Synthetic Milestones in f Element Inorganic Chemistry

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Abstract. This paper highlights the chemical ingenuity and craftsmanship of Professor Gerd Meyer and his inorganic chemistry colleagues who have extended the tradition of synthesis of pure rare earth and actinide compounds. Inorganic synthesis is an intellectual discipline that is essential to most chemical, materials science, and solid state physics research. It requires broad understanding of principles of chemical thermodynamics, kinetics, acid-base chemistry, and chemical bonding relationships, as well as specialized skills and intuition that few scientists have mastered.

Keywords: f Elements; Solid State Chemistry; Coordination Chemistry

1 Introduction

Discovery is at the heart of many scientific disciplines. The preparation of novel chemical compounds of high purity is at the heart of chemistry. Many chemists recall their proudest and most inspiring moments when they viewed beautiful crystals of a new or purified substance before their eyes. John Corbett captured the essence of synthetic inorganic chemistry in many of his papers with his phrase "First comes the synthesis."

Chemical synthesis is both an artistic and a scientific endeavor. Rather than attempting to be comprehensive, this paper highlights the combination of artistic talent and scientific scholarship that has distinguished the essence of inorganic f-element compound synthesis as well as the careers of Gerd Meyer, his mentors, and his colleagues.

In this paper the term "lanthanides" includes all elements lanthanum through lutetium, abbreviated Ln. "Rare earths" includes Sc and Y. "Actinides" includes all elements actinium through lawrencium, abbreviated An.

2 Metals, Intermetallics, and Other Metal-Bonded Systems

The preparation of a pure chemical element in its elemental form has always been a goal of chemists and materials scientists. To reduce oxides or halides to metals, the synthetic inorganic chemist needs to select and design refractory containers and must be skillful to degas them to reduce compounds of the electropositive f elements to the pure metals. Of historical interest during the Manhattan Project, Leo Brewer's insights led to the use of cerium sulfide to manufacture refractory containers for reduction of plutonium [1, 2]. The use of degassed tantalum crucibles for synthesis of rare earth metals was pioneered by Spedding and Daane [3]. Corbett [4], Meyer, and others extended the use of tantalum crucibles in many studies of reduced metal halides.

Synthesis of pure actinide metals requires adroitness with materials in solid, liquid, and gas phases. Neptunium metal has recently been made by reduction via electrodeposition from solution, amalgamation at a mercury cathode, and purification by distillation [5].

3 Binary compounds

Lanthanide and actinide oxides
Most chemists consider that oxides are easy compounds to synthesize, because most metallic elements form oxides in air. The term "rare earths" refers to oxidic minerals in which many of the 4f elements are found in nature. Oxides of f elements are sufficiently basic that they must be purified from carbonate from atmospheric

CO_2. The stoichiometry of many oxides, for example those of Pr, Tb, U, Cm, and Cf, varies with preparative conditions, in particular with temperature and quenching conditions.

Oxides of unusually low and high oxidation state are special synthetic challenges. Among the binary f-element oxides in the latter category, four syntheses stand out:

Sesquioxides of the lanthanides and of most actinides are very well characterized. However there are no sesquioxides of Th, Pa, U, or Np. Even Ce_2O_3 and Pu_2O_3 must be reduced from dioxide via conproportionation with metal or other reductants at 1500 °C or higher. This may seem surprising because the trivalent aqueous ions Ce^{3+}, U^{3+}, Np^{3+}, and Pu^{3+} and many trivalent compounds of these elements are well known. The reason for the synthetic obstacle is thermodynamic as well as kinetic: the fluorite-structure dioxides are both very stable (creating miscibility gaps between An and AnO_2 in the Th-Np oxide phase diagrams) and very inert (requiring high temperatures to achieve solid-solid reactions). The marginally stable sesquioxides Ce_2O_3 and Pu_2O_3 (with respect to disproportionation) can only be synthesized under exotic high-temperature conditions [6-8].

Neptunium pentoxide: The stoichiometry and all other properties of the highest neptunium oxide was unknown for several decades. Neptunium pentoxide, Np_2O_5, was prepared by several unusual routes. Finally single crystals were synthesized recently under mild hydrothermal conditions [9], a relatively new tool in the synthetic chemist's toolbox.

Hyperstoichiometric plutonium dioxide, PuO_{2+x}, was probably seen by many plutonium scientists in colorful "dioxide" samples prepared by various routes [10]. Haschke et al. [11] succeeded in convincing most of the world's actinide chemists that PuO_{2+x} with $x \leq 0.3$ really can be produced by careful reaction of PuO_2 with water vapor or moist air at about 350 °C.

Monoxides. Other than EuO, Eu_3O_4, and possibly YbO, there are no stable solid f-element monoxides [7]. Synthesis of EuO and Eu_3O_4 requires reducing high-temperature conditions similar to those for Ce_2O_3. Metastable solid monoxides of several other lanthanides have been synthesized from a mixture of metal and sesquioxide at high pressures (15-80 kbar and 500-1200 °C). These monoxides are metallic in character, with electronic structures represented as $(Ln^{3+})(O^{2-})(e^-)$. Upon rapid cooling they do not disproportionate. They are metastable at room temperature but stable at high pressure because the molar volume of the solid product $(Ln^{3+})(O^{2-})(e^-)$ is less than that of the solid reactants $(LnO_{1.5} + 0.5Ln)$, i.e. there is a negative $P\Delta V$ term in the free energy that makes the free energy of the conproportionation reaction favorable (negative) at high pressure.

Monoxides, dioxides, and trioxides of most lanthanide and of many actinide elements are known in the gas phase. Although there are reports of solid monoxides of some actinides (in particular UO, NpO, PuO, and AmO) the reports are usually based on X-ray powder patterns of rock salt structures that in some cases have been shown to be surface impurities such as oxynitrides. This author is unaware of attempts or successes to prepare bulk actinide monoxides either by vapor deposition or by high-pressure conproportionation. Such syntheses remain a challenge for the next generation of synthetic chemists.

Lanthanide and actinide hydrides

Hydrides of most f elements are best synthesized from the elements. Because the only method of synthesis is from the elements, the kinetics of the metal-hydrogen reaction at the solid-gas interface dominate discussions of syntheses [12]. For the lanthanides and for actinides Np-Cf the product is typically $LnH_{2+\delta}$ or $AnH_{2+\delta}$ where $\delta \leq 0.9$ [13]. Some dihydrides have also been prepared. Protactinium and uranium form stoichiometric or nearly stoichiometric AnH_3. Thorium is the only element for which a higher hydride (Th_4H_{15}) is known.

Lanthanide and actinide trichlorides, tribromides, and triiodides

These and many other halides are very hygroscopic. Pure trihalides typically require specialized apparatus and great skill to prepare. As is the case with oxides, these and other halides are of fundamental and applied interest. Synthesis of anhydrous halides is also important because they are synthetic precursors for complex halides and organometallic compounds.

Synthetic procedures for lanthanide and actinide trichlorides are found in many places. The monograph by Brown [14] is comprehensive, describing syntheses known by 1968. The most comprehensive and recent synthetic procedures are those pioneered by Meyer [15].

Actinide hexafluorides and lower binary fluorides

Among the first hexafluoride synthesized were those of osmium and uranium [16], both from the elements. More elegant methods have been developed, but almost all use elemental fluorine. Perhaps the most elegant synthesis of a thermodynamically unstable compound is that of PtF_6, made as an unstable byproduct of the combustion of Pt in the form of a hot wire with elemental fluorine [17].

Almost all hexafluoride syntheses require elemental fluorine, typically at temperatures where a significant fraction of F_2 is dissociated. UF_6 can be prepared without use of fluorine [18]:

$$UF_4 + O_2 \rightarrow UF_6 + UO_2F_2 \ .$$

Synthetic procedures for lanthanide fluorides were reviewed by Brown in 1968 [13] and more recently by Müller [18a]. Synthetic procedures for actinide fluorides were reviewed by Freestone and Holloway [18b].

The pentafluorides are synthetic challenges because of their marginal stability, between stable tetrafluorides and volatile hexafluorides. Neptunium pentafluoride has been prepared from precursors [18c], the most recent being by reaction of $NONpF_6$ with LiF and BF_3 in anhydrous HF [19]. The precursor $NONpF_6$ is also an unusual Np(V) compound, synthesized [20] from FNO and NpF_6 under UV irradiation. Plutonium pentafluoride has thus far escaped synthesis, despite innovative attempts in the solid [21] and gas phase [22]. It is believed to be unstable with respect to disproportionation [18b]. However, $NOPuF_6$ has been synthesized [20] from FNO and PuF_6, without the need for UV irradiation.

Halides with f-element oxidation state equal to or less than 2.0

Reduced lanthanide halides (typically $LnCl_2$ but also sesquihalides such as Gd_2Cl_3 and ternary halides such as $CsDyCl_3$) require strongly reducing conditions. In general these are synthesized by metallothermic reduction: conproportionation of trihalide and metal (lanthanide metal for $LnCl_2$, Gd_2Cl_3, etc., or alkali metal for $CsLnCl_3$, etc.) in sealed fused silica or tantalum vessels [29, 29a]. Dihalides of Am, Cf, and Es have been synthesized by milder methods, such as reaction of Am metal with HgX_2 or even reduction of trihalide with hydrogen, because Am is the actinide analogue of Eu, in which the dipositive ion is slightly stabilized by the f^7 electron configuration and because the actinides heavier than Bk show increasingly stable +2 oxidation states. In general these syntheses remain to be reproduced because of the difficulty in obtaining long-lived Am-Es isotopes, even in national laboratories, and in handling these isotopes on microgram or larger scale [29b].

Synthesis of Bk dihalides was attempted by a nuclear "hot chemistry" technique: observing the phase transformations upon allowing β^- decay of the [249]Bk in the [249]Bk trihalides over a period of more than a year. It was conjectured that the electrons released in β^- decay might reduce the Bk or its progeny Cf. This did not occur; the trihalides transformed into $(Bk\text{-}Cf)X_3$ solid solutions, ultimately into Cf trihalides [29c].

As is the case for monoxides, the author is unaware of bulk syntheses of any reduced (divalent) actinide halides, either binary or polynary, of actinides lighter than Am or of Cm. This is another challenge for future synthesis.

A summary of the production of reduced halides containing divalent rare earths has been published by Meyer [29d]. In his paper, dedicated to his "doctor father" R. Hoppe, he focused on metallothermic reduction as developed for the first production of rare earth metals by W. Klemm, his "doctor grandfather" and other pioneer synthetic chemists.

4 Complex compounds

Polynary oxides and halides

This section is restricted to those polynary compounds in which f-element ions of unique oxidation state or coordination have been created.

During the preparation of Li_4NpO_5 and other Np(VI) oxides, Keller *et al.* [23] found that some of these materials dissolved in alkaline solution to produce green solutions. They did not recognize that Np(VII) was produced. Finally in 1967 Krot and Gel'man [24] announced the synthesis of Np(VII) and Pu(VII) in alkaline solution. Within a few years a large number of Np(VII) and Pu(VII) polynary oxides had been synthesized. Several more years were required to characterize these compounds structurally. One of the first to be discovered, Li_5NpO_6, was only partially characterized by X-ray powder diffraction because, like many complex oxides containing both low-Z and high-Z elements, only the actinide element has a high X-ray scattering factor. It was more recently characterized by neutron powder diffraction [25].

The +3 through +6 oxidation states of plutonium were established in USA during the Second World War [26]. During the Manhattan Project studies, electrolytic oxidation of alkaline solutions of Pu(VI) and chemical oxidation with Ag(II) in dilute HNO_3(aq) showed no evidence of further oxidation of Pu(VI) [27]. Several ternary Pu(VII) oxides are now known. Evidence for Pu(VIII) in a ternary oxide has recently been published.

Most of these polynary oxides display actinide oxidation states that are unknown in binary oxides: Li_4PuO_5 is a Pu(VI) oxide but anhydrous PuO_3 is not known; Li_5NpO_6 is a Np(VII) oxide but anhydrous Np_2O_7 is not known. Thus the synthetic chemist can find new oxidation states in complex compounds that stabilize unusual metal oxidation states.

It should be noted that much interest in synthesis of rare earth complex oxides has been focused since the first announcement in 1987 of the many high-temperature superconducting (HTSC) oxides that contain Y^{3+}, La^{3+}, and other rare earths. This paper does not discuss the synthetic techniques used to prepare these compounds in polycrystalline form, as single crystals, as thin films, and as components of wires: sol-gel techniques, metal-organic chemical vapor deposition, "soft chemistry" (chimie douce) from coordination-complex precursors, spray pyrolysis, freeze drying, etc. It notes simply that many HTSC oxides required careful duplication or improved syntheses in other laboratories to establish their purity and their unique properties.

Complex f-element trichlorides, tribromides, and triiodides have been comprehensively studied, beginning with synthesis and following through to structural, spectroscopic, and electronic-structure characterization, by Meyer [28] and coworkers. He has mentored many colleagues and students in this area, including the author of this article. He reviewed the syntheses of these compounds, "dry" (from anhydrous binary halide precursors), "wet" (from aqueous or other solutions), ammonium-halide-complex, melts, or other routes [28].

Just as polynary oxides can be synthesized with higher f-element oxidation states than the corresponding binary oxides can be synthesized, unique oxidized polynary halides can be similarly synthesized. The simplest example is Cs_2CeCl_6, first synthesized in 1966 [30]. It is interesting to note that the corresponding complex chloride of plutonium was synthesized much earlier, and those of americium and berkelium later. The author has attempted but not succeeded to prepare the corresponding tetrachlorides $CeCl_4$ and $PuCl_4$ by inert matrix deposition and metathesis (unpublished studies). There is evidence for higher oxides and halides such as PuO_3 and $PuCl_4$ in the gas phase, so these also remain as challenges for future syntheses. A parallel exists for lanthanide tetrafluorides; only CeF_4, PrF_4, and TbF_4 are known as pure solids whereas complex tetrafluorides of unstable Pr^{4+}, Tb^{4+}, and the very unstable Nd^{4+} and Dy^{4+}, have been prepared by fluorination [18a, 28a].

5 Coordination compounds and organometallic compounds

Synthesis of the coordination complexes and organometallic compounds of the five elements is beyond the scope of this article. Because organometallic compounds usually require strictly anhydrous and oxygen-free conditions, polar solvents such as acetonitrile, Schlenk lines and inert-atmosphere box techniques are primary tools of organolanthanide and organoactinide chemists.

6 Concluding remarks

This paper describes how Professor Gerd Meyer and his contemporary synthetic inorganic chemist colleagues have built on the long tradition of inorganic synthesis in the area of f elements. The author is well aware of many other monographs and reference works that have been written for the synthetic inorganic chemist, in particular the *Inorganic Syntheses* series begun by Booth [30a]. The most recent volume in this series is volume 35 [31]. Encyclopedic treatises have been compiled by Brauer [32], Hagenmuller [33], Zuckerman and Hagen [34]. Monographs on techniques of inorganic synthesis include those by Jolly [35], Rao [36], and Herrmann [37]. The *Gmelin Handbuch der Anorganischen Chemie*, with multiple volumes on each element and its compounds, published until at least 1997 and still available in many research libraries, is authoritative and comprehensive. As in the case for many other disciplines, Gerd Meyer and his colleagues "have stood on the shoulders of giants."

The tradition of synthetic chemistry is to prepare chemical substances as pure as the state of the synthetic chemist's art will allow. This tradition was considered by some as an end in itself but nowadays the synthetic chemist is usuallly a member of a team motivated by the unique properties of specific chemical substances. Synthesis is typically followed by chemical analysis and structure determination. Determination of important physical properties (spectroscopic, magnetic, thermodynamic, etc.) requires that substances be sufficiently pure (including "minor" impurities that give rise to spurious magnetic or spectroscopic signals, as well as amorphous phases not detected by crystallography) that materials scientists, catalytic chemists, and engineers of many disciplines will be able to utilize these properties for productive applications.

Many chemists of the past centuries were sufficiently "generalists" rather than specialists so that they could be skilled in synthesis as well as in structure determination, and elucidation of physical properties. Synthetic chemists of this century typically work in teams. Their skills are essential to many other disciplines

(physical chemistry, spectroscopy, materials science). It is essential that specialists in a wide rande of scientific and engineering disciplines recognize and appreciate how important it is that, as John Corbett wrote, "First comes the synthesis."

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