Rare-Earth and Transition Metal
Solid State and Coordination Chemistry

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Abstract. The research programme at the Chair of Inorganic Chemistry I at the Department of Chemistry of the Universität zu Köln is reviewed briefly.

Introduction

Transition (d block) and rare-earth (f block) metal halide chemistry is rich of oxidation states. In solid state chemistry, such oxidations states are of special interest that are lower than the respective group number.

Elaborate synthetic routes have been developed to explore the respective systems and to grow crystals for structure determination and to prepare pure samples for further characterization.

Coordination chemistry of a number of transition metal and rare-earth metals takes closed-shell ions or such with high magnetic moments as cetral ions and O- or N-donor ligands into accunt.

Solid State Chemistry: The Reduction of Rare-Earth Metal Halides with Unlike Metals – Wöhler's "Metallothermic Reduction"[1]

Metal halides (such as PrI_3) are reduced with alkali metals yielding not only binary halides (as PrI_2 and Pr_2I_5) but also cluster complexes ($Cs_4Pr_6I_{13}C_2$, with some carbon in the reaction mixture). These cluster complexes are in fact *anti*-Werner complexes[2] when re-written as $\{(C_2)Pr_6\}I_{13}Cs_4$: A dicarbon unit is encapsulated in a praseodymium octahedron ("cluster") which is surrounded by and connected through iodine ligands with additional cesium atoms filling space and contributing electrons.

Cluster complexes may be molecules such as in $\{Sc_4C_{10}Sc_{20}\}I_{30}$, consisting of a truncated hollow T4 supertetrahedron of iodine stuffed with a T3 supertetrahedron of scandium that encapsulates the adamantoid cluster Sc_4C_{10},[3] Fig. 1.
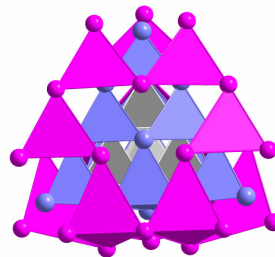

Figure 1: The molecular $\{Sc_4C_{10}Sc_{20}\}I_{30}$ cluster complex.

They may also be extended solids with various dimensionalities. Oligomeric cluster complexes are observed in $\{Ru_4Ho_{16}\}I_{28}\{Ho_4\}$[4] (Fig. 2), for example. The alternative to oligomers are chains, as seen, e.g., in $\{Os_3Sc_{12}\}Br_{16}Sc$[5] (Fig. 3) with eight-coordinate endohedral osmium atoms. The additional scandium atom is needed for its three electrons which makes for a 47-electron cluster complex, isoelectronic with $\{Ir_3Sc_{12}\}Br_{16}$. With $\{RuPr_3\}Cl_3$,[6] a first example of a seven-coordinate endohedral transition metal ion has been accomplished, see Fig. 4.

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[1] G. Meyer, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2537-2552.
[2] G. Meyer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2729-2736.

[3] L. Jongen, A.-V. Mudring, G. Meyer, *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 1886-1889.
[4] K. Daub, *Dissertation*, Universität zu Köln, **2009**.
[5] S. Zimmermann, *Dissertation*, Universität zu Köln, **2008.**
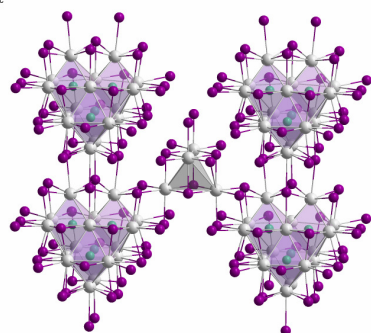[6] N. Herzmann, A.-V. Mudring, G. Meyer, *Inorg. Chem.* **2008**, *47*, 7954-7956.

Figure 2: Crystal structure of $\{Ru_4Ho_{16}\}I_{28}\{Ho_4\}$.

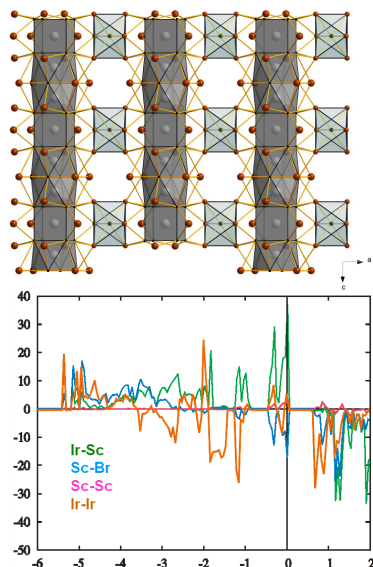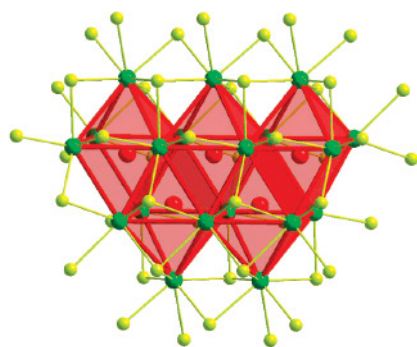**Figure 3:** Crystal and electronic structures of $\{Os_3Sc_{12}\}Br_{16}Sc$.

Figure 4: Chains of face-connected $\{RuPr_7\}$ clusters as observed in $\{RuPr_3\}Cl_3$.

Transition metal halides in low oxidation states are by no means understood. This becomes obvious by the crystal structure of TaI_4 which was only recently determined.[7] Against the dogma that it would be isostructural with NbI_4, the structure contains isolated tetramers (Fig. 4).
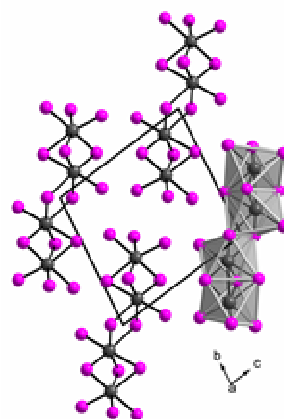

Figure 4: Crystal structure of $TaI_4 = Ta_4I_{16}$.

The enigma of "tantalum tribromide" of which crystals have been grown by reduction of $TaBr_5$ with aluminium has recently been solved. It includes, although statistically distributed, 70% $[TaBr_6]^-$ anions in the large hole of the structure of $\{Ta_6\}Br_{15}$ according to $\{Ta_6\}Br_{15}[TaBr_6]_{0,7}$,[8] see Fig. 5.
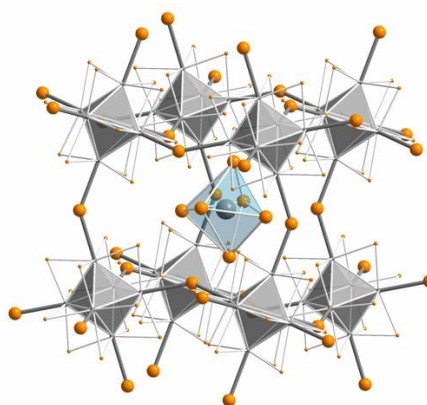
Figure 5: Crystal structure of "$TaBr_3$" = $TaBr_{2.74}$ = $\{Ta_6\}Br_{15}@[TaBr_6]_{0.7}$.

The Oxidation of Metals with Liebig Acids[9]

Except for Wöhler's Metallothermic Reduction a second synthetic route has been extraordinarily prolific throughout the years, the oxidation of non-noble metals with Liebig acids. These are all compounds with an acid hydrogen atom. There is a large variety of organic compounds with HO– or HN– functions with acid constants that allow for substitution of the hydrogen atom by a metal atom.

We have especially explored carboxylic acids yielding a large variety of new simple and complex salts, mostly coordination polymers. These include alkanoates as the isotypic propionates $M(OPr)_2$ (M =

[7] G. Meyer, R. Wiglusz, I. Pantenburg, A.-V. Mudring, *Z. Anorg. Allg. Chem.* **2008**, *634*, 825-828.

[8] K. Habermehl, *Dissertation*, Universität zu Köln, **2009**.

[9] G. Meyer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 201-222.

Mn, Fe; Fig. 6)[10] as well as benzoates like $Mn_{19}(OBz)_{38}(HOBz)_2$, anhydrous acetates like $Nd(OAc)_3$ or the complicated $[Eu_2(OAc)_6(HOAc)_2(H_2O)_2](HOAc)_4$ or heterobimetallic complexes as $[Dy_2Co(OAc)_4(H_2O)_2](HOAc)_2$.
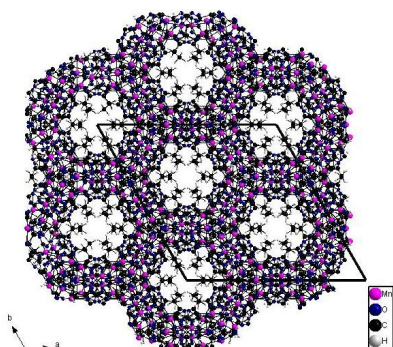
Figure 6: A view down the channels of the proprionates $M(OPr)_2$ (M = Mn, Fe).

The ammonium ion, $(NH_4)^+$, represents a special Liebig acid. It is available in a large variety of salts and may react as an acid/oxidant or as a (base)/reductant and is also a pseudo alkali-metal cation. Again, a large variety of compounds has been obtained by reaction of $(NH_4)X$ (X = F, Cl, Br) with non-noble metals: $Si(NH_3)_2F_4$ or $(NH_4)[Si(NH_3)F_5]$, $[Ni(NH_3)_6]-[TaF_6]_2$ and $(NH_4)_4[Ni(TaF_6)_6]$ as well as $(NH_4)_3[YCl_6]$, $[Zn(NH_3)_2]Cl_2$, $[Al(NH_3)_4Cl_2]-[Al(NH_3)_2Cl_4]$ including cluster complexes like $(NH_4)_6[Ta_5(NH)_4Cl_{17}]$, $K_4[Ta_6Cl_{12}]Cl_6$ and $[Fe(NH_3)_6]_3[Fe_8Br_{14}]$, to name only a few.

Transition Metal Coordination Chemistry

Further activities are located in the coordination chemistry of various transition metals (mercury, silver, nickel, platinum, iron, manganese) to explore the competition between N and O (multi-)donor ligands and auxiliary ligands.[11]

Many single and multi-N ligands have been explored. Of these, the ligand Tris-pyridyl-triazin (Tpt) has been especially prolific, even with simple co-ligands, like nitrate, see Fig. 7.

In certain cases, new ligands could also be synthesized under the influence of, for example, Hg(II), see the formation of the bis(N-imino-methyl-formamidate anion in $Hg(Imf)_2$[12] by ring-opening of 1,2,4-triazole, see Fig. 8.
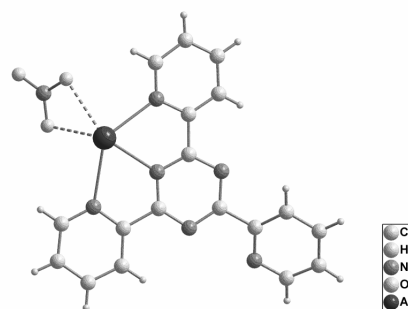
[10] S. Gomez Torres, *Dissertation*, Universität zu Köln, **2007**; Th. Bierke, *unpublished research*, **2008**.

[11] G. Meyer, P. Nockemann, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1447-1461; G. Meyer, M. Sehabi, I. Pantenburg, in: *Design and Construction of Coordination Polymer*s (M.-C. Hong, L. Chen, editors), Wiley-Interscience, **2009**.

[12] P. Nockemann, I. Pantenburg, G. Meyer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 613-615.
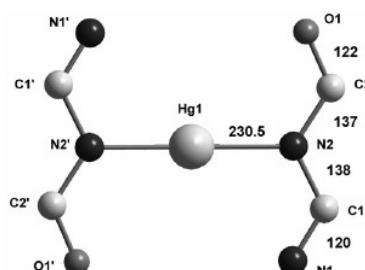

Figure 7: The complex $Ag(Tpt)(NO_3)$ in the solid state.

Figure 8: The $Hg(Imf)_2$ molecule in the solid state.

Mercurous complexes with N-donor ligands have also been explored, and are possible with bases less basic than pyridine. In certain cases also oxygen-containing mercurous compounds have been obtained with anti-SiO_2 type structures, as for example $[(Hg_2)_2O][Pb(NO_3)_3]_2$,[13] see Fig. 9.

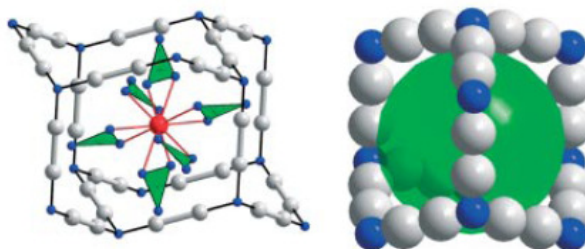**Figure 9:** Part of the crystal structure of $[(Hg_2)_2O]-[Pb(NO_3)_3]_2$, featuring the anti-cristobalite type cages incorporating nitratoplumbate anions.

Polyiodides and poly-interhalides

The influenece of the cation on the formation of polyiodide or poly-interhalogenide anions, isolated or polymeric, is also being studied. The cations are mostly encapsulated in crowns and cryptands, see for example $[Fe(12\text{-crown-}4)]I_{16}$[14] with the rare I_{16}^{2-} anion, Fig. 10.

[13] G. Meyer, M. Nolte, R. Berners, *Z. Anorg. Allg. Chem.* **2006**, *632*, 2184-2186.
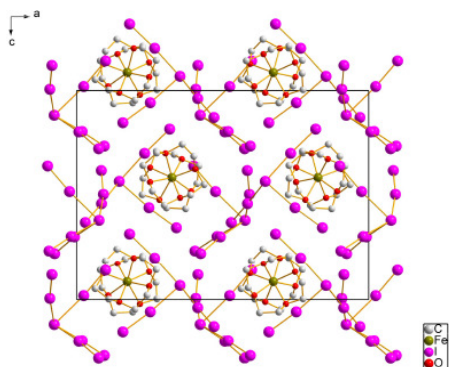
[14] C. Fiolka, *unpublished research*, **2009**.

Figure 10: Projection of the crystal structure of [Fe(12crown4)]I$_{16}$.

In some cases, rare-earth cations included in crown ethers have also been applied, as for example in [Gd(OH)(H$_2$O)(benzo-18-crown-6)]I(I$_3$)(CH$_3$CN)[15] which contains hydroxide-bridged dimers as well as iodide and triiodide anions, see Fig. 11.

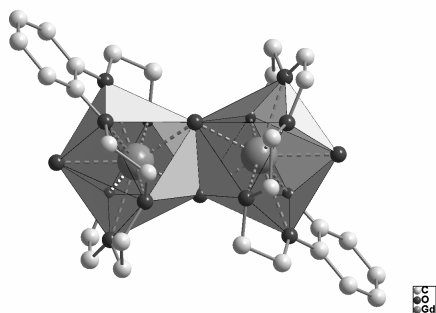**Figure 11:** The hydroxide bridged dimers as they appear in the crystal structure of [Gd(OH)(H$_2$O)-(benzo-18-crown-6)]I(I$_3$)(CH$_3$CN).

Anionic transition metal complexes have been introduced to compete with the polyiodide network. One observation is a chain of [Pd$_2$I$_6$]$^{2-}$ anions including iodine molecules,[16] see Fig. 12.

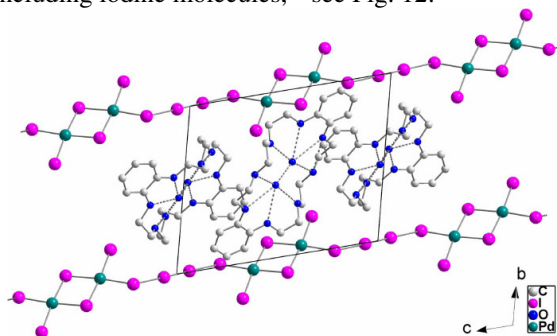**Figure 12:** Projection of the crystal structure of [(H$_5$O$_2$)(Dibenzo-24-crown-8)]$_2$[Pd$_2$I$_6$(I$_2$)].

Experimental Section

Synthesis. Starting materials were either purchased from usual commercial sources or made in the laboratory. Moisture and/or air-sensitive compounds were handled in nitrogen or argon filled dry boxes (Mbraun, Garching, Germany).

Crystal structures. Single crystals were selected under a microscope and sealed in thin-walled glass capillaries. Their quality was checked on a single-crystal X-ray diffractometer (Stoe Image Plate Diffraction System, IPDS I or II) and a complete intensity data set was collected using graphite-monochromated Mo-K$_\alpha$ radiation. The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data.[17] The programs used are Stoe's X-Area,[18] including X-RED and X-Shape for data reduction and absorption correction,[19] and the WinGX suite of programs,[20] including SIR-92[21] and SHELXL-97 [22] for structure solution and refinement. The last refinement cycles included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all of the hydrogen atoms. Crystallographic data for the respective structure have been deposited with the Cambridge Crystallographic Data Centre or at the Fachinformationszentrum Karlsruhe.

Crystal data for [Gd(OH)(H$_2$O)(b18c6)]-I(I$_3$)CH$_3$CN: C$_{18}$H$_{30}$NO$_8$GdI$_4$, 1053.28 g mol^{-1}; diffractometer IPDS-II, T = 170(2) K; $2\theta_{max}$ = 54.8°; 0° ≤ ω ≤ 180°, φ = 0°, 0° ≤ ω ≤ 180°, φ = 90°, $\Delta\omega$ = 2°, 180 images; -14 ≤ h ≤ 15, -24 ≤ k ≤ 24, -15 ≤ l ≤ 15; ρ_{calc} = 2.428 g cm^{-3}; 37766 measured reflections of which 6263 were symmetrically independent; R$_{int}$ = 0.1524; F(000) = 1940; μ = 6.626 mm^{-1}. Monoclinic, $P2_1/a$ (no. 14), a = 1233.8(1), b = 1925.0(2), c = 1252.3(1) pm, β = 104.38(1)°, V = 2881.2(5) 10^6·pm^3, Z = 4; R values: R$_1$/wR$_2$ for 4516 reflections with [I$_0$>2σ(I$_0$)]: 0.0542 / 0.1262, for all data: 0.0739 / 0.1371; S$_{all}$ = 1.027.

[15] C. Walbaum, I. Pantenburg, G. Meyer, , *Z. Anorg. Allg. Chem.* **2009**, *635*, in press.

[16] C. Walbaum, I. Pantenburg, G. Meyer, *Cryst. Res. Technol.* **2008**, *43*, 1183-1186.

[17] X-Shape 1.06, Crystal Optimisation for Numerical Absorption Correction (C), Stoe & Cie GmbH, Darmstadt, **1999**.

[18] X-Area 1.16, Stoe & Cie GmbH, Darmstadt, **2003**.

[19] X-RED 1.22, Stoe Data Reduction Program (C), Stoe & Cie GmbH, Darmstadt, **2001**.

[20] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

[21] A. Altomare, G. Cascarano, C. Giacovazzo, *J. Appl. Crystallogr.* **1993**, *26*, 343.

[22] G. M. Sheldrick, SHELXL-97; Programs for Crystal Structure Analysis, Universität Göttingen, 1997.