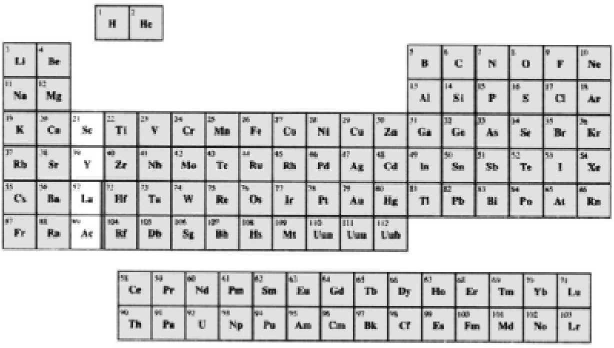

20

Scandium, Yttrium, Lanthanum and Actinium

20.1 Introduction

In 1794 the Finnish chemist J. Gadolin, while examining a mineral that had recently been discovered in a quarry at Ytterby, near Stockholm, isolated what he thought was a new oxide (or "earth") which A. G. Ekeberg in 1797 named yttria. In fact it was a mixture of a number of metal oxides from which yttrium oxide was separated by C. G. Mosander in 1843. This is actually part of the fascinating story of the "rare earths" to which we shall return in Chapter 30. The first sample of yttrium metal, albeit very impure, was obtained by F. Wöhler in 1828 by the reduction of the trichloride by potassium.

Four years before isolating yttria, Mosander extracted lanthanum oxide as an impurity from cerium nitrate (hence the name from Greek λανθάνειν, to hide), but it was not until 1923 that metallic lanthanum in a relatively pure form was obtained, by electrolysis of fused halides.

Scandium, the first member of the group, is also present in the Swedish ores from which yttrium and lanthanum had been extracted, but in only very small amounts and, probably for this reason, its discovery was delayed until 1879 when L. F. Nilsen isolated a new oxide and named it scandia. A few years later and with larger amounts at his disposal, P. T. Cleve prepared a large number of salts from this oxide and was able to show that it was the oxide of a new element whose properties tallied very closely indeed with those predicted by D. I. Mendeleev for ekaboron, an element missing from his classification (p. 29). It was only in 1937 that the metal itself was prepared by the electrolysis of molten chlorides of potassium, lithium and scandium, and only in 1960 that the first pound of 99% pure metal was produced.

The final member of the group, actinium, was identified in uranium minerals by A. Debierne in 1899, the year after P. and M. Curie had discovered polonium and radium in the same minerals. However, the naturally occurring isotope, ^{227}Ac, is a β^- emitter with a half-life of 21.77 y and the intense γ activity of its decay products makes it difficult to study.

20.2 The Elements(1,2,3)

20.2.1 Terrestrial abundance and distribution

With the exception of actinium, which is found naturally only in traces in uranium ores, these elements are by no means rare though they were once thought to be so: Sc 25, Y 31, La 35 ppm of the earth's crustal rocks, (cf. Co 29 ppm). This was, no doubt, at least partly because of the considerable difficulty experienced in separating them from other constituent rare earths. As might be expected for class-a metals, in most of their minerals they are associated with oxoanions such as phosphate, silicate and to a lesser extent carbonate.

Scandium is very widely but thinly distributed and its only rich mineral is the rare thortveitite, $Sc_2Si_2O_7$ (p. 348), found in Norway, but since scandium has only small-scale commercial use, and can be obtained as a byproduct in the extraction of other materials, this is not a critical problem. Yttrium and lanthanum are invariably associated with lanthanide elements, the former (Y) with the heavier or "Yttrium group" lanthanides in minerals such as xenotime, $M^{III}PO_4$ and gadolinite, $M_2^{III}M_3^{II}Si_2O_{10}$ (M^{II} = Fe, Be), and the latter (La) with the lighter or "cerium group" lanthanides in minerals such as monazite, $M^{III}PO_4$ and bastnaesite, $M^{III}CO_3F$. This association of similar metals is a reflection of their ionic radii. While La^{III} is similar in size to the early lanthanides which immediately follow it in the periodic table, Y^{III}, because of the steady fall in ionic radius along the lanthanide series (p. 1234), is more akin to the later lanthanides.

20.2.2 Preparation and uses of the metals

Some scandium is obtained from thortveitite, which contains 35–40% Sc_2O_3, but most is obtained as a byproduct in the processing of uranium ores which contain only about 0.02% Sc_2O_3, and in the production of tungsten. Its applications, for instance in laser crystals and coatings, are highly specialized and the amount consumed is low, though increasing.

Yttrium and lanthanum are both obtained from lanthanide minerals and the method of extraction depends on the particular mineral involved. Digestions with hydrochloric acid, sulfuric acid, or caustic soda are all used to extract the mixture of metal salts. Prior to the Second World War the separation of these mixtures was effected by fractional crystallizations, sometimes numbered in their thousands. However, during the period 1940–45 the main interest in separating these elements was in order to purify and characterize them more fully. The realization that they are also major constituents of the products of nuclear fission effected a dramatic sharpening of interest in the USA. As a result, ion-exchange techniques were developed and, together with selective complexation and solvent extraction, these have now completely supplanted the older methods of separation (p. 1228). In cases where the free metals are required, reduction of the trifluorides with metallic calcium can be used.

Yttrium has important roles in the field of electronics, providing the basis of the phosphors used to produce the red colour on television screens and, in the form of garnets such as $Y_3Fe_5O_{12}$, being employed as microwave filters in radar. Because of its low neutron absorption cross-section, yttrium has potential as a moderator in nuclear reactors though this use has yet to be developed. It was, however, the announcement in 1986/87 of the *high temperature superconductors*, $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-x}$ which produced the highest, though as yet unfulfilled, hopes of commercial exploitation. The latter compound has a critical temperature, $T_c \sim 95\,K$, below which it is

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[1] R. C. VICKERY, Scandium, yttrium and lanthanum, Chap. 31 in *Comprehensive Inorganic Chemistry*, Vol. 3, pp. 329–53, Pergamon Press, Oxford, 1973, and references therein. C. T. HOROVITZ (ed.), *Scandium: Its Occurrence, Chemistry, Physics, Metallurgy, Biology and Technology*, Academic Press, London, 1975, 598 pp.

[2] S. COTTON, *Lanthanides and Actinides*, Macmillan, Basingstoke, 1991, 192 pp.

[3] K. A. GSCHNEIDER and L. EYRING (eds) *Handbook of the Physics and Chemistry of Rare Earths*, Vols 1–21, 1978–1995, Elsevier, Amersterdam.

superconducting. This temperature, crucially, can be attained using liquid nitrogen rather than liquid helium as refrigerant and a continuing spate of publications on these and related materials has been generated (p. 1182).

Lanthanum has also found modest uses. Its oxide is an additive in high-quality optical glasses to which it imparts a high refractive index (sparkle) and has been suggested for a variety of catalytic uses. "Mischmetal", an unseparated mixture of lanthanide metals containing about 25% La, is used in making lighter flints, and more importantly in the production of alloy steels. (p. 1232).

Actinium occurs naturally as a decay product of ^{235}U:

$$^{235}_{92}\mathrm{U} \xrightarrow[7.04\times10^{8}\,\mathrm{y}]{\alpha} {}^{231}_{90}\mathrm{Th} \xrightarrow[25.52\,\mathrm{h}]{\beta^-} {}^{231}_{91}\mathrm{Pa} \xrightarrow[3.28\times10^{4}\,\mathrm{y}]{\alpha}$$

$$^{227}_{89}\mathrm{Ac} \xrightarrow[21.77\,\mathrm{y}]{\beta^-} {}^{227}_{90}\mathrm{Th} \dashrightarrow$$

but the half-lives are such that one tonne of the naturally occurring uranium ore contains on average only about 0.2 mg of Ac. An alternative source is the neutron irradiation of ^{226}Ra in a nuclear reactor:

$$^{226}_{88}\mathrm{Ra} + {}^{1}_{0}n \longrightarrow {}^{227}_{88}\mathrm{Ra} \xrightarrow[42.2\,\mathrm{min}]{\beta^-} {}^{227}_{89}\mathrm{Ac} \dashrightarrow$$

In either case, ion-exchange or solvent extraction techniques are needed to separate the element and, at best, it can be produced in no more than milligram quantities. Large-scale use is therefore impossible even if desired.

20.2.3 Properties of the elements

A number of the properties of Group 3 elements are summarized in Table 20.1. Each of the elements has an odd atomic number and so has few stable isotopes. All are rather soft, silvery-white metals, and they display the gradation in properties that might be expected for elements immediately following the strongly electropositive alkaline-earth metals and preceding the transition elements proper. Each is less electropositive than its predecessor in Group 2 but more electropositive than its successors in transition series, while the increasingly electropositive character of the heavier elements of the group is in keeping with the increase in size. The inverse trends in electronegativity are illustrated in Fig. 20.1.

As is the case for boron and aluminium (in Group 13), the underlying electron cores are those of the preceding noble gases and indeed, as was pointed out in Chapter 7, a much more

Table 20.1 Some properties of Group 3 elements

Property	Sc	Y	La	Ac
Atomic number	21	39	57	89
Number of naturally occurring isotopes	1	1	2	(2)
Atomic weight	44.955910(8)	88.90585(2)	138.9055(2)	227.0277[(a)]
Electronic configuration	[Ar]$3d^1 4s^2$	[Kr]$4d^1 5s^2$	[Xe]$5d^1 6s^2$	[Rn]$6d^1 7s^2$
Electronegativity	1.3	1.2	1.1	1.1
Metal radius (12-coordinate)/pm	162	180	187	—
Ionic radius (6-coordinate)/pm	74.5	90.0	103.2	112
$E^\circ(\mathrm{M}^{3+} + 3\mathrm{e}^- = \mathrm{M(s)})$/V	−2.03	−2.37	−2.37	−2.6
MP/°C	1539	1530	920	817
BP/°C	2748	3264	3420	2470
$\Delta H_{\mathrm{fus}}/\mathrm{kJ\,mol^{-1}}$	15.77	11.5	8.5	(10.5)
$\Delta H_{\mathrm{vap}}/\mathrm{kJ\,mol^{-1}}$	332.71	367	402	(293)
ΔH_{f} (monatomic gas)/kJ mol^{-1}	376 (±20)	425 (±8)	423 (±6)	—
Density (20°C)/g cm^{-3}	3.0	4.5	6.17	—
Electrical resistivity (20°C)/μohm cm	50–61	57–70	57–80	—

(a) This value is for the radioisotope with the longest half-life (^{227}Ac).

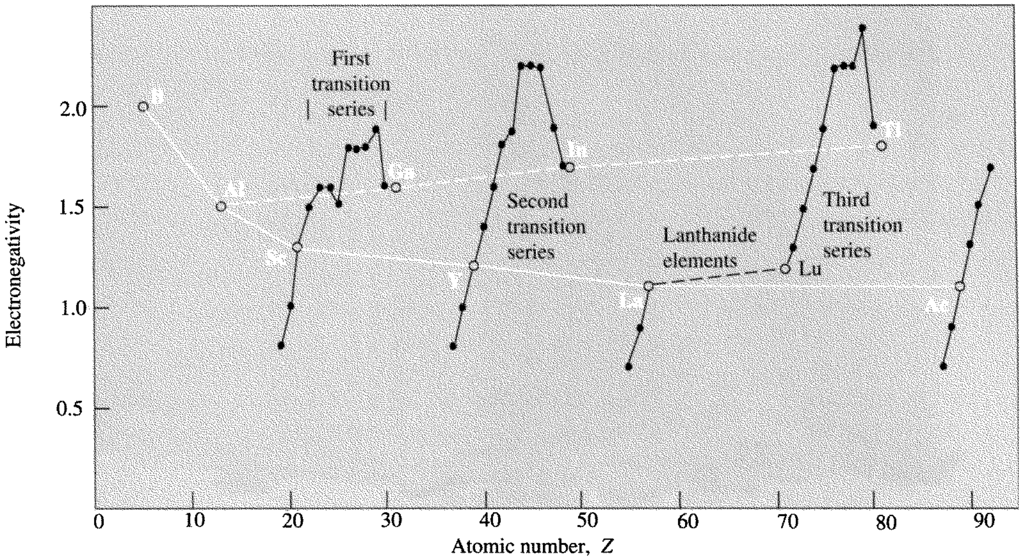

Figure 20.1 Electronegativity of the elements in Groups 3 and 13.

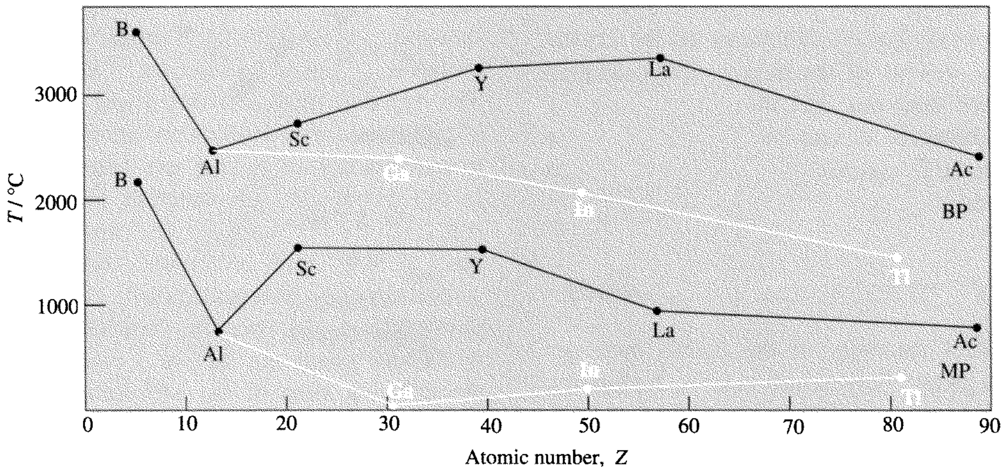

Figure 20.2 Mps and bps of the elements in Groups 3 and 13.

regular variation in atomic properties occurs in passing from B and Al to Group 3 than to heavier congeners in Group 13 (p. 223). However, the presence of a d electron on each of the atoms of this group (in contrast to the p electron in the atoms of B, Al and the other elements in Group 13) has consequences which can be seen in some of the bulk properties of the metals. For instance, the mps and bps (Fig. 20.2), along with the enthalpies associated with these transitions, all show discontinuous increases in passing from Al to Sc rather than to Ga, indicating that the d electron has a more cohesive effect than the p electron. It appears that this is due to d electrons forming more localized bonds within the metals. Thus, although Sc, Y and La have typically metallic (hcp) structures (with other metallic modifications at higher temperatures),

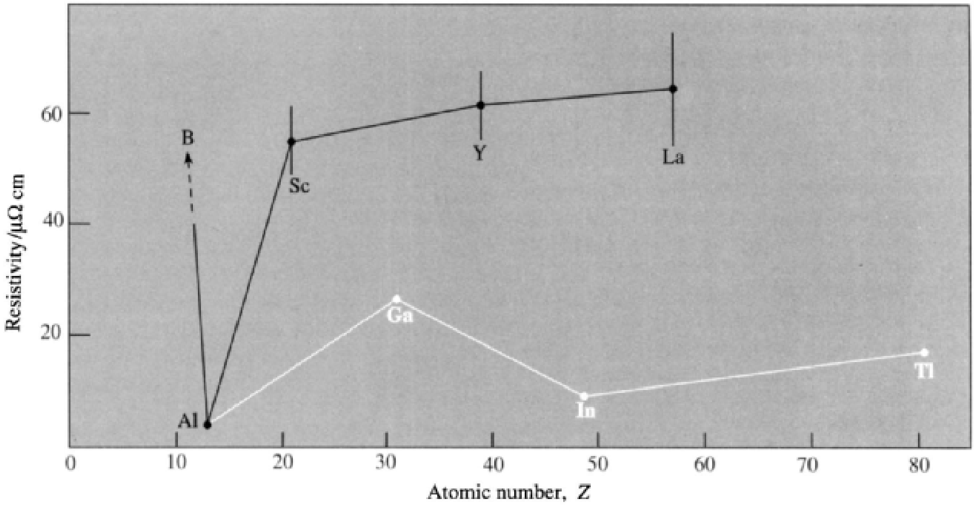

Figure 20.3 Resistivities of the elements in Groups 3 and 13.

their electrical resistivities are much higher than that of Al (Fig. 20.3). Admittedly, resistivity is a function of thermal vibrations of the crystal lattice as well as of the degree of localization of valence electrons, but even so the marked changes between Al and Sc seem to indicate a marked reduction in the mobility of the d electron of the latter.

20.2.4 Chemical reactivity and trends

The general reactivity of the metals increases down the group. They tarnish in air — La rapidly, but Y much more slowly because of the formation of a protective oxide coating — and all burn easily to give the oxides M_2O_3. They react with halogens at room temperature and with most non-metals on warming. They reduce water with evolution of hydrogen, particularly if finely divided or heated, and all dissolve in dilute acid. Strong acids produce soluble salts whereas weak acids such as HF, H_3PO_4 and $H_2C_2O_4$ produce sparingly soluble or insoluble salts.

In the main, the chemistry of these elements concerns the formation of a predominantly ionic +3 oxidation state arising from the loss of all 3 valence electrons and giving a well-defined cationic aqueous chemistry. Because of this, although each member of this group is the first member of a transition series, its chemistry is largely atypical of the transition elements. The variable oxidation states and the marked ability to form coordination compounds with a wide variety of ligands are barely hinted at in this group although materials containing the metals in low oxidation states can be prepared (see p. 949) and a limited organometallic (predominantly cyclopentadienyl) chemistry has developed. Differences in chemical behaviour within the group are largely a consequence of the differing sizes of the M^{III} ions. Scandium, the lightest of these elements, with the smallest ionic radius, is the least basic and the strongest complexing agent, with properties not unlike those of aluminium. Its aqueous solutions are appreciably hydrolysed and its oxide has some acidic properties. On the other hand, lanthanum and actinium (in so far as its properties have been examined) show basic properties approaching those of calcium.

Most structural studies have relied exclusively on the use of X-ray techniques but these elements have nuclei, ^{45}Sc, ^{89}Y and ^{139}La with abundances in excess of 99.9% and $I = \frac{7}{2}, \frac{1}{2}, \frac{7}{2}$ respectively. The application of nmr studies is therefore becoming increasingly important,[4] mainly on solutions but also for solid-state work.[5]

20.3 Compounds of Scandium, Yttrium, Lanthanum and Actinium

20.3.1 Simple compounds[6]

The oxides, M_2O_3, are white solids which can be prepared directly from the elements. In Sc_2O_3 and Y_2O_3 the metals are 6-coordinate but the larger La^{III} ion adopts this structure only at elevated temperatures, a 7-coordinate structure being normally more stable. When water is added to La_2O_3 it "slakes" like lime with evolution of much heat and a hissing sound. The hydroxides, $M(OH)_3$, (or in the case of scandium possibly the hydrated oxide) are obtained as gelatinous precipitates from aqueous solutions of the metal salts by addition of alkali hydroxide. In the case of scandium only, this precipitate can be dissolved in an excess of conc NaOH to give anionic species such as $[Sc(OH)_6]^{3-}$. Yttrium and lanthanum hydroxides possess only basic properties, and the latter especially will absorb atmospheric CO_2 to form basic carbonates.

Dissolution of the oxide or hydroxide in the appropriate acid provides the most convenient method for producing the salts of the colourless, diamagnetic M^{III} ions. Such solutions, especially those of Sc^{III}, are significantly hydrolysed with the formation of polymeric hydroxy species.

With the exception of the fluorides, the halides are all very water-soluble and deliquescent. Precipitation of the insoluble fluorides can be used as a qualitative test for these elements. The distinctive ability of Sc^{III} to form complexes is illustrated by the fact that an excess of F^- causes the first-precipitated ScF_3 to redissolve as $[ScF_6]^{3-}$; indeed, $M_3[ScF_6]$, $M = NH_4$, Na, K, were isolated as long ago as 1914. The anhydrous halides are best prepared by direct reaction of the elements rather than by heating the hydrates which causes hydrolysis. Heating the hydrated chlorides, for instance, gives Sc_2O_3, YOCl and LaOCl respectively, though to produce AcOCl it is necessary to use superheated steam. The anhydrous halides illustrate nicely the effects of ionic size on the coordination number of the metal[2]. In all four of its halides scandium is 6-coordinate. So too is yttrium except in its fluoride where it has eight near neighbours and one slightly further away (8 + 1). The larger lanthanum however has 9 + 2 coordination in its fluoride, but is 9-coordinate in its chloride and bromide and 8-coordinate in its iodide.

Sulfates and nitrates are known and in all cases they decompose to the oxides on heating. Double sulfates of the type $M_2^{III}(SO_4)_3.3Na_2SO_4.12H_2O$ can be prepared, and La (unlike Sc and Y) forms a double nitrate, $La(NO_3)_3.2NH_4NO_3.4H_2O$, which is of the type once used extensively in fractional crystallization procedures for separating individual lanthanides.

Reaction of the metals with hydrogen produces highly conducting materials with the composition MH_2, similar to the metallic nonstoichiometric hydrides of the subsequent transition elements (pp. 66–7). Except in the case of ScH_2, further H_2 can then be absorbed causing a diminution of electrical conductivity until materials similar to the ionic hydrides of the alkaline-earth metals, and with the limiting composition MH_3, are produced. The dihydrides, though ostensibly containing the divalent metals, are probably best considered as pseudo-ionic compounds of M^{3+} and $2H^-$ with the extra electron in a conduction band. However, the question of the type of bonding is still controversial, as was explained more fully in Chapter 3 (p. 66).

Another example of a "divalent" metal of this group, but which in fact is probably entirely analogous to the dihydrides, is LaI_2. However, the most extensive set of examples of these metals in low formal oxidation states is provided by the binary and ternary halides produced by

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[4] J. MASON, *Polyhedron* **8**, 1657–68 (1989).

[5] A. R. THOMPSON and E. OLDFIELD, *J. Chem. Soc., Chem. Commun.*, 27–9 (1987).

[6] G. MEYER and L. R. MORSS (eds.), *Synthesis of Lanthanide and Actinide Compounds*, Kluwer Acad. Publ., Dordrecht, 1991, 367 pp.

prolonged heating of the reactants in sealed tantalum or niobium vessels to temperatures sometimes in excess of 1000°C. Starting with ScX_3 and Sc metal along with the appropriate alkali metal halide, several compounds of the series M^IScX_3 have been obtained containing octahedrally coordinated Sc^{II} in linear $[ScX_3^-]$ chains⁽⁷⁾. $ScCl_3 + Sc$ yield no less than five reduced phases, dark-coloured and sensitive to oxygen and moisture⁽⁸⁾:

> Sc_7Cl_{12} consists of discrete $[Sc_6Cl_{12}]^{3-}$ clusters, similar to the M_6Cl_{12} clusters of Nb and Ta (p. 991), along with separate Sc^{3+} ions;
>
> Sc_5Cl_8 is best regarded as $(ScCl_2^+)_n$-$(Sc_4Cl_6^-)_n$ in which edge-sharing $ScCl_6$ octahedra and edge-sharing Sc_6 octahedra lie in parallel chains;
>
> Sc_2Cl_3 and its Br analogue are of unknown structure, as are reported La_2X_3 phases, though Y_2Cl_3 and Y_2Br_3 have been shown to consist of parallel chains of Y_6 octahedra, the chains being linked by Cl atoms;
>
> Sc_7Cl_{10} is composed of a double chain of Sc_6 octahedra sharing edges, and a parallel chain of $ScCl_6$ octahedra⁽⁹⁾;
>
> ScCl, made up of close-packed layers of Sc and Cl atoms in the sequence Cl-Sc-Sc-Cl has, like analogous Y and La materials with Cl and Br, since been shown to have been stabilised by interstitial H impurity.⁽¹⁰⁾

The ability of B, C and N as well as H to stabilize many of these reduced phases is at once a major preparative problem⁽¹¹⁾ and also a source of an expanding area of cluster chemistry of which $Sc_7X_{12}Z$ (Z = C; X = Br, I. Z = B; X = I), best regarded as $Sc(Sc_6X_{12}Z)$, are examples.⁽¹²⁾

20.3.2 Complexes⁽¹³,¹⁴⁾

Compared to later elements in their respective transition series, scandium, yttrium and lanthanum have rather poorly developed coordination chemistries and form weaker coordinate bonds, lanthanum generally being even less inclined to form strong coordinate bonds than scandium. This is reflected in the stability constants of a number of relevant 1:1 metal-edta complexes:

Metal ion	Sc^{III}	Y^{III}	La^{III}	Fe^{III}	Co^{III}
$\log_{10} K_1$	23.1	18.1	15.5	25.5	36.0

This may seem somewhat surprising in view of the charge of +3 ions, but this is coupled with appreciably larger ionic radii and also with greater electropositive character which inhibits covalent contribution to their bonding. Lanthanum of course exhibits these characteristics more clearly than Sc, and, while La and Y closely resemble the lanthanide elements, Sc has more similarity with Al. Even Sc however is a class-a acceptor, complexing most readily with *O*-donor ligands particularly if chelating. Complexes with *N*-donor and halide ligands are less well-characterized and those with *S*-donors are largely confined to the Y and La complexes with dithiocarbamates and dithiophosphinates, $[M(S_2CNEt_2)_3]$ and $[M\{S_2P(C_6H_{11})_2\}_3]$.

The complex anion $[ScF_6]^{3-}$ has already been mentioned and, while there is a fairly extensive series of halo complexes with a

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[7] A. Lachgar, D. S. Dudis, P. K. Dorhout and J. D. Corbett, *Inorg. Chem.* **30**, 3321-6 (1991).

[8] J. D. Corbett, *Acc. Chem. Res.* **14**, 239-46 (1981).

[9] F. J. Di Salvo, J. V. Waszczak, W. M. Walsh, Jr., L. W. Rupp and J. D. Corbett, *Inorg. Chem.* **24**, 4624-5 (1985).

[10] See p. 176 of A. Simon, *Angew. Chem. Int. Edn. Engl.*, **27**, 159-83 (1988). Hj. Mattausch, R. Eger, J. D. Corbett and A. Simon, *Z. anorg. allg. Chem.* **616**, 157-61 (1992).

[11] J. D. Corbett in *Synthesis of Lanthanide and Actinide Compounds*, pp. 159-73, Kluwer Acad. Publ., Dordrecht, (1991).

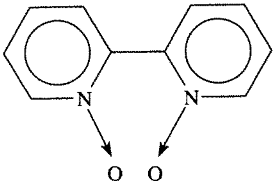
[12] D. S. Dudis, J. D. Corbett and S-J. Hwu, *Inorg. Chem.* **25**, 3434-8 (1986).

[13] G. A. Melson and R. W. Stotz, *Coord. Chem. Revs.* **7**, 133-60 (1971).

[14] F. A. Hart, Scandium, Yttrium and the Lanthanides, in *Comprehensive Coordination Chemistry*, Vol. 3, pp. 1059-127, Pergamon Press, Oxford, 1987.

variety of stereochemistries, they must normally be prepared[15] by dry methods to avoid hydrolysis, and iodo complexes are invariably unstable. Other complexes such as $[Sc(dmso)_6]^{3+}$ (where dmso is dimethylsulfoxide, Me_2SO), $[Sc(bipy)_3]^{3+}$, $[Sc(bipy)_2(NCS)_2]^+$ and $[Sc(bipy)_2Cl_2]^+$ exhibit scandium's usual coordination number of 6. Data for corresponding Y and La compounds are limited but in $[Y(OH)(H_2O)_2(phen)_2]_2Cl_4.2(phen).MeOH$ the yttrium is 8-coordinate with square antiprismatic geometry,[16] and in $[La(NO_3)_3(bipy)_2]$ the lanthanum is 10-coordinate. This is illustrative of the general trend in moving down the group that coordination numbers greater than 6 become the rule rather than the exception. It seems likely that in aqueous solutions, in the absence of other preferred ligands, Y^{III} is directly coordinated to 8 water molecules and La^{III} to 9 and in $M(OH)_3$, (M = Y, La) the metal ion is 9-coordinate with a stereochemistry approximating to tri-capped trigonal prismatic.

A coordination number of 8 is probably the most characteristic of La and possibly even of Y, with the square antiprism and the dodecahedron being the preferred stereochemistries. The acac complexes referred to below are good examples of the former type, while $Cs[Y(CF_3COCHCOCF_3)_4]$ typifies the latter. On the basis of ligand–ligand repulsions the cubic arrangement is expected to be much less favoured in discrete complexes, but, nonetheless, the complex $[La(bipyO_2)_4]ClO_4$, in which $bipyO_2$ is 2,2′-bipyridine dioxide, has been shown to be very nearly cubic.



The gradation of properties within this group is also illustrated by the oxalates and β-diketonates which are formed. On addition of alkali-metal oxalate to aqueous solutions of M^{III}, oxalate precipitates form but their solubilities in an excess of the alkali-metal oxalate decrease very markedly down the group. Scandium oxalate dissolves readily with evidence of such anionic species as $[Sc(C_2O_4)_2]^-$. Yttrium oxalate also dissolves to some extent but lanthanum oxalate dissolves only slightly. All three elements form acetylacetonates: that of scandium is usually anhydrous, $[Sc(acac)_3]$, and presumably pseudo-octahedral: $[Y(acac)_3(H_2O)]$ is 7-coordinate with a capped trigonal prismatic structure (p. 916); $[Y(acac)_3(H_2O)_2].H_2O$ and $[La(acac)_3(H_2O)_2]$ are 8-coordinate with distorted square-antiprismatic structures (p. 917); the scandium compound can be sublimed without decomposition whereas the yttrium and lanthanum compounds decompose at about 500°C and dehydration without decomposition or polymerization is difficult.

The alkoxides and aryloxides, particularly of yttrium have excited recent interest.[17] This is because of their potential use in the production of electronic and ceramic materials,[18] in particular high temperature superconductors, by the deposition of pure oxides (metallo-organic chemical vapour deposition, MOCVD). They are moisture sensitive but mostly polymeric and involatile and so attempts have been made to inhibit polymerization and produce the required volatility by using bulky alkoxide ligands. $M(OR)_3$, R = 2,6-di-*tert*-butyl-4-methylphenoxide, are indeed 3-coordinate (pyramidal) monomers but still not sufficiently volatile. More success has been achieved with fluorinated alkoxides, prepared by reacting the parent alcohols with the metal tris-(bis-trimethylsilylamides):

$$[M\{N(SiMe_3)_2\}_3] + 3ROH \longrightarrow M(OR)_3 + 3(Me_3Si)_2NH, \text{ eg } R = (CF_3)_2MeC-$$

The Y and La compounds, though polymeric, are surprisingly volatile but, using

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[15] G. MEYER, p. 145–58 in ref. 6.

[16] M. D. GRILLONE, F. BENETOLLO and G. BOMBIERI *Polyhedron* **10**, 2171–7 (1991).

[17] R. C. MEHROTRA, A. SINGH and U. M. TRIPATHI, *Chem. Revs.* **91**, 1287–303 (1991).

[18] D. C. BRADLEY, *Chem. Revs.* **89**, 1317–22 (1989).

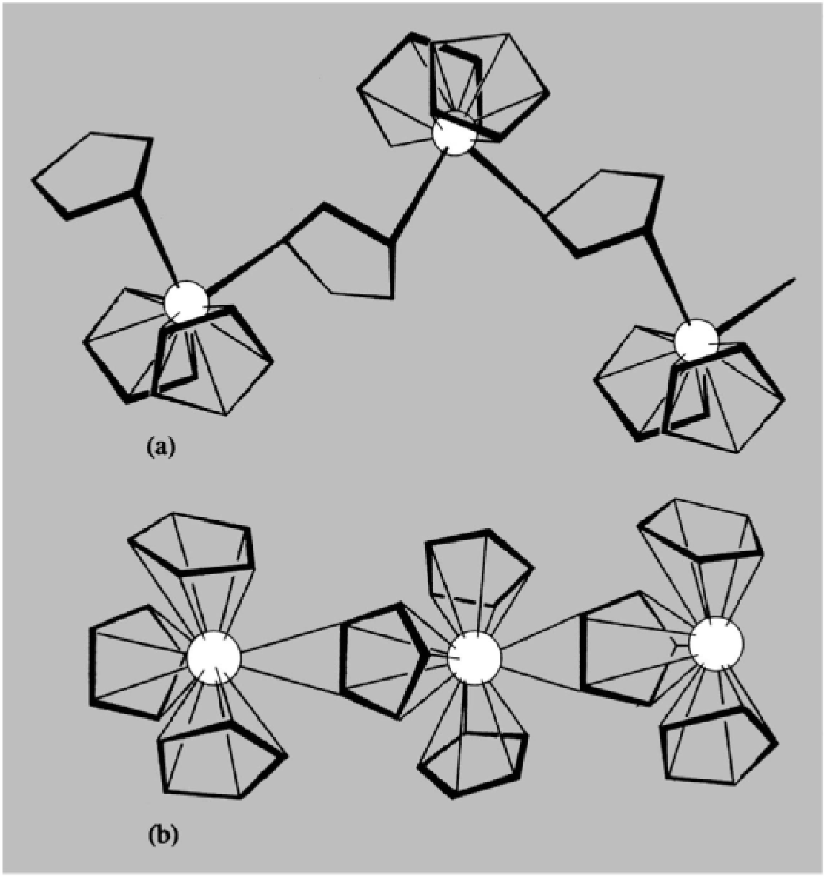

Figure 20.4 (a) The structure of $[Sc(C_5H_5)_3]$. (b) The structure of $[La(C_5H_5)_3]$. Note that the "total connectivity" of the ligands around each Sc atom is 12 as compared to 17 for the larger La.

thf as solvent, volatile octahedral monomers $[M(OR)_3(thf)_3]$, M = Y, La, are obtained.$^{(19)}$ With 2,6-diphenylphenolate ligands the coordination number 5 is stabilized in the distorted trigonal-bipyramidal $[La(Odpp)_3(thf)_2].(thf)$.$^{(20)}$

EDTA complexes of La and the lanthanides are known. $K[La(edta)(H_2O)_3].5H_2O$ is a 9-coordinate complex but steric constraints imposed by the edta produce deviations from a tricapped trigonal prismatic structure. $[La(edtaH)(H_2O)_4].3H_2O$ is 10-coordinate and its structure is probably best regarded as being based on the same structure but with an extra water "squeezed" between the three coordinated water molecules.

The highest coordination numbers of all are attained with the aid of chelating ligands, such as SO_4^{2-} and NO_3^-, with very small "bites" (p. 917). In $La_2(SO_4)_3.9H_2O$ there are actually two types of La^{III}, one being coordinated to 12 oxygens in SO_4^{2-} ions while the other is coordinated to 6 water molecules and 3 oxygens in SO_4^{2-} ions. In $[Y(NO_3)_5]^{2-}$ the Y^{III} is 10-coordinate and in $[Sc(NO_3)_5]^{2-}$, even though one of the nitrate ions is only unidentate (p. 469), the coordination number of 9 is extraordinarily high for scandium.

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The low symmetries of many of the above highly coordinated species, which appear to be determined largely by the stereochemical requirements of the ligands, together with the fact that these high coordination numbers are attained almost exclusively with oxygen-donor ligands, are consistent with the belief that the bonding is essentially of an electrostatic rather than a directional covalent character.

20.3.3 Organometallic compounds (2,21,22)

In view of the electronic structures of the elements of this group, little interaction with π-acceptor ligands is to be expected, though cocondensation of metal vapours with an excess of the bulky ligand, 1,3,5-tri-*tert*-butylbenzene at 77 K yields the unstable sandwich compounds $[M(\eta^6\text{-Bu}^t_3C_6H_3)_2]$, M = Sc, Y which are the first examples of these metals in oxidation state zero.(23) The organometallic chemistry of this group, as of the lanthanides, is instead dominated by compounds involving cyclopentadiene and its methyl-substituted derivatives.(23) Though many are thermally stable, they are invariably sensitive to moisture and oxygen. The first to be prepared were the ionic cyclopentadienides, $M(C_5H_5)_3$, formed by the reactions of anhydrous MCl_3 with NaC_5H_5 in tetrahydrofuran and purified by vacuum sublimation at 200–250°C. The solids are polymeric, $[Sc(C_5H_5)_3]$ being made up of zig-zag chains of $\{Sc(\eta^5\text{-}C_5H_5)_2\}$ groups joined by $\eta^1{:}\eta^1\text{-}C_5H_5$ bridges,(24) (Fig. 20.4a), whereas in the lanthanum analogue the zig-zag chains of $\{La(\eta^5\text{-}C_5H_5)_2\}$ groups are joined by $\eta^5{:}\eta^2\text{-}C_5H_5$ bridges(25) (Fig. 20.4b). They are reactive compounds and form "tetrahedral" monomers, $[M(C_5H_5)_3L]$ with neutral ligands such as ammonia and phosphines.

The $M(C_5H_5)_2Cl$ compounds, which are actually Cl-bridged dimers, $[(C_5H_5)M(\mu\text{-Cl})_2M(C_5H_5)]$, provide an extensive substitution chemistry in which μ-Cl can be replaced by a variety of ligands including H, CN, NH_2, MeO and alkyl groups.

Monomeric alkyl compounds of the form MR_3 have also been obtained for Sc and Y, where the alkyl groups are of the types Me_3SiCH_2 and Me_3CCH_2 which are bulky and contain no β hydrogen atoms (p. 926).

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