.

Transparent crystals enabled us to study spectroscopic properties, like absorption and emission of ytterbium ions in LGOB crystal, at room and low temperature (10K). Emission spectrum at room temperature exhibits several zero-phonon lines and a broad emission spectral range (from 975 to 1080 nm) (Figure 1 b), due to the distribution of ytterbium ions in several types of coordination polyhedra. This is suitable for tunable laser application or ultra short pulses laser generation.

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Structural and Optical Characterization of Rare-Earth Doped Yttrium Aluminoborate Laser Glasses and Glass Ceramics

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Keywords: Yttrium aluminoborates, laser glasses and vitroceramics, solid state NMR, optical properties

Glasses of the ternary system Y_2O_3-Al_2O_3-B_2O_3 have been introduced as interesting alternatives to single crystalline materials for special laser applications involving self-frequency doubling or self-sum frequency mixing.[1] Yet, at the present time, no detailed discussion of the structure of these glasses as a function of composition is available. In particular, the local environment and spatial distribution of the fluorescent rare earth ions in these (and other types of) glasses is completely unknown to date. Owing to its element-selectivity, its local selectivity and its inherently quantitative character, solid state NMR is an ideally suited method for providing such kind of structural information in glasses. The difficulty (and challenge) lies in the $4f^n$-paramagnetism of the rare earth ions, which broadens their NMR signals beyond detectability. A potential solution to this problem is the study of diamagnetic mimics,[2] such as yttrium ions, via NMR spectroscopy. In this contribution we introduce high resolution ^{89}Y solid state NMR as a new tool to investigate rare earth ion coordination and distribution in glassy and ceramic optical and laser materials. Despite its 100% natural abundance and spin ½ - character, the ^{89}Y isotope poses serious difficulties to solid state NMR studies owing to its low gyromagnetic ratio, resulting in low detection sensitivity and long spin-lattice relaxation times. Because of these difficulties, ^{89}Y NMR has never before been used for structural studies of glasses, to the best of our knowledge. Here we show that static and MAS-NMR spectra with excellent signal to noise ratios can be obtained by using a combination of paramagnetic doping and direct acquisition of Carr-Purcell spin echo trains. Based on such measurements, we discuss compositional trends in the local rare earth environments on the basis of chemical shift data and explore the effects of the paramagnetic dopants Nd^{3+} and Er^{3+} upon the NMR peak positions, linewidths and relaxation behavior. A detailed description of the framework structure of these glasses, based on high-resolution single and double resonance ^{11}B and ^{27}Al NMR experiments, is also developed. Furthermore, the structural information is correlated with the absorption, luminescence and excited state lifetime characteristics of these materials.

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Synthesis and optical characterization of re-dispersible Tb^{3+}– doped $GdPO_4$ crystalline nanoparticles

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Keywords: lanthanides; luminescence; nanoparticles; re-dispersible

Nanoparticles doped with lanthanide ions act as a potential candidates for many applications, such as lamp phosphors, fiber amplifiers, high-density optical storage materials and electro – luminescent display devices. [1,2]. Green-emitting phosphors Tb^{3+} doped Gadolinium phosphate ($GdPO_4$) (Tb^{3+} = 0, 2, 5, 7, 10, 20 and 30) nanoparticles are prepared at relatively low temperature of 160 °C in ethylene glycol medium. They crystallize in monoclinic structure with average crystallite size of 40-50 nm. From the luminescence study of Tb^{3+} doped $GdPO_4$ (Fig. 1), the magnetic dipole transition ($^5D_4 \rightarrow {}^7F_5$) at 545 nm (green) is more prominent than the electric dipole transition ($^5D_4 \rightarrow {}^7F_6$) 484 nm (blue).This is due to the substitution of Tb^{3+} in $GdPO_4$ with a center of symmetry. Maximum luminescence intensity and lifetime is observed for Tb^{3+} concentration of 10 at.%. With the increase in Tb^{3+} concentration, decrease in luminescence is observed. This is attributed to concentration quenching effect, due to the cross – relaxation of excited energy among Tb^{3+} ions. Excitation peaks at ~254, 274 and 320-400 nm are observed. The peak at 320-400nm is due to 4f –transition t 274nm due to of Tb^{3+}, whereas the former at 254 nm is of the 4f – 5d transition of Tb^{3+}. The peak at 274 nm is due to $^8S_{7/2} \rightarrow {}^6I_{11/2}$ of Gd^{3+}. The maximum excitation due to 4f transition of Gd^{3+} shows $GdPO_4$ as a potential host for Tb^{3+}, consequently a significant emission is obtained. These nanoparticles are re-dispersible in water, ethanol or chloroform. They can be incorporated in polymer-based materials to get the green emitting phosphors polymer film. They are also a potential candidate for biological labeling.

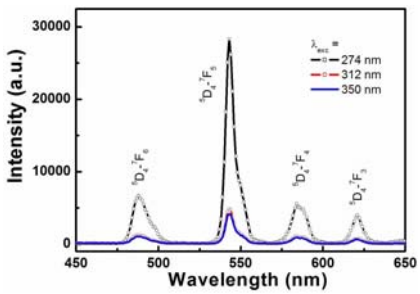

Figure 1. Emission spectra of 10 at.% Tb^{3+} doped $GdPO_4$ nanoparticles at different excitation.

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Lanthanide and Actinide Chemistry in Ionic Liquids

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Keywords: Lanthanides, Actinides, Ionic Liquids, Coordination

Ionic liquids are increasingly attracting the attention of inorganic and materials chemists.[1] The incorporation of functional groups in so-called *task-specific ionic liquids* can impart particular capabilities to an ionic liquid, such as the ability to interact with a metal center and an enhanced solubility for metal salts.[2] The dissolution process and speciation of lanthanide and actinide compounds in ionic liquids were investigated. We applied a multiple-technique approach to reveal the solvate species of the metal in solution. One example that is presented is the functionalised ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf_2N], which is able to dissolve stoichiometric amounts of rare-earth and uranium oxides.[3]

Figure 1: Dissociation of a dimeric europium(III) complex in an ionic liquid.

The crystal structures of the rare-earth complexes were found to consist of dimers. The speciation of the metal complexes after dissolution in ionic liquids was investigated by luminescence spectroscopy, ^{1}H, ^{13}C, and ^{89}Y NMR spectroscopy, and by the synchrotron radiation techniques EXAFS (extended X-ray absorption fine structure) and HEXS (high-energy X-ray scattering). The combination of these complementary analytical techniques revealed that the cationic dimers dissociate into monomers after dissolution of the complexes in the ionic liquids. Deeper insight into the coordination chemistry of metal compounds in ionic liquids is desirable for applications in the field of electrochemistry, catalysis and materials chemistry.

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Crystal Structures and Photophysical Properties of Ln(III) Complexes with Ethylenediaminetetrakis(methylenephosphonic acid) H_8EDTMP

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Keywords: Lanthanides; Coordination Chemistry; Structure; Spectroscopy

Crystal structures of lanthanide organophosphonates are still poorly recognized even though these compounds have found many practical applications in new technologies and medicine [1]. For example the complex of radioactive isotope of $^{153}Sm^{3+}$ with EDTMP is used for pain relief from metastatic bone cancer [2]. The biodistribution and pharmacokinetics of this compound is good, whereas that of the $^{166}Ho^{3+}$ complex, which could be a better radiopharmaceutical due to its β emitting properties, is rather poor [3]. To understand differences between both Ln^{3+} complexes, we have undertaken studies on structural and photophysical properties of light and heavy Ln^{3+} ions with EDTMP ligand.

Crystals of the formula $[C(NH_2)_3]_7[Ln(EDTMP)(CO_3)]\cdot 10H_2O$ (where Ln^{3+} = Pr, Nd, Sm, Eu [4], Gd, Tb, Er) and $K_xH_{5-x}[Ln(EDTMP)]\cdot yH_2O$ (where Ln^{3+} = Nd, Eu [5]) were synthesized and their structures have been determined by the X-ray diffraction method. The EDTMP ligand links to the Ln^{3+} ion with 2 nitrogen atoms and 4 oxygen atoms (one from each phosphonate group). The remaining coordination sites in $[Ln(EDTMP)(CO_3)]^{7-}$ are filled by 2 oxygen atoms from the bidentate carbonate anion (Fig. 1A). The exception is the holmium structure, where two symmetry independent Ho^{3+} ions adopt 8- and 7-coordinate geometries which result from the bidentate or monodentate coordination of the carbonate ligand. In the crystal structures of the potassium salts (Fig. 1B) two additional donor atoms in the inner sphere of the Ln^{3+} ion come from an adjacent tridentate phosphonate group, what gives thus rise to formation of cyclic tetramers (Fig. 1C).

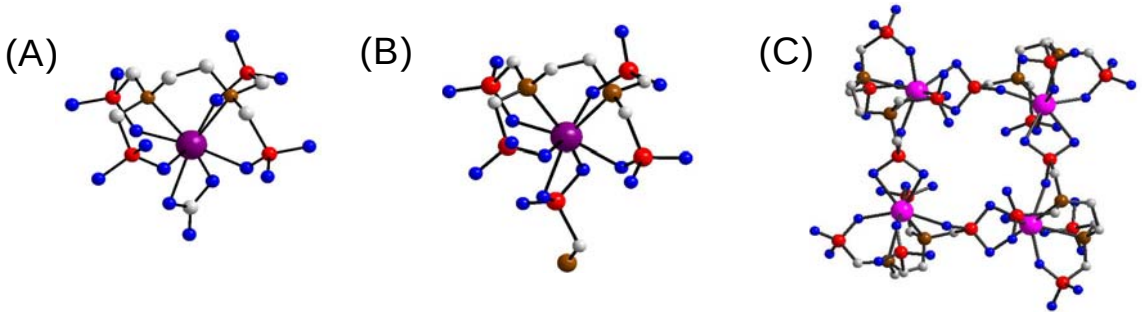

Figure 1. Molecular structures of A) $[Nd(EDTMP)CO_3]^{7-}$, B) $[Nd(EDTMP)]^{5-}$ and C) $[Eu(EDTMP)]^{5-}$ anions.

The variation of Ln–O and Ln–N bond distances for light and heavy lanthanide ions in the EDTMP complexes will be discussed and its influence on photophysical properties will be demonstrated (UV-vis absorption and emission spectra, emission lifetimes of excited states). The results will be compared to the data obtained for the Ln^{3+}–EDTA and Ln^{3+}–CDTMP (where CDTMP is *trans*-cyclohexane-1,2-diamine-*N,N,N′,N′*-tetrakis(methylenephosphonic acid)) [6] complexes.

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Rare Earth Activated Nano Clays: Particles With Multifunctional Properties

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Keywords: Lanthanides; Layered Materials; Clays; Spectroscopy

Embeddings of luminescent rare earths complexes in suitable host materials are of considerable interest for eventual devices, as the predominantly molecular nature of otherwise efficient complexes can significantly hamper their applicability and performance. Numerous hosts have thus been employed, among them (crystalline) hosts such as zeolites or (amorphous) sol-gel materials and polymers.

Surprisingly little work has been reported on the accommodation of molecular rare earth species in 2D confined matrices, as provided in, e.g., layered silicates and layered double hydroxides (LDHs), although the few known examples displayed rather high optical emission efficiencies [1,2,3]. In addition, the 2D confinement can be held responsible for interesting structure – efficiency relationships. Furthermore, via delamination, such layered materials also readily grant access to the nanoscale. The interaction of complexes of Eu^{3+} and Tb^{3+} with nanoscopic hectorites (or laponite®, resp., s. fig.1., displaying a strong geometric anisotropy with a diameter of the primary nanocrystallites of 30 nm at a thickness of only 1 nm) was thus investigated. As rare earth complexes, we made use of well-known β-diketonates (e.g. Tris(1-(2-thenyl)-3,3,3-trifluor-butan-1,3-dionato)Eu(III), "$Eu(ttfa)_3$") and co-coordinating ligands (1,10-phenantholine, "phen") to activate the laponite, and were rewarded with intensely luminescing, powderous materials.

Furthermore, due to the peculiar surface chemistry of these layered silicates (high degree of surface ionization), they can be rendered soluble in aqueous solution. In addition to the optical functionalization, we were thus able to produce materials that could be redispersed in water, which at the same time maintained most of their luminescence efficiencies. Next to the solid, powderous samples, which, due to the materials' anisotropy, may be employed to yield thin, but robust luminescent films, we also consider the redispersability of the nano hybrids to be of particular value, as it opens pathways as bioassays (the particles are highly endocytic, non-toxic, and should even suppress undesired immunoreactions).

It is additionally possible to equip the surfaces of the nano clays with various organic pendants such as to achieve solubility in organic media. To this end, we were able to produce solutions in DMF, which makes combinations of functional laponites with the backbones of polymers very conceivable as well - it might be noteworthy that clays are widely used as polymer additives already.

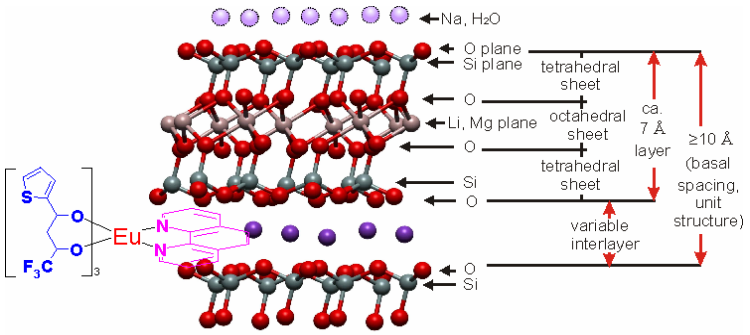

Figure 1. Principle structure of the hectorites (laponites); the insertion of $Eu(ttfa)_3$phen is indicated

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Cytotoxicity of $Gd_2O_3:Ln^{3+}$ Nanostructures and their Potential as Biomarkers

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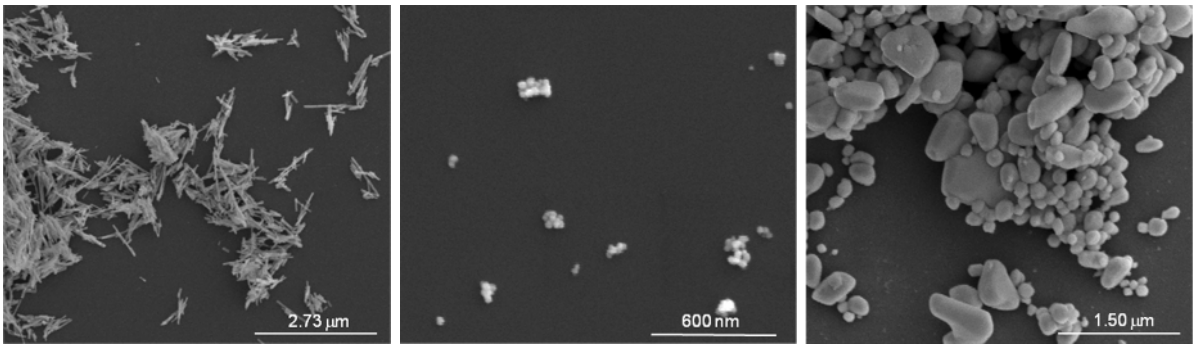
Keywords: Gadolinium oxide; Cytotoxicity; Upconversion luminescence; Biomarkers

Fluorescent markers like commonly used organic dyes or recently investigated quantum dots have been applied for bioimaging, but suffered from colour fading and their toxicity. Further problems are auto-fluorescence and photo toxicity as well as scattering when ultraviolet light is used as excitation source. The outstanding optical and magnetic properties of lanthanides make inorganic materials doped with lanthanide ions be promising candidates to overcome these problems. Recently, upconverting phosphors that absorb infrared radiation and emit in the visible spectrum like Er^{3+}-doped Y_2O_3 are attracting attention and were successfully applied in fluorescence biolabelling [1, 2].

In this study erbium and ytterbium doped gadolinium oxide nanostructures were synthesized. To investigate the influence of morphology on the optical and biological properties of the obtained powders, three different types of nanoparticles were synthesized; first, $Gd(OH)_3:Er^{3+},Yb^{3+}$ nanorods of approx. 40 nm in width and several 100 nm in length were synthesized by hydrothermal method, which could be transformed into the oxide phase by post-thermal treatment. Enzymatic and alkaline precipitation methods were used to prepare nanoparticles of approx. 40 nm in diameter and larger particles with less homogeneous size distribution in the range from 100 nm to 1 μm, respectively. (Fig. 1)



(a) (b) (c)

Figure 1. Scanning electron micrographs of $Gd_2O_3:Er^{3+},Yb^{3+}$ nanorods and particles obtained by hydrothermal synthesis (a), enzymatic (b) and alkaline (c) precipitation method.

Investigation of their optical properties, in particular upconversion emission and near-infrared emission, revealed the potential use of the obtained nanostructures for applications as biomarkers.

In this context, morphology and size effects on the cytotoxicity of Ln^{3+}-doped gadolinium oxide were investigated. B-cell hybridomas, were incubated with different concentrations of rod-shaped and spherical $Gd_2O_3:Er^{3+},Yb^{3+}$. In a first assay, cell viability was analysed by counting cells in a hemocytometer. To determine viability of cells and proliferation of cells, hybridomas were stained with CFSE before cultivation. The cultured cells were then stained with propidium iodide and flow cytometric analysis was performed. In both assays and independent from morphology and concentrations, no cytotoxic effect was observed.

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Luminescent lanthanide nanoparticles via metal vapour synthesis in ionic liquids

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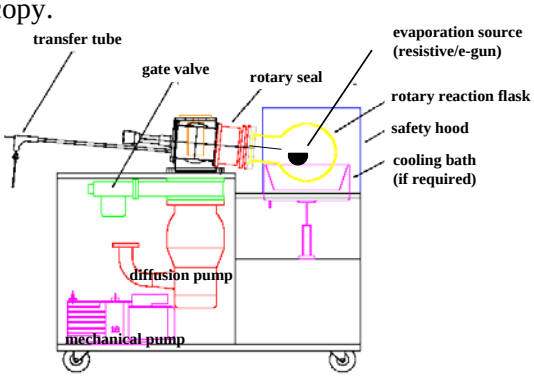
Keywords: ionic liquids; lanthanides; evaporation; nanoparticles

Ionic liquids (IL) are a unique class of salts with a melting point below 100 °C consisting typically of a large, organic cation and a weakly, most times inorganic anion. Some are even liquid at room temperature (RTIL). Due to the possibility of combining many different ions, ILs have tuneable physical and chemical properties, like polarity, viscosity, miscibility with water, or other solvents, and solubility of salts, for example. By the choice of the right cation-anion combination they may be designed in such a way that they are non volatile, thermally stable salts. Because of their ionic character, ILs are able to stabilize nanoparticles by forming electrostatic shells around leading to monodisperse particles and at the same time avoiding particle agglomeration [1]. Rare-earth based compounds and their superior luminescent properties are important in many applications such as in lasers, biosensors, light emitting diodes (LEDs), displays, and lamps. Normally, for such applications well-defined uniform nanoparticles are needed. Until now, classical route to nanoparticles involve wet chemical route such as precipitation, hydrothermal-, microwave-, or ultrasonic methods.

A new method to synthesize size-controlled nanoparticles [2, 3] is the evaporation of lanthanide materials into RTILs. The evaporation accessory based upon the design of Timms [4] is shown in figure 1. The crucible containing the sample, surrounded by a tungsten wire basket heater, is fixed between two water-cooled electrodes. The rotating reaction flask contains the desired RTIL (water content below 50 ppm, 1 ml/mg sample). A pump systems allows the evacuation of the reaction chamber to a pressure of 1.07 mPa. While the crucible is heated by resistive heating, the rotating flask is water-cooled and the IL is stirred, so that the metal-charged surface of the solvent is mixed with the pure IL, which causes diffusion of the particles into the IL. During the evaporation, in which the pressure increases to 2.67 mPa, agglomeration will be prevented, if the evaporation rate is smaller than the diffusion of the particles into the ionic liquid. This synthesis method allows to obtain lanthanide nanoparticles, with a well defined size distribution and morphology. The materials are characterized by XRD, TEM, and optical spectroscopy.



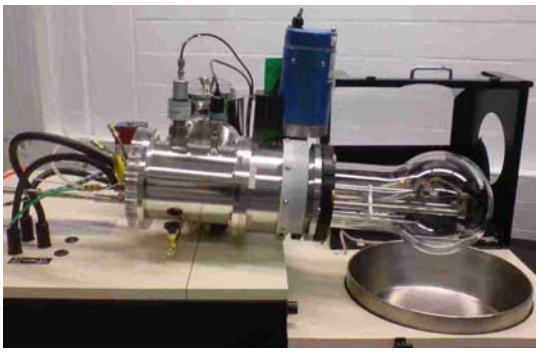


Figure 1. Scheme of the rotary metal vapour synthesis reactor (left) as well as a photo of the evaporation accessory including the reaction flask with a volume of 3 l and the rotary section of the (right).

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Crown-ether-templated uranyl selenates: principles of structure formation

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Keywords: Actinides; Crystal chemistry; Organic-inorganic composites; Structure; Uranyl selenates

Single crystals of $[(H_3O)(H_2O)](H_9O_4)[C_8H_{16}O_4][(UO_2)_2(SeO_4)_3(H_2O)]$ (1), $(H_5O_2)_2(H_3O)_2[(C_{10}H_{20}O_5)_2]$-$[(UO_2)_3(SeO_4)_5(H_2O)]$ (**2**), $(H_5O_2)(H_3O)_3[C_{10}H_{20}O_5][(UO_2)_3(SeO_4)_5(H_2O)]$ (**3**) and $K[C_{10}H_{20}O_5][(UO_2)$-$(SeO_4)(HSeO_4)(H_2O)]$ (**4**) were prepared by isothermal evaporation from aqueous solution of uranyl nitrate, selenic acid and corresponding crown ether, also for the **4** compound potassium hydroxide was used. Data were collected by means of a STOE IPDS II difractometer using monochromatic MoKα radiation and frame widths of 2° in ω. The unit cell parameters were refined by least square techniques: **1** (monoclinic $P2_1/c$, a = 10.7328(6) Å, b = 12.2828(5) Å, c = 22.7085(17) Å, β = 110.102(5) °, V = 2811.3(3) Å^3, R_1 = 0.0704 for 5192 reflections with $|F_o| \geq 4\sigma_F$), **2** (monoclinic $C2/c$, a = 24.584(3) Å, b = 11.7316(10) Å, c = 19.0712(17) Å, β = 103.261(11) °, V = 5353.7(9) Å^3, R_1 = 0.0744 for 4937 reflections with $|F_o| \geq 4\sigma_F$), **3** (monoclinic $P2_1/m$, a = 11.6754(5), b = 18.9887(10), c = 12.2047(5) Å, β = 112.282(3) °, V = 2503.7(2) Å^3, R_1 = 0. 0679 for 4882 reflections with $|F_o| \geq 4\sigma_F$) and **4** (orthorhombic $Pna2_1$, a = 15.376(5), b = 13.262(5), c = 10.775(5) Å, V = 2197.2(15) Å^3, R_1 = 0. 0684 for 3815 reflections with $|F_o| \geq 4\sigma_F$).

As typical for uranyl selenates, the structures of the compounds **1**–**4** contain U and Se atoms in pentagonal bipyramidal and tetrahedral coordinations, respectively. The U^{6+} cations form two short U^{6-}–O bonds resulting in linear uranyl ions, $[UO_2]^{2+}$. The uranyl ions are coordinated in the equatorial plane by five anions each. The Se^{6+} cations are tetrahedrally coordinated by four O atoms each. The UO_7 and SeO_4 polyhedra polymerize by sharing common O atoms to form chains (compound **4**) or sheets (compounds **1**, **2** and **3**).

The structure of **1** is based upon $[(UO_2)_2(SeO_4)_3(H_2O)]^{2-}$ layered complexes, parallel to the (110) plane. There is one crystallographically independent molecule of 12-crown-4 ether between uranyl selenate layers. A charge of an inorganic layer is compensated by $(H_9O_4)^+$ and $[(H_3O)(H_2O)]^+$ complexes providing 3D connection between organic and inorganic parts of a structure via hydrogen bonds.

Compound **2** is a layered uranyl selenate composite with $[(UO_2)_3(SeO_4)_5(H_2O)]^{4-}$ inorganic layers parallel to a (100) plane. There is one nonequivalent molecule of 15-crown-5 ether between inorganic layers. The $(H_5O_2)^+$ and $(H_3O)^+$ complexes combine inorganic layers with molecules of crown ether by the strong hydrogen interactions.

The structure of **3** is also based upon layered complexes of the same chemical composition and topology as in the structure of **2**. There are two independent molecules of 15-crown-5 ether in the interlayer space that are connected with uranyl selenate layers by the hydrogen bonding of three $(H_3O)^+$ complexes and one $(H_5O_2)^+$.

The structure of **4** is based upon $[(UO_2)(SeO_4)(HSeO_4)(H_2O)]^-$ chains running parallel to the c axis. Their packing pattern corresponds to close packing of cylindrical rods. There is one crystallographically independent molecule of 15-crown-5 ether and one K^+ cation between uranyl selenate chains. The K^+ cations are coordinated by eight ligands belonging to crown ether rings and unshared vertices of selenate tetrahedra.

The basic structural principle of organic-inorganic uranyl composites templated by such electroneutral molecules as crown ethers is the translation of interactions between organic and inorganic components by the means of protonated water molecule complexes (structures **1**–**3**) or monovalent cations (structure **4**)

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Influence of the alkaline cations on the crystal structure of new uranyl molybdates $CsNa_3[(UO_2)_4O_4(Mo_2O_8)]$ and $Cs_2Na_8[(UO_2)_8O_8(Mo_5O_{20})]$

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Keywords: Actinides; Chemistry; Synthesis, Structure.

Uranyl molybdates are of interest from the mineralogical, environmental and technological points of view. These compounds form as a result of alteration of spent nuclear fuel (SNF). From a more fundamental point of view, uranyl molybdates show outstanding structural diversity. Mo^{6+} cations occur in tetrahedral, trigonal, bipyramidal, tetragonal pyramidal or octahedral coordination [**1**]. Uranyl molybdates show extreme variation of the angular characteristics of the different structural units, in agreement with their strong tendency to form 3-D framework structures. To date, detailed chemical and structural information is available for pure Li, Na, K, Rb and Cs uranyl molybdates, whereas little is known about mixed alkaline systems such as Na-Cs. However, these systems are of particular importance because of the presence of mixed alkaline uranyl molybdates in SNF.

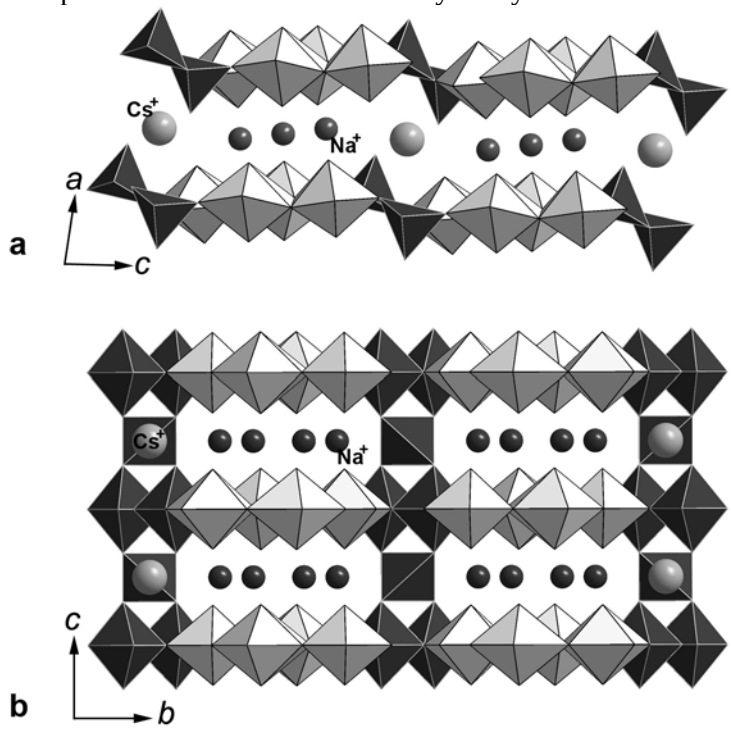

Figure 1. Projection of the crystal structures of $CsNa_3[(UO_2)_4O_4(Mo_2O_8)]$ along the *b* axis (a) and of $Cs_2Na_8[(UO_2)_8O_8(Mo_5O_{20})]$ along the *a* axis (b) (legend: UO_7 polyhedra = light; MoO_5, MoO_4 and MoO_6 polyhedra = dark-grey). Cs-O and Na-O bonds are omitted for clarity..

The structures of $CsNa_3[(UO_2)_4O_4(Mo_2O_8)]$ (**1**) and $Cs_2Na_8[(UO_2)_8O_8(Mo_5O_{20})]$ (**2**) contain two symmetrically unique U^{6+} cations, each of which being strongly bonded to two oxygen atoms to form nearly linear uranyl $(UO_2)^{2+}$ ions. Each uranyl ion is coordinated by five additional O atoms located at the equatorial vertices of pentagonal bipyramids, the apical vertices of which are the O_{Ur} atoms. Bond lengths within the uranyl ions range from 1.80 to 1.85 Å, whereas the U–O bond lengths corresponding

to the equatorial ligands range from 2.15 to 2.58 Å. There is one Mo site in the structure of **1**. It is coordinated by five O atoms thus forming MoO_5 polyhedra. Four Mo-O bonds are in the range 1.72–1.87 Å, and the fifth is at 2.37 Å. There are two symmetrically distinct Mo^{6+} cations in the structure of **2**. The Mo(2) atom is tetrahedrally coordinated by four O atoms, which is typical for synthetic uranyl molybdates. The Mo(1) atom is coordinated by six O atoms in a strongly distorted octahedral arrangement. Cs and Na alkaline atoms are present in both studied compounds. There are, respectively, one or two symmetrically unique positions for Cs and Na in **1**. The same numbers of non-equivalent alkaline atoms are found in the structure of **2**.

The structure of **1** contains complex sheets parallel to (001) of composition $[(UO_2)_2O_2(MoO_5)]$ built from *Ur*O_5 pentagonal bipyramids and Mo polyhedra. Within the sheets, *Ur*O_5 bipyramids share equatorial edges, resulting in complex chains parallel to the *a* axis. The chains are linked by edge- and corner-sharing with edge-sharing dimers of MoO_5 polyhedra. Na and Cs atoms are located in the interlayer space. Note that Cs atoms are situated between the molybdenum clusters whereas Na atoms are segregated between the uranyl complexes. Such location of alkaline metal cations is due to the difference in their ionic radii. The large Cs^+ cations (ionic radius - 2.65 Å) are localized between the Mo_2O_9 groups and force the Mo polyhedra to rotate relative to the $[(UO_2)_2O_2(MoO_5)]$ sheet plane. Thus the effective distance between the layers is increasing. Such rotation is impossible for U^{6+} polyhedra due to their rigid edge-sharing complexes. The distance between the U^{6+} polyhedra vertices of neighboring layers is 3.8 Å, which allows Na^+ (ionic radius 1.86 Å) cation to position between the uranyl groups.

The crystal structure of **2** is based upon a framework built up from *Ur*O_5 bipyramids, MoO_6 octahedra and MoO_4 tetrahedra. The framework consists of the $[(UO_2)_2O_2(MoO_5)]$ sheets parallel to (010) and composed from *Ur*O_5 bipyramids and MoO_6 distorted octahedra. The sheets are linked into 3-D framework by sharing vertices with the $Mo(2)O_4$ tetrahedra, located between the sheets. The MoO_4 tetrahedron shares two corners with two MoO_6 octahedra in the sheet above, and two with MoO_6 octahedra of the sheet below. Thus four MoO_6 octahedra and one MoO_4 tetrahedron form chains of composition Mo_5O_{18}. The resulting framework has a system of channels occupied by the Cs^+ and Na^+ cations. As in the structure of **1**, flexibility of the Mo complexes allows Cs atoms to locate between the Mo groups and Na between the uranyl polyhedra.

Comparison with other alkaline uranyl molybdates is given.

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Highly efficient NCN-ligand stabilized organolanthanide catalysts for the coordinative chain transfer ethylene polymerization

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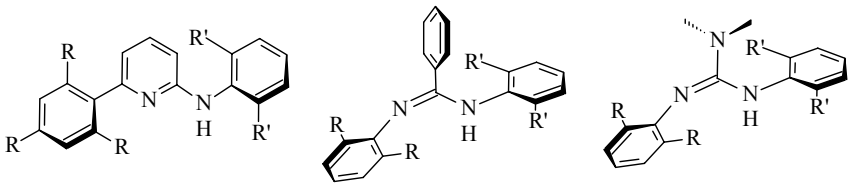
Keywords: Lanthanides, Organometallics, Polymerization, Al-Alkyles

Neutral complexes of group 3 and rare earth metals have been the subject of intensive investigations over the past two decades because of their unique activities in selective organic synthesis and catalytic olefin transformations.[1]

However, recent studies have shown that cationic lanthanide metal alkyls are highly efficient polymerization catalysts with often higher activities then their neutral congeners.[2]

Recently we could show that aminopyridinato (ApH) stabilized cationic yttrium alkyls are thermally very stable, highly efficient catalysts for the coordinative chain transfer polymerization of ethylene in presence of $(R_2AlO)_2$ Alumoxane scavengers (Al/Y > 20), with an extremely narrow polydispersity (Mw/Mn < 1.1) and relative high molecular weight.[3]

The use of Al trialkyls instead of Alumoxane decreases the polymerization activity dramatically and reduces the average molecular weight.



ApH **AmH** **GuaH**

Figure 1. NCN-framework ligands

However, replacing the Ap-ligand for stronger π-donating amidinate or guanidinate NCN ligands drives the system back into a highly reversible chain transfer catalyst system, which produces exclusively tailor made alumina terminated polyethylene.

Such functionalized polyolefin chains can be easily transformed and are valuable starting materials for numerous applications.[4,5]

Scope and mechanism will be presented.

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Interaction of Hydroxylaminato Rare-Earth Metal Complexes with $AlMe_3$, $GaMe_3$ and $InMe_3$

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Keywords: Lanthanides; Chemistry; Coordination; Structure

Rare-earth metal alkoxide bis(cyclopentadienyl) complexes have been reported since the early 1980´s.[1] This type of complexes shows high activity in several catalysis mechanisms like ethene and styrene polymerisation or ring opening reactions.[2] Hydroxylaminato ligands with the general constitution $[R_2NO^-]$ can be perceived as a special type of alkoxides as they mostly interact via the oxygen donor function towards the metal atoms. As MAO and other aluminium-alkyl derivates are used as co-catalysts in these catalysis-mechanisms we have recently started to investigate the reactivity of rare-earth metal hydroxylaminato complexes of towards trialkyl earth-metals.

Reactions of $HON(C_2H_4\text{-}o\text{-}Py)_2$ - as a double donor functionalised hydroxylamine - with rare-earth metal triscyclopentadienyls leading to three novel coordination modes of the ligand depending on the ionic radius of the rare-earth metal ions. The complexes of the late rare-earth metals exhibit two further reactive positions, namely the hydroxylaminato oxygen and the free pyridine nitrogen. The reaction of these complexes with LEWIS acidic earth-metal alkyls opens up different combinations to hetero-bimetallic complexes. The earth-metal alkyls first coordinate to the hard hydroxylaminato oxygen and second to the comparatively soft pyridine nitrogen. This way it is also possible to synthesise hetero-trimetallic compounds combining yttrium, aluminium and gallium in one complex.

The complexes of medium sized metal ions - here exemplified with Nd^{3+} - undergo interesting structural changes upon interaction with $AlMe_3$, $GaMe_3$ and $InMe_3$. In this case the decrease of the electron density at the oxygen atom leads to monomerisation of the complex and an increase of the coordination number at Nd^{3+} (Figure 1).

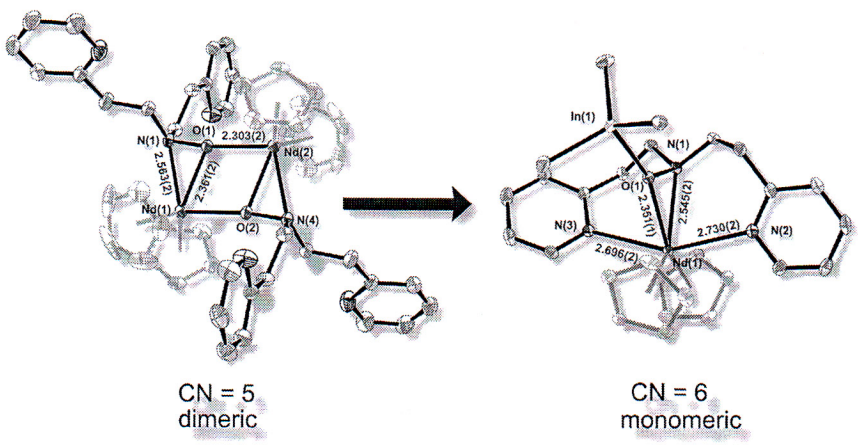

Figure 1: Monomerisation of $[Cp_2NdON(C_2H_4\text{-}o\text{-}Py)_2]_2$ by application of $InMe_3$.

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Hemilabile Hydroxylaminato Complexes of Rare-Earth Metals

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Keywords: Lanthanides; Chemistry; Coordination; Structure

Before our group focused on rare earth chemistry, only Evans *et al.* had reported a hydroxylamine related complex. This compound $[(C_5H_6Me_4NO)_2Sm(\mu\text{-}ONC_5H_6Me_4)]_2$ contains hydroxylaminato ligands introduced via the stable radical TEMPO in a redox process.[1] We realized that *N,N*-dialkylhydroxylamines could be ideal protioligands to complex rare earth metals, since they posses an additional nitrogen donor function directly adjacent to the oxygen atom binding to the metal centre. This leads to a saturation of the metal ions coordination sphere by a minimum of atoms.

Unfortunately, by utilizing these hydroxylamines, the metal ions demand for electron density was not saturated and dimerisation was observed, even when using bulky ligands.[2,3,4,5] We therefore considered introducing donor-functionalized hydroxylamines, which could lead to monomeric compounds. The ligand bis(2-{pyrid-2-yl}ethyl)hydroxylamine $[HON(C_2H_4\text{-}o\text{-}Py)_2]$ employed by Bauer, Shoeb and Agwada has, in addition to the hydroxylamine unit, two further donor functions, which are able to interact with the metal ions.[6]

In here we present the first rare earth metal complexes combined with a multi donor functionalized hydroxylaminato ligand. This ligand displays three different coordination modes towards rare earth metal ions. Co-ordination of one pyridyl function to the metal ions is observed for the monomeric species of the small metal ions. Dimerisation is observed for medium ion sizes, here exemplified with Nd^{3+} and Pr^{3+} complexes. In this case no pyridine coordination is observed. A combined motif is found for even larger ionic radii as demonstrated for the case of the dimeric La^{3+} complex (Figure 1).

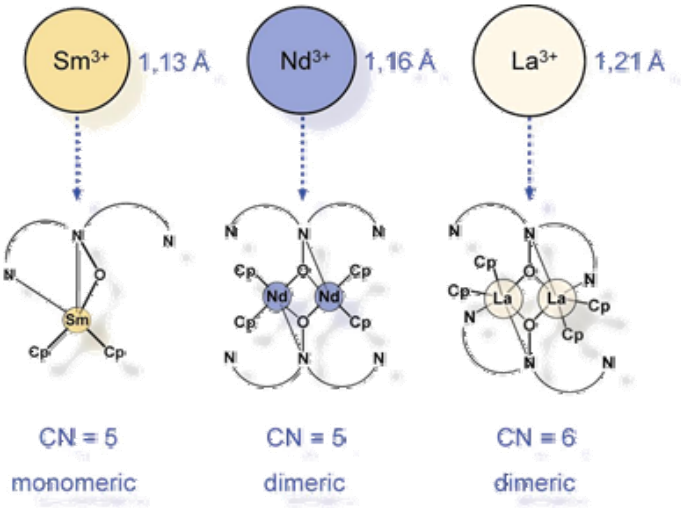

Figure 1: Different aggregation motifs in dependency of ionic radii.

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C-H activation in Rare-Earth Metal Tetramethylaluminates Induced by a Neutral Ligand

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Keywords: Lanthanides; C-H activation; Carbide

C–H bond activation in the coordination sphere of metals and alkane elimination reactions from metal bound alkyl substituents are key steps for the understanding of many important chemical processes. These include catalytic transformations, heterogenic as well as homogenous ones. Such reactions have been studied particularly in the context of olefin polymerization.
Recently Anwander and co-workers contributed a series of examples, where C-H activation reactions take place in the coordination sphere of rare-earth metals. They found that the action of PMe_3 onto $[La\{Al(CH_3)_4\}]_4$ lead to the formation of complex aggregates containing methylene, methine and carbide units, where the carbide is coordinated by five metal atoms.[1]
We have now observed even the formation of hexacoordinated carbon atoms of the carbide type in reactions of rare-earth tris(tetramethylaluminates) (M = La, Sm, Y) with the neutral tridendate ligand TMTAC (1,3,5-trimethyl-1,3,5-triazacyclohexane). Our initial intention was to use the mixed metal precursors $[Ln\{Al(CH_3)_4\}_3]$ to deprotonate TMTAC, leading to doubly amino-substituted carbanions, as recently described by us for a lithiated derivative $[LiCH(NMeCH_2)_2NMe]$, which can serve as a nucleophilic acylation reagent analogous to the Corey-Seebach reagent.[2]

The reaction products point to a mechanism of sterically induced condensation of $Al(CH_3)_4$ groups in close proximity in the coordination spheres of the rare-earth metal atoms, which is dependent on the size of these metal atoms.
The reaction of $[Sm\{Al(CH_3)_4\}_3]$ with TMTAC combines products of an intra- and intermolecular reaction pathway, by isolating $[(TMTAC)Sm\{(\mu_2\text{-}CH_3)(CH_3)_2Al\}_2\{(\mu_3\text{-}CH_2)_2Al\text{-}(CH_3)_2\}]$, the product of a double intramolecular condensation and the carbide species. A possible mechanism for this reactivity is based on the complex-induced proximity effect (CIPE), a concept which proved to be very successful in typical carbanion chemistry.[3]

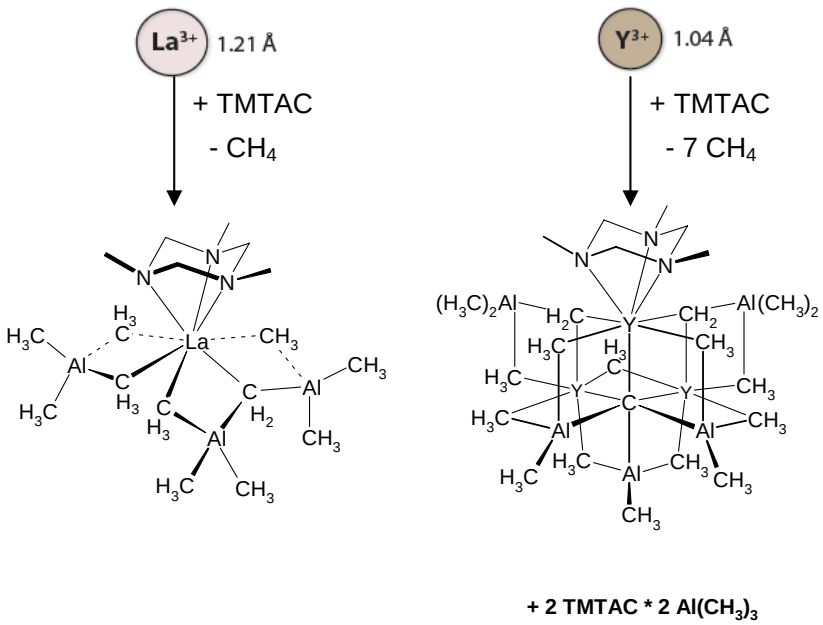

Figure 1: Reactions of $[La\{Al(CH_3)_4\}_3]$ and $[Y\{Al(CH_3)_4\}_3]$ with TMTAC

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Cyclopentadienylphosphazene Constrained Geometry Complexes of Rare-Earth Metals and their application in Hydroamination Reactions

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Keywords: Cyclopentadienylphosphazene; Constrained Geometry Complexes; Hydroamination

Constrained geometry catalysts (CGCs) of rare-earth metals, based upon the cyclopentadienyl-silylamido (*CpSiN*) type ligand system, have an extraordinary potential as catalysts in intramolecular hydroamination reactions.[1] In order to improve their catalytic properties a new class of constrained geometry ligands was recently developed by our own working group in which a phosphazene unit displaces the silylamido moiety.[2] Three-valent metal complexes based on monoanionic *CpPN*-type ligands are isolobal, in case of group 3 metals even isoelectronic, with the classical CGCs involving dianionic *CpSiN* ligands and group 4 metals (Figure 1).

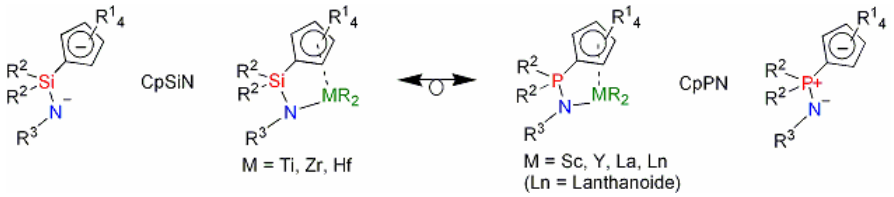

Figure 1. Isolobal relationship between the classical CGCs and the CG-*CpPN*-systems.

A series of rare-earth metal CGC-type complexes with the cyclopentadienylidene-*P*-amino-phosphorane ligands were synthesized and fully characterized. Figure 2 gives an overview of those *CpPN*-complexes.

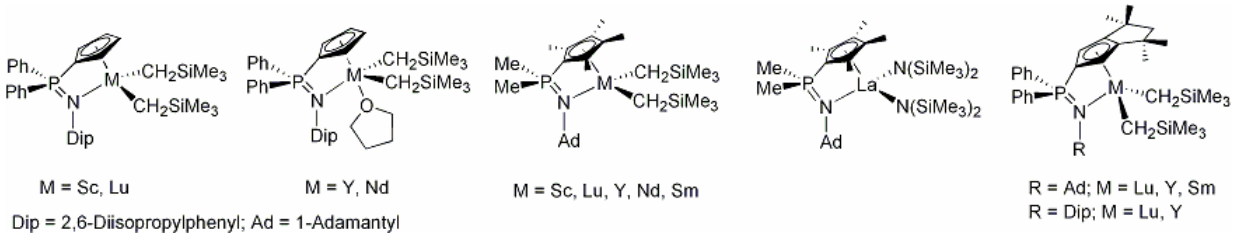

Figure 2. Synthesized *CpPN*-CGCs of rare-earth metals.

Additionally, intramolecular olefin hydroamination reactions on *gem*-substituted penten-4-ylamines were investigated. The synthesized *CpPN*-CGCs with Y, Nd, Sm and La are active precatalysts for the intramolecular hydroamination of 2,2-dimethylpentenamine with TOF values of up to 120 h^{-1} at ambient temperature.

We thankfully acknowledge financial support by the **DFG priority program SPP 1166**.

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New Cyclopentadienyl-*N*-silylphosphazene and Cyclopentadienyliden-phosphorane complexes of Rare-Earth Metals

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Keywords: Constrained Geometry Complexes, Cyclopentadienyl-*N*-silylphosphazene, Lewis acid-base adduct complex, trialkylphosphonium cyclopentadienylide

The development of constrained geometry complexes for polymerization catalysis in the nineties was an enormous improvement of stereoselective polymerization of long-chain olefins. In the classical dianionic ligand system a cyclopentadienyl-group acts as a η^5-coordinating fragment and an amidogroup as a η^1-coordinating chelate fragment bonded over a silyl bridge (*CpSiN*).

Now we report the investigation of four new monoanionic ligands in which the amido moiety is displaced by a basic phosphazene donor function (*CpSiNP*). They were established in a convergent multi-stage synthesis and fully characterized (Figure 1).

The ligands showed themselves to be unreactive towards metallation with various metal alkyls and amides. The remarkable low acidity of these ligands is very contrary to the protic character of the cyclopentadienyl(phosphazene)-ligands with a intracyclic phosphazene unit (*CpPN*) developed in our own working group[1]. The synthesis of the first *CpSiNP*-complexes of lanthanides (Figure 2) was achieved by the aryl elimination pathway using chelate stabilized arene complexes of the REMs[2].

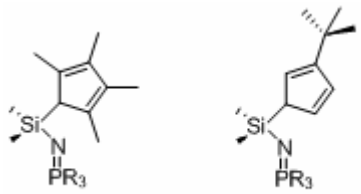

Figure 1. New *CpSiNP*-ligands (R = NMe_2, *t*Bu).

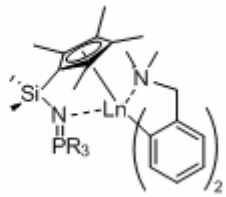

Figure 2. *CpSiNP*-complexes (Ln = Lu, Y).

The recently developed trialkylphosphonium cyclopentadienylide ligand, $C_5Me_4PMe_3$ reacts with $[CrCl_3(thf)_3]$ to yield the novel neutral Lewis acid-base complex.[3] The molecular structures of this complex has been established by X-ray diffraction and a highly zwitterionic P-C_{Cp} bond is confirmed. This result leads to the consideration of developing analogous complexes with group 3 elements. The related zwitterionic halfsandwich complexes of Y, Sc, La were prepared and characterized (Figure 3).

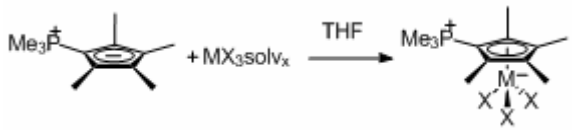

Figure 3. Complexes of the new ligand with rare earth metals (M = Y, La, Sc; X = Cl, Br; solv = thf, dme).

We thankfully acknowledge financial support by the **DFG priority program SPP 1166.**

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Homoleptic *Tris*-Aryl Complexes of the Rare Earth Metals

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Keywords: Lanthanide aryl complexes

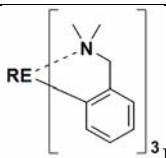
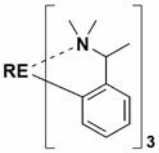
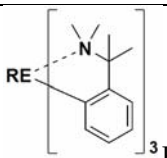
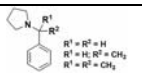
Crystalline homoleptic trisalkyl or trisaryl rare earth compounds stable at ambient temperatures are important precursors for a "salt-free" synthetic access to organometallic rare earth complexes. Furthermore they are a promising class of compounds for the use in catalytic applications.

WAYDA reported that with *ortho*-lithiated *N*,*N*-dimethylbenzylamine ligand (dmba) only the corresponding $Ln(dmba)_3$ complexes (Ln = Er, Yb, Lu) for the late lanthanides with small ionic radii can be obtained.[1] All attempts to synthesize the homoleptic complexes of the early and even middle lanthanides were unsuccessful.

To avoid thermal decomposition via C-H-activation in the benzylic position of the ligand, we report the effect of stepwise replacement of these protons by methyl groups. This modification leads to a significant enhancement of the thermal stability of the homoleptic early and middle lanthanide complexes which is a precondition to their use in synthesis and catalysis.

The synthesis of a series of stable, crystalline homoleptic aryl complexes of the early (Nd, Sm), middle (Gd, Dy) and late (Er, Yb) lanthanides is reported here. The results are summarized in Table 1.

Table 1: Known and newly synthesized homoleptic aryl complexes of the rare earth metals (compounds marked with * are also crystallographically characterized).

	 $RE(dmba)_3$	 $RE(tmba)_3$	 $RE(cuda)_3$	
late lanthanides (Er – Lu & Sc)	Er *, Yb * & Lu * [1]	---	---	---
middle lanthanides (Eu – Ho & Y)	only Y * [3]	Y *, Dy *	Y	Y
early lanthanides (Ce – Sm & La)	No stable complexes [2]	Nd *, Sm [2]	Sm * [2]	---

By reacting two equivalents of the lithiiated ligands with RE halogenides we were able to obtain also bis-aryl-chloro-complexes of the type $RE(Ar)_2Cl$ (RE = Sc, Lu[2], Y) which are in the case of Lu and Y crystallographically characterized. This new class of compounds is of great interest for further salt-metathesis or ligand-exchange reactions with a potential for catalysis.

We thankfully acknowledge financial support by the **DFG priority program SPP 1166**.

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Rare-earth metal complexes bearing bulky phenyl(trimethylsilyl)amide ligands

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Keywords: amide; borohydride; structural characterization; synthesis

Heteroleptic amide/chloride complexes of the rare-earth metals are readily activated for 1,3-diene polymerization according to a chlorination-alkylation sequence.[1] Control of the organoaluminum-promoted amido/alkyl ligand exchange is hampered by ligand redistribution reactions of the mixed amide/chloride precursor compounds as revealed by $[N(SiMe_3)_2]$ and $[N(SiHMe_2)_2]$ derivatives.[1, 2]

Herein we present the synthesis and characterization of corresponding rare-earth metal complexes bearing the bulky $[N(SiMe_3)(C_6H_3iPr_2\text{-}2,6)]$ amido ligand. It was found previously by SCHUMANN et al. that the coordination behavior of this ligand can be readily tuned via the aryl substitution pattern.[3] Using different synthesis protocols we now investigated into solvent (thf vs. hexane) and the implications of distinct alkali metal amide precursors (lithium vs. potassium) for the product formation. Intrinsic ate complexation and concomitant oligomerization were observed as well as discrete heteroleptic and homoleptic species, examples being the lanthanum and neodymium borohydride derivatives shown in Figure 1.

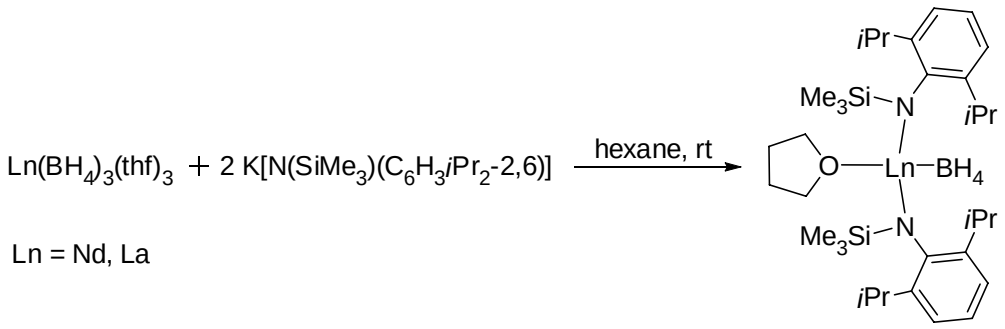

Figure 1. Synthesis of heteroleptic amide borohydride complexes.

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Synthesis and structures of some pseudo-lanthanoid(II) aryloxides by retralex reactions with alkaline earth metals, and the effect of solvent variation

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Keywords: Pseudo-lanthanide; Chemistry; Coordination; Structure

The alkaline-earth metals, calcium, strontium, and barium have been used as pseudo-lanthanoids(II) in redox transmetallation/ ligand exchange reactions with 2,4-di-*tert*-butylphenol. The reactions were carried out in the donor solvents tetrahydrofuran (thf) and dimethoxyether (dme) and the resulting complexes structurally characterised by X-ray crystallography. The steric coordination numbers[1] of tetrahydrofuran and dimethoxyethane are 1.21 and 1.78 respectively, and this difference is shown to have a large impact on the structure of the reaction product. Complexes were of the general form $AE_n(L)_{2n}(solv)_x$ (where AE = Ca or Sr; L = 2,4-di-tert-butylphenolate; solv = thf or dme; n and x vary with solvent and metal choice), except for barium complexes which were large clusters of the form $Ba_8(L)_{12}(OH)_4$.

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Low coordinate lanthanoid aryloxides by retralex reactions

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Keywords: Lanthanides; Theory; Coordination; Structures

New trivalent lanthanoid aryloxide complexes have been prepared by redox transmetallation ligand exchange (retralex) reactions using 2,4-di-*tert*-butylphenol (2,4-^{t}BupH). Mononuclear complexes from thf (tetrahydrofuran) were of the type Ln(2,4-^{t}Bup)$_3$(thf)$_3$ (Ln = La(1), Pr(2), Nd(3), Gd(4), Er(5)). The 'lanthanoid contraction effect' resulted in the rather subtle change in conformation from meridional (La, Pr, Nd, Gd) to facial (Er). Dinuclear complexes of the type Ln$_2$(2,4-tBup)$_6$(thf)$_2$ were obtained when any of **1-5** were recrystallised from toluene. A similar structural motif was observed when the reaction was carried out in diethylether {Nd$_2$(2,4-^{t}Bup)$_6$(Et$_2$O)$_2$}**(6)**, and in the absence of a solvent {Nd$_2$(2,4-^{t}Bup)$_6$(2,4-^{t}BupH)$_2$}**(7)**

Synthesis and characterisation of bis(diphenylphosphinocyclopentadienyl)-rare earth and -alkaline earth mono- and bi- metallic complexes

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Keywords: Lanthanides; Organometallics; Chemistry; Synthesis

The redox transmetallation reaction provides an excellent, high yield, synthetic route to give divalent rare earth [2] and alkaline earth complexes $[(AE(RE)(C_5H_4PPh_2)_2(THF)]$ (AE = Ca, Sr, Ba and RE = Yb). From the monometallic complexes mentioned above, a series of heterobimetallic complexes $[M(THF)(C_5H_4PPh_2)_2M^*(L)_2]$ (M = Yb, Ca, Sr, Ba; M* = Pt; L = CH_3 or C_6H_5) were prepared. The first example of such a complex was unusual for f/d bimetallics as the f-block element was in the donor part of the molecule [1]. In this example, the reaction of $[Yb(C_5H_4PPh_2)_2(THF)]$ with $PtMe_2(cod)$ (cod = cyclooctadiene) in toluene afforded $[Yb(THF)_2(C_5H_4PPh_2)_2PtMe_2].(PhMe)$ which when recrystallised gave $[Yb(THF)_2(C_5H_4PPh_2)_2PtMe_2].THF$ [1]. The alkaline earth and lanthanoid bimetallic complexes mentioned above were characterised using ^1H, ^{31}P and ^{13}C NMR spectroscopy. The formation of lanthanoid (alkaline earth)-transition metal bimetallic complexes was achieved by using $C_5H_4PPh_2$ as the bridging ligand. The phosphine groups of the above metallocene complexes readily displace neutral ligands (1,5 - cyclooctadiene) from Pt^{II} centres and the metallocene complex acts as a chelating biphosphine metalloligand. Two of the complexes were structurally authenticated by single crystal X-ray diffraction: $[Ca(C_5H_4PPh_2)_2(DME)]$ (**Figure 1**), a discrete neutral monomeric molecule in which the phosphorus atoms are not coordinated to the calcium ion. $[Sr(C_5H_4PPh_2)_2(THF)Pt(CH_3)_2]$ (**Figure 1**) shows the strontium fragment acting as a chelating metalloligand attached to the platinum. The strontium environment is 9-coordinate, with two staggered η^5-$C_5H_4PPh_2$ rings and three THF ligands bound.

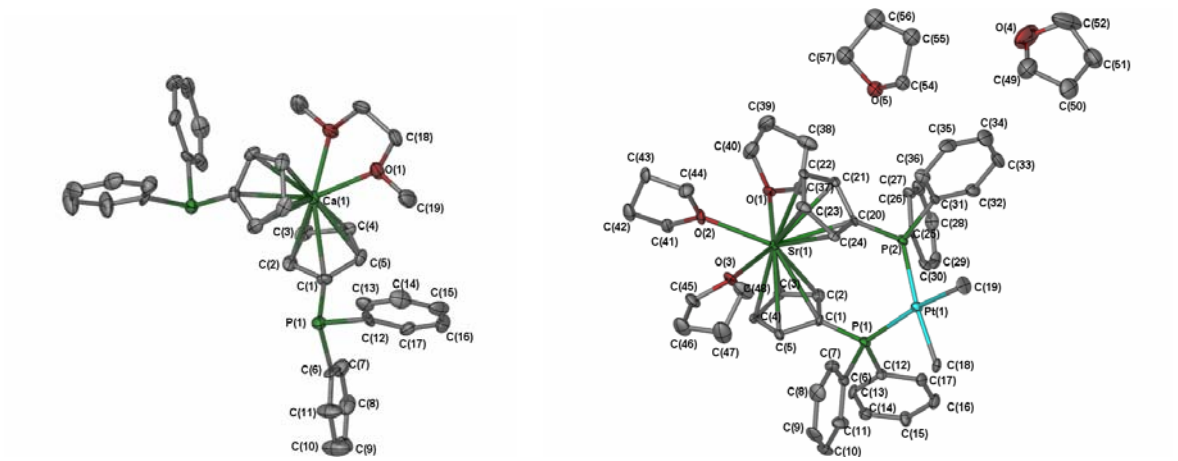

Figure 1. X-ray crystal structures of $[(Ca(C_5H_4PPh_2)_2(DME)]$ and $[Sr(C_5H_4PPh_2)_2(THF)_3Pt(CH_3)_2].(THF)_2$. Hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability level.

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Rare Earth Metal Alkyl Complexes Supported by Imidazolin-2-Iminato Ligands: Synthesis, Structural Characterisation and Catalytic Application

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Keywords: Lanthanides; Applications; Catalysis; Synthesis

Organolanthanide chemistry has witnessed a spectacular growth during the past two decades. In this process, the design and application of organolanthanide complexes as catalysts for polymerisation and organic synthesis have been of particular interest. So far, organolanthanide chemistry has been dominated by metallocene complexes; however, there has recently been a remarkable impetus toward the search for new ligand systems to extend lanthanide chemistry beyond the traditional realm of metallocene complexes [1].

Our group reported a new synthetic approach to imidazolin-2-iminato rare earth metal dichlorides of type **1** [2, 3]. These proved to be excellent starting materials for the synthesis of a large number of mononuclear lanthanide imido complexes as described in Figure 1. Beside the structural investigations performed with these complexes, our study was focused on their application in homogeneous catalysis. The complexes, resulted after the reaction with two equivalents of $LiCH_2SiMe_3$, showed to be highly efficient catalysts for hydroamination and hydrosilylation reactions and for the catalytic addition of primary amines to carbodiimines. Future work will be aimed at further exploring the potential of imidazolin-2-iminato ligands as ancillary ligands in homogenous rare earth metal catalysis.

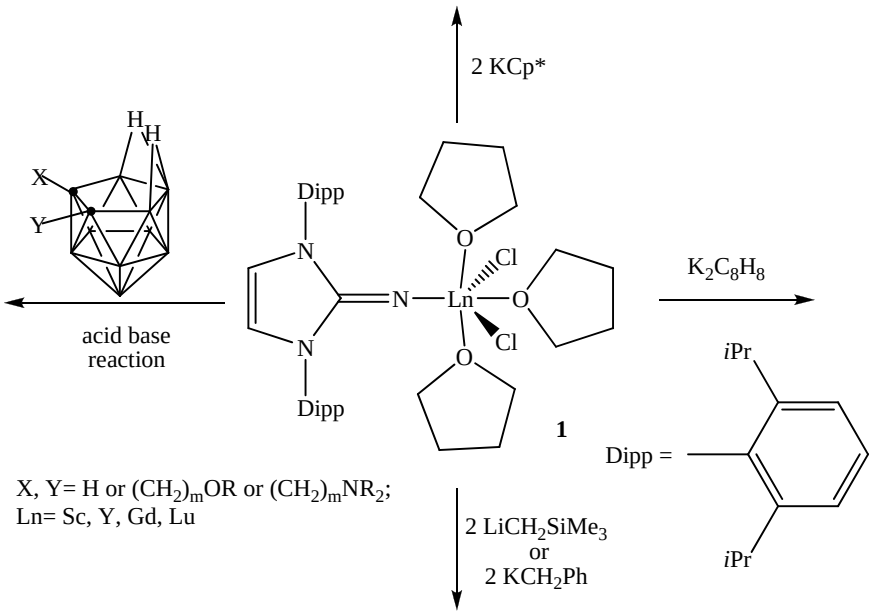

Figure 1. Imidazolin-2-iminato rare earth metal complexes.

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Investigations of a Novel Bora-Amidinate Ligand in Lanthanide Chemistry

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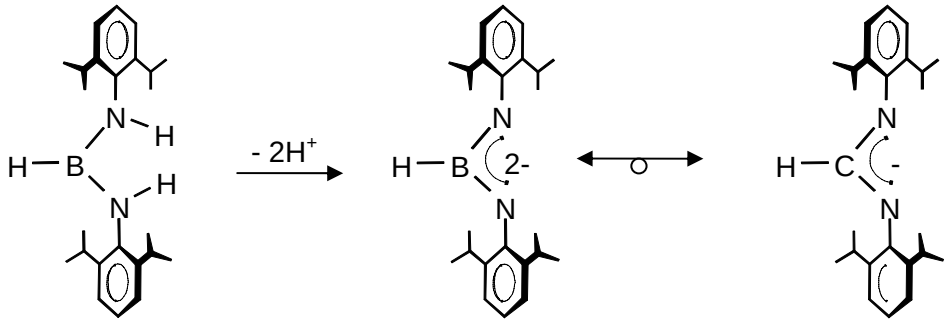
Keywords: Lanthanides, Organometallics

Bora-amidinate ligands (*bam*) have been recently reviewed by Chivers [1]. The chemistry of these dianionic ligands in *s*, *p* and *d* group metal chemistry is thoroughly investigated, however, hitherto no lanthanide chemistry of this unique ligand has been reported.

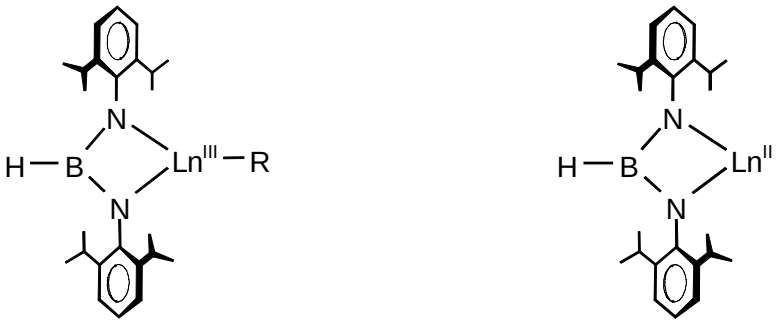
Most *bam* ligands hold a sterically demanding group in the backbone (phenyl, mesityl, *t*Bu or iPr_2N). We recently developed a convenient, atom economical synthetic route to a new *bam* ligand with a BH unit and sterically demanding DIPP-substituents (DIPP = 2, 6-di-*i*Pr-phenyl) at the nitrogen atoms. This dianionic ligand is isolectronic to the corresponding monoanionic adiminate (*am*) ligand which has been extensively studied [2].



Our goals in lanthanide chemistry are defined as follows:

i) Syntheses of *bam*-lanthanide(II) complexes in which only one side of the metal is protected by ligand bulk and the other side is completely accessible for interesting redox chemistry.

ii) Syntheses of heteroleptic lanthanide(III) complexes of the general form (*bam*)$Ln^{III}R$ in which R is a reactive group for further catalytic studies.



Here we describe our preliminary results.

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Synthesis and Reactivity of Phosphorus-Stabilised Lanthanide Carbene Complexes

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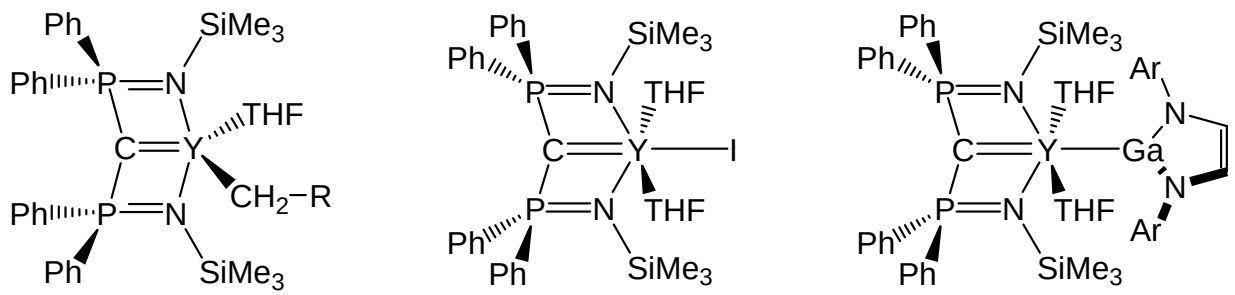
Keywords: Lanthanides; Carbenes; Organometallics; Synthesis

The chemistry of lanthanide carbenes is relatively undeveloped in comparison to that of related transition metal complexes, and structurally characterised lanthanide carbene complexes that do not derive from stable free carbenes are sparse.[1]



R = $SiMe_3$ **1a**, Ph **1b** **2** **3**

Figure 1. Complexes **1a-b**, **2** and **3**

Our group has reported the facile syntheses of the yttrium alkyl-carbene complexes, **1a-b**, by the double deprotonation of a bis-iminophosphoranomethane ligand (BIPM-H_2, $H_2C(PPh_2NSiMe_3)_2$) by yttrium trialkyl precursors.[2,3] We have recently extended this methodology to synthesise a range of lanthanide carbene complexes, such as **2**, and have demonstrated their synthetic utility by preparing a yttrium-gallyl complex, **3**, which exhibits the first structurally authenticated Ga-Y bond.[4] We have reported initial investigations into the reactivity of **1b** with diphenyldiazene and benzophenone to afford insertion products and dimeric bridging methandiide complexes.[3] More recently, we have observed insertion and cycloaddition carbene reactivity of **1a-b** and **2** with carbodiimides and isocyanates and an unprecedented C-H activation and C-C bond forming reaction of benzophenone.

We thank the Royal Society, the UK EPSRC and the University of Nottingham for funding, and the NSCCS for the use of computational facilities.

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Theoretical description of the energy transfer in the lanthanide materials

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Keywords: Lanthanides; Theory; Organometallics; Spectroscopy.

The magnitude of the quantum yield of the sensitized luminescence of the lanthanide-organic chelates is the result of the competition between all the photophysical processes that occur in the system. The energy transfer between the ligand/antenna and the central ion plays the crucial role in the spectroscopic properties of the considered systems. Indeed, this process enables the emission from the lanthanide ion. As a consequence, the efficiency of the energy transfer is one of the leading factors that determines the quantum yield of the sensitized luminescence. Therefore, the knowledge of the efficiency of the energy transfer is crucial for designing effective luminescent lanthanide-organic chelates. The present work is devoted to the calculation of the energy transfer rate that consists of two parts, namely the matrix element of the operator, which describes the interaction between the central ion and antenna, and the spectral overlap integral. The matrix element is expressed in the terms of the effective operators by means of the Racah Algebra with the inclusion of the perturbing influence of the crystal field potential and electron correlation effects [1]. This part of the energy transfer rate allows one to perform ab initio type calculations when the perturbed function approach is applied. This theoretical model is also formulated in the relativistic version [2], which is in addition to the possibility of taking into account the exchange interactions if the wave functions of the whole system (lanthanide ion and ligands) are totally antisymmetrized[3].

The dependence of the energy transfer rate (and consequently, of the quantum yield of the sensitized luminescence) on factors that determine the magnitude of the overlapping of the spectral bands of the ligand/antenna and the lanthanide ion is also considered [4]. As for example, the results of numerical calculations performed for Tb^{3+} and Yb^{3+} complexes are analyzed and compared to the experimentally observed correlation between the quantum yield of the sensitized luminescence of the lanthanide complexes and the position of the lowest triplet energy level of the ligand/antenna [5].

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Quantum Mechanical *TM–RE* Bonding Analysis in Position Space: Methodology and Application

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Keywords: Lanthanides; Theory; Bonding analysis

Based on standard quantum chemical calculations, modern theoretical approaches can provide insights into bonding situations in systems under investigation (molecules, clusters or solids). The methods for position-space analysis of chemical bonding can be combined together to obtain more detailed picture of shared-type interaction in the system.

In the QTAIM method [1] the position space is divided into non-overlapping atomic domains defined by the topology of the electron density. This way the atomic charges are uniquely defined for the current system and the distributions of such atom-assigned charges can be analysed.

In the ELI-D approach [2] both the electron density and the pair density is used to define the unique subdivision of the position space into the core and valence regions where among the latter the lone-pair and shared-interaction (bonding) ones can be distinguished. The integration of the electron density in these regions provides an average number of electrons assigned to atomic cores, lone pairs and bonds.

The combination of the two methods is used to determine the polarity of the bonds. Additionally, the delocalization indices [3] between atomic domains are calculated to characterize the shared-type interaction.

The described methodology is applied to analyse the bonding situations in *TM–RE* contacts in different heterobimetallic complexes. It turns out that in considered systems the *TM–RE* bonds are of a polar donor-acceptor type with peculiarities specific for electronic interactions involving penultimate atomic shells.

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Crystal Field Analysis of Nd^{3+} Electronic Levels in $[Nd_4(EDTMP)_4]$ Anion

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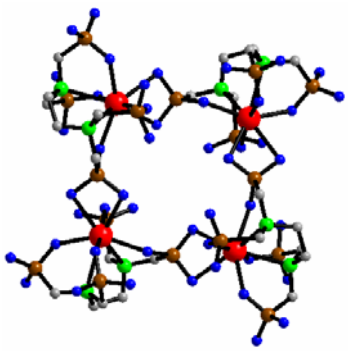
Keywords: Crystal field parameters; Coordination Chemistry; Spectroscopy

The compound $K_{17}H_3[Nd_4(EDTMP)_4]\cdot 36H_2O$ (where EDTMP is ethylenediaminetetra-(metylenephosphonic ligand)) crystallizes in P-4n2 space group. The octacoordinate Nd^{3+} cation is surrounded by two nitrogen atoms and six oxygen atoms from phosphonic groups. The coordination polyhedron of the first coordination sphere of the Nd^{3+} ion may be described as a distorted square antiprism (symmetry – C_1). The EDTMP anion is involved in bonds with two neighbouring Nd^{3+} cations. Three of the ligand phosphonic groups are monodendate, whereas the fourth one is three-coordinate, *i.e.* one of its oxygen atom coordinates to the metal ion Nd1 and the two others coordinate to a neighbouring (generated by symmetry from Nd1) neodymium ion. In this way four [Nd(EDTMP)] entities are bonded together to create a cyclic tetramer (symmetry S_4).



The high resolution absorption spectra of $K_{17}H_3[Nd_4(EDTMP)_4]\cdot 36H_2O$ crystal were measured at room and liquid helium temperatures. The experimentally determined energy levels were simulated using a semi-empirical Hamiltonian representing the combined free-ion and crystal-field interactions for Nd^{3+} ion in the real C_1 as well as in the approximated C_{2v} symmetry sites. The reliable starting values of CFPs were provided by the superposition model.

Structure Optimization and Electronic Structure of the $SrAl_2O_4:Eu^{2+}$ Persistent Luminescence Material by DFT Calculations

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Keywords: Lanthanides; Persistent Luminescence; Solid State; DFT Calculations

The alkaline earth aluminates (MAl_2O_4, M: Ca, Sr and Ba) doped with Eu^{2+} and co-doped with selected rare earth (R^{3+}) ions as Dy^{3+} and Nd^{3+}, are efficient blue/green emitting persistent luminescence materials used *e.g.* in luminous paints [1]. The proposed persistent luminescence mechanisms (*e.g.* [2, 3]) have not yet been thoroughly proven since essential experimental data is missing or contradictory. The connection between the electronic band structure of the host as well as the energy levels of intrinsic lattice defects (vacancies, interstitials *etc.*) and the rare earth (co-)dopants needs to be clarified to fully solve the energy storage mechanism of the persistent luminescence materials. Systematic development of new efficient materials will only be possible when the mechanism is understood.

In this work, the electronic structure of the Eu^{2+} doped strontium aluminate ($SrAl_2O_4:Eu^{2+}$) material was studied with density functional theory (DFT) calculations which used the WIEN2k package [4]. The energy positions of the strontium and oxygen vacancies were calculated. The inclusion of Eu^{2+} in the $SrAl_2O_4$ material is expected to create locally important structural modifications of the host structure. Accordingly, the changes in the local environment of Eu^{2+} as well as in the electronic structure due to optimization of the crystal structure were studied, too.

Good agreement was found between the experimental and calculated band gap energies in the $SrAl_2O_4:Eu^{2+}$ material. The Sr vacancy states were located very close to the top of the valence band corresponding to shallow hole traps in the material. Oxygen vacancy states were located close to the bottom of the conduction band. These states correspond to shallow electron traps which can be readily quenched by thermal energy. Additional oxygen vacancy states were found deep in the energy gap of the host. However, electrons in the deep traps can not participate in the persistent luminescence mechanism due to the high amount of energy required to bleach the traps.

Changes in the environment of Eu^{2+} were observed when the crystal structure of the $SrAl_2O_4:Eu^{2+}$ material was optimized. The Eu-O distances were slightly shorter in the optimized structure compared to the original Sr-O distances, irrespective of Eu^{2+} locating in the Sr1 or Sr2 site. This resulted in an increase in the electron repulsion shifting the Eu^{2+} 4f ground state higher in the energy gap. Despite the small structural differences in the two Sr sites with structure optimization, a significant energy difference of 0.41 eV between the luminescence bands from the two sites has been observed experimentally. The difference may be explained rather by the difference in the $4f^65d^1$ level position than in the 4f ground state position of Eu^{2+} in the Sr1 and Sr2 site. Accordingly, the effect of the local environment – *e.g.* the presence of defects and defect aggregates – on the luminescence from the Eu^{2+} center has to be studied even more closely.

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Modeling Biological U(VI) Coordination from First Principles

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Keywords: Actinides; Theory; Coordination; Structure/Spectroscopy

Model bioligand coordination by UO_2^{2+} has been computationally investigated within a combined experimental and theoretical study [1,2] of the microbial influence on environmental actinide chemistry [3,4]. Molecular structures, UO_2^{2+}−ligand binding energies, and electronic excitation spectra of $UO2^{2+}$ salicylhydroxamate, benzohydroxamate, and benzoate systems have been calculated on a hybrid-type DFT and TD-DFT level of theory to complement experimental data. Solvation effects have been addressed by both discrete UO_2^{2+} hydration and a continuum SCRF model. The calculated quantities agree with experimental X-ray absorption (EXAFS) experiments, stability constants, and UV−vis spectra. It has been found that thorough consideration of salvation is necessary to provide consistent molecular and electronic structure models by otherwise routine quantum chemistry methods.

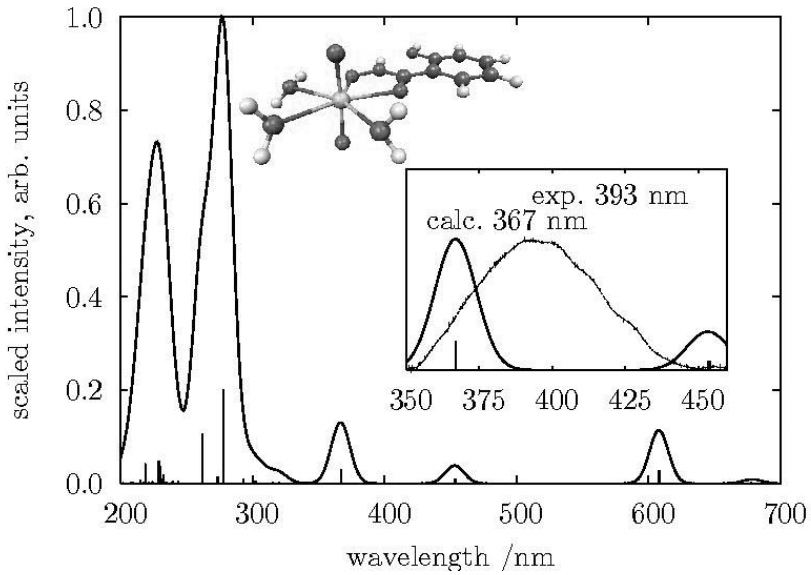

Figure 1. Calculated B3LYP-TD-DFT excitation spectrum of uranylsalicylhydroxamate, considering three discrete OH_2 solvent molecules at the UO_2^{2+} subsystem, and experimental UV−vis spectrum.

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Investigation of Electronic Structure and Properties of Solid EuC_2 and YbC_2

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Keywords: Lanthanides; Theory; Solid State; Structure

EuC_2 crystallizes in a different space group (C2/c) in comparison to all other rare earth carbides (I4/mmm) [1] that have been synthesized.

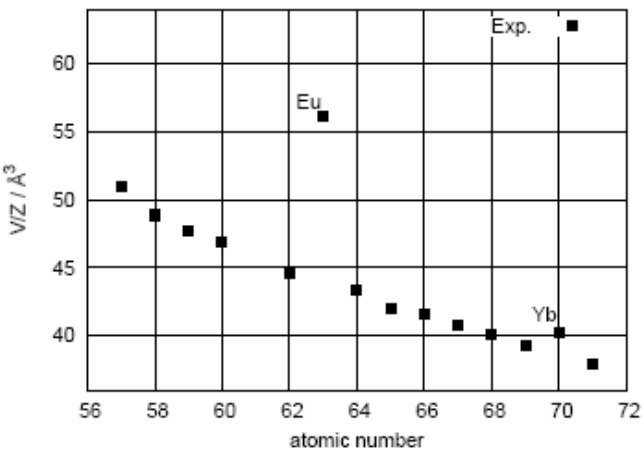

Figure 1. Cell volumes per formula unit.

In addition the unit cell volumes of solid EuC_2 and YbC_2 do not fit in the lanthanide row (cf. figure 1). It has been proposed that this effect might be caused by a difference in the valence of the lanthanide atoms (Ln^{2+} vs. Ln^{3+}). Generally rare earth atoms prefer a valence of 3+ in molecules and crystals. It is possible that the rare earth atoms in EuC_2 and YbC_2 may better be described as a Ln^{2+} than a Ln^{3+} since a half and fully occupied 4f-shell (Eu^{2+}: $4f^{7}$, Yb^{2+}: $4f^{14}$) is favoured.

In our work we focussed on the structures of EuC_2 and YbC_2. The calculations were carried out with the CRYSTAL06 program. Geometries of both carbide compounds have been fully optimized. Band structures were derived and frequencies were analyzed.

Our results agree with experimental presumptions. We could show that Eu is more likely to show a 2+ valence in the carbide compound and Yb a 3+ valence, respectively.

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A MCDHF/DCB-Adjusted Energy-Consistent Pseudopotential for U and its Application to U^{4+}, U^{5+} and UH

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Keywords: Actinides; Theory

The accurate description of the electronic structure of lanthanide and actinide systems requires an inclusion of relativistic and electron correlation effects [1]. Effective core potential methods restrict the explicit quantum chemical treatment to the valence space, thus lead to computational savings compared to all-electron methods and allow a straightforward implicit inclusion of relativistic contributions [2]. Therefore effective core potentials, especially pseudopotentials, are frequently used tools in heavy element quantum chemistry.

A new relativistic energy-consistent small-core pseudopotential (SPP) for uranium, i.e., 1s-4f shells (60 electrons) are included in the core, as well as the corresponding (14s13p10d8f6g)/[6s6p5d4f3g] ANO basis set in a generalized contraction scheme, have been developed [3]. The four-component all-electron reference data , i.e., at the multiconfiguration Dirac-Hartree-Fock level using the Dirac-Coulomb Hamiltonian with a Fermi nucleus charge distribution and perturbatively including the Breit interaction, comprised 100 non-relativistic configurations yielding a total of 30190 J levels which was obtained for U-U^{7+} and included a wide spectrum of occupations in the 5f, 6d, 7s, and 7p valence shells, but also additional configurations with holes in the core/semi-core orbitals 5s, 5p, 5d, 6s, and 6p as well as configurations with electrons in the 6f-9f, 7d-9d, 8p-9p, and 8s-9s shells. The mean square error for the total valence energies of configurations was 16 cm-1 , and for the 30190 J levels 306 cm^{-1} [1]. The new SPP and the basis sets have been applied to U^{4+} [4] and U^{5+} [4] combined with the spin-orbit configuration interaction (SOCI) [5] and Fock-space coupled-cluster methods [6, 7], as well as the diatomic molecule UH [3]. The results have been compared with those of an older scalar Wood-Boring-adjusted pseudopotential, supplemented by a valence spin-orbit term [8], as well as other computational and experimental data from the literature. The accuracy of results obtained with the new pseudopotential is similar to the one of the best available all-electron calculations, however they are obtained at a significantly lower computational cost.

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Hydrothermal synthesis and 2.04 μm emission of Ho^{3+}-doped $NaGd(WO_4)_2$

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Keywords: Synthesis; Lanthanides; Spectroscopy; Nanophotonics

Double alkaline rare-earth molybdates and tungstates $M^+T^{3+}(X^{6+}O_4)_2$ where M= monovalent alkali metal Li or Na, T=Bi, La, Y, Gd, Lu, and X=Mo, W, constitute a wide family of $CaWO_4$-related inorganic compounds having tetragonal $I\bar{4}$ symmetry.[1] These solids are transparent in the mid infrared up to about λ≈5 μm. Single crystals of these compounds have been grown previously in air either from their own melt or using M_2WO_4 and $M_2W_2O_7$ fluxes. In all cases the crystals were free of OH^- radicals or other contaminants introducing optical losses.

Recently, efficient mode-locked sub-100 fs laser generation at λ≈1 μm has been obtained with Yb^{3+} doped crystals,[3] its origin being the large bandwidth of the optical transitions due to the structural disorder.[4] With regard to ordered crystals, this effect is particularly noticeable for Dy^{3+}, Ho^{3+} and Er^{3+} ions. It is expected that the performances of $MT(XO_4)_2$ compounds already shown at λ≈1 μm can be expanded to the mid infrared emissions of lasant lanthanides.

Unfortunately, the thermal conductivity of these single crystals is relatively low, i.e. 1.5-2 W/m×K, limiting power applications. Therefore, it is required to incorporate them in hybrid composites to allow a more efficient cooling of the optical medium. A first step in this direction is the synthesis of nanocrystalline particles able to infiltrate or merge with other materials also transparent in the mid-infrared.

In this work we explore mild (170 ºC, pH=6-7.5) hydrothermal processes to synthesize tetragonal nanoparticulate Ho^{3+}-doped and Tm^{3+} and Ho^{3+}-codoped $NaGd(WO_4)_2$ materials. In particular, it has been observed that the products obtained from pH=7-7.5 solutions and reaction times t lasting 8 h≤ t ≤ 14 h are constituted by a single $I\bar{4}$ crystalline phase, and present an unique size distribution of octahedral particles. The observed room temperature photoluminescence up to 2.1 μm and the lifetimes up to ~400 μs of Ho^{3+} in two series of $NaGd_{1-x}Ho_x(WO_4)_2$ (x=0.005, 0.01, 0.02, 0.05, 0.1, 0.25) morphologically controlled samples prepared during 8h and 14 h, are of interest for coherent mid infrared light sources when incorporated in hybrid photonic composites

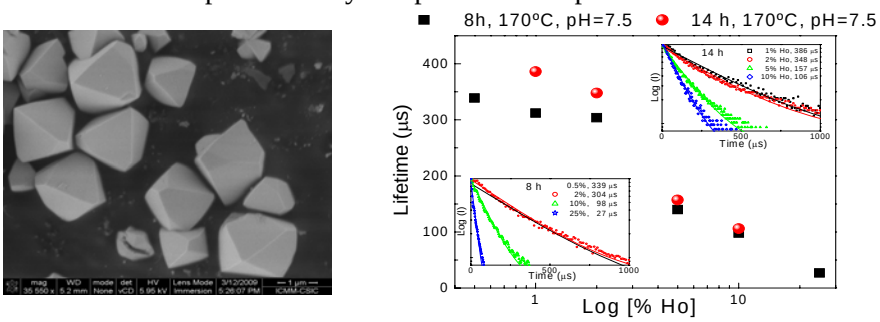

Figure 1. Left, SEM image of $NaGd_{0.95}Ho_{0.05}(WO_4)_2$ hydrothermally prepared at 170 ºC, pH=7.5 and 14 h; Right, lifetimes for Ho^{3+} (λ_{emi}=2041 nm, λ_{exc}=1190 nm) of $NaGd_{1-x}Ho_x(WO_4)_2$ samples prepared at pH=7.5, 14 h or 8 h.

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VUV, UV and Vis Spectroscopic Behaviour of $Lu_2O_3:Pr^{3+}/Pr^{4+}$ Nanosize Phosphors

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Keywords: Nanocrystallites, Combustion Synthesis, Pr^{3+}

There is a challenge in recent years to produce a new nanosize efficient phosphors for medical application and X-ray and γ-ray detectors. Investigations were directed to reveal the influence of synthesis conditions, which affect the morphology of samples, the doping level and size of the nanoparticles on overall optical behaviour of the phosphors.
$Lu_2O_3:Pr^{3+}/Pr^{4+}$ nanosize phosphors were successfully synthesized via a new combustion route [1]. Two series of the nanocrystalline $Lu_2O_3:Pr^{3+}/Pr^{4+}$ for different composition of a fuel and concentration of the active ions (1-10 wt%) were obtained. The samples were heated in different atmospheres; one series in air and a second in N_2 and further H_2 and cover the size range 6-8 nm Optical absorption and VUV and UV excited luminescence spectra were measured at room, 77 and 10 K. Structural characteristic of the samples is presented and correlate with the decay profile of the Pr^{3+} emission The role of the CT state of Pr^{4+} as well as a self trapped emission (STE) of the host on efficiency of the overall emission of nanosize $Lu_2O_3:Pr^{3+}/Pr^{4+}$ phosphors will be discussed.

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Photoionisation investigation in Ce^{3+} doped $LiY_{1-x}Lu_xF_4$ laser crystals

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Keywords: rare-earths; laser crystals, solarisation, microwave cavity, photoconductivity

Ce^{3+} doped $LiYF_4$ and $LiLuF_4$ crystals are known as active media for the ultraviolet (UV) spectral range [1]. $LiLuF_4$: Ce exhibits record energy characteristics among all known solid-state active media in the UV range [2]. However, in its homological analog $LiYF_4$:Ce, lasing is hampered by color centers induced by exciting radiation. By varying the chemical composition of $LiY_{1-x}Lu_xF_4$:Ce^{3+} fluoride crystals with the scheelite structure, one can change the spectral properties[3] and the parameters of losses induced by solarization effects. In this work, we experimentally studied the photoinization effects induced by the UV laser irradiation. This analyze will help also in the choice of the excitation and emission wavelengths in order to avoid losses by excited state absorption mechanisms from the 5d emitting band.

Photoconductivity spectra have been recorded in 1% Ce^{3+} doped YLF and LLF crystals as well as in the mixed $LiY_{0.4}Lu_{0.6}F_4$ solid solution, using the microwave resonant cavity technique [4] which is based on the measurement of dielectric losses when a doped crystal put in a resonator is irradiated by a pulsed tunable laser source. Furthermore the transient signals give access to the kinetic of free carriers in the conduction band. A fast recombination lifetime of the electron either on the active Ce^{3+} ion or on color certers or traps of few tens of nanoseconds is measured. The dependences of the reflected microwave signal intensity with the mean laser excitation permits to establish the photoionisation mechanisms[5]: a linear process corresponding to the direct transition from the rare-earth 5d level to the conduction band is observed shorter than 270 nm whereas a two step- or higher order process is observed for longer wavelength after revealing excited state absorption. It is then possible to locate the rare earth ion energy levels inside the wide band gap of these fluoride crystals. We have estimated that the 4f-ground state energy level of Ce^{3+} ions is located around 5,7 eV above the valence band in $LiYF_4$ crystal

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Size effect on the phase transitions, structure and optical characterization of pure and Pr^{3+} doped $CePO_4$ nanocrystals

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Keywords: Lanthanides; Nanocrystalline Materials; Synthesis; Spectroscopy

The pure and Pr^{3+} doped phosphates $CePO_4$ were prepared in the nanocrystalline form by the hydrothermal method in acid or alkaline environment. Subsequently the powders were calcined at different temperatures. It was established that the samples grown from acid solution (pH = 1) and calcined at the temperatures higher than 600ºC, transform from the hexagonal phase to monoclinic one.

The results of temperature studies showed that two transformations are observed for the phosphate nanoparticles. First is related with the release of zeolite water at about 220ºC and a second corresponds to the irreversible structural phase transition at about 620ºC. The symmetry of the cerium phosphates with zeolite water is pseudohexagonal and the materials free of zeolite water with the hexagonal symmetry transform into the monoclinic phase.

The grain diameter is about 18 – 28 nm depending on the calcination temperature. The size of the particles was determined from the X-ray powder diffraction data with the Scherrer equation and was verified by electron microscopy studies.

The effect of particle size on the phase transformation of $CePO_4$ and $CePO_4$:Pr^{3+} nanopowders was also studied using vibrational and optical spectroscopy. Vibrational spectra showed significant changes as a function of the grain size what can be explained as a result of phonon confinement effect.

Synthesis and photophysical properties of nanomaterials based on lanthanides oxyfluorides

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Keywords: lanthanides; materials; solid state; spectroscopy

The study of nanomaterials is one of the most interesting and active part of the science. The size of crystallites or particles, which compose the nanomaterial, is nanometric and usually not exceeding 100 nm. Nanodimension materials, in contrast to bulk counterparts, show changes in optical, electrical and magnetic properties, depending on their size. Nanomaterials activated by lanthanide ions, Ln^{3+}, were extensively investigated in last years due to their unique and attractive spectroscopic properties, corresponding to f-f transitions. Potential applications of these materials were found in high-performance displays and optoelectronic devices like plasma display devices (PDP), field emission displays (FED), cathode ray tubes (CRT) and electroluminescent displays (EL) [1,2,3,4]. Laser materials, optical amplifiers and photocatalysts are also areas where the nanostructural materials doped with Ln^{3+} ions were used. One of the most promising materials for above mentioned applications are lanthanide oxyfluorides activated by doping with appropriate luminescent ions, like Eu^{3+} or Tb^{3+}.

Gadolinium ($GdOF:Eu^{3+}$, $GdOF:Tb^{3+}$) and lanthanum ($LaOF:Eu^{3+}$, $LaOF:Tb^{3+}$) oxyfluorides were obtained by precipitation of the fluorides in molten stearic acid and in glycerine. Prepared precursors were calcined at range of temperatures to find the best for luminescence and structure, conditions. X-ray diffraction and transmission microscopy were applied to analyze the obtained products. Potoluminescent properties of the prepared nanopowders with the Eu^{3+} and Tb^{3+} ions (concentration ~5 % mol) were investigated by analyzing their luminescence (excitation and emission) spectra and emission lifetimes, measured at room temperature. The luminescence properties, characteristic for Eu^{3+} or Tb^{3+} ions, and structural properties observed for the obtained materials strongly depend on the synthetic method used. Those methods allow to obtain the product at low temperatures. Also, luminescence and structural properties of the material obtained in this way are satisfactory.

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The temperature effect of Ce^{3+} doped CAS and LSCAS glasses luminescence

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Keywords: rare-earths; optical glasses, thermoluminescence

There is currently a great deal of interest in the progress of new luminescent materials that emit at shorter wavelengths. Such materials are desired for photonic applications in imaging, optical data recording, solid state lasers, scintillations and displays. Rare earth ion-doped glasses have been often studied for this purpose. Among them, trivalent rare earth ion Ce^{3+} in glasses/crystals has $4f^1$ electronic configuration of the ground state and $5d^1$ electronic configuration of the excited state. The absorption and luminescence transitions between these states are allowed electric dipole transitions, resulting in large absorption in the UV region and shorter luminescence lifetime. These transitions play an important role in luminescent materials development, which are interesting for those kind of applications.

In this study, two kinds of optical glasses were compared. The first one was prepared with silica content of 7 wt% (LSCAS) and the second one with silica content ~30 wt% (CAS). The interest in these glasses as host material is because they are OH^- free and transparent in the spectral range from ~250 nm to 5 μm, when melted under vacuum conditions. Furthermore, previous work has showed these classes of glasses are a good candidate for solid state laser media hosts due to their thermal, optical and mechanical properties [1, 2]. A broad visible emission was observed for both glasses. The observed emission band of Ce^{3+}:LSCAS is centered near 550 nm, covering the blue and red spectral ranges, and Ce^{3+}:CAS presents a strong blue emission centered around 480 nm.

In this study, temperature-dependent emission spectra of Ce^{3+} doped CAS and LSCAS glasses were investigated. The thermal quenching was analyzed in terms of the activation energy ΔE obtained using an Arrhenius function. An understanding of the origin of temperature quenching is helpful to development of new luminescent materials for photonic applications, like white LED and solid state lasers.

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Preparation and Up-Conversion Luminescence Properties of $NaYF_4:Yb^{3+},Er^{3+}$ Nanomaterials

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Keywords: Lanthanides; Nanomaterials; Up-conversion Luminescence

Up-conversion phosphors are materials which can produce visible emission after excitation with infrared radiation. The up-conversion luminescence of rare earth ions draws more and more attention due to their potential applications in the field of optoelectronics (*e.g.* lasers, displays) or security printing (*e.g.* bank notes, bonds) [1]. As a novel field of application, nanomaterials with efficient up-conversion luminescence may be used in the homogeneous label technology for quantitative all-in-one whole blood immunoassay [2].

The $NaYF_4$ host material has been recognized as one of the most feasible hosts for efficient up-conversion [3]. In this work, up-converting $NaYF_4:Yb^{3+},Er^{3+}$ (x_{Yb}: 0.17, x_{Er}: 0.03) nanomaterials were obtained with a co-precipitation synthesis [4] using NaF and RCl_3 (R: Y, Yb, Er) as the precursor materials. The $NaRF_4$ materials were further heated between 200 and 700 ^oC in N_2, N_2 + 10 % H_2 gas sphere or in air. Impurities were analyzed with FT-IR spectroscopy. The crystallite size and morphology was characterized with transmission electron microscopy (TEM) while the crystal structure was studied with X-ray powder diffraction. The crystallite sizes were also estimated with the Scherrer formula [5] from diffraction data. Up-conversion luminescence was studied with pulsed IR laser excitation at 970 nm.

The FT-IR spectra revealed no impurities in the $NaYF_4:Yb^{3+},Er^{3+}$ nanomaterials. The TEM images showed that the particles were spherical and slightly aggregated. The particle sizes were between. 100 and 150 nm. According to the XPD measurements, both the efficient hexagonal and the less performant cubic phase were present, depending, among other things, on the heating temperature and time as well as on the gas sphere. The calculated crystallite size of the nanomaterials was *ca.* 100 and 150 nm for the cubic and hexagonal phases, respectively, agreeing well with the sizes approximated from the TEM images. The up-conversion luminescence spectra showed both strong red (640-685 nm) and green (515-560 nm) emission due to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ and $(^2H_{11/2}, {}^4S_{3/2}) \rightarrow {}^4I_{15/2}$ transitions of Er^{3+}, respectively. The red-to-green luminescence intensity ratios of the nanomaterials were *ca.* 2. The most intense up-conversion luminescence was obtained when the material was heated at 700 ^oC for 3 hours in static N_2.

This study was partly supported by the Finnish Funding Agency for Technology and Innovation (Tekes).

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Rhombic YbF_3 and GdF_3:Yb^{3+} nanoparticles synthesized in ionic liquids

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Keywords: ionic liquids; nanoparticles; ytterbium; luminescence

Lanthanide fluorides are excellent for the use as luminescent materials due to their low vibrational energies yielding in a minimization of fluorescence quenching. In fact, there are plenty of applications of such luminescent materials including lasers, LEDs, luminescent marker in biomedicine or optoelectronics [1]. Especially, Yb^{3+} doped compounds are suitable for laser materials as the intense and broad Yb^{3+} absorption lines is favourable for IR diode laser pumping. Moreover, neither excited state absorption nor cross-relaxation processes can occur which would reduce the effective laser cross-section. The purpose of Yb^{3+} as a sensitizer for other rare earth species has been described recently[2]. Resulting from the ground electronic configuration $4f^{13}$, which corresponds to a single hole in the complete 4f electronic shell, the Yb^{3+} ion exhibits a very simple energy scheme. In consequence, there is a unique spectral term, ^2F, which is split by the spin–orbit coupling into two energy manifolds, $^2F_{7/2}$ and $^2F_{5/2}$, which separated from each other by approximately 10000 cm^{-1}. In some crystal lattices broad bands in the UV spectral range could be observed for the Yb^{3+} ions under high energy excitation (VUV). Such an emission could be assigned to charge transfer processes, involving allowed transitions between the 4f states of Yb^{3+} and empty ligand centered energy levels [2].

Ionic liquids (ILs) are salts with melting points below 100 °C, many of them are even liquid at room temperature. They often consist of large organic cations combined with weakly coordinating inorganic anions. This offers the possibility to design a IL with properties for a specific applications (task-specific ionic liquids (TSILs)) by choosing the appropriate cation-anion combination. In terms of nanoparticle synthesis, the stabilizing properties based on the coloumbic potential can be used to avoid particle growth and agglomeration. For the synthesis of YbF_3 nanoparticles we have employed the task-specific ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (C_4mimBF_4). It is well known that the tetrafluoroborate anion can serve as a mild source of fluoride anions. Fast ionothermal conversion of suitable ytterbium precursors into YbF_3 can be easily achieved in an autoclave at 120 °. Imaged by TEM, the YbF_3 particles exhibit a rhombic shape with averaged edge lengths of 260 nm (Fig. 1a). Higher resolution reveals that the rhombs are constituted of smaller particles with an averaged diameter of 20 nm. SAED (single area electron diffraction) indicates confirm the single crystallinity of the single particles. By using a microwave synthesis for YbF_3 from C_4mimBF_4 , we obtained YbF_3 of different morphology (Fig. 1b) . Here YbF_3 forms bundles (length 800 nm) of particles with an averaged diameter of 20 nm (Fig. 1b).

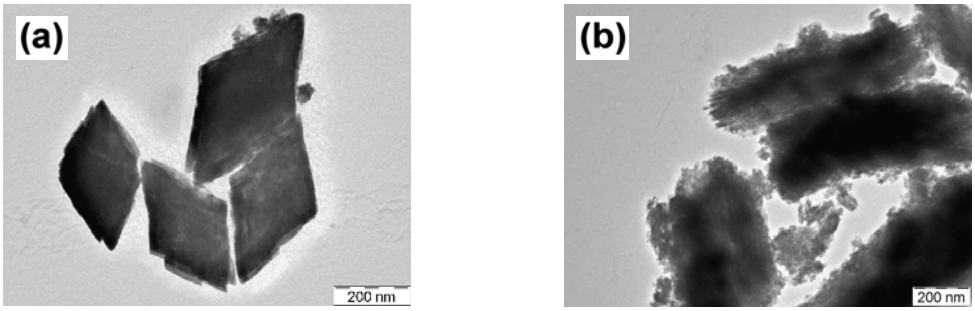

Figure 1. Rhombic YbF_3 (a, autoclave) and YbF_3 as bundles (b, microwave) of particles are imaged by TEM.

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Luminescent lanthanide nanoparticles via metal vapour synthesis in ionic liquids

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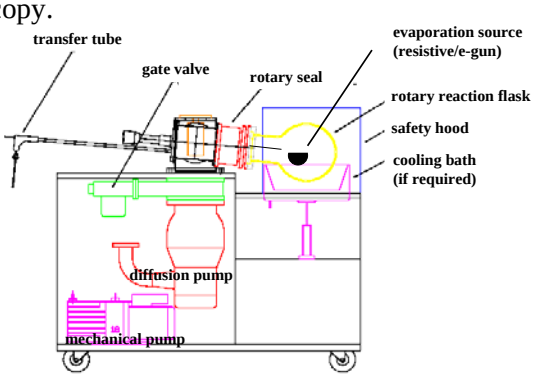
Keywords: ionic liquids; lanthanides; evaporation; nanoparticles

Ionic liquids (IL) are a unique class of salts with a melting point below 100 °C consisting typically of a large, organic cation and a weakly, most times inorganic anion. Some are even liquid at room temperature (RTIL). Due to the possibility of combining many different ions, ILs have tuneable physical and chemical properties, like polarity, viscosity, miscibility with water, or other solvents, and solubility of salts, for example. By the choice of the right cation-anion combination they may be designed in such a way that they are non volatile, thermally stable salts. Because of their ionic character, ILs are able to stabilize nanoparticles by forming electrostatic shells around leading to monodisperse particles and at the same time avoiding particle agglomeration [1]. Rare-earth based compounds and their superior luminescent properties are important in many applications such as in lasers, biosensors, light emitting diodes (LEDs), displays, and lamps. Normally, for such applications well-defined uniform nanoparticles are needed. Until now, classical route to nanoparticles involve wet chemical route such as precipitation, hydrothermal-, microwave-, or ultrasonic methods.

A new method to synthesize size-controlled nanoparticles [2, 3] is the evaporation of lanthanide materials into RTILs. The evaporation accessory based upon the design of Timms [4] is shown in figure 1. The crucible containing the sample, surrounded by a tungsten wire basket heater, is fixed between two water-cooled electrodes. The rotating reaction flask contains the desired RTIL (water content below 50 ppm, 1 ml/mg sample). A pump systems allows the evacuation of the reaction chamber to a pressure of 1.07 mPa. While the crucible is heated by resistive heating, the rotating flask is water-cooled and the IL is stirred, so that the metal-charged surface of the solvent is mixed with the pure IL, which causes diffusion of the particles into the IL. During the evaporation, in which the pressure increases to 2.67 mPa, agglomeration will be prevented, if the evaporation rate is smaller than the diffusion of the particles into the ionic liquid. This synthesis method allows to obtain lanthanide nanoparticles, with a well defined size distribution and morphology. The materials are characterized by XRD, TEM, and optical spectroscopy.



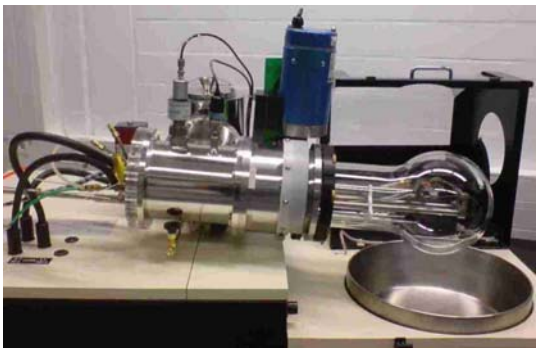


Figure 1. Scheme of the rotary metal vapour synthesis reactor (left) as well as a photo of the evaporation accessory including the reaction flask with a volume of 3 l and the rotary section of the (right).

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Lanthanide-containing Ionic Liquid Crystals

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Keywords: liquid crystals · ionic liquid crystals· ionic metallomesogens · lanthanides

Liquid crystals (LCs) are substances which have properties at an intermediate stage between the perfectly ordered periodic structure of crystalline solids and the perfectly disordered structure of isotropic liquids, gases and amorphous solids. Such an intermediate state of matter is called a mesomorphic state or liquid crystalline state of matter [1,2]. Most LCs are neutral organic compounds with either a rod-like or disc-like shape. Because of their structural flexibility, the orientation of molecules in LCs can be influenced by applying an external electric or magnetic field. A comparatively new field of research is the design of LC-metal complexes.These so called metallomesogens combine the properties of LCs and d- or f-block elements [3, 4].

Ionic liquid crystals (ILCs) represent a number of compounds that are constituted of discrete cations and anions and are able to exhibit a mesomorphic state, thus they combine the properties of LCs and ionic liquids [2, 3]. Ionic liquids (ILs) are salts with a melting point below 100 °C and are often be considered as 'designer' and 'green solvents'. The properties of ILs like viscosity, density, and miscibility with solvents can be tuned by variation of the anions and the cations and their combination [3]. The interest in designing lanthanide-containing ILCs is increasing because of the unique physical properties of several lanthanide ions like magnetism and luminescence [4]. The aim of our work is to design lanthanide-containing ILCs, which combine the properties of lanthanide-ions, ILs and LCs by variation of the ions (as it is shown in Fig.1). Their thermal and optical properties are studied by DSC (Differential Scanning Calorimetry), POM (Polarized Optical Microscopy) and optical spectroscopy (luminescence measurements).

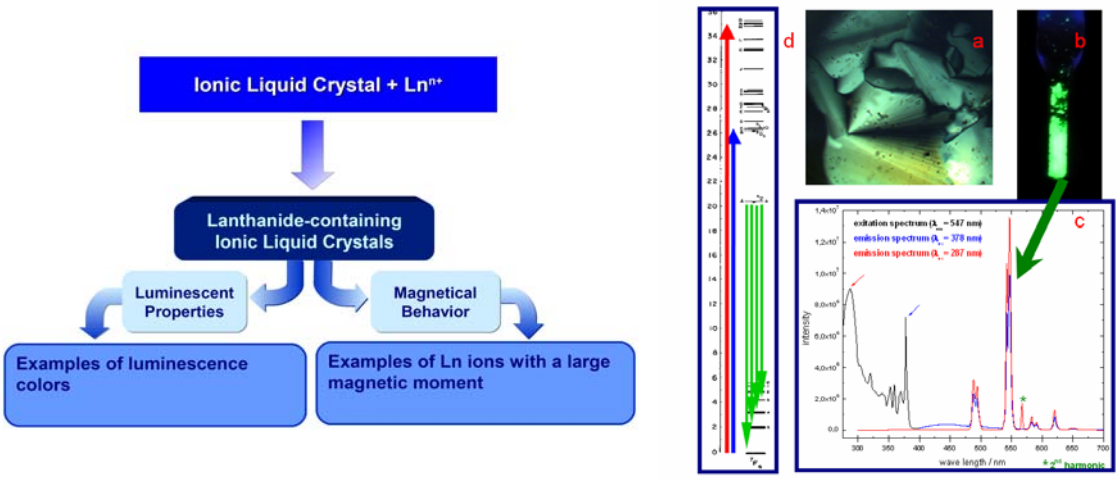

Figure 1. Scheme of the strategy to gain lanthanide-containing ILCs (left) and an example for a ILC under investigation based on $[C_{12}mim]_3[TbBr_6]$ (right): (a): POM microgaphs at 100 °C. (b): Intensiv green luminescence up on UV excitation. (c): Excitation and emission spectra. (d): A cut of Dieke-diagram.

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Toward Rationally Designed Lanthanidomesogens

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Keywords: Lanthanides; Liquid Crystals

The combination of a tridentate coordination unit with different dendrimeric arms yields ligands that form complexes with lanthanide ions, which are potential candidates for forming liquid crystals.

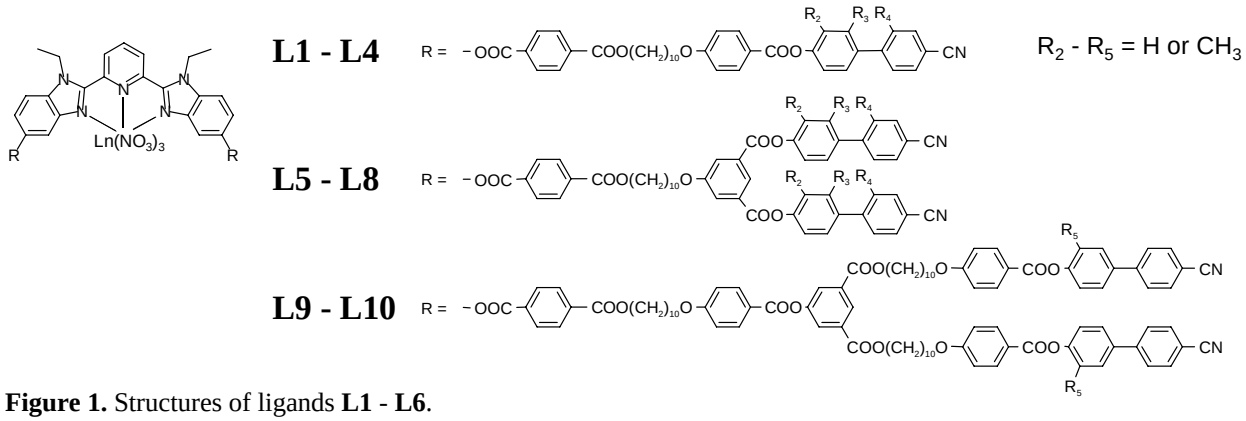

Figure 1. Structures of ligands **L1** - **L6**.

The properties of the complexes have been investigated by means of DSC, POM and SAXS. Whereas complexes of the smaller **L1**-**L4** exhibit no mesogenic behaviour, complexes of the larger **L9** of general composition [Ln(**L9**)$(NO_3)_3$] form smectic phases over large temperatures with clearing temperatures around 186 - 200 °C. Introduction of methyl groups in **L10** leads to lower clearing temperatures (144 - 159 °C) as well as the formation of nematic phases in a narrow temperature domain.

The influence of the methyl groups on the sequences of the mesophases is compared with enthalpic and entropic parameters for the 2 [Ln(**L**)$(NO_3)_3$] ⇆ [Ln(**L**)$(NO_3)_3]_2$ (**L** = **L1** - **L10**) dimerization processes which have been studied in CD_2Cl_2 solution by variable temperature ^{1}H NMR.

For the intermediate ligands **L5** - **L8**, more organised cubic mesophases are suspected on the basis of POM.

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Broad and intense near infrared luminescence induced by structural changes in Pr^{3+}:Tellurite glasses

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Keywords: Lanthanides, Luminescence, Tellurite Glass, Pr^{3+}

Telurite glasses are interesting materials for development of new optical devices due to their low melting point, high refractive index combined with the lowest phonon energy presented among oxide glasses [1,2]. Trivalent praseodymium possess several metastable states providing the possibility of emission over the visible and near infrared spectra and is one of the rare earth ions that can irradiate around 1,3µm, the so called second telecom window [3].

Samples from the composition of $[(100\text{-}x)/100(80TeO_2 + 15Li_2O + 5TiO_2) + (x)Pr_6O_{11}]$ and $[(100\text{-}x)/100(80TeO_2 + 15Li_2O + 5WO_3) + (x)Pr_6O_{11}]$ with x ranging from 0.125 to 0.75 (%mol), were prepared under melt quenching technique. Batches of 10 grams were mixture manually over one hour in a porcelain mortar, placed in a platinum crucible and fusion was performed at 1173K in an electrical furnace. The molten glass was poured into the pre-heated brass mold and brought to furnace for annealing. The spectroscopic properties were investigated through optical absorption and luminescence under 476.5nm, 990nm and 1064nm excitation, using an Ar^+ laser, a diode laser and a Nd^{3+}:YAG laser.

The samples showed absorption bands over the visible and near infrared spectra characteristics from the dopant ion. The emission spectra under 476.5nm excitation showed several bands over the visible region due to the radiative decay from the levels $^3P_1$, $^3P_0$ and $^1D_2$ to the lower lying levels, the transition from $^3P_0$ to $^3F_2$ showed a very sharp red emission. Over 990nm and 1064nm excitation the samples showed a band centered at 1325nm as shown in Figure 1.

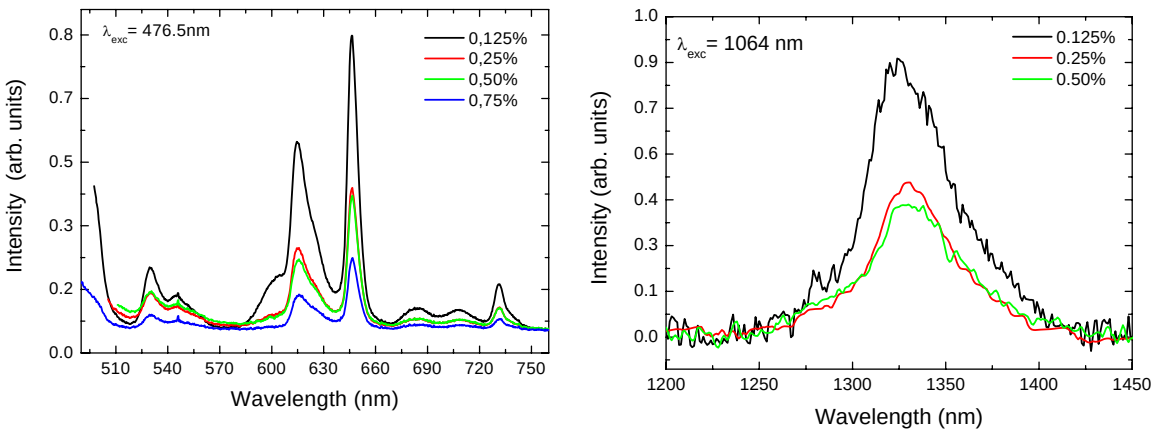

Figure 1. Emission spectra of the samples containing titanium with different concentration (%mol) of Pr^{3+} over the visible region under excitation of 476.5nm and over near infrared region under excitation of 1064nm.

For the set of samples containing tungsten, it was possible to observed a structural change on the glass network through the monitoring of the near infrared emission band when a Nd^{3+}:YAG laser was used as excitation source at high powers. It is known that the basic structural units for tellurite glasses are the TeO_4 trigonal bipyramid and TeO_3 trigonal pyramid, and the increase of temperature can change one in another [4].The local heating of the sample doped with 0.25% mol of Pr^{3+} provided a different number of sites for the doping ion in the sample influencing the intensity of the emission band. This structural change also modified the width of the band centered around 1325nm as it appeared a shoulder at 1270nm as shown in Figure 2.

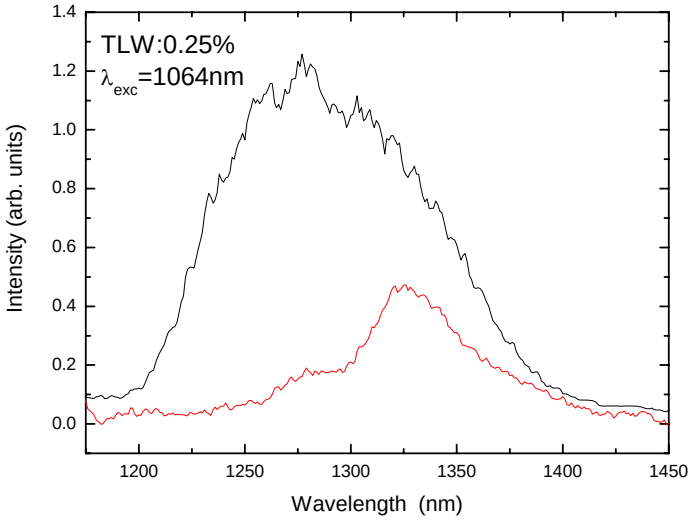

Figure 2. Near Infrared emission band for the sample containing tungsten doped with 0.25%mol of Pr^{3+}. Red line-before annealing, black line after annealing.

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Control of the morphology in hydrothermal synthesis processes and emission near 2 μm of Tm^{3+}- doped Lu_2O_3 nanostructures

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Keywords: Synthesis; Structure; Spectroscopy; Nanophotonics

Due to the conjunction of excellent thermo-mechanical properties, high optical cross-sections and high doping potential for rare-earth laser cations, the sesquioxides Sc_2O_3, Y_2O_3 and Lu_2O_3 are attractive hosts for high power solid-state lasers [1]. Giving its very similar mass and size the latter is the choice material for the favorable incorporation of the highest concentration of Tm^{3+}. The 1.95 μm eye-safe laser emission operating in the $^3F_4 \rightarrow {}^3H_6$ of Tm^{3+} can advantageously replace the traditionally used Ho^{3+}-doped analogue crystal, in the same spectral range, when pumping with high power AlGaAs diode lasers.
However, the high melting temperature, ~2500 ºC, of Lu_2O_3 supposes serious difficulties for the production of bulk crystals. As an alternative, diverse low temperature methodologies have been extensively applied to prepare nanocrystals of this phase, mainly intended for fabricating transparent laser ceramics [2]. Another possibility to be explored is the incorporation of these nanoparticles in hybrid composites. A first step in this direction is the synthesis of Tm^{3+}-Lu_2O_3 nanocrystals with size and morphologies suitable for dense sintering or for infiltration or merging with other materials also transparent in the mid-infrared.

In this work a simple hydrothermal route to synthesize nanoparticles of $Lu_{2-x}Tm_xO_3$ is presented. Two distinct shapes such as micron size rods with ~ 90 nm ∅ and nanosquare sheets have been obtained for Tm^{3+} concentrations ranging from 50% mol to 0.2% mol Tm (i.e., $1.0 \geq x \geq 0.004$) by choosing the starting reagents and adjusting the pH value, 7.5 and 12 respectively, of the reacting solution, which lasted in all cases the same time, 24h. Powder X-ray analyses indicate that both prepared structures are the pure cubic $Ia\bar{3}$ phase, while FESEM and TEM images confirm the formation of different morphologies, as shown in Figure 1. The photoluminescence at ~1.95 μm of Tm^{3+} and emission lifetimes in these materials have been measured, and the dependence with the concentration and morphology is analyzed.

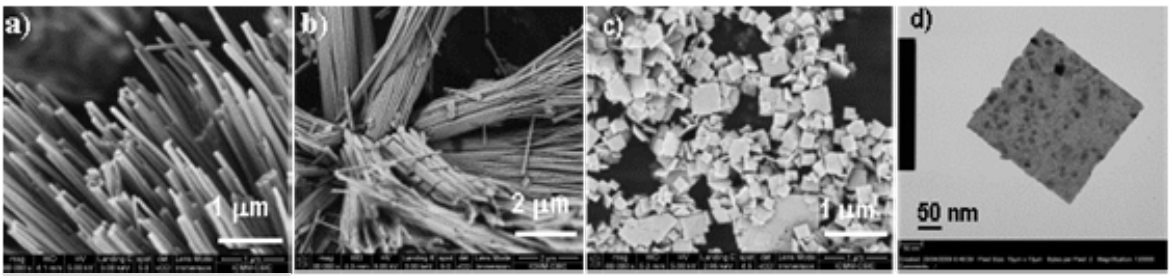

Figure 1. a) FESEM image of micron size nanowires constituting the product of the hydrothermal synthesis of $Lu_{2-x}Tm_xO_3$ (x=0.04) from chloride precursors; b) FESEM image of the final calcined product (x=0.04), where the predominant morphology consists of rods 15 μm×90 nm ∅; c) and d) FESEM and TEM images of $Lu_{2-x}Tm_xO_3$ (x=0.1) hydrothermally prepared from nitrate precursors consisting of ~150 nm square nanosheets

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Biocompatibility of Eu^{3+}-doped Gadolinium Hydroxide and Oxide Nanorods

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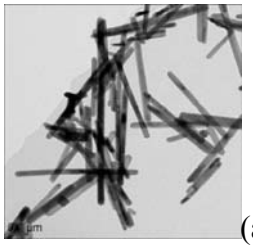
Keywords: Gadolinium Hydroxide; Gadolinium Oxide; Europium-doped Nanostructures; Cytotoxicity

With regard to new imaging diagnostic tools materials showing magnetic and luminescent properties are of growing interest. Due to the efficient luminescence, Eu^{3+}-doped inorganic host materials turn to promising candidates for applications as contrast agents in MRI, bio-sensors or markers that may overcome the toxicity of recently used semiconductor quantum dots [1, 2]. Gd_2O_3:Eu^{3+} nanoparticles have been investigated with regard to their optical properties and suitability as fluorescent markers [3, 4]. In this study, we focus on the synthesis and characterization of Eu^{3+}-doped Gd-containing nanorods. $Gd(OH)_3$ nanorods of 500 nm in length and 30 nm in width were prepared by solvothermal decomposition of Gd-containing molecular precursors (figure 1a) [5]. Hydrothermal treatment of $Gd(OH)_3$ with $EuCl_3 \cdot 6\,H_2O$ resulted in $Gd(OH)_3$:Eu^{3+}, which was transformed into gadolinium oxide by subsequent annealing where-as the rod-like nanostructure was persistent.

Our interest lies in the preparation of Ln-containing nanomaterials with respect to future applications in biomedicine or diagnostic. In this context *in vitro* experiments have to be performed to test the potential cytotoxicity. Therefore, cytotoxicity experiments were performed for synthesized nanorods by using human colon epithelial cells (Caco2) and human lung epithelial cells (A549). After two different exposure times the effect of the doped Gd_2O_3 nanostructures was determined via analyzing the following parameters: metabolic activity of the cell (WST-1), cell proliferation (BrdU), cell membrane homogeneity (LDH) and viability (Live/Dead staining, figure 1b). The cytotoxicity of Eu^{3+}-doped, as well as malleabilized Eu^{3+}-doped Gd_2O_3 nanorods was tested till the concentration of 250 µg/ml. In the case of both cell culture systems the malleabilized and non-malleabilized Eu^{3+}-doped Gd_2O_3 showed no cytotoxic effects regarding the test parameters.


(a)

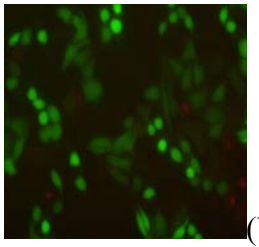

(b)

Figure 1. TEM image of $Gd(OH)_3$ nanorods (a) and fluorescence microscopic image of A549 cells after incubation with Gd_2O_3:Eu^{3+} nanorods for 24 hours (green: Fluoresceindiacetat, red: Propidiumiodide).

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Lanthanide complexes of tripodal ligands derived from hydroxoyquinolinate with potential application in magnetic resonance imaging

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Keywords: MRI agents; relaxation theory

Magnetic resonance imaging is a commonly used diagnostic method in medicinal practice as well as in biological and preclinical research. However, the relaxivity of commercial CAs is only a few percent of the theoretically predicted relaxivity while the "new generation" target specific CAs require higher relaxivity. The simultaneous optimization of the molecular parameters determining the relaxivity (number of coordinated water molecules, water-exchange rate, rotation dynamics of the whole complex, electronic relaxation, ion-nuclear distance, solvation) is essential to prepare more efficient contrast agents.

We have recently become interested in the design of new ligands containing 8-hydroxyquinoline groups. For a better understanding of the influence of this group, we have synthesized two tripodal ligands based on nitrogen anchors to change both the pre-organization of the lanthanide complexes and the numbers of water in the first coordination sphere of the ion.

We have already reported the photophysical properties of tripodal 8-hydroxyquinolinate ligands [1]. Here are presented the synthesis, the thermodynamic and relaxometric properties of two new hydroxiquinolinate based Ln(III) complexes.

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Synthesis and Characterization of Novel Tridentate Receptors for the Preparation of Luminescent Lanthanide-Containing Materials

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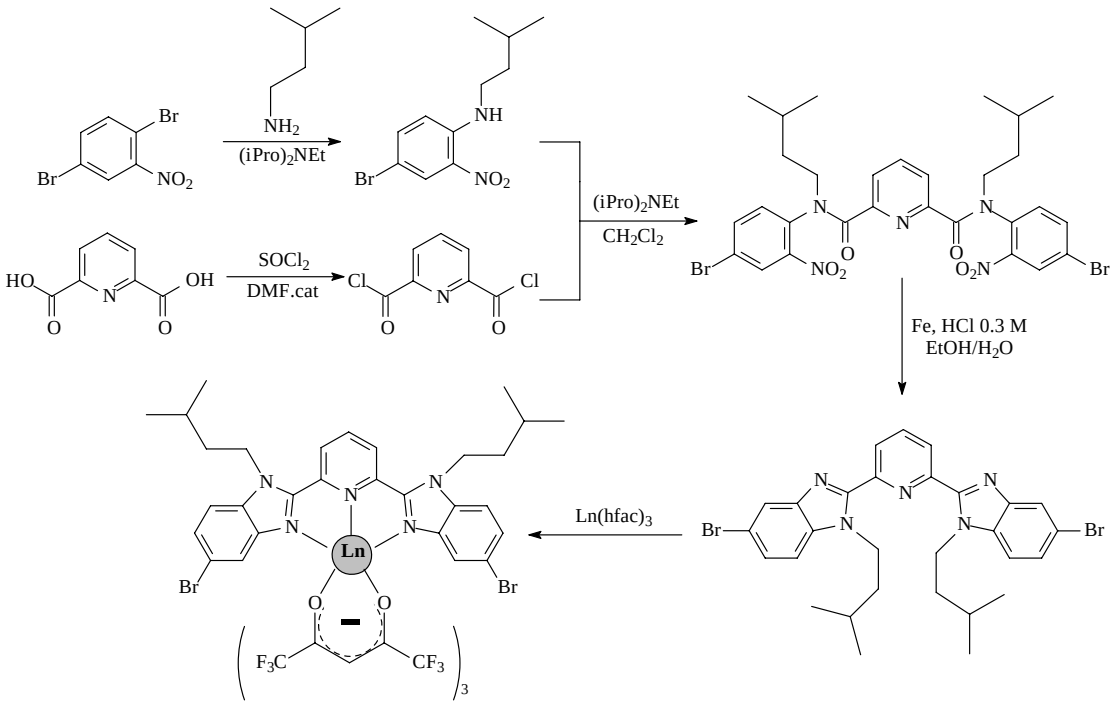
Keywords: lanthanide; luminescent materials;

In recent years, considerable effort has been focussed on the development of new luminescent materials based on lanthanide metal–ion complexes.[1] A new synthetic strategy has been developed to obtain bent aromatic tridentate 2,6-bis(benzimidazol-2'-yl)pyridine cores functionalized with two bromine atoms. A series of new lanthanide complexes has been synthesised by treating the bromo-substituted tridentate receptors with the lanthanide hexafluoroacetylacetonates, $Ln^{III}(hfac)_3$. In order to understand the effect of the bromine substituents on the stability and on the electronic properties of these complexes, analogous non-substituted tridentate receptors have been prepared. The thermodynamic and photophysical properties of these two families of lanthanides complexes will be discussed.



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Lanthanide-polymer hybrid nanoparticles prepared by the miniemulsion technique - Design, characterization and application

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Keywords: Lanthanides, Miniemulsion, EPR-spectroscopy, Film formation

Complexes, clusters or solid state materials based on lanthanides are used for screens, catalysts, magnets and contrast agents. Their optical and magnetic properties are responsible for this variety of applications. For some lanthanide compounds there are difficulties in handling because they are sensitive towards moisture or air. Therefore it is necessary to protect them in order to maintain their unique properties and be able to make use of them. This can be achieved by embedding lanthanide compounds in a polymer matrix. Polymer dispersions containing polymer nanoparticles with the embedded lanthanide components are easy to process. Such polymer dispersions can be printed and they are able to form polymer films.

The miniemulsion technique is a suitable method for the preparation of polymer nanoparticles containing different compounds. By using this technique lanthanide-polymer hybrid nanoparticles dispersed in water can be obtained.

By using the miniemulsion process hybrid particles from a great variety of hydrophobic lanthanide complexes (e.g. $Ln(tmhd)_3$) were prepared. The particle size can be adjusted from 80 to 300 nm. For the polymer matrix different types of monomers (e.g. styrene, acrylates and methacrylates) can be used.

The particle structure and morphology are influenced by the lanthanide coumpound, the surfactant type and the polymer. $Ln(tmhd)_3$-type complexes induce the formation of onion-like or lamellar ordered structures (Figure 1). The layer distance can be adjusted from 2-5 nm dependent on the chain length of the applied surfactant. The structure formation can be characterized by electron paramagnetic resonance (EPR) spectroscopy. The double electron-electron resonance (DEER) method, which can measure the dipolar interaction of two or more electron spins, enables the determination of interlayer distances in the range of 2-8 nm. The interaction of coordinating surfactants (e.g. alkyl sulfates) with free coordination site(s) of the lanthanide complex is responsible for the structure formation. Also complexes without accessible coordination sites are dispersed in the polymer matrix. It could be shown that their optical properties are retained after embedding in a polymer matrix.

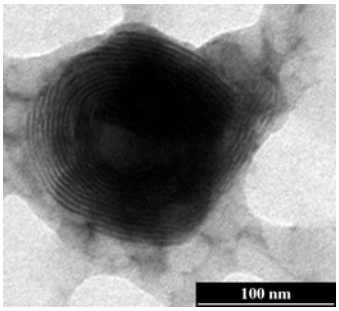

Figure 1. $Gd(tmhd)_3$-Polymer hybrid nanoparticles.

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Gold Nanoparticles Functionalized with Gadolinium Chelates as High Relaxivity MRI Contrast Agents

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Keywords: Lanthanide; MRI; Contrast agent; Magnetism

We developed small, stable, water-dispersible, DTTA[1] thiol functionalized gold nanoparticles (DtNP) complexed with paramagnetic gadolinium or diamagnetic yttrium rare earth ions (Gd-DtNP and Y-DtNP).
Characterizations using TEM images, dynamic light scattering technique and STEM with EDX analysis indicate a particle size distribution from 2-15 nm. Molecular modelling (Figure 1) shows a thickness of the coating shell of roughly 1.3 nm as measured between the rare earth ions and the gold core surface.
Accurate Au and Gd or Y concentrations have been determined with ICP-MS technique. Bulk magnetic susceptibility measurements at high magnetic field of different concentrations of Gd-DtNP and Y-DtNP samples showed the absence of a significant magnetic contribution due to the gold core.
NMRD profiles of Gd-DtNP solutions at 25°C show very high relaxivities with marked relaxivity humps between 10 and 60 MHz indicating slow rotational motion (Figure 2).

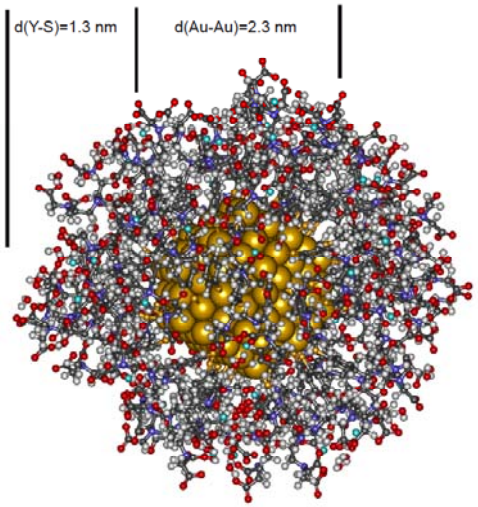

Figure 1. Partially optimized structure (MM3 force field) of Y-DtNP containing 201 gold atoms, 56 Y-Dt chelates and 112 water molecules.

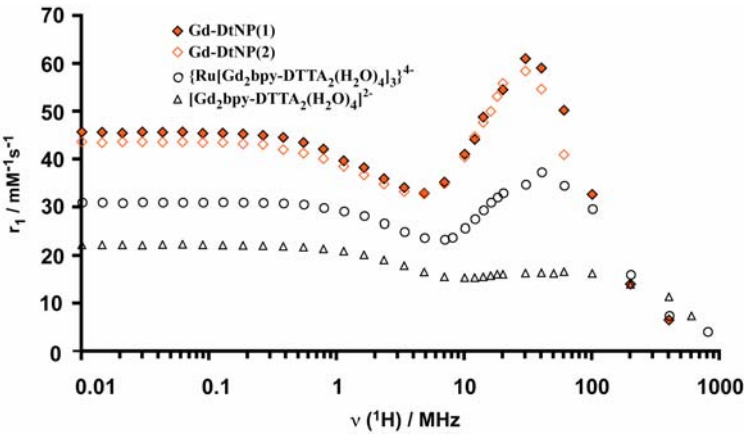

Figure 2. ^{1}H nuclear magnetic relaxation dispersion (NMRD) profiles, recorded at 25°C of Gd-DtNP(1), Gd-DtNP(2), Ru-based metallostar $\{Ru[Gd_2bpy\text{-}DTTA_2(H_2O)_4]_3\}^{4-}$ and the bimetallic complex $[Gd_2bpy\text{-}DTTA_2(H_2O)_4]^{2-}$.

The "modified Florence approach"[2] fits well the experimental points of the NMRD profile of Gd-DtNP(1) even at high frequencies indicating that the nanoparticles behave as rigid units. The fitted parameters describing the electron spin relaxation are finally in good coherence with what was expected from the Ru-based metallostar values.[3]

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Lanthanide complexes encapsulated in silica nanoparticles

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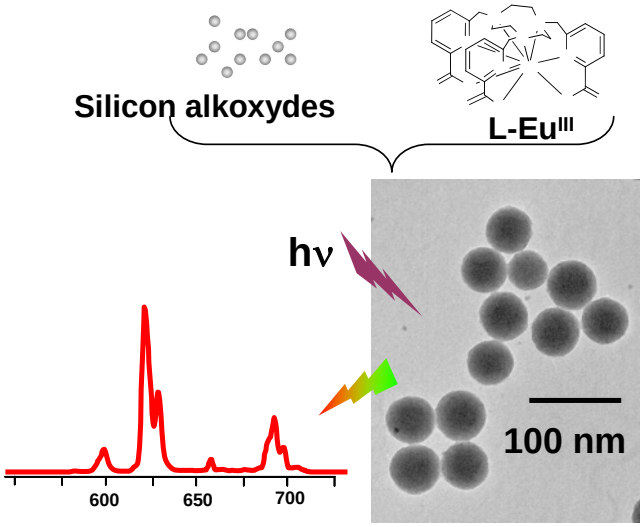
Keywords: Lanthanides; Chemistry; nanoparticles; Spectroscopy; Luminescence

This project is based on the preparation of hybrid silicate nanoparticles including molecular fluorophores for the development of fluorescent tags for material (luminescent materials, fluorescent tracers, counterfeiting, sensors of ground pollutant agents…) and *in vitro, in vivo* biological (biophotonics or phototherapy…) labeling and imaging. The approach to the development of lanthanide based tags is based on the incorporation of lanthanide compounds in materials capable of silica nanoparticles which allow protection of the chelate, improvement of the luminescence efficiency and easy vectorisation and furthermore can provide a route to multimodal tags.



Here we focus on the sol-gel processes using micro-emulsions. These processes imply the incorporation of the lanthanide chelates in silica particles of nanometric size with a random distribution. Sizes from 50 to 70 nm are obtained and the synthetic methods allow to promote the incorporation of the lanthanide chelates in silica by adequate choices of surfactant and co-surfactant. Interesting results have allowed us to validate the synthetic methods involving sol-gel processing with silica precursors. The TEM images show porous particles with homogeneous sizes. The photophysical studies have confirmed that the complexes are incorporated and produce good luminescence quantum yields (suspension in water) and that the lanthanides ions are not released in the media. Moreover we have shown dual emission in various emission ranges. The Tb^{III}- and Eu^{III} containing nanoparticles display good luminescence quantum yields and a sizeable near-IR luminescence emission is observed for the Yb^{III} and Nd^{III} complexes.

Structural and spectroscopy characterization of rare-earth ion doped PLZT ferroelectric ceramics

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Keywords: PLZT transparent ceramics; rare earth ions; solid state NMR, laser active media

In recent years, there has been a great interest for rare-earth (RE) doped transparent ceramics as near-infrared laser active media due to their feasible fabrication, better mechanical, thermal and chemical stabilities than crystals and glasses [1]. Although the composition of lead lanthanum zirconate titanate (PLZT) ceramics, with La/Zr/Ti proportion 9/65/35, is mostly known for its ferroelectric and electro-optic properties, characteristics such as extensive transmission window, fairly low phonon energy and high refractive index, also make it a very interesting host for RE ions. Recently, several works have reported Nd^{3+}-, Er^{3+}- and Tm^{3+}-doped PLZT transparent ceramics as potential near-infrared laser active media and amplifiers[2-4]. In particular, transparent PLZT:Nd was reported as the most promising candidate for 1.06 μm emission. However, as the dopant concentration was increased from 1.0 at%, the optical quality of the ceramic was gradually worsened by the presence of secondary phases, so that the required conditions for laser action could not be achieved. Since the structural quality of samples has a direct implication on their spectroscopic and optical qualities, the goals pursued in this work are to present means to obtain highly transparent samples with higher dopant incorporation, as well as to understand some fundamental questions regarding the distribution and incorporation of different RE ions in the PLZT host matrix [5,6]. With this purpose, an alternative method, based on the use of RE-doped precursor oxides, is presented for the synthesis of PLZT:RE. The samples are characterized by several techniques (XRD, DTA-TG, FT-IR, Raman, NMR and Luminescence), as a function of doping concentration (0.1 – 4.0 wt% RE_2O_3). XRD results show formation of significantly lower contents of secondary phases for samples doped with Nd^{3+}, Y^{3+} and Yb^{3+} prepared by the alternative method. In addition, solid state NMR spectroscopy of ^{207}Pb proved to be a very useful tool for the understanding of these complex systems. Because active RE ions are paramagnetic, and thus inaccessible by NMR, the strategy used for the characterization of their spatial distribution was to study the paramagnetic influence of ^{207}Pb powder pattern. NMR measurements allowed us to make proposals about dopant ion insertion considering secondary phase formation and showed homogeneous distribution of dopants in the matrix. Finally, luminescence studies indicate efficient emission of these materials with no evidence of quenching in the concentration ranges studied.

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Optical Materials on the Basis of the CeO_2:Ln Nanoparticles

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Keywords: Lanthanides, Materials, Structure, Luminescence

Technology of synthesis of silica gel-glasses, inorganic films, powders and ceramics activated by the CeO_2:Ln (Ln ≠ Ce) nanoparticles has been elaborated and their spectral-luminescent properties when Ln = Nd, Sm, Eu, Tb, Dy, Ho, Er and Tm are considered.

It has been shown by the methods of small-angle neutron scattering, electron microscopy and X-ray diffractometry that the nanoparticles possess by the O_h symmetry with coordination number of the cations 8 and their sizes distributed within the 5–200 nm range for the glasses and about 50 nm for the powders and ceramic. It has been established that the relative concentration and sizes of the CeO_2:Ln nanoparticles in glasses can be varied in a wide range by technological methods and entering of compensator of local charge.

It has been established that optical centers forming in the nanoparticles are characterized by the following spectral features: intense absorption at wavelength shorter than 400 nm; narrowband luminescence spectra with a high relative intensity of magnetic-dipole transitions caused by the Ln^{3+} ions; weak vibronic interaction of the Ln^{3+} ions with the glassy host-matrix; an effective sensitization of the Ln^{3+} ions luminescence by the labile photoreduced ions $(Ce^{4+})^-$ which can occur both by non-radiative transfer of energy by the exchange-resonance mechanism and by reversible transfer of an electron to the Ln^{3+} ions prone to the lowering of their charge state. In certain cases, the sensitization by transfer of electron can lead to luminescence of photoreduced $(Ln^{3+})^-$ ions. At heat treatment in hydrogen, the reduction of Ce^{4+} to Ce^{3+} in the nanoparticles can occurred both without relaxation of local environment to the new charge state of the activator and with such relaxation. In the first case, an effective (quantum yield close to 100%) sensitization of luminescence of Ln^{3+} ions by Ce^{3+} ions takes place, and formation of effective luminescent centers with essentially modified spectra is realized in the second case.

With formation of the nanoparticles, some share of isolated simple Ln^{3+} and complicated Ce^{4+}–Ln^{3+} centers can be formed too. These centers are characterized by a low symmetry and by the broadening spectra with relatively large intensity of the electric-dipole transitions as well as do not display the sensitization of the Ln^{3+} ions luminescence in the complicated centers. A presence of the nanoparticles and the isolated centers in the activated matrixes is a cause of switching from narrowband spectrum with a high intensity of magnetic-dipole transitions to broadband spectrum with a high intensity of electric-dipole transitions depending on wavelength excitation.

The materials potential applications as laser media, optical switchers, and ultradispersed luminophors are discussed.

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Lanthanide Containing Nanostructures: Microwave-assisted Synthesis

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Keywords: Lanthanides; Organometallics; Nanostructures

Recently, one-dimensional (1D) nanostructures have gained great attention due to their unique chemical, physical and mechanical properties [1, 2]. Especially, hydroxide and oxide of lanthanide (Ln)-based compounds have a huge potential for the application for luminescent devices, catalyst, magnets and other functional materials.

Up to now, several methods such as hydrothermal [3], solvothermal synthesis [4] and chemical reactions [5] are applied to synthesize nanoparticles with rare earth elements. In this work, we are presenting our results of Ln-based nanomaterials prepared by microwave-assisted method. The Tb(OH)3 nanomaterial is obtained by decomposition of
Tb(oleat)3 with ionic liquid [bmim]BF4. Subsequent calcination treatment of Tb(OH)3 nanomaterial at high temperature leads to form Tb2O3 nanostructures. Depending on the operating parameters of microwave oven (temperature, exposure time, pressure etc.) and then different types of nanostructures characterized by XRD, SEM and TEM.

New nanostructures prepared by a pore filling of template AAO with different lanthanide containing precursors as well as doping of other rare earth elements in the microwave oven are under investigation.

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Formation and microstructure of thermal stable La-containing complex oxide nanoparticles in catalytic alumina support

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Keywords: Lanthanum; Solid-state reaction; Alumina; Catalyst support

Lanthanum modified γ-alumina support that embedded highly dispersed La-containg oxide nano-particles in γ-alumina matrix was prepared by impregnation process. La-containg alumina was heated in the temperature range of 600-1200□ and characterized by surface area measurement, X-ray powder diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM). The added lanthanum should react with γ-Al_2O_3 to form $LaAlO_3$ nano-particles in the secondary particle of alumina. $LaAlO_3$ nano-particles with average crystallite size of about 10 nm were found after heat treatment at 800□, and the crystallite size of $LaAlO_3$ nano-particles increased with the rise of heat treatment temperature. Work partially supported by City-area project of Western-Tono, “Development of environmentally conscious ceramics” .

Development of environmental conscious ceramics using some rare earth doped compouds

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Keywords: rare earths, joint research, ceramics

Gifu area in Japan island has clustered unique technologies with potential specific field about ceramics. Japanese government will promotion the relationship between industry-academia , and Prefectures government cooperation toward unique/innovative technologies. Our program about use of rare earths for new ceramics is focusing on utilizing technical seeds or intelligence of universities as well as industrial potential in Western-Tono (Gifu) region in Japan. This region has many factories for ceramics and pottery products. This paper reports the author's project about new generation environmental ceramics by using rare earth elements and compouds. In addition, the aims to create new business and local industries as well as research and development through promotion and encouragement of industry-academia-government joint research that utilizes unique regional resources. Work supported by City-area project of Western-Tono, "Development of environmentally conscious ceramics".

Surface Modification and Oxygen Storage Capacity of CeO_2-containing Nanoparticlate Composite Prepared by Precipitaion Process

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Keywords: cerium, oxygen storage, nanoparticles, precipitaion

Oxygen removal reactions and OSC of ceria catalyst on oxide support were examined by temperature programmed reduction (TPR) and oxygen pulse injection. TPR traces of ceria catalyst on alumina and zirconia show two peaks at 420 and 560 . The OSC per weight increases with CeO_2-content as-prepared state. The OSC per Ce decreases with CeO_2-content, however in the case of zirconia support, the performance of OSC was influenced by the composite state or interface between oxides. The activation energies of the first peak at 460 was increase slightly with Ce-content, but that of the first peak at 560 was decrease with Ce-content. it result indicated that there are the relationship between the properties under reducing atmosphere depending on the interaction between support and ceria. This phenomena is useful the design of support-catalyst interaction when two comonents are both oxides.
Work supported by City-area project of Western-Tono, “Development of environmentally conscious ceramics” .

Internal friction and oxygen relaxation of some rare earth doped zirconia ceramics

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Keywords: yttrium oxygen relaxation, internal friction, zirconia

The solid solution oxides of CeO_2 and ZrO_2 are useful crystals as solid state ionics, which are applied to sensors, solid eletctrolytes and other advanced devices such as SOFC. Since CeO_2 is easily reduced in reducing atmosphere, the fabrication of composites with ZrO_2 is considered for the design of components in the fuel cell operating at moderate temperatures. However, in this ternary system of CeO_2-ZrO_2-Ln_2O_3 (Ln: rare earths), the decrease in oxide ion conductivity is observed by mixing ZrO_2 and CeO_2. In this work, the oxygen movement and the doping effect of CeO_2 to ZrO_2-Y_2O_2 are examined by the mechanical loss measurement of polycrystalline bodies. We discuss the difference of the mobility of oxygen, which is the origin of mechanical loss in the crystals, by comparing the mechanical loss peaks in a series of solid solutions. The starting powders were obtained by a coprecipitation process of aqueous metal nitrates with ammonia solution. The as-precipitated powders with the selected compositions were filtered, washed with distilled water, and the calcined at 1027K for 3h in air. The sintered bodies were prepared by a heating procedure of the compact bodies at 1827K for 3h in air. Specimens with dimensions of $40\times4\times0.5mm^3$ were cut from them. The mechanical loss measurements at the temperatures up to 823K were carried out with a torsion pendulum system with the frequency range of 0.1–9.0 Hz. The apparatus is attached with the detector of the strain and load in connection with a PC-controlled measuring system. The Q was evaluated by the direct measurement of the difference of phase between stress and strain. The low temperature mechanical loss spectra were measured. We observed two loss maxima of Debye-type relaxation which are related to local jumps of oxygen, and their strong Ce-doping level dependence.

Spectroscopic proprieties of new class tungstates; the role of co-doping d-electron ions

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Keywords: d-electron ions, neodymium, luminescence

The inorganic compounds doped with RE ions are widely known as multifunctional materials having unique physical and chemical properties. In recent years, great interest has been focused on lanthanide complexes with d-electron or diamagnetic transition metal ions. The introducing d-electron ions plays the important role in modulating magnetic and spectroscopic properties. Among the lanthanide ions' series, the Eu^{3+} ion has a great advantage because of its non-degenerate ground and emitting states, which allow to use this ion as a structural probe. We have investigated the clastering process and the role of chain formations in lanthanide tungstates and molibdates on the optical behaviour mainly on radiative transitions probabilities and nonradiative phenomena [1].

New families of the zinc, cadmium and copper tungstates doped with the europium ions were synthesized by a solid-state reaction between Eu_2WO_6 and MWO_4. The studies of reactivity between divalent metal tungstate (MWO_4) (M = Zn, Cd, Co, Cu) with some of the rare-earth metals' tungstates RE_2WO_6 (RE=Y, Nd, Sm, Eu, Gd, Dy, Ho) were described in our previous papers [2]. The RE_2WO_6 compounds show polymorphism. The structure of the low-temperature modifications of RE_2WO_6 (RE=Pr-Dy) is closely related to the scheelite-type structure and can be described by the following formula $RE^{[7]}RE^{[8]}[W^{[6]}O_6]$ when RE=Ho-Lu. The $ZnEu_4W_3O_{16}$ phase crystallizes in the orthorhombic system and it is not isostructural with known $CdRE_4Mo_3O_{16}$ compounds. The $MEu_2W_2O_{10}$ (M=Cu, Cd) compounds crystallize in the monoclinic system and have a layered-type structure. The anion lattice of these phases is built by structural elements $[(W_2O_9)^{6-}]_\infty$.

The electronic transitions probabilities, emission, excitation spectra and fluorescence lifetimes of novel type tungstates were investigated at 293, 77 and 4 K in the 200-2000 nm spectral range. The fine structure of the electronic levels were analyzed and used in the structure and symmetry determination. For diluted yttrium compounds the emission from $^5D_1$ level was observed. Basing on a standard Judd-Ofelt analysis, radiative transition probabilities branching ratios and quantum efficiencies of most emission transitions were estimated. The X-ray data and IR spectra are useful for better understanding of the Eu(III) ion behaviour. The influence of the d-electron metal on the intensities and splitting of the bands were observed. The distinct vibronic coupling in the absorption, emission and excitation spectra occur. The single ion relaxation processes and cooperative interactions will be disused.

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The photoluminescence properties of Eu^{3+} and Gd^{3+}- doped sodium doubles phosphates under VUV/UV excitation

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Keywords: energy transfer, gadolinium, europium

The strong demands for phosphors suitable to excitation in vacuum ultraviolet (VUV) regions is important challenge in the field of luminescent materials, typically for plasma display panels and mercury- free fluorescent lamps. The Gd-Eu couple is well known for efficient conversion of the absorbed high-energy photons into two visible ones [1]. Through two-step energy transfer from Gd^{3+} to Eu^{3+}, two red emission photons of Eu^{3+} may be realized with quantum efficiency close to 200%. The two-step energy transfer process was investigated mainly for fluoride compounds and only few oxide hosts doped with RE ions were tested. Among them Eu^{3+} doped $GdBO_3$ has found commercially application in PDP devices.

The alkali metal double phosphates, such as $Na_3M(PO_4)_2$ (M = Y, Lu, RE) show strong VUV absorption around 165 nm and are good candidates for various luminescent materials. The sodium double phosphates with different concentration of Gd^{3+} and Eu^{3+} ions were synthesized by solid state reaction. The optical properties were studied basing on the emission and excitation spectra measured under VUV/UV excitation at room and low temperatures. The measurements with different energy of the excitation lines were used to characterize the energy transfer between pair ions in the compounds under investigations. The role Gd^{3+} in enhancing Eu^{3+} luminescence $Na_3Lu(PO_4)_2$:Eu^{3+} under excitation by vacuum ultraviolet light was investigated.

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A spectroscopic study of potassium lanthanide ternary chlorides doped by Pr^{3+} and Yb^{3+} ions

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Keywords: luminescence, praseodymium, ytterbium

The wide band gap materials, like chlorides and other halides co-doped with lanthanide ions are important in obtaining valuable insights into many aspects of luminescence centers as well as for wide applications [1-5]. The most interesting optical properties of chloride materials is their high transparency arising from low energy phonons on one hand and high ionicity on the other hand [4]. These intrinsic properties extend transmission to far UV and IR, and lead to less absolute fundamental absorption with respect to other oxide or sulphide materials. Moreover, in many chemical compositions exhibiting high solubility for rare earth ions together with crystal field effects, high doping level is achievable. Altogether, it makes the chlorides the very efficient materials, which are used in a wide range of optical applications from phosphors to lasers [5]. Among lot of different isolators especially lanthanide ternary halides seem to be very promising lattice to study cooperative interaction between active ions and interaction matrix-ions.

A series of potassium lanthanum praseodymium ternary chlorides K_2LnCl_5 and KLn_2Cl_7 (Ln=Gd, La) complexes codoped by Pr^{3+} and Yb^{3+}, with wide range of concentration of active ions, was grown with Bridgman techniques. Spectroscopic measurements relevant to laser applications, high resolution absorption and emission spectra at 293, 77 and 4 K as well as emission decay times have been studied. The influence of codoping by Yb^{3+} ions on the optical properties of KLn_2Cl_7 and K_2LnCl_5:Pr^{3+} single crystals will be discussed.

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Sensitised near-infrared luminescence of Ln(III) complexes

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Keywords: Lanthanide, Spectroscopy, Ligand-to Metal Energy Transfer, Structure.

A serie of new lanthanide complexes with sulfonylamide derivatives of a general formula $C_6H_5SO_2NHPO(R)_2$ was synthesized ($\{Na[Ln(SB)_4]\}_n$, $\{Na[Ln(SK)_4]\}_n$ where Ln = Yb^{III}, Er^{III}, Nd^{III}, Lu^{III} and Gd^{III}) and the crystal structure of ($\{Na[Er(SB)_4]\}_n$ and $\{Na[Yb(SK)_4]\}_n$ were resolved. Absorption, emission, IR and Ramman spectra at 300, 77 and 4 K as well as luminescence decay time measurements were used to characterize the phothophysical properties of Nd^{III}, Er^{III} and Yb^{III} complexes in solid state, methanolic solution and silica gel. Effective energy transfer from ligands to the Ln^{III} ion was demonstrated. On the basis of low-temperature, high-resolution absorption and luminescence spectra, the ligand-field splittings of the excited and ground states of Yb^{III} complexes were determined.

Effective LMCT of Eu(III) and Tb(III) complexes with sulfonylamide derivatives

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Keywords: Lanthanide, Spectroscopy, Ligand-to Metal Energy Transfer

A serie of new lanthanide complexes with sulfonylamide derivatives of a general formula $C_6H_5SO_2NHPO(R)_2$ was synthesized ($\{Na[Ln(SB)_4]\}_n$, $\{Na[Ln(SK)_4]\}_n$ where Ln = Eu^{III}, Tb^{III} and Gd^{III}) and the crystal structure of ($\{Na[Ln(SB)_4]\}_n$ and $\{Na[Ln(SK)_4]\}_n$ were resolved. Absorption, emission, IR and Ramman spectra at 300, 77 and 4 K as well as luminescence decay time and quantum yield measurements were used to characterize the dynamics of the excited states and to determine the ligand-to-metal energy transfer mechanism for the Eu^{III} and Tb^{III} complexes in solid state, silica gel and methanolic solution. The role of the C-T state in these processes and influence of the complex structure has been analysed.

Thermosensible photoluminescent coating with Cr^{3+} and Eu^{3+} dopand ions

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Keywords: Al_2O_3, Cr^{3+}, Eu^{3+}

In recent years, a great deal of research on rare-earth (RE) and transition metal (TM) ions doped nanostructure materials has been focused to find their potential applications in photonic applications, such as up-conversion lasing, display and phosphors.

Sintered Al_2O_3-ceramics are increasingly used in industrial applications because of their unique properties, like high thermal, chemical and mechanical stability (very hard material), high melting point and fine optical and dielectric characteristics. In researching of the well emitting materials the main effort is focused on incorporating the emitting ions into host materials with low phonon energies. A suitable host must also present large optical band gap combined with good solubility and stability. In this point of view alumina is attractive host because it presents a high transparency window from ultraviolet to near infrared (it is an insulator with a band gap (9eV)). It has a wide range of technological applications, such as high-temperature structural materials, laser emitters and electrical devices. One of the main application of α - Al_2O_3 in optics is determined by its excellent emitting properties when it is doped with Cr^{3+} ions. In the corundum trivalent chromium ions substitute aluminum ions and show well-known an intense pair of luminescence lines at 693 nm and 694 nm (R-lines), which can be easily excited by light sources emitting in the near ultraviolet, blue or green spectral range.

We used α alumina oxide transition ion and rare earth ion doped as a thermosensitive photoluminescent coating. The research base on change of luminescence intensity of the substitutional Cr^{3+} ion, which are used as an intrinsic probe for temperature.

Introducing the second ions (Eu^{3+}), which intensity of luminescence will not vary in function of temperature allows us to control the thickness of the coating before and after heat treatments. Using very popular combustion method we succeeded to obtain Eu^{3+} and Cr^{3+} doped corundum, in spite of big differences in ionic radii of Al^{3+} (0.53Å), Cr^{3+} (0.68Å) and Eu^{3+} (1.07 Å) ions. The samples were heated in a different temperatures (the range of heat-treatment very large). The excitation, emission and decay times of luminescence were measured at room temperature. The changes of crystal structure of Al_2O_3 doped with Eu^{3+} and Cr^{3+} doped according to the heat-treatment temperatures were analyzed by the X-ray diffraction and optical measurement of Cr^{3+} and Eu^{3+} ions. Room-temperature photoluminescence indicated a strong red emission, which is due to characteristic transitions of $^2E \rightarrow {}^4T_2$ of Cr^{3+} and $^5D_0 \rightarrow {}^7F_J$, J=0,1,2,3,4 of Eu^{3+} for these phosphors. The differences in luminescence intensity ($^2E \rightarrow {}^4T_2$ of Cr^{3+}) could appear with change of concentration of active ions and could be used as an intrinsic probe for temperature especially as it is well known the luminescence properties of ruby nanocrystals strongly depend on phase, the concentration of Cr^{3+} ions and the sintering temperature. The heat treatment of the powders produces an enhancement of the luminescence intensity.

Influence of Ce^{3+} to Tb^{3+} energy transfer on Tb^{3+} emission in nanocrystalline Lu_2SiO_5 and $Lu_2Si_2O_7$ host lattices

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Keywords: Terbium, Cerium; Lutetium silicate, Nanocrystallites, Energy transfer, Colour coordinates

Nanocrystalline phosphors, Lu_2SiO_5:Tb^{3+}, Ce^{3+} (LSO:Tb,Ce) and $Lu_2Si_2O_7$:Ce^{3+} (LPS:Tb,Ce) were obtained at 1100 and 1250 ^oC respectively by the reaction of nanostructured Lu_2O_3 and colloidal SiO_2. X-ray diffraction analysis confirmed crystallization of a single phases of LSO and LPS in the indicated temperatures. Different concentrations of the active ions allowed to study the influence of the Ce^{3+} co-doping on the Tb^{3+} emission. Tb^{3+} doped LSO or LPS yield both the blue emission $^5D_3 \rightarrow {}^7F_J$ (J = 3, 4, 5, 6) and green emission $^5D_4 \rightarrow {}^7F_J$ (J = 3, 4, 5, 6) of Tb^{3+}. The green emission of Tb^{3+} is remarkably enhanced due to energy transfer from Ce^{3+} to Tb^{3+} when present together in the host lattice. Basing on optical luminescence and luminescence excitation spectra the optimal Tb^{3+} doping level for maximum light output was established to be 10 mol% and the highest enhancement of Tb^{3+} luminescence by Ce^{3+} co-doping was detected for Ce^{3+}:Tb^{3+} concentrations ratio 1:6. The effect of active ions concentration on the colorimetric characteristic of the emission of the compounds are presented.

Photoluminescence Properties of Eu^{2+} doped in $CsMgCl_3$ and $CsCaCl_3$

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Keywords: Lanthanides; Materials; Spectroscopy; Eu^{2+}

The d↔f luminescence of divalent Europium has already been investigated in a large number of different host lattices [1]. The luminescence of the Perowskite type host lattice $CsMgCl_3$ doped with Eu^{2+} is very unusual because of the presence of three broad emission bands between 420 nm and 500 nm (Fig.1). This unusual spectroscopic behavior could be explained by excitonic luminescence like in $CsCdBr_3$:Eu^{2+} [2] and by different cationic sites occupied by Eu^{2+} in the host lattice. The luminescence properties of pure $CsMgCl_3$ as well as that after doping with Eu^{3+} or Sr^{2+} have been investigated in order to identify the provenance of the different emission bands. Because of the emission at relatively low energy of $CsMgCl_3$:Eu^{2+} for a chloride host lattice, we expected that Eu^{2+} occupies the small Mg^{2+} site rather bthan that of the Cs^{+} site. This hypothesis could be verified with EXAFS measurements at ESRF in Grenoble by determining the coordination number of Eu^{2+} and the Eu-Cl distances in $CsMgCl_3$:3%Eu^{2+}. Furthermore, with the analysis of the luminescence of $CsMgCl_3$: 0, 1% Sr^{2+}, 0, 0.01% Eu^{2+} we could establish that the emission at 428nm (23 365 cm^{-1}) originates from excitons and that an energy transfer process from Eu^{2+} excited states to excitons is responsible for this very intense luminescence. The bands caused by Eu^{2+} 5d → 4f emission could be assigned 490 nm (20 400 cm^{-1}) after comparison of the Eu^{2+} emission band of $CsCaCl_3$:Eu^{2+}.

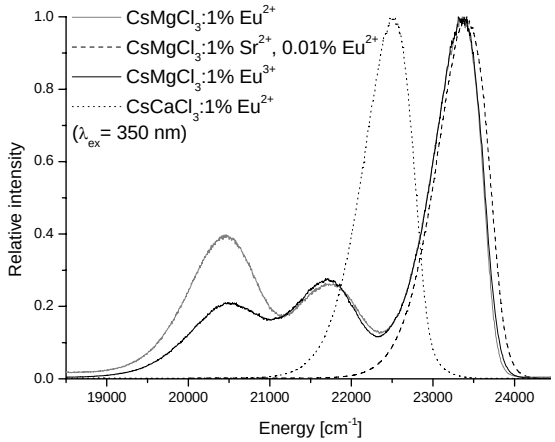

Figure 1. Emission spectra of CsMgCl3 :X (X = Eu2+, Eu3+, Sr2+) and CsCaCl3 :Eu2+

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Spectroscopy of $KGd(WO_4)_2$ single crystals doped with Eu^{3+} and Ho^{3+} ions

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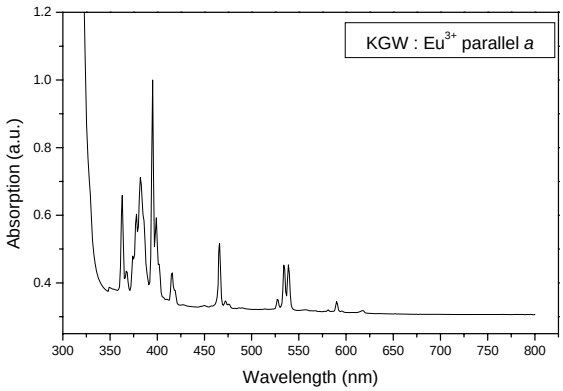
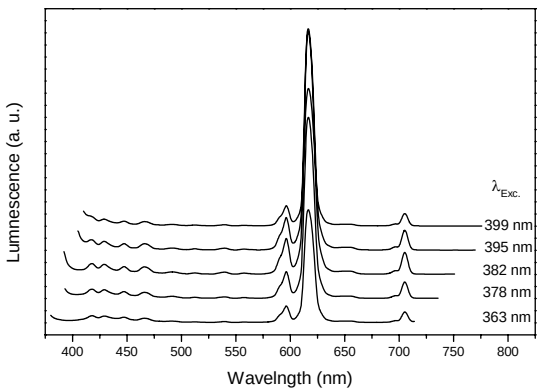
Keywords: Lanthanides; Monoclinic Double Tungstates; Solid State

Potassium gadolinium tungstate crystals $KGd(WO_4)_2$ (KGW) doped with rare earth ions are very attractive solid state laser materials [1]. When activated with trivalent lanthanide ions, KGW shows high efficiency of stimulated emission at low pumping energies under laser diode excitation [2]. In the present work we report the results of the detailed spectroscopic studies of the Eu^{3+} and Ho^{3+} ions in KGW. The crystals were grown by the top seeded solution growth method; the doping concentration of Eu^{3+} and Ho^{3+} ions was 5 at.% and 1 at.%, respectively. The room-temperature absorption spectra of KGW:Nd^{3+} and KGW:Er^{3+} crystals were recorded using the Cary 400 spectrophotometer in the 300 to 800 nm spectral range. The absorption spectra were detected for three possible orientations of the samples: when the incident light is parallel to the *a*,*b* axes and *c** direction (perpendicular to the *ab* plane) of the crystal. The fluorescence spectra were recorded with HITACHI F-7000 fluorescence spectrometer. The measurements were carried out for different excitation from 200-900 nm spectral range. Analysis of the obtained absorption spectra was performed using the conventional Judd-Ofelt theory and actual dependence of the refractive index on the wavelength. In this way, the Judd-Ofelt intensity parameters, branching ratios and radiative lifetimes were all evaluated and compared with experimental and literature data. Below we show the absorption (left) and luminescence (right) spectra for KGW : Eu^{3+}.





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A Sweet Luminescent Ionic Liquid

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Keywords: Lanthanides; Ionic Liquids; Luminescence; Metal-Containing Ionic liquids

Ionic liquids (ILs) are attracting more and more attention due to their unique chemical and physical properties which may include low vapor pressure, wide liquid range, large electrochemical window, and so on.[1-2] Metal-containing ionic liquid are a special kind of ILs which contain metal ion(s) in the anion or cation. Compared with ordinary organic ionic liquids, metal-containing ionic liquids combine both the properties of ionic liquids and those of the metal incorporated in the complex anion which can be special magnetic, photophysical/optical or catalytic properties [3]

$[C_4mim]_3[Eu(Sac)_6(H_2O)_2]$ (**1**) (C_4mim = 1-butyl-1-methylimidazolium; Sac = saccharinate) was obtained by reacting (C_4mim)(Sac) with $Eu(Sac)_3$ $(H_2O)_4$ at 90 °C. Colorless block-shaped crystals formed after the solution was slowly cooled to room temperature. It crystallizes in the orthorhombic space group *Pna*2_1, with four formula units in the unit cell (a = 25.574(5), b = 16.470(3), c = 15.648(3) Å, V = 7645(3) Å^3). The asymmetric unit contains one Eu(III) ion, six Sac^- anions, three $[C_4mim]^+$ cations and two aqua ligands (see Figure 1). DSC (differential scanning calorimetry) measurement shows the compound to melt at about 79 °C (onset), therefore it is a true ionic liquid.

Compound **1** shows the typical luminescence of Eu (III) complexes (see Figure 2). When monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at 611 nm, the excitation spectrum of **1** shows several discrete f-f transitions at 360.5, 364.5 ($^7F_0 \rightarrow {}^5D_4$), 372, 374.5 ($^7F_{0/1} \rightarrow {}^5G_J$), 379.5, 382.5 ($^7F_{0/1} \rightarrow {}^5L_7$, ^5G_J), 393 ($^7F_0 \rightarrow {}^5L_6$), 414 ($^7F_0 \rightarrow {}^5D_3$), 463.5 ($^7F_0 \rightarrow {}^5D_2$), 524.5 ($^7F_0 \rightarrow {}^5D_1$), and 533 nm ($^7F_1 \rightarrow {}^5D_1$). The emission spectrum of **1** under excitation of 393 nm light exhibits five characteristic emission bands of the europium (III) ion: (578.5 ($^5D_0 \rightarrow {}^7F_0$), 591 ($^5D_0 \rightarrow {}^7F_1$), 611 ($^5D_0 \rightarrow {}^7F_2$), 653 ($^5D_0 \rightarrow {}^7F_3$) and 690, 698 nm ($^5D_0 \rightarrow {}^7F_4$). The Eu ($^5D_0$) lifetime of **1** for $\lambda_{ex,em}$= 393, 611 nm in the solid state is about 0.55 ms.

Figure 1. Coordination environment in compound **1**.

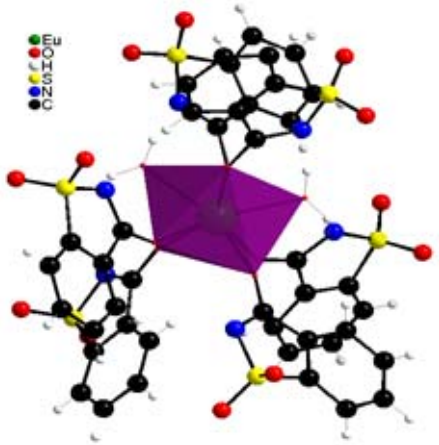
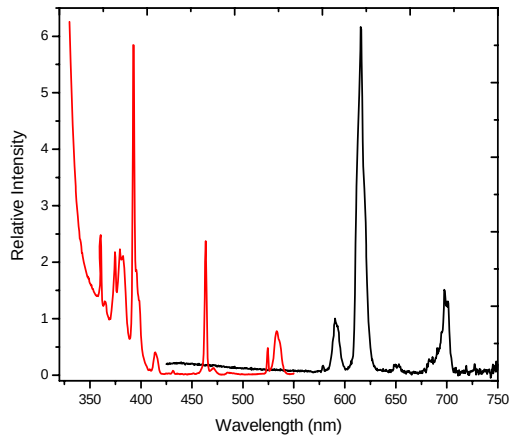


Figure 2. Excitation and emission spectra of **1**.



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Photoluminescence of Tm^{2+} Ions in Several Chloride Host Lattices

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Keywords: Luminescence, Tm^{2+},

The luminescence properties of trivalent rare earth ions are well known for a long time. The energy states of these ions were calculated and published in 1968 [1]. The weak 4f-4f-transitions of the trivalent ions are not influenced by the ligands because the 4f-orbital is shielded by the 5s- and 5p-orbitals. In contrast, the intense emissions of the parity-allowed 5d → 4f transitions of the divalent rare earth ions depend strongly on the surrounding. The luminescence of the most stable one, Eu^{2+}, has been investigated in numerous host lattices. On the other hand, the luminescence properties of Tm^{2+} are very rarely described in the past due to its much lower stability [2-5].
In this work we present the investigation of the luminescence of Tm^{2+} in different chloride host lattices which results in a surprisingly large number of different emission bands. The host lattices $AMCl_3$ (A = K, Rb, Cs; M = Sr, Ba) and $CaCl_2$ doped with Tm^{2+} showed a very intensive emission of the parity-forbidden transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$ at room temperature. From the lowest 5d level a spin-allowed (LS) and also a spin-forbidden transition (HS) into the $^2F_{7/2}$ state was detected at 10 K and room temperature (Fig. 1). Additionally, it was possible to observe emission from a higher 5d (LS) state ($^3H_5$) into the $^2F_{5/2}$ level. In the systems $BaCl_2$:Tm^{2+} and CaFCl:Tm^{2+} HS and LS emission bands starting from higher 5d levels ($^3H_4$ and $^3H_5$) into the $^2F_{7/2}$ ground state could be detected. The influence of the host lattices on the splitting of the HS and LS states could be investigated for the first time by the comparison of different systems.

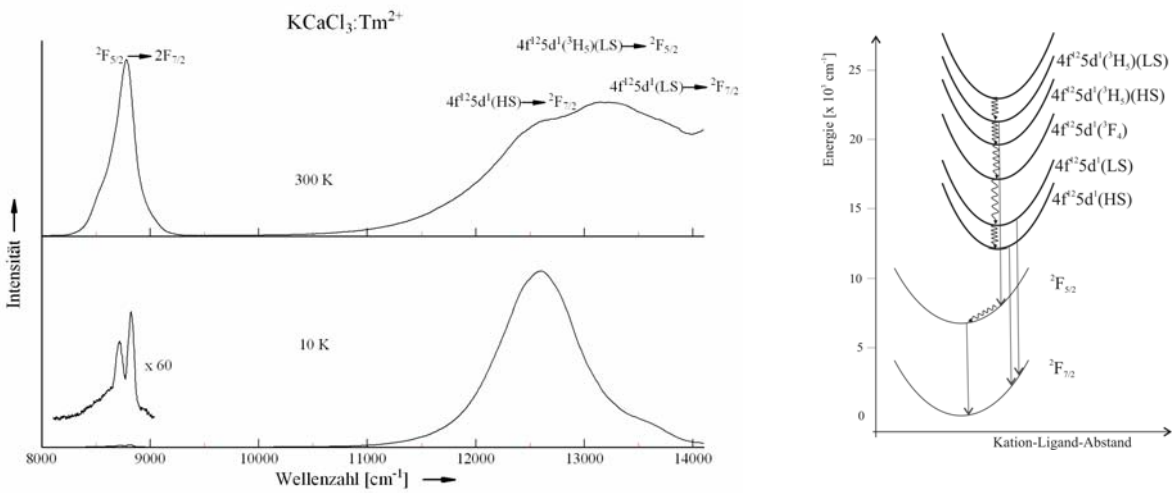

Figure 1: Emissions spectra at 10 K and 300 K (left) and energy-level-diagram (right) of $KCaCl_3$:Tm^{2+}

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Effect of Grinding on the Persistent Luminescence of $SrAl_2O_4:Eu^{2+},Dy^{3+}$

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Keywords: Lanthanides, solid state, persistent luminescence, grinding

Persistent luminescence is a phenomenon where the material emits in visible after the irradiation source has been removed. These materials have found applications where light is needed in the dark without external energy sources. Such uses include traffic and emergency signs, watches, clocks, and textile prints. One of the best persistent luminescence materials at present is the Eu^{2+} and Dy^{3+} doped strontium aluminate ($SrAl_2O_4:Eu^{2+},Dy^{3+}$) [1] which can emit in green for up to 15-25 hours. The exact mechanism of persistent luminescence is not known but it is often connected to the trapping of electrons and/or holes to defects. The electrons/holes are thermally activated from traps which process is followed by the Eu^{2+} emission [2,3]. Dy^{3+} co-doping improves both the duration and intensity of persistent luminescence which effect is probably due to the increased number of traps gained by adding co-dopants [4]. In this work, the effect of grinding on the UV excited, persistent and thermoluminescence of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ was studied. Also a comparison to the commercial product was carried out.

The polycrystalline $SrAl_2O_4:Eu^{2+},Dy^{3+}$ material was prepared with a solid state reaction by annealing $SrCO_3$, Al_2O_3, Eu_2O_3 and Dy_2O_3 at 900 °C for 1 h and at 1300 °C for 4 h in a reducing N_2 + 10 % H_2 sphere. B_2O_3 was added to the mixture as a flux. The nominal concentrations of the Eu^{2+} and Dy^{3+} ions were 1 and 2 mole-% of the strontium amount, respectively. The product was divided into four parts and each part was ground in an agate mortar for one to ten minutes. A sample of the commercial product Luminova (United Mineral & Chemical Corp.) was ground for 10 minutes, as well.

According to the X-ray powder diffraction measurements, both the fresh and commercial materials consist of the monoclinic $SrAl_2O_4$ structure. Grinding does not cause significant changes in the shape and width of the reflections. This means that the mean particle size remains almost unchanged despite the grinding.

The emission of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ consists of a broad band at 520 nm (λ_{exc}: 350 nm) due to the $4f^65d^1 \rightarrow 4f^7$ emission of Eu^{2+}. Grinding weakens the UV excited luminescence of both products. The persistent luminescence emission spectra were measured after the fluorescent lamp irradiation. Persistent luminescence emission consists of a broad band which also has a maximum at 520 nm. There is a clear decrease in the persistent luminescence intensity with increasing grinding time.

Thermoluminescence (TL) glow curves of the fresh materials have a peak at *ca.* 90 °C which corresponds to the shallowest traps. Above this temperature, a broad band at *ca.* 130-300 °C probably embraces several different peaks corresponding to deep traps. The intensity of the latter band decreases with increasing grinding time compared to the band at 90 °C. The TL glow curves of the commercial product consist of a very strong and broad band in the range of 40-250 °C. The grinding of the commercial material did not cause any significant changes to the TL curves of this material.

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Importance of Using Circularly Polarized Luminescence Spectroscopy for the Chiroptical Characterization of Lanthanide(III) Complexes

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Keywords: Lanthanide; Chirality; Spectroscopy

Circular Dichroism (CD) has long been used to determine if a protein is in its native folded or unfolded form and to further characterize the secondary and tertiary structures of folded proteins. [1]

Chirality is an intrinsic property of a majority of biological systems, due to the primary structures consisting of amino acid residues. CD is able to examine these kinds of chiral environments from the ground state but it does so in an additive manner. The CD signal obtained usually gives information for the entire molecule and is not specific to one particular chromophore in solution, but it gives information pertaining to the entire population of molecules within a solution.

Circularly Polarized Luminescence (CPL) spectroscopy is the emission analogue of CD. [2] CPL examines the chiroptical properties of molecular species from the excited state. The advantage of using CPL over or in accordance with CD is that CPL is extremely sensitive to its surrounding environment. CPL is much more selective in that it has the ability to selectively characterize luminescent chromophores that are present within a system of interest.

In the present study, we report on a series of our accomplishments aimed at increasing the use of this still underemployed technique for probing chiral structural changes.

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Excitation energy transfer in europium 1- and 2- naphthylcarboxylates

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Keywords: Lanthanides; Physics; Coordination; Spectroscopy

This work contains the results of investigations of the effects of Eu^{3+} luminescence excitation in a number of europium naphthylcarboxylates. Two series of europium compounds of compositions $Eu(RCOO)_3 \cdot nH_2O$ and $Eu(RCOO)_3 \cdot Phen$ (Phen - 1,10-phenanthroline) with 1- and 2-naphthoic ($C_{10}H_7COOH$), 1- and 2-naphthylacetic ($C_{10}H_7CH_2COOH$), 1- and 2-naphthoxyacetic ($C_{10}H_7OCH_2COOH$) acids were investigated. Some europium compounds with 1- and 3-hydroxy-2-naphthoic acids ($C_{10}H_6OHCOOH$) were also considered. The effect of the methylene bridges breaking the pi-pi- or p-pi-conjugation in the ligand on the structure of compounds and on the excitation energy transfer to Eu^{3+} ions was examined. The influence of OH-groups inserted in 1- or 3-position of naphthoic ligand on the excitation energy transfer was also analyzed.

Luminescence and luminescence excitation spectra of europium compounds were investigated. The lifetimes of $^5D_0$ state and luminescence efficiencies of Eu^{3+} ion were studied. To obtain the energy of the lowest excited triplet state of the ligands the phosphorescence spectra of gadolinium compounds registered with time delay were considered. Vibrational spectra were analyzed.

It was demonstrated that introduction of the methylene bridges between the carboxylic group and naphthalene rings of ligand weakens the steric hindrances in the structures of compounds. Judging from the luminescence spectra, the nearest surroundings of Eu^{3+} ion becomes more symmetric (Fig. 1). The decoupling of ligand pi-electronic system leads to strengthening the Eu-O bonds and lowering the energy of "ligand – metal ion" charge transfer states (LM CTS) in europium carboxylates studied. So, the probability of participation of the LM CTS in the degradation of excitation energy increases.

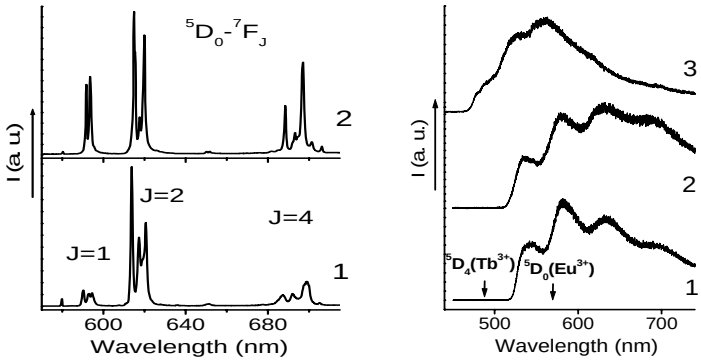

Figure 1. The luminescence spectra of $Eu(1\text{-Naphth})_3 \cdot Phen$ (1), $Eu(1\text{-NaphthOAc})_3 \cdot Phen$ (2) at 77 K.
Figure 2. The phosphorescence spectra of $Gd(1\text{-Naphth})_3$ (1), $Gd(1\text{-Naphth})_3 \cdot Phen$ (2), $GdCl_3 \cdot Phen \cdot nH_2O$ (3) registered with 1 ms time delay at 77 K.

The energies of the lowest triplet states of both the ligands in $Eu(RCOO)_3.Phen$ were determined. It was derived that the lowest triplet state of compound relates to the naphthylcarboxylate anion (Fig. 2). The dependence of the triplet energy and of the lifetime of $^5D_0$ (Eu^{3+}) state on architecture of the naphthylcarboxylate ligands was investigated. It was shown that the lowest triplet energy can become ~1000 cm^{-1} higher and can reach $^5D_4$ (Tb^{3+}) level at introduction of the methylene group in the ligand. In this case, the luminescence of terbium naphthylcarboxylates can be observed.

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NIR emitting hydroxyquinoline-based complexes

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Keywords: Hydroxyquinoline; Lanthanides; Luminescence

Near-infrared (NIR) emitting materials gained worldwide interest recently due to potential applications in biochemical analysis and telecommunications technology. 8- hydroxyquinoline subunits are well known as chromophores for sensitization of NIR emitting lanthanides (Nd(III), Er(III), Yb(III)) due to their low energy triplet state (500-600 nm). However, the complexation studies with bidentate 8-hydroxyquinolines show versatile coordination chemistry [1]. The bidentate hydroxyquinoline ligand does not form stable self organized complexes. Several donor functional groups have been attached to quinoline group that increase the coordination number in order to shield the metal against solvent coordination and also to modulate the luminescence properties [2].

The incorporation of tetrazole groups as carboxylic acid replacements for the sensitization of lanthanide emission has recently been described for the first time by our group [3]. Here we present the X-ray structure and photophysical properties of synthesized stable tris lanthanide complexes with two different dianionic tridentate hydroxyquinoline based ligands which are 8-hydroxyquinoline-2-carboxylic acid (H_2hqa) and 2-(1H-tetrazol-5-yl)- quinolin-8-ol (H_2hqt) that have O,N,O and N,N,O coordinating units respectively. The effect of tetrazole groups on molar absorptivity and light harvesting properties of the complexes will be presented.

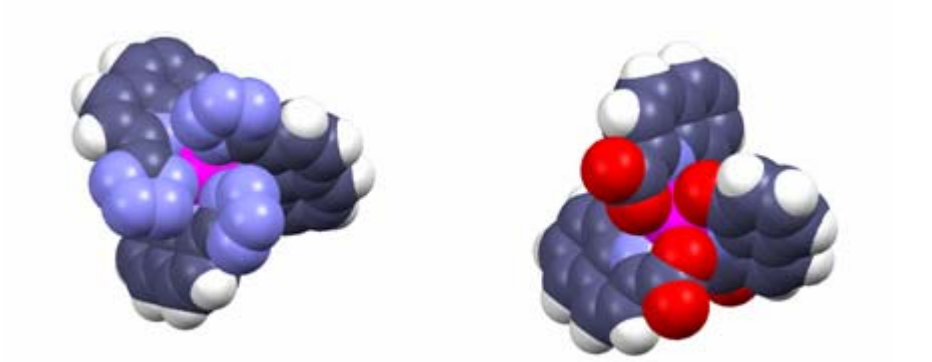

Figure 1. Space filling representation of the X-ray structures of $[Nd(Hqt)_3]^{-3}$ (left) and $[Nd(Hqa)_3]^{-3}$ (right) complexes showing syn and anti configuration respectively .

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Spectroscopic properties of europium-doped $Ti_xSn_{1-x}O_2$

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Keywords: oxides; lanthanides; sol-gel; spectroscopy

It is well known that several phosphors currently used in modern lighting devices (e.g. phosphor-converted LEDs) have complicated preparation routes or stability issues. In addition, narrowband red emitters (based on Eu^{3+}) are desired due to their higher lumen equivalent and stability. Various oxides can be easily prepared and doped with rare earths by using sol-gel techniques. Wide-gap semiconducting TiO_2 and SnO_2 are especially interesting as their mixture exhibits a miscibility gap so that their solid solution could be considered as a tunable optical material.

Europium-doped $Ti_xSn_{1-x}O_2$ powders (x=0, 0.25, 0.5, 0.75, 1) were prepared by using a sol-gel route. Subsequent heat treatment up to 1000°C was applied. According to Raman-spectra, the solid solution with $x \geq 0.5$ has a vibrational pattern similar to that of TiO_2 rutile (except for pure TiO_2, which is anatase at low heat treatments), whereas higher content of tin leads to a fairly abrupt relaxation to SnO_2-like rutile structure.

Steady-state and time-resolved photoluminescence characterization of the materials were performed by using various excitation sources. All materials exposed some form of Eu^{3+} emission. Photoluminescence spectra revealed several different sites for the impurity ion in the host depending on the Ti/Sn ratio and the crystalline phase (anatase vs rutile). The direct excitation of europium prevailed in mixtures containing an essential amount of titania whereas only host-sensitized emission could be observed in SnO_2. By far most efficient emission originates from directly excited europium ions in an amorphous TiO_2 surrounding although energy transfer from host to Eu ions in crystalline surrounding was also clearly detected. The results are in contrast to TiO_2:Sm where the host-sensitized rare earth emission is essential [1].

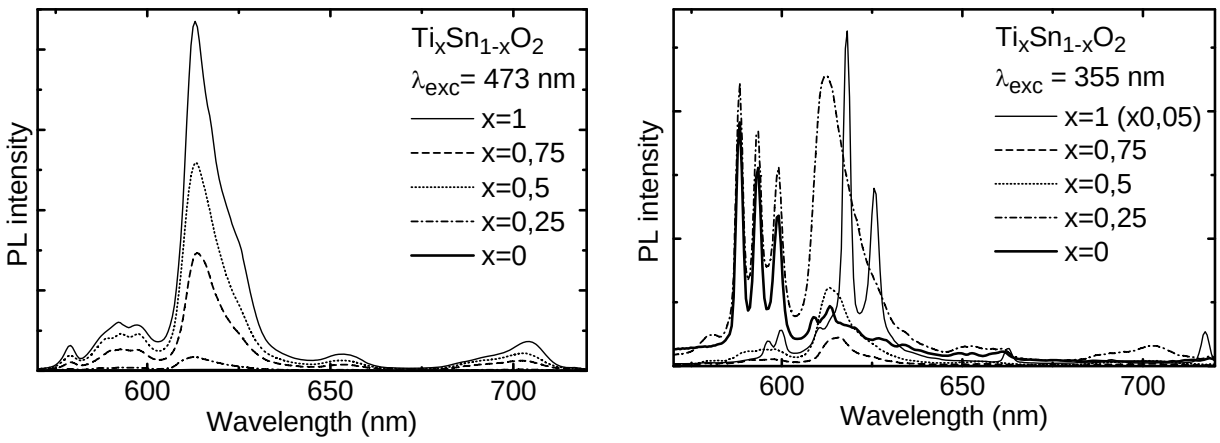

Figure 1. PL spectra of $Ti_xSn_{1-x}O_2$ Eu^{3+} (annealed at 800°C) under 473 and 355 nm laser excitation demonstrating Eu ions in amorphous and crystalline surrounding, respectively.

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Single crystal and nanocrystalline Pr^{3+} doped lutetium phosphate: a comparative analysis of the *f-f* luminescence properties

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Keywords: Lanthanides, Materials, Spectroscopy, Structure

Lanthanide doped phosphate hosts of composition $LnPO_4$ (Ln=La, Y, Gd) are interesting luminescent materials. These phosphate hosts have very good chemical and physical properties. In particular, they have a high chemical stability and a high transparency in the near-UV and visible regions. These properties, together with high emission intensities of the luminescent lanthanide ions, present as dopants, make phosphate based materials suitable for many technological applications, such as in the field of scintillators and phosphors [1].Lanthanide phosphate nanoparticles have demonstrated valuable applications also in the field of bio-labelling [2].

Lutetium phosphate ($LuPO_4$) doped with luminescent lanthanide ions is an interesting material which has been seldom investigated in the literature. Owing to the good properties of Pr^{3+} as a luminescent ions, we found it interesting to investigate and compare the *f-f* transitions of Pr^{3+} doped $LuPO_4$ in single crystal and nanocrystalline forms.

1% Pr^{3+} doped single crystals were prepared using the flux-grow technique while a nanocrystalline sample of the same composition was synthesised by coprecipitation in aqueous solution. Structural investigations for the nanocrystalline sample was performed by Raman spectroscopy and Rietveld refinement of the X-ray powder diffraction patterns, from which an average particle size of about 50 nm is obtained. The sample resulted to be single phase (tetragonal, $I4_1/amd$ space group). The morphological properties of the nanocrystalline sample were investigated using transmission electron microscopy (TEM).

The room temperature laser excited (λ_{exc}=460 nm) emission spectra show, for both single crystal and nanocrystalline samples, a strong emission in the red region (600-650 nm) due to transitions starting from $^3P_0$ and $^1D_2$ excited levels of the Pr^{3+} ion. Differences in the relative intensity of the $^3P_0$ and $^1D_2$ emission bands were observed for the nanocrystalline and single crystal samples. The emission decay curves were measured and analysed. The comparison between the decay times of the $^3P_0$ and $^1D_2$ levels suggests different de-excitation pathways for the nanocrystalline and single crystal samples.

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High-pressure luminescence studies of f-f radiative transitions of Yb^{3+} ions in $GdPO_4$

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Keywords: Lanthanides; Materials; Solid State; Spectroscopy

Yb^{3+} ion is nowadays attracting a lot of attention as an active dopant ion for solid state laser materials. Moreover, Yb^{3+} doped phosphates have been of considerable interest for the possible applications of these materials in new lighting devices as well as for fundamental studies. However only a very limited number of papers exists on the spectroscopic studies of ytterbium doped orthophosphates.

The special electronic configuration of Yb^{3+} ions ($4f^{13}$) makes the $4f$ electrons less shielded than in other ions of the lanthanide series, and hence the electrons show a higher tendency to interact with the lattice and with neighbouring ions. Therefore one could expect that the radiative transition probability of the optical transitions between the excited and the ground states of Yb^{3+} could be strongly influenced by the interaction with ligands, contrary to the expectation for the other trivalent lanthanide ions. Thus these ions could be a good probe of the host crystal structure and its pressure changes.

In this work we present the study of the absorption, luminescence and radiative decay times of the intrashell f-f transitions of Yb^{3+} ions in bulk $GdPO_4$:Yb(1%) crystal at different temperatures and at high hydrostatic pressure. $GdPO_4$ at ambient pressure has a monoclinic monazite structure. The local symmetry of Yb^{3+} is C_1.

Experiments at ambient pressure were performed at temperatures from 10 to 295 K whereas measurements at high pressure were performed in a diamond-anvil cell at 10 K at pressures up to 170 kbar. The radiative de-excitation probability of the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition within the $4f$ electronic shell of Yb^{3+} in $GdPO_4$ crystals exhibits a strong increase with increasing hydrostatic pressure. At the same time only very small, almost negligible and nonlinear changes of the transition energy with pressure are observed. The obtained results can be ascribed to pressure-induced energy structure changes of the Yb^{3+} center which are most probably caused by the first or higher order phase transition of the $GdPO_4$ crystal. [1, 2].

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High-pressure spectroscopy of ytterbium doped YPO_4

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Keywords: Lanthanides; Materials; Solid State; Spectroscopy

The intra-*4f* shell luminescence of rare-earth (RE) ions doped to different crystal hosts has been attracting keen interest both for optical applications as laser active materials and for fundamental studies. Despite the wide occurrence it is still little known about spectral properties of rare earth phosphates activated by small quantities of various rare earths.

In this work we present the study of the absorption, luminescence spectra and radiative decay times of the intrashell f-f transitions of Yb^{3+} ions in bulk YPO_4:Yb(1%) crystal at different temperatures and at high hydrostatic pressure. YPO_4 at ambient pressure has the tetragonal zircon structure. The local symmetry of Yb^{3+} is D_{2d}. Experiments at ambient pressure were performed at temperatures from 10 to 295 K whereas measurements at high pressure were performed in a diamond-anvil cell at 10 K with pressure up to 160 kbar.

We have observed through decay kinetics measurements under pressure that the probability of the *f-f* radiative transitions ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) of Yb^{3+} ions in YPO_4 crystals is sensitive to the applied hydrostatic pressure and exhibits various behaviour. With increasing pressure the probability is almost constant up to about 70 kbar and then increases. It is accompanied by a linear shift of the transition energies in the whole pressure range. The linear changes of the photoluminescence energies, generally referred to as the pressure coefficients dE_{PL}/dp, are very small and negative (-0.4 – -0.7 cm^{-1}/kbar) for all but one *f-f* radiative transitions, for which it is equal to 0.44 cm^{-1}/kbar.

The obtained results can be ascribed to pressure-induced energy structure changes of the Yb^{3+} center which are probably caused by a phase transition of the YPO_4 crystal from tetragonal zircon to scheelite-type structure. [1, 2, 3]. A clear explanation needs some further studies which are under way.

Acknowledgements: This work was supported by the grant of the Polish Ministry of Science and Higher Education during years 2008-2010.

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Vacuum ultraviolet excitation spectra of lanthanide doped hexafluoroelpasolites

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Keywords: Lanthanides; VUV, Elpasolite, 4f – 5d, Crystal field

Vacuum ultraviolet excitation spectra at ~10 K have been recorded for $4f^N \rightarrow 4f^{N-1}5d$ transitions of $Cs_2NaMF_6:Ln^{3+}$ (M = Y, Ga; Ln = Nd, Sm, Tb, Ho, Er, Tm). In these high band gap hosts the lanthanide ions occupy octahedral symmetry sites. The spectra comprise broad, structured bands and in most cases the individual vibronic structure is not resolved. Simulations of the relative intensities and band positions in the spectra have been made by using parameter values from previous studies and/or by employing values from similar systems or estimating trends across the lanthanide series, without data-fitting or parameter adjustments. The agreement with experimental results is reasonable except where the luminescent state being monitored is not efficiently populated nonradiatively from the $4f^{N-1}5d$ state, or where additional bands are present. The latter are readily assigned to charge transfer transitions. The figure shows the VUV excitation spectrum and simulation for $Cs_2NaYF_6:Sm^{3+}$. Comparison of the lanthanide hexafluoroelpasolite spectra has been made with those of other high symmetry lanthanide ion systems.

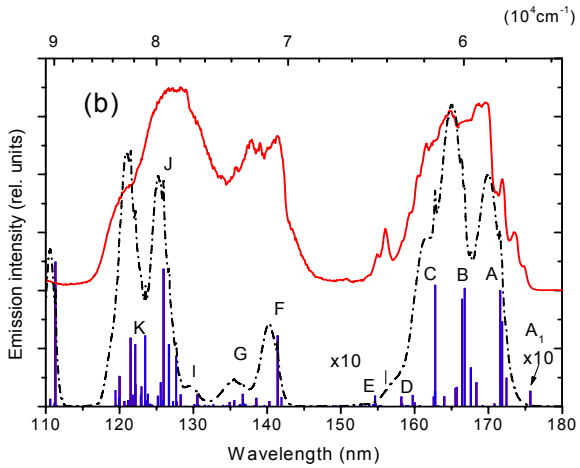

Figure. Experimental excitation spectrum (full line: λ_{em} = 598.6 nm, T = 12.4 K) and simulated $4f^N - 4f^{N-1}5d$ absorption spectrum (dashed lines) for $Cs_2NaYF_6:Sm^{3+}$. The vertical bars show the calculated locations and relative intensities of pure electronic transitions. The simulated convolutions employ E_{shift} = 600 cm^{-1} and E_{width} = 1000 cm^{-1}. The zero-phonon lines are enlarged by 10 times for clearer display in the ranges 175-180 nm and 145-156 nm.

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Valence transformation upconversion for oxides in vacuum

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Keywords: Lanthanides; Materials; White light; Upconversion

Under a vacuum of ~10^{-2} torr, the neat and high purity lanthanide sesquioxide powders Nd_2O_3, Yb_2O_3, Er_2O_3 and Tm_2O_3 have been excited by an unfocussed 975 nm diode laser at powers up to 1 W. The excitation leads to the production of charge carriers which can then undergo reaction or trapping. Broad band emission is observed over the visible spectral region which is characterized by multiphoton excitation quanta of between 3 and 4. The broad emission band is assigned to emission from a self-trapped exciton state below the conduction band. Emission is also detected from the divalent lanthanide ion species Tm^{2+}, showing that electron trapping occurs, as well as from intraconfigurational $4f^N$ -$4f^N$ transitions. The emissions are characterized by rise times of several seconds, depending upon the laser power. The emission intensity is several orders of magnitude greater than that for the doped lanthanide species Y_2O_3:Yb^{3+}, Er^{3+} in air. Moreover, the colour purity of emission from neat Yb_2O_3 is close to that of white light, with CIE coordinates (0.329, 0.335).

Fig. 1(a) shows the upconversion spectrum for Yb_2O_3 under various excitation powers, as well as the log-log plot of emission intensity and excitation power. Note the saturation at higher powers. Fig. 1(b) shows the corresponding plot for Nd_2O_3.

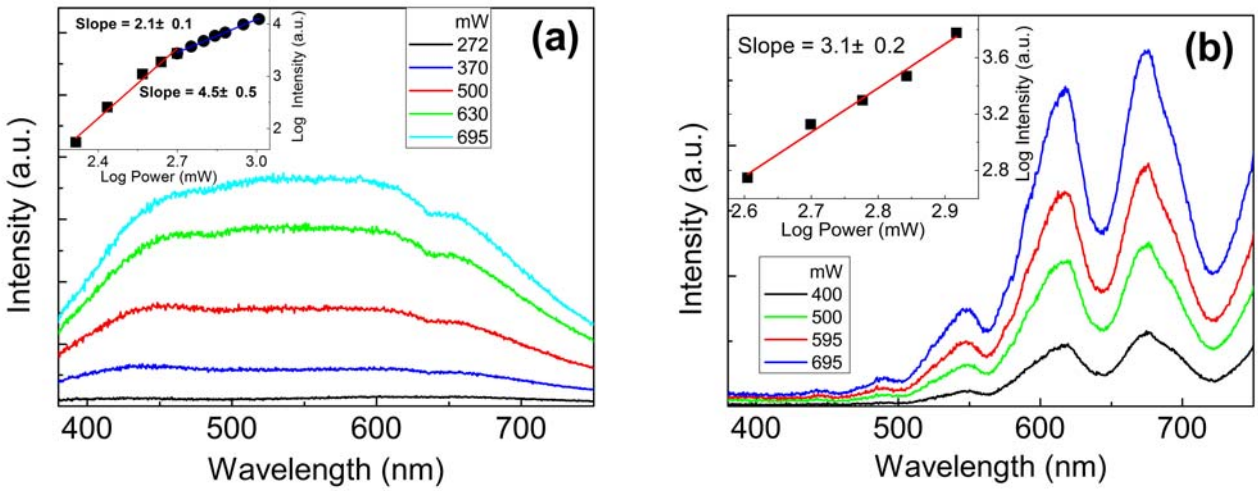

Figure 1. 975 nm upconversion of lanthanide sesquioxide powders between 380-720 nm with powers as marked, under 10^{-2} torr: (a) Yb_2O_3; (b) Nd_2O_3. The figure insets are log-log plots of upconversion emission intensity versus laser power, with the slopes marked.

Acknowledgement
The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China [Project No. CityU 102308].

Luminescent Ln(III) complexes based on alternative ligands

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Keywords: Lanthanides; Chemistry; Coordination; Spectroscopy

Summary Luminescent Ln(III) complexes are being widely explored and in the last two years a series of complexes have been prepared for studies of lanthanide emission. All these compounds share a common tetraazamacrocyclic ring, bearing a variety of sensitising chromophores.[1,2] Our research is directed to the synthesis of new ligands for Eu^{3+} and Tb^{3+} and has focused on the synthesis of new ligands, based on alternative substructures. The synthesis of novel compounds is presented, derived from original molecular skeletons (Fig. 1). The first ligand is based on the 6-aminoperhydro-1,4-diazepine (AMPED) ring, whose functionalized derivatives have been shown to complex efficiently lanthanide ions.[3] Some preliminary luminescence properties have recently been reported.[4] The second system relies on an unusual dihydrazino-*s*-triazine (DHT) substructure bearing on the heterocyclic ring the light-absorbing residues. The synthesis and the photophysical properties of these novel derivatives are reported.

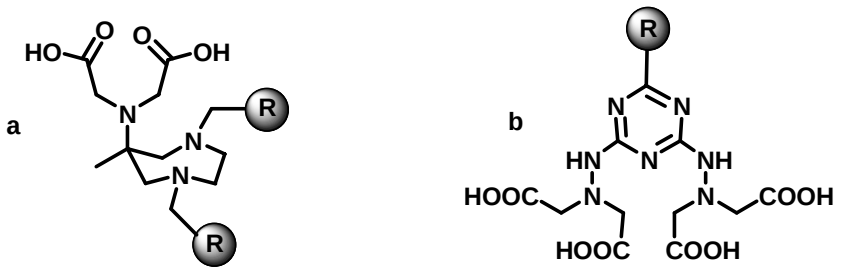

Figure 1. New ligands for emission spectroscopy based on AMPED core (a), and DHT substructure (b).

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Structural regularities and luminescence properties of dimeric europium and terbium carboxylates with 1,10-phenanthroline (C.N. = 9)

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Keywords: Lanthanides; Physics; Coordination; Spectroscopy

Using methods of optical spectroscopy and X-ray crystallography we have investigated the effect of architecture of carboxylate anions on the structure of Ln^{3+} coordination centre and on paths of the excitation energy transfer in a family of dimeric lanthanide carboxylates with 1,10-phenanthroline $Ln(RCOO)_3 \cdot Phen$ (Ln = Eu, Gd, Tb). 1-Naphthylcarboxylates, benzoates, 2-furancarboxylates, phenoxyacetates, caproates, 3-nitropropionates, acetates (1-7) and other compounds (8-11) with known structures were examined. Luminescence and phosphorescence spectra of compounds, the $^5D_4$ (Tb^{3+}) and $^5D_0$ (Eu^{3+}) lifetimes and the Ln^{3+} luminescence efficiencies were studied.

The crystal structures of 3-nitropropionates $Ln(NO_2C_2H_4COO)_3 \cdot Phen$ (Ln = Eu, Tb) were determined by X-ray diffraction method. Space group for both compounds is P-1, unit cell dimensions for Eu and Tb nitropropionates are **a** = 8.4676(8), **b** = 10.5393(9), **c** = 13.4681(13), a = 93.281(2), b = 92.836(2), g = 94.3076(17) and **a** = 10.0094(7), **b** = 11.5769(8), **c** = 12.2513(9), a = 114.807(2), b = 97.052(2), g = 106.693(2), respectively. In all investigated compounds, the two Ln^{3+} ions of dimer are bonded by two bidentate-bridging and two "tridentate" bridging-cyclic carboxylic groups. In addition, each Ln^{3+} ion coordinates bidentate-cyclic carboxylic group and one Phen molecule.

The influence of steric hindrances on Eu^{3+} coordination centre is weakening at change of the type and size of radical attached to COO^- anion in the listed row of compounds. This is accompanied by the gradual changes of Eu-O bond lengths due to the "tridentate" COO^- groups, of the Eu-Eu separations in dimer and of the shape of Eu^{3+} polyhedron, which correlate with the Stark splitting of the Eu^{3+} electronic levels and intensity distribution in the Eu^{3+} luminescence spectra (Fig. 1).

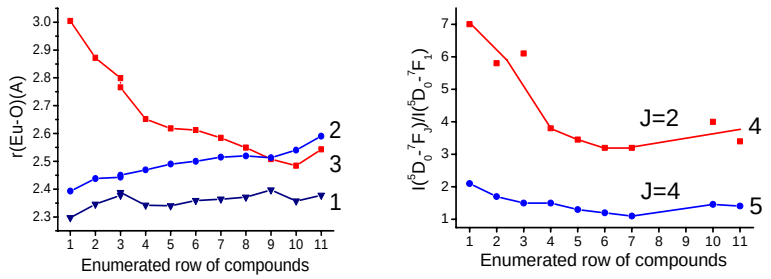

Figure 1. The changes of Eu-O bond lengths with "tridentate" bridging-cyclic COO^- -group (1, 2, 3) and relative integral intensities of $^5D_0$-$^7F_2$ and $^5D_0$-$^7F_4$ transitions of Eu^{3+} ion (4, 5) in investigated row of compounds.

The influence of relative positions of the lowest triplet state of the complex referred to Phen and $^5D_4$ (Tb^{3+}) or $^5D_0$ (Eu^{3+}) electronic states on the energy transfer was investigated. Connection between the triplet energy, the Ln-N bond lengths and the electronic density distribution in the Phen molecule was analyzed. It was found that the lifetime of $^5D_4$ state and the Tb^{3+} luminescence efficiency decrease noticeably in some investigated compounds at increasing the temperature owing to the energy back transfer. It was demonstrated that the luminescence quenching in terbium nitropropionate is the lowest.

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Diethoxy, monoethoxy and dihydroxy 6-phosphoryl picolinic acid as luminescent lanthanide sensitizers

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Keywords: Lanthanides; Chemistry; Coordination (incl. Supramolecular); Synthesis and Spectroscopy

Derivatives of dipicolinic acid (DPA) have shown great potential as efficient and stable lanthanide sensitizers. However, modification of the coordinating moieties, *i.e.* replacement of one or two of the carboxylic groups with other simple coordinating functional groups, remains, to our knowledge, poorly documented. Phosphoryl derivatives are one of the major alternatives to carbonyl coordinating units, and have already been used in various ligand structures.
Thus, we have synthesized three 6-phosphoryl picolinic acid derivatives, replacing one of the coordinating carboxylic functional group of dipicolinic acid. The phosphoryl moiety was introduced according to known procedures; deprotection of the diethoxyphosphoryl group to form the monoethoxy and dihydroxy phosphoryl was then achieved through careful control of sodium hydroxide amounts and temperature.

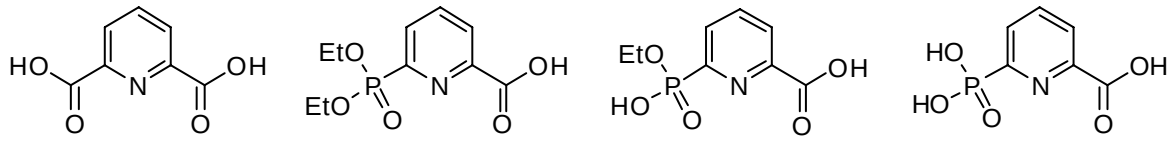

Figure 1. Structures of dipicolinic acid (DPA), diethoxy-6-phosphoryl picolinic acid (DEPPA), monoethoxy-6-phosphoryl picolinic acid (MEPPA), and dihydroxy-6-phosphoryl picolinic acid (DHPPA).

A complete study of the ligands and europium complexes was carried out in aqueous solution. Problems of solubility were encountered with the dihydroxyphosphoryl picolinic acid ligand (DHPPA), however a poor efficiency for the sensitization of europium has been observed at low concentration. Increasing efficiencies were found for europium 1:3 monoethoxyphosphoryl (MEPPA) and diethoxyphosphoryl (DEPPA) complexes, up to 1.89(4) ms lifetime and 15 % quantum yield for europium tris-(diethoxy-6-phosphorylpicolinate). The neutral diethoxyphosphoryl moiety seems therefore to be a better sensitizer than partially or fully de-protected derivatives. Sizeable solubility and complex stability were observed in water, as well as maximum emission under slightly acidic conditions (pH = 4.8). These photophysical properties are compared to the ones of the europium tris(dipicolinate) standard and exhibit interesting complementarities.

Urea Route to Homoleptic Cyanates - Characterization and Luminescence Properties of $[M(OCN)_2(urea)]$ and $M(OCN)_2$ with M = Sr, Eu

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Keywords: Lanthanides; Solid State Chemistry; Structure; Spectroscopy

A novel approach for the synthesis of urea-complexes and homoleptic cyanates of alkaline earth metals and europium is described. Direct reaction above 120 °C of urea with elemental Sr or Eu in closed ampoules yields $[M(OCN)_2(urea)]$ with M = Sr, Eu. According to single-crystal X-ray diffraction the isotypic complexes exhibit a layer structure ($[Eu(OCN)_2(urea)]$: $P2_1/c$, a = 7.826(2) Å, b = 7.130(1) Å, c = 12.916(3) Å, β = 99.76(3)°, Z = 4, V = 710.3(2) Å^3). They were furthermore characterized by vibrational spectroscopy, thermal analysis, magnetic measurements and photoluminescence studies. Thermal treatment of compounds $[M(OCN)_2(urea)]$ to 160 - 240 °C affords evaporation of urea and subsequent formation of solvent-free homoleptic cyanates of Sr and Eu, respectively. The crystal structures of $Sr(OCN)_2$ and $Eu(OCN)_2$ were determined from X-ray powder diffraction data and refined by the Rietveld method. Both compounds crystallize in the orthorhombic space group *Fddd* and adopt the $Sr(N_3)_2$ type of structure ($Sr(OCN)_2$, a = 6.1510(4) Å, b = 11.268(1) Å, c = 11.848(1) Å, V = 821.1(2) Å^3; $Eu(OCN)_2$, a = 6.1514(6) Å, b = 11.2863(12) Å, c = 11.8201(12) Å, V = 820.63(15) Å^3). The cyanates are stable up to 450 °C. Above 500 °C β-$SrCN_2$ and $Eu_2O_2CN_2$ are formed, respectively. Excitation and emission spectra of $Eu(OCN)_2$·Urea, $Sr(OCN)_2$·Urea:Eu^{2+}, $Eu(OCN)_2$, $Sr(OCN)_2$:Eu^{2+} at different temperatures are reported. A strong green emission for all examined Eu-containing compounds due to $4f^65d^1$-$4f^7$ transition is observed at low temperatures. As oxidic and nitridic Eu^{2+} doped host lattices play an important role for the development of new luminescence materials,[1] the luminescence properties are discussed in detail and are comparable to those of oxides and nitrides. A blue shift of the emission bands is observed due to the high ionicity of the lattice. Furthermore, the obtained compounds are promising precursors for the synthesis of new oxidic as well as nitridic materials, as they are easy to synthesize from line chemicals (e.g. urea).[2]

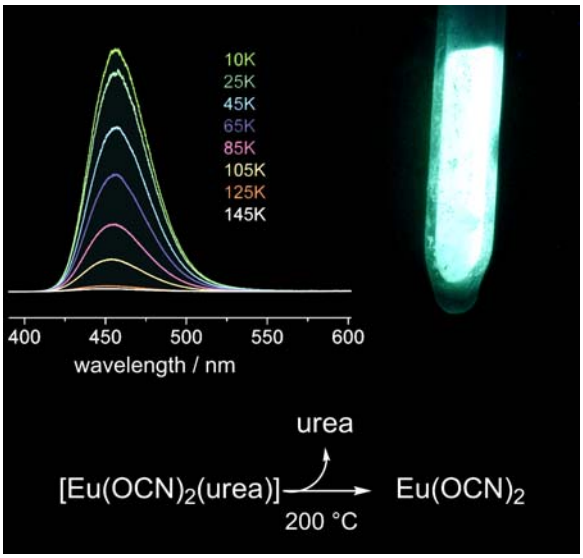

Figure 1. Emission spectra of $Sr(OCN)_2$:Eu^{2+} at different temperatures and reaction scheme.

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Luminescence of Sm^{2+} doped in BaFBr

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Keywords: Samarium, luminescence, pressure, lifetime

Alkaline earth fluride halides (MFX) doped with divalent lanthanide ions show a wide range of spectroscopic properties with many practical applications. BaFCl and BaFBr doped with $Eu^{2+}$are commercially used in X-ray detectors. Sm^{2+} in those crystals can be used as pressure sensors [1] and has been shown to be the first compound which allows room temperature hole burning [2]. BaFBr doped with Sm^{2+} presents rich luminescence spectra. In this work we studied the effect of pressure and temperature on the CF energy levels of Sm^{2+}doped BaFBr.

Sharp Sm^{2+} crystal field (CF) f-f emission bands are observed. There is no evidence of any f-d emission at low or room temperature, but at high temperature (more than 450K) we observed broad emission originating from the lowest $4f^5 5d^1$ state. The CF energy levels were determined from the $^5D_{0,1,2} \rightarrow {}^7F_j$ (where j=0-4) transitions. The CF parameters were refined to reproduce the experimental CF energy levels within error less than 10 cm^{-1} using the program written by S. Edvardsson et al.[3].

The pressure has the ability to tune the CF energy levels. The pressure up to 8 GPa results red shift of luminescence bands. $^5D_{0,2} \rightarrow {}^7F_0$ band shift with pressure showed very good linear dependence with pressure. The $^5D_0 \rightarrow {}^7F_0$ shift is three times stronger than R_1 lineshift of ruby and the shift increases with temperature. The pressure induced study also revealed the reduction of the splitting between the two $^7F_1$ CF energy levels (A_2 and E).

Temperature has a great influence on the lifetime of the excited states. The radiative lifetimes of $^5D_{0,1,2}$ state decrease with temperature, the radiative lifetime of $^5D_1$ decreases much faster than $^5D_0$. The energy of the lowest excited state of the configuration $4f^5 5d^1$ was determined by fitting the lifetime values of $^5D_1$ state.

This work is supported by the Swiss National Science Foundation.

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New acridone-benzimidazole fused ligands: towards the sensitization of Eu luminescence with excitation wavelength in the visible range

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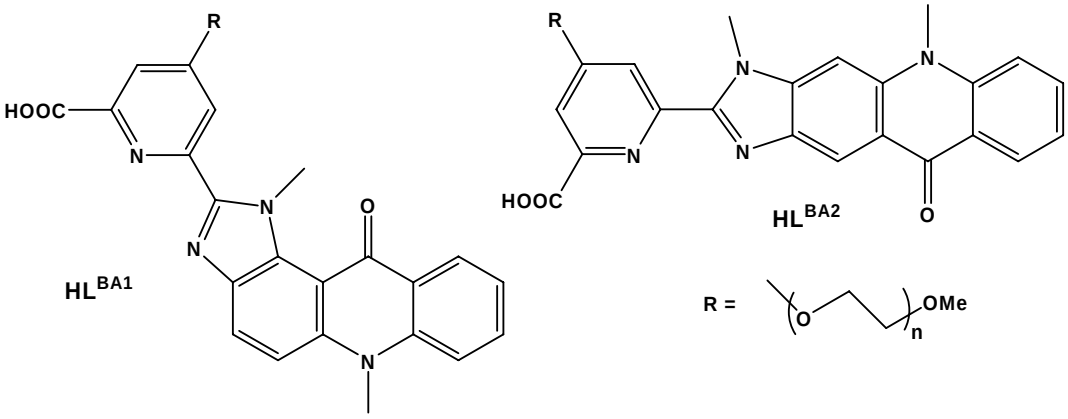
Keywords: Lanthanides; Chemistry; Coordination; Luminescence

Numerous europium complexes, including very stable neutral homobimetallic $[Eu_2(L^{CX})_3]$ (X=1-6) helicates [1,2], have been previously studied by our group with the aim of providing them as luminescent biological probes in aqueous media.

One of the actual challenges consists in circumventing the intrinsic limitations of energetic UV-light excitation. Indeed, excitation below 340 nm suffers from several drawbacks for *in cellulo* applications including cell-damages, need for costly quartz optics, and large induced auto-fluorescence. Thus, the combination between a sensitizer which possesses a long excitation wavelength could be a promising system towards cell imaging experiments in confocal luminescence microscopy which requires excitation wavelength of, at least, 405 nm [1].

Acridone ring is known to sensitize Eu^{III} luminescence, *via* the commonly observed singlet-to-triplet conversion inside the ligand and the subsequent ligand-to-Eu^{III} energy transfer with excitation wavelength above 400 nm [3]. Thus, the idea of the present work is to keep intact the benzimidazole substituted pyridine-2-carboxylic acid coordinating unit present in the former water-soluble helicates with the concomitant fusion of both *N*-methylacridone and *N*-methylbenzimidazole rings on the 6,7 or 7,8-positions of the latter heterocycle to form two new tridentate ligands. After complexation with Eu^{III}, these ligands afford $[Eu\ (L^{BAX})_3]$ (X=1 or 2) complexes. Additional organic and water-solubility is ensured by the presence of polyoxyethylene chains on the 4-position of the pyridine heterocycle.

We report here on the physico-chemical as well as photophysical properties of this new class of nonacoordinate Eu^{III} complexes.



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Surprisingly Efficient Near-Infrared Luminescence of Ytterbium Complexes with Benzoxazole-Substituted 8-Hydroxyquinolines

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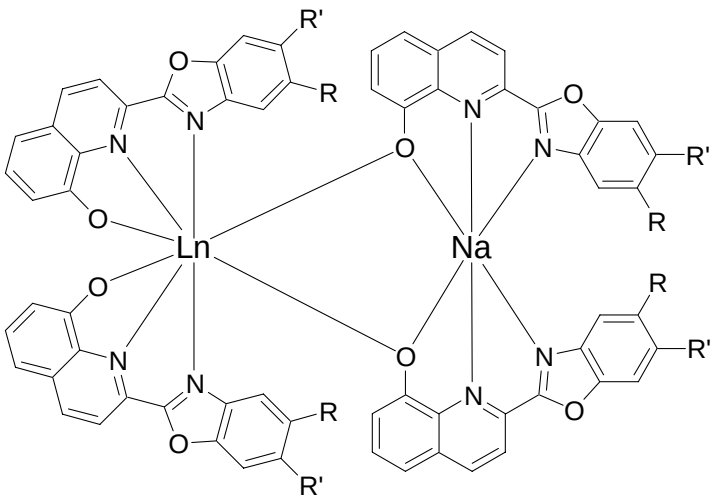
Keywords: Ytterbium; Chemistry; Coordination; Luminescence

Heterobinuclear Yb^{III}-Na^{I} complexes with benzoxazole substituted 8-hydroxyquinolines [1], in which a sodium complex acts as one of the ligands, display efficient near-infrared emission of ytterbium at 925-1075 nm. The solid state structure of the complexes has been established by X-ray crystallography while ^{1}H NMR spectroscopy confirmed that the complexes remain intact in 10^{-3} M CH_2Cl_2 solution. The absorption transitions of the complexes span UV and visible spectral range and allow excitation of infrared luminescence with visible light up to 600 nm. The luminescence lifetime and quantum yield of the complexes reach 22 μs and 3.7%, in the solid state, and 20 μs and 2.6% in CH_2Cl_2 solution [2].



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Spectroscopic properties of $GdF_3:Eu^{3+}$ nanocrystals synthesized via microwave synthesis in ionic liquids

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Keywords: europium; nanoparticles; luminescence

Fluorides and other halides of metals, which are wide band gap materials, co-doped with lanthanide ions in variable concentration are important in obtaining valuable insights into general aspects of lanthanide luminescence as well as for optical applications [1]. The most interesting optical properties of fluoride materials are their high transparency arising from low energy phonons on one hand and high ionicity on the other hand [2]. These intrinsic properties extend transmission to far UV and IR, leading to less absolute fundamental absorption compared to oxide or sulfide materials. Altogether, it turns the fluorides into very efficient materials, which are used in a wide range of optical applications from phosphors to lasers [3]. A very important goal is the development of new luminescent materials, which exhibit very high quantum efficiencies, in some cases even higher than 100% [1]. The most promising system for the realization of such a quantum cutting material where one VUV photon is converted to two VIS photons is the system of GdF_3:Eu [4]. In order to obtain a system with such a high quantum yield it is very important to synthesize the compounds under strict inert conditions to exclude any contamination of oxygen. In the case of Eu^{3+} oxygen would allow for non-radiative relaxation via europium–oxygen charge transfer states followed by emission from these levels.

In order to synthesize the europium doped GdF_3 nanocrystals, the corresponding acetate precursors were converted in the desired molar ration via microwave irradiation in the task-specific ionic liquid $[C_4mim][BF_4]$ (C_4mim = 1-butyl-3-methylimidazolium). The optical properties of the obtained materials will be presented in detail.

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IR and Vis emission of K_2LnCl_5 (Ln=Gd,La) crystals doped by Tb^{3+} and Yb^{3+} ions

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Keywords: luminescence, terbium, ytterbium

For many years optical properties of rare-earth ions in different host materials have been investigated, because of the importance of such materials in lasers, scintillators and nonlinear optics [1,2]. To study the physical processes the most suitable materials are large band gap inorganic solids doped with optically active rare earth ions. Ternary alkali metal halides have turned out to be appropriate host matrices. Especially chloride compounds are very effective due to their low phonon energy resulting in low multiphonon relaxation rates and high emission efficiencies. Optical excitations in these systems result either in a direct excitation of the luminescence center or in an excitation of the host lattice which partially transfers this energy to the emitting states of the activator.

A series of single crystals of potassium ternary chlorides K_2LnCl_5 (Ln = Gd, La) [3] codoped with Tb^{3+} and Yb^{3+} in a wide range of concentration was grown with Bridgman techniques. The compounds crystallize isotypic with K_2PrCl_5. This crystal structure features the lanthanide cation in a monocapped prismatic sourrounding. The $[LnCl_7]$ units form 1D-chains by sharing common edges. The ${}^{1}_{\infty}[LnCl_7]$ chains form a hexagonal arrangement. The close proximity of neighboring lanthanide ions makes cooperative interactions possible. High resolution emission and excitation spectra at 293 K and 77 K, as well as luminescence decay time measurements at different excitation wavelengths (including synchrotron radiation as excitation source) are used to characterize the energy transfer between ion pairs in the compounds studied.

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Using Lanthanide Ion Probe Spectroscopy (LIPS) to Monitor Polyelectrolyte Conformation

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Keywords: Poly Acrylic Acid; Time-Resolved Emission Spectroscopy; Lanthanide Ions; Energy Transfer

The speciation and subsequently the retardation and release of (heavy) metal ions in the bio- and geosphere is of great interest. Parameters such as toxicity and mobility are mainly governed by the oxidation state of the metal ion and the interaction of the metal ion with surrounding minerals and/or natural occurring organic material. As a useful tool for the monitoring of complexation of metal ions Lanthanide Ion Probe Spectroscopy (LIPS) can be applied [1]. Complexation of lanthanide ions (Ln(III)) by ligands results in changes in the luminescence decay time of the Ln(III) and in case of Europium (Eu(III)) additional changes in the spectral shape of the luminescence emission spectrum are observed.
As in the bio- and geosphere the distribution of minerals and natural occurring organics is very heterogeneous, it is useful to approach such complex systems using suitable model compounds. Natural organic material is known to consist of complex structures composed of aromatic, benzoic acid like substructures and aliphatic moieties. As the substructures also bear protonateable functional groups, e.g. carboxylic and phenolic groups, the natural organic material can be described in terms of polyelectrolytes [2, 3]. Promising steps to approach the "real" system (metal ions and organic phases) are i) the investigation of substructures and subsequent interactions of these simpler organic substances with metal ions and ii) to characterise the polyelectrolyte properties of natural occurring organics in detail.
With this paper, the polyelectrolytic properties (e.g., conformation) of natural organic material were investigated. LIPS was applied to investigate complexes of two different poly acrylic acids (PAA) with Eu(III) and Terbium (Tb(III)) at different pH values. In the experiments, the changes in the Eu(III) and Tb(III) luminescence are monitored and related to the concentration of Ln(III) and the pH of the solution. In additional experiments, Neodymium (Nd(III)) was added to Ln(III)-PAA complexes. Nd(III) can act as an acceptor of energy. By an inter-lanthanide energy transfer from Tb(III) or Eu(III) to Nd(III), part of the energy is transferred from Eu(III) or Tb(III) to Nd(III). The inter-lanthanide energy transfer shows up in a decrease of the luminescence decay time of Eu(III) and Tb(III), respectively. The efficiency of these energy transfer depends on the distance between the donor ion (Eu(III) or Tb(III)) and the acceptor ion (Nd(III)). Using this inter-lanthanide energy transfer, it is possible to calculate distances of binding sites in polyelectrolyte-Ln(III) complexes. These distances again can be evaluated with respect to Ln(III) concentration and pH of the solution. Changes in the deduced Ln(III)-Ln(III) distances are closely related to conformational changes in the polyelectrolyte structure.

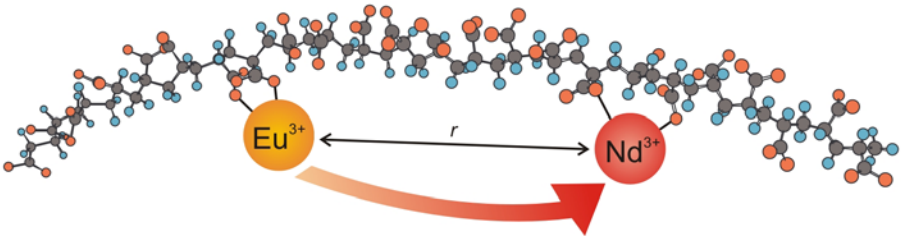

Figure 1. Scheme of the inter-lanthanide energy transfer. Energy can be transferred from Eu(III) to Nd(III). The transfer efficiency is a function of the distance *r* between donor (Eu(III)) and acceptor (Nd(III)).

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Luminescence Properties of Divalent Samarium-Doped Strontium Tetraborate

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Keywords: samarium; tetraborate; solid state; spectroscopy

Strontium tetraborate, SrB_4O_7, is a suitable host lattice for luminescent divalent rare earth ions, such as Eu^{2+}, Sm^{2+}, Yb^{2+}, Tm^{2+} and these divalent ions can be very stable even when heated in air at high temperature. This is attributed to the structural framework in SrB_4O_7, all the boron atoms are tetrahedrally coordinated with oxygen atoms and form a three-dimensional borate network [1].

In this work, the reduction process for samarium from trivalent to divalent state is reported. Samples were synthesized by conventional solid-state procedure. The luminescence of Sm^{2+} in this host is studied as a function of dopant concentration, annealing time and temperature.

The emission spectra at room temperature of Sm^{2+} in SrB_4O_7 prepared in air are shown in Figure 1. The emission spectra shows that the luminescence of Sm^{2+} in SrB_4O_7 prepared in air consist of four groups of lines at 685, 700, 725, and 760 nm that correspond to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3) transitions in Sm^{2+}, respectively. A group of weak lines at 560, 600, and 640 nm correspond to $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2, respectively) transitions in Sm^{3+} ion [2].

Weak Sm^{3+} emission is detected regardless of annealing time or temperature during sample preparation. This can be due to glassy phase remaining in samples.

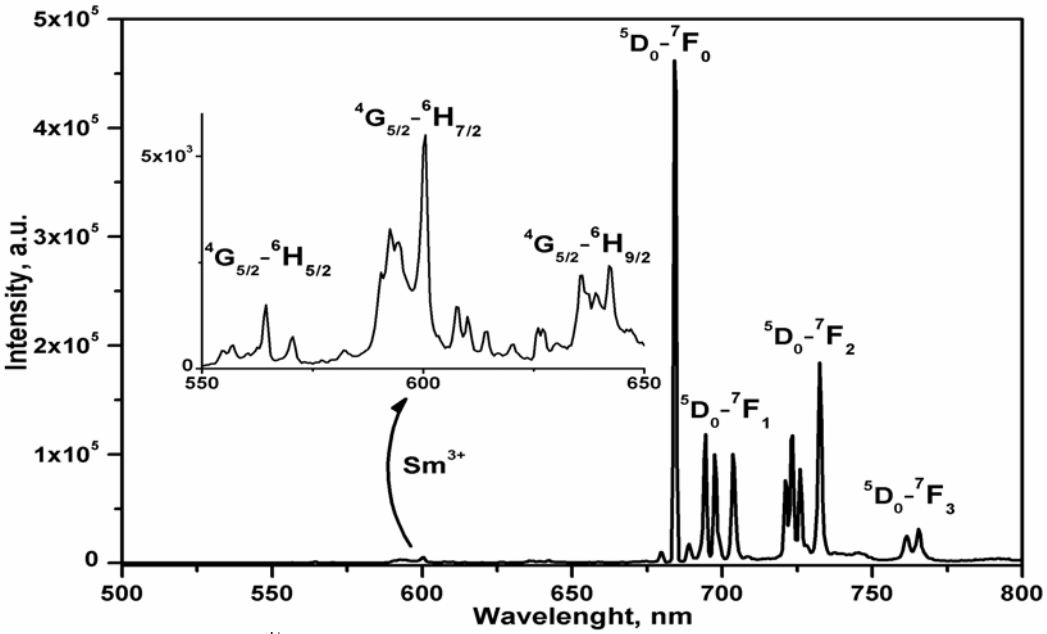

Figure 1. Emission spectra of Sm^{2+} in SrB_4O_7 prepared in air (λ_{ex} = 404 nm) at room temperature (The inset shows the enlargement of the Sm^{3+} emission in the range from 550 to 650 nm).

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Synthesis and Optical Properties of $CaY_2Al_4SiO_{12}:Ce^{3+}$

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Keywords: Cerium, Synthesis, Spectroscopy

A series of Ce^{3+} doped $CaY_2Al_4SiO_{12}$ samples were synthesized by sol-gel method employing ethylene glycol as a chelating agent. Samples were characterized by powder X-ray diffraction (XRD) and photoluminescence (PL) techniques.

The XRD measurements showed that the garnet phase was already formed if powders were annealed at 1400°C (see Fig. 1) for several hours under CO atmosphere. A further increase of the annealing temperature (> 1500°C) resulted in molten samples, suggesting that the melting point of the target materials are between 1400 and 1500°C.

Photoluminescence measurements revealed that the spectral position of Ce^{3+} emission band is sensitive to the Ce^{3+} concentration of the target samples. It turned out that emission maximum has shifted to the red spectral region if Ce^{3+} concentration was increased. This can be explained by re-absorption of emitted photons by the activator. Target samples possessed strong absorption in the blue spectral region and high transmittance at the longer wavelengths (see Fig. 2) making them very attractive for application in pcLEDs.

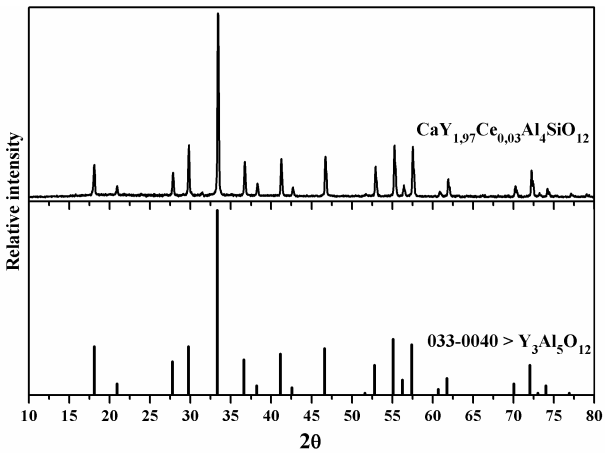

Figure 1. XRD pattern of $CaY_{1,97}Ce_{0,03}Al_4SiO_{12}$ annealed at 1400°C.

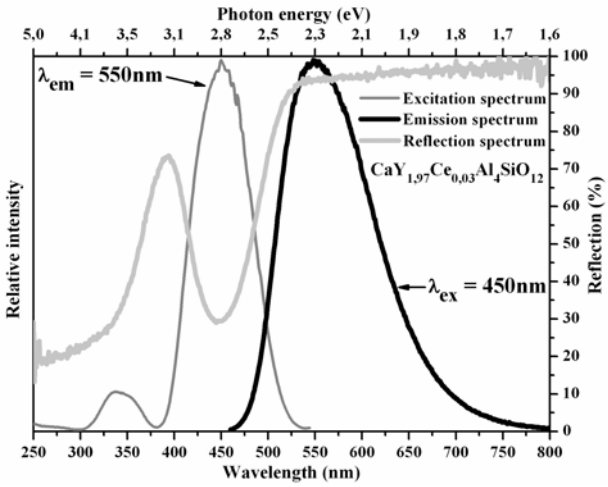

Figure 2. Emission, excitation and reflection spectra of $CaY_{1,97}Ce_{0,03}Al_4SiO_{12}$ annealed at 1400°C.

The emission maximum of the phosphors is centred at around 550 nm (green-yellow spectral region) and is slightly shifted towards the blue spectral range relative to conventional YAG:Ce phosphors emitting at 560 nm.

Optical properties of the phosphor powders were studied as a function of Ce^{3+} concentration on the dodecahedral lattice site. Furthermore, quantum efficiencies (QE), lumen equivalents (LE) and CIE 1931 colour points were also calculated and will be discussed.

Luminescence of Lanthanides in Complexes with Phosphorus- and Carboxycalix[4]arenes

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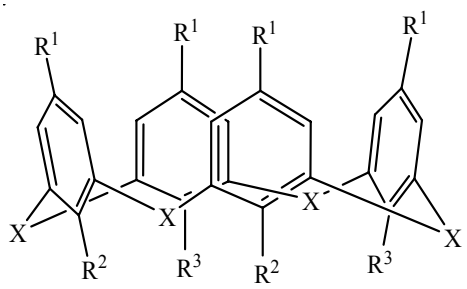
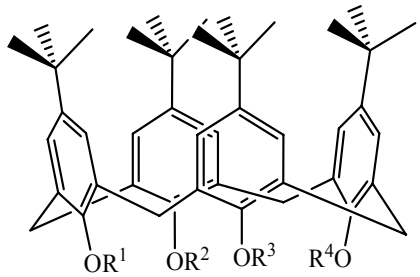
Keywords: Lanthanides; Chemistry; Coordination; Spectroscopy

There is a considerable interest in lanthanide calix[4]arene complexes which most of them are related to luminescence and extraction [1,2]. Besides, the incorporation of functional groups into the structures of calix[4]arenes and formation of molecular devices capable of performing various duties is a very essential target in nowadays research. In the present work we report about the most recent results obtained in the spectroscopic characterization of lanthanide complexes (Ln = Tb, Eu, Sm, Dy, Yb) with phosphorus containing pendant arms calix[4]arenes (L^1-L^6) and carboxycalix[4]arenes (L^7-L^9) (Fig.1). All ligands and complexes have been characterized by elemental analysis, mass-spectrometry, IR- and NMR-spectroscopy. The absorption, excitation and luminescence spectra of complexes were investigated and their spectral-luminescence characteristics at room temperature and 77K were discussed. The influence some of organic solvents on the luminescence intensity of complexes was studied. It was established that a change of pH shows a highly sensitive influence on the 4f-luminescence of water-soluble complexes with L^1-L^6.



L_1: X= CH_2 $R^1 = CH_2P(O)(C_2H_5)_2$ $R^2 = R^3 =$ OH
L_2: X= CH_2 $R^1 = CH_2P(O)(OH)(C_2H_5)$ $R^2 = R^3 = OC_3H_7$
L_3: X= CH_2 $R^1 = CH_2P(O)(C_3H_7)_2$ $R^2 = OH$ $R^3 = OP(O)(OH)_2$
L_4: X= S $R^1 = CH_2P(O)(C_2H_5)_2$ $R^2 = R^3 = OH$
L_5: X= S $R^1 = CH_2P(O)(OH)_2$ $R^2 = R^3 = OH$
L_6: X= S $R^1 = CH_2P(O)(C_6H_5)_2$ $R^2 = R^3 = OH$



L_7: $R^1 = R^2 = R^3 = H$ $R^4 = CH_2COOH$
L_8: $R^1 = R^3 = H$ $R^2 = R^4 = CH_2COOH$
L_9: $R^1 = R^2 = R^3 = R^4 = CH_2COOH$

Figure 1. Structures of ligands studied.

In order to increase of 4f-luminescence efficiently the methods dealing with the optimization of ligand structure were discussed in detail.

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Intramolecular Energy Transfer of *d-f* Heterodinuclear Complexes

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Keywords: Lanthanides; Chemistry; Coordination; Spectroscopy

A *d*-Metal complex can be a suitable sensitizer of lanthanide near-infrared emission, because it generally has strong visible-light absorption and a tendency to generate excited states with different spin multiplicity.[1] The differences between the coordination natures of *d*- and *f*-metal ions make it difficult to prepare multidentate ligands for *d-f* heteronuclear complexes. In this study, a macrocycle-based multidentate ligand was synthesized to form dioxorhenium(V)-lanthanide(III) heteronuclear complexes by the stepwise complexation method. The near-infrared luminescence via effective intramolecular energy transfer from *d*-metal complex moiety to the lanthanide ion were investigated.

All the employed lanthanide cations from La^{3+} to Lu^{3+} gave similar crystals of heterodinuclear complexes with C_4 symmetric structures. The lanthanide contraction from La^{3+} to Lu^{3+} gave gradual changes on the chemical properties of the dioxorhenium complex unit such as photo-absorption energy, redox potential ($Re^{V/VI}$), Re-O bond lengths, and resonance raman intensity of the Re=O bond, indicating that this type of dinuclear complexes can be used for fine-tuning of chemical properties of *d*-metal complexes.

Complex **1** has strong absorption bands by metal-to-ligand charge transfer and *d-d* transitions of the rhenium complex moiety. When the complex **1** (Ln = Nd, Yb) was photo-excited by these absorption bands in acetonitrile, near-infrared emission from Nd^{3+} and Yb^{3+} was obtained with the quantum yields of 0.28% and 0.52%, respectively. These values were much larger than those of the corresponding mononuclear lanthanide complexes **2**. Since dinuclear complex **1** and mononuclear complex **2** showed almost the same luminescence lifetimes, it is concluded that the enhancement in the luminescence quantum yield is mainly caused by efficient energy transfer from the rhenium complex to the lanthanide ion.

Water-soluble iodide salts of **1** were also obtained. Decomplexation did not occur at low concentration (1 μM), while the near-infrared emission could still be detected. Since this type of *d-f* heteronuclear complexes can work as near-infrared emissive molecule in aqueous solutions, it can be a useful molecular probe with near-infrared light detection.

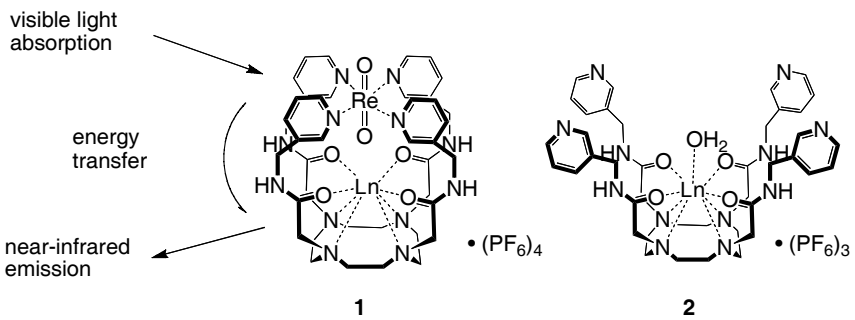

Figure 1. Structures of *d-f* dinuclear complex **1** and mononuclear complex **2**.

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Structure-photoluminescence relationships in europium doped microporous and mesoporous materials

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Keywords: time-resolved photoluminescence, europium, maximum-entropy method, decay-associated spectra

To obtain innovative lanthanide-doped materials of potential interest for photoluminescence (PL)-based applications, information related to the distribution of the lanthanides ions and their detailed coordination environment is essential. Time-resolved emission (photoluminescence) spectroscopy (TRES) is a very powerful tool providing high-resolution details on the photoluminescence processes involved such as the excited-state dynamics and the corresponding species-related spectra. In contrast to regular time-gated single photon counting techniques, which often only measure the decay at a particular emission wavelength, from TRES superior information in two independent experimental dimensions are obtained: emission wavelength λ and PL intensity at different times t after excitation. From the TRES, both PL decays and PL spectra can be extracted, providing a detailed insight in the photophysics of the system under investigation [1].

Here, we report the application of the maximum entropy method and decay-associated spectra to the analysis of the time-resolved luminescence spectra of europium in the microporous and mesoporous materials [2-4]. Due to the well–known sensitivity of europium PL properties to the local environments, we are able to describe the structure-PL relationships in terms of *individual species* that contribute to the total emission of the system. Based on the photoluminescence lifetimes and spectra derived for each of the europium species present in the samples, detailed information on the local symmetry at the europium sites, heterogeneity effects and quantum efficiency of the PL is extracted from the TRES and discussed in detail. Moreover, the relative contribution of the radiative and non-radiative relaxation to the overall PL of europium in the investigated materials is analyzed with respect to the Si/Al ratio, moisture content (due to surface treatment), and polymer embedding (grafting), respectively.

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Luminescent Properties of Modified Eu^{3+} / Tb^{3+} Picolinates and Dipicolinates

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Keywords: Lanthanides; Coordination Compounds; Luminescence; Energy Transfer

Luminescence properties of mixed Eu^{3+} and Tb^{3+} complexes with α-picolinic ("Pic") and 2,6-dipicolinic ("Dipic") acids and their derivatives with NH_2- and OH- substituents were studied for the purpose of analytical and imaging applications in biological, polymer and colloidal systems. Complexes of both lanthanide ions with the principle compositions $NaLn(Pic)_4$ and $Na_3Ln(Dipic)_3$, respectively, show high quantum yields and long life times of the excited states [1, 2]. Substitutions of the aromatic rings change the electronic structure of the ligands, thus causing shifts of the ligand triplet states and Eu – O^{2-} charge transfer state positions with subsequent changes in luminescent characteristics. This holds true for mixed compositions also, i.e. partial replacement of Pic and Dipic ligands by Pic-X and Dipic-X (X = $-NH_2$, -OH), to yield complexes of the type $Na_3Ln(Dipic)_2$Dipic-X (Fig.1). NH_2- and OH- substituents were chosen for the goal of subsequent coupling reactions with isocyanato-, isothiocyanato-, epoxy- and carboxylic groups of analytical and other substrates of interest, e.g. polymer backbones. The effects of coupling of the primary ligands to aliphatic isocyanates and isothiocyanates on the luminescent properties are investigated. Thus, in the solid state, energy transfer from Tb^{3+} to Eu^{3+} species strikingly differs in efficiency for the series $Ln(Pic)_3$, $NaLn(Pic)_4$ and $Na_3Ln(Dipic)_3$. Energy transfer is found to be particularly efficient in trispicolinates $Ln(Pic)_3$, in which carboxylic groups coordinate two rare earth ions at the same time to accomplish a sufficiently high coordination number, while it is much less efficient in the monomeric dipicolinates ($Ln(Dipic)_3^{3-}$, coordination number 9), where ligand-to-ligand resonant energy transfer mechanisms dominate. Using a covalently linked spacer molecule between Tb^{3+} and Eu^{3+} complex units, intramolecular energy transfer processes were studied in the resulting dinuclear complexes in the solid state and in solution.

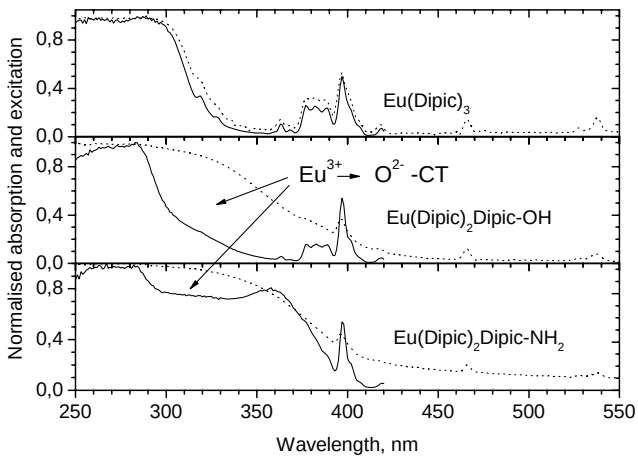

Figure 1. Normalised absorption (dotted line) and excitation (solid line) spectra of $Na_3Eu(Dipic)_2$Dipic-X complexes

The ligands L were linked in the manner $[L\text{-}O\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}O\text{-}L]^{m-}$ and $[L\text{-}NH\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}NH\text{-}L]^{m-}$, (m = 2 for L = Pic and m = 4 for L = Dipic), thereby enabling the evaluation of possible Tb^{3+} / Eu^{3+} FRET complex pairs rather than the 'conventional' systems comprising a rare earth complex and purely organic luminescence quencher dye.

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Luminescence characteristics of Dy^{3+}-doped Zn-Al-K-Na phosphate glasses

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Keywords: Lanthanides; Spectroscopy; Dy^{3+} ions; Glasses;

Dysprosium ion doped Zn-Al-K-Na phosphate glasses with composition of PZAKNDy: (46-x/2) P_2O_5 + 10 Al_2O_3 + 15K_2O + 10 Na_2O + (19-x/2) ZnO + x Dy_2O_3 (x = 0.05, 0.1, 1.0, 2.0 and 3.0 mol %) have been prepared by melt quenching technique and are characterized by optical absorption, emission spectra and fluorescence lifetime measurements [1,2]. The observed bands in the absorption spectrum are analyzed by using free-ion Hamiltonian model. The Judd-Ofelt analysis has been performed and the intensity parameters ($\Omega_{\lambda,}$ λ = 2, 4, 6) have been evaluated which are used to predict radiative properties. From emission spectra, the effective bandwidth ($\Delta\lambda_{eff}$) and the stimulated emission cross-section ($\sigma(\lambda_p)$) were evaluated. The fluorescence decay from the $^4F_{9/2}$ level of Dy^{3+} ions have been measured by monitoring the intense $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition (573 nm). The fluorescence lifetimes (τ_{exp}) are found to decrease with increasing concentration due to concentration quenching. The decay curves are perfectly single exponential for lower concentrations and gradually changes to non-exponential for higher concentrations.

The non-exponential decay curves are well fitted to the Inokuti-Hirayama model for S = 6 which indicates that the energy transfer between the donor and acceptor is of dipole-dipole type. Infra red emission and decay curve properties at 1.32 μm originating from the $^6F_{11/2} \rightarrow {}^6H_{9/2}$ level are also examined as it is interesting for application to the fiber amplifiers in the optical transmission systems. The systematic analysis on decay measurements reveals that the energy transfer mechanism strongly depends on concentration as well as glass composition. These results are compared with those of reported Dy^{3+}-doped phosphate, fluorophosphate, fluoride and chalcogenide glasses and glass ceramics [1-4] to find the similarities/differences/applications/challenges as well as to derive the future scope of work in the field of lanthanide ion-doped systems, specifically to design Ln^{3+}-based photonic/laser devices besides quantitative estimation of interaction parameters.

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Eu and (Eu,Li)-Activated HfO_2 Phosphors – Phase Purity and Spectroscopic Properties

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Keywords: Lanthanides, Materials, Structure, Spectroscopy

It has been reported, recentely [1,2] that Eu-doped HfO_2 powders exhibit interesting properties as X-ray phosphors. The interests in HfO_2:Eu compositions comes from high density (~9.7 g/cm^3), and high effective atomic number (Z_{eff}=67.2) of the host which ensure effective absorption of X-rays and gamma particles. Hafnia crystallizes in variety of structures - cubic, monoclinic, tetragonal, orthorhombic. However, up to about 2000K monoclinic phase is the stable one. Yet, doping HfO_2 with trivalent lanthanides perturbs this equilibrium and even at lower temperatures it tends to crystallize in different structures. Furthermore, doping hafina with trivalent ions of lanthanides forces incorporation of defects to balance the lower charge of the activator compared to Hf^{4+}. We shell report on the dependence of structural and spectroscopic properties of HfO_2:Eu and HfO_2:Eu,Li on the dopants concentrations and temperature of the powders preparation.

Powders of HfO_2:Eu and HfO_2:Eu,Li with different content of the activators (0, 0.5, 1, 3, 5 at.%) were prepared with the classic Pechini method. The raw powders were heat-treated at various temperatures in the range of 600-1700 °C. The co-doping with Li^+ was anticipated to increase the efficiency of energy transfer from the excited HfO_2 host to the Eu^{3+} emitting ions. The real influence of the Li^+ on the photo- and radioluminescence of HfO_2:Eu powders will be presented and analyzed.

A significant, broad-band radioluminescence peaking around 520 nm is observed from undoped HfO_2. Its efficiency becomes clearly stronger with increasing temperature of preparation. This emission can also be stimulated with UV radiation. After ceasing of the irradiation a significant afterglow was observed, see Fig. 1. Addition of Eu^{3+} caused its emission came into view. However, for samples prepared at high temperatures the red luminescence of Eu^{3+} was accompanied with the broad-band intrinsic bluish green emission of the host. This was especially clearly seen upon UV excitation. Consequently, for materials prepared at low temperatures the emission was orange-red, while for those made at high temperatures it was basically white, see Fig. 1.

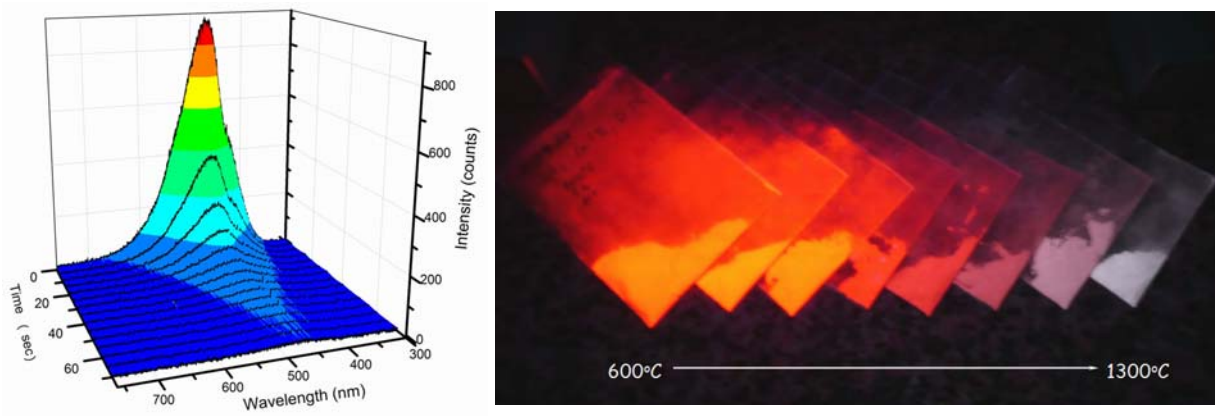

Figure 1. Afterglow luminescence of undoped HfO_2 prepared at 1500 °C (left), and variation of luminescence colour of HfO_2:Eu5%,Li5% as the function of preparation temperature (right).

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Persistent luminescence in rare-earth codoped $Ca_2Si_5N_8:Eu^{2+}$

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Keywords: Lanthanides; Physics; Solid State; Persistent Luminescence

Persistent luminescent materials are able to emit light up to hours, sometimes even days, after they were excited, without needing a constant energy input [1]. Obviously, this has applications in for example security lighting. The origin of this persistent luminescence is not yet fully understood, but most probably it is due to the existence of specific charge traps in the material. Many persistent materials have been developed over the past few years. However, stable and efficient persistent light emitting compounds in the orange to red part of the visible spectrum are relatively scarce. One of the ways to achieve this is turning to different host materials, other than the more popular oxides and sulfides.

We focused on the thermally and chemically stable compound $Ca_2Si_5N_8$ as a host material, produced from calcium nitride and silicon nitride through a solid state reaction at 1300°C. Small amounts of Eu^{2+} were added as luminescent centers. The emission spectrum of this material peaks in the orange region at around 610nm. The influence of codoping with different rare earths (Nd, Dy, Sm, Ho and Tm) on the persistent luminescence was investigated and compared with samples without codoping. It is shown that the effect of adding Nd, Dy and Ho is negligible, while Sm has a detrimental effect [2]. Tm enhances the persistence considerably, with a main decay constant of about one hour. The best results were achieved when 0.75-1% of the Ca-sites in the material are occupied by Tm atoms. Thermoluminescence (TL) measurements revealed that the addition of Nd, Dy and Ho leads to relatively shallow traps, as the TL peaks occur below room temperature. The addition of Tm on the other hand leads to TL peaks above room temperature. The TL results are interpreted with the lanthanide energy level scheme as discussed by Dorenbos [3].

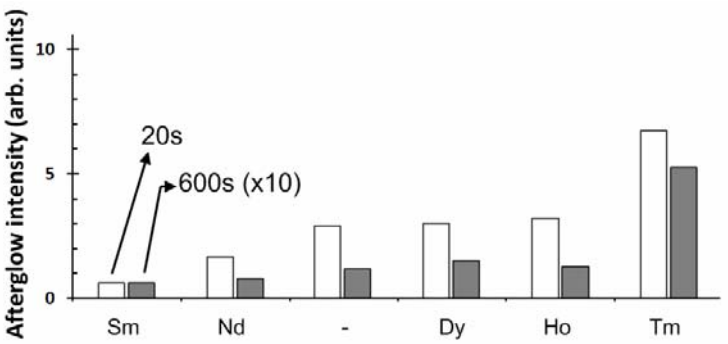

Figure 1: Relative intensity of the persistent luminescence of $Ca_2Si_5N_8:Eu^{2+}$ codoped with different rare-earths, 20 seconds and 10 minutes after the excitation

Furthermore, we have found that the intensity of the persistent luminescence is positively influenced when the rare earths are added to the initial mixture as fluorides instead of oxides. Also, a small deficit of calcium nitride appears to enhance the phosphorescence of the resulting material.

It is possible to excite the persistent emission with visible light, which is useful for practical (especially indoor) applications where UV excitation is not always available.

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Luminescent and structural behaviour of copper(I)-doped rare earth containing ionic liquids

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Keywords:

Cu^+ ions known to exhibit strong, broad band luminescence corresponding to a $3d^94s \rightarrow 3d^{10}$ transition. Such a transition is parity forbidden in the free ion and partially allowed in a host matrix through coupling of lattice vibrations of odd parity. In the compounds $[C_4mim]_3[LnCl_6]_x[CuCl_4]_{1-x}$ the Cu^+ is embedded in a host matrix of $[C_4mim]_3[LnCl_6]$, wherein the Lanthanide ion is octahedrally coordinated by six ligands. The samples exhibits very intensive emission, the colour of emission is strongly depend on the temperature and turns from orange to blue-green with decreasing temperature. In all three compounds we can find an efficient energy transfer from the imidazolium ring of the ionic liquid to Cu^+. However, the emission of the lanthanide ions Tb^{3+} and Dy^{3+} is independent of the local environment and we not able to observed any energy transfer from the imidazolium rings to the Ln^{3+} ions. At low temperature, the Tb^{3+} emission is overlapped by the strong emission of the Cu^+ ions.

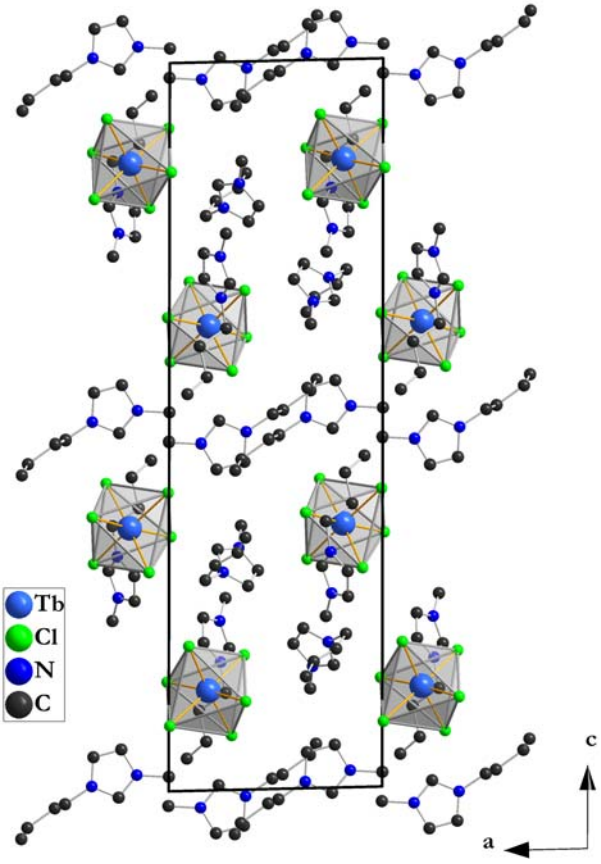

Fig. 1: Crystal structure of $[C_4mim]_3[TbCl_6]_{1-x}[CuCl_4]_x$ along [010].

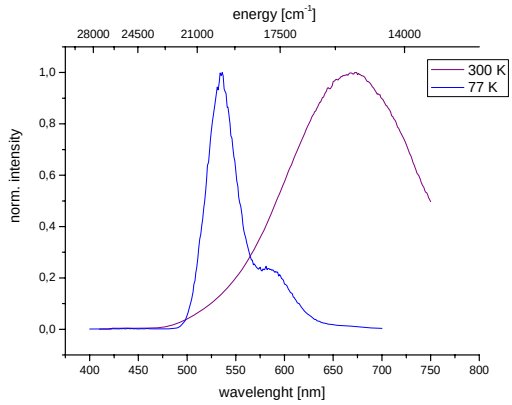

Fig. 2: Emission spectra of $[C_4mim]_3[GdCl_6]_{1-x}[CuCl_4]_x$ at 300 and 77 K (λ_{excit} = 360 nm).

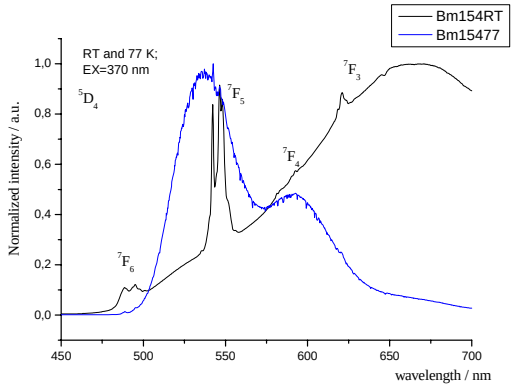

Fig. 3: Emission spectra of $[C_4mim]_3[TbCl_6]_{1-x}[CuCl_4]_x$ at 300 and 77 K (λ_{excit} = 360 nm).

Magnetic Interactions in Lanthanide containing Systems: From Synthesis to Characterization

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Keywords: Lanthanides; Chemistry; Coordination; Magnetism

Heterodinuclear copper-lanthanide complexes based on compartmental salen-type ligand (N,N'-bis(3-methoxysalicyliden)-1,3-diamino propane [L]) have been successfully used to build-up 1-D coordination polymers using pyrazine-2,3-dicarboxylic acid as bridging ligand. A series of isostructual compounds containing Ln ions (Ln = La to Dy) were crystalographically characterized[1]. The temperature dependence of the magnetic susceptibility was measured in the temperature range of 2 - 300 K. Evaluation of the temperature dependence of the $\chi_M T$ product indicates that the Cu-Gd coupling interaction within the heterodinuclear units is ferromagnetic (J = 4.7 cm^{-1} with $\mathbf{H} = -J\ \mathbf{S_1S_2}$). ESR measurements gave additional insights into the electronic structures. From the obtained g values the tilting of the principle axis of the copper and lanthanide g tensors can be correlated to structural features.

When reacted in 2:1 stoichiometry (copper precursor: lanthanide) with salicylic acid as additional blocking ligand, trinuclear Cu_2Ln complexes are obtained (Ln = La, Pr, Sm, Eu and Gd). The lanthanide ion is in a O_{10}-coordination environment. They have been characterized according to their magnetic properties in terms of the thermal dependence of the magnetic susceptibility and ESR spectroscopy.

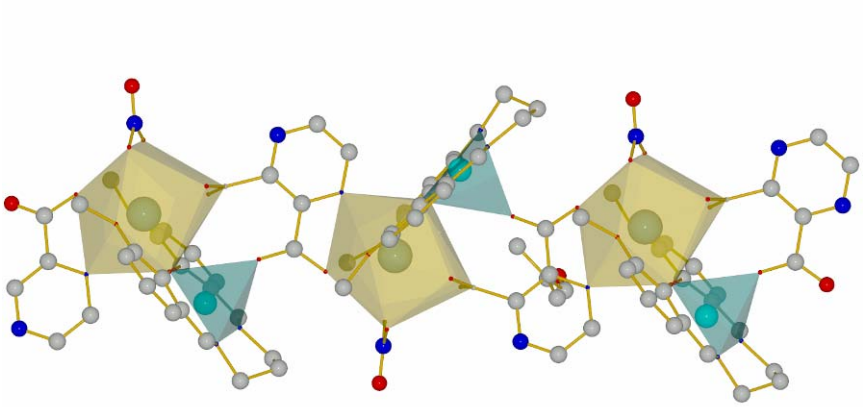

Figure 1. Schematic representation of the 1-D Cu-Ln coordination polymers with the coordination polyhedra around the copper and lanthanide ions highlighted.

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A europium(II) complex with dibenzo-30-crown-10

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Keywords: Divalent europium; crown ether

Crown ethers are one of the few classes of ligands that may efficiently stabilize the divalent lanthanide cations, and apart from that their Ln(II) complexes are good luminophors, what is uncommon among the organic complexes of of divalent lanthanides. For these reasons they are interesting objects of investigations and in a further perspective, of some practical applications.

The stability of the Ln(II)-crown ether complexes was recognized in the eighties of the XX century [1] and the spectroscopic properties mainly of the Eu(II) complexes in methanolic solutions were extensively presented sixteen years later [2].

Then, to get an insight into their structures and the structural factors that may influence their spectroscopic properties, synthesis of the crystalline complexes was inevitable. Previously complexes of Eu(I) and Sm(II) with a few crown ethers (e.g. 12-crown-4, 15-crown-5 and 18-crown-6) were described [3,4].

Dibenzo-30-crown-10 is in some way particular in this family, because it is one of the most potent stabilizers of the divalent state of the lanthanides [1]. Paradoxically, its Eu(II) complex was rather difficult to prepare.

The [Eu(dibenzo-30-crown-10](ClO$_4$)$_2$·H$_2$O complex has been prepared by electrolytic reduction at a controlled potential and its crystal structure has been elucidated (see Fig. 1 for a view of the complex cation).

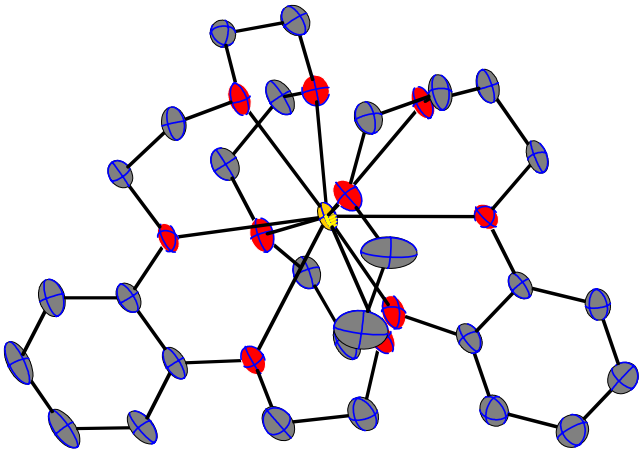

Figure 1. A view of the [Eu(dibenzo-30-crown-10]$^{2+}$ cation.

The complex shows a strong blue-violet emission with maximum at 403 nm.

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Polymorphism of octahedral hexanuclear compounds

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Keywords: Lanthanides; Chemistry; Coordination; Synthesis; Polymorphism

Hexanuclear compounds of general formula $[Ln_6O(OH)_8(NO_3)_6(H_2O)_n]2NO_3.mH_2O$ with Ln=Pr,Nd,Sm-Lu present a generous polymorphism as hydrated, partially dried and anhydrous phases.

First, we synthesized and studied the hydrated phases, which possess 12 or 14 coordination water molecules depending on the ionic radius of the involved lanthanide, and a number of 2, 4, 5 or 6 crystallisation water molecules varying with the hydration rate of the reaction medium[1-5]. Synthesis in dried ethanol leads to $[Ln_6O(OH)_8(NO_3)_6(H_2O)_{12}]2NO_3.2H_2O$ with Ln=Sm-Lu, the less hydrated phase. When exposed to wet atmosphere this phase binds more and more water molecules, and in the end, after a few days, decomposes into amorphous lanthanide oxo-hydroxy-nitrate phases.

We also studied the anhydrous phases, obtained by heating any hydrated phase for about 1 hour at 180°C[3-5] : 4 out of the 6 nitrato groups that were connected only to one metallic ion in a bidentate manner become bridging ligands between 2 different octahedral complexes in a tridentate manner. Their crystal structure is the same for Ln=Pr-Lu ; their chemical formula is $[Ln_6O(OH)_8(NO_3)_8]_\infty$[6].

Finally we found another structure, partially dehydrated, obtained via lyophilisation or nitrogen flux drying. By these means 6 water molecules remain per octahedral hexanuclear motif, one per metallic ion. The chemical formula is $[Ln_6O(OH)_8(NO_3)_6(H_2O)_6]2NO_3$, the compounds are isostructural for Ln=Pr-Lu. We report here the whole hydration/dehydration process for these compounds.

Table 1. polymorphism of hexanuclear lanthanide based compounds

$[Ln_6O(OH)_8(NO_3)_6(H_2O)_n]2NO_3.mH_2O$

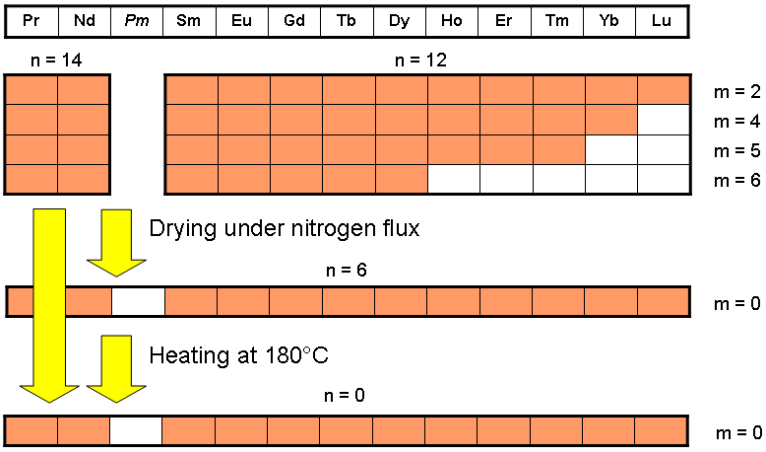
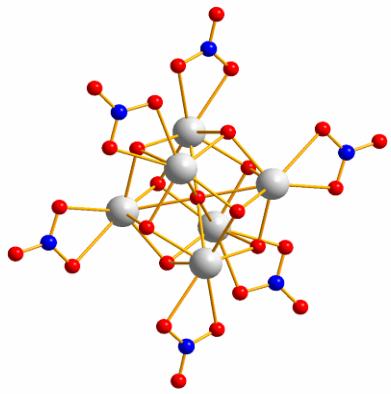


Figure 1. octahedral hexanuclear core $[Ln_6O(OH)_8(NO_3)_6]^{2+}$



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A new familly of porous lanthanide-containing coordination polymers : $Ln_2(C_2O_4)_3(H_2O)_6$ with Ln = Eu – Yb or Y.

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Keywords: Lanthanides; Chemistry; Coordination; Structure, Porosity

Lanthanide oxalate coordination polymers have been extensively studied because they are convenient molecular precursors to condensed phases. It is well established that these compounds with general formula $Ln_2(C_2O_4)_3.10H_2O$ exhibit 2-D crystal structure with honeycomb-like bi-dimensional molecular layers. Our group has recently succeeded in synthesizing, at low temperature, three dimensional coordination polymers with general formula $Ln_2(C_2O_4)_3(H_2O)_6.12H_2O$ with Ln = Eu – Yb and Y [1]. All of them are isotructural. Their crystal structure exhibits large channels with hexagonal sections filled by crystallization water molecules. These crystallization water molecules can be removed by freeze-drying without destroying the molecular structure leading to a new family of porous lanthanide-containing coordination polymers with general chemical formula $Ln_2(C_2O_4)_3(H_2O)_6$ with Ln = Eu – Yb and Y. The porosity of the obtained lyophilized compounds has been estimated to roughly $483 m^2g^{-1}$ by computational methods [2, 3]. The luminescent properties of the terbium(III) and europium(III) containing compounds are also briefly described.

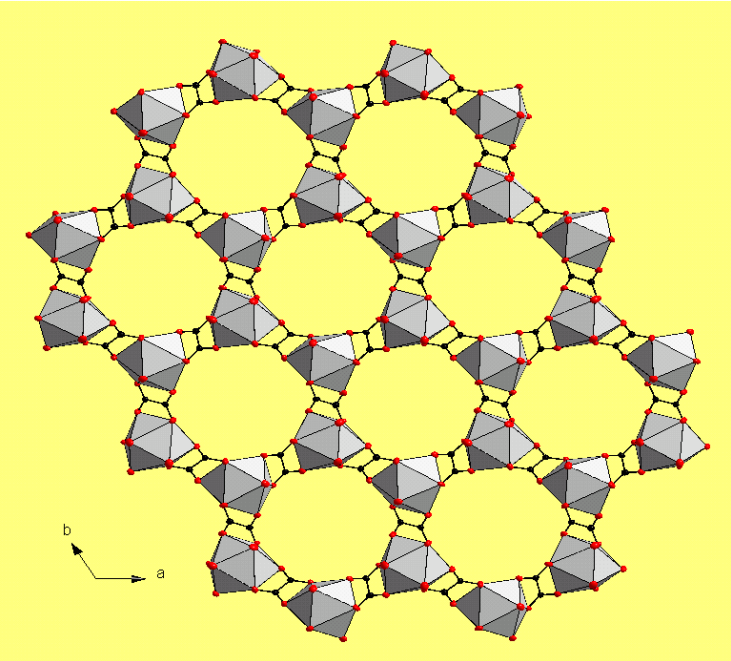

Figure 1. Projection view of $Er_2(C_2O_4)_3(H_2O)_6$.

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The lanthanide terephthalate coordination polymers : A family with highly tuneable luminescent properties.

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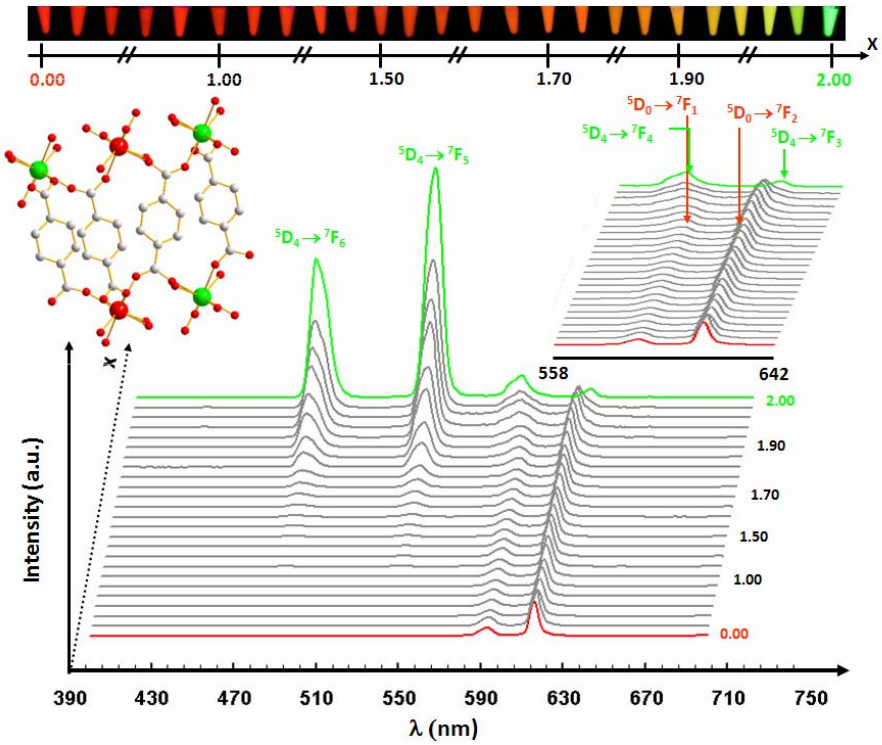
Keywords: Lanthanides; Chemistry; Coordination; structure; Luminescence

Lanthanide-containing coordination polymers, thanks to the similar chemical behaviour of lanthanide ions generally constitute families of isostructural compounds exhibiting different physical properties. This tuneable character of the physical properties has often been stressed and has motivated numerous studies. Actually, most often, results of these studies were disappointing because of the lanthanide contraction effect that reduces the families to only a few compounds.

We wish to describe here a family of heteropolynuclear lanthanide based coordination polymers containing millions of isostructural compounds exhibiting tunable luminescent properties.



These coordination polymers have general chemical formula $\left[\left(\sum_{i=1}^{13} Ln^{i}_{x_i}\right)(C_8H_4O_4)_3(H_2O)_4\right]_{\infty}$ with $\sum_{i=1}^{13} x_i = 2$ and where the Ln^i respectively symbolize one of the lanthanide ions comprised between La and Tm (except Pm) or Y and where $C_8H_4O_4^{2-}$ stands for terephthalate[1]. This infinite family of compounds constitutes an excellent object for studying the physical phenomena governing the luminescent properties. We have undertaken a systematic study. The first results will be presented.

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Structural study of hetero-poly-nuclear coordination polymers.

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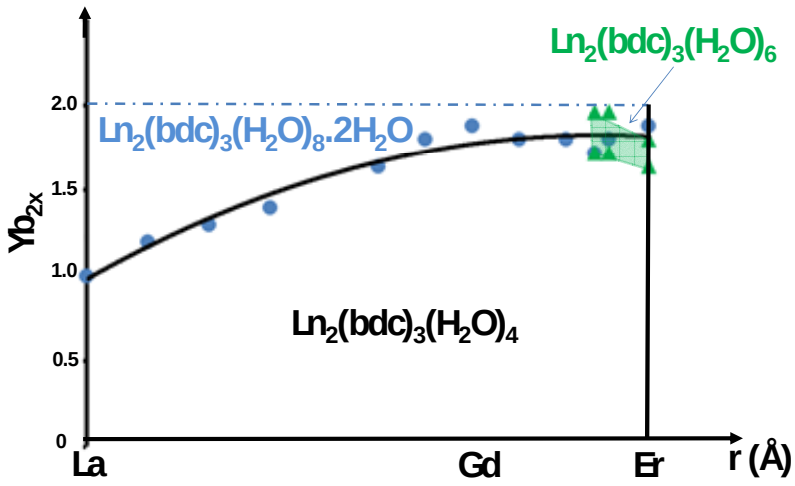
Keywords: Lanthanides, spectroscopy, coordination, synthesis

Reactions in water between a lanthanide chloride and the sodium salt of 1,4 benzene dicarboxylic acid lead to two different families of isostructural coordination polymers depending on the involved lanthanide ion : The compounds belonging to the first family are obtained when Ln = La – Tm or Y. Their general chemical formula is $[Ln_2(bdc)_3(H_2O)_4]_\infty$. It has already been shown [1] that this structural family also contains hetero-poly-metallic compounds with general chemical formula $\left[\left(\sum_{i=1}^{13} Ln^i_{x_i}\right)(C_8H_4O_4)_3(H_2O)_4\right]_\infty$ with $\sum_{i=1}^{13} x_i = 2$ and where the Ln^i respectively symbolize one of the lanthanide ions comprised between La and Tm (except Pm) or Y. The second family contains coordination polymers with general chemical formula $[Ln_2(bdc)_3(H_2O)_8.2H_2O]_\infty$ with Ln = Yb-Lu [2]. Considering the high stability of the first structural type we have tempted the synthesis of hetero-bi-nuclear compounds involving simultaneously one lanthanide ion comprises between La and Tm and one Yb(III) ion. The obtained compounds with general chemical formula $[(Yb_{2x}Ln_{2-2x})(bdc)_3(H_2O)_n.mH_2O]_\infty$ with $0 \leq x \leq 1$ have been structurally characterized by X-ray diffraction. The results of this structural study are reported here. They clearly show that it is possible to obtain hetero-di-nuclear compounds belonging either to the first structural type, either to the second one depending on the relative ratio of both lanthanide ions. As an illustration the hetero-pentadeca-nuclear coordination polymer involving all the fifteen lanthanide ions in equal proportions is synthesized and structurally described.



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Non-covalent d-block containing cryptates for encapsulation of labile trivalent lanthanides

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Keywords: Lanthanides; Helicates; Heterobimetallic complexes; Energy transfer

The stoichiometric mixing of the segmental ligand L (3eq) with $Ln(CF_3SO_3)_3$ (1eq) and $Cr(CF_3SO_3)_2$ (2 eq) followed by oxidation provides the bimetallic inert cryptate *HHH*-$[CrLnCrL_3]^{9+}$ (Ln=La-Lu).[1] The X-ray crystal structure of $[CrEuCrL_3]^{9+}$ confirms the formation of a trinuclear triple helix, in which the metals are regularly spaced by c.a. 9 Å, while NMR data collected on the analogous complex $[ZnEuZnL_3]^{9+}$ indicates that the wrapped structure is maintained in acetonitrile. Photophysical data demonstrate the operation of intramolecular intermetallic $Ln^{III}\leftrightarrow Cr^{III}$ energy transfer whose magnitude and direction can be tuned by a judicious choice of the central lanthanide cation. Reaction of $[CrEuCrL_3]^{9+}$ with strong donor for trivalent lanthanides (water, DMSO, DMF, fluoride) selectively produces the kinetically inert receptor *HHH*-$[Cr_2L_3]^{9+}$, which is highly preorganized for further lanthanide re-complexation.

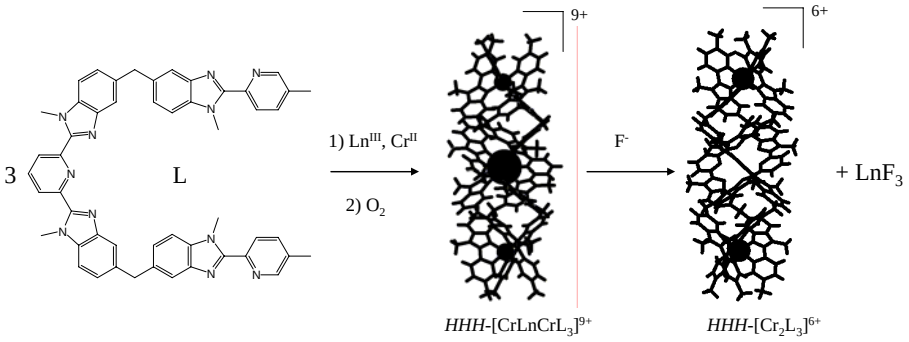

Figure 1. Self-assembly with post-modification of *HHH*-$[CrLnCrL_3]^{9+}$ followed by selective decomplexation of the central lanthanide.

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Some Insight into Physicochemical Properties of Lanthanide Carbonate Complexes

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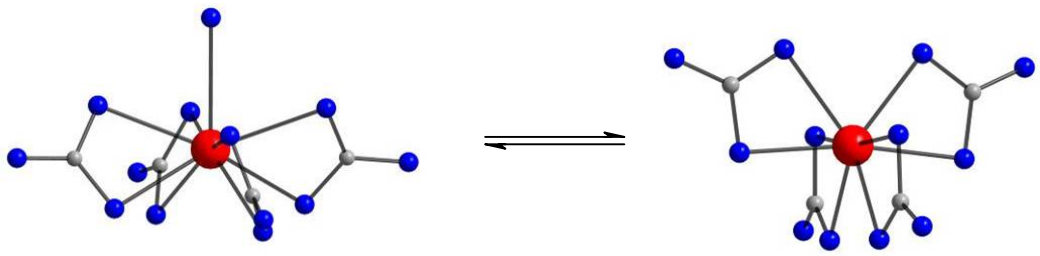
Keywords: Lanthanides; Carbonate; Structure; Spectroscopy

Majority of lanthanide carbonates have been studied using X–ray diffraction of powders [1,2]. They were synthesized hydrothermally and molecules of the complexes formed polymeric chains. Our studies have been focused on the synthesis of crystalline monomeric complexes of the formula $[Ln(CO_3)_4(H_2O)]^{5-}$ (where Ln^{3+} = Nd [3], Eu) and $[Yb(CO_3)_4]^{5-}$, which were obtained by slow evaporation of aqueous solutions.

The Nd and Eu crystals are isomorphous and the lanthanide ion is nine-coordinate, whereas in the Yb^{3+} complex the metal ion is eight-coordinate. In all three complexes the carbonate anions are bidendate. The change of Ln^{3+} ion coordination number, connected with elimination of a water molecule, is accompanied by significant rearrangement of carbonate anions as shown below.



Spectroscopic properties of these compounds (monocrystals and aqueous solutions) have been also determined and discussed.

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Selective Separation of Lanthanides: Receptors based on Azacrowns with Picolinate Pendants

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Keywords: Lanthanide; Selectivity; Coordination; Structure

The design of systems that can selectively recognize a given Ln(III) íon, or at least a particular group of them, remains a challenging task for coordination chemistry. The stability trends for Ln(III) complexes in aqueous solution usually fall within one of the following categories: (i) in the most common case, the stability constants increase form La(III) to Lu(III) due to the increase of charge density of the metal íons; (ii) the stability increases across the series, reaches a plateau and then declines; and, (iii) only with a very few ligands, the stability decreases along the lanthanide series. However, independently of the stability trend, most of ligands provide limited discirmination along this series, except for a few cases where an important selectivity was found for the hevier lanthanides.[1] Within this field, we have decided to exploit the favorable coordination properties toward the Ln(III) íons of the picolinate groups, together with the selectivity that the crown derivatives show for large metal íons, to design new ligands with potential application in the Ln(III) separation technologies. Thus, herein we report the coordination properties of the receptors *N,N'*-bis[(6-carboxy-2-pyridyl)methyl]-1,7-diaza-12-crown-4 (**L**^{1}), *N,N'*-bis[(6-carboxy-2-pyridyl)methyl]-1,10-diaza-15-crown-5 (**L**^{2}), *N,N'*-bis[(6-carboxy-2-pyridyl)methyl]-4,13-diaza-18-crown-6 (**L**^{3}) towards the Ln(III) series based on potentiometric studies, ^{1}H and ^{13}C NMR spectroscopy, single crystal X-ray diffraction, and theoretical calculations peformed at the DF (B3LYP) level.

The stability of the complexes of **L**^{1} falls within the category (ii), as the stability increases along the series, reaches a maximum and then smoothly declines and no selectivity has been observed. However, we have found that the stability of the Ln(III) complexes with **L**^{3} follows the less common trend (iii): the stability decreases along the lanthanide series (Figure 1), and our potentiometric measurements evidence an unprecedented selectivity of the receptor **L**^{3} derived from the largest crown, 4,13-diaza-18-crown-6, for the large Ln(III) ions. Among the different Ln(III) ions, La(III) and Ce(III) show the highest logK_{ML}3 values, with a dramatic drop of the stability observed from Ce(III) to Lu(III) as the ionic radius of the Ln(III) ions decreases (logK_{CeL}3 – logK_{LuL}3 = 6.9). The selectivity that our receptor **L**^{3} shows for the large Ln(III) ions can be attributed to the better fit between the light Ln(III) ions and the relatively large crown fragment of the ligand. Indeed, our DFT calculations indicate that the interaction between the Ln(III) ion and several donor atoms of the crown moiety is weakened as the ionic radius of the metal ion decreases.

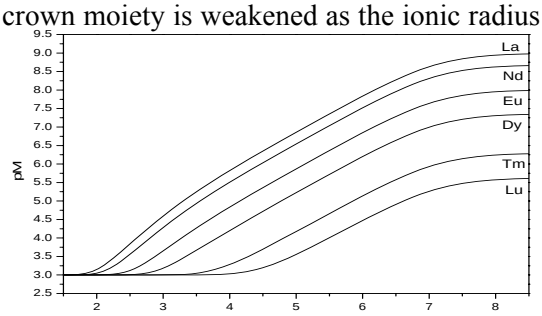

Figure 1. pM = -Log[Ln(III)]$_{free}$ as a function of pH calculated in aqueous 0.1M KCl at 298K with [**L**^{3}]$_0$ = 10^{-3}M and [Ln(III)]$_0$ = 10^{-3}M.

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Exploiting the consequences of effective concentration for designing novel neutral binuclear lanthanide triple-helices

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Keywords: Lanthanides; Coordination; Materials

The development of new hybrid functional materials according to a chemical strategy, often referred to as the "bottom-up" approach, uses the bond making tools of the chemists for producing increasingly more complex molecules, starting from atoms or elementary molecular units. Thanks to the impressive progresses gained during the last decade in supramolecular chemistry, high complexity in bulk material is currently obtained via the thermodynamically-driven self-organization of sophisticated building blocks. The combination of the specificities of each partners, organic and inorganic, produces unprecedented and innovative properties. In this context, tridentate ligand LAH_2 (Figure 1a) containing 8-hydroxyquinoline was synthesized. Its complexation behaviour with Ln(III) ions was studied in both solution and solid state, revealing the formation of neutral $[Ln_2(LA)_3]$ cylindrical helical architectures (Figure 1a) [1]. Those complexes are particularly interesting because they can potentially be converted into calamitic metal-containing liquid crystalline materials by adequate substitutions of the axial positions. This point is a crucial advantage compared to the well-known carboxylate $[Ln_2(LB)_3]$ helical complexes which have no possible axial extensions [2] (Figure 1b).

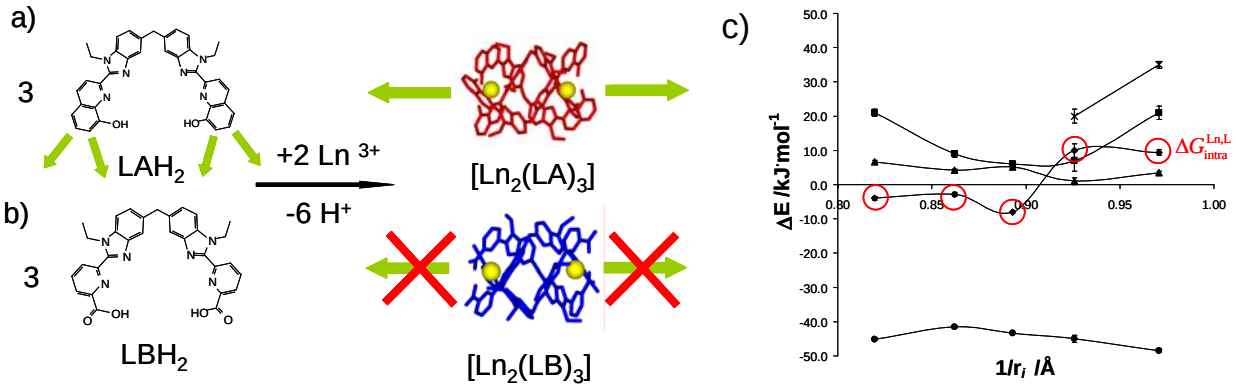

Figure 1. a) New LAH_2 ligand and related $[Ln_2(LA)_3]$ complexes. b) LBH_2 Ligand and related $[Ln_2(LA)_3]$ complexes. c) Thermodynamic data gained from the thermodynamic model.

The solution behaviour of this novel family of complexes was quantitatively analyzed with a simple thermodynamic model [3,4], revealing the importance of the effective concentration ($\Delta G_{intra}^{Ln,L}$) (Figure 1c), which controls the intramolecular ring-closing reactions. This key parameter is a measure of the receptor preorganization, and it allows us to explain the higher stability constants of $[Ln_2(LA)_3]$ complexes with larger lanthanides.

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A Ten-Coordinated La^{III} Complex obtained from benzene-1,2,4,5-tetracarboxylic Acid and 4,4'-bipyridine; Hydrothermal Synthesis and Crystal Structure

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Keywords: Lanthanides; Chemistry; Coordination (incl. Supramolecular); Hydrothermal Synthesis

Rare earth coordination complexes possess a wide range of interesting connectivities and topologies due in no small part to the relatively unpredictable coordination geometries of the 4f series and different potential applications [1–3]. The large ionic radii of rare earth elements allow for many interactions, typically between 7 and 10 coordinate, with a decrease often observed across the period due to the lanthanide contraction.

Here we report the synthesis, characterization and crystal structure of the $\{(bpyH_2)[La(btc)(H_2O)_4(NO_3)] \cdot 2H_2O\}_n$ complex, obtained from the reaction of Lanthanum(III) nitrate hexahydrate with the benzene-1,2,4,5-tetracarboxylic acid ($btcH_4$) and 4,4′-bipyridine (bpy) in 1:1:1 molar ratio in basic media under hydrothermal condition. Polymeric complex was characterized by FT-IR spectroscopy, elemental analysis and X-ray diffraction. X-ray crystal structural analysis reveals that the compound belongs to the monoclinic space group *C*2/*c* with cell parameters a = 14.2806(7) Å, b = 11.0258(5) Å, c = 16.0333(8) Å and β = 101.9400(10)°. Each metal is connected to two neighboring ones, through four μ_2-oxo bridges, to form infinite metal–metal chain running in a zigzag fashion along the c crystal axis, Fig. 1. The La^{III} atom is ten coordinated in a distorted tetracapped trigonal prism. In the crystal structure, a wide range of noncovalent interactions consisting of hydrogen bonding (of the types of O–H···O, N–H···O and C–H···O) and ion pairing interactions connect the various components into a supramolecular structure.

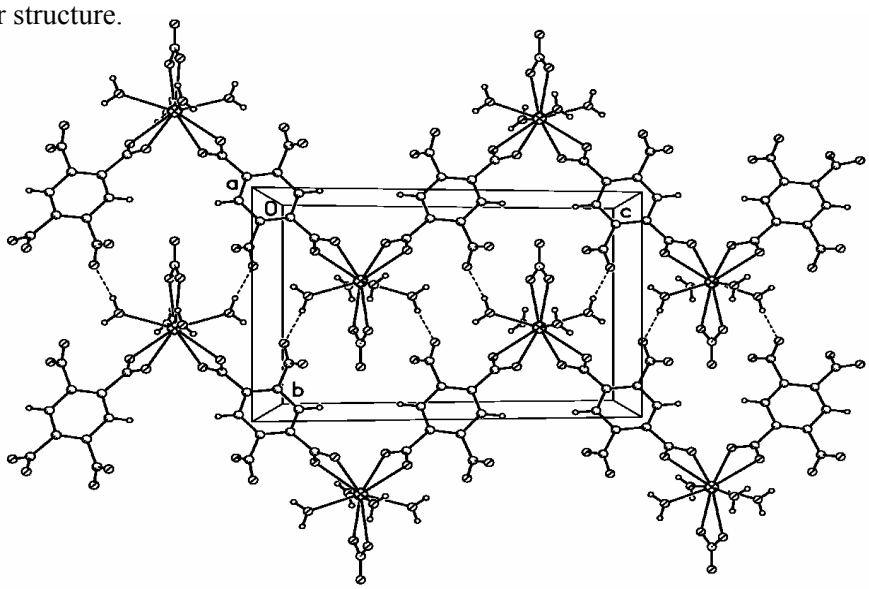

Figure 1 Anionic layer (parallel to (0 1 1) crystal plane) which formed by H-bonded chains (the 4,4′-bipyridinium ions have been omitted for clarity).

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Hydrothermal Synthesis and Structural Studies of a new Co-crystal of a Cerium(III) complex and 2,2′-bipyridine

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Keywords: Synthesise, Lanthanides, crystal structure, coordination

In the few past years, lanthanide chemistry has attached great interesting for the various molecular structures with different potential applications. Lanthanide compounds posses potential properties in magnetic, optic and luminescent but also they generate diversities of structures by selecting bridging ligands. A lot of work have been done to direct synthesize of target structure and to impart desired properties to lanthanide chelates [1].

Hydrothermal synthesis refers to the synthesis by chemical reaction of substances in a sealed heated solution above ambient temperature and pressure. This technique provides a powerful tool for the construction of materials containing unique structures and special properties [2].

In continuation of our research on hydrothermal synthesis of transition metals complexes with polycarboxylate ligands [3] in the present work, we report the hydrothermal synthesis of a new complex of Ce(III) with bridged carboxylate groups, formulated as, $\{[Ce_2(pydc)_2(NO_3)(H_2O)_9]_2[Ce_2(pydc)_4(H_2O)_4]$. (byp). $4H_2O$ (fig. 1), (pydc = pyridine-2,6-dicarboxylat, bpy = 2,2′-bipyridine). Complex was characterized by FT-IR spectra, elemental analysis and X-ray diffraction. X-ray crystal structural analysis reveals that the compound belongs to the triclinic space group *P-1* with cell parameters a = 12.7966(6), b = 13.3615(7), c = 15.9559(8) Å, α = 101.090(2)˚, β = 113.247(1)˚ and γ = 100.783(1)˚. The compound is contained of two cationic and an anionic binuclear Ce^{III} complex. The crystal structure of cationic moiety, $[Ce_2(pydc)_2(NO_3)(H_2O)_9]^+$, contains two types of Ce centers. Ce1 and Ce2 are linked by one O atom from bridged pyridine-2,6-dicarboxylat. The molecular structure of the anionic moiety shows a binuclear complex in which the two central atoms are connected together *via* a four-membered ring Ce2O2. This connecting ring is formed by two $(pydc)^{2-}$ fragments which act as bridge ligands. A coordination number of nine is observed for the central atoms in cationic and anionic complex. An interesting feature of the crystal structure is 2,2′-bipyridine as a co-crystal.

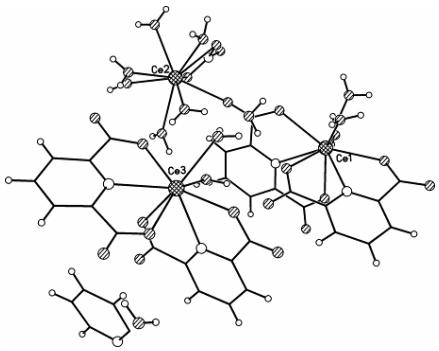

Figure 1. Symmetrically independent part of unit cell

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Helicates: Triple-stranded Dinuclear Complexes of Rare Earth Metals

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Keywords: Lanthanides; Chemistry; Coordination; Structure; Helicate

Helicates as structural motives are of peculiar interest in the field of supramolecular chemistry and can be obtained by coordination of two or more ligands to at least two metal centres. The influence of polydentate ligands based on 8-hydroxyquinoline on the luminescent behavior of lanthanides was impressively described in former publications. Starting from those perceptions we want to extend the family of ligands and investigate the energy transfer systematically.

Starting from 8-hydroxyquinoline-2-carbonitrile, 2-(benzoxazole-2-yl)-quinoline-8-ol **1** was synthesised in two reaction steps. Complexation studies of the tridentate building block **1** with different lanthanide ions (La^{3+}, Pr^{3+}, Nd^{3+}, Er^{3+}, Yb^{3+}) resulted in triple-stranded helicate-type complexes [(**1**)$_3$Ln]. X-Ray quality crystals of the Nd(III)-complex **2** were obtained from DMF. Our final goal was the preparation of triple-stranded dinuclear lanthanide helicates. Therefore **1** was coupled twice to an isobutenylidene unit followed by rearrangemet yielding the hexadentate ligand **3**. The helicates [(**3**)$_3$Ln$_2$] **4** were formed by complexation with the lanthanide ions mentioned before. Recently 2-(oxazole-2-yl)-quinoline-8-ol **5** and 2-(oxazine-2-yl)-quinoline-8-ol **6** are obtained as new building blocks.

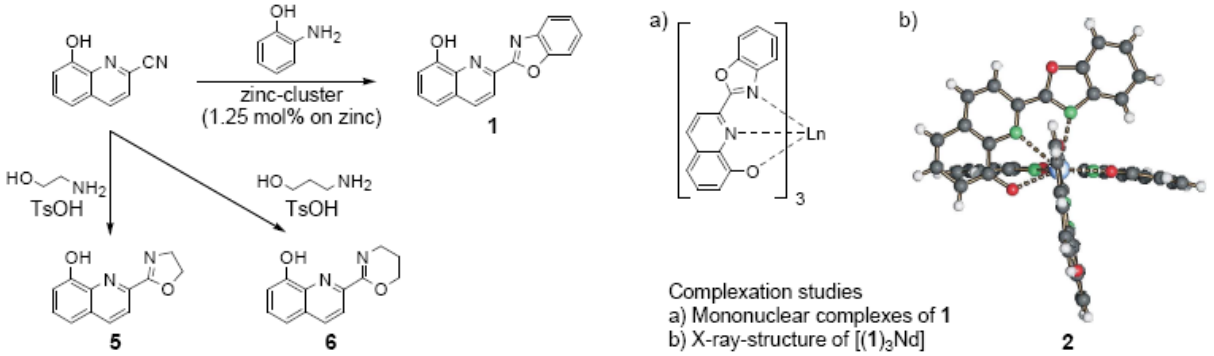

Figure 1. Tridentate building blocks

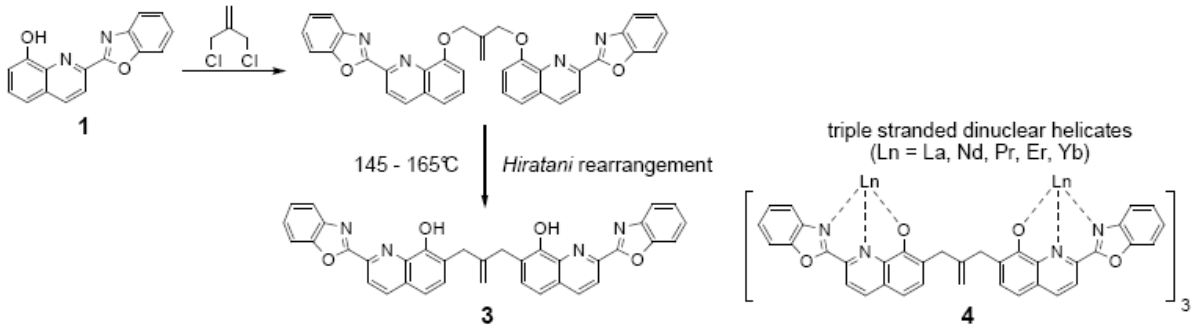

Figure 2. Hexadentate ligands

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Investigation of lanthanide (III) coordination compounds with 4-pentenoic and 3-butenoic acids

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Keywords: Spectroscopy; Lanthanide; Carboxylates

The presented investigations confirm application of the spectroscopic studies as an useful way to consider the Ln – L bond nature. The parameters determined on the basis of absorption spectra and their variation point out the changes in polarity and strength Ln – L bond, what qualifies the lanthanide carboxylates as precursors of catalysts.

A new type of coordination compounds of formula $Ln(C_5H_7O_2)$. 2 H_2O (where Ln = Pr, Nd, Eu; $C_5H_7O_2$ = 4-pentenoic anion (I)) and $Ln(C_4H_5O_2)$. 2 H_2O (where Ln = Pr, Nd, Eu, Ho, Er; $C_4H_5O_2$ = 3-butenoic anion (II)) were obtained in the aqueous solutions and as crystals.

The surrounding of Ln^{3+} ions both in the solution and in the crystal was characterized by UV-Vis electronic spectroscopy at room and low temperatures. The parameter values determined on the basis of these spectra (eg. the nephelauxetic ratio β, $R = I_{vib.}/I_{0\text{-}phonon}$ rates as quantity of vibronic coupling and others) and their variations were analysed. The correlation between the vibronic coupling and covalency is discussed. In the lanthanide series from La^{3+} to Lu^{3+} the ionic contributions to the metal – ligand bond increase less than the covalent ones and depend on the metal atomic number. This dependence is not linear. We observed the minimum for europium compounds. The relation between hypersensitivity and covalency is also discussed.

Heterobimetallic $[Zn(\mu–MO1)(\mu_2–CF_3COO)Ln(hfa)_2]$ (Ln = La^{III}, Nd^{III}, Sm^{III}–Dy^{III}) complexes: synthesis, structure and photophysical properties

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Keywords: Lanthanides; Coordination chemistry; Structure; Luminescence; heterometallic

Zinc complexes with Schiff bases are adequate sensitizers of lanthanide luminescence in both the visible and near-infrared (NIR) ranges [1, 2]. This work presents a series of Zn^{II}–Ln^{III} heterobimetallic complexes with general formula $[Zn(\mu–MO1)(\mu_2–CF_3COO)Ln(hfa)_2]$ (Ln = La, Nd, Sm–Dy, Yb). According to X-ray single crystal analysis all complexes are isostructural; the lanthanide ion is 9-coordinated with distorted mono-capped square antiprismatic environment while Zn adopts a square-pyramidal geometry (Fig. 1a).

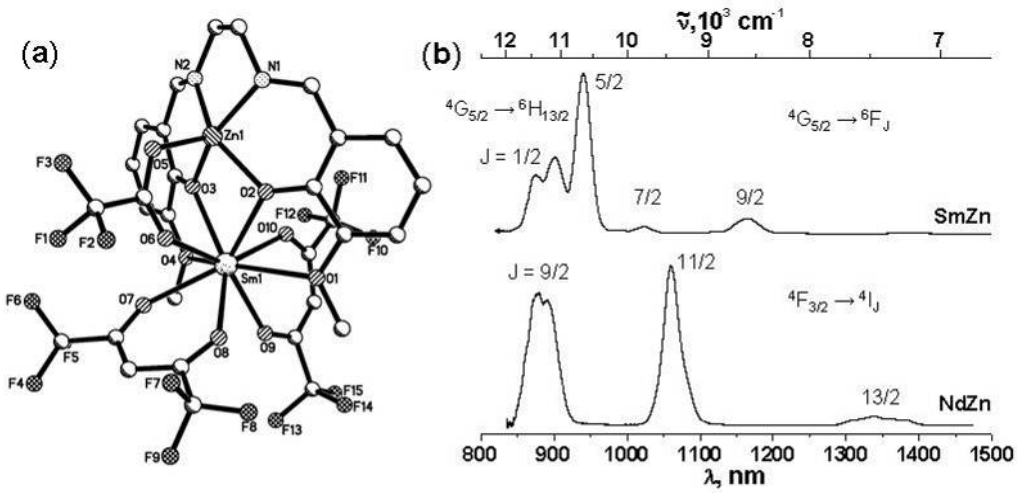

Figure 1. $[Zn(\mu–MO1)(\mu_2–CF_3COO)Ln(hfa)_2]$: (a) crystal structure (Ln = Sm); (b) NIR-sensitized luminescence (Ln = Nd, Sm).

Ligand-centred as well as visible (Ln = Eu^{III}, Tb^{III}) and NIR (Ln = Nd^{III}, Sm^{III}, Yb^{III}) sensitized luminescent properties (spectra, lifetimes, and absolute quantum yields) of the Zn^{II}-Ln^{III} complexes are investigated in detail and compared with the parent $ZnMO1·H_2O$ and $Ln(hfa)_3·2H_2O$ complexes.

This work is supported by Russian Foundation of Basic Research (grant № 09-03-00850-a).

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3d/4f Heterometallic and polycarbonatolanthanoid complexes

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Keywords: Lanthanides; Chemistry; Coordination (incl. Supramolecular); Synthesis

The pseudohalide ligand dicyanonitrosomethanide (dcnm) may undergo nulceophilic addition to a nitrile group,[1,2] resulting in a class of ligands which offers diverse coordination chemistry, providing access to novel 3d/4f heterometallic clusters and high nuclearity lanthanoid clusters.

The nitroso functional group allows for an unusual symmetrical η^2 bonding mode to lanthanoids, forming the complexes $[R_4N]_3[Ln(dcnm/ccnm)_6]$ (R = Me, Et; Ln = La – Gd; ccnm = carbamoylcyanonitrosomethanide).[3] Through the introduction of co-ligands such as 18-crown-6 and 1,10-phenanthroline or by the presence of intramolecular hydrogen bonding the symmetry of the nitroso bond may be influenced.

The transition metal promoted *in situ* ligand synthesis is observed in the formation of heterometallic clusters such as the trinuclear complex $[Me_4N][\{TM(cmnm)_3\}_2RE(cmnm)_2]$ (TM = Ni, Fe; RE = La – Gd, cmnm = cyano(imino(methoxy)methyl)nitrosomethanide. Alternative reaction conditions yields the complex $[Ln_2Mn^{III}{}_2O_2(ccnm)_6(dcnm)_2(H_2O)_2]$ (Ln = Gd, Tb, Er) which has a butterfly core geometry infrequently observed in 3d/4f complexes.

"Lanthaballs", $[Ln_{13}(1,10\text{-phenanthroline})_{18}(ccnm)_6(CO_3)_{14}(H_2O)_6]^{5+}$ (Ln = La - Nd) (Figure 1), are the highest nuclearity polycarbanatolanthanoid species known to date and contain a unprecedented $[Ln_{13}(CO_3)_6]$ core. Their synthesis demonstrates the utility of carbonate in forming clusters with novel core geometries and increasing nuclearities.

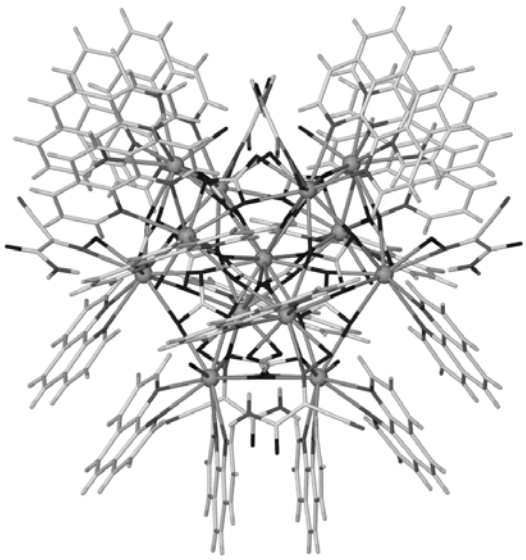

Figure 1. The "lanthaball" complex

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Molecular Solid State Synthesis of Ionic Coordination Polymers by Synthetic Rare Earth Crystal Engineering

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Keywords: Lanthanides; Chemistry; Coordination; Crystal Engineering

Rare earth crystal engineering is a challenging field in chemistry. This is due to the high number of parameters to be considered when developing a synthetic bottom-up approach wherein crystallographic and chemical knowledge in rare earth chemistry is used to design and construct building blocks (tectons). These may then be used to prepare new materials in a controlled manner with specific optical or magnetic properties.[1,2]

In this work, penta-anionic tetraoxalato lanthanide complexes were used to obtain new crystalline ionic lanthanide-organic coordination polymers. The compounds were conveniently synthesized by grinding and kneading methods and their structures, luminescence, and magnetic properties have been characterized.

Using this approach we combined anionic Ln-containing building blocks $[Ln(C_2O_4)_4]^{5-}$ (Ln = Ce, Eu, Gd, Dy, Ho, Yb [3]) with various organic linker cations such as EDTA, aza-crown ethers, and melamine. In these species the lanthanide ion has nearly regular cubic antiprismatic coordination geometry (**Fig. 1**), which makes this new class of lanthanide coordination polymers interesting for applications in materials science.

By the formation of hydrogen bonded salts of these complex anions with melamine, compounds with interesting structural and optical properties have been discovered. Europium compounds show strong luminescence properties with unusually long life times.

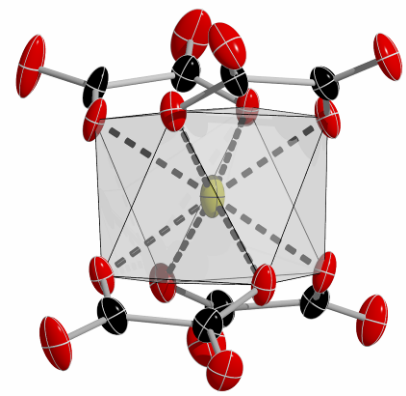

Figure 1. Molecular structure of $[Ln(C_2O_4)_4]^{5-}$ used as a building block for coordination salts.

Due to the low solubility in water of both the lanthanide complex and the organic tectons, crystallization of the products proved problematic. Whereas the ytterbium containing complex $[Hmel]_6[Yb(C_2O_4)_4][NO_3]\cdot(H_2O)_{3\text{-}4}$ (mel = melamine) [3] was synthesized by refluxing the aqueous reaction mixture under harsh conditions for several days, the analogous Ln compounds (Ln = Ce, Eu, Gd, Dy, Ho) have been synthesized for the first time by simple ball milling of the reagents with only catalytic amounts of water. Repeating this procedure three times resulted in X-ray pure products.

Protonated melamine and pentaaza-5-crown-15 were used as organic tectons, which allowed us to engineer crystals consisting of a layered and cross-linked coordination salt structure. The chelating oxalate ligands act as hydrogen bond acceptors linking the protonated tectons while simultaneously saturating the coordination sphere of the lanthanide ion.

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Engineering of peptides for the complexation of Ln(III) ions

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Keywords: Lanthanides, Chemistry, Coordination, Peptides

Biocompatible chelators for lanthanide(III) ions (Ln^{3+}) are of interest as magnetic resonance imaging agents (Gd^{3+})[1] or luminescent probes for biology.[2] As peptides are hydrophilic scaffolds adapted to the biological environment, recent efforts by our laboratory [3a] and others[3b] aimed at the development of efficient Ln-binding peptides. However, stability constants in physiological conditions of Ln^{3+} complexes with peptides containing only natural amino acids (coordination through mono- or bidentate carboxylates) are insufficient for *in vivo* applications.

In order to improve the stability of the complexes, we designed $\mathbf{P^n}$ peptides including unnatural chelating amino acids with aminodiacetate side-chains. The latter groups were linked to the peptide scaffold through alkyl spacers of variable length n. These unnatural amino acids are abbreviated Ada_n with n = 1, 2, 3 carbons. The Ln^{3+} complexes of the first model hexadentate ligands obtained by this strategy were studied by luminescence, circular dichroism, mass spectrometry and structural NMR. In the best case (n = 2), the exclusive formation of a monometallic complex is observed and this complex is more stable in aqueous solution at pH 7 than optimized complexes with peptides containing only natural amino acids.[3b] Indeed, the peptide backbone behaves as a non-innocent spacer between coordinating groups. A synergy may exist between metal coordination and the establishment of secondary structure elements in the lanthanide-peptide complex, which enhances the complex stability.[4]

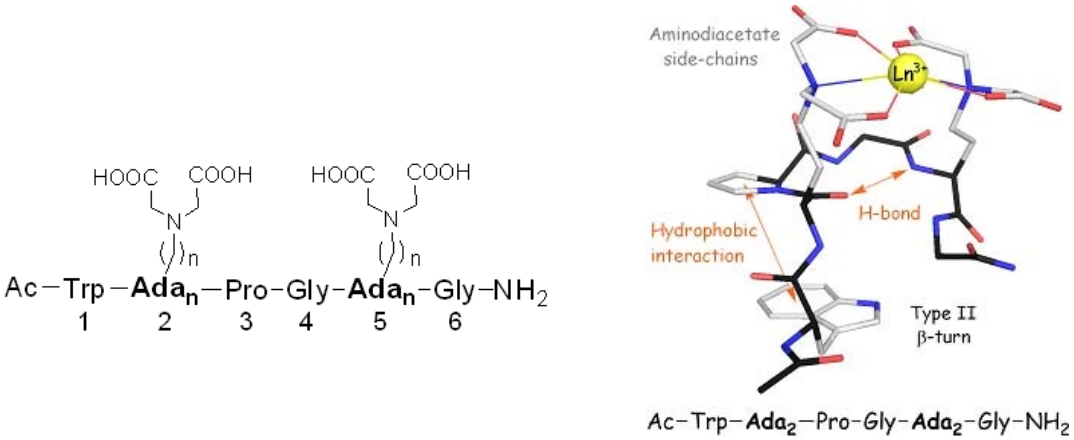

Figure 1. Sequence of the $\mathbf{P^n}$ peptides and solution NMR structure of the La$\mathbf{P^2}$ complex.

These results may be utilized for the design of higher denticity peptides interesting for the above-mentioned biological applications. Research in this direction is currently undergoing in our laboratory.

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The Solvent Free Melt Synthesis – A Way to Generate Highly Aggregated Systems with Promising Properties

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Keywords: Lanthanides; Hybrid Materials; Ln-N-Coordination Chemistry; Metal Organic Frameworks (MOFs)

Beside cyclopentadienyl and complexes with oxygen containing ligands amides form another pillar of rare earth metal coordination chemistry [1]. Solvent containing reaction routes dominate all fields thereof. Many compounds which were synthesized in this manner are solvates and are therefore heteroleptic unless the ligands are multi-chelating. Furthermore the co-coordination of solvent molecules mostly leads to small molecular units, such as monomers, dimers or oligomers. In order to avoid both facts we successfully elaborated a solvent free melt synthesis within DFG SPP-1166 including crystallization under the melt conditions. Self-consuming amine melts oxidize rare earth metals at rather high temperatures concerning the ligands combined with an activation of the metals by catalytic amounts of mercury, micro waves or ammonia, yielding homoleptic amides [2].

Depending on the organic ligands, in particular on the number and positions of N atoms within an aromatic heterocycle, the dimensionality of the resulting rare earth amides can be influenced. N-donor ligands that contain only one N atom are exclusively able to link the metal atoms by forming additional π-interactions. Multi-N-ligands that contain N atoms on opposite sides of the ring are able to link the metal centres by more stable μ-bridging σ-coordination modes [3]. Accordingly, two-, or three-dimensional framework structures are accessible. Cavities in these structures can be tuned by variation of the rare earth metals or the extension of the organic ligands [4] (Fig 1). Compared to O-donor linked frameworks Ln-N-MOFs have significantly higher thermal stabilities, up to 650°C. In addition, luminescence properties [3] render some of these compounds attractive as phosphors and for sensoring.

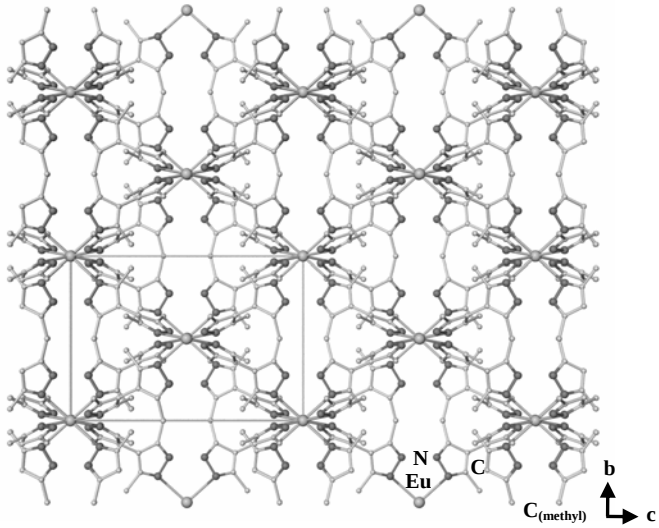

Figure 1. Crystal structure of $^{3}_{\infty}[Eu(Me_4BpzH)_3(Me_4BpzH_2)]$, Me_4BpzH^- = tetramethylbipyrazolate anion, Me_4BpzH_2 = tetramethylbipyrazole, as an example of a Ln-N-MOF with a view along [100]. Eu atoms are depicted as large grey balls, N atoms as dark, C atoms as light grey balls. H atoms are omitted for clarity.

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New isotypic rare earth–silver 2D coordination polymers $Ag_2SE(Aba)_4(NO_3)_5$

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Keywords: lanthanides, coordination, 4-aminobenzamide, silver

Ligands containing O-donor atoms, such as 4-amino-benzamide, easily connect to rare earth ions while ligands containing N-donor atoms easily connect to soft transition metal ions like the Ag(I) ion. In the current research 4-aminobenzamide (Aba) was chosen with both O and N donor atoms to link rare earth and silver ions. As expected, the amino group connects to silver ions, while the carbonyl group connects to rare earth ions.

For $Ag_2SE(Aba)_4(NO_3)_5$ 4-aminobenzamide, $SE(NO_3)_3(H_2O)_x$ and $AgNO_3$ in a 1:1:1 ratio were dissolved in 80 ml of ethanol. Polyhedral crystals grew by slow evaporation of the solvent at ambient temperature. In all cases the crystal structures were determined from complete X-ray diffraction data sets. $Ag_2SE(Aba)_4(NO_3)_5$ crystallize in the monoclinic space group C2/c (no. 15). Crystal data are listed in Table 1.

The SE(III) ions are coordinated by four carbonyl groups of four 4-aminobenzamide ligands and four oxygen atoms of two nitrate ions (Figure 1). The SE-O bond lengths are in the expected range [La = 243.9(4)-274.47(4) pm, Ce = 241.4(8)-267.7(4)pm , Nd = 237.49(5)-269.47(4), Gd = 232.42(4)-268.55(3)]. Because the ionic radii decrease from La(III) to Gd(III), the SE-O bond lengths decrease in this way, too. These SE-coordination units are linked via Ag(I) ions. Each Ag(I) ion is coordinated linearly via two amino groups from two Aba ligands [Ag-N [pm]: La = 217.6(4)/218.2(4), Ce = 216.9(8)/218.5(8), Nd = 217.8(6)/218.0(6), Gd = 216.78(2)/217.07(2)]. These are typical bond lengths for linearly coordinated Ag(I) ions. These compounds present a two-dimensional network based on the SE coordination units linked via Ag(I) ions.

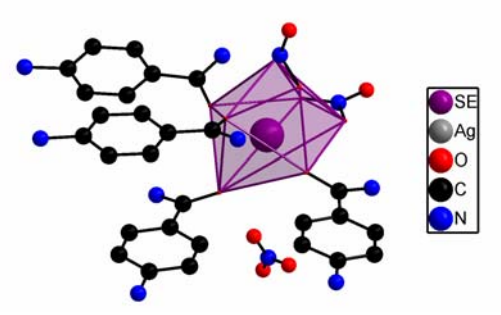

Figure 1. Coordination sphere of SE(III).

	SE=La	SE=Ce	SE=Nd	SE=Gd
a [pm]	1860.9(3)	1868.1(2)	1855.6(3)	1842.1(2)
b [pm]	1389.2(2)	1386.6(2)	1385.4(3)	1381.5(2)
c [pm]	1630.7(2)	1627.4(2)	1624.7(2)	1619.7(2)
ß [°]	101.95(1)	101.89(1)	102.42(2)	102.75(2)
Z	4	4	4	4
V [10^6pm^3]	4124.3(9)	4124.8(8)	4079(1)	4020.1(8)
R_1	0.0403/	0.0639/	0.0552/	0.0502/
	0.0578	0.087	0.0788	0.0726
wR_2	0.1018/	0.1531/	0.1406/	0.1239/
	0.1079	0.1695	0.1516	0.131
Goof	1.014	1.054	0.969	1.027

Table 1. Crystal data of $Ag_2SE(Aba)_4(NO_3)_5$.

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A new anhydrous lanthanide carboxylate: $Tb_2(OPr)_6(HOPr)$

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Keywords: lanthanides, metal-organics, crystal structure, terbium propionate

Only one anhydrous lanthanide propionate, $Nd_2(OPr)_6(HOPr)_2$ [1] has been reported until today. Other propionates contain further ligands or water as in $Pr(OPr)_3(H_2O)_3$ [2] subject to their preparation from metal and carboxylic salts from solution. The non-noble lanthanide metals such as terbium can simply be oxidized directly with a thermally stable carboxylic acid such as propionic acid to yield an anhydrous salt. For $Tb_2(OPr)_6(HOPr)$, terbium and propionic acid in a 1:5 ratio were sealed under vacuum in a glass ampoule and heated to 160°C for one day, cooled to 70°C within 24 hours and held there for three days.

In the crystal structure of $Tb_2(OPr)_6(HOPr)$ [triclinic, P-1, Z = 2, a = 1273.0(3), b = 1303.2(2), c = 2071.1(4) pm, α = 75.68(1)°, β = 74.84(1)°, γ = 68.99(1)°, R1 [I>2σ(I)] = 0.0584] four independent terbium(III) cations are alternately coordinated by eight oxygen atoms of propionate anions (Tb3 and Tb4), or by eight oxygen atoms of propionate anions and one oxygen atom of the additional propionic acid molecule (Tb1 and Tb2). The coordination polymers are linked by one edge and built into curled one-dimensional chains (Figs. 1 and 2). Two of these chains are found in the unit cell (Fig. 1). Because of the shielding of the nonpolar rests of the propionate anions, no connection between the chains is found. Mean Tb-O distances are 243.7(1), 244.0(1), 238.5(1) and 239.4(1) pm, respectively, for the four crystallographically independent Tb sites. Tb-Tb distances range from 396.2(2) to 405.7(2) pm.

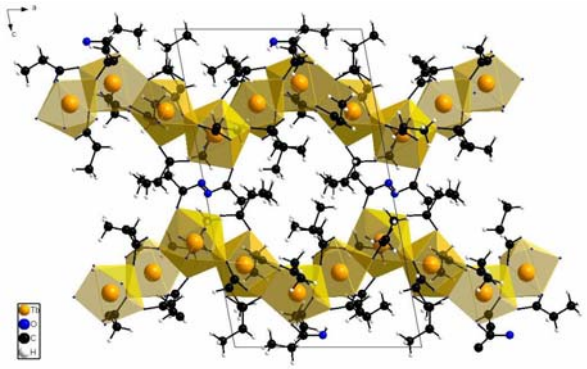

Figure 1. Chains of coordination polymers along [010]

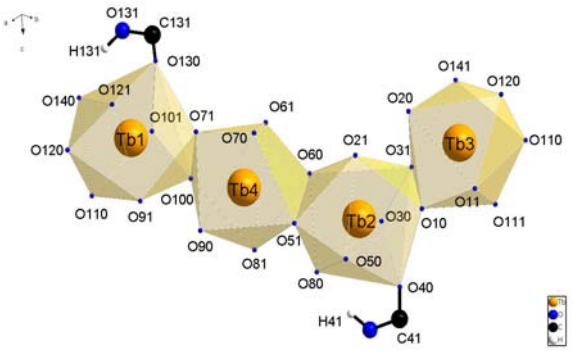

Figure 2. Coordination spheres around Tb1 – Tb4

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Four different polyiodide anions in the crystal structure of $[Lu(db18c6)(H_2O)_3(thf)_6]_4(I_3)_2(I_5)_6(I_8)(I_{12})$

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Keywords: Lanthanides; Polyiodides; Crown ether

One focus of our research in the area of polyhalides is to elucidate the formation of different polyiodide anions by varying shape, charge and size of the corresponding counter cation. Among others the rare earth cations in their trivalent state seem to stabilize higher-order polyiodide anions when these are treated with an excess of iodine.
The especially iodine rich compound $Lu(db18c6)(H_2O)_3(thf)_6I_{14}$ crystallizes in the monoclinic space group $P2_1/c$ (a = 2132.80(8), b = 2871.52(9), c = 2658.64(9) pm, β = 112.792(2), V = 15011.1(9) $10^6 \cdot pm^3$, Z = 8). Each of the two crystallographically independent Lu^{3+}-cations are incorporated in a dibenzo-18-crown-6 molecule and have coordination number 9 through three coordinating water molecules which are attached to two thf molecules each such that the complex cation is $[Lu(db18c6)(H_2O)_3(thf)_6]^{3+}$, see Fig. 1, with d(La-O(crown)) = 234(2)-253(2) pm, d(La-O(H_2O)) = 228(2)-236(2) pm and d(O(H_2O)-O(thf)) = 250(3)-270(3) pm. A coordination number of nine for the rare earth cation with the 18-membered crown ether is typical as the examples of $[Dy_2(db18c6)_2Cl_4][Dy_2(CH_3CN)_2Cl_8]$ [**1**] and $[SmI_3(db18c6)]$ [**2**] may show. In the asymmetric unit there are 28 iodine atoms (Fig. 2). These built one triiodide anion, three pentaiodide anions and one half octaiodide and dodecaiodide anions each such that the complete formula must be written as $[Lu(db18c6)(H_2O)_3(thf)_6]_4(I_3)_2(I_5)_6(I_8)(I_{12})$. These four different polyiodide anions are connected via distances of more than 360 pm to a 3D network that incorporates the complex cations.

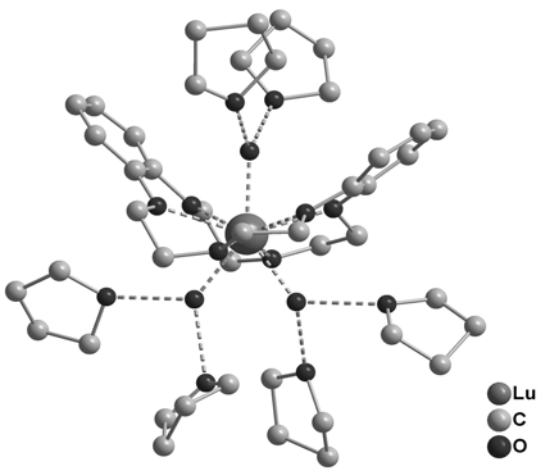

Figure 1. $[Lu(db18c6)(H_2O)_3(thf)_6]^{3+}$ cations.

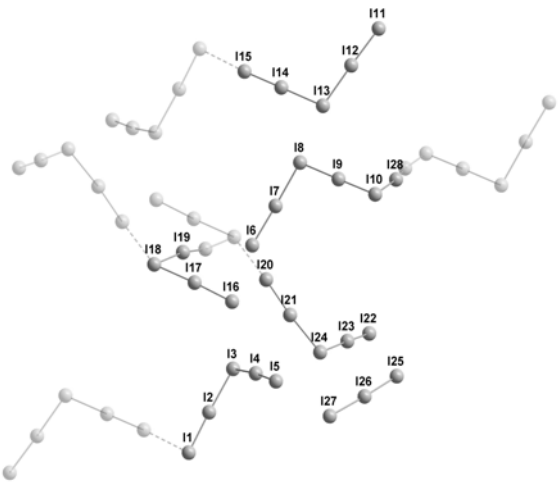

Figure 2. The four different polyiodide anions in the crystal structure of $[Lu(db18c6)(H_2O)_3(thf)_6]_4$-$(I_3)_2(I_5)_6(I_8)(I_{12})$ with their atomic numbering scheme. Atoms that do not belong to the asymmetric unit are drawn transparently.

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Chloride-oxo-arsenates(III) of the lanthanides with zinc and iron

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Keywords: Lanthanides, Arsenites, Chlorides

In order to extend our work on oxo-selenates(IV) of the rare earth elements we recently started to investigate the respective oxo-arsenates(III) [1]. The AsO_3^{3-} ion is isosteric to the SeO_3^{2-} ion but its higher charge should allow for different structural architectures. [1]. As first results we presented the crystal structures of the chloride oxo-arsenates(III) $RE_5(AsO_3)_4Cl_3$ (RE = La, Pr, Nd). The crystal structures of the lanthanum and praseodymium compound isotypic with the previously reported cerium compound [2], the neodymium phase has slightly different symmetry [3]. Now we have successfully prepared the new chloride-oxo-arsenates(III) $RE_3(AsO_3)(As_2O_5)Cl_2$ (RE = Sm, Eu) and the structurally strongly related compounds $RE_2Zn(AsO_3)(As_2O_5)Cl$ (Fig.1) (RE = Dy, Ho) and$RE_2Fe(AsO_3)(As_2O_5)Cl$ (RE = Sm, Gd). They were synthesized from the reactions of the oxides RE_2O_3, As_2O_3, $ZnCl_2$ and $FeCl_2$, respectively. The components were filled into silica tubes under nitrogen atmosphere, torch sealed under vacuum and finally fired at 800 °C in a resistance furnace for three days. Formation of single crystals is enhanced enormously, if an excess of the chlorides is used.

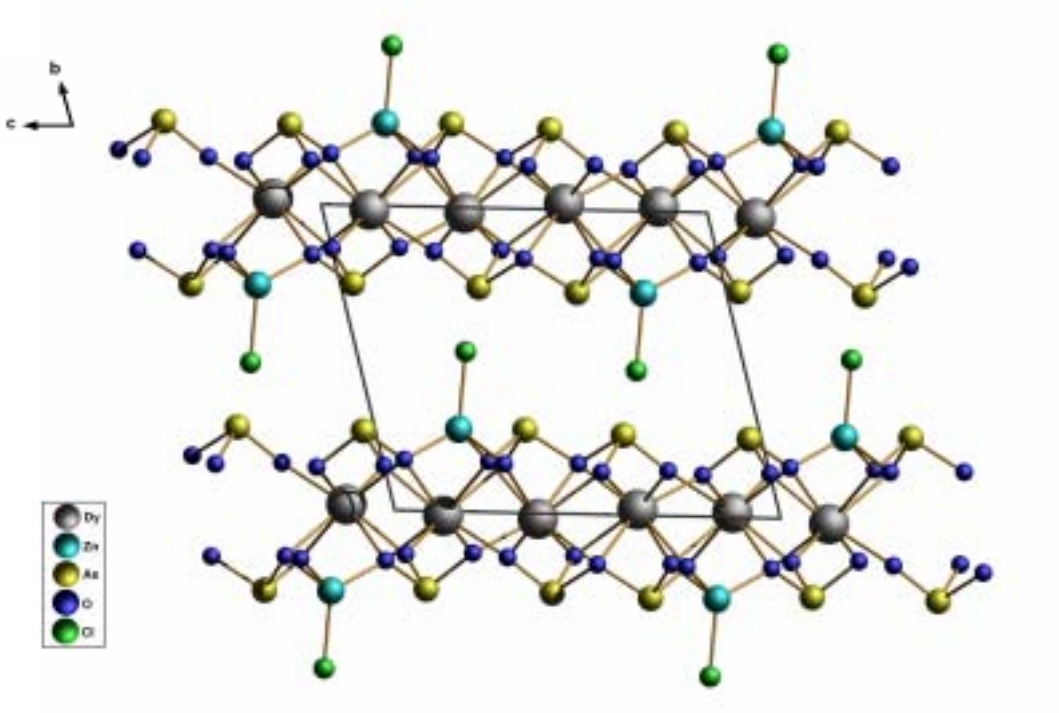

Figure 1. Projection of the crystal structure of $Dy_2Zn(AsO_3)(As_2O_5)Cl$ onto (100).

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In search for tuneable intramolecular intermetallic interactions in polynuclear lanthanide complexes.

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Keywords: Lanthanides; Chemistry; Coordination

The deep understanding of the thermodynamic factors which control self-assembly processes is essential for the rational preparation of polynuclear lanthanide complexes.

In this contribution, we report on the detailed coordination and thermodynamic behaviour of the unsymmetrical tridentate 2-benzimidazolyl-6-carboxamido pyridine binding units in the ligands **L1** et **L2** with neutral $Ln(NO_3)_3$ (Ln is a trivalent lanthanide), which gives mononuclear [Ln(**L1**)$(NO_3)_3$(Solvent)] and binuclear [Ln_2(**L2**)$(NO_3)_6$(Solvent)$_2$] complexes. In the solid state, the bis–tridentate ligand **L2** shows variable helical conformations of its central diphenylmethane spacer in its uncoordinated form and in its complexed form in [Eu_2(**L2**)$(NO_3)_6(H_2O)_2$], which puts the two metals at a contact distance of 8.564(1)Å. In solution, fast rearrangement yield an average planar extended conformation of the spacer , which increases the intramolecular intermetallic contact distance by 30% (≈ 12Å)[1] (Figure 1b).

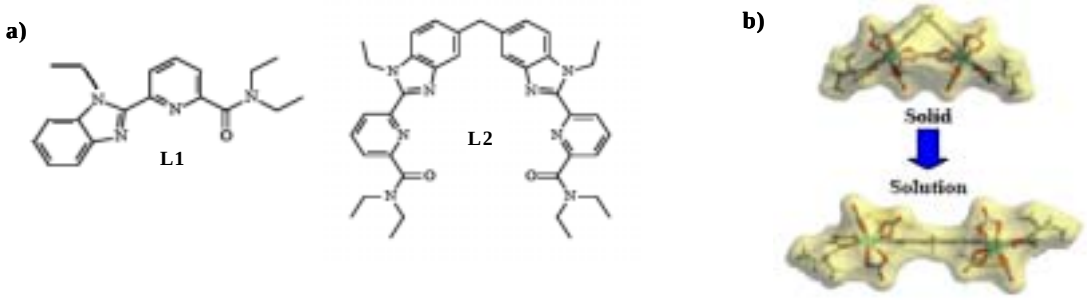

Figure 1. a) Chemical structures of ligands **L1** and **L2**; b) CPK representations of [Eu_2**L2**$(NO_3)_6(H_2O)_2$] in the crystal structure and in solution with distal of the diphenylmethane spacer.

The experimental macroscopic formation constants (log $\beta_{ij}^{Ln,L}$) were rationalized by application of a simple *site-binding* thermodynamic model [2], based on (i) an absolute affinity of the N_2O tridentate binding unit of each ligand for $Ln(NO_3)_3$ ($\Delta G^{Ln,L}$) and (ii) an intramolecular intermetallic interaction operating in the binuclear complexes (ΔE^{LnLn}). Surprisingly, the free energies $\Delta G^{Ln,L}$ and ΔE^{LnLn} in [Ln_2**L2**$(NO_3)_6$] are comparable with those found in the highly charged triple-stranded helicates $[Ln_2(\mathbf{L2})_3]^{6+}$ (Ln··Ln≈9Å) despite (i) the different nature of the entering metalls and (i) the different intramolecular intermetallic contact distance. These results support the current interpretation of intramolecular intermetallic interactions in polynuclear complexes as arising from two opposite contributions of comparable and huge magnitudes, one brought by intramolecular electrostatic interactions and the other associated with macroscopic solvation changes [3]

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Towards the Microscopic Structure of $Na_5Lu_9F_{32}$, a'cubic $NaLuF_4$'

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Keywords: $Na_5Lu_9F_{32}$; sodium rare earth fluoride; structure

Sodium rare earth fluorides presently attract a lot of interest as infrared to visible upconversion phosphors. Their average structures have been investigated already more than 40 years ago [1]. The hexagonal compounds β-$NaYF_4$: Yb, Er and β-$NaYF_4$: Yb, Tm are the best upconversion phosphors hitherto know for green and blue emission, respectively [2]. The microscopic structure of the hexagonal phase was determined from diffuse scattering to provide a basis for explaining the extraordinary optical properties of these materials [3]. After our work on the hexagonal phase we started an effort to determine the microscopic structure of the 'cubic' α-phase.

'Cubic' crystals were grown from a melt of composition 5 NaF + 9 LuF_3 by the Bridgman technique. They were investigated with both laboratory and synchrotron (ESRF) X-rays. Obviously, the diffraction pattern is quite complex, see Fig. 1. The strong reflections belong to a pseudo-cubic CaF_2 type cell with $a_c \approx 5.46$ Å. The weaker superstructure reflections may be indexed assuming a larger orthorhombic unit cell and sixfold twinning. Two orthorhombic axes are located along face diagonals of the cubic cell. The relation of the orthorhombic to the cubic cell is $a \approx 5\sqrt{2}\, a_c$, $b \approx \sqrt{2}\, a_c$, $c \approx a_c$. The orthorhombic super cell becomes obvious from Figure 1 *right*, where twin reflections and diffuse scattering were removed from the upper right quadrant. A detailed structure solution taking into account the orthorhombic cell and the diffuse scattering is currently in progress.

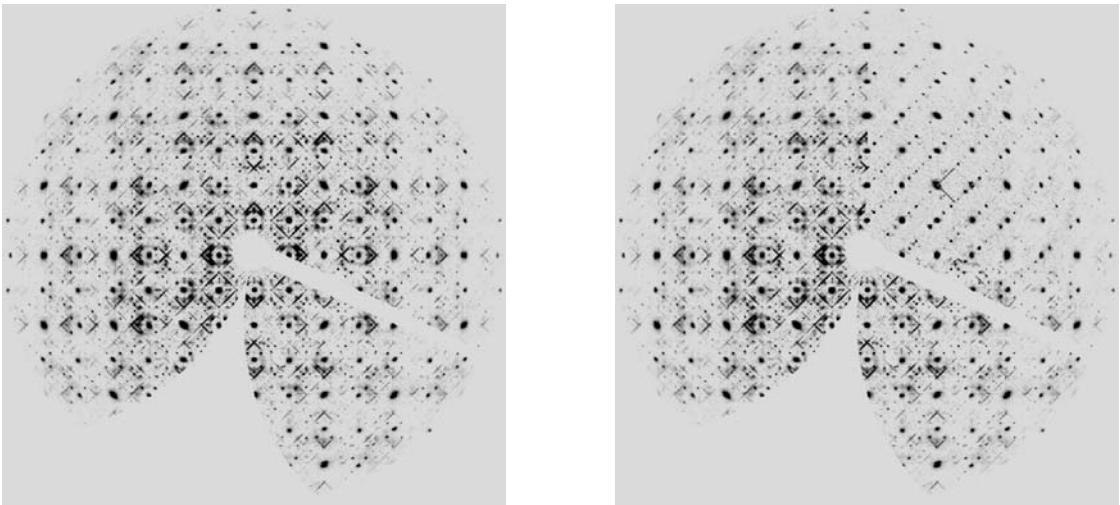

Figure 1. *Left:* Diffraction pattern of the hk0 layer of $Na_5Lu_9F_{32}$ showing the strong CaF_2 type reflections, week superstructure reflections, and diffuse scattering. *Right:* The superstructure becomes obvious after removing the twin reflections and the diffuse scattering from the upper right quadrant.

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Crystal Structure, Vibrational Spectra and Activation of $BaCa(P_4O_{12})$ with Eu^{2+} Compared with β-$Sr(PO_3)_2$:Eu

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Keywords: Lanthanides; Chemistry; Solid State; Spectroscopy

Inorganic solid state compounds with condensed anions doped with rare-earth metal cations like Eu^{2+} are of broad interest for optical applications like white light LEDs or scintillators [1]. We recently reported about the host material α-$Sr(PO_3)_2$ [2] which was then co-doped with Eu^{2+} and Mn^{2+} to give white light under UV excitation [3]. The polyphosphates β-$Sr(PO_3)_2$ and $BaCa(PO_3)_4$ were doped with Eu^{2+}; $BaCa(PO_3)_4$ was structurally characterised for the first time. Both phosphors were analysed by fluorescence spectroscopy. β-$Sr(PO_3)_2$:Eu and $BaCa(PO_3)_4$:Eu were found to emit blue light at 424 nm and 418 nm, respectively, with a broader emission band compared with α-$Sr(PO_3)_2$:Eu. Both phosphors can be excited at 330 nm. The crystal structure of $BaCa(PO_3)_4$ has been determined based on single-crystal data ($P2_1/n$, Z=4, a=723.00(11), b=917.05(19), c=1524.7(2) pm, β=90.995(12)°, $R1$=0.050, $wR2$=0.099, 1748 reflections, 164 parameters). $BaCa(PO_3)_4$ is not homeotypic with β-$Sr(PO_3)_2$ and α-$Sr(PO_3)_2$ but isotypic with $BaCd(PO_3)_4$ [4].

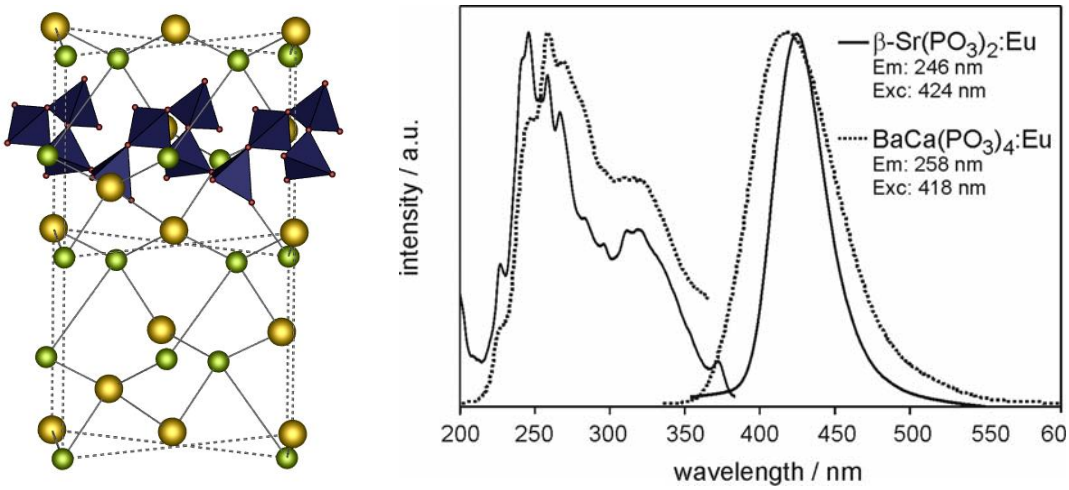

Figure 1. Visualisation of the diamond-like cationic network structure in $BaCa(PO_3)_4$ (left) and the fluorescence emission spectra of $BaCa(PO_3)_4$:Eu and β-$Sr(PO_3)_2$:Eu.

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Phase transitions of the Polyphosphates $Ln(PO_3)_3$ (Ln = Y, Tb...Yb)

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Keywords: Lanthanides; Chemistry; Solid State; Phase Transition, Incommensurately modulated

Crystalline compounds of rare-earth metals with condensed anions are of broad interest for optical applications [1], but unfortunately there is still a lack of knowledge of structural details in many condensed phosphates [2]. Recently, the room-temperature structures of the polyphosphates $Ln(PO_3)_3$ with Ln = Gd…Lu of the late rare earth metal ions have been elucidated. Contrary to previous crystal structure analyses [2] the crystal structures of the late lanthanoids' *catena*-polyphosphates $Ln(PO_3)_3$ (Ln=Tb…Yb) are incommensurately modulated [3]. We also examined the crystal structures of $Sc(PO_3)_3$, which is isotypic with $Lu(PO_3)_3$ and *C*-type phosphates, and that of $Y(PO_3)_3$, which is isotypic with incommensurate β-$Dy(PO_3)_3$.

At low temperature we determined the lock-in phases of the above mentioned incommensurately modulated polyphosphates. These adopt in parts already known structure types but also exhibit a novel structure type both of which are centrosymmetric. All observed phase transitions can be described using group-subgroup relationships and finally lead to an overall structure concept of the lanthanide polyphosphates based on the basic structure unit cell of the incommensurate phases [4].

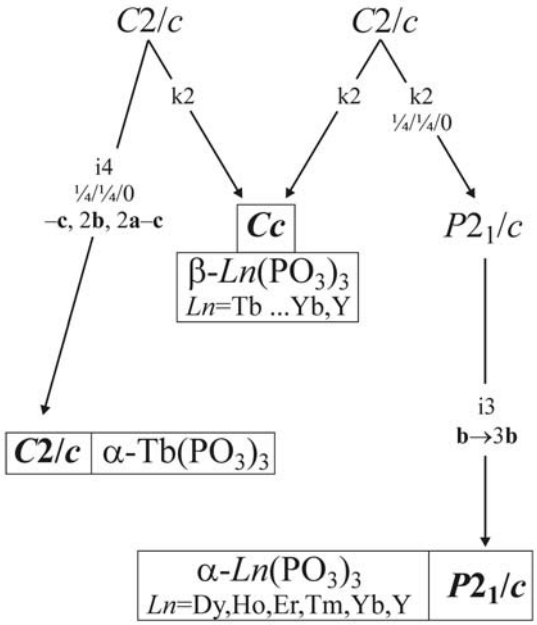

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Figure 1. Group-subgroup relation schemes of the phase transitions from incommensurate β-$Dy(PO_3)_3$ to α-$Dy(PO_3)_3$ and β-$Tb(PO_3)_3$ to α-$Tb(PO_3)_3$

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Some new lanthanide sulphate hydrates

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Keywords: Lanthanides; Chemistry; Solid State; Structure, Spectroscopy

Trivalent rare-earth ions can act as a quantum cutter or induce high-energy photons from low-energy photons (upconversion). Upconversion phosphors are interesting for the coating of solar cells [1,2]. Therefore we investigate phosphates, thiophosphates as well as fluorophosphates. On the way to fluorophosphates we characterized some new rare-earth sulphates, which can be used as model compounds for fluorophosphates, because fluorophosphoric acid and sulphuric acid are isoelectronic.

In this contribution we report about the synthesis, structure and optical properties of $Ho_2(SO_4)_3{\cdot}8H_2O$ and $KLn(SO_4)_2{\cdot}H_2O$ (*Ln*=Sm, Eu, Gd, Dy). The octahydrates of the rare-earth sulphates show one structure type and crystallize in the monoclinic space group C2/c [3]. The holmium cations are eightfold-coordinated and form slightly undulating layers. Between the layers there are voids where the sulphate tetrahedra and water molecules are located.

The structures of the $KLn(SO_4)_2{\cdot}H_2O$ consist of hexagonal undulating layers of alternating Ln and K atoms perpendicular the bc-layer. In between these layers there are two different kinds of distorted voids: the S1 sulphate anions are located in the hexagonal prismatic voids and the S2 sulphate anions are found in the trigonal prismatic voids. The coordination environment of the rare-earth ions is different in the case of the Sm (Gd) and the Dy (Eu) compound, respectively. The Sm and Gd double sulphates show the same structure type as $KCe(SO_4)_2{\cdot}H_2O$ [4] where the *Ln* atom is ninefold-coordinated in contrast to $KDy(SO_4)_2{\cdot}H_2O$ where the *Ln* ion is eightfold-coordinated by oxygen atoms (**Fig.1**).

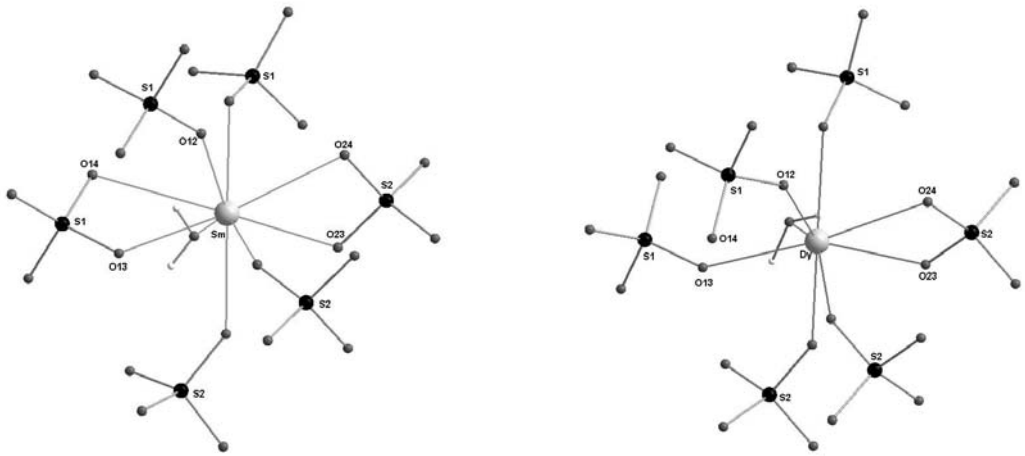

Figure 1. Coordination geometry for the rare-earth ions in $KSm(SO_4)_2 \cdot H_2O$ (left) and $KDy(SO_4)_2 \cdot H_2O$ (right).

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Crystal structure of the $TbMn_{1.76}In_{0.23}$ compound

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Keywords: Rare-earth elements; *f*-elements; crystal structure

For the systems R–Mn–In (R = Y, Gd, Tb, Dy, Ho, Tm, Yb, Lu), the formation of particular compounds has been studied only. The isothermal section RMn_2–"RIn_2" was studied meticulously, where the formation of the Laves phases $MgCu_2$, $MgZn_2$, $MgNi_2$ and compounds with AlB_2 and $CaIn_2$ structure types was observed [1-3]. The isothermal section of Er–Mn–In phase diagram was constructed [3].

New compound $TbMn_{1.76}In_{0.23}$ was found during investigation of the phase equilibria in the Tb–Mn–In system. The sample was prepared by arc-melting under argon atmosphere and annealed at 600°C. The crystal structure was determined by single crystal X-ray diffraction (CAD-4T diffractometer, Mo*K*α radiation). The structure belongs to $TbFe_2$ structure type, which can be described as deformed variant of $MgCu_2$ structure type (space group *R*-3*m*). The structure refinement was accomplished using WinCSD software [4].

Table 1 - Atomic coordinates and displacement parameters for $TbMn_{1.76}In_{0.23}$

(ST $TbFe_2$, space group *R*-3*m*, Pearson code *hR*18, a = 5.570(1), c = 13.648(4) Å, ρ = 8.116(6) g/cm^3, R = 0.0632, R_w = 0.0653, T = 295 K)

Site	Wyckoff position	x	y	z	U_{eq} (Å^2)	G
Tb	6	0	0	0.37477(6)	0.0110(1)	1
Mn1	9	1/2	0	1/2	0.0103(4)	0.84(3)
In	9	1/2	0	1/2	0.0103(4)	0.15(3)
Mn2	3	0	0	0	0.010(2)	1

Table 2 - Anisotropic displacement parameters for $TbMn_{1.76}In_{0.23}$

Site	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
Tb	0.0084(2)	0.0084(2)	0.0134(3)	0.00210(4)	0	0
Mn1	0.0084(4)	0.0071(5)	0.0126(6)	0.0017(1)	0.0001(2)	0.0002(3)
In	0.0084(4)	0.0071(5)	0.0126(6)	0.0017(1)	0.0001(2)	0.0002(3)
Mn2	0.008(2)	0.008(2)	0.011(3)	0.0021(4)	0	0

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Structural and magnetic characterization of ordered Sr_2LnSbO_6 (Ln=rare earth) perosvkites

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Keywords: Lanthanides; Solid State; Magnetism; Crystal Field

The double perovskites A_2LnMO_6 (A = Sr^{2+} and Ba^{2+}; Ln = trivalent lanthanide cation; M = pentavalent 4d or 5d transition elements) have been widely studied concerning their structure and properties [1]. If the Ln and M cations are ordered within the B-perosvkite sites the symmetry and size of the unit cell change when are compared to the ideal cubic aristotype. Woodward predicted 15 possible space groups for the ordered $A_2BB'O_6$ perovskites when the cation ordering and the octahedral tilting around the pseudo-cubic axes take place simultaneously [2]. The ordered double perovskites A_2LnMO_6 with only one of the two B-sites carrying magnetic moment, namely Ln, show a magnetic sublattice consisting of edge-sharing tetrahedral, which represents a frustrating magnetic geometry in three dimensions. More recently, the structure of double perovskites Sr_2LnSbO_6 (Ln= Dy, Ho, Gd, Y and In) has been investigated, and the monoclinic symmetry of the space group $P2_1/n$, with Ln and Sb elements ordered in the B-sites, was reported [3, 4].

We report the preparation of the whole family of double perovskites Sr_2LnSbO_6 (Ln = La-Lu), which crystallize with the $P2_1/n$ space group, with lattice parameters $a=\sqrt{2}a_p$, $b=\sqrt{2}a_p$ and $c=2a_p$ (β~90 º), being a_p the lattice parameter of the cubic aristotype. A progressive decreasing was observed in lattice parameters with the increasing of the atomic number of the Ln cation, according with the well-known lanthanide contraction.

Magnetic susceptibility measurements for this family of compounds reveal a paramagnetic behaviour in a very wide temperature range. From experimental spectroscopic data as well as from a semi-empirical estimation (Simple Overlap Model SOM [5]) of the crystal-field parameters corresponding to the point site symmetry of the magnetically active Ln, O_h, and using the wavefunctions associated with the energy levels obtained, the paramagnetic susceptibility and its evolution *vs* temperature is simulated according to the van Vleck formalism. The observed deviation from the Curie–Weiss behaviour at low temperature, very well reproduced in each case, reflects the splitting of the ground state of the corresponding Ln cation under the influence of the crystal field. Thus, magnetic frustration or cooperative interactions do not need to be considered to explain the mentioned low temperature deviation from the linearity of Curie-Weiss plots.

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Magnetoresistance in rare earth half-Heusler compounds

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Keywords:

Ternary intermetallic half- Heulser rare earth compounds *REYZ* (*RE* = lanthanide element, *Y* = transition metal, *Z* = sp element), have been investigated by the means of magnetic, resistance and magnetoresistance measurements. Most of the compounds with half-Heusler (MgAgAs) structure are semiconducting although they are made out of metal elements [1, 2]. Additionally for some of these compounds a metal-insulator transition was found. The metal - insulator transition temperature depends strongly on the preparation conditions.

Some of these compounds show a negative giant magnetoresistance (GMR) even above the magnetic ordering temperature in the paramagnetic temperature regime. This magnetoresistance scales roughly with the square of the magnetization in the paramagnetic state, and is related to the metal-insulator transition [3].

The nonmagnetic semiconducting LuNiBi compound shows a large postitve MR effect of 25% at room temperature (figure 1). The positive MR may be due to metallic bismuth impurities in the sample that cause an extraordinary magnetoresistance (EMR) [4].

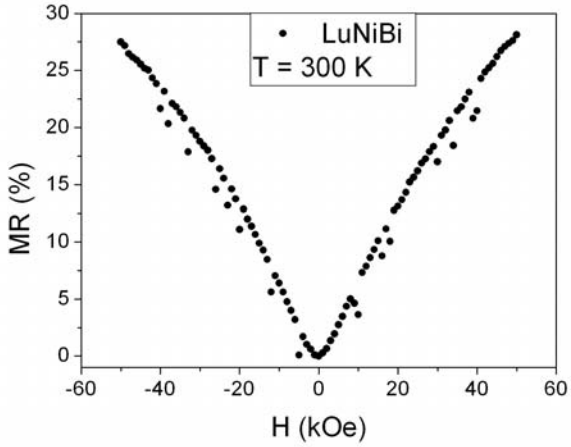

Figure 1: Magnetoresistance of LuNiBi at 300 K

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High Pressure Luminescence Studies of GaN Epilayer Implanted with Praseodymium Ions

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Keywords: lanthanide, materials, solid state, spectroscopy,

The optical activity of rare earth ions in III-nitride semiconductors has been extensively investigated for optoelectronics and phosphor applications during the last decade. It was shown that the output light color of these materials can be tuned to cover the UV-visible-NIR spectral region by selecting the right rare earth impurity and engineering the properties of III-nitride alloy hosts. Despite the efforts dedicated to study these materials our understanding of the RE^{3+} ions excitation/de-excitation mechanisms, issues of paramount importance from the application stand point, is inadequate. In this paper, the high pressure luminescence spectra of praseodymium implanted GaN epilayers grown by MOCVD on (0001) sapphire are presented for the first time. The implanted samples were thermally annealed at a temperature of 1000°C in N_2 at atmospheric pressure to recover from implantation damage and activate the rare earth ions. Hydrostatic pressures up to 120 kbar were applied with a diamond anvil at room temperature. High pressure luminescence spectra of Pr-doped GaN when excited at 325 nm (above bandgap) are characterized by the band at about 370 nm related to the GaN excitonic emission transitions, broad band centered at 520 nm due to the deep defects recombination transitions in GaN epilayers and the sharp structures in the visible region attributed to the transitions from ^3P_J (J=0,1) and $^1D_2$ levels of Pr^{3+} ion. The same Pr^{3+} ion lines structure was detected when excited with 532 nm (resonant excitation to the $^1D_2$ level). We observed that for higher pressures the $^3P_0$ emission at 650 nm is considerably quenched when excited above bandgap and resonantly to the 4f level. This observation is in the direct contrast to our recent reports on the significant increase of the Eu^{3+} emission intensity in GaN when subjected to hydrostatic pressure [1]. The $^3P_0 \rightarrow {}^3F_2$ emission line shifts with pressure toward the lower energies with the rate of +0.654 cm^{-1} $kbar^{-1}$. Furthermore, the new Pr^{3+} transition lines originating from $^3P_1$ level were observed in the region between 473 nm – 515 nm when the ambient pressure was close to 36 kbar. The Pr-doped GaN emission intensity decrease and modifications of the observed luminescence spectra will be discussed in the light of the change of energy of the bound exciton with pressure. Furthermore, our results will be compared with other material systems for which similar observations were reported.

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The Laves phases $Eu_{1-x}M_xMg_2$ (M = La, Ce, Sm) and their hydrides: synthesis, structures and properties

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Keywords:

Crystal structure, magnetic, electrical and optical properties of rare earth intermetallics may be strongly influenced by the incorporation of hydrogen. A systematic crystal chemical exploration of the hydrides formed hereby revealed many new compounds, the most interesting from a structural point of view being $EuMg_2H_6$ [1]. This ferromagnetic semiconductor (T_C = 27 K) crystallizes in a new structure type (anti-type: $Na_5[NiO_2][CO_3]$ [2]) related to that of cubic perovskite (Figure 1). In order to map the field of existence of this unitary structure type iso- and aliovalent substitution of europium is of interest.

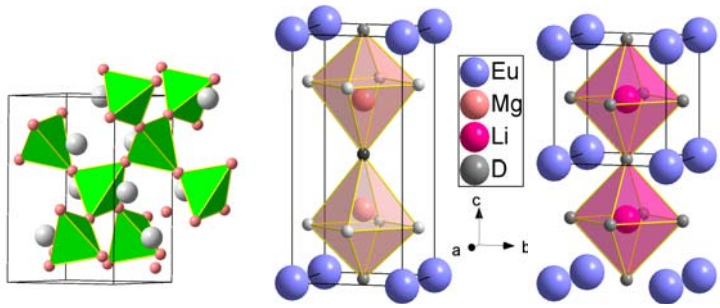

Figure 1: Crystal structures of $SmMg_2H_7$ (left, hydrogen atoms omitted for clarity), $EuMg_2H_6$ (middle) and cubic perovskite type $EuLiH_3$ (right)

Isovalent substitution by strontium yields a complete solid solution series for the hexagonal Laves phases $Eu_{1-x}Sr_xMg_2$. Ferromagnetic (15 K $\leq T_C \leq$ 27 K) hydrides $Eu_{1-x}Sr_xMg_2H_6$ ($x \leq 0.6$) with a $EuMg_2H_6$ type of structure are produced upon hydrogenation [3].

Aliovalent substitution of europium by lanthanides preferring the trivalent oxidation state in hydrides was also explored by investigating the pseudo-binary systems $LnMg_2$-$EuMg_2$ (Ln = La, Ce, Sm). The solubility of the hexagonal Laves phase $EuMg_2$ in the cubic Laves phases $LnMg_2$ reaches up to 50%, while vice versa only 20% $LnMg_2$ is soluble in $EuMg_2$ [4]. The hydrogenation of the cubic Laves phases $Ln_{1-x}Eu_xMg_2$ follows two different reaction pathways depending on reaction conditions: 1) Quickly increasing hydrogen pressure and temperature yields mixtures of binary lanthanide hydrides and magnesium. 2) Hydrogen absorption at room temperature followed by annealing at moderate temperatures yields hydrides of the formula $Ln_{1-x}Eu_xMg_2H_{7-x}$, which are structurally related to the filled Laves phase hydride $SmMg_2H_7$ [5].

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Two Modifications of the Novel Oxosilicate $NaTbSi_2O_6$ in Comparison

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Keywords: Lanthanides, Chemistry, Solid State, Structure

Until now, no compound in the quaternary system Na / Tb / Si / O is known to literature. But by preparative studies in this system, two modifications of the formula type $NaTbSi_2O_6$ were obtained from the same reaction mixture of Tb_4O_7, SiO_2, NaBr and TeO_2 as fluxing agent in evacuated silica ampoules by tempering at 800 °C for 100 h. The colourless single crystals of both structure types are lath-shaped and can not be distinguished optically. The first resulting modification, α-$NaTbSi_2O_6$, crystallizes monoclinically in space group $P2_1/c$ with a = 542.57(4), b = 1376.54(9), c = 762.83(5) pm, β = 110.086(3)° and V_m = 80.557 cm^3/mol with four formula units per unit cell and is isostructural to the normal-pressure phase of $NaYSi_2O_6$ [1], whereas the high-pressure structure of $NaYSi_2O_6$ needs to be described in the monoclinic space group $C2/c$ [2]. The also known monoclinic compound $NaScSi_2O_6$ [3] (space group $C2/c$ as well) is realizing a third structure type for the composition $NaMSi_2O_6$. A fourth novel high-temperature modification could now be achieved for the second form of sodium terbium oxosilicate, β-$NaTbSi_2O_6$ namely, which crystallizes triclinically in space group $P\overline{1}$ (a = 549.41(4), b = 938.65(6), c = 972.30(7) pm, α = 117.263(2), β = 97.239(2), γ = 99.676(2)°, Z = 3, V_m = 85.798 cm^3/mol).

In the monoclinic phase α-$NaTbSi_2O_6$, the two crystallographically different oxosilicate tetrahedra $[SiO_4]^{4-}$ (d(Si–O) = 159 – 167 pm) build up zig-zag-shaped, infinite unbranched *vierer* single chains ${}^1_\infty\{[SiO^v_{2/2}O^t_{2/1}]^{3-}\}$ running along [001] (figure 1) via vertex sharing. Viewing along [010], a layer of crystallographically unique Tb^{3+} cations, each surrounded by seven O^{2-} anions in the shape of a pentagonal bipyramid (d(Tb–O) = 226 – 256 pm), are located between these chains, while the only kind of Na^+ cations is situated inside of them. The Na^+ cations themselves are coordinated as capped trigonal prisms (d(Na–O) = 232 – 292 + *309* pm, CN = 6 + 1). In contrast, the triclinic structure of β-$NaTbSi_2O_6$ belongs to the *cyclo*-oxosilicates according to $Na_3Tb_3[Si_6O_{18}]$, in which the three crystallographically different oxosilicate tetrahedra $[SiO_4]^{4-}$ (d(Si–O) = 159 – 165 pm) are vertex -connected to corrugated six-membered rings $[Si_6O_{18}]^{12-}$ (figure 2) lying in the (100) plane. The two types of Tb^{3+} cations are coordinated as distorted trigonal antiprisms with oxygen atoms (d(Tb–O) = 223 – 235 pm). In (100), the condensed $[TbO_6]^{9-}$ polyhedra arrange alternatively with layers containing the oxosilicate rings and the Na^+ cations with Na–O distances ranging from 230 to 274 pm. While the fivefold coordinated $(Na1)^+$ cations are situated between the isolated *cyclo*-oxosilicate units, the $(Na2)^+$ cations can be found inside the rings. These $(Na2)^+$ cations are surrounded by the six bridging O^{2-} anions of the *cyclo*-$[Si_6O_{18}]^{12-}$ units in a hexagonal *quasi*-planar coordination sphere.

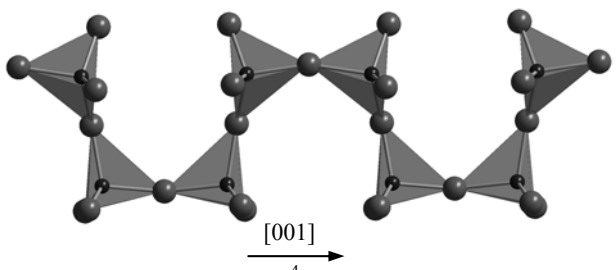

Figure 1. Linkage of the $[SiO_4]^{4-}$ tetrahedra in α-$NaTbSi_2O_6$

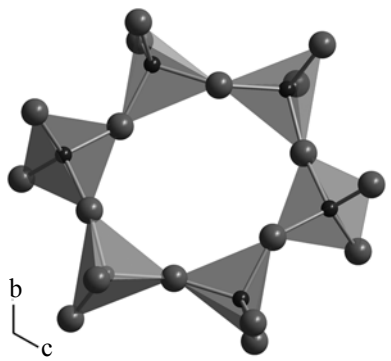

Figure 2. $[Si_6O_{18}]^{12-}$ unit in β-$NaTbSi_2O_6$

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The New Modification of a Well-Known Compound: *C-Type* $LaTaO_4$

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Keywords: Lanthanides, Chemistry, Solid State, Structure

The simple ternary oxotantalates(V) of the trivalent rare-earth elements with the composition $MTaO_4$ have been published in 2005 [1], where two different modifications were reported. With the early and light lanthanides (M = La – Pr) they crystallize in the monoclinic *A-type* modification in space group $P2_1/c$ with lattice constants of a = 762(±1), b = 553(±4), c = 777(±4) pm, β = 101(±1)° and four formula units per unit cell. With M = Nd, Sm – Lu, the monoclinic *B-type* (space group $P2/c$) is formed, where the cell dimensions shrink to lattice constants like a = 516(±9), b = 551(±9), c = 534(±9) pm, β = 96.5(±0.3)° with only two formula units present in the unit cell. The M^{3+} cations exhibit a coordination sphere of eight oxygen atoms in both structure types, but while the larger ones are surrounded by distorted square antiprisms, the smaller ones are coordinated by trigonal dodecahedra. The coordination environments of the Ta^{5+} cations can be described as octahedral, slightly distorted in the *A-type*, but highly distorted in the *B-type* structure of $MTaO_4$. The novel *C-type* modification of $LaTaO_4$ also crystallizes monoclinically, but in the space group $P2_1/n$ with a = 539.37(4), b = 514.32(4), c = 1269.58(9) pm and β = 94.109(3)° with four formula units in the unit cell. Unlike in the *A*- and *B-type* structure the La^{3+} cations in *C-type* $LaTaO_4$ display a sevenfold oxygen coordination sphere with the shape of a monocapped octahedron (figure 1; d(La–O) = 234 – 254 + *294* pm, CN = 6 + 1). The oxotantalate(V) units in *C*-$LaTaO_4$ again form distorted $[TaO_6]^{7-}$ octahedra (d(Ta–O) = 189 – 215 pm), which are connected via two edges (O1···O1' and O2···O2') to other anions to generate one-dimensional strands $^1_\infty\{[TaO^e_{4/2}O^t_{2/1}]^{3-}\}$ along [010] (figure 2). Surrounded and interconnected by La^{3+} cations, they arrange like a hexagonal rod packing. A very similar architecture occurs in monoclinic β-$PrSbO_4$ [2], which also crystallizes in space group $P2_1/n$ as the title compound and shows quite similar lattice parameters (a ≈ 531, b ≈ 509, c ≈ 1282 pm, β = 92°), but the Pr^{3+} cations in this particular case have only coordination numbers of six (d(Pr–O) = 236 – 244 pm) and even the $[SbO_6]^{7-}$ octahedra (d(Sb–O) = 193 – 204 pm) appear more perfect.

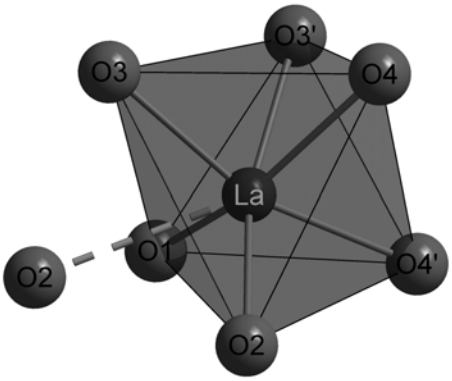

Figure 1. Capped octahedral surrounding of the La^{3+} cations in *C-type* $LaTaO_4$

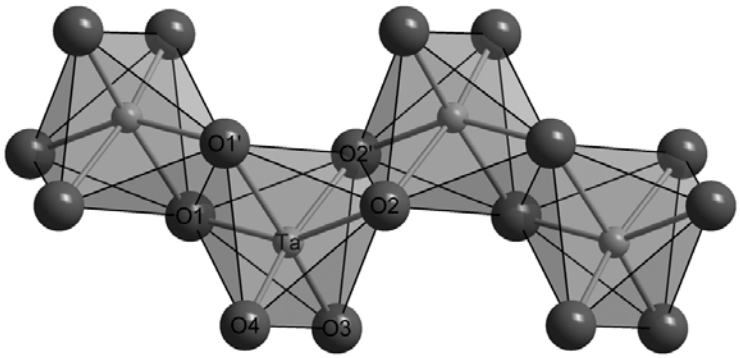

Figure 2. One-dimensional chain $^1_\infty\{[TaO^e_{4/2}O^t_{2/1}]^{3-}\}$ of edge-connected $[TaO_6]^{7-}$ octahedra running along [010] in *C*-$LaTaO_4$.

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Formation of Gd^{3+} trap states in $NaGdF_4$

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Keywords: Lanthanides; Physics; Solid State; Spectroscopy

Alkali gadolinium fluorides are most attractive from the viewpoint of the development of phosphors for fluorescent lamps, since they exhibit efficient excitation energy transfer from the Gd^{3+} ions to the other ions yielding visible photons, such as Eu^{3+} and Tb^{3+} ions. Early work by Kiliaan *et al.* on $NaGdF_4$: Ce^{3+}, Eu^{3+} showed that, the Ce^{3+} ion excited by ultraviolet (UV) light (wavelength: ~250 nm) gives the excitation energy to the Gd^{3+} ion; and then, almost all the excitation energy is transferred to the Eu^{3+} ion yielding a red photon through the excitation energy migration among Gd^{3+} ions [1]. Recent work by Wegh *et al*. demonstrated that a two-step energy transfer from one Gd^{3+} ion excited by vacuum ultraviolet (VUV) light (~200 nm) to two Eu^{3+} ions in $LiGdF_4$: Eu^{3+} offers conversion of one VUV photon to two red photons [2]. Energy migration among Gd^{3+} ions plays a key role in the two-step energy transfer.

Energy migration among Gd^{3+} ions in gadolinium compounds has been studied by several research groups. Mori *et al*. reported the scintilation mechanisms of Gd_2SiO_5: Ce^{3+} crystals [3]. They proposed that the energy migration among Gd^{3+} ions is regarded as the diffusion of core excitons formed by the 4*f* states in Gd^{3+} ions; the long-distance diffusion of the free core excitons is resposible for the scintilation of Ce^{3+} ions at room temperature. In addition, they found that the core excitons are bound to defects at low temperatures (< 30 K). Earlier work by Mahiou *et al*. showed that the free and bound exciton-like states are formed by the 4*f* states of Gd^{3+} ions on different crystallographic sites in $NaGdF_4$ [4]. The authors called the two states "Gd^{3+} intrinsic and trap states", respectively.

We have recently investigated photoluminescence (PL) and photoluminescence excitation (PLE) spectra for the Gd^{3+} intrinsic and trap states in $NaGdF_4$ in more detail [5]. It was found that the PLE spectrum for PL of the Gd^{3+} intrinsic states shows additional excitation bands peaking at ~160 nm at room temperature, although it does not show at 10 K. Since the PLE spectrum for PL of the Gd^{3+} trap states shows similar excitation bands at 10 K and the PL spectra at various temperatures suggest the thermal activation from the trap states to the intrinsic ones, we attributed the excitation bands to transitions (probably 4f-5d transitions) of the Gd^{3+} trap states.

In this study, in order to clarify the role of $NaGdF_4$ crystal lattice in the formation of the Gd^{3+} trap states, we have measured PL spectra at various temperatures (10–300 K) and PLE spectra at 10 K and 300 K for $NaY_{1-x}Gd_xF_4$ (x=0.01 and 0.10), and compared with those for $NaGdF_4$ (x=1). It is found that the luminescence line and the excitation bands originating from the Gd^{3+} trap states are absent in the PL and PLE spectra at x=0.01; they appear in the PL and PLE spectra at x=0.10. We discuss the formation process of Gd^{3+} trap states in $NaGdF_4$.

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Isolated Tetrahedra and capped trigonal Prisms: Pr_5CCl_{10}

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Keywords: Praseodymium; Chloride; Tetrahedra; Prisms

Depending on the interstitial atoms different kinds of polyhedra occur in the structures of rare-earth metal halides. In the case of carbon the structure usually contains octahedra or seldom trigonal prisms, which are centered by C_2 dumbbells or single carbon atoms. Nitrides and oxides of the rare-earth metal halides are more often constituted of tetrahedra, which occur isolated, as double tetrahedra or as infinite chains.

A first example for the tetrahedral surrounding of C^{4-} ions in RE_6C_2 double tetrahedra was found with $La_6C_2Br_{10}$ [1]. Recently $Pr_6C_2Cl_{10}$ could be synthesized in the same formula type, crystallizing in the same space group type but with different crystal structure [2]. The compounds are electron precise, explaining the transparency of the yellow crystals.

Now, a first rare-earth carbide halide with a discrete C centered tetrahedral arrangement of Pr atoms could be synthesized. In this contribution we present the new compound Pr_5CCl_{10} with trigonal symmetry. For the synthesis a mixture of Pr, $PrCl_3$ and C in a ratio of 5:10:3 was arc-sealed in a Ta capsule and to prevent oxidation sealed in silica glass. The mixture was annealed for 34 days at 825 °C. The yield was approx. 90%. The compound formed irregular black-green crystals, which look olive-green and transparent in fragments.

Pr_5CCl_{10} crystallizes in *P*3 with a = 14.0202(15) Å and c = 7.3209(80) Å. Besides Pr_4C tetrahedra the structure contains isolated Pr atoms, that are nine-fold coordinated by Cl atoms and represent the center of a distorted three-fold capped trigonal prism. All Cl atoms connect the tetrahedra via all edges.

TEM investigations were performed, which confirmed the space group as well as the structure. High resolution images showed the structural building blocks in detail.

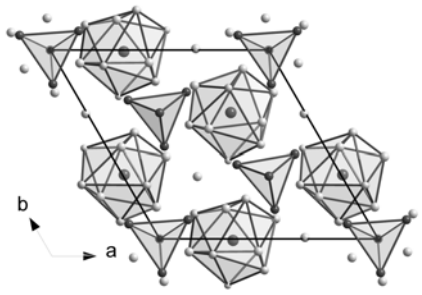

Figure 1. Projection of Pr_5CCl_{10} along [001] with the emphasized Pr_4C tetrahedra and the distorted three-fold capped trigonal prisms of Cl, surrounding the isolated Pr atoms (big grey).

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Magnetic Properties of $EuLn_2O_4$ (Ln = Lanthanides)

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Keywords: Lanthanides; Chemistry; Solid State; Magnetism

Magnetic properties of ternary lanthanide oxides $EuLn_2O_4$ (Ln = Gd, Dy-Lu) have been studied. They crystallized in an orthorhombic structure with space group *Pnma*. Figure 1 shows the crystal structure of $EuLn_2O_4$. Ln ions occupy two different crystallographic sites (Ln1 and Ln2) and are coordinated by six oxide ions in an octahedral manner. The $Ln1O_6$ and $Ln2O_6$ octahedra form the zigzag chains along the *b* axis, respectively. These chains connect with each other and build up the honeycomb-like framework. The Eu ions locate in the tunnel of the honeycomb structure.

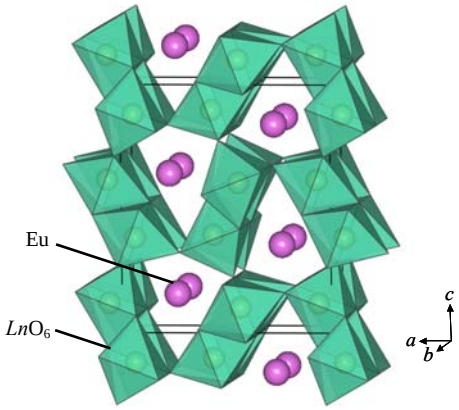

Figure 1. Crystal structure of $EuLn_2O_4$

The ^{151}Eu Mössbauer spectrum for $EuYb_2O_4$ (Fig. 2) shows strongly that the Eu ions are in the divalent state. The 12 possible transitions (eight allowed transitions and four forbidden transitions) due to a quadrupole interaction were taken into account; the observed data were fitted with the sum of these Lorentzian lines. The fitting parameters, the isomer shift (IS), the quadrupole coupling constant (QS) and the asymmetry parameter (η) are listed in Table 1.

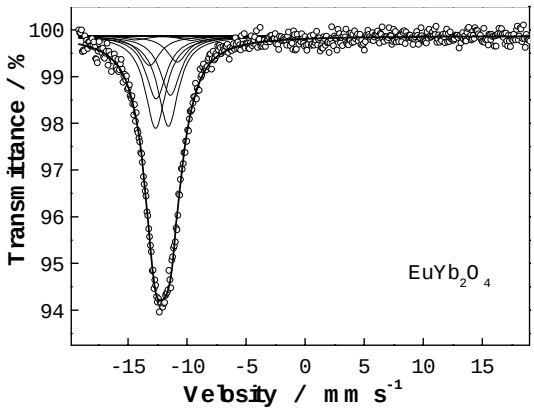

Figure 2. ^{151}Eu Mössbauer spectrum of $EuYb_2O_4$ at room temperature

Figure 3 shows the temperature dependence of magnetic susceptibility of $EuLu_2O_4$. All these compounds indicate an antiferromagnetic transition at 4.2-6.3 K. From the positive Weiss constant and the saturation of magnetization for $EuLu_2O_4$, it is considered that ferromagnetic chains of Eu^{2+} are aligned along the *b* axis of the orthorhombic unit cell, with neighboring Eu^{2+} chains antiparallel. When Ln = Gd-Yb, ferromagnetically aligned Eu^{2+} ions interact with the Ln^{3+} ions, which would overcome the magnetic frustration of triangularly aligned Ln^{3+} ions and the $EuLn_2O_4$ compounds show a simple antiferromagnetic behavior. A suggested magnetic structure for $EuLn_2O_4$ will be discussed.

Figure 3. Magnetic susceptibility vs. temperature of $EuLu_2O_4$

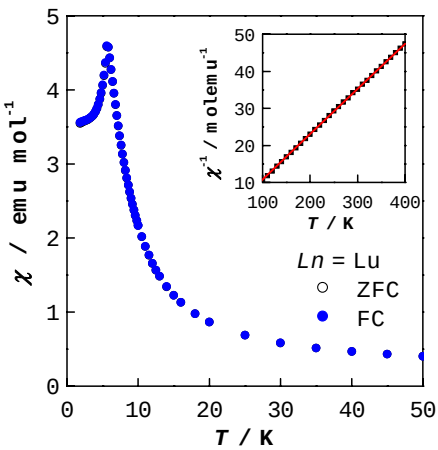

Table 1. Mössbauer parameters for $EuLn_2O_4$

Ln	IS / mm s^{-1}	QS / mm s^{-1}	η
Gd	–12.29(1)	8.2(1)	0.40(4)
Dy	–12.23(1)	7.6(1)	0.56(3)
Ho	–12.15(1)	7.3(1)	0.72(2)
Er	–12.12(1)	7.3(1)	0.85(3)
Tm	–12.09(1)	7.5(1)	0.89(4)
Yb	–12.09(1)	6.9(1)	0.95(8)
Lu	–12.10(1)	7.5(1)	1.0(1)

Preparation of Cerium Nitride by Taking Advantage of the Reaction of Cerium Hydride with Ammonia

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Keywords: Materials; Solid State; Catalysis; Synthesis

It has been recently found that rare earth nitrides show specific activity as a catalyst; thus EuN and YbN are active as a selective catalyst for the partial hydrogenation of benzene to cyclohexene [1]. Europium amide ($Eu(NH_2)_2$) and ytterbium amide ($Yb(NH_2)_2$ and $Yb(NH_2)_3$) obtained by taking advantage of the solubility of europium and ytterbium metals in liquid ammonia become effective precursors for EuN and YbN, respectively; thus the thermal decomposition of these amides leads to catalytically active rare earth nitrides [2,3].

Other rare earth metals than Eu and Yb exhibit the poor solubility toward liquid ammonia, and hence a similar procedure for the preparation of rare earth nitride can not be adopted. For the preparation of CeN, the direct reaction of cerium metals with ammonia at elevated temperatures has been previously studied, but it is difficult to prepare stoichiometric cerium nitrides [2]. In this study, the use of cerium amides as a precursor of cerium nitride was investigated to synthesize active nanocrystalline cerium nitride. There is much expectation of the synthesis of cerium amide in good yield by taking advantage of the reaction of cerium hydride and ammonia. The preparation of CeN using cerium amide thus obtained has been studied extensively by X-ray diffraction analysis (XRD) and temperature-programmed desorption (TPD) combined with mass spectrometer.

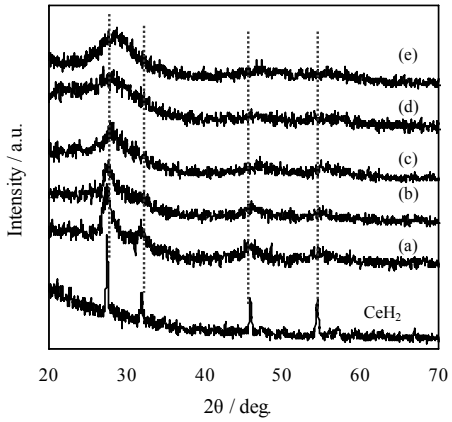

Fig. 1 Changes in XRD with ball-milling of CeH_2 and NH_3; (a) 0.25 h, (b) 1 h, (c) 3.5 h, (d) 7 h and (e) 20 h

The formation of cerium amide as a precursor of nitride was important in the whole steps for the preparation. As shown in Fig. 1, nanocrystalline cerium amide was obtained upon reactive ball milling of CeH_2 under 0.3 MPa ammonia pressure. The cerium amide product obtained by ball milling for 7 h was subjected to the thermal treatment to be converted into cerium nitride (Fig. 2). The conversion processes of cerium amide into nitride were evaluated with XRD and TPD. Consequently, it can be presumed that the cerium amide decomposes to imide (CeNH) with evolution of ammonia around 600 K, followed by conversion into nitride (CeN) around 800 K with evolution of hydrogen.

$$Ce(NH_2)_2 \rightarrow CeNH + NH_3$$
$$CeNH \rightarrow CeN + 1/2H_2$$

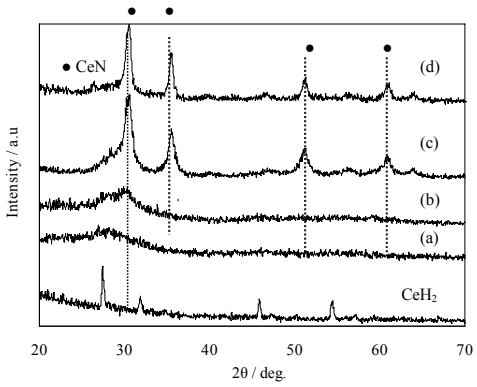

Fig. 2 Changes in XRD of (a) ball-milling products of CeH_2 and NH_3 with the thermal treatment.
The products were subjected to evacuation for 1 h at the following temperatures: (b) 673 K, (c) 873 K and (d) 1073 K.

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Temperature study of Ho^{3+}, Yb^{3+} and Tm^{3+} tridoped $KGd(WO_4)_2$ crystals by Raman spectroscopy

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Keywords: Lanthanides; Monoclinic Double Tungstates; Solid State; Raman Spectroscopy

In the last few years much attention has been paid to development of novel rare earth doped solid state laser materials based upon infrared to visible frequency up-conversion, because of their potential applications as optoelectronic devices such as colour display, optical data storage, biomedical diagnostic, sensors [1,2]. The lanthanide doubly doped $KGd(WO_4)_2$ host crystals have been recognized as one of the most efficient up-conversion materials. In the present work the vibrational properties of the Ho^{3+}, Yb^{3+} and Tm^{3+} tridoped $KGd(WO_4)_2$ crystals have been studied by Raman spectroscopy. The vibrational studies of the $KGd(WO_4)_2$ host lattice are particularly important due to its role in transfer of excitation energy between Ho^{3+}, Yb^{3+} and Tm^{3+} ions in the energy conversion process.

The tridoped $KGd(WO_4)_2$:(Ho, Yb, Tm) crystals were obtained by the Top Seeded Solution Growth method. The doping concentration of Ho^{3+}, Yb^{3+} and Tm^{3+} ions was 20 at.%, 5 at.% and 5at.%, respectively.

The vibrational properties of $KGd(WO_4)_2$: (Ho, Yb, Tm) crystals have been investigated using Renishaw In-Via Raman spectrometer equipped with confocal DM 2500 Leica optical microscope, Ren-cam CCD detector and Ar^+ ion laser with excited light at 488 nm wavelength. The temperature-dependent polarized Raman spectra of $KGd(WO_4)_2$: (Ho, Yb, Tm) crystals were recorded in the spectral range 100 – 1000 cm^{-1} in the *y(xx)z* and *y(xy)z* scattering geometry over the 77 – 300K temperature range. The strongest low-temperature changes in the Raman spectra of $KGd(WO_4)_2$: (Ho, Yb, Tm) crystals were observed in the range of the stretching vibrations of WO_4^{2-} tetrahedra and WOOW oxygen bridge bonds (650 – 950 cm^{-1} spectral range). The frequency of the bands located at 685, 747 and 901 cm^{-1} increases, while that of the band at 761 cm^{-1} decreases with lowering temperature. Moreover, the temperature dependences of some selected bands show different slopes below and above 150K. The observed anomalies in the spectral parameters of selected Raman bands at about 150K have been related with the local distortion of WO_4^{2-} tetrahedral and elongation of W–O bonds in the WOOW bridge bonds. The results obtained have been discussed in terms of the influence of the temperature and doping concentration on the lattice dynamics and crystal structure.

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Study of $Li_6Ln(BO_3)_3$: Yb (Ln= Gd, Y) crystals : crystal growth, thermal, mechanical and optical characterizations

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Keywords: Lanthanides; Solid State; Materials; Spectroscopy

For high-power laser applications, the laser beam must have a very good spatial quality, which depends on the thermal, mechanical and optical properties of the crystal. The latter ensure production of a laser effect, which may have tunable properties, or generate ultra short pulses.
Mechanical properties are also important for shaping: easy cleavage and crystal brittleness can hinder cutting and polishing process. Moreover, a soft material can easily be scratched or broken. In order to achieve a good beam quality, the surface of the crystal must be optically polished (without scratches).
Thermal properties also play a key role. If the materials tend to store too much heat during pumping process, problems of stability or even cracks in the crystal may occur. So a high thermal conductivity is needed.
Accordingly, studies of thermal, mechanical and optical properties are necessary for characterizing laser crystals.
The borate $Li_6Y(BO_3)_3$ has shown interesting laser properties [1; 2] (κ=2.6 $W.m^{-1}.K^{-1}$; P_{out} =2W; tunable laser). We plan to improve these preliminary results by means of crystal chemical engineering.
We report the study of the solid solution: $Li_6(Gd_xY_{(1-x)})_{0.75}Yb_{0.25}(BO_3)_3$ with x = 0, 0.25, 0.5, 0.75, 1 and a constant ytterbium concentration of 25%.
Gadolinium ion has a bigger ion radius and also a higher molar mass than yttrium ion. The substitution modifies the unit cell parameters, but also the thermal conductivity. Indeed, the ionic radius difference induces a distortion of the rare earth polyhedra and affects the crystal field at the Yb site (r(Gd) = 1.06 Å; r(Y)= 1.02 Å; r(Yb) = 0.98 Å). The thermal conductivity evolution of doped compounds depends on the mass difference between the doped element and the rare earth [3].
Crystals of each composition were grown by the Czochralski method. The resulting crystals compositions were checked by ICP and their indexes measured by the Brewster angle method. Several thermal and mechanical characterizations have been made, like hardness, thermal expansion and thermal conductivity. The spectroscopic study, including thermal extinction and lifetime measurements, was performed at room and low temperature in order to attribute the different emission lines. A more detailed investigation of the emission, at low temperature, of the $Li_6Ln(BO_3)_3$ Ytterbium doped crystal revealed in fact two zero phonon lines corresponding to two manifolds, where the second one cannot be explained by crystallographic data.
Understanding the crystal fundamental properties is a key parameter for obtaining efficient high power laser operation.

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22-Isopolytungstate Fragment $[H_2W_{22}O_{74}]^{14-}$ Coordinated to Lanthanide Ions

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Keywords: Lanthanides; Polyoxometalates; Synthesis; X-ray Crystal Structure

Polyoxometalates (POMs) represent a large class of nanosized metal-oxygen cluster anions [1]. Lanthanide-containing POMs can be of interest due to photoluminescence as well as catalytic, electrochemical, and magnetic properties. Peacock and Weakley have prepared a family of mono-lanthanide substituted decatungstates with the formula $[Ln(W_5O_{18})_2]^{n-}$ (Ln = lanthanide ion) [2], but to date no other isopolytungstates based on lanthanides have been structurally characterized.

Here, we present the synthesis and characterization of the 22-isopolytungstate coordinated two external lanthanide ions, $[Ln_2W_{22}O_{71}(OH)_2(H_2O)_{10}]^{8-}$ (Ln = La (1), Ce (2), Tb (3), Dy (4), Ho (5), Er (6), Tm (7), Yb (8), Lu (9), and Y (10)). Polyanions 1-10 are isostructural, and the coordination number of the lanthanide ions correlates with their sizes, Fig. 1. All compounds have been fully characterized in the solid state (FTIR, XRD, TGA) [3].

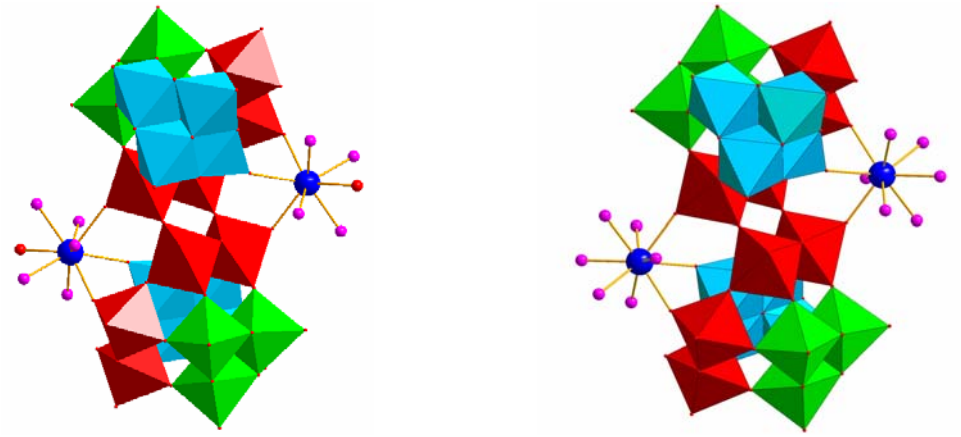

Figure 1. Polyhedral representation of $[Ln_2\mathbf{(H_2O)_{10}}W_{22}O_{72}(OH)_2]^{8-}$ (**1-2**) (left) and $[Ln_2\mathbf{(H_2O)_{10}}W_{22}O_{72}(OH)_2]^{8-}$ (**3-10**) (right). The structures of both polyanions are virtually identical, except the coordination number (8 vs 9) of the lanthanide ions. The color code is as follows: WO_6 octahedra (light blue, green, red); Ln (blue); H_2O (pink), O (red). The WO_6 octahedra were colored differently for clarity.

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Structural relationships between the rare-earth halide cluster phases $\{ZRE_6\}X_{12}RE$ and $\{ZRE_6\}X_{10}$

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Keywords: Reduced rare-earth halides; endohedral transition metals; cluster

New cluster compounds in the system Tb/X/Z containing endohedral transition metal atoms (Z) have been obtained via conproportionation reactions[1] of the corresponding terbium trihalide and the rare-earth metal itself. The respective encapsulated transition metals were added to the reaction mixture as pure elements. The reactions were carried out in sealed tantalum containers within the temperature range 900-1100°C for 10-14 days.

All products are air and moisture sensitive and were, hence, handled in a glove-box under a dry nitrogen atmosphere. The compounds were obtained as single crystals and data sets were collected at ambient temperature on STOE IPDS I/II diffractometers.

The recently synthesized compounds $\{ZTb_6\}I_{12}Tb$ (Z = Fe, Co) and $\{FeTb_6\}Br_{12}Tb$ are isostructural with $\{NSc_6\}Cl_{12}Sc$[2] whereas $\{ZTb_6\}Br_{10}$ (Z = Ni, Ir) are similar to the $\{RuY_6\}I_{10}$-type[3] of structure. The structural relationships between the $\{ZRE_6\}X_{12}RE$ and $\{ZRE_6\}X_{10}$ phases are based on the common packing of the halogen atoms and the endohedral transition metal atoms. The packing atoms are arranged in layers which are stacked in an ABC manner and can therefore be described as the motif of a cubic closest packing. In the $\{ZRE_6\}X_{12}RE$ phase there are seven out of thirteen octahedral voids occupied by rare-earth metal atoms, while in $\{ZRE_6\}X_{10}$ six out of eleven octahedral voids are filled accordingly. It can be shown that these two structures may be interconverted through a shear plane under the formal loss of a rare-earth dihalide in accordance to the formulae $RE_7X_{12}Z$ and $RE_6X_{10}Z$, respectively.

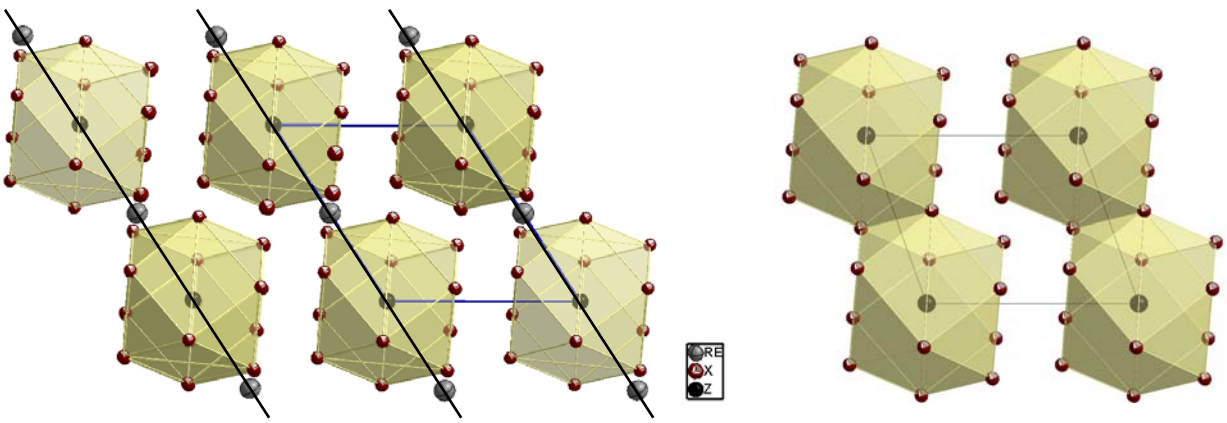

Figure 1. Interconversion between $\{ZRE_6\}X_{12}RE$ (*left*) and $\{ZRE_6\}X_{10}$ structures (*right*) under formal loss of "REX_2" through a shear plane. Due to clarity those metal atoms which build up octahedral clusters are omitted.

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$\{Ir_3Gd_{11}\}Br_{15}$ – a novel structure type in rare-earth halide chemistry

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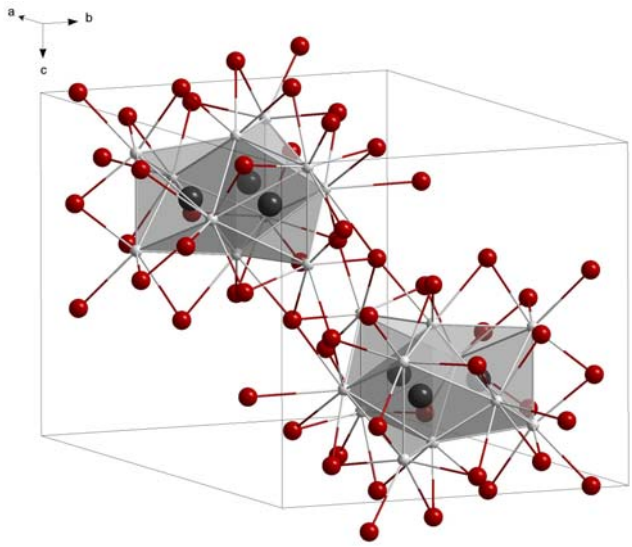
Keywords: Reduced rare-earth halides; endohedral transition metals; cluster

With $\{Ir_3Gd_{11}\}Br_{15}$ we have obtained a compound with a previously unknown structure type in rare-earth halide chemistry. Main structural features are isolated clusters trimers which are built by three face-sharing octahedral units. The endohedral iridium atoms form a triangle with internuclear distances of 295.5(1) pm. The packing can be described as a distorted hexagonal closest packing of the cluster units that form 3^6 nets which are stacked in an ABA manner. The trimeric clusters are interconnected through bridging halogen atoms.
The $\{Ir_3Gd_{11}\}$ cluster units link topologically lanthanide with alkali-metal cluster chemistry. The clusters in $\{O_3Cs_{11}\}$[1], a cesium suboxide structurally characterized in 1972, are likewise build by eleven cesium atoms which can be described as face-sharing octahedra centered by endohedral oxygen atoms.
The similarity of the cluster units in$\{Ir_3Gd_{11}\}Br_{15}$ and $\{O_3Cs_{11}\}$ shows the quite simple but impressive principles in solid state chemistry. Apparently, nature's purpose is to constitute stable structures in respect to stoichiometry and thermodynamic conditions. The example shows once more that certain structures and patterns are not limited to particular sorts of elements. Moreover, structures which are exclusively known from specific atoms or groups can be used as templates for others in exploratory synthesis.
To summarize, the new compound $\{Ir_3Gd_{11}\}Br_{15}$ features a unique structure in lanthanide chemistry with oligomeric cluster units, that were hitherto only known from the alkali suboxide $\{O_3Cs_{11}\}$. Together with the cluster arrangement in the sense of a hexagonal closest packing of the metal building blocks, it becomes clear that the imposing structure of $\{Ir_3Gd_{11}\}Br_{15}$ is no more and no less an principal example of structural concepts in the solid state.



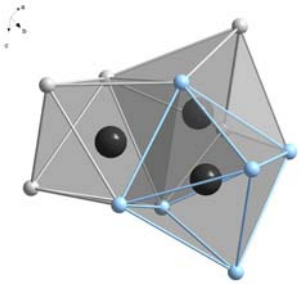


Figure 1
Left: Unit cell of $\{Ir_3Gd_{11}\}Br_{15}$.
Right: Trimeric cluster with one emphasized octahedron and all halide ligands omitted.

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$R\{R_6Z\}I_{12}$ with R = Dy, Ho

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Keywords: Lanthanides; Solid State Chemistry; Synthesis

Rare earth cluster compounds of the general formula $R\{ZR_6\}I_{12}$, where Z is an interstitial atom, primarily a d metal or a main group element, have been well explored for the rare earth elements Sc, Y, Pr and Gd [1]. Additionally, compounds of the formula type $A_x\{ZR_6\}I_{12+y}$, where A is an alkali metal (Rb or Cs) with x = 1-4 and y = 0-1 and Z = C, C_2, are known for the rare earth elements Pr and Er [2,3].

With $Ho\{ZHo_6\}I_{12}$ (Z = Fe-Ni, Ir, C) and $Dy\{(C_2)Dy_6\}I_{12}$, we were able to extend the knowledge of this structure type to the elements holmium and dysprosium [4, 5]. Both compounds crystallize in the space group R-3 and consist of isolated $\{ZR_6\}$ clusters, i.e. the metal atoms are not shared with other clusters. The cluster cores are surrounded by edge-capping and terminal iodide ligands that either connect the clusters to each other directly or via RI_6 units (Fig. 1). In $Ho\{ZHo_6\}I_{12}$, the $\{ZHo_6\}$ octahedra have -3 symmetry, only slightly deviating from regular octahedral symmetry whereas in the case of $Dy\{(C_2)Dy_6\}I_{12}$, the C_2 interstitial causes a significant elongation of the octahedron parallel to the axis of the C_2 dumbbell (Fig. 2). Since the C_2 units can be orientated parallel to each of the three 4-fold axes of the regular octahedron, they appear to be statistically disordered with a site occupation factor of 1/3 for each C atom. As a consequence, the Dy atoms of the clusters reveal a corresponding disorder.

Remarkably, the attempt to stabilize the $\{Dy_6\}$ cluster by adding a transition metal as a possible interstitial failed. Only the mixed compound $Dy\{CoDy_{4.43}Y_{1.47}\}I_{12}$ has been obtained so far. In contrast to its neighbour Dy, the $\{Ho_6\}$ clusters seem to encapsulate transition metals in particular, probably resulting from electronic reasons.

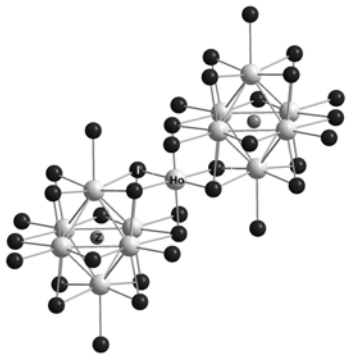

Figure 1 $\{ZHo_6\}$ octahedra surrounded by iodine atoms and their connection via HoI_6 entities.

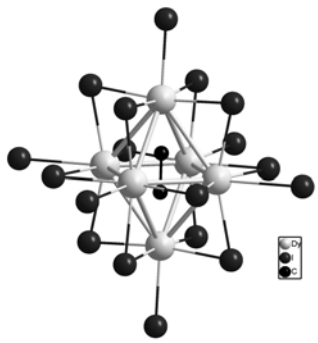

Figure 2 One $\{Dy_6\}I_{18}$ cluster unit encapsulating a C_2 dumbbell.

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Seven-Coordinate Ruthenium in the New Praseodymium Cluster Chloride $\{RuPr_3\}Cl_3$

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Keywords: Praseodymiumchloride; Cluster ; Bonding

Recently, we have succeeded to contribute a new structure type to the ZR_3X_3 (R = rare earth, Z = transition metal, X = halide) family. $\{RuPr_3\}Cl_3$ is the first rare-earth metal halide with a seven-coordinate interstitial.[1] As depicted in Fig. 1, the Ru atom is surrounded by a rather distorted monocapped trigonal prism (TP) of Pr atoms. The TP's share two common rectangular faces to form double chains which run down the short crystallographic *b* axis (4.004 Å). This leads to the *Niggli* formulation $\{RuPr_1Pr_{6/3}\}Cl_3$. The compound crystallizes in the orthorhombic space group *Pnma* (*no.* 62). Fig. 1 (right) refers to the bonding situation. The interactions are dominated by ionic Pr-Cl and covalent Pr-Ru bonding. In addition, there is an interplay between the Ru atoms, but only a minor one.

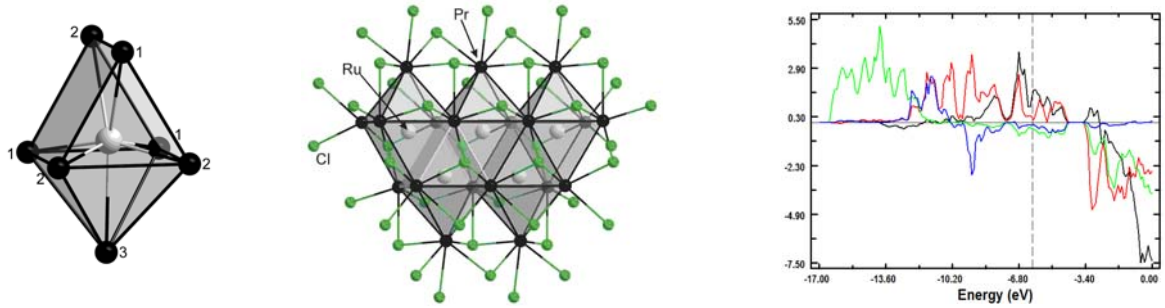

Figure 1. $\{RuPr_7\}$ cluster in $\{RuPr_3\}Cl_3$ (left), chain of face-sharing monocapped TP's (middle). COOPs for $\{RuPr_3\}Cl_3$. Green curves represent Pr-Cl (14x), blue Ru-Ru (2x), red Pr-Ru (7x) and black Pr-Pr (10x) interactions interactions (right).

Apparently isoelectronic compounds within the $\{ZR_3\}X_3$ family exhibit significantly different structures. Our new member does not resemble any of the known structure types, although the $\{RuPr_3\}$ chain is similar to that found in the distorted monoclinic $\{ZR_3\}I_3$ subgroup. However, the halide sheath around the chain and the connection of adjacent chains is, again, different. The analogous bromide and iodide compounds show as main building units fairly regular Pr_6X_{12} type octahedra centred by ruthenium atoms. They crystallize in the monoclinic space group $P2_1/m$ (*no.* 11).[2, 3]

The distortions and the structural diversity and, therefore, stability trends may be discussed in terms of better mixing of R and Z valence d orbitals. These follow the I1 + I2 sums for the R elements rather well. The larger values are considered to reflect better mixing and more covalent bonding character, whereas the smaller values and a larger energy difference indicate more salt-like interactions.[4,5]

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Influence of crystal structure on valence states of Ytterbium and Europium in dicarbide solid solutions

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Keywords: Carbides; Crystal Structure; Lanthanides; Solid State; Valence changes

Among the rare earth metal dicarbides EuC_2 and YbC_2 are of special interest, as Eu and Yb are known to exist as either trivalent or divalent cations. EuC_2, as the only compound of composition REC_2, crystallizes in the monoclinic ThC_2 type structure (C2/c, Z = 4). Using ^{151}Eu mössbauer spectroscopy it was shown that Eu is clearly divalent in EuC_2. YbC_2 crystallizes in the tetragonal CaC_2 type structure (I4/mmm, Z = 2). Magnetisation measurements resulted in a mixed valency with approx. 80 % Yb^{3+}, a value that was also found by Atoji et al. using paramagnetic neutron scattering [1].
As the different valences in these compounds go along with different crystal structures we started to explore the influence of crystal structure on the valence states of Eu and Yb by synthesizing solid solutions of composition $Eu_xSr_{1-x}C_2$ and $Yb_xCa_{1-x}C_2$. These solid solutions show a variety of different modifications. ThC_2 type structure and CaC_2 type structure are found in both systems, additionally the CaC_2-III type structure (C2/m, Z = 4) is found in $Yb_xCa_{1-x}C_2$ at low Yb contents. First hints on valence effects were obtained from the unit cell volumes per formula unit. At x ≈ 0.75 two modifications coexist (ThC_2 and CaC_2 type structure) for which a large volume difference of ΔV/V ≈ 12 % is observed (see figure 1). Only the tetragonal modifications follow Vegard´s law, whereas the volumes of the monoclinic modifications are too large. In $Eu_xSr_{1-x}C_2$ no similar effects were observed, tetragonal as well as monoclinic modifications lie on a Vegard straight line. The larger volumes of the monoclinic modifications in $Yb_xCa_{1-x}C_2$ may be explained by a lower valence state of Yb. This would argue for the assumption that the ThC_2 type structure shows a preference for the divalent state of Yb.

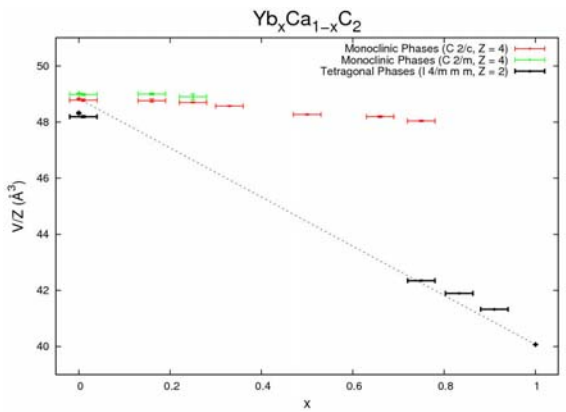

Figure 1. Unit cell volume per formula unit of solid solutions $Yb_xCa_{1-x}C_2$ as a function of x.

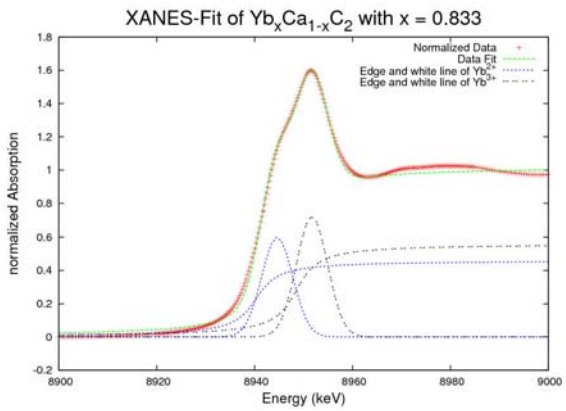

Figure 2. XANES fit of tetragonal $Yb_xCa_{1-x}C_2$ with x ≈ 0.833.

XANES spectra at the Yb-L_{III} edge (Hasylab, beamline C) clearly show that this is indeed the case. A tetragonal modification with x ≈ 0.833 shows two white lines separated by 7 eV, one belonging to Yb^{3+}, the other to Yb^{2+}. A fit results in a substance containing 55 % of Yb^{3+} and a mean valence of 2.55. For x ≈ 0.67 (monoclinic modification) only one white line is observed, which is shifted by 7 eV against the Yb^{3+} line of the Yb_2O_3 reference. This compound is therefore purely divalent. Temperature dependent XANES measurements at different compositions are planned to corroborate these results.

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Europium-based assays to monitor GPCR activation.

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Keywords: 1; europium, 2;GTP binding, GPCR, QFRET 3; drug discovery

Luminescent lanthanide chelates provide very practical tools for drug discovery e.g. in monitoring signaling cascades from the ligand interaction to cellular surfaces, through receptor activation, primary and secondary signaling cascades into nuclear receptor activation and expression.

A challenge in screening of novel targets has been to find out suitable, generic, robust and sensitive assays to enable high-throughput screening of large libraries in miniaturized volumes. To make assays for ligand binding in homogeneous format generally requires specific labeling of each ligand – or agonist/antagonist – and to follow up receptor activation by secondary messengers, such as cAMP and IP3, set demands to finding good binding partners and find rapid assay kinetics.

We will describe how europium-labeled GTP can be used as a generic tool to measure GPCR activation through GTP binding assay. GTP labeled with highly luminescent europium terpyridine chelate using a linkage making it non-hydrolysable upon binding to G-protein can be used to monitor ligand binding and receptor activation. We have developed both heterogeneous and homogeneous assays to GTP binding assay, as well as assay for ligand binding, and assays for various secondary messengers based on europium chelates.

Application of an external quencher into the assay allows us to develop direct homogeneous assays without any specific secondary binder carrying energy acceptor. QRET is exemplified here in an assay for GTP binding GPCR and in assay for cAMP as secondary messenger.

Paramagnetic pH-sensitive liposomes with improved MRI properties

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Keywords: Lanthanides; Applications; MR Imaging agents; pH-responsive probes

The MRI visualization of drug release needs the development of probes whose MRI response can be sensitive to endogenous and external applied stimuli that can induce the drug release from the nanocarrier, thus modulating and promoting the drug efficiency.[1] Liposomes are phospholipid-based bilayered nanovesicles entrapping an aqueous cavity that are widely used in drug delivery applications. In this work, paramagnetic liposomes exhibiting T_1 contrast enhancement due to pH-triggered probe release from the liposomal cavity were prepared and tested.

pH sensitive paramagnetic liposomes were formulated with a bilayer made of POPE (palmitoyl-oleoyl-phosphatdyl-ethanolamine), THS (α-tocopherol-hemisuccinate) and cholesterol (44/11/44 in mol%). The vesicles were encapsulated with different hydrophilic paramagnetic Gd(III) complexes and were tested in buffers at different pH values.

At physiological pH, the relaxivity of the system is controlled by the water permeability of the liposome, whereas upon acidification, the protonation of THS simultaneously induces the aggregation of the liposomes and a destabilization of the membrane with the consequent release of the entrapped MRI agent, thus resulting in a relaxivity enhancement. The probe release represents a good improvement with respect to pH sensitive MR liposomal preparations reported so far.[2]

pH-sensitive liposomes encapsulating a Gd(III) complex are promising candidates for in vivo visualization of drug delivery and drug release using MRI. Such probes may be useful for monitoring pathology where physiological parameters are altered. Moreover, they may be used for the quantification of *in situ* drug availability and delivery by exploiting the excellent spatio-temporal resolution of the MRI technique.

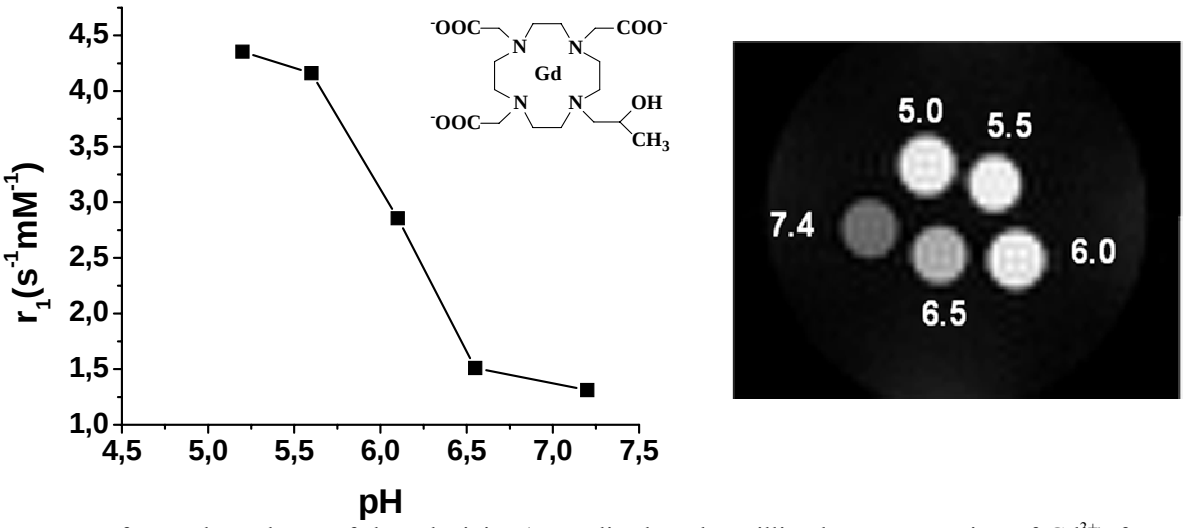

Figure 1. Left: pH dependence of the relaxivity (normalized to the millimolar concentration of Gd^{3+}) for a pH sensitive liposomes encapsulated with the clinically approved complex Gd-HPDO3A (25°C, 0.47 T). Right: T1w-MR image of a phantom containing the liposome suspension at different pH values. (25°C, 7 T).

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Self-assembled heteropolymetallic complexes as MRI contrast agents.

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Keywords: Lanthanides; Chemistry; Coordination

Magnetic resonance imaging (MRI) is currently routinely used as a diagnostic tool in various medical procedures. In recent years, efforts have been directed towards the finding of contrast agents with improved characteristics such as increased efficiency and organ specificity. Our approach in achieving such goals explores slowing down the rotational motion of the contrast agent by formation of large molecular weight supramolecular structures. A new promising class of these supramolecular structures is the so-called **metallostars**. These are metal complexes build by self-assembly containing a central d-metal ion and peripheral lanthanide ions. For the synthesis of the complexes, novel ditopic ligands were developed. These ligands contain a DTPA-derivative as a binding unit for the lanthanide ion and a catechol, a 8-hydroxyquinoline or a 1,10-phenantroline derivative as a binding unit for Fe(III), Al(III), Ga(III) or Ru(II) ions. The luminescence studies show a clear indication for the formation of supramolecular complexes. Further studies towards the relaxivity, biodistribution and phisico-chemical properties of the complexes are underway.

Insights into The Self-Assembly of a New Family of Dissymmetric Tripodal Ligands with Lanthanides

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Keywords: Lanthanides; Bimetallic Helicates; Dissymetric Tripodal Ligands

The improvement of the Ln(III) luminescent and magnetic properties requires a judicious design of ligands, in particular tripods[1]. In this work, two new asymmetric tripodal ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ differing by the length of the bidentate pendant arm (see Figure 1) have been synthesized, and their self-assembly with Ln(III) was investigated. The complexes were characterized in acetonitrile solution by means of spectrophotometry, ES-MS and luminescence. These ligands are supposed to provide a coordination cavity for eight-coordinated lanthanide cations, and to form monometallic complexes. However, the X-ray crystal structure of the europium complex with $\mathbf{L^1}$ ([M]/[**L**] = 1:1) revealed a dimeric form in the solid state. Herein, the solution properties of Ln(III) complexes with both ligands and the effects of the spacer length will be discussed.

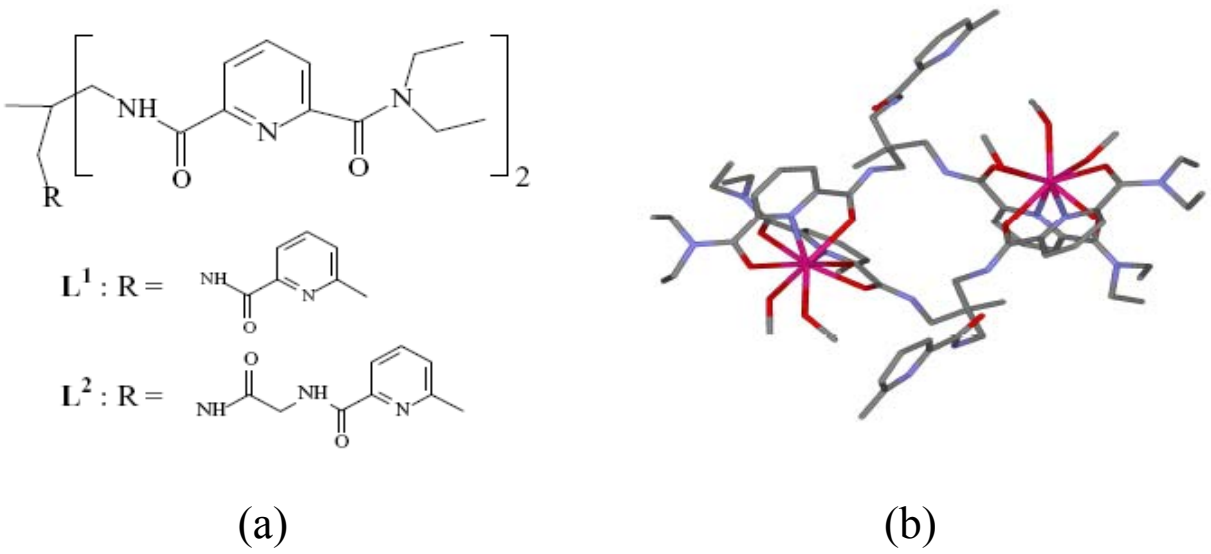

Figure 1. (a) Chemical structure of $\mathbf{L^1}$ and $\mathbf{L^2}$ showing different bidentate arms. (b) X-ray crystal structure of the bimetallic complex $[Eu_2\mathbf{L^1}_2(CH_3OH)_6]^{6+}$.

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Fluorinated Responsive Lanthanide Complexes for 19-F MRS/MRI

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Keywords: Lanthanides; Chemistry; Coordination, Spectroscopy.

Summary Fluorinated probes are an attractive tool for MR spectroscopy and imaging applications for biological studies *in vivo*, thanks to high NMR sensitivity, large chemical shift range (>300ppm), accompanied by a near – zero endogenous background. The slow longitudinal relaxation rate of the ^{19}F nucleus (1 s^{-1} in CF_3 groups) limits the number of transients acquired in a given time interval. A solution to this problem is to place the ^{19}F nucleus close to a paramagnetic lanthanide ion, in a kinetically stable complex or conjugate, leading to much shorter T_1 (and T_2) relaxation times. This allows faster signal acquisition, and the amplification of the chemical shift sensitivity to changes in the microenvironment. These properties are being studied to develop responsive probes able to monitor pH and enzyme activity.
A series of fluorinated lanthanide (III) complexes of mono-amide ligands based on 1,4,7,10-tetraazacyclododecane has been synthesised, Fig. 1, and their ^{19}F NMR spectral properties assessed. The electron-withdrawing nature of the substituents in the aromatic ring determines the pK_a of the amide proton which reflects in the variation of the chemical shift of the CF_3 group, as a pH responsive feature. The acid-base equilibrium is fast on the NMR timescale, therefore only one signal is observed, corresponding to the weighted average of the chemical shifts of the amide and its conjugate base.
The introduction of an ester group allows probes to monitor the activity of enzymes such as esterases. For certain ortho-substituted complexes, two isomers are observed with a chemical shift non-equivalence of 50 ppm. Ester hydrolysis may be monitored by following the change of the relative intensity of the two resonances.

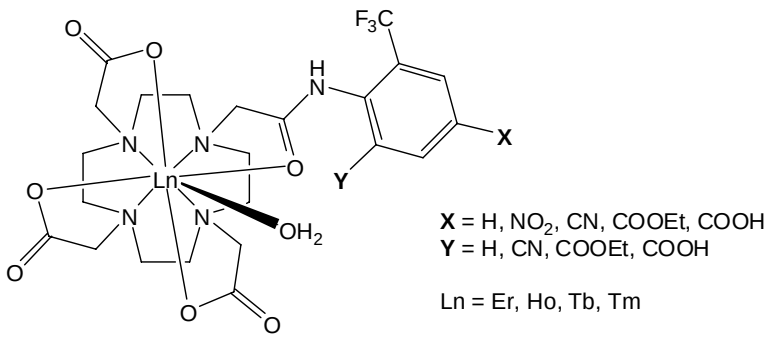

Figure 1 General structure of fluorinated macrocyclic lanthanide complexes.

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On-chip Multiplexed Immunohistochemical Assays based on Lanthanide Luminescence bioprobes

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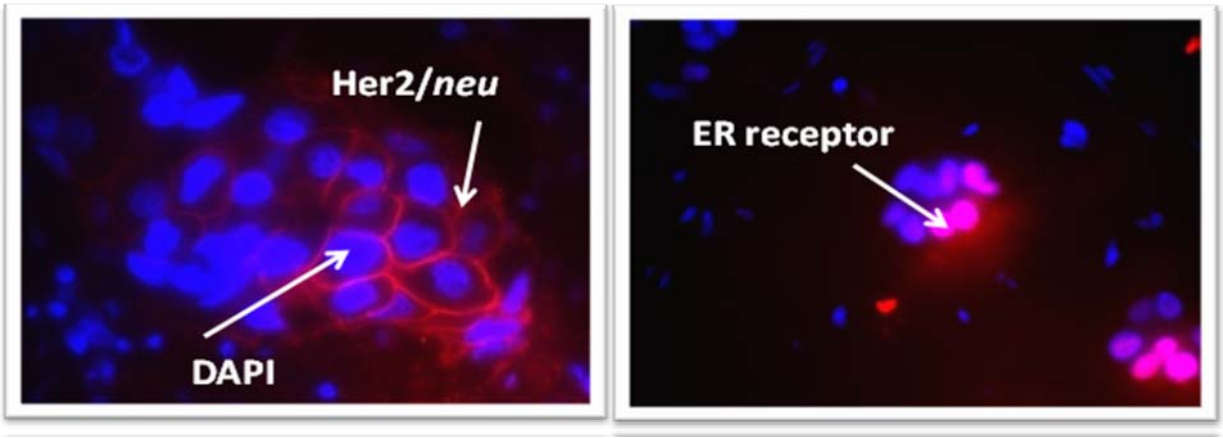
Keywords: Lanthanide; bioprobe; bioinorganic chemistry; Lab-on-Chip; Immunohistochemistry

The development of miniaturized bio-analytical systems is an ever-growing field of research[1] for the characterization of predictive biomarkers in malignant tumours and the follow-up of the disease during treatment.[2] We present here a quite innovative effort in integrating the benefits of time-resolved lanthanide luminescent probes in a microfluidic device, for the fast multiplexed analyses of tumour markers on cancerous tissues. This approach involves the development of a panel of Ln-labelled tumour-associated antibodies which allow time-resolved imaging. In this way, the localization of the tumour markers can be easily traced on the cancerous tissue where the immune complexes have bound.

The red-emitting Eu-W8044 and green-emitting Tb-W14016 chelates (PerkinElmer) were used in this assay, as they feature adequate photophysical properties and possess an active group for easy protein coupling. Duplex assays featuring simultaneous detection of estrogen receptors (ER) and the human epidermal growth factor receptors 2 (Her2/*neu*) on breast cancer tissue sections are shown. The Lab-on-a-Chip lanthanide-based assay shows good specificity and an enhanced sensitivity compared to conventional organic dyes.



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Investigations of Lanthanides Complexes with Short Symmetrical Tripodal Ligands

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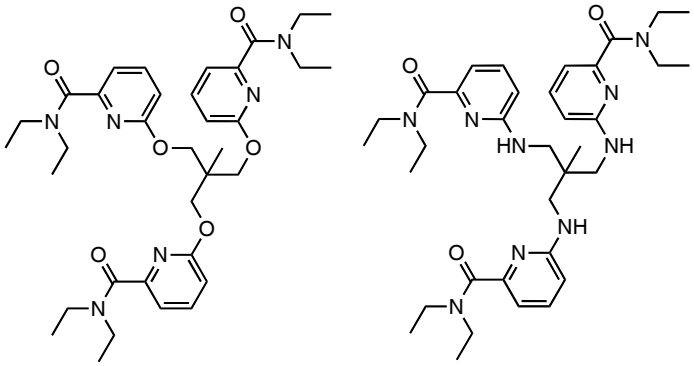
Keywords: tripodal ligands, lanthanides, coordination chemistry, crystal structure

Recently, the short tripodal receptors have been designed for the preparation of three-dimensional tetrametallic helicates.[1] In this work, the multistep synthesis of two structurally similar symmetric tripodal ligands **L1** and **L2** has been prepared using a modified catalytic procedure.[2] The lanthanide complexation is achieved by the coordination units of the type 'O-N-O' or 'N-N-O', respectively. The reaction of **L1** with europium leads to the formation of a monometallic tripodal complex, which has been characterised by X-ray crystallography. The luminescent and thermodynamic properties of the complexes along the lanthanide series will be discussed in view of potential applications for sensing purposes.



L1 **L2**

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Enlarging the capability of lanthanide helicates as bioprobes: nanoparticles and multi-photon excitation

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Keywords: Lanthanide; Bioprobe; Spectroscopy

Recently, many unique advantages of using bimetallic triple helicates as lanthanide luminescent bioprobes (LLB) have been demonstrated. [1] In this work we explore enlarging the capability of these compounds by using multi-photon excitation and by formation of surface-functionalized nanoparticles. In particular, $[Ln_2(L^{C2})_3]$ (Ln = Eu^{III}, Tb^{III}) [2] and $[Eu_2(L^{C5})_3]$ [3] were found to exhibit three- and two-photon sensitized luminescence, respectively, when excited at 800 nm by a femtosecond laser. Moreover, on the way to increase the sensitivity of LLBs, $[Eu_2(L^{C2})_3]$ was encapsulated into silica nanoparticles (~60 nm) the surface of which was functionalized with –SH or $–NH_2$ groups. The photophysical properties remain reasonable for $[Eu_2(L^{C2})_3]$@SiO_2/–SH with almost the same overall quantum yield (20%) and slightly decreased lifetime (3.1 ms) compared with surface-unmodified nanoparticles (25%, 3.4 ms), while for $[Eu_2(L^{C2})_3]$@SiO_2/$–NH_2$ significant decrease in Q^L_{Eu} was observed. So, $[Eu_2(L^{C2})_3]$@SiO_2/–SH can be considered to be a promising precursor for further bioconjugation with proteins and *in cellulo* tests.

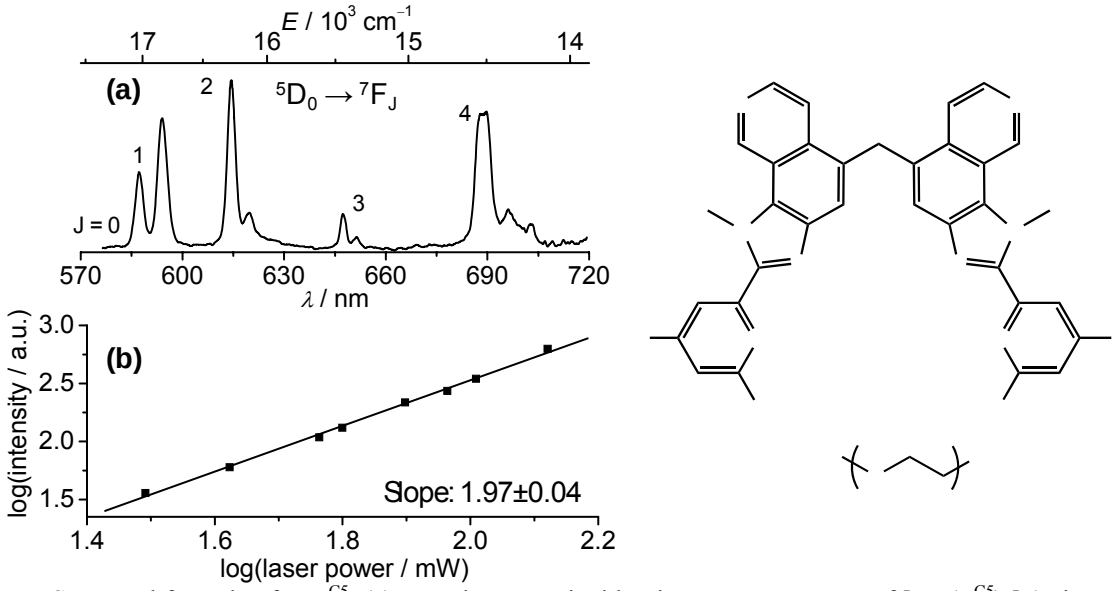

Figure 1. Structural formula of H_2L^{C5}; (a) two-photon excited luminescence spectrum of $[Eu_2(L^{C5})_3]$ (Tris-HCl, c = $1.67 \cdot 10^{-4}$ M, pH = 7.4) and (b) dependence of sensitized luminescence *vs.* incident laser power.

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Lanthanide Complexes as Bioprobes

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Keywords: Lanthanides; Chemistry; Coordination; Spectroscopy

Summary One of the fundamental goals in biology is to understand the complex spatio-temporal interplay of biomolecules from the cellular to the integrative level. To study these interactions, we have utilized the unique photophysical properties of lanthanides to develop systems for specific localization and to act as bifunctional molecular probes. In this report, we seek to develop optical probes for both cellular imaging and in vitro assay detection.

Recently, we have examined different methods of probing biological structures using various functionalised lanthanide complexes as emissive probes. Lanthanide systems for singlet oxygen generation, imaging of cell proliferation in cancer cells and sensing of biological species have been explored with different techniques such as spectral imaging and two photon excitation [1, 2].

Current efforts focus on the design and synthesis of next generation probes, based upon the design of certain azaxanthone systems that show very good photophysical properties for cellular imaging, to study various biological functions and pathways.

The improvement in our mechanistic understanding of such systems has opened up the possibility of studying more complex intracellular behaviour at a sub-cellular level.

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Self-Assembly of Tridimentional Tetranuclear Helicates with Lanthanides

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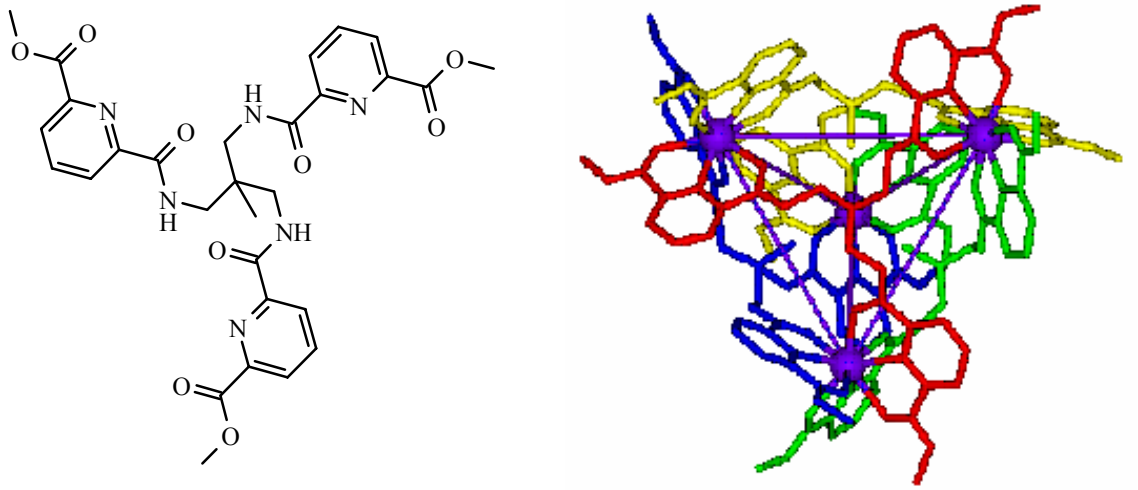
Keywords: Lanthanides; 3D Helicates; Tripodal Ligand; Self-Assembly

Recently, several Ln(III) complexes with tripodal ligands [1] were prepared in order to develop stable luminescent and paramagnetic devices. Herein, we report on the synthesis and the coordination properties of a tripodal ligand **L**, which has been designed for Ln(III) coordination by taking advantage of the chelating effect of 2,6-dicarbonylpyridine subunits. These subunits are connected by a short spacer to prevent the formation of mononuclear complexes.

The self-assembly process of the receptors **L** with lanthanides cations at stoechiometric conditions results in the formation of discrete tetranuclear complexes $[Ln_4\mathbf{L}_4]^{12+}$.[2] X-ray crystallography shows that nine-coordinated cations are linked by ligands to provide regular tetrahedral complexes in the solid state, in which every ligand **L** coordinates three different Ln^{3+} cations (one by arm) and each metal center is complexed by three different ligands. Structural parameters will be compared with analogous complexes bearing terminal carboxamide groups. These remarkable, highly charged 3D edifices are maintained in solution as demonstrated by NMR spectroscopy, ESI-MS and spectrophotometric batch titrations. Formation kinetics, thermodynamic parameters and photophysical properties of Ln(III) complexes (Eu-Lu) with **L** will be discussed.



L $[Lu_4\mathbf{L}_4]^{12+}$

Figure 1: Schema of **L** and the X-ray crystal structure of $[Lu_4\mathbf{L}_4]^{12+}$

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Poly-β-Cycldextrin based Platform for pH mapping via a ratiometric $^{19}F/^{1}H$ MRI method

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Keywords: Lanthanides; MRI applications; supramolecular structures; pH mapping

Mapping pH is an important task in Medical Imaging as changes in pH usually accompany the development of various pathologies including tumors, stroke, infection,…
Several paramagnetic metal complexes whose relaxivity is pH-dependent have been reported. However none of them have been yet succesfully applied in vivo because in order to have images reporting the pH map it is necessary to transform the observed changes in relaxation rates (R_1) in changes of relaxivities (r_1). This transformation requires the knowledge of the local concentration of the metal complex. A route to acquire this information may be pursued through the acquisition of the MR image of a heteronuclear signal originated from a molecule that displays the same "in vivo" biodistribution of the paramagnetic complex. Herein we report a supramolecular construct formed by: i) a Polycyclodextrin substrate that hosts ii) a suitably functionalized pH responsive Gd(III)complex and iii) an analogously functionalized ^{19}F-containing molecule (Fig 1). The binding to the PolyCD substrate is pursued through the introduction of an adamantane group on both Gd and F containing systems. Adamantane is known to have a high binding affinity to β-CD cavities. The proof of concept of this approach has been obtained by acquiring the ^{1}H and ^{19}F-MRI images of a phantom consisting of four tubes filled with solutions of Gd/F/PolyCD adduct at different values of concentration and pH. As shown in Figure 1A the ^{1}H-MR image does not account for a proportional change in contrast with pH because the observed R_1 is dependent on both pH and concentration. Through the acquisition of the ^{19}F-MR image it has been possible to assess the concentration of the adduct in the four tubes thus allowing the $R_1 \rightarrow r_1$ transformation (Fig. 1B). The method proved to work well with a small (1-2%) error in the pH assessment. Finally the Poly-CD/F/Gd adduct can be edowed with targeting properties by hosting in one of the empty β-CD cavities an adamantane functionalized moiety able to provide the system with the proper recognition towards the target of interest.

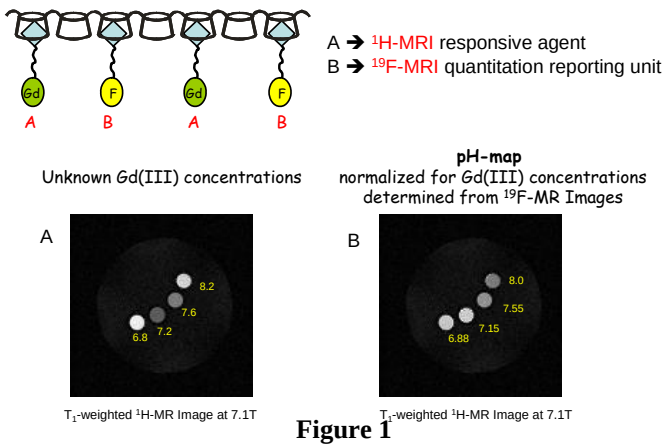

Figure 1

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