

																1		2																	
3		4																		5		6		7		8		9		10					
Li		Be																		B		C		N		O		F		Ne					
11		12																		13		14		15		16		17		18					
Na		Mg																		Al		Si		P		S		Cl		Ar					
19		20		21		22		23		24		25		26		27		28		29		30		31		32		33		34		35		36	
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr	
37		38		39		40		41		42		43		44		45		46		47		48		49		50		51		52		53		54	
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe	
55		56		57		58		59		60		61		62		63		64		65		66		67		68		69		70		71		72	
Cs		Ba		La		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn	
87		88		89		90		91		92		93		94		95		96		97		98		99		100		101		102		103		104	
Fr		Ra		Ac		Rf		Db		Sg		Bh		Hs		Mt		Uun		Uuu		Uub													
59		60		61		62		63		64		65		66		67		68		69		70		71		72		73		74		75			
Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu									
90		91		92		93		94		95		96		97		98		99		100		101		102		103		104		105					
Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr									

30

The Lanthanide Elements ($Z = 58 - 71$)

30.1 Introduction⁽¹⁾

Not least of the confusions associated with this group of elements is that of terminology. The name “rare earth” was originally used to describe almost any naturally occurring but unfamiliar oxide and even until about 1920 generally included both ThO_2 and ZrO_2 . About that time the name began to be applied to the elements themselves rather than their oxides, and also to be restricted to that group of elements which could only be separated from each other with great difficulty. On the basis of their separability it was convenient to divide these elements into the “cerium group” or “light earths” (La to about Eu) and the “yttrium group” or “heavy earths” (Gd to Lu plus Y which, though much lighter than the others, has a comparable ionic radius and is

consequently found in the same ores, usually as the major component). It is now accepted that the “rare-earth elements” comprise the fourteen elements from $_{58}\text{Ce}$ to $_{71}\text{Lu}$, but are commonly taken to include $_{57}\text{La}$ and sometimes Sc and Y as well.

To avoid this confusion, and because many of the elements are actually far from rare, the terms “lanthanide”, “lanthanon” and “lanthanoid” have been introduced. Even now, however, there is no general agreement about the position of La, i.e. whether the group is made up of the elements La to Lu or Ce to Lu. Throughout this chapter the term “lanthanide” and the general symbol, Ln, will be used to refer to the fourteen elements cerium to lutetium inclusive, the Group 3 elements, scandium, yttrium and lanthanum having already been dealt with in Chapter 20.

The lanthanides comprise the largest naturally-occurring group in the periodic table. Their properties are so similar that from 1794, when J. Gadolin isolated “yttria” which he thought was the oxide of a single new element, until 1907, when lutetium was discovered, nearly a hundred claims were made for the discovery of elements

¹ K. A. Gschneider Jr. and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, North-Holland, Amsterdam, Vol. 1, (1978) to Vol. 21, (1995). An authoritative source of information on all topics associated with lanthanide elements.

History of the Lanthanides⁽²⁻⁴⁾

In 1751 the Swedish mineralogist, A. F. Cronstedt, discovered a heavy mineral from which in 1803 M. H. Klaproth in Germany and, independently, J. J. Berzelius and W. Hisinger in Sweden, isolated what was thought to be a new oxide (or "earth") which was named *ceria* after the recently discovered asteroid, Ceres. Between 1839 and 1843 this earth, and the previously isolated *yttria* (p. 944), were shown by the Swedish surgeon C. G. Mosander to be mixtures from which, by 1907, the oxides of Sc, Y, La and the thirteen lanthanides other than Pm were to be isolated. The small village of Ytterby near Stockholm is celebrated in the names of no less than four of these elements (Table 30.1).

The classical methods used to separate the lanthanides from aqueous solutions depended on: (i) differences in basicity, the less-basic hydroxides of the heavy lanthanides precipitating before those of the lighter ones on gradual addition of alkali; (ii) differences in solubility of salts such as oxalates, double sulfates, and double nitrates; and (iii) conversion, if possible, to an oxidation state other than +3, e.g. Ce(IV), Eu(II). This latter process provided the cleanest method but was only occasionally applicable. Methods (i) and (ii) required much repetition to be effective, and fractional recrystallizations were sometimes repeated thousands of times. (In 1911 the American C. James performed 15 000 recrystallizations in order to obtain pure thulium bromate).

The minerals on which the work was performed during the nineteenth century were indeed rare, and the materials isolated were of no interest outside the laboratory. By 1891, however, the Austrian chemist C. A. von Welsbach had perfected the thoria gas "mantle" to improve the low luminosity of the coal-gas flames then used for lighting. Woven cotton or artificial silk of the required shape was soaked in an aqueous solution of the nitrates of appropriate metals and the fibre then burned off and the nitrates converted to oxides. A mixture of 99% ThO₂ and 1% CeO₂ was used and has not since been bettered. CeO₂ catalyses the combustion of the gas and apparently, because of the poor thermal conductivity of the ThO₂, particles of CeO₂ become hotter and so brighter than would otherwise be possible. The commercial success of the gas mantle was immense and produced a worldwide search for thorium. Its major ore is monazite, which rarely contains more than 12% ThO₂ but about 45% Ln₂O₃. Not only did the search reveal that thorium, and hence the lanthanides, are more plentiful than had previously been thought, but the extraction of the thorium produced large amounts of lanthanides for which there was at first little use.

Applications were immediately sought and it was found that electrolysis of the fused chloride of the residue left after the removal of Th yielded the pyrophoric "mischmetall" (approximately 50% Ce, 25% La, 25% other light lanthanides) which, when alloyed with 30% Fe, is ideal as a lighter flint. Besides small amounts of lanthanides used in special glasses to control absorption at particular wavelengths, this was the pattern of usage until the 1940s. Before then there was little need for the pure metals and, because of the difficulty in obtaining them (high mps and very easily oxidized), such samples as were produced were usually impure. Attempts were also made to find element 61, which had not been found in the early studies, and in 1926 unconfirmed reports of its discovery from Illinois and Florence produced the temporary names *illinium* and *florentium*.

During the 1939–45 war, Mg-based alloys incorporating lanthanides were developed for aeronautical components and the addition of small amounts of mischmetall to cast-iron, by causing the separation of carbon in nodular rather than flake form, was found to improve the mechanical properties. But, more significantly from the chemical point of view, work on nuclear fission requiring the complete removal of the lanthanide elements from uranium and thorium ores, coupled with the fact that the lanthanides constitute a considerable proportion of the fission products, stimulated a great surge of interest. Solvent extraction and, more especially, ion-exchange techniques were developed, the work of F. H. Spedding and coworkers at Iowa State University being particularly notable.

As a result, in 1947, J. A. Marinsky, L. E. Glendenin, and C. D. Coryell at Oak Ridge, Tennessee, finally established the existence of element 61 in the fission products of ²³⁵U and at the suggestion of Coryell's wife it was named *promethium* (later *promethium*) after Prometheus who, according to Greek mythology, stole fire from heaven for the use of mankind. Since about 1955, individual lanthanides have been obtainable in increasing amounts in elemental as well as combined forms.

belonging to this group. In view of the absence at that time of a conclusive test to determine whether or not a mixture was involved, this is not surprising. Indeed, there was a general lack of understanding of the large number of elements

involved since the periodic table of the time could accommodate only one element, namely La. Not until 1913, as a result of H. G. J. Moseley's work on atomic numbers, was it realized that there were just fourteen elements between La and Hf, and in 1918 Niels Bohr interpreted this as an expansion of the fourth quantum group from 18 to 32 electrons. More information is in the Panel above and in Table 30.1.

² F. SZABADVARY, pp. 33–80, Vol. 11 (1988) of ref. 1.

³ C. K. JØRGENSEN, pp. 197–215, Vol. 11 (1988) of ref. 1.

⁴ C. H. EVANS, *Chem. in Brit.* **25**, 880–2 (1989).

Table 30.1 The discovery of the oxides of Group 3 and the lanthanide elements^(2,4)

Element	Discoverer	Date	Origin of name
<i>From ceria</i>			
Cerium, Ce	C. G. Mosander	1839	The asteroid, Ceres
Lanthanum, La	C. G. Mosander	1839	Greek <i>λανθάνειν</i> , <i>lanthanein</i> , to escape notice
Praseodymium, Pr	C. A. von Welsbach	1885	Greek <i>πρασιος</i> + <i>διδυμος</i> praseos + didymos, leek green + twin
Neodymium, Nd	C. A. von Welsbach	1885	Greek <i>νέος</i> + <i>διδυμος</i> , <i>neos</i> + <i>didymos</i> , new twin
Samarium, Sm	L. de Boisbaudran	1879	The mineral, samarskite
Europium, Eu	E. A. Demarcay	1901	Europe
<i>From yttria</i>			
Yttrium, Y	C. G. Mosander	1843	Ytterby
Terbium, Tb ^(a)	C. G. Mosander	1843	Ytterby
Erbium, Er ^(a)	C. G. Mosander	1843	Ytterby
Ytterbium, Yb	J. C. G. de Marignac	1878	Ytterby
Scandium, Sc	L. F. Nilson	1879	Scandinavia
Holmium, Ho	P. T. Cleve	1879	Latin <i>Holmia</i> : Stockholm
Thulium, Tm	P. T. Cleve	1879	Latin <i>Thule</i> , "most northerly land"
Gadolinium, Gd	J. C. G. de Marignac	1880	Finnish chemist, J. Gadolin
Dysprosium, Dy	L. de Boisbaudran	1886	Greek <i>δυσπροσιτος</i> , <i>dysprositos</i> , hard to get
Lutetium, Lu ^(b)	G. Urbain C. A. von Welsbach C. James	1907	Latin <i>Lutetia</i> : Paris

^(a)Terbium and erbium were originally named in the reverse order.

^(b)Originally spelled lutecium, but changed to lutetium in 1949.

30.2 The Elements

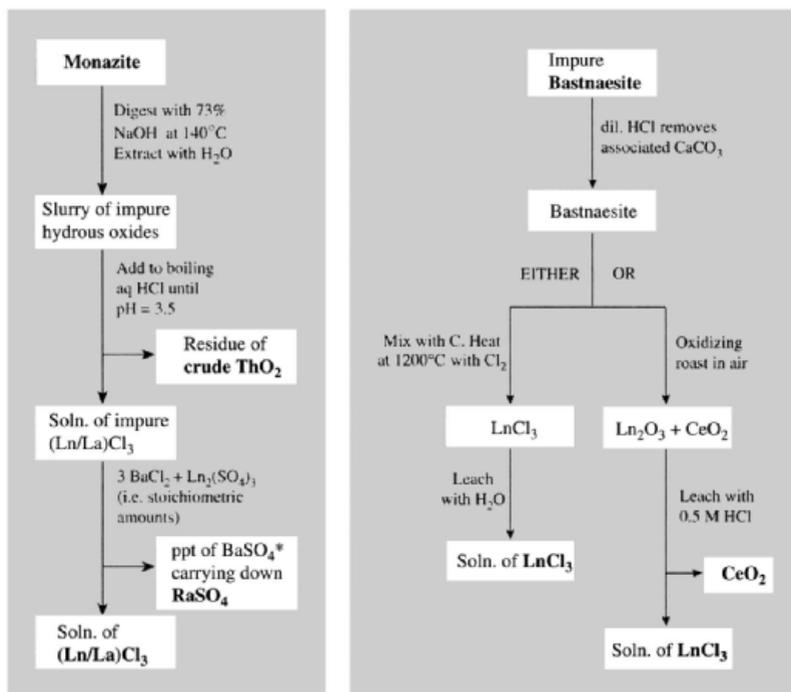
30.2.1 Terrestrial abundance and distribution

Apart from the unstable ¹⁴⁷Pm (half-life 2.623 y) of which traces occur in uranium ores, the lanthanides are actually not rare. Cerium (66 ppm in the earth's crust) is the twenty-sixth most abundant of all elements, being half as abundant as Cl and 5 times as abundant as Pb. Even Tm (0.5 ppm), the rarest after Pm, is rather more abundant in the earth's crust than is iodine.

There are over 100 minerals known to contain lanthanides but the only two of commercial importance are monazite, a mixed La, Th, Ln phosphate, and bastnaesite, an La, Ln fluorocarbonate (M^{III}CO₃F). Monazite is widely but sparsely distributed in many rocks but, because of its high density and inertness, it is concentrated by weathering into sands on beaches and river beds, often in the presence of other

similarly concentrated minerals such as ilmenite (FeTiO₃) and cassiterite (SnO₂). Deposits occur in southern India, South Africa, Brazil, Australia and Malaysia and, until the 1960s, these provided the bulk of the world's La, Ln and Th. Then, however, a vast deposit of bastnaesite, which had been discovered in 1949 in the Sierra Nevada Mountains in the USA, came into production. Bastnaesite is also now extracted in China in large quantities, and has become the most important single source of La and Ln.

The bulk of both monazite and bastnaesite is made up of Ce, La, Nd and Pr (in that order) but, whereas monazite typically contains around 5–10% ThO₂ and 3% yttrium earths, these and the heavy lanthanides are virtually absent in bastnaesite. Although thorium is only weakly radioactive it is contaminated with daughter elements such as ²²⁸Ra which are more active and therefore require careful handling during the processing of monazite. This is a complication not encountered in the processing of bastnaesite.



*These residues contain ²²⁸Ra, a daughter element of Th and an active γ -emitter, and must therefore be handled with care

Figure 30.1 Flow diagram for the extraction of the lanthanide elements.

30.2.2 Preparation and uses of the elements⁽⁵⁻⁸⁾

Conventional mineral dressing yields concentrates of the minerals of better than 90% purity. These can then be broken down (“opened”) by either acidic or alkaline attack, the latter being more usual nowadays. Details vary considerably since they depend on the ore being used and on the extent to which the metals are to be separated from each other, but the schemes

⁵ Kirk-Othmer *Encyclopedia of Chemical Technology*, Vol. 14, pp. 1091-115 4th edn., Interscience, New York, 1995.

⁶ B. JEZOWSKA-TRZEBIATOWSKA, S. KOPACZ and T. MIKULSKI, *The Rare Earth Elements, Occurrence and Technology*, Elsevier, Amsterdam, 1990, 540 pp.

⁷ K. L. NASH and G. R. CHOPPIN (eds.), *Separations of Elements*, Plenum, New York, 1995, 286 pp.

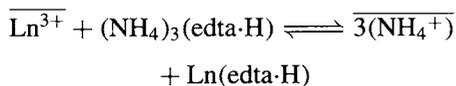
⁸ R. G. BAUTISTA and N. JACKSON (eds.), *Rare Earths, Resources, Science Technology and Applications*, TMS, Warrendale USA, 1991, pp. 466.

outlined in Fig. 30.1 are typical of those used for monazite and bastnaesite to obtain solutions of the mixed chlorides. At this point the classical methods (see Panel, p. 1228) were formerly employed to separate the individual elements where this was required and, indeed the separation of lanthanum by the fractional crystallization of $\text{La}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ is still used. However the separations can now be effected on a large scale by solvent extraction^(7,9) using aqueous solutions of the nitrates and a solvent such as tri-*n*-butylphosphate, $(\text{Bu}^n\text{O})_3\text{PO}$ (often with kerosene as an inert diluent), in which the solubility of Ln^{III} increases with its atomic weight. This type of process has the advantage of being continuous and is ideal where the product and feed are not to be changed.

Alternatively, for high-purity or smaller-scale production the more easily adapted ion-exchange

⁹ R. G. BAUTISTA, pp. 1-28, Vol. 21 (1995) of ref 1.

techniques are ideal, the best of these being "displacement chromatography". Two separate columns of cation exchange resin are generally employed for this purpose. The first column is loaded with the Ln^{III} mixture and the second, or development, column is loaded with a so-called "retaining ion" such as Cu^{II} (Zn^{II} and Fe^{III} have also been used), and the two columns are coupled together. An aqueous solution (the "eluant") of a complexing agent, of which the triammonium salt of edta^{4-} is typical, is then passed through the columns, and Ln^{III} is displaced from the first column (barred species are bound to the resin):



The reaction at any point in the column becomes progressively displaced to the right as fresh complexing agent arrives and the reaction products are removed. The solution of $\text{Ln}(\text{edta}\cdot\text{H})$ and $(\text{NH}_4)_3(\text{edta}\cdot\text{H})$ then reaches the development column where Cu^{II} is displaced and Ln^{III} redeposited in a compact band at the top of the column:



This occurs because Cu^{II} , being smaller than Ln^{III} , is able to form in the solution phase, a complex with $(\text{edta}\cdot\text{H})^{3-}$ of comparable stability, in spite of its lower charge. The Cu^{II} serves the additional purpose of keeping the complexing agent in a soluble form. If the resin were loaded instead with H^+ , $\text{edta}\cdot\text{H}_4$ would be precipitated and would clog the resin. Even using Cu^{II} the composition of the eluant must be carefully controlled. The concentration of edta must not exceed 0.015 M, otherwise $\text{Cu}_2(\text{edta})\cdot 5\text{H}_2\text{O}$ precipitates, and it is to encourage the formation of the more soluble salt of $(\text{edta}\cdot\text{H})^{3-}$ that an acidic rather than neutral ammonium salt of edta^{4-} is used.

Once the Ln^{III} ions have been deposited on to the resin they are displaced yet again by the NH_4^+ in the eluant. Now, the affinity of Ln^{III} ions for the resin decreases with increasing atomic weight, but so slightly that elution of the development column

with NH_4^+ ions alone would not discriminate to an effective extent between the different lanthanides. However, the values of ΔG° (and therefore of $\log K$) for the formation of $\text{Ln}(\text{edta}\cdot\text{H})$ complexes, increase steadily along the series by a total of *ca.* 25% from Ce^{III} to Lu^{III} . Thus in the presence of the complexing agent, the tendency to leave the resin and go into solution is significantly greater for the heavy than for the light lanthanides. As a result, displacement of the Ln^{III} ions from the resin concentrates the heavier cations in the solution. The Ln^{III} ions therefore pass down the development column in a band, being repeatedly deposited and redissolved in what is effectively an automatic fractionation process, concentrating the heavier members in the solution phase. The result is that when all the copper has come off the column the lanthanides emerge in succession, heaviest first. They may then be precipitated from the eluant as insoluble oxalates and ignited to the oxides.

The production of mischmetal by the electrolysis of fused $(\text{Ln},\text{La})\text{Cl}_3$, and the difficulties in obtaining pure metals because of their high mps and ease of oxidation, have already been mentioned (Panel, p. 1228). Two methods are in fact available for producing the metals.

(i) *Electrolysis of fused salts.* A mixture of LnCl_3 with either NaCl or CaCl_2 is fused and electrolysed in a graphite or refractory-lined steel cell, which serves as the cathode, with a graphite rod as anode. This is used primarily for mischmetal, the lighter, lower-melting Ce, and for Sm, Eu and Yb for which method (ii) yields Ln^{II} ions.

(ii) *Metallothermic reduction.* This consists of the reduction of the anhydrous halides with calcium metal. Fluorides are preferred, since they are non-hygroscopic and the CaF_2 produced is stable, unlike the other Ca halides which are liable to boil at the temperatures reached in the process. $\text{LnF}_3 + \text{Ca}$ are heated in a tantalum crucible to a temperature 50° above the mp of Ln under an atmosphere of argon. After completion of the reaction, the charge is cooled and the slag and metal (of 97–99% purity) broken apart. The main impurity is Ca which is removed by melting

under vacuum. With the exceptions of Sm, Eu and Yb this method has general applicability.

In 1995 total world production of "rare earth oxides" was 68 000 tonnes of which China and the USA produced 30 000 and 29 000 tonnes of bastnaesite respectively with smaller quantities of monazite from Australia (as a by-product of TiO_2 production) and India. The bulk of output is used without separation of individual lanthanides. Major uses are in the production of low alloy steels for plate and pipe where $< 1\%$ Ln/La added in the form of mischmetall or silicides greatly improves strength and workability, and in petroleum "cracking" catalysis where various mixed metal oxides are employed. The walls of domestic "self-cleaning" ovens are treated with CeO_2 which prevents the formation of tarry deposits, and CeO_2 of varying purity is used to polish glass. Other small-scale uses include that of mischmetall in Mg-based alloys to produce lighter flints, while Ln/Co alloys are used for the construction of permanent magnets, and individual Ln oxides are used as phosphors in television screens and similar fluorescent surfaces.

Current availability of individual lanthanides (plus Y and La) in a state of high purity and relatively low cost has stimulated research into potential new applications. These are mainly in the field of solid state chemistry and include solid oxide fuel cells, new phosphors and perhaps most significantly high temperature superconductors (p. 1182.)

30.2.3 Properties of the elements

The metals are silvery in appearance (except for Eu and Yb which are pale yellow, see p. 112 and below) and are rather soft, but become harder across the series. Most of them exist in more than one crystallographic form, of which hcp is the most common; all are based on typically metallic close-packed arrangements, but their conductivities are appreciably lower than those of other close-packed metals.

The more important physical properties of the elements are summarized in Table 30.2. The alternation between several and few stable

isotopes for even and odd atomic number respectively, is mirrored by an even-odd variation in the natural abundances of the elements (see p. 4) and in the uncertainty of their atomic weights (see p. 17).

The electronic configurations of the free atoms are determined only with difficulty because of the complexity of their atomic spectra, but it is generally agreed that they are nearly all $[\text{Xe}]4f^n 5d^0 6s^2$. The exceptions are:

- (1) Cerium, for which the sudden contraction and reduction in energy of the 4f orbitals immediately after La is not yet sufficient to avoid occupancy of the 5d orbital.
- (2) Gd, which reflects the stability of the half-filled 4f shell;
- (3) Lu, at which point the shell has been filled.

However, only in the case of cerium (see below) does this have any marked effect on the aqueous solution chemistry, which is otherwise dominated by the +3 oxidation state, for which the configuration varies regularly from $4f^1$ (Ce^{III}) to $4f^{14}$ (Lu^{III}). It is notable that a regular variation is found for any property for which this $4f^n$ configuration is maintained across the series, whereas the variation in those properties for which this configuration is not maintained can be highly irregular. This is illustrated dramatically in size variations (Fig. 30.2). On the one hand, the radii of Ln^{III} ions decrease regularly from La^{III} (included for completeness) to Lu^{III} . This "lanthanide contraction" occurs because, although each increase in nuclear charge is exactly balanced by a simultaneous increase in electronic charge, the directional characteristics of the 4f orbitals cause the $4f^n$ electrons to shield themselves and other electrons from the nuclear charge only imperfectly. Thus, each unit increase in nuclear charge produces a net increase in attraction for the whole extranuclear electron charge cloud and each ion shrinks slightly in comparison with its predecessor. On the other hand, although a similar overall reduction is seen in the metal radii, Eu and Yb are spectacularly irregular. The reason is that most of the metals are composed of a lattice of Ln^{III} ions with a $4f^n$ configuration and 3 electrons in the

Table 30.2 Some properties of the lanthanide elements

Property	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic number	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Number of naturally occurring isotopes	4	1	7	—	7	2	7	1	7	1	6	1	7	2
Outer electron configuration	4f ¹ 5d ¹ 6s ²	4f ³ 6s ²	4f ⁴ 6s ²	4f ⁵ 6s ²	4f ⁶ 6s ²	4f ⁷ 6s ²	4f ⁷ 5d ¹ 6s ²	4f ⁹ 6s ²	4f ¹⁰ 6s ²	4f ¹¹ 6s ²	4f ¹² 6s ²	4f ¹³ 6s ²	4f ¹⁴ 6s ²	4f ¹⁴ 5d ¹ 6s ²
Atomic weight	140.116(1)	140.90765(2)	144.24(3)	—	150.36(3)	151.964(1)	157.25(3)	158.92534(2)	162.50(3)	164.93032(2)	167.26(3)	168.93421(2)	173.04(3)	174.967(1)
Metal radius (CN 6)/pm	181.8	182.4	181.4	183.4	180.4	208.4	180.4	177.3	178.1	176.2	176.1	175.9	193.3	173.8
Ionic radius (CN 6)/pm														
IV	87	85	—	—	—	—	—	76	—	—	—	—	—	—
III	102	99	98.3	97	95.8	94.7	93.8	92.3	91.2	90.1	89.0	88.0	86.8	86.1
II	—	—	129 ^(a)	—	122 ^(b)	117	—	—	107	—	—	103	102	—
$E^\circ(\text{M}^{4+}/\text{M}^{3+})/\text{V}$	1.72	3.2 ^(c)	4.9 ^(c)	—	—	—	—	3.1 ^(c)	5.4 ^(c)	—	—	—	—	—
$E^\circ(\text{M}^{3+}/\text{M}^{2+})/\text{V}$	—	—	—2.6	—	—1.55	—0.35	—	—	—2.5	—	—	—2.3	—1.05	—
$E^\circ(\text{M}^{3+}/\text{M})/\text{V}$	—2.34	—2.35	—2.32	—2.29	—2.30	—1.99	—2.28	—2.31	—2.29	—2.33	—2.32	—2.32	—2.22	—2.30
MP/°C	798	931	1021	1042	1074	822	1313	1365	1412	1474	1529	1545	819	1663
BP/°C	3433	3520	3074	(3000)	1794	1429	3273	3230	2567	2700	2868	1950	1196	3402
$\Delta H_{\text{fus}}/\text{kJ mol}^{-1}$	5.2(±1.2)	11.3(±2.1)	7.13	—	8.9(±0.4)	—	—	—	—	—	—	—	3.35	—
$\Delta H_{\text{vap}}/\text{kJ mol}^{-1}$	398	331	289	—	165(±17)	176	301	293	280	280	280	247	159	414
ΔH_f (monatomic gas)/kJ mol ⁻¹	419	356	328	301	207	178	398	389	291	301	317	232	152	—
Ionization energies/ kJ mol ⁻¹														
1st	541	522	530	536	542	547	595	569	567	574	581	589	603	513
2nd	1047	1018	1034	1052	1068	1085	1172	1112	1126	1139	1151	1163	1175	1341
3rd	1940	2090	2128	2140	2285	2425	1999	2122	2230	2221	2207	2305	2408	2054
ΔH (hydration L _n ³⁺)/kJ mol ⁻¹	3370	3413	3442	3478	3515	3547	3571	3605	3637	3667	3691	3717	3739	3760
Density(25°C)/ g cm ⁻³	6.770	6.773	7.007	—	7.520	5.234	7.900	8.229	8.550	8.795	9.066	9.321	6.965	9.840
Electrical resistivity (25°C)/μ ohm cm	73	68	64	(50)	88	90	134	114	57	87	87	79	29	79

^(a)CN = 8.^(b)CN = 7.^(c)Estimated values since these M^{IV} are not stable in aqueous solution.

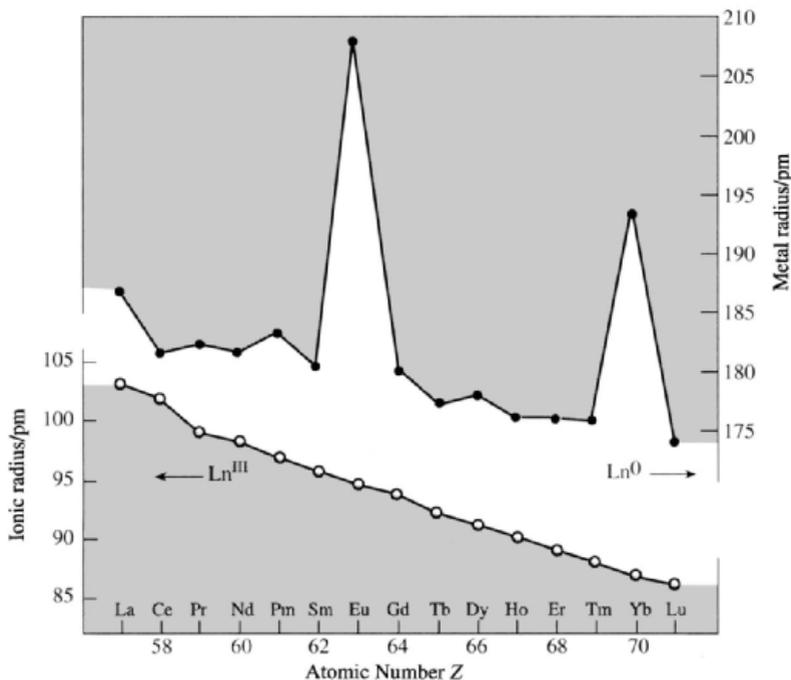


Figure 30.2 Variation of metal radius and 3+ ionic radius for La and the lanthanides. Other data for Ln^{II} and Ln^{IV} are in Table 30.2.

5d/6s conduction band. Metallic Eu and Yb, however, are composed predominantly of the larger Ln^{II} ions with $4f^{n+1}$ configurations and only 2 electrons in the conduction band. The smaller and opposite irregularity for metallic Ce is due to the presence of ions in an oxidation state somewhat above +3. Similar discontinuities are found in other properties of the metals, particularly at Eu and Yb.

A contraction resulting from the filling of the 4f electron shell is of course not exceptional. Similar contractions occur in each row of the periodic table and, in the d block for instance, the ionic radii decrease by 20.5 pm from Sc^{III} to Cu^{III} , and by 15 pm from Y^{III} to Ag^{III} . The importance of the lanthanide contraction arises from its consequences:

- (1) The reduction in size from one Ln^{III} to the next makes their separation possible, but the smallness and regularity of the reduction makes the separation difficult.

- (2) By the time Ho is reached the Ln^{III} radius has been sufficiently reduced to be almost identical with that of Y^{III} which is why this much lighter element is invariably associated with the heavier lanthanides.
- (3) The total lanthanide contraction is of a similar magnitude to the expansion found in passing from the first to the second transition series, and which might therefore have been expected to occur also in passing from second to third. The interpolation of the lanthanides in fact almost exactly cancels this anticipated increase with the result, noted in preceding chapters, that in each group of transition elements the second and third members have very similar sizes and properties.

Redox processes, which of necessity entail a change in the occupancy of the 4f shell, vary in a very irregular manner across the series. Quantitative data from direct measurements are

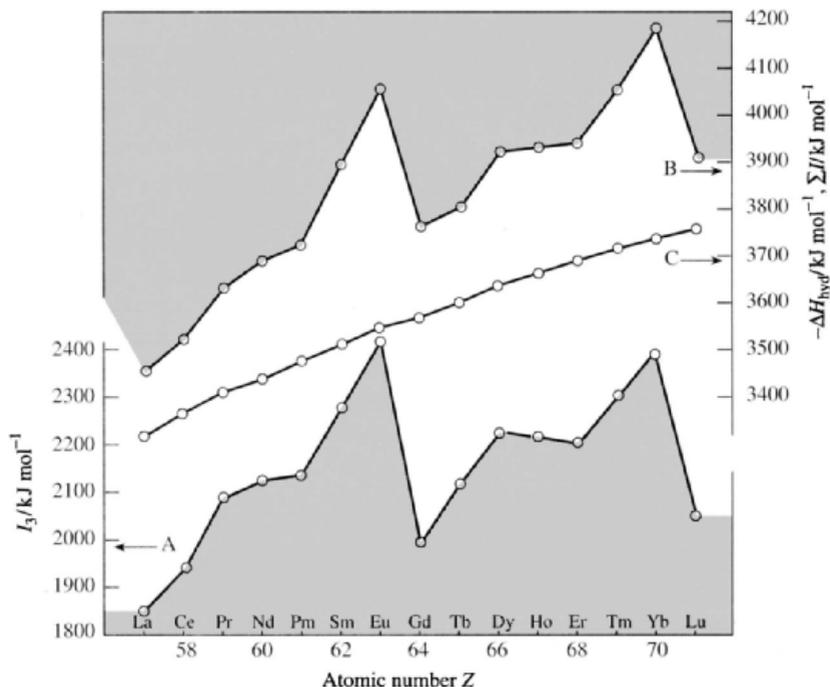


Figure 30.3 Variation with atomic number of some properties of La and the lanthanides: A, the third ionization energy (I_3); B, the sum of the first three ionization energies (ΣI); C, the enthalpy of hydration of the gaseous trivalent ions ($-\Delta H_{\text{hyd}}$). The irregular variations in I_3 and ΣI , which refer to redox processes, should be contrasted with the smooth variation in ΔH_{hyd} , for which the $4f^n$ configuration of Ln^{III} is unaltered.

far from complete for such processes, but the use of thermodynamic (Born–Haber) cycles⁽¹⁰⁾ greatly improves the situation. Enthalpies of atomization (ΔH_f) and ionization energies are given in Table 30.2 and the variations of I_3 and ΣI are shown in Fig. 30.3. I_3 refers to the 1-electron change, $4f^{n+1}(\text{Ln}^{2+}) \rightarrow 4f^n(\text{Ln}^{3+})$ and the close similarity of the two curves indicates that this change is the dominant factor in determining the shape of the ΣI curve. The variation of I_3 across the series is in fact typical of the variation in energy of any process (e.g. $-\Delta H_f$ which refers essentially to $4f^{n+1}6s^2 \rightarrow 4f^n 5d^1 6s^2$) which involves the reduction of Ln^{3+} to Ln^{2+} . It is characterized by an increase in energy, first as each of the $4f$ orbitals of the Ln^{II} ions are singly occupied and the stability of the $4f$

shell steadily increases due to the corresponding increase in nuclear charge (La \rightarrow Eu); then again as each $4f$ orbital is doubly occupied (Gd \rightarrow Lu). The sudden falls at Gd and Lu reflect the ease with which it is possible to remove the single electrons in excess of the stable $4f^7$ and $4f^{14}$ configurations. Explanations have been given for the smaller irregularities at the quarter- and three-quarter-shell stages, but require a careful consideration of interelectronic repulsion, as well as exchange energy, terms.⁽¹¹⁾

30.2.4 Chemical reactivity and trends

The lanthanides are very electropositive and reactive metals. With the exception of Yb

¹⁰ D. A. JOHNSON, *J. Chem. Ed.* **57**, 475–7 (1980).

¹¹ D. A. JOHNSON, *Adv. Inorg. Chem. Radiochem.* **20**, 1–132 (1977).

their reactivity apparently depends on size so that Eu which has the largest metal radius is much the most reactive. They tarnish in air and, if ignited in air or O_2 , burn readily to give Ln_2O_3 or, in the case of cerium, CeO_2 (praseodymium and terbium yield nonstoichiometric products approximating to Pr_6O_{11} and Tb_4O_7 respectively). When heated, they also burn in halogens producing LnX_3 , and in hydrogen producing LnH_2 and LnH_3 (see below). They will, indeed, react, though usually less vigorously, with most non-metals if heated. Treatment with water yields hydrous oxides, and the metals dissolve rapidly in dilute acids, even in the cold, to give aqueous solutions of Ln^{III} salts.

The great bulk of lanthanide chemistry is of the +3 oxidation state where, because of the large sizes of the Ln^{III} ions, the bonding is predominantly ionic in character, and the cations display the typical class-a preference of O -donor ligands (p. 909). Three-dimensional lattices, characteristic of ionic character, are common and the coordination chemistry is quite different from, and less extensive than, that of the d-transition metals. Coordination numbers are generally high and stereochemistries, being determined largely by the requirements of the ligands and lacking the directional constraints of covalency, are frequently ill-defined, and the complexes distinctly labile. Thus, in spite of widespread opportunities for isomerism, there appears to be no confirmed example of a lanthanide complex existing in more than one molecular arrangement. Furthermore, only strongly complexing (i.e. usually chelating) ligands yield products which can be isolated from aqueous solution, and the comparative tenacity of the small H_2O molecule commonly leads to its inclusion, often with consequent uncertainty as to the coordination number involved. This is not to say that other types of complex cannot be obtained, but complexes with uncharged monodentate ligands, or ligands with donor atoms other than O , must usually be prepared in the absence of water.

Some typical compounds are listed in Table 30.3. Coordination numbers below 6 are found only with very bulky ligands and even

the coordination number of 6 itself is unusual, 7, 8 and 9 being more characteristic. Coordination numbers of 10 and over require chelating ligands with small "bites" (p. 917), such as NO_3^- or SO_4^{2-} , and are confined to compounds of the larger, lighter lanthanides. The stereochemistries quoted, especially for the high coordination numbers, are idealized and in most cases appreciable distortions are in fact found.

A number of trends connected with ionic radii are noticeable across the series. In keeping with Fajans' rules, salts become somewhat less ionic as the Ln^{III} radius decreases; reduced ionic character in the hydroxide implies a reduction in basic properties and, at the end of the series, $Yb(OH)_3$ and $Lu(OH)_3$, though undoubtedly mainly basic, can with difficulty be made to dissolve in hot conc $NaOH$. Paralleling this change, the $[Ln(H_2O)_x]^{3+}$ ions are subject to an increasing tendency to hydrolyse, and hydrolysis can only be prevented by use of increasingly acidic solutions.

However, solubility, depending as it does on the rather small difference between solvation energy and lattice energy (both large quantities which themselves increase as cation size decreases) and on entropy effects, cannot be simply related to cation radius. No consistent trends are apparent in aqueous, or for that matter nonaqueous, solutions but an empirical distinction can often be made between the lighter "cerium" lanthanides and the heavier "yttrium" lanthanides. Thus oxalates, double sulfates and double nitrates of the former are rather less soluble and basic nitrates more soluble than those of the latter. The differences are by no means sharp, but classical separation procedures depended on them.

Although lanthanide chemistry is dominated by the +3 oxidation state, and a number of binary compounds which ostensibly involve Ln^{II} are actually better formulated as involving Ln^{III} with an electron in a delocalized conduction band, genuine oxidation states of +2 and +4 can be obtained. Ce^{IV} and Eu^{II} are stable in water and, though they are respectively strongly oxidizing and strongly reducing, they have well-established

Table 30.3 Oxidation states and stereochemistries of compounds of the lanthanides^(a)

Oxidation state	Coordination number	Stereochemistry	Examples
2	6	Octahedral	LnZ (Ln = Sm, Eu, Yb; Z = S, Se, Te)
	8	Cubic	LnF_2 (Ln = Sm, Eu, Yb)
3	3	Pyramidal	$[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (Ln = Nd, Eu, Yb)
	4	Tetrahedral	$[\text{Lu}(2,6\text{-dimethylphenyl})_4]^-$
		Distorted tetrahedral	$[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3(\text{OPPh}_3)]$ (Ln = Eu, Lu)
	6	Octahedral	$[\text{LnX}_6]^{3-}$ (X = Cl, Br; LnCl_3 (Ln = Dy–Lu))
	7	Capped trigonal prismatic	$[\text{Dy}(\text{dpm})_3(\text{H}_2\text{O})]^{(b)}$
		Capped octahedral	$[\text{Ho}\{\text{PhC}(\text{O})\text{CH}=\text{C}(\text{O})\text{Ph}_3\}(\text{H}_2\text{O})]$
	8	Dodecahedral	$[\text{Ho}(\text{tropolonate})_4]^-$
		Square antiprismatic	$[\text{Eu}(\text{acac})_3(\text{phen})]$
		Bicapped trigonal prismatic	LnF_3 (Ln = Sm–Lu)
	9	Tricapped trigonal prismatic	$[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$, $[\text{Eu}(\text{terpy})_3]^{3+}$
		Capped square antiprismatic	$[\text{Pr}(\text{terpy})\text{Cl}_3(\text{H}_2\text{O})_5] \cdot 3\text{H}_2\text{O}$
		Bicapped dodecahedral	$[\text{Ln}(\text{NO}_3)_5]^{2-}$ (Ln = Ce, Eu)
4	12	Icosahedral	$[\text{Ce}(\text{NO}_3)_6]^{3-(c)}$
	15	See p. 1249	$[\text{Sm}(\eta^5\text{-C}_9\text{H}_7)_3]$
	16	See pp. 1248, 1249	$[\text{Nd}(\eta^5\text{-C}_5\text{H}_4\text{Me})_3]_4$, $[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)_2]^-$
	6	Octahedral	$[\text{CeCl}_6]^{2-}$
	8	Cubic	LnO_2 (Ln = Ce, Pr, Tb)
		Square antiprismatic	$[\text{Ce}(\text{acac})_4]$, LnF_4 (Ln = Ce, Pr, Tb)
	10	Complex	$[\text{Ce}(\text{NO}_3)_4(\text{OPPh}_3)_2]^{(c)}$
	12	Icosahedral	$[\text{Ce}(\text{NO}_3)_6]^{2-(c)}$

^(a)Except where otherwise stated, Ln is used rather loosely to mean most of the lanthanides; the Pm compound, for instance, is usually missing simply because of the scarcity and consequent expense of Pm.

^(b)dpm = dipivaloylmethane, $\text{Me}_3\text{CC}(\text{O})\text{CH}=\text{C}(\text{O}^-)\text{CMe}_3$.

^(c)The structure can be visualized as octahedral if each NO_3^- is considered to occupy a single coordination site (p. 1245).

aqueous chemistries. Ln^{IV} (Ln = Pr, Nd, Tb, Dy) and Ln^{II} (Ln = Nd, Sm, Eu, Dy, Tm, Yb) also are known in the solid state but are unstable in water. The rather restricted aqueous redox chemistry which this implies is summarized in the oxidation state diagram (Fig. 30.4).

The prevalence of the +3 oxidation state is a result of the stabilizing effects exerted on different orbitals by increasing ionic charge. As successive electrons are removed from a neutral lanthanide atom, the stabilizing effect on the orbitals is in the order $4f > 5d > 6s$, this being the order in which the orbitals penetrate through the inert core of electrons towards the nucleus. By the time an ionic charge of +3 has been reached, the preferential stabilization of the 4f orbitals is such that in all cases the 6s and 5d orbitals have been emptied. Also, in most cases, the electrons remaining in the 4f orbitals are themselves so far

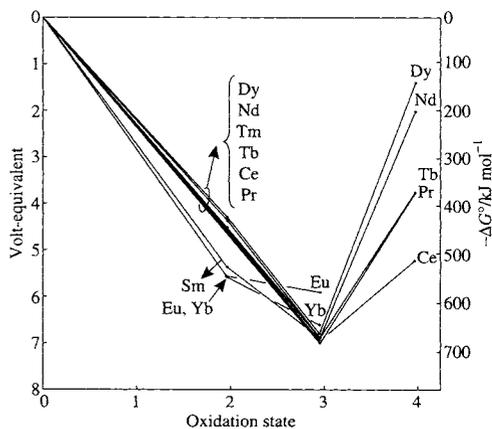


Figure 30.4 Volt-equivalent versus oxidation state for lanthanides with more than one oxidation state.

embedded in the inert core as to be immovable by chemical means. Exceptions are Ce and, to

a lesser extent, Pr which are at the beginning of the series where, as already noted, the 4f orbitals are still at a comparatively high energy and can therefore lose a further electron. Tb^{IV} presumably owes its existence to the stability of the $4f^7$ configuration.

The stabilizing effects of half, and completely, filled shells can be similarly invoked to explain the occurrence of the divalent state in $Eu^{II}(4f^7)$ and $Yb^{II}(4f^{14})$ while these, and the other known divalent ions are of just those elements which occupy elevated positions on the I_3 plot (Fig. 30.3).

The absence of 5d electrons and the inertness of the lanthanides' 4f shell makes π backbonding energetically unfavourable and simple carbonyls, for instance, have only been obtained in argon matrices at 8–12 K. On the other hand, essentially ionic cyclopentadienides are well known and an increasing number of σ -bonded Ln–C compounds have been produced (see section 30.3.5).

30.3 Compounds of the Lanthanides^(12–15)

The reaction between H_2 and the gently heated (300–350°C) metals produces black, reactive and highly conducting solids, LnH_2 . These hydrides have the fcc fluorite structure (p. 118) and are evidently composed of Ln^{III} , $2H^-$, e^- , the electron being delocalized in a metallic conduction band. Further hydrogen can be accommodated in the interstices of the lattice and, with the exceptions of Eu and Yb, which are the two lanthanides

¹² S. COTTON, *Lanthanides and Actinides*, Macmillan, Basingstoke, 1991, 192 pp.

¹³ G. MEYER and L. R. MORSS (eds.), *Synthesis of Lanthanide and Actinide Compounds*, Kluwer, Dordrecht, 1991, 367 pp.

¹⁴ M. LESKALÄ and L. NIINISTÖ, pp. 203–334, Vol. 8 (1986) and pp. 91–320, Vol. 9 (1987) of ref. 1.

¹⁵ T. MOELLER, The lanthanides, Chap. 44, pp. 1–101, in *Comprehensive Inorganic Chemistry*, Vol. 4, Pergamon Press, Oxford, 1973; Lanthanides and actinides, Vol. 7, *MTP International Review of Science, Inorganic Chemistry* (Series Two) (K. W. BAGNALL, ed.), Butterworths, London, 1975, 329 pp.

most favourably disposed to divalency, a limiting stoichiometry of LnH_3 can be achieved if high pressures are employed (p. 66). The composition of LnH_3 is Ln^{III} , $3H^-$ with conductivity correspondingly reduced as the additional H atom traps the previously delocalized electron (to form H^-).

Metallic conductivity, arising from the presence of Ln^{III} ions with the balance of electrons situated in a conduction band, is also found in some of the borides (p. 145) and carbides (p. 297).

30.3.1 Oxides and chalcogenides^(16,17)

Ln_2O_3 are all well characterized. With three exceptions they are the final products of combustion of the metals or ignition of the hydroxides, carbonate, nitrate, etc. The exceptions are Ce, Pr and Tb, the most oxidized products of which are the dioxides, from which the sesquioxides can be obtained by controlled reduction with H_2 . Ln_2O_3 adopt three structure types conventionally classified as:⁽¹⁸⁾

A-type, consisting of $\{LnO_7\}$ units which approximate to capped octahedral geometry, and favoured by the lightest lanthanides.

B-type, also consisting of $\{LnO_7\}$ units but now of three types, two are capped trigonal prisms and one is a capped octahedron; favoured by the middle lanthanides.

C-type, related to the fluorite structure but with one-quarter of the anions removed in such a way as to reduce the metal coordination number from 8 to 6 (but not octahedral); favoured by the middle and heavy lanthanides.

Ln_2O_3 are strongly basic and the lighter, more basic, ones resemble the oxides of Group 2

¹⁶ R. G. HAIRE and L. EYRING, pp. 413–506, Vol. 18 (1994) of ref. 1.

¹⁷ L. EYRING, pp. 187–224 of ref. 13 for oxides; M. GUITTARD and J. FLAHAUT, pp. 321–52 of ref. 13 for sulfides.

¹⁸ A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., pp. 544–7, Oxford University Press, Oxford, 1984.

in this respect. All are insoluble in water but absorb it to form hydroxides. They dissolve readily in aqueous acids to yield solutions which, providing they are kept on the acid side of pH 5 to avoid hydrolysis, contain the $[\text{Ln}(\text{H}_2\text{O})_x]^{3+}$ ions. Hydrous hydroxides can be precipitated from these solutions by addition of ammonia or aqueous alkali. Crystalline $\text{Ln}(\text{OH})_3$ have a 9-coordinate, tricapped, trigonal prismatic structure, and may be obtained by prolonged treatment of Ln_2O_3 with conc NaOH at high temperature and pressure (hydrothermal ageing).

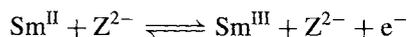
The pale-yellow CeO_2 is a rather inert material when prepared by ignition, but in the hydrous, freshly precipitated form it redissolves quite easily in acids. The analogous dark-coloured PrO_2 and TbO_2 can be obtained by ignition but require more extreme conditions (O_2 at 282 bar and 400°C for PrO_2 , and atomic oxygen at 450°C for TbO_2). All three dioxides have the fluorite structure. Since this is the structure on which C-type Ln_2O_3 is based (by removing a quarter of the anions) it is not surprising that these three oxide systems involve a whole series of nonstoichiometric phases between the extremes represented by $\text{LnO}_{1.5}$ and LnO_2 (p. 643). The compositions and structures of these phases arise because the basic unit from which they are built is a so-called "coordination defect", $[\text{M}_2^{\text{III}}\text{M}_{1.5}^{\text{IV}}\square\text{O}_6]^{(19)}$.

Claims for the existence of several lower oxides, LnO , have been made but most have been rejected, and it seems that only NdO , SmO (both lustrous golden yellow), EuO (dark red) and YbO (greyish-white) are genuine. They are obtained by reducing Ln_2O_3 with the metal at high temperatures and, except for EuO , at high pressures. They have the NaCl structure but whereas EuO and YbO are composed of Ln^{II} and are insulators or semiconductors, NdO and SmO like the dihydrides consist essentially of Ln^{III} ions with the extra electrons forming a conduction band. EuO was unexpectedly found to be ferromagnetic at low temperatures. The

absence of conduction electrons, and the presence of 4f orbitals which are probably too contracted to allow overlap between adjacent cations, makes it difficult to explain the mechanism of the ferromagnetic interaction. EuO and the monochalcogenides have potential applications in memory devices.⁽²⁰⁾

Chalcogenides of similar stoichiometry to the oxides, but for a wider range of metals, are known, though their characterization is made more difficult by the prevalence of nonstoichiometry and the occurrence of phase changes in several instances. In general the chalcogenides are stable in dry air but are hydrolysed if moisture is present. If heated in air they oxidize (sulfides especially) to basic salts of the corresponding oxo-anion and they show varying susceptibility to attack by acids with evolution of H_2Z .

Monochalcogenides, LnZ ($\text{Z} = \text{S}, \text{Se}, \text{Te}$), have been prepared for all the lanthanides except Pm, mostly by direct combination.⁽¹⁷⁾ They are almost black and, like the monoxides, have the NaCl structure. However, with the exceptions of SmZ , EuZ , YbZ , TmSe and TmTe , they have metallic conductivity and evidently consist of $\text{Ln}^{\text{III}} + \text{Z}^{2-}$ ions with 1 electron from each cation delocalized in a conduction band. EuZ and YbZ , by contrast, are semiconductors or insulators with genuinely divalent cations, but SmZ seem to be intermediate and may involve the equilibrium:



Trivalent chalcogenides, Ln_2Z_3 , can be obtained by a variety of methods which include direct combination and, in the case of the sulfides, the action of H_2S on the chloride or oxide. As with Ln_2O_3 , various crystalline modifications occur. When Ln_2Z_3 are heated with an excess of chalcogen in a sealed tube at 600°C , products with compositions up to or nearing LnZ_2 are obtained. They seem to be polychalcogenides, however, with the metal uniformly in the +3 state; Ln^{IV} chalcogenides are not known.

¹⁹ B. F. HOSKINS and R. L. MARTIN, *Aust. J. Chem.* **48**, 709–39 (1995).

²⁰ Pages 23–41 of ref. 11.

30.3.2 Halides^(12,13,21)

Halides of the lanthanides are listed in Table 30.4 and are of the types LnX_4 , LnX_3 and LnX_2 . Not surprisingly, LnX_4 occur only as the fluorides of Ce^{IV} , Pr^{IV} and Tb^{IV} . CeF_4 is comparatively stable and can be prepared either directly from the elements or by the action of F^- on aqueous solutions of Ce^{IV} when it crystallizes as the monohydrate. The other tetrafluorides are thermally unstable and, as they oxidize water, can only be prepared dry; TbF_4 from $\text{TbF}_3 + \text{F}_2$ at 320°C , and PrF_4 by the rather complex procedure of fluorinating a mixture of NaF and PrF_3 with F_2 ($\rightarrow \text{Na}_2\text{PrF}_6$) and then extracting NaF from the reaction mixture with liquid HF .

Promethium apart, all possible trihalides (52) are known. The trifluorides, being very insoluble, can be precipitated as $\text{LnF}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ by the action of HF on aqueous $\text{Ln}(\text{NO}_3)_3$. Aqueous solutions of the other trihalides are obtained by simply dissolving the oxides or carbonates in aqueous HX . Hydrated ($6\text{--}8\text{H}_2\text{O}$) salts can be crystallized, though with difficulty because of their high solubilities. Preparation of the anhydrous trihalides by thermal dehydration of these hydrates is possible for fluorides and chlorides of the lighter lanthanides, and an atmosphere of HX extends the applicability of the method to heavier lanthanides. Because of the possible formation of oxohalides in preparations involving halides and oxygen-containing materials, direct combination, which is a completely general method, is often preferred for the anhydrous halides.

The anhydrous trihalides are ionic, high melting, crystalline substances which, apart from the trifluorides are extremely deliquescent. As can be seen from Table 30.4, the coordination number of the Ln^{III} changes with the radii of the ions, from 9 for the trifluorides of the large lanthanides to 6 for the triiodides of the smaller lanthanides. Their chief importance has been as materials from which the pure metals can be prepared.

The dihalides are obtained from the corresponding trihalides, most generally by reduction with the lanthanide metal itself⁽²²⁾ or with an alkali metal^(23,24) and also, in the case of the more stable of the diiodides (SmI_2 , EuI_2 , YbI_2), by thermal decomposition.[†] SmI_2 and YbI_2 can also be conveniently prepared in quantitative yield by reacting the metal with 1,2-diiodoethane in anhydrous tetrahydrofuran at room temperature:⁽²⁵⁾ $\text{Ln} + \text{ICH}_2\text{CH}_2\text{I} \rightarrow \text{LnI}_2 + \text{CH}_2=\text{CH}_2$. With the exception of EuX_2 , all the dihalides are very easily oxidized and will liberate hydrogen from water. The occurrence of these dihalides parallels the occurrence of high values of the third ionization energy amongst the metals^(10,11) (Fig. 30.3), with the reasonable qualification that, in this low oxidation state, iodides are more numerous than fluorides. The same types of structures are found as for the alkaline earth dihalides with the coordination number of the cation ranging from 9 to 6 and, like CaI_2 , the diiodides of Dy, Tm and Yb form layer structures (CdCl_2 , CdI_2 ; see Fig. 29.2) typical of compounds with large anions where marked polarization effects are expected.

The isomorphous diiodides of Ce, Pr and Gd stand apart from all the other, salt-like, dihalides. These three, like LaI_2 , are notable for their metallic lustre and very high conductivities and are best formulated as $\{\text{Ln}^{\text{III}}, 2\text{I}^-, e^-\}$, the electron being in a delocalized conduction band. Besides the dihalides, other reduced species have been obtained such as $\text{Ln}_5\text{Cl}_{11}$ ($\text{Ln} = \text{Sm}, \text{Gd}, \text{Ho}$). They have fluorite-related structures (p. 118) in which the anionic sublattice is partially rearranged to accommodate additional anions,

²² J. D. CORBETT, pp. 159–73 of ref. 13.

²³ G. MEYER, *Chem. Rev.* **88**, 93–107 (1988); G. MEYER, and T. SCHLEID, pp. 175–85 of ref. 13.

²⁴ A. SIMON, H. MATTAUSCH, G. J. MILLER, W. BAUHOFFER and R. K. KREMER, pp. 191–285, Vol. 15 (1991) of ref. 1.

[†] Dilute solid solutions of Ln^{III} ions in CaF_2 may be reduced by Ca vapour to produce Ln^{II} ions trapped in the crystal lattice. By their use it has been possible to obtain the electronic spectra of Ln^{II} ions.

²⁵ P. GIRARD, J. L. NAMY and H. B. KAGAN, *J. Am. Chem. Soc.* **102**, 2693–8 (1980).

²¹ H. A. EICK, pp. 365–412, Vol. 18 (1994) of ref. 1.

Table 30.4 Properties of lanthanide halides: colour, mp/°C and coordination^(a)

	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LnF ₄	white 400 dec 8 sa	white dec 8 sa	--	--	--	--	white dec 8 sa	--	--	--	--	--	--
LnF ₃	white 1430 9 ttp	green 1395 9 ttp	violet 1374 9 ttp	white 1306 9 ttp	white 1276 9 ttp	white 1231 8 btp	white 1172 8 btp	green 1154 8 btp	pink 1143 8 btp	pink 1140 8 btp	white 1158 8 btp	white 1157 8 btp	white 1182 8 btp
LnCl ₃	white 817 9 ttp	green 786 9 ttp	mauve 758 9 ttp	yellow 682 9 ttp	yellow dec 9 ttp	white 602 9 ttp	white 582 8 btp	white 647 6 o	yellow 720 6 o	violet 776 6 o	yellow 824 6 o	white 865 6 o	white 925 6 o
LnBr ₃	white 733 9 ttp	green 691 9 ttp	violet 682 8 btp	yellow 640 8 btp	grey dec 8 btp	white 770 6 o	white 828 6 o	white 879 6 o	yellow 919 6 o	violet 923 6 o	white 954 6 o	white dec 6 o	white 1025 6 o
LnI ₃	yellow 766 8 btp	737 8btp	green 784 8 btp	orange 850 6 o	dec 6 o	yellow 925 6 o	957 6 o	green 978 6 o	yellow 994 6 o	violet 1015 6 o	yellow 1021 6 o	white dec 6 o	brown 1050 6 o
LnF ₂	--	--	--	purple 1417 8 c	yellow 1416 8 c	--	--	--	--	--	--	grey (1407) 8 c	--
LnCl ₂	--	--	green 841 9 ttp	brown 859 9 ttp	white 731 9 ttp	--	--	black 721 dec 8, 7	--	--	green 718 7 co	green 720 7 co	--
LnBr ₂	--	--	green 725 9 ttp	brown 669 8, 7	white 683 8, 7	--	--	black 7 co	--	--	green 7 co	yellow 673 6 o	--
LnI ₂	bronze 808	bronze 758	violet 562 8, 7	green 520 7 co	green 580 7 co	bronze 831	--	purple 721 dec 6 ol	--	--	black 756 6 ol	yellow 780 6 ol	--

^(a)9 ttp = 9-coordinate tricapped trigonal prismatic; 8 sa = 8-coordinate square antiprismatic; 8 btp = 8-coordinate bicapped trigonal prismatic; 8 c = 8-coordinate cubic (fluorite); 8, 7 = mixed 8- and 7-coordinate (SrBr₂ structure); 7 co = 7-coordinate capped octahedral; 6 o = 6-coordinate octahedral; 6 ol = 6-coordinate octahedral layered.

Table 30.5 Stoichiometries and structures of reduced halides ($X/M < 2$) of scandium, yttrium, lanthanum and the lanthanides

Average oxidation state	Examples	Structural features
1.714	Sc ₇ Cl ₁₂ M ₇ I ₁₂ (La, Pr, Tb)	Discrete M ₆ X ₁₂ clusters
1.600	Sc ₅ Cl ₈	Discrete M ₆ X ₁₂ clusters
1.500	M ₂ Cl ₃ (Y, Gd, Tb, Er, Lu) M ₂ Br ₃ (Y, Gd)	Single chains of edge-sharing metal octahedra with M ₆ X ₁₂ -type environment (edge-capped by X) along with parallel chains of edge-sharing MX ₆ octahedra
1.429	Sc ₇ Cl ₁₀	Single chains of edge-sharing metal octahedra with M ₆ X ₈ -type environment (face-capped by X)
1.000	MXH _n (X = Cl, Br)(Sc, Y, Gd, Lu and probably other Ln)	Double chains of edge-sharing metal octahedra with M ₆ X ₈ -type environment with parallel chains of edge-sharing MCl ₆ octahedra
		Double metal layers of edge-sharing metal octahedra, M ₆ X ₈ -type environment but with encapsulated H atoms

leading to irregular 7- and 8-coordination of the cations. In the case of Gd and Tb, further reduction gives rise to Ln₂Cl₃ phases which are constructed from Ln₆ octahedra sharing *trans*-edges and sheathed with chlorine atoms which bridge adjacent chains. Gd₂Cl₃ is a semiconductor and provided the first example of a lanthanide in an oxidation state $< +2$. Continued reduction finally produces “graphite-like” LnCl phases originally thought to be binary halides like ZrX (p. 966) but in fact, like ScCl (p. 950), requiring the presence of interstitial H atoms to stabilize the structure. They are therefore formulated as LnXH_n. Structural characteristics are summarised in Table 30.5.^(22,26–28)

Other interstitial atoms stabilizing such clusters are B, C, N and O.⁽²²⁾ Examples of carbon stabilized clusters include: isolated metal octahedra in Cs[Ln₆I₁₂C] (Ln = Er, Lu)⁽²⁹⁾ and Gd[Gd₆Cl₁₂C]; pairs of edge-sharing metal octahedra in Gd₁₀Cl₁₈(C₂)₂; and chains of edge-sharing metal octahedra in Gd₄I₅C.

30.3.3 Magnetic and spectroscopic properties⁽¹²⁾

The electronic configurations of the lanthanides are described by using the Russell–Saunders coupling scheme. Values of the quantum numbers S and L corresponding to the lowest energy are derived in the conventional manner.⁽¹²⁾ These are then expressed for each ion in the form of a ground term with the symbolism that $S, P, D, F, G, H, I, \dots$ correspond to $L = 0, 1, 2, 3, 4, 5, 6, \dots$ in that order. The angular momentum vectors associated with S and L couple together (spin–orbit coupling) to produce a resultant angular momentum associated with an overall quantum number J . Because the 4f electrons of lanthanide ions are largely buried in the inner core, they are effectively shielded from their chemical environments. As a result, spin–orbit coupling is much larger than the crystal field (of the order of 2000 cm⁻¹ compared to 100 cm⁻¹) and must be considered first. Note that this is precisely the reverse of the situation in the d-block elements where the d electrons are exposed directly to the influence of neighbouring groups and the crystal field is therefore much greater than the spin–orbit coupling.

J can take the values $J = L + S, L + S - 1, \dots, L - S$ (or $S - L$ if $S > L$), each corresponding to a different energy, so that a “term” (defined

²⁶ A. SIMON, *Angew. Chem. Int. Edn. Engl.* **27**, 159–83 (1988).

²⁷ R. P. ZIEBARTH and J. CORBETT, *Acc. Chem. Res.* **22**, 256–62 (1989).

²⁸ H. MATTAUSCH, R. EGER, J. D. CORBETT and A. SIMON, *Z. anorg. allg. Chem.* **616**, 157–61 (1992).

²⁹ H. M. ARTELT, T. SCHLEID and G. MEYER, *Z. anorg. allg. Chem.* **618**, 18–25 (1992).

Table 30.6 Magnetic and spectroscopic properties of Ln^{III} ions in hydrated salts

Ln	Unpaired electrons	Ground state	Colour	μ_e /BM	
				$g\sqrt{J(J+1)}$	Observed
Ce	1 (4f ¹)	² F _{5/2}	Colourless	2.54	2.3–2.5
Pr	2 (4f ²)	³ H ₄	Green	3.58	3.4–3.6
Nd	3 (4f ³)	⁴ I _{9/2}	Lilac	3.62	3.5–3.6
Pm	4 (4f ⁴)	⁵ I ₄	Pink	2.68	—
Sm	5 (4f ⁵)	⁶ H _{5/2}	Yellow	0.85	1.4–1.7 ^(a)
Eu	6 (4f ⁶)	⁷ F ₀	Very pale pink	0	3.3–3.5 ^(a)
Gd	7 (4f ⁷)	⁸ S _{7/2}	Colourless	7.94	7.9–8.0
Tb	6 (4f ⁸)	⁷ F ₆	Very pale pink	9.72	9.5–9.8
Dy	5 (4f ⁹)	⁶ H _{15/2}	Yellow	10.65	10.4–10.6
Ho	4 (4f ¹⁰)	⁵ I ₈	Yellow	10.60	10.4–10.7
Er	3 (4f ¹¹)	⁴ I _{15/2}	Rose-pink	9.58	9.4–9.6
Tm	2 (4f ¹²)	³ H ₆	Pale green	7.56	7.1–7.5
Yb	1 (4f ¹³)	² F _{7/2}	Colourless	4.54	4.3–4.9
Lu	0 (4f ¹⁴)	¹ S ₀	Colourless	0	0

^(a)These are the values of μ_e at room temperature. The values fall as the temperature is reduced (see text).

by a pair of S and L values) is said to split into a number of component “states” (each defined by the same S and L values plus a value of J). The “ground state” of the ion is that with $J = L - S$ (or $S - L$) if the f shell is less than half-full, and that with $J = L + S$ if the f shell is more than half-full. It is indicated simply by adding this value of J as a subscript to the symbol for the “ground term”.

The magnitude of the separation between the adjacent states of a term indicates the strength of the spin-orbit coupling, and in all but two cases (Sm^{III} and Eu^{III}) it is sufficient to render the first excited state of the Ln^{III} ions thermally inaccessible, and so the magnetic properties are determined solely by the ground state. It can be shown that the magnetic moment expected for such a situation is given by:

$$\mu_e = g\sqrt{J(J+1)} \text{ BM,}$$

$$\text{where } g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

As can be seen in Table 30.6, this agrees very well with experimental values except for Sm^{III} and Eu^{III} and agreement is reasonable for these

also if allowance is made for the temperature-dependent population of excited states.

Electronic absorption spectra are produced when electromagnetic radiation promotes the ions from their ground state to excited states. For the lanthanides the most common of such transitions involve excited states which are either components of the ground term[†] or else belong to excited terms which arise from the same 4f^{*n*} configuration as the ground term. In either case the transitions therefore involve only a redistribution of electrons within the 4f orbitals (i.e. f→f transitions) and so are orbitally forbidden just like d→d transitions. In the case of the latter the rule is partially relaxed by a mechanism which depends on the effect of the crystal field in distorting the symmetry of the metal ion. However, it has already been pointed out that crystal field effects are very much smaller in the case of Ln^{III} ions and they

[†] The separation of these component states being, as pointed out above, of the order of a few thousand wavenumbers, such transitions produce absorptions in the infrared region of the spectrum. Ions which have no terms other than the ground term will therefore be colourless, having no transitions of sufficiently high energy to absorb in the visible region. This accounts for the colourless ions listed in Table 30.6.

cannot therefore produce the same relaxation of the selection rule. Consequently, the colours of Ln^{III} compounds are usually less intense. A further consequence of the relatively small effect of the crystal field is that the energies of the electronic states are only slightly affected by the nature of the ligands or by thermal vibrations, and so the absorption bands are very much sharper than those for $d \rightarrow d$ transitions. Because of this they provide a useful means of characterizing, and quantitatively estimating, Ln^{III} ions.

Nevertheless, crystal fields cannot be completely ignored. The intensities of a number of bands ("hypersensitive" bands) show a distinct dependence on the actual ligands which are coordinated. Also, in the same way that crystal fields lift some of the orbital degeneracy ($2L + 1$) of the terms of d^n ions, so they lift some of the $2J + 1$ degeneracy of the states of f^n ions, though in this case only by the order of 100 cm^{-1} . This produces fine structure in some bands of Ln^{III} spectra.

Ce^{III} and Tb^{III} are exceptional in providing (in the ultraviolet) bands of appreciably higher intensity than usual. The reason is that the particular transitions involved are of the type $4f^n \rightarrow 4f^{n-1}5d^1$, and so are not orbitally forbidden. These 2 ions have 1 electron more than an empty f shell and 1 electron more than a half-full f shell, respectively, and the promotion of this extra electron is thereby easier than for other ions.

Sm, Dy but more especially Eu and Tb have excited states which are only slightly lower in energy than excited states of typical ligands. If electrons on the ligand are excited, the possibility therefore exists that, instead of falling back to the ground state of the ligand, they may pass first to the excited state of the Ln^{III} and then fall to the metal ground state, emitting radiation of characteristic frequency in doing so (fluorescence or, more generally, luminescence). This is the basis of the commercial use of oxide phosphors of these elements on TV screens where the excitation is provided by electrical discharge. Excitation by uv light produces luminescence spectra

which yield information about the donor atoms and co-ordination symmetry.^(30,31)

It has been possible, as already noted (footnote, p. 1240) to study the spectra of Ln^{II} ions stabilized in CaF_2 crystals. It might be expected that these spectra would resemble those of the +3 ions of the next element in the series. However, because of the lower ionic charge of the Ln^{II} ions their $4f$ orbitals have not been stabilized relative to the $5d$ to the same extent as those of the Ln^{III} ions. Ln^{II} spectra therefore consist of rather broad, orbitally allowed, $4f \rightarrow 5d$ bands overlaid with weaker and much sharper $f \rightarrow f$ bands.

30.3.4 Complexes^(12,14,32)

Oxidation state IV

The +4 oxidation state is found in LnO_2 , LnF_4 , the ternary oxides M_2LnO_3 and Li_8LnO_6 ($\text{Ln} = \text{Ce, Pr, Tb}$), and in the ternary fluorides M_3LnF_7 ($\text{Ln} = \text{Ce, Pr, Tb, Nd, Dy}$). $\text{M}^{\text{IV}}\text{TbIO}_6 \cdot x\text{H}_2\text{O}$ has been obtained from aqueous alkaline solution⁽³³⁾ but Ce is the only lanthanide with a significant aqueous or co-ordination chemistry in this oxidation state. Fig. 30.4 shows that this situation is in no way surprising.

Aqueous "ceric" solutions are widely used as oxidants in quantitative analysis; they can be prepared by the oxidation of Ce^{III} ("cerous") solutions with strong oxidizing agents such as peroxodisulfate, $\text{S}_2\text{O}_8^{2-}$, or bismuthate, BiO_3^- . Complexation and hydrolysis combine to render $E(\text{Ce}^{4+}/\text{Ce}^{3+})$ markedly dependent on anion and acid concentration. In relatively strong perchloric acid the aquo ion is present but in other acids coordination of the anion is likely. Also, if the pH is increased, hydrolysis to

³⁰ N. SABBATINI, M. GUARDIGOLI and J.-M. LEHN, *Coord. Chem. Revs.* **123**, 201–28 (1993).

³¹ J. V. BEITZ, pp. 159–96, Vol. 18 (1994) of ref. 1.

³² F. A. HART, Scandium, Yttrium and the Lanthanides, Chap. 39, pp. 1059–127, in *Comprehensive Coordination Chemistry*, Vol. 3, Pergamon Press, Oxford, 1987.

³³ Y. YING and Y. RU-DONG, *Polyhedron* **11**, 963–6 (1992).

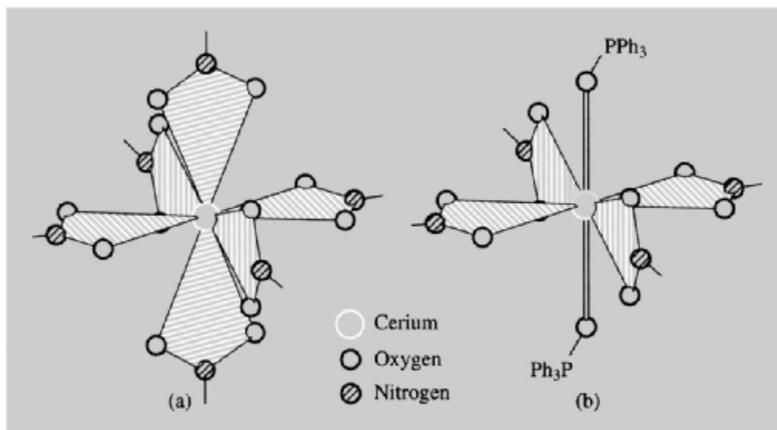


Figure 30.5 Nitrate complexes of Ce^{IV} . (a) $[\text{Ce}(\text{NO}_3)_6]^{2-}$: the Ce^{IV} is surrounded by 12 oxygen atoms from 6 bidentate nitrate ions in the form of an icosahedron (in each case the third oxygen is omitted for clarity). Note that this implies an octahedral disposition of the 6 nitrogen atoms. (b) $[\text{Ce}(\text{NO}_3)_4(\text{OPPh}_3)_2]$.

$\text{Ce}(\text{OH})^{3+}$ occurs followed by polymerization and finally, as the solution becomes alkaline, by precipitation of the yellow, gelatinous $\text{CeO}_2 \cdot x\text{H}_2\text{O}$.

Of the various salts which can be isolated from aqueous solution, probably the most important is the water-soluble double nitrate, $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$, which is the compound generally used in Ce^{IV} oxidations. The anion involves 12-coordinated Ce (Fig. 30.5a). Two *trans*-nitrates of this complex can be replaced by Ph_3PO to give the orange 10-coordinate neutral complex $[\text{Ce}(\text{NO}_3)_4(\text{OPPh}_3)_2]$ (Fig. 30.5b). The sulfates $\text{Ce}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 0, 4, 8, 12$) and $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_3$, and the iodate are also known. Also obtainable from aqueous solutions are complexes with other *O*-donor ligands such as β -diketonates, and fluoro complexes such as $[\text{CeF}_8]^{4-}$ and $[\text{CeF}_6]^{2-}$. This last ion is not in fact 6-coordinated but achieves an 8-coordinate, square-antiprismatic geometry with the aid of fluoride bridges. In the orange $[\text{CeCl}_6]^{2-}$ by contrast, the larger halide is able to stabilize a 6-coordinate, octahedral geometry. It is prepared by treatment of CeO_2 with HCl but, because Ce^{IV} in aqueous solution oxidizes HCl to Cl_2 , the reaction must be performed in a nonaqueous solvent such as pyridine or dioxan.

Oxidation state III

The coordination chemistry of the large, electropositive Ln^{III} ions is complicated, especially in solution, by ill-defined stereochemistries and uncertain coordination numbers. This is well illustrated by the aquo ions themselves.⁽³⁴⁾ These are known for all the lanthanides, providing the solutions are moderately acidic to prevent hydrolysis, with hydration numbers probably about 8 or 9 but with reported values depending on the methods used to measure them. It is likely that the primary hydration number decreases as the cationic radius falls across the series. However, confusion arises because the polarization of the H_2O molecules attached directly to the cation facilitates hydrogen bonding to other H_2O molecules. As this tendency will be the greater, the smaller the cation, it is quite reasonable that the secondary hydration number increases across the series.

Hydrated salts with all the common anions can be crystallized from aqueous solutions and frequently, but by no means invariably, they contain the $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$ ion. An enormous number of salts of organic acids such as oxalic, citric and

³⁴ E. N. RIZKALLA and G. R. CHOPPIN, pp. 529–58, Vol. 18 (1994) of ref. 1; T. KOWALL, F. FOGLIA, L. HELM and A. E. MERBACH, *J. Am. Chem. Soc.* **117**, 3790–9 (1995).

tartaric have been studied,⁽³⁵⁾ often for use in separation methods. These anions are, in fact, chelating *O* ligands which as a class provide the most extensive series of Ln^{III} complexes. NO₃⁻ is an inorganic counterpart and is notable for the high coordination numbers it yields, as in the 10-coordinate bicapped dodecahedral [Ce(NO₃)₅]²⁻, and in [Ce(NO₃)₆]³⁻ which like its Ce^{IV} analogue, has the 12-coordinate icosahedral geometry (Fig. 30.5a) (see also p. 469).

β -diketonates (L-L) provide further important examples of this class of ligand, and yield complexes of the type [Ln(L-L)₃L'] (L' = H₂O, py, etc.) and [Ln(L-L)₄]⁻, which are respectively 7- and 8-coordinate. Dehydration, under vacuum, of the hydrated tris-diketonates produces [Ln(L-L)₃] complexes which probably increase their coordination by dimerizing or polymerizing. They may be sublimed, the most volatile and thermally stable being those with bulky alkyl groups R in [RC(O)CHC(O)R]⁻; they are soluble in non-polar solvents, and have received much attention as "nmr shift" reagents. Thus, in the case of organic molecules which are able to coordinate to Ln^{III} (i.e. if they contain groups such as -OH or -COO⁻), the addition of one of these coordinatively unsaturated reagents produces a labile adduct; because this adduct is anisotropic the paramagnetic Ln^{III} ion shifts the resonance line of each proton by an amount which is critically dependent on the spatial relationship of the Ln^{III} and the proton. Greatly improved resolution is thereby obtained along with the possibility of distinguishing between alternative structures of the organic molecule.

Various crown ethers (p. 96) with differing cavity diameters provide a range of coordination numbers and stoichiometries, although crystallographic data are sparse. An interesting series, illustrating the dependence of coordination number on cationic radius and ligand cavity diameter, is provided by the complexes formed by the lanthanide nitrates and the 18-crown-6 ether (i.e. 1,4,7,10,13,16-

hexaoxacyclo-octadecane). For Ln = La–Gd the most thermally-stable product is that with a ratio of Ln:crown ether = 4:3, but the larger of these lanthanides (i.e. La, Ce, Pr and Nd) also form a 1:1 complex. This is [Ln(NO₃)₃L] in which the Ln^{III} is 12-coordinate⁽³⁶⁾ (Fig. 30.6a). The 4:3 complex, on the other hand, is probably [Ln(NO₃)₂L]₃[Ln(NO₃)₆] in which, compared to the 1:1 complex, the Ln^{III} in the complex cation has lost one NO₃⁻, so reducing its coordination number to 10. The remaining, still smaller lanthanides (Tb–Lu) find the cavity of this ligand too large and form [Ln(NO₃)₃(H₂O)₃]L, in which the ligand is uncoordinated.

Unidentate *O* donors such as pyridine-*N*-oxide and triphenylphosphine oxide also form many complexes, as do alkoxides. This last group, like the alkoxides of Sc and Y (p. 951) is of special interest because of possible applications in the deposition of pure metal oxides by MOCVD techniques.⁽³⁷⁾ Attempts to prepare Ln(OR)₃ usually produce polynuclear clusters. Two examples will suffice: [Nd₆(OPr^{*i*})₁₇Cl], made up of 6 Nd atoms held together around a central Cl atom by means of bridging OCHMe₂ groups⁽³⁸⁾ (Fig. 30.6b). [Yb₅O(OPr^{*i*})₁₃] which consists of a square pyramid of Yb atoms containing a μ_5 -O. Four μ_2 -OPr^{*i*} groups cap the faces of the square pyramid. A single terminal alkoxide completes a distorted octahedral coordination sphere for each metal atom.⁽³⁹⁾

Complexes with *O*-donor ligands are more numerous than those with *N* donors, probably because the former ligands are more often negatively charged — a clear advantage when forming essentially ionic bonds. However, by using polar organic solvents such as ethanol, acetone or acetonitrile in order to avoid competitive coordination by water, complexes with

³⁶ J.-C. G. BÜNZLI, B. KLEIN and D. WESSNER, *Inorg. Chim. Acta* **44**, L147–9 (1980).

³⁷ D. C. BRADLEY, *Chem. Revs.* **89**, 1317–22 (1989).

³⁸ R. A. ANDERSEN, D. H. TEMPLETON and A. ZALKIN, *Inorg. Chem.* **17**, 1962–5 (1978).

³⁹ D. C. BRADLEY, H. CHUDZYNSKA, D. M. FRIGO, M. E. HAMMON, M. B. HURSTHOUSE and M. A. MAZID, *Polyhedron* **9**, 719–26 (1990).

³⁵ A. OUCHI, Y. SUZUKI, Y. OHKI and Y. KOIZUMI, *Coord. Chem. Revs.* **92**, 29–43 (1988).

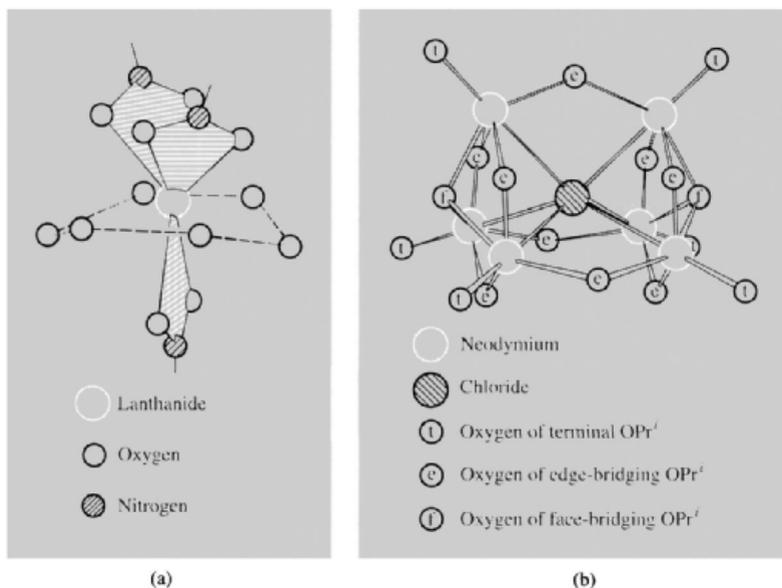
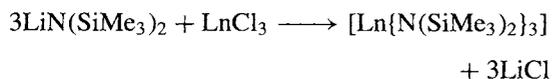


Figure 30.6 (a) $\text{Ln}(\text{NO}_3)_3$ (18-crown-6). For clarity only 2 of the oxygen atoms of each nitrate ion are shown, and only the 6 oxygen atoms of the crown ether. (Note the boat conformation of the crown ether which allows access to two NO_3^- on the open side and only one on the hindered side.) (b) $[\text{Nd}_6(\text{OPr}^i)_{17}\text{Cl}]$. Only the oxygens of the OPr^i groups are shown. Note that the 6 Nd atoms surrounding the Cl atom are situated at the corners of a trigonal prism, held together by 2 face-bridging and 9 edge-bridging alkoxides.

chelating ligands such as en, dien, bipy,^(39a) and terpy can be prepared. Coordination numbers of 8, 9 and 10 as in $[\text{Ln}(\text{en})_4]^{3+}$, $[\text{Ln}(\text{terpy})_3]^{3+}$ and $[\text{Ln}(\text{dien})_4(\text{NO}_3)_2]^{2+}$ are typical. Nor do complexes such as the well-known $[\text{Ln}(\text{edta})(\text{H}_2\text{O})_3]^-$ show any destabilization because of the *N* donor atoms (edta has 4 oxygen and 2 nitrogen donor atoms). More pertinently, whereas the complexes of 18-crown-6-ethers mentioned above dissociate instantly in water, complexes of the *N*-donor analogues are sufficiently stable to remain unchanged.

As with other transition elements, the lanthanides can be induced to form complexes with exceptionally low coordination numbers by use of the very bulky ligand, $\text{N}(\text{SiMe}_3)_2^-$:



The volatile, but air-sensitive, and very easily hydrolysed products have a coordination number of 3, the lowest found for the lanthanides; they are apparently planar in solution (zero dipole moment) but pyramidal in the solid state. With Ph_3PO the 4-coordinate distorted tetrahedral adducts $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3(\text{OPPh}_3)]$ are obtained. So difficult is it to expand the coordination sphere that attempts to prepare bis- (Ph_3PO) adducts produce instead the dimeric peroxo bridged complex, $[(\text{Ph}_3\text{PO})\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{LnO}_2\text{-Ln}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{OPPh}_3)]$ (see p. 619).

Coordination by halide ions is rather weak, that of I^- especially so, but from non-aqueous solutions it is possible to isolate anionic complexes of the type $[\text{LnX}_6]^{3-}$. These are apparently, and unusually for Ln^{III} , 6-coordinate and octahedral. The heavier donor atoms S, Se, $\text{P}^{(40)}$ and As form only a few

⁴⁰ M. D. FRYZUK, T. S. HADDAD and D. J. BERG, *Coord. Chem. Revs.* **99**, 137–212 (1990).

^{39a} E. C. CONSTABLE, *Adv. Inorg. Chem.* **34**, 1–64 (1989).

compounds. Chelating dithiocarbamate ligands provide the best known examples such as $[\text{Ln}(\text{S}_2\text{CNMe}_2)_3]$ and $[\text{Ln}(\text{S}_2\text{CNMe}_2)_4]^-$. Trigonal planar $[\text{Sm}(\text{SAr})_3]$, ($\text{Ar} = \text{C}_6\text{H}_2\text{Bu}_3^{1-2,4,6}$) is a rare example of an Ln complex with a unidentate S-donor ligand and also an unusually low coordination number.⁽⁴⁰⁾

Oxidation state II⁽¹¹⁾

The coordination chemistry in this oxidation state is essentially confined to the ions Sm^{II} , Eu^{II} and Yb^{II} . These are the only ones with an aqueous chemistry and their solutions may be prepared by electrolytic reduction of the Ln^{III} solutions or, in the case of Eu^{II} , by reduction with amalgamated Zn. These solutions are blood-red for Sm^{II} , colourless or pale greenish-yellow for Eu^{II} and yellow for Yb^{II} , and presumably contain the aquo ions. All are rapidly oxidized by air, and Sm^{II} and Yb^{II} are also oxidized by water itself although aqueous Eu^{II} is relatively stable, especially in the dark.

A number of salts have been isolated but, especially those of Sm^{II} and Yb^{II} , are susceptible to oxidation even by their own water of crystallization. Carbonates and sulfates, however, have been characterized and shown to be isomorphous with those of Sr^{II} and Ba^{II} .

Europium and Yb display further similarity with the alkaline earth metals in dissolving in liquid ammonia to give intense blue solutions, characteristic of solvated electrons and presumably also containing $[\text{Ln}(\text{NH}_3)_x]^{2+}$. The solutions are strongly reducing and decompose on standing with the precipitation of orange $\text{Eu}(\text{NH}_2)_2$ and brown $\text{Yb}(\text{NH}_2)_2$ (always contaminated with $\text{Yb}(\text{NH}_2)_3$) which are isostructural with the Ca and Sr amides.

30.3.5 Organometallic compounds⁽⁴¹⁾

The organometallic chemistry of lanthanides is far less extensive than that of transition elements

but, in spite of the lanthanides' inability to engage in π backbonding, it is one which has shown appreciable growth in the last quarter of a century. The compounds are of two main types: the predominantly ionic cyclopentadienides, and the σ -bonded alkyls and aryls. Organolanthanides of any type are usually thermally stable, but unstable with respect to water and air.

Cyclopentadienides and related compounds

The series $[\text{Ln}(\text{C}_5\text{H}_5)_3]$, $[\text{Ln}(\text{C}_5\text{H}_5)_2\text{Cl}]$ and the less numerous $[\text{Ln}(\text{C}_5\text{H}_5)\text{Cl}_2]$ are salts of the C_5H_5^- anion and their most general preparation is by the reaction of anhydrous LnCl_3 and NaC_5H_5 in appropriate molar ratios in thf. The metal atoms in these compounds display an apparent tendency to increase their coordination numbers: solvates and other adducts are readily formed. In polar solvents, where they are no doubt solvated, they are monomeric but, in non-polar solvents the $\text{tris}(\text{C}_5\text{H}_5)$ compounds are insoluble, while the $\text{bis}(\text{C}_5\text{H}_5)$ compounds dimerize. In the solid state the $\text{tris}(\text{C}_5\text{H}_5)$ compounds show considerable structural diversity. Those of Er and Tm have η^5 rings arranged in a trigonal plane around the metal and those of Lu and Pr are isostructural with the Sc and La analogues respectively (p. 953). In the Sm compound each C_5H_5^- ion is pentahapto towards 1 metal atom but some also act as bridges by presenting a ring vertex (η^1) or edge (η^2) towards an adjacent metal atom, so producing a chain structure.[†] In a less complicated way the blue $[\text{Nd}(\text{C}_5\text{H}_4\text{Me})_3]$ is actually tetrameric, each Nd being attached to three rings in a pentahapto mode with one ring being further attached in a monohapto manner to an adjacent Nd. In spite of the steric bulk of the ligand, $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_3]$ has been obtained.⁽⁴²⁾ $[\text{Ln}(\text{C}_5\text{H}_5)_2\text{Cl}]$

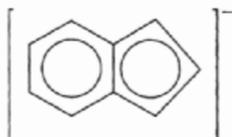
[†] Ring bridges of these types are found in alkaline earth cyclopentadienides such as $[\text{Ca}(\text{C}_5\text{H}_5)_2]$ and are characteristic of the electrostatic nature of the bonding.

⁴² W. J. EVANS, S. L. GONZALES and J. W. ZILLER, *J. Am. Chem. Soc.* **113**, 7423–4 (1991).

⁴¹ C. J. SCHAEVERIEN, *Adv. Organometallic Chem.* **36**, 283–362 (1994).

are actually dimers $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ln}(\mu\text{-Cl})_2\text{Ln}(\eta^5\text{-C}_5\text{H}_5)_2]$. The Cl bridges can be replaced by, for instance, H, CN and OR and donor solvents will cleave the bridges. Most mono (C_5H_5) and (C_5Me_5) compounds are tris solvates such as $[\text{Ln}(\eta^5\text{-C}_5\text{H}_5)_2(\text{thf})_3]$.

Complexes with the two analogous ligands, indenide, C_9H_7^- ,

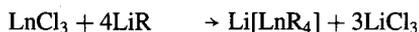


and cyclooctatetraenide, cot , $\text{C}_8\text{H}_8^{2-}$, ions can be prepared by similar means. In solid $[\text{Sm}(\text{C}_9\text{H}_7)_3]$ the 5-membered rings of the 3 ligands are bonded in a pentahapto manner and the compound shows little tendency to solvate, presumably because of the bulky nature of the C_9H_7^- ions. The lighter (and therefore larger) Ln^{III} ions form $\text{K}[\text{Ln}(\eta^8\text{-C}_8\text{H}_8)_2]$. The Ce^{III} member of the series has a similar “sandwich” structure to the so-called “uranocene” (p. 1279). The other members of the series have the same infrared spectrum and so also are presumed to have this structure.

Cyclopentadienyl derivatives of divalent lanthanides are also known⁽⁴³⁾ $[\text{Ln}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2]$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$) might be expected to be isostructural with ferrocene but are “bent” i.e. rather than the two rings being parallel they are tilted relative to each other.

Alkyls and aryls

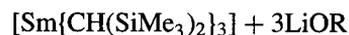
These are prepared by metathesis in thf or ether solutions:



⁴³ W. J. EVANS, *Polyhedron*, **6**, 803–35 (1987).

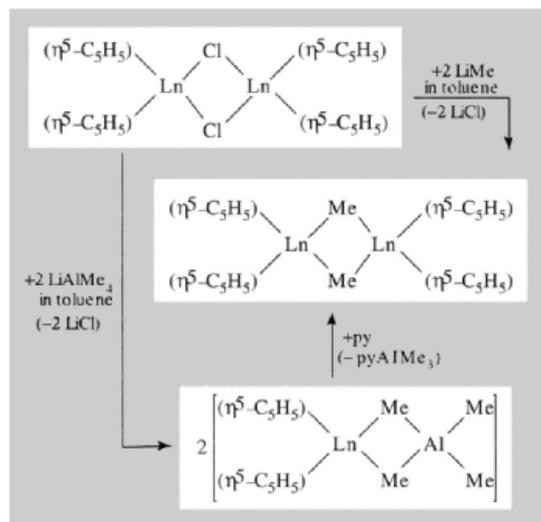
The triphenyls are probably polymeric and the first fully-characterized compound was $[\text{Li}(\text{thf})_4][\text{Lu}(\text{C}_6\text{H}_3\text{Me}_2)_4]$ in which the Lu is tetrahedrally coordinated to four σ -aryl groups. More stable products, of the form $[\text{LnR}_3(\text{thf})_2]$, are obtained by the use of bulky alkyl groups such as $-\text{CH}_2\text{CMe}_3$ and $-\text{CH}_2\text{SiMe}_3$.

Methyl derivatives, octahedral $[\text{LnMe}_6]^{3-}$ species, are known for most of the lanthanides. The first homoleptic, neutral lanthanide alkyl⁽⁴⁴⁾ was obtained using the bulky alkyl $\text{CH}(\text{SiMe}_3)_2$:



Compounds containing lanthanide–carbon σ -bonds have recently been reviewed.⁽⁴⁵⁾

Novel, mixed alkyl cyclopentadienides have also been prepared for the heavy lanthanides:⁽⁴⁶⁾



⁴⁴ P. B. HITCHCOCK, M. F. LAPPERT, R. G. SMITH, R. A. BARTLETT and P. P. POWER, *J. Chem. Soc., Chem. Commun.*, 1007–9 (1988).

⁴⁵ S. A. COTTON, *Coord. Chem. Revs.* **160**, 93–127 (1997).

⁴⁶ J. HOLTON, M. F. LAPPERT, D. G. H. BALLARD, R. PEARCE, J. L. ATWOOD and W. E. HUNTER, *J. Chem. Soc., Dalton Trans.*, 45–61 (1979).