

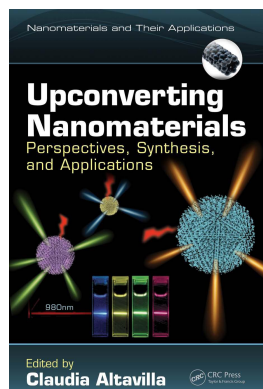
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Claudia Altavilla

A Perspective on Lanthanide Chemistry

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Section I

Syntheses, Mechanism, and Functionalization



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A Perspective on Lanthanide Chemistry

Simon A. Cotton

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1.1 Introduction

Although we now see lanthanides as a mature area of chemistry, lanthanide chemistry was slower to develop than the chemistry of the transition metals, and it is instructive to consider the reasons for this.

1.2 How Many Lanthanides?

Although the first ores of these elements were isolated at the end of the eighteenth century, it was over a century before scientists knew how many lanthanides were there (Evans 1996). In 1787, Arrhenius discovered ytterbite (soon renamed as gadolinite), which was later found to principally contain yttrium, lanthanum, cerium, and neodymium, along with smaller amounts of several other lanthanides. It was Johan Gadolin, who in 1794, isolated yttrium oxide from this ore.

The scene was set for a period of a confused endeavor. The similarity in the properties of the lanthanides made the separations, particularly of adjacent

elements, extremely difficult, depending as they did on the techniques such as fractional crystallization. One of the greatest of the early rare-earth researchers, Charles James (a British-born chemist carrying out his research in the United States), reported that “The most important point proved by this work is that the element, giving the characteristic absorption bands of thulium, cannot be separated into simpler substances. After about 15,000 operations the absorption spectrum underwent no change” (James 1911, p. 1342). James was one of the three researchers, who in 1907, discovered lutetium, the last stable lanthanide waiting to be found, and the other two researchers being the Frenchman Georges Urbain and the Austrian Carl Auer von Welsbach, and the priority was usually being given to Urbain.

An application of spectral analysis, following the invention of the spectroscope in 1859, both helped and hindered. The observation of the previous unseen spectral lines not only showed the presence of undiscovered elements, but also led to confusion through an incorrect identification. Mendeleev’s periodic classification was severely challenged by the lanthanides (Laing 2005; Scerri 2006). People had no idea on how many lanthanides were there until Moseley’s work on x-ray spectroscopy (1913), which led to the concept of an atomic number, which showed that, following the discovery of lutetium, just one rare earth remained to be unearthed, element 61 (Fontani et al. 2014).

In fact, the existence of an element between neodymium and samarium had been postulated in 1902. This suggestion had been advanced by the Czech chemist Bohuslav Brauner, another of the great forgotten figures of lanthanide chemistry, who spent much of his research career working on the exacting business of determining the accurate atomic masses for the lanthanides. The precise positioning of the lanthanides was also problematic. In 1900, “Brauner put forward the view that the rare-earth elements should be regarded as a sort of zone or belt of closely related individuals occupying the place of a single element in the table, using as an analogy the existence of asteroid belts in the solar system” (Levy 1935, p. 1887). (It was, incidentally, Brauner who suggested a test for fluorine, involving inhaling it and noting whether fumes of hydrofluoric acid issued from the nose; he did live up to the age of 79 though.) Claims for the discovery of element 61 in the 1920s (“florentium” and “illinium”) rested on a misassignment of spectral lines, and it was eventually realized that the element had no stable isotopes, and it was not until 1947 that promethium was discovered among uranium fission products, and the lanthanide series was complete (Marinsky et al. 1947).

1.3 High-Coordination Numbers

At almost the same time as Moseley’s discovery, the formulation of Bragg’s law (1912) made it possible to determine the position of atoms in crystals by

x-ray diffraction, and this has eventually proved to be vital to our knowledge of lanthanide chemistry. Alfred Werner had relied on the fact that some transition metals—most notably Co(III)—invariably exhibit an octahedral six coordination in their complexes—or as he would explain it, every metal has a fixed number of secondary valencies, that is, a unique coordination number (Constable and Housecroft 2013). This enabled him to rationalize structures of the ammine complexes of CoCl_3 , where compounds with the formulae $\text{CoCl}_3 \cdot n\text{NH}_3$ ($n = 3\text{--}6$) were known, with the help of conductivity measurements and silver ion precipitation of chloride to confirm the number of ions that are present, enabling him to show that their formulae were $[\text{Co}(\text{NH}_3)_6]^{3+} (\text{Cl}^-)_3$; $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} (\text{Cl}^-)_2$; $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ (\text{Cl}^-)$; and $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$. Likewise, he was able to account for the two isomers of $\text{CoCl}_3 \cdot 4\text{NH}_3$, what we now know as purple *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \text{Cl}^-$ and green *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \text{Cl}^-$.

Within a few years of Bragg's law, x-ray diffraction studies reported by R. W. G. Wyckoff and R. G. Dickinson in 1921–1922 had confirmed an octahedral coordination in complexes such as $(\text{NH}_4)_2[\text{PtCl}_6]$ and $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$; similarly that $\text{K}_2[\text{PtCl}_4]$, $(\text{NH}_4)_2[\text{PdCl}_4]$, and $\text{K}_2[\text{PdCl}_4]$ all involved a square-planar coordination (Dickinson 1922; Wyckoff 1922). Of course, the isolation of two isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ (first made in 1844–1845), showed that these complexes had square-planar geometries, which were not tetrahedral (where only one isomer would exist). Perhaps surprisingly, no structure was reported until much later of any cobalt(III) ammine (Pauling 1994). Lanthanide complexes, of course, exhibit strikingly variable coordination numbers, and the complexes are so labile that very few examples of isolable isomers are known, an exception being the *fac*- and *mer*- $[\text{Ln}(\text{OP}(\text{NMe}_2)_3)_3\text{Cl}_3]$ (Petriček et al. 2000). The structures of several hydrated ethylsulfates $[\text{Ln}(\text{H}_2\text{O})_9] (\text{EtSO}_4)_3$ ($\text{Ln} = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{and Dy}$) were reported in 1937 (Ketelaar 1937) and that of hydrated neodymium bromate, $[\text{Nd}(\text{H}_2\text{O})_9] (\text{BrO}_3)_3$, was reported in 1939 (Helmholz 1939), showing a tricapped trigonal prismatic nine-coordination geometry for the metals. Their significance was not appreciated at the time.

1.4 Complexing Agents for Lanthanides

The Manhattan Project had one particularly important spin-off affecting lanthanide chemistry, with the use of ion-exchange resins for separations. At first, citrate was used to elute individual lanthanides from the resin, but soon, EDTA was recognized as being superior (Choppin and Wong 1994). A 1953 paper showed how the stability constant of the lanthanide–EDTA complexes increases with an increasing atomic number (and decreasing ionic radius). The hexadentate nature of EDTA binding was recognized for

the lighter lanthanides at least, but the possibility of water coordination was not discussed (Wheelwright et al. 1953). In a study of lanthanide–EDTA complexes 2 years later, Moeller et al. assumed a six coordination for the lanthanides, but the study of discontinuities in stability-constant data (the “gadolinium break”) led to the idea that this was due to a possible change in the denticity of EDTA (Moeller et al. 1955). This point was not clarified for another decade. A logical extension led to the study of the potentially octadentate DTPA, which has complexes with stability constants of at least four orders of magnitude than those of the corresponding EDTA complexes (Harder and Chabarek 1959; Moeller and Thompson 1962). Even at the beginning of the 1960s, when ligand field theory was being successfully applied to the burgeoning area of transition metal coordination chemistry, and new discoveries were being reported daily in transition metal organometallic chemistry—all aided by the application of instrumental methods (nuclear magnetic resonance [NMR], ultraviolet [UV]–visible, and infrared [IR] spectroscopy, as well as magnetic susceptibility measurements)—university-teaching texts had little to say about the lanthanides.

Although the pioneering crystal structures of $[\text{Ln}(\text{H}_2\text{O})_9] (\text{EtSO}_4)_3$ and $[\text{Nd}(\text{H}_2\text{O})_9] (\text{BrO}_3)_3$ had revealed tricapped trigonal prismatic nine coordination as far back as 1937–1939, their significance was not widely appreciated. Right into the 1960s, x-ray diffraction was a relatively slow technique, until the coming of automatic diffractometers and high-speed computing; so, very few structures of lanthanide complexes were determined, reflected in the textbooks of the time. It was generally assumed that yttrium and the lanthanides formed six-coordinate complexes such as the majority of transition metals, despite an increasing evidence to the contrary (Hart and Laming 1963). The presence of bidentate nitrates, leading to 12-coordination in the $[\text{Ce}(\text{NO}_3)_6]^{3-}$ units in $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ was recognized in 1963 (Zalkin et al. 1963); the ability of the coordinated nitrate group with its small bite angle to afford high-coordination numbers is now well recognized. However, the first compounds to really challenge the prevailing orthodoxy were the EDTA complexes. J. L. Hoard recognized that while EDTA could wrap itself around small 3d metals and achieve an octahedral coordination of the metal, the Ln^{3+} ions were too large for that to happen. He showed that the compound $\text{La}(\text{EDTAH}) \cdot 7\text{H}_2\text{O}$ contained 10-coordinate $[\text{La}(\text{EDTAH})(\text{OH})_4]$ units while $\text{K La}(\text{EDTA}) \cdot 8\text{H}_2\text{O}$ proved to contain nine-coordinate $[\text{La}(\text{EDTA})(\text{OH})_3]^-$ ions. It was also noted that $\text{MLn}(\text{EDTA}) \cdot 8\text{H}_2\text{O}$ ($\text{M} = \text{K}$, $\text{Ln} = \text{La}$, Nd , or Gd ; $\text{M} = \text{Na}$, $\text{Ln} = \text{Nd}$, Tb , or Er ; and $\text{M} = \text{NH}_4^+$, $\text{Ln} = \text{Nd}$, or Gd) were isomorphous, arguing for the persistence of nine-coordinate $[\text{La}(\text{EDTA})(\text{OH})_3]^-$ ions over a range of ionic radii (Hoard et al. 1965; Lind et al. 1965). A subsequent study showed that the later lanthanides could form eight-coordinate $[\text{La}(\text{EDTA})(\text{OH})_2]^-$ ions and that in some cases the counterion could influence which complex crystallized. For example, $\text{Na}[\text{Ho}(\text{EDTA})(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}$ and $\text{K}[\text{Ho}(\text{EDTA})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ contain nine-coordinate $[\text{Ho}(\text{EDTA})(\text{H}_2\text{O})_3]^-$ ions but $\text{K}[\text{Ho}(\text{EDTA})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ has eight-coordinate

[Ho(EDTA)(H₂O)₂]⁻ ions. A solid [C(NH₂)₃]₂[Er(EDTA)(H₂O)₂] ClO₄·6H₂O contains an eight-coordinate Er³⁺, while Na[Er(EDTA)(H₂O)₃]·5H₂O contains a nine-coordinate Er³⁺ (Janicki and Mondry 2014).

In the early 1960s, Alan Hart initiated a program of syntheses of the complexes of lanthanide salts with N- and O-donor ligands, including 1,10-phenanthroline, 2,2'-bipyridyl, and triphenylphosphine oxide (Hart and Laming 1964, 1965a, b). IR evidence that the nitrate groups were coordinated in the complexes [Ln(phen)₂(NO₃)₃] and [Ln(bipy)₂(NO₃)₃] indicated coordination numbers greater than six, subsequently confirmed by x-ray diffraction studies (Al-Karaghoulis and Wood 1972; Fréchet et al. 1992; Kepert et al. 1996) on [La(bipy)₂(NO₃)₃], [La(phen)₂(NO₃)₃], [Lu(phen)₂(NO₃)₃], and [Lu(bipy)₂(NO₃)₃], showing that the nitrates have a symmetrical bidentate coordination (with rare exceptions, this is the norm for lanthanide complexes). Likewise, the structure of [Eu(terpy)₃] (ClO₄)₃ (terpy = 2, 2', 6', 2''-terpyridine) showed that three terpyridyl ligands might fit around a lanthanide ion, affording a coordination number of 9 (Frost et al. 1969).

Thus, by 1970, as a result of increased activity in lanthanide chemistry, the high-coordination numbers in lanthanide complexes were generally recognized (Choppin 1971).

1.5 β-Diketonate Complexes and Luminescence

At around the same time, β-diketonate complexes of the lanthanides came into prominence (for a review, see Binnemans 2005). Although lanthanide ions are efficient luminescent materials, the overall emission of “inorganic” lanthanide compounds is poor because they are weak absorbers. As long ago as 1942, Weissman recognized that the coordinating organic ligands, including β-diketonates such as benzoylacetone and dibenzoylmethane, resulted in a strong absorption by the organic moiety, and that this could be transferred to a Eu³⁺ ion for subsequent emission, which is the “antenna effect” (Weissman 1942).

Formally similar to the established β-diketonate complexes formed by the transition metals, [Ln(diketonate)₃] had been known since 1897, with the report of hydrated tris acetylacetonate complexes of lanthanum and gadolinium (Urbain 1897). The 3d metals form a number of anhydrous M(acac)₃ (e.g., M = Sc, Cr, Mn, Fe, and Co) that contain octahedrally coordinated metals, but several structures reported in the late 1960s showed coordination numbers greater than six for lanthanide compounds. Thus, Y(acac)₃·3H₂O contained eight-coordinate [Y(acac)₃(H₂O)₂] molecules (Cunningham et al. 1967), which was the same coordination number also found in La(acac)₃·3H₂O (which is [La(acac)₃(H₂O)₂]·H₂O (Phillips et al. 1968)) and Cs[M(acac)₄] (M = Y, Eu) (Burns and Danford 1969). Using the bulkier 1-phenyl-1,3-butanedionato

ligand (Cotton and Legzdins 1968), only one water could coordinate in seven-coordinate $[Y(C_6H_5COCHCOCH_3)_3 \cdot H_2O]$, and with the even-bulkier tmhd (dpm) ligand, monomeric six-coordinate complexes are obtained (De Villiers and Boeyens 1972) for the later (and smaller) lanthanides, $[Ln(dpm)_3]$ or $[Ln(tmhd)_3]$ ($Ln = Ho-Lu$).

A strong red emission from Eu^{3+} in Y_2O_3 had been noted as far back as 1906 by Georges Urbain (Urbain 1906) but it was not for over half a century that this found an application. In 1962, Schimitschek and Schwarz suggested that europium complexes had suitable optical properties for laser materials (Schimitschek and Schwarz 1962), and laser emission was duly observed in 1963–1964 (Brecher et al. 1965; Lempicki and Samelson 1963; Samelson et al. 1964) in $Eu(\text{diketonate})_3 \cdot xH_2O$ and piperidinium $[Eu(\text{diketonate})_4]$ (diketonate, e.g., acac, benzoylacetate, dibenzoylmethane, and benzoyltrifluoroacetate). New europium-based phosphors made mass-produced color television (TV) feasible in the early 1960s, as hitherto the weakness of the available red phosphors had been a limiting factor. Initially the way was led by the discovery that $YVO_4: Eu^{3+}$ was “far superior in both colour and brightness” (Levine and Palilla 1964) to silver-activated zinc cadmium sulfide, hitherto the standard. Within a few years, it in its turn had been superseded by $Y_2O_2S: Eu^{3+}$ (Sovers and Yoshioka 1968) described (Haynes and Brown 1968) as “bright as $YVO_4: Eu$ and distinctly more “red.”” The study of Eu^{3+} emission in materials such as $NaInO_2$ and $NaGdO_2$ had shown that the change in site symmetry from centrosymmetric in the former to noncentrosymmetric in the latter was accompanied by pronounced changes in the emission, from predominantly ${}^5D_0 \rightarrow {}^7F_1$ in the former to ${}^5D_0 \rightarrow {}^7F_2$ in the latter, resulting in a significant shift in color of the emission (Blasse and Bril 1969).

Although lanthanide chelates made very efficient phosphors, they were not employed in TVs (or in similar commercial applications) as the complexes exhibited poor air stability and also tended to degrade under UV irradiation, where the “inorganic” materials were proving to be superior. Likewise, after the discovery of the Nd:YAG (yttrium aluminum garnet) laser in 1964, it has been materials such as $Y_3Al_5O_{12}$ (YAlG), $Y_3Gd_5O_{12}$ (YGaG), and $Gd_3Ga_5O_{12}$ (GdGaG) lattices that have had the desired properties for a laser host material, being stable, hard, optically isotropic, and accepting substitutionally trivalent ions (Geusic et al. 1964; Reisfeld and Jørgensen 1977). Increasingly, uses are being sought such as phosphors in organic light-emitting diodes (LEDs), and stability problems are being circumvented by dispersing the lanthanide complex in a host matrix. The most popular luminescent rare-earth complex is the strong red emitter $[Eu(\text{tta})_3(\text{phen})]$ (Kido and Okamoto 2002; Sanó et al. 1995), and ways are continually sought to improve its efficiency (Zhou et al. 2016).

The volatility of the β -diketonate complexes makes them suitable for a number of applications, including the precursors for metal-organic chemical vapor deposition and atomic layer deposition (Binnemans 2005; Hsu et al. 2014) while $[Ln(\text{fod})_3]$ complexes are also used as Lewis acid catalysts in

organic reactions, such as Diels–Alder syntheses (Bednarski and Danishefsky 1983; Binnemans 2005).

As already noted, the lanthanide β -diketonates form adducts with Lewis bases, usually with one or two donor atoms, thus acting as Lewis acids toward O- and N-donor ligands in particular, and this property was soon to be exploited in NMR-shift reagents (probably the first time that many chemists encountered lanthanides). Originally Hinckley used a pyridine adduct $[\text{Eu}(\text{dpm})_3\text{py}_2]$ to simplify the NMR spectrum of cholesterol (Hinckley 1969), but it was soon realized (Sanders and Williams 1970) that the base-free europium chelate would be superior, and that $[\text{Pr}(\text{dpm})_3]$ would give much-greater shifts to a high field, rather than a low field (Briggs et al. 1970). Soon, the fluorinated complex $[\text{Eu}(\text{fod})_3]$ was found to be even better, on account of its greater solubility in non-polar-covalent NMR solvents and for its greater Lewis acidity, due to the electron-withdrawing fluorines (Rondeau and Sievers 1971). Within a few years, the coming of high-frequency NMR spectrometers rendered the common applications of lanthanide-shift reagents redundant, though niche applications remain, like chiral lanthanide-shift reagents, such as $\text{Eu}(\text{facam})_3$ and $\text{Eu}(\text{hfbc})_3$ (Goering et al. 1974; McCreary et al. 1974; Viswanathan and Toland 1995).

1.6 Low-Coordination Numbers

As already noted, by 1970, it was recognized that lanthanides frequently exhibited high-coordination numbers in their complexes, with the 12-coordination represented by complexes such as $[\text{Ce}(\text{NO}_3)_6]^{3-}$. Even six coordination personified in compounds such as $\text{Cs}_2\text{NaLnCl}_6$ (elpasolite structure) was on the low side for the lanthanides (Morss et al. 1970). Up until that time, “low”-coordination numbers of 2 and 3 in transition metal chemistry were confined to certain compounds of the metals with d^{10} electron configurations, such as $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Au}(\text{CN})_2]^-$, and $[\text{Hg}(\text{CH}_3)_2]$, soon to be joined by $[\text{M}(\text{PR}_3)_2]$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{PR}_3 =$ bulky phosphine, e.g., P^tBu_3 , PPh^tBu_2) (Matsumoto et al. 1974).

It was found that by using the bulky bis(trimethylsilyl)amide ligand, steric effects could enforce low-coordination numbers of 3d metals. Three coordination was realized in $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (Bradley et al. 1969), soon to be joined by the Ti, V, and Cr analogs (Alyea et al. 1972), while it was subsequently determined for M(II) compounds such as $[\{\text{Fe}(\text{N}(\text{SiMe}_3)_2)_2\}_2]$, $[\{\text{Fe}(\text{NPh}_2)_2\}_2]$, and $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})]$ (Olmstead et al. 1991).

A natural extension of this reasoning led to attempts to make corresponding lanthanide bis(trimethylsilyl)amides, resulting in the successful isolation of the three-coordinated lanthanide complexes $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$, where $\text{Ln} = \text{Y}, \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Ho}, \text{Yb}, \text{and Lu}$, which were the first three-coordinate compounds of these metals (Bradley et al. 1973; Ghotra et al. 1973).

Four coordination was first realized in $[\text{Li}(\text{thf})_4]$, $[\text{Lu}(2,6\text{-dimethylphenyl})_4]$, and the ytterbium analog, by making use of a hindered aryl group (Cotton et al. 1972). In the Ln(II) state, two coordination was more recently achieved, again by using a very bulky ligand, in $[\text{Yb}\{\text{C}(\text{SiMe}_3)_3\}_2]$ (Eaborn et al. 1994; van den Hende et al. 1995). Three-coordinate Yb(II) is similarly found in $[\text{Li}(\text{thf})_4][\text{YbR}_3]$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$) (Hitchcock et al. 2002).

1.7 MRI Agents

Following the first experiments on NMR imaging in humans (1977), the strongly paramagnetic Mn(II) was used to enhance tissue discrimination, before it was realized that the even-more paramagnetic Gd^{3+} had the desirable properties for imaging. Linking to research of over 30 years earlier, it was realized that the use of chelating agents would sequester sufficient gadolinium, so that the concentration of free $\text{Gd}^{3+}(\text{aq})$ ions would be at manageable levels. In practice, hexadentate EDTA did not form a strong-enough complex ($\log K \sim 17$) but octadentate DTPA formed a sufficiently stable complex for the job ($\log K \sim 22\text{--}23$) (Carr et al. 1984a, b; Weinmann et al. 1984). DTPA had originally been studied as a complexing agent for eluting lanthanide ions in rare-earth fractionation (Harder and Chabarek 1959; Moeller and Thompson 1962) and has found uses in sequestering transition metals to stabilize H_2O_2 and to remove Ca^{2+} and Mg^{2+} ions in a wide range of cosmetic products.

The first gadolinium-based magnetic resonance imaging (MRI) agent to come into clinical use was $[\text{Gd}(\text{DTPA})(\text{H}_2\text{O})]^{2-}$ as Magnevist[®], in 1988. An alternative strategy uses a ligand based on a macrocyclic ring with the added donor groups attached, with complexes in commercial use including $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^-$ (Dotarem[®]) and $[\text{Gd}(\text{HP-DO3A})(\text{H}_2\text{O})]$ (Prohance[®]) that involve a N_4 macrocycle bearing additional donors (mainly carboxylates) and have slightly greater stability constants than $[\text{Gd}(\text{DTPA})(\text{H}_2\text{O})]^{2-}$, using a ligand of the same denticity as DOTA. Another type is closely related to $[\text{Gd}(\text{DTPA})(\text{H}_2\text{O})]^{2-}$, but with two carboxylates replaced by neutral donor groups like amides, affording neutral molecules, such as $[\text{Gd}(\text{DTPA-BMA})(\text{H}_2\text{O})]$ (Omniscan) (Bottrill et al. 2006; Caravan 2006; Caravan et al. 1999; Merbach et al. 2013). The comparative stability constants (Kumar et al. 1994) are 17.7 for $[\text{Gd}(\text{EDTA})]^-$, 22.2 for $[\text{Gd}(\text{DTPA})]^{2-}$, 21.0 for $[\text{Gd}(\text{DO3A})]$, and 25.3 for $[\text{Gd}(\text{DOTA})]^-$.

1.8 Superconductors and Alkoxides

The 1986 report of superconductivity below ~ 35 K in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ stimulated a new interest (Bednorz and Müller 1986) and frenetic activity in the

rare earths, as this superconducting transition temperature was some 10° higher than found hitherto for any material. Within a year, superconductivity had been described in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at 93 K (above the boiling point of liquid nitrogen) and “warm” superconductors were thus known (Hazen et al. 1987; Wu et al. 1987; for a recent review, see Keimer et al. 2015).

Attempts to find the best ways of making $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (also known as “YBCO”) stimulated research into lanthanide alkoxides as the potential sources of metal oxides by vapor deposition. Compounds such as yttrium isopropoxide had been prepared many years before (Mazdiasni et al. 1966a, b, 1967) and their formulae were taken to be of the type $[\text{Y}(\text{OPr}^i)_3]$. The yttrium compound has been used in the sol–gel process to make yttrium-stabilized zirconia. Now, in an age of sophisticated spectroscopic techniques and high-speed crystallographic structural determination, it was shown that yttrium isopropoxide was in fact $[\text{Y}_5\text{O}(\text{OPr}^i)_{13}]$ and had a considerably more complex structure, $[\text{Y}_5(\mu_5-\text{O})(\mu_3-\text{OPr}^i)_4(\mu_2-\text{OPr}^i)_4(\text{OPr}^i)_5]$ (Bradley et al. 1990; Poncelet et al. 1989). Subsequently, using the three-coordinate $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$ has afforded a useful route for preparing chloride-free alkoxides, such as trimeric $[\text{La}_3(\text{OBu}^t)_9(\text{Bu}^t\text{OH})_2]$ as well as the neopentoxides $[\text{Ln}(\text{ONep})_3]$ (Nep = $\text{OCH}_2\text{C}(\text{CH}_3)_3$; Ln = Sc, Y, and La–Lu except Pm) (Boyle et al. 2007; Bradley et al. 1991). All the neopentoxides have the tetrameric structure $[\text{Ln}(\mu-\text{ONep})_2(\text{ONep})_4]$ and afford Ln_2O_3 nanoparticles on hydrolysis. The volatile $[\text{Ce}(\text{OCMe}_2\text{Pr}^i)_4]$, a precursor for CeO_2 films, is a loosely bound dimer, $[(\text{Me}_2\text{Pr}^i\text{O})_3\text{Ce}(\mu_2-\text{OCMe}_2\text{Pr}^i)_2\text{Ce}(\text{OCMe}_2\text{Pr}^i)_3]$ (Suh et al. 2004). Other oxo alkoxides have been discovered; thus refluxing toluene solutions of $[\text{Ln}_3(\text{OBu}^t)_9(\text{Bu}^t\text{OH})_2]$ (Ln = La, Nd, and Pr) gives compounds $[\text{Ln}_5(\mu_5-\text{O})(\mu_3-\text{OBu}^t)_4(\mu_2-\text{OBu}^t)_4(\text{OBu}^t)_5]$, analogous to the isopropoxide (Daniele et al. 2000). Desolvation of $[\text{Ce}_2(\text{OPr}^i)_8(\text{Pr}^i\text{OH})_2]$ gives $[\text{Ce}_4\text{O}(\text{OPr}^i)_{14}]$, with the structure $[\text{Ce}_4(\mu_4-\text{O})(\mu_3-\text{OPr}^i)_2(\mu-\text{OPr}^i)_6(\text{OPr}^i)_6]$ (Sirio et al. 1997), while an attempted synthesis of $[\text{Ce}(\text{ONep})_4]$ from alcoholysis of $[\text{Ce}(\text{OBu}^t)_4]$ gives $[\text{Ce}_3\text{O}(\text{OBu}^t)(\text{ONep})_9]$, which has the structure $[\text{Ce}_3(\mu_3-\text{O})(\mu_3-\text{OBu}^t)(\mu_2-\text{ONep})_3(\text{ONep})_6]$ (Aspinall et al. 2011). Although these compounds have not proved of any great synthetic utility in the synthesis of materials such as YBCO, they nevertheless have provided new insights into the structures of lanthanide compounds.

This brings us to upconversion and nanomaterials, which are the subjects of this book.

1.9 Upconversion and Nanomaterials

Upconversion was first observed, in the 1960s, by Auzel and independently by Ovsyankin and Feofilov (Auzel 1966; Ovsyankin and Feofilov 1966). The phenomenon has been reviewed (Auzel 2004). It was not for another 30 years

that it started to come into its own, when nanotechnology began to take off. Luminescent lanthanide nanoparticles have been proved to be extremely useful for bioimaging, biolabels, and bioassays. $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$ was found (Menyuk et al. 1972) to be an efficient upconversion phosphor as early as 1972 but it is only more recently that codoped $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$ (as a green emitter) and $\text{NaYF}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$ (as a blue emitter) have been identified as a material with very high upconversion efficiencies (Krämer et al. 2004), which are capable of upconversion multi-color fine-tuning (Wang and Liu 2008). Various syntheses have been developed to synthesize $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$ and similar nanomaterials (Boyer et al. 2006; Liu et al. 2011), notably one involving the thermal decomposition (Boyer et al. 2006) of a mixture of CF_3COONa and *in situ*-synthesized $(\text{CF}_3\text{COO})_3\text{Ln}$, a method originating in previous studies of the thermal decomposition of $(\text{CF}_3\text{COO})_3\text{Ln}$ up to some 30 years earlier (Rillings and Roberts 1974; Russell 1993).

1.10 Conclusion

We have traveled a long way from the beginnings of lanthanide chemistry to our present sophisticated materials, capable of doing almost anything that we require. Nevertheless, we should always remember that we build on what has gone before; to use the expression attributed to Newton, *"If I have seen further it is by standing on the shoulders of giants."*

Abbreviations

bipy = 2,2'-bipyridyl
 DOTA = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate
 dpm = 2,2,6,6-tetramethylhepta-3,5-dionato (also known as dipivaloylmethane, dpm)
 DTPA = diethylene triamine pentaacetate
 DTPA-BMA = diethylenetriamine pentaacetic acid-bismethylamide
 EDTA = ethylenediaminetetraacetate
 facam = 3-trifluoroacetyl-d-camphorato
 fod = 7,7-dimethyl-1,1,2,2,2,3,3-heptafluoroocta-7,7-dimethyl-4,6-dionato
 hfbc = 3-heptafluorobutyryl-d-camphorato
 HP-DO3A = 10-(2-hydroxypropyl)-1,4,7-tetraazacyclododecane-1,4,7-triacetate
 Htta = 2-thenoyltrifluoroacetone (Htta), 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione
 phen = 1,10-phenanthroline

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