Terres rares

Two centuries
of the rare earths

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Abstract

The rare earths are important in the history of the Periodic Table, not least because no one knew how many there were. Their separation was also a challenge, owing to the similarity of properties of neighbouring elements, a manifestation of the lanthanide contraction. After initial uncertainty, it was realised that these elements exhibited predominantly the +3 oxidation state, but over the past century compounds of a few elements in the +2 state have been synthesised, and with recent breakthroughs all lanthanides have been forced into the +2 state, with the right choice of ligand. Certain elements, notably cerium, exhibit the +4 oxidation state in their chemistry. Studying the structures of compounds of the elements has been very rewarding, with a wide range of coordination numbers from 2 to 12. Among these compounds, diketonate complexes have had many applications, from lanthanide shift reagents to organic light-emitting diodes.

Applications bring lanthanides into all homes, whether with batteries, lighting, computer hard drives, fibre optics or wind turbines. Since the discovery of yttrium, the first rare earth, over two centuries have passed; now, with the latest discovery that lanthanides have a role in enzymes, we can say that these elements have come into their own.

Keywords
Rare earth; lanthanides; Periodic Table.

Back in 2017, the United Nations designated 2019 as the International Year of the Periodic Table of the Chemical Elements. Dmitri Mendeleev first presented his periodic table in 1869. The elements were arranged according to their atomic mass, with certain additional modifications which distinguished it from previous tables. For instance, some gaps were left blank for elements that remained to be discovered (e.g., Sc, Ge, Ga).

1. Discovery

The first five rare earth elements were known when Mendeleev proposed his first periodic table, starting with Carl Axel Arrhenius's discovery of a black stone at a mine near Ytterby in 1787, consequently named ytterbite. In 1794 Johan Gadolin went further with the isolation of the oxide of a new element which he named yttrium. Later on, this small village gave its name to other three elements, namely erbium, terbium, and ytterbium. Together with the much lighter scandium, yttrium and the lanthanides are often referred to collectively as the rare earths. This is a double misnomer, as 'earths' are strictly the oxides of elements, and they are certainly not rare (Figure 1). Although not as abundant as lighter elements, they are more common than well-known elements such as platinum metals, mercury, silver, and gold. Yttrium is considered as a lanthanide element due to its similarities, in both atomic size and chemistry, with heavier

lanthanides, most notably holmium. The reduced size and mass of scandium involve important differences in its chemistry. High-abundance ores containing a specific rare earth element are missing, and therefore, the separation of mixtures of similar elements into distinct species is an important part of the extraction process.

The term 'lanthanide' derives from the similarity of this series of elements to the first member, lanthanum, which itself gets its name from the Greek word *lanqaneiv* (*lanthanein*), 'to be hidden', as it was first discovered as an impurity in cerium.

2. Rare earth ores

Looking first at their overall global abundance, within the lanthanide series the lighter lanthanides are more abundant than the heavier ones; secondly, that the elements with even atomic number are more abundant than those with odd atomic number.

Among the principal ores, bastnasite, $LnFCO_3$, and monazite, $(Ln,Th)PO_4$, are both richer in earlier lanthanides, espcially La and Ce; in contrast, xenotime (Y, La)PO_4, is richer in later lanthanides (e.g. Gd-Lu) and strikingly more so in yttrium. The other very important source of these elements is a type only found in southern China, the 'ion-absorption ores'. These are formed by slow weathering of lanthanide-containing igneous rocks (e.g. granite) then the Ln^{3+} ions are adsorbed by kaolinic clays. These ores have a low abundance of rare earths (ca. 0.1%) but are very abundant and are also easy to mine. Their composition varies from place to place; they generally contain significant amounts of the middle lanthanides (e.g. Gd to Er) and also yttrium, but sometimes the lanthanum content is significant. Although their content of heavy lanthanides like holmium, thulium and lutetium is low, these ores have become the main source of the heavier lanthanides in particular because of the sheer scale of these deposits, [1, 2].

At the time that Mendeleev created his first Periodic Table, only five of the rare earths were known – yttrium, lanthanum, cerium, erbium and terbium. It was not until the later part of the 19th century that improved separation techniques, along with spectroscopic analysis, allowed the
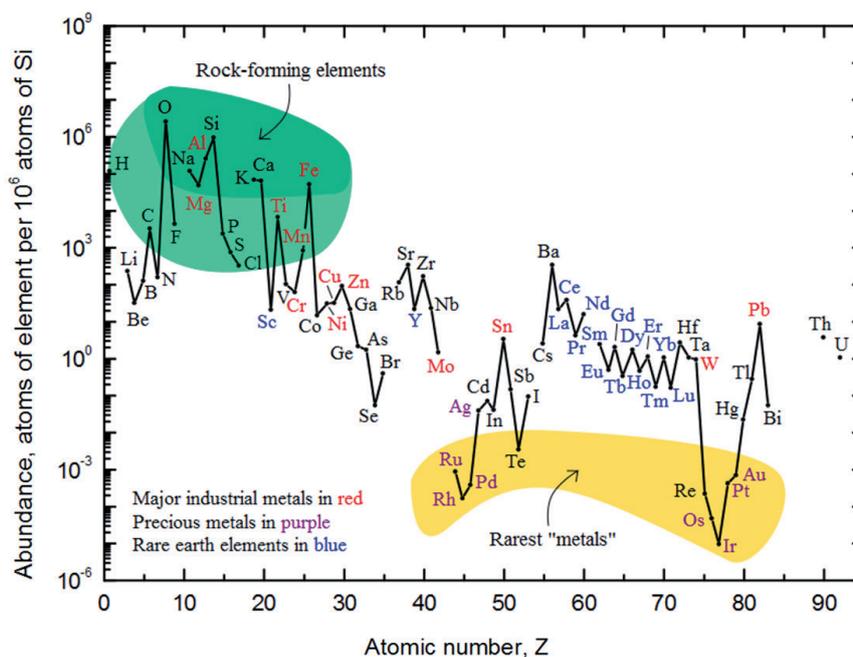
Figure 1. Abundances of the chemical elements.
Source: http://upload.wikimedia.org/wikipedia/commons/0/09/Elemental_abundances.svg
[from WikiCommons]

discovery and isolation of all but one of the elements by 1907 (Lutetium).

Initially, Mendeleev faced some problems in positioning these elements [3], as he assumed that like many metals they typically had oxidation states of +2 in their compounds, leading to incorrect atomic masses (Fig. 2).

Figure 2. Mendeleev's paper (1869) entitled "On the Relationship of the Properties of the Elements to their Atomic Weights".

'One orders the elements according to increasing atomic weight in vertical rows so that the horizontal rows contain analogous elements, still ordered by increasing atomic weight, one obtains the following arrangement, from which a few general conclusions may be derived.'

In points 1-3 he says: - 1. If arranged according to their atomic weights, the elements show an evident gradual variation of properties. 2. Chemically analogous elements have either similar atomic weights (Pt, Ir, Os), or weights which increase by equal increments (K, Rb, Cs). 3. The arrangement according to atomic weight corresponds to the *valency* of the element and to a certain extent the difference in chemical behaviour, for example Li, Be, B, C, N, O, F. He lists (in order of increasing mass) erbium, yttrium, cerium, lanthanum and didymium. Note that Di refers to 'didymium', the mixture of Pr, Nd and Sm which was at that time considered to be an element. Yt was then the symbol for yttrium; a space has been left for an element of atomic mass 45, now known to be scandium. D. Mendeleev, *Zeitschrift für Chemie*,

1869, **12**, 405-406 and https://web.lemoyne.edu/giunta/EA/MENDELEEVann.HTML

By 1871 he had changed his ideas [4], taking the formulae of the oxides to be M_2O_3, leading to atomic masses in line with today's values, though he appeared to believe that lanthanum had an oxidation state of (+4).

Whilst in the latter part of the 19th century new lanthanides were rapidly being discovered, no one knew how many there were until H. G. J. Moseley (1887-1915) and his study of X-ray spectra of the elements introduced the concept of atomic number. Moseley's Law showed that the square root of the frequency of the emitted X-ray is proportional to the atomic number, and revealed that the only rare earth remaining to be discovered was element 61. [5]

Several claims for this element were made by researchers, notably in 1926 when "Illinium" and "Florentium" were simultaneously reported by American and Italian researchers. [6] None of these claims could be supported by other researchers. Lines in spectra claimed to be from element 61 were found to be due to other elements, present as impurities.

It was realised that Element 61 would be radioactive and too short-lived to be found on earth, and it was finally recognised in 1946 among the fission products of uranium. [7]

3. Oxidation states and separating the elements

All the lanthanides form stable Ln^{3+} ions in aqueous solution, and since there is very little significant aqueous chemistry in other states, this affects separating and purifying the individual elements. Neighbouring elements have very similarly sized ions, so that their compounds have similar solubilities. Initially, however, fractional crystallisation, which takes advantage of small differences in solubility of compounds of neighbouring metals, was employed, though multiple stages were necessary, most famously in the case of thulium, where 15 000 operations were necessary to remove the last traces of erbium.[8]

Lanthanides are prominent among the fission products of uranium, so that during the Manhattan project new separation methods were developed, notably cation-exchange chromatography, where the elements are eluted from ion-exchange resins. Initially complexing agents like citrate or α-hydroxy-isobutyrate were employed, but subsequently the complexes of EDTA (Ethylenediaminetetraacetate) were found to have much higher stability constants. [9]

Such separations work very well on the small scale to produce high-purity samples of individual lanthanides, but on the industrial scale solvent extraction is the preferred technique. Typically, an aqueous solution of the mixed lanthanides is extracted using a complexing agent like tributyl phosphate (TBP) or di-2-ethylhexyl phosphoric acid (HDEHP) in kerosene, complexes such as $[Ln(NO_3)_3(TBP)_3]$ becoming more stable and more soluble in kerosene with increasing atomic number. Counter-current methods are employed to provide a multistage process that gives enhanced separations. [10]

4. The lanthanide contraction

These separations work because of the lanthanide contraction (a term coined in 1925 by the Norwegian mineralogist Victor Goldschmidt), the decreasing size of the lanthanide atoms and ions with increasing atomic number [11]. This accounts for subtle and progressive changes often observed in properties of lanthanide compounds, though the ionic radii are the most obvious manifestation. This impinges on bond lengths in lanthanide compounds, so that in a series of isostructural compounds with the same coordination number, the lanthanide – bond length decreases steadily with increasing atomic number.

Thus for the family $[Ln(terpy)(NO_3)_3(H_2O)_n]$ (terpy = 2,2';6',2"-terpyridine) the trends in the Ln-N, Ln-O and Ln-OH$_2$ are illustrated in Fig. 3. There is a smooth variation with increasing atomic number (and decreasing ionic radius) of the lanthanide, with discontinuities at the point of coordination number change. Thus there is a gradual decrease in bond length with increasing Z for the 10 coordinate series $[Ln(terpy)(NO_3)_3(H_2O)]$ (Ln = Ce-Ho), but there
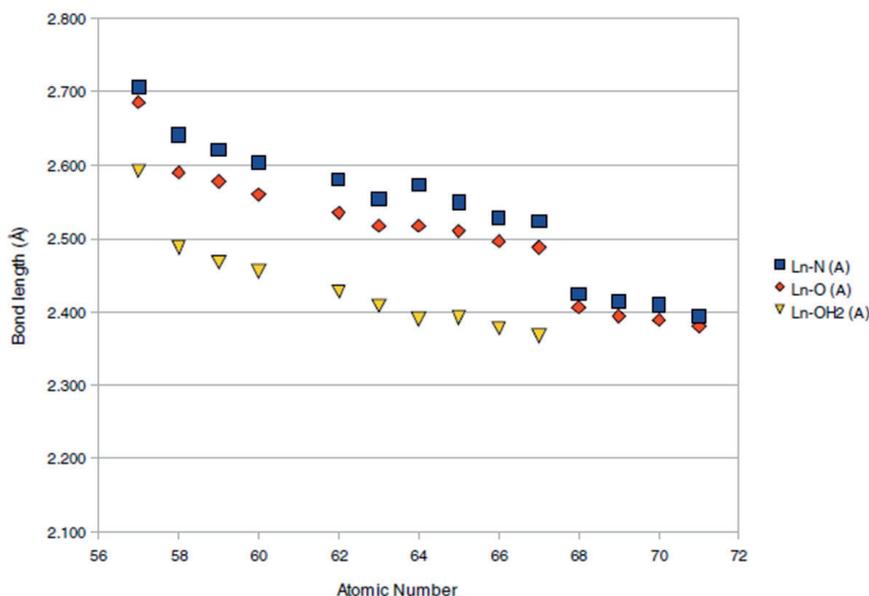
Figure 3. Bond lengths in the family $[Ln(terpy)(NO_3)_3(H_2O)_n]$.
(with permission from S. A. Cotton and P. R. Raithby, *Co-ordination Chem. Revs.*, 2017, **340**, 220-231)

is a sharp step up to the 11 coordinate [La(terpy)(NO$_3$)$_3$(H$_2$O)] at one end, and the 9 coordinate [Er(terpy)(NO$_3$)$_3$] at the other [12].

5. Coordination numbers in lanthanide compounds

The propensity of many transition metal ions, notably Co^{3+}, to indulge predominantly in forming six coordinate, octahedral compounds was a cornerstone of Alfred Werner's coordination theory [13]. Chemists tended to assume that the lanthanides behaved similarly. It took some time for X-ray diffraction to be applied to lanthanide complexes, so that it was not until the late 1930s that structures were reported of the hydrated ethylsulfates [Ln(H$_2$O)$_9$] (EtSO$_4$)$_3$ (Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Dy) (Ketelaar, 1937) and hydrated neodymium bromate, [Nd(H$_2$O)$_9$] (BrO$_3$)$_3$, in 1939 (Helmholz 1939), which revealed tricapped trigonal prismatic nine coordination. Despite that, the view that lanthanides adopted six coordination persisted into the 1960s.

The report of 12-coordinate [Ce(NO$_3$)$_6$]$^{3-}$ ions in Ce$_2$Mg$_3$(NO$_3$)$_{12}$. 24H$_2$O [15] was followed by the realisation that the familiar complexing agent EDTA was not big enough to totally encapsulate Ln^{3+} ions, leaving space for water molecules enter the coordination sphere, with Lynn Hoard's group discovering nine-coordinate [La(EDTA)(OH$_2$)$_3$]$^-$ ions in K La(EDTA). 8H$_2$O. Not only can heavier lanthanides can form eight coordinate ions such as [Er(EDTA)(OH$_2$)$_2$]$^-$, but sometimes the counter-ion can affect which complex ion crystallises, with nine coordination in Na [Er(EDTA)(H$_2$O)$_3$].5H$_2$O and eight coordination in NH$_4$ [Er(EDTA)(OH$_2$)$_2$]$^-$ and [C(NH$_2$)$_3$]$_2$[Er(EDTA)(H$_2$O)$_2$]ClO$_4$.6H$_2$O [17]. Likewise, whilst the ethylsulfate, bromate and triflate salts of the hydrated lanthanide ions all contain 9 coordinate [Ln(H$_2$O)$_9$]$^{3+}$ ions [18] the perchlorates have octahedral [Ln(H$_2$O)$_6$]$^{3+}$ ions [19]. The most normal coordination number for the lanthanide ions is 8 or 9 [20].

Research from the late 1960s in the laboratory of D. C. Bradley at Queen Mary College London led to the isolation of [M{N(SiMe$_3$)$_2$}$_3$] (M = Sc, Ti, V, Cr, Fe) with the unprecedented coordination number for these metals of three, enforced by the very bulky bis(trimethylsilyl)amide ligand [21]. A natural extension of this was to use this ligand to attempt the synthesis of similar lanthanide compounds, success being achieved in the three-coordinate [Ln{N(SiMe$_3$)$_2$}$_3$] (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Yb, and Lu), making these the first compounds of these metals with this coordination number [22]. Unlike the d-block analogues, the coordination geometry here is trigonal pyramidal, a distortion ascribed to the presence of β-Si−C agostic interactions, a view supported by density functional theory (DFT) calculations [23]. Very bulky ligands were also employed in the synthesis of the first four coordinate compounds, [Li(thf)$_4$] [Ln(2,6-dimethylphenyl)$_4$] (Ln = Yb, Lu) [24], and in the two coordinate [Yb{C(SiMe$_3$)$_3$}$_2$] [25].

6. β-diketonate complexes and their applications.

Lanthanide β-diketonates were among the first lanthanide complexes to be reported; syntheses including [La(acac)$_3$(H$_2$O)$_2$] and [Ce(acac)$_4$] (Hacac = acetylacetone or pentane-2,4-dione), were published by Georges Urbain in 1897 [26] and many others have followed. The diketonate ligands (R$_1$COCHCOR$_2$$^-$) afford a wide range of easily synthesised lanthanide complexes, which have found numerous applications discussed below.

Unlike the familiar octahedrally coordinated [M(acac)$_3$] (M = Sc-Co), the lanthanides expand their coordination sphere by adduct formation with Lewis bases (unless the diketonate has very bulky substituents). Thus [Ln(acac)$_3$(H$_2$O)$_2$] (Ln = La-Ho, Y) are eight coordinate and [Yb(acac)$_3$(H$_2$O)$_2$] is seven coordinate – only a few complexes with very bulky substituents, such as [Lu(tmhd)$_3$] (Htmhd = 2,2,6,6-tetramethyl-3,5-heptanedione (also known as Hdpm)), have sic coordination, and even these tend to accept additional donors. In contrast, [Ho(hfac)$_3$(bipy)$_2$] (Hhfac = hexafluoroacetylacetone, 1,1,1,5,5,5-hex-afluoro-2,4-pentanedione; bipy = 2,2'bipyridyl)

has ten coordinate holmium [27]. Some complexes like [Ln(tmhd)$_3$] and [Ln(tmhd)$_3$]$_2$](Ln = Tb-Ho) and adopt monomeric six coordinate or dimeric seven coordinate structures depending upon crystal growth conditions [28].

The volatility of many β-diketonate complexes makes them suitable for a number of applications, including precursors for metal-organic chemical vapour deposition (MOCVD) and atomic layer deposition (ALD) [27]. Compounds like [Ln{tmhd}$_3$] have both advantages and disadvantages in comparison with alternative precursors, such as [Ln{(CpR}$_3$] (R e.g. Me, Et, ^{i}Pr), alkoxides and |[Ln(N(SiMe$_3$)$_2$)$_3$] [27, 29]. Thus their lower reactivity and ease of synthesis makes the diketonate complexes easier to make and handle than the cyclopentadienyls or the bis(trimethylsilyl)amides, but the diketonates are harder to activate and require higher growth temperatures. Their propensity for adduct formation has been useful in several aspects of the chemistry of these complexes. From 1969 [30], paramagnetic complexes such as [Ln(tmhd)$_3$] (Ln = Eu, Pr) and [Eu(fod)$_3$] (Hfod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione) enjoyed considerable success as NMR shift reagents (probably the first time that many organic chemists encountered lanthanides), which simplified ^{1}H NMR spectra of organic compounds by reducing overlap of signals and giving well resolved spectra [31]. This relied on the molecule being studied (e.g. an alcohol) forming an adduct with [Ln(diketonate)$_3$]. Within two decades, the coming of high-frequency NMR spectrometers rendered common applications of lanthanide shift reagents redundant, though niche applications remain, like chiral lanthanide shift reagents. [Ln(fod)$_3$] complexes are also used as Lewis acid catalysts in organic reactions, such as Diels-Alder syntheses [27].

7. Properties and applications of lanthanide-based compounds

Electronic spectra

With the exception of La^{3+} and Lu^{3+}, the Ln^{3+} (Ln = lanthanide) ions have a partly filled 4f subshell.

They absorb electromagnetic radiation, exciting the ion from its electronic ground state to a higher excited state. Because the 4f orbitals are well shielded by outer (5s, 5p) filled subshells, they play little part in bonding and are little influenced by surrounding ligands. Consequently, the transitions in their absorption spectra are typically sharp and line-like, in contrast to d-d transitions in spectra of transition metals ions [32, 33]. A few ions, such as Nd^{3+}, have spectra containing certain "hypersensitive" transitions, absorptions whose intensity and structure varies with their environment (though much less than observed with d block ions) [34].

Lasers

Lasers rely on stimulated emission of light. The most popular rare earth lasers are rods made of yttrium aluminium garnet (YAG; Y$_3$Al$_5$O$_{12}$) containing Nd^{3+} ions. They are fitted with mirrors at each end, one a partly reflecting mirror. A lamp is used to 'pump' the system so that an excess of the neodymium ions are in an excited state (e.g. ^{4}F$_{5/2}$ or ^{4}F$_{7/2}$); this means that more ions can emit electrons than absorb. These excited ions undergo a non-radiative decay to the long-lived ^{4}F$_{3/2}$ excited state, creating a 'population inversion', where an excess of the Nd^{3+} ions are in this state. The ^{4}F$_{3/2}$ state can relax to the ^{4}I$_{11/2}$ state radiatively, emitting a photon. This emission process can be triggered by an incident photon of appropriate energy, 'stimulated emission'. The emitted photons can be reflected backwards and forwards in the rod, stimulating the release of more and more photons. Eventually there is such a large build-up of photons that they emerge from the rod as an intense beam of coherent monochromatic light, the laser beam [35].

Luminescence

Many Ln^{3+} ions are important for their luminescence under UV irradiation. The most important emitters of visible light are Eu^{3+} (red) and Tb^{3+} (green), whilst several, such as Yb^{3+}, Nd^{3+} and Er^{3+}, luminesce in the near-IR. Red emission from Eu^{3+}, in Y$_2$O$_3$, was first noted in 1906 by Georges Urbain [36], and in 1942, Weissman rec-

ognized that coordinating organic ligands, including β-diketonates, absorbed strongly and that this could be transferred to a Eu^{3+} ion for subsequent emission, which is the "antenna effect" [37]. Initial excitation of the ligand to its first excited singlet state can be followed successively by intersystem crossing to the triplet state, followed by another non radiative transition to an excited state of the europium ion, which can emit back to its ground state by photoluminescence. This can be applied to other lanthanides, of course. [Eu(TTA)$_3$(phen)] (Htta = 2-thenoyltrifluoroacetone, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione; phen = 1,10-phenanthroline) (Fig. 4) is one of the brightest red emitters known; widely used as a red emitter in OLEDs (organic light-emitting diodes) [38].

Figure 4. The complex [Eu(TTA)$_3$(phen)], important in red-emitting devices.

One application of the antenna effect was conceived in the wake of the terrorist attacks in New York on September 11th 2001, when envelopes containing anthrax spores (*Bacillus anthracis*) were delivered to two USA Senators and to several media outlets; five people were killed. Anthrax spores contain around 10% by mass of calcium dipicolinate (DPA^{2-}), which acts as a biomarker. The Tb^{3+} aqua ion is only weakly luminescent because of vibronic coupling between O-H groups in the coordinated water molecules with the excited Tb^{3+} ion, which provides a nonradiative decay pathway. Adding DPA^{2-} to Tb^{3+} ions produces an enhancement of luminescence by three orders of magnitude, as dipicolinate acts as an antenna, whose lowest triplet state matches the lowest emitting level of the Tb^{3+} ion. The effect can be enhanced further, by additionally including the

hexadentate macrocylic ligand DO2A^{2-} (DO2A = 1,4,7,10-tetraazacyclododecane-1,7-diacetate); the resulting nine coordinate complex (Fig. 5) has no deactivating waters in the coordination sphere and has even higher emission [39].

Figure 5. The structure of the [Tb(DO2A)(DPA)]$^-$ complex (DO2A^{2-} = 1,4,7,10-tetraazacyclododecane-1,7-diacetate; DPA^{2-} = dipicolinate)

Lanthanides are especially important because of their lighting and display applications. This first became important when colour televisions became widespread from the 1960s, particularly the red emitters based in Eu(III), still used today. Following on from this, lanthanide phosphors were applied to fluorescent tubes; materials used have included red: Y$_2$O$_2$S or Y$_2$O$_3$: Eu^{3+}; green: LaPO$_4$: Ce^{3+}, Tb^{3+}, CeMgAl$_{11}$O$_{19}$:Tb^{3+} or Y$_2$O$_2$S: Tb^{3+}: blue: BaMgAl$_{10}$O$_{17}$:Eu^{II}. Uses have spread to compact fluorescent lamps, plasma TVs and computer monitors, successive generations of phosphor being chosen for greater energy efficiency [40].

Chemistry and oxidation states in lanthanide compounds

As already noted, when Mendeleev conceived his table, it was widely believed that rare earths like La, Ce and Y had oxidation states of +2 in their compounds, like most other metals. This meant that compounds of the elements were assigned the wrong formulae (e.g. MO), leading to incorrect atomic masses and problems with positioning them in the Periodic Table in 1869 [3]. By 1871, he had modified his ideas, recognising that the oxides were M$_2$O$_3$, and his values of the atomic

masses were in the correct region (e.g. Y 88, Ce 140, Er 178), though he seems to have thought that lanthanum was tetravalent, leading to an atomic mass of 180 [4]. Even though many lanthanide elements were not identified yet at that time, Mendeleev tried to accommodate the existing rare earths along with the other elements. It was eventually achieved in 1905 with Alfred Werner who positioned all lanthanides in a horizontal block of their own [41].

Until recent times, it was recognised that the chemistry of the lanthanides was largely that of the +3 oxidation state [42]. Cerium was known additionally to form compounds in the +4 state, most familiarly the well known oxidant $(NH_4)_2[Ce(NO_3)_6]$, widely used by organic chemists. As the 20th century proceeded, halides of certain divalent lanthanides were synthesised, usually by hydrogenic reduction of the trihalides, such as $SmCl_2$ (1906), followed by $EuCl_2$ (1911), YbI_2 (1929) and the other LnX_2 (X = F, Cl, Br, I; Ln = Sm, Eu, Yb) [43]. The Eu^{2+} aqua ion was found to be reasonably stable in the absence of oxygen, less so the corresponding ions of samarium and ytterbium. So for many years, the +2 oxidation state was associated with Sm^{2+} (f^6); Eu^{2+} (f^7) and Yb^{2+} (f^{14}), and the idea grew that these were stable because of the half-filled or filled 4f subshells. Subsequently it was found that the +2 state was accessible for other lanthanides by means of comproportionation reactions, high-temperature 'metallothermic reduction' affording further dihalides, notably $NdCl_2$, NdI_2, DyI_2 and TmI_2, with electron configurations away from the half-filled or filled sub-shell, Nd^{2+} (f^4); Dy^{2+} (f^{10}); Tm^{2+} (f^{13}) [44].

$$Nd + 2\ NdCl_3 \rightarrow 3\ NdCl_2$$
$$Tm + 2\ TmI_3 \rightarrow 3\ TmI_2$$
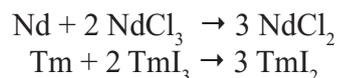
These were later found to be convertible into molecular complexes [45], such as seven coordinate $NdI_2(THF)_5$; eight coordinate $DyI_2(DME)_3$ and seven coordinate $TmI_2(DME)_3$ (note the lanthanide contraction at work).

Over the past half-century, these developments have been followed by a developing chemistry of the +2 state in lanthanide organometallic chemistry, most notably research carried out by Evans on Sm(II) compounds like $[Sm(C_5Me_5)_2]$ [46]. This has paled by comparison with Evans' most recent work, showing that the +2 state is accessible for all lanthanides, provided that the right ligand set is used, in the right geometry [47].

'Flash' reduction of $[Ln(C_5H_4SiMe_3)_3]$ using KC_8 on a column at -35-C, with all isolation steps carried out at that temperature, leads to $[K(18\text{-crown-}6)][Cp'_3Ln]$ (Ln = Y, La-Nd, Sm-Lu; Figure 6) and also $[K(2.2.2\text{-cryptand})]$ $[Cp'_3Ln]$ (Cp' = $C_5H_4SiMe_3$). Study of the magnetic and spectroscopic properties of these compounds indicates that the Sm, Eu, Tm and Yb compounds have f^n electron configurations, whilst the compounds of La-Nd, Gd-Er and Lu are have $f^{n-1}d^1$ electron configurations. So the electronic ground state of the Dy(II) and Nd(II) compounds depend on the ligand environment, something unprecedented in lanthanide chemistry, as the $[Cp'_3Ln]^-$ ions
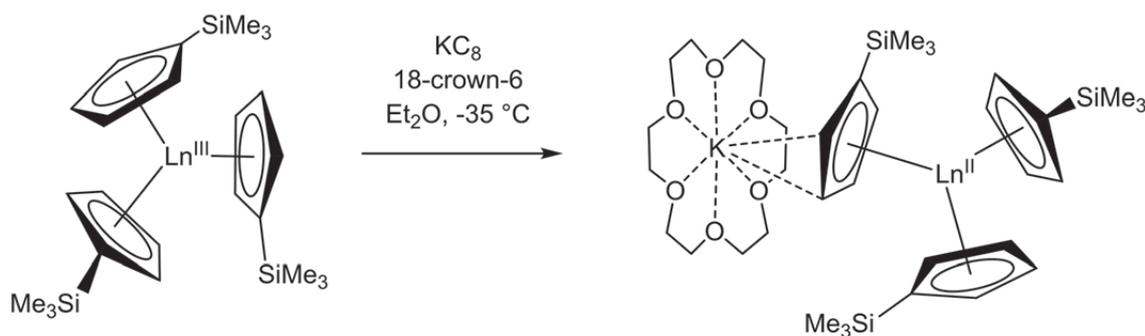
Figure 6. Synthesis of the Ln(II) compounds [K(18-crown-6)][Cp′₃Ln]

of Dy^{2+} and Nd^{2+} are $4f^9\,5d^1$ and $4f^3\,5d^1$, respectively, whereas in earlier compounds like $[NdI_2(THF)_5]$ and $[DyI_2(DME)_3]$ they are $4f^{10}$ and $4f^4$ respectively. The $C_5H_4SiMe_3$ ligand has created an environment such that – for the first time ever – the electronic ground state of a particular lanthanide ion can be changed by changing its environment. The choice of the cyclopentadienyl ligand is important, as the corresponding $[Cp''_3Ln]^-$ ion ($[C_5H_3(SiMe_3)_2]$ = (Cp'')) has only been obtained for Ln = La, Ce, Pr, Nd [48]; likewise, the $[Cp^{tet}_3Ln]^-$ ion has been isolated for Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, and Dy (Cp^{tet} = C_5Me_4H) [49].

Magnetism

The past half century has seen lanthanide-based magnets replace traditional iron-containing magnets in many applications. They produce stronger magnetic fields, owing to the higher magnetic moments of the lanthanides. The two main materials concerned are $SmCo_5$ and $Nd_2Fe_{14}B$. The former is more expensive but can operate at higher temperatures than the cheaper $Nd_2Fe_{14}B$. Both are more brittle than the robust iron magnets. Their higher strength means that they are more compact. Modern motor cars use them in many devices, notably traction motors in electric cars, as do computer hard drives, headphones and wind turbines [50].

Lanthanide containing single molecule magnets (SMMs) are an active area of research. They exhibit supermagnetic behaviour below a certain temperature (the 'blocking temperature') and are potentially magnetic memory units, capable of making up a quantum computer [51]. Materials like $[Dy(Cp^{ttt})_2][B(C_6F_5)_4]$ (Cp^{ttt}=1,2,4-tri(*tert*-butyl)cyclopentadienide) show promise [52], with blocking temperatures above 50K, though materials operating at liquid nitrogen temperatures and above are actively being sought.

All the Ln^{3+} except for La^{3+} and Lu^{3+} ions are paramagnetic, in some cases very strongly so. The most important application of this in recent years has been the use of gadolinium complexes in magnetic resonance imaging (MRI) agents used
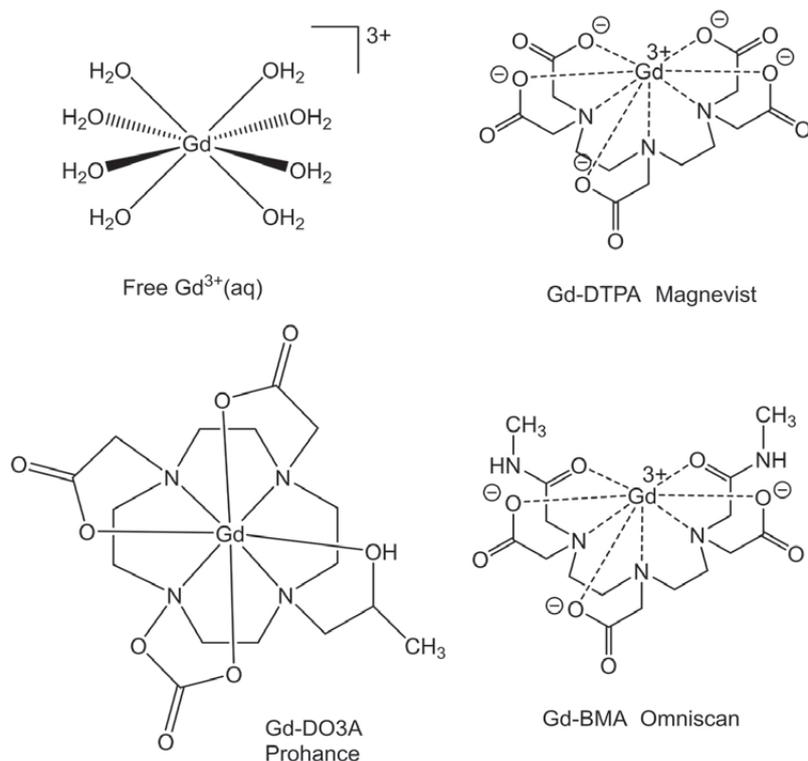
Figure 7. The structures of the gadolinium aqua ion, too toxic to be used in MRI, and three commercial MRI agents.

in medical diagnosis [53, 54]. MRI scanners are essentially pulsed NMR spectrometers, detecting signals from ^1H nuclei in water molecules; the contrast agents improve the images of bodily organs and structures, like tumours and blood supply. They work by shortening the relaxation times of ^1H nuclei inside tissues, and differentiate between healthy and diseased tissue. Free $Gd^{3+}(aq)$ is too toxic for use, so gadolinium complexes are required. Structures of some of these are shown in Figure 7.

For their first twenty years of use, MRI agents were regarded as totally safe. Recently, complications have emerged with patients with renal failure, so that with these patients MRI scans have been restricted. There has also been concern about Gd^{3+} deposition in neural tissues, including the brain (even in people with intact blood-brain barriers and normal renal functions) and the use of the more stable macrocyclic contrast agents promoted [55].

The latest development in magnetic materials lies in certain layered ceramic compounds, called MAX phases, incorporating certain rare earth elements [56]; this family of compounds has the general formula $[(Mo_{2/3}Ln_{1/3})_2AlC]$ (Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu) and exhibits "a plethora of ground states, resulting from an interplay of competing magnetic interactions in the presence of magnetocrystalline anisotropy". They have the potential of being used in future spintronics applications.

Catalysts

Lanthanides have a number of important applications, several on a large scale. Lanthanum and cerium are added to zeolite cracking catalysts in the petrochemical industry [57]. Because of its ability to switch oxidation states between +3 and +4, cerium is widely used in oxidation catalysts, often as CeO_2. Thus in self-cleaning ovens the CeO_2 catalyst oxidises molecules like fatty acids [58]. Cerium oxide is used in automobile three-way catalysts (TWC), not least as an oxygen store to smooth out the oxidising performance of the system. Its role includes improving low-temperature performance. Cerium oxide

nanoparticles have been widely employed as a diesel fuel additive in vehicles, with a view to catalysing the regeneration of particulate filters through oxidising soot particles. Diesel particulate emissions are reduced, but there is concern over metallic nanoparticle emissions [59].

Lanthanides in Biology

Until recently, it was a given that the rare earth elements had no function in any living system. Yet had been known for years that some properties of the lanthanides resembled other metal ions, and it was commonplace to use them as spectroscopic probes for 'silent' ions (e.g. Ca^{2+}) - Eu^{3+} for its luminescence for example. In 2011, however, it was reported that XoxF, a methanol dehydrogenase (MDH) protein that converts methanol into methanal as an energy source, was lanthanide-dependent (and indeed was expressed when lanthanides were added to a culture medium) [60]. Shortly afterwards it was found that the thermoacidophilic bacterium *Methylacidiphilum fumariolicum SolV*, isolated from a volcanic mudpot in Italy, needed lanthanides to exist, and in 2014 the crystal structure [61] of XoxF isolated from *Methylacidiphilum fumariolicum SolV* showed cerium ions at the active site (structures of lanthanum and europium analogues have also been reported). In many ways, such as the aminoacid ligands utilised, it strongly resembles Ca^{2+}-dependent MDH enzymes, but with one extra carboxylate ligand, resulting in an increase in coordination number to 9, from 7 in Ca-MDH. It is believed to be widespread in marine environments.

The coordination sphere of the lanthanides (Figure 8) includes four amino acids, as well as the redox cofactor pyrroloquinoline quinone (PQQ), and an active site that binds the methanol. The lanthanides appear to act as Lewis acids; despite the fact that the later, smaller, lanthanides are stronger Lewis acids, early lanthanides are preferred by these organisms. This may mean that the organisms came to acquire and use the more abundant early lanthanides like La and Ce.

Lanmodulin, a protein more recently identified in the lanthanide-dependent *Methylobacterium extorquens,* binds lanthanides at picomolar levels,

with 10^8 fold selectivity for La^{3+} over Ca^{2+}. It has been suggested that there exists a Ln^{3+} uptake system that uses a chelator analogous to the use of siderophores by bacteria wanting to acquire Fe^{3+}. When lanmodulin binds lanthanides, it undergoes a considerable conformational change from a substantially disordered state to a very compact one [62]. There is a growing interest in this scientific area which continues to develop [63].
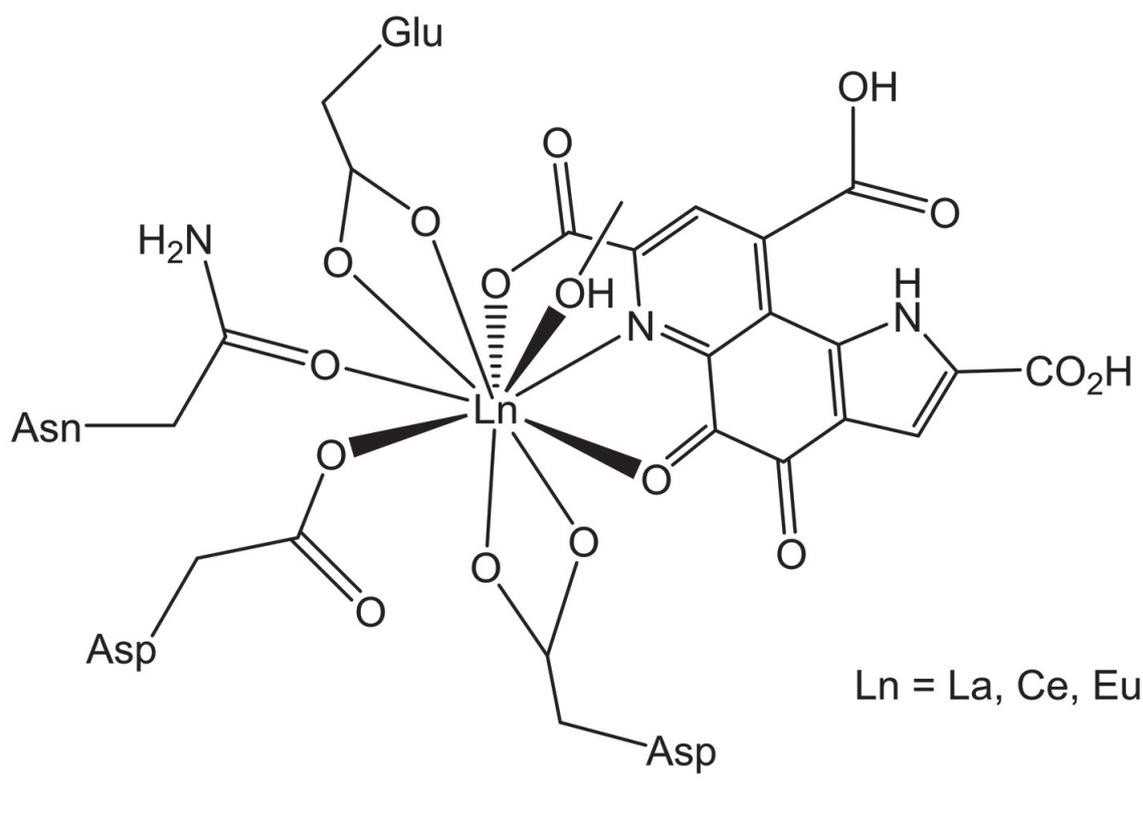
Fig. 8. The coordination sphere in the lanthanide-dependent MDH enzymes, with methanol substrate bound to the lanthanide (MDH = methanol dehydrogenase).

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