ELSEVIER

Coordination Chemistry Reviews
181 (1999) 121–145

COORDINATION
CHEMISTRY
REVIEWS

Structural chemistry of Sc(III): an overview

Paul R. Meehan, Damian R. Aris, Gerald R. Willey *

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

Received 4 June 1998; received in revised form 11 August 1998; accepted 7 October 1998

Contents

Abstract

Structural aspects of the chemistry of organometallic/coordination compounds of scandium(III) are reviewed. Individual compounds are classified and discussed in terms of coordination number and associated metal geometry through the range CN = 3–9. The present review provides an exhaustive literature coverage 1926–1998 (April). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Scandium(III) complexes; X-ray crystal structures; Coordination number; Metal geometry

---

* Corresponding author. Tel.: + 44-1203-523227; fax: + 44-1203-524112; e-mail: msrep@snow.csv.warwick.ac.uk.

PII: S0010-8545(98)00214-8

1. Introduction and scope of review

In this review we shall consider the structural chemistry of coordination compounds and organometallo complexes involving Sc(III) starting with the first reported structure determination in 1926 of $Sc(acac)_3$ [1] and continuing through to the present. The use of the Cambridge Crystallographic Centres' database has proved invaluable, not only for tracking down the wide range of reported structures but also for providing the necessary atom coordinates to facilitate redrawal of the individual structures presented in the text [2].

Previous literature coverage of scandium compounds includes reviews by Melson and Stotz [3] (coordination chemistry describing complexes with different donor atom ligands), Cloke [4] (zero oxidation state compounds) and the succinct annual surveys provided initially by Fay and continued by Constable and, more recently, Housecroft [5].

First some simple statistics:

- The total number of structurally-determined scandium(III) compounds is 95 (up to and including April 1998). Despite the apparent initial neglect, more probably a reflection of high material costs rather than chemical indifference, there is clearly a rapidly growing interest in the structural coordination chemistry of this particular Group 3 metal i.e. compare publication listings 1926 (1), 1950–1959 (1), 1960–1969 (1), 1970–1979 (21),1980–1989 (16) and 1990–to date (45).
- Various estimates of the ionic radius of Sc^{3+}, depending on the coordination sphere, have emerged from these structural studies: these include 0.68 Å (six-coordinate), 0.885 Å (eight-coordinate) and 0.867 Å (nine-coordinate). Other values cited elsewhere for the effective ionic radius of Sc^{3+} include 0.745 Å (six-coordinate), 0.870 Å (eight-coordinate) [6] and 0.81 Å [7].
- For convenience, individual compounds are organised into groups according to the coordination number exhibited by the metal centre(s); this allocation is summarised in Table 1. The fact that such a small (relatively) ion can accommodate a coordination number range from 3 to 9 is surprising and noteworthy in itself. Variations of metal geometry, subtle or otherwise, within each sub-group are highlighted in the discussion.

Table 1
Number of scandium structures per coordination number

Coordination number	Number of structures
3	13
4	17
5	10
6	33
7	10
8	10
9	2

2. Coordination number 3

Hitchcock et al. [8] have shown that $[Sc(OC_6H_2Me\text{-}4\text{-}^tBu_2\text{-}2,6)_3]$ adopts a classical trigonal planar (D_{3h}) geometry, with O–Sc–O mean 119.5°. The Sc–O bond length is relatively short at mean 1.869(15) Å. The bulky nature of the ligand is exemplified by Sc–O–C mean 168.4(5)° which, additionally, highlights the steric crowding around the metal.

The requirement for sterically-bulky ligands to enforce such a low coordination number around scandium is equally demonstrated in the case of $Sc[N(SiMe_3)_2]_3$. Initially reported by Aylea et al. [9] in 1972, structural elucidation came the following year when Ghotra and co-workers [10] reported the tris-silylamide adopts pyramidal geometry. Aware that dipole moment studies on the compound in solution pointed towards planarity, Ghotra argued that intramolecular van der Waals' attractions draw the ligands together during recrystallisation thereby 'squeezing' the metal atom out of the coordination plane and hence conferring pyramidal geometry, Sc–N mean 2.049 Å (calculations using a theoretical planar model give a value of 1.963 Å).

In 1987, Schaefer and Bercaw [11] reported the synthesis of $Cp^*_2ScCH_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$) via the reaction between Cp^*_2ScCl and methyllithium A study of the electronic properties of this first cyclopentadienyl–Sc(III) compound pointed towards a 14-electron environment, with the possibility of an agostic $Sc\text{–}CH_3$ interaction. However the observed metal geometry is trigonal planar; the methyl group exhibits conventional σ-bonding, Sc–C 2.24(1) Å, with the two Cp* ring centroids at 2.1701(12) and 2.1710(11) Å, respectively, from the scandium atom.

Used in the role of catalyst for alkene polymerisation, permethylscandocene alkyls readily polymerise ethylene but not higher olefins [12]. The reaction between the permethylscandocene methyl derivative and acetylene (as the parent alkyne) proceeds via σ-bond metathesis with alkane elimination as illustrated in Eq. (1).

$$Cp^*_2Sc\text{–}CH_3 + H\text{–}C{\equiv}CH \rightarrow Cp^*_2Sc\text{–}C{\equiv}CH + CH_4 \tag{1}$$

Attempted recrystallisation led to a novel crystalline product, $Cp^*_2Sc\text{–}C{\equiv}C\text{–}ScCp^*_2$ [13]; this dinuclear product can also be obtained from the direct 2:1 stoichiometric reaction of the permethylscandocene methyl reagent and acetylene. Interestingly the C–C bond length, 1.224(9) Å, of the acetylene bridging fragment is only slightly enhanced from the value of 1.21 Å noted for acetylene itself. The related $Cp^*_2ScCH_2(cyclo\text{-}C_5H_8)$ decomposes in cyclohexane to give the dimeric crystalline product $[Cp^*Sc\{\mu\text{-}(\eta^5,\eta^1)\text{-}C_5(CH_3)_4CH_2\}]_2$ [14] in which two symmetry-related scandium atoms are bridged by the (η^5,η^1)Cp* group; the link arises from the C–H activation of one of the ligand methyl groups. The penta-hapto Cp* groups bind in an essentially unaltered manner. The reactions of $[Cp^*ScCl_2]_x$ with $Na_2(C_2B_9H_{11})$ or $[Cp^*ScMe_2]_x$ with $C_2B_9H_{13}$ followed by treatment with THF lead to the formation of $Cp^*(C_2B_9H_{11})Sc(THF)_3$. Alkylation of this product using the bulky $Li^+[CH(SiMe_3)_2]^-$ gives an essentially quantitative yield of $[Li(THF)_3]^+Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2]^-$. Subsequent recrystallisation from pentane/toluene provides the pale yellow crystalline product $[Li(THF)_3]^+\{[Cp^*(C_2B_9H_{11})ScCH(SiMe_3)_2]_2Li\}^-$.

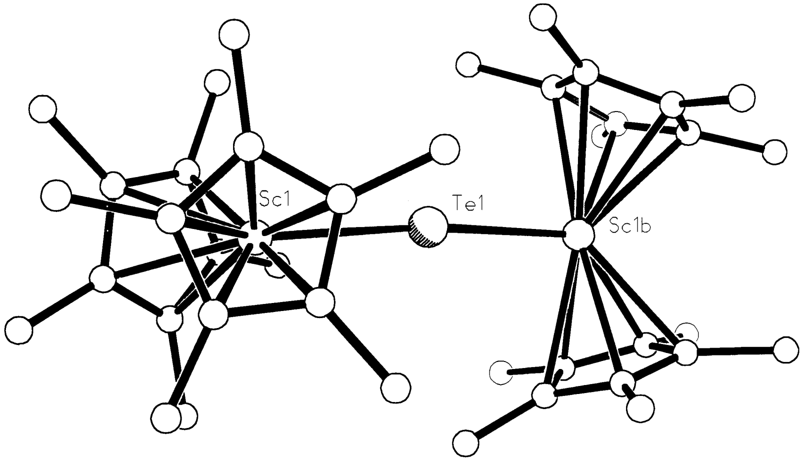


Fig. 1.

The structure consists of a discrete solvated lithium cation and a complex anion comprising two scandium atoms each of which is sandwiched between a Cp* group and a dicarbollide ligand both bonded in penta-hapto fashion, Sc–Cp*(centroid) 2.205, 2.192 Å, Sc–dicarbollide(centroid) 2.126, 2.142 Å. Each scandium atom carries an attendant $CH(SiMe_3)_2$ group and there is a lithium ion loosely bonded between two triangular [BH] faces of the two $C_2B_9H_{11}^{2-}$ ligands. Clearly the low coordination number is enforced by the bulky nature of the three bound ligands [15,16].

The structure of the scandium–alkyl derivative $\{(\eta^5\text{-}C_5Me_4)SiMe_2[\eta^5\text{-}C_5H_3CH_2CH_2P^tBu_2]\}ScCH(SiMe_3)_2$ involving a silicon bridge between the constituent Cp and Cp* rings and a tertiary phosphine group associated with the Cp ring is described in terms of a trigonal planar metal geometry with a metal–alkyl bond distance Sc–C 2.271(7) Å [17].

More recent three-coordinate scandium structures feature permethylscandocene tellurolates (and selenolates), isolated via the insertion of tellurium (selenium) into the Sc–C bond of an alkyl derivative. Subsequent thermal decomposition yielded dimeric scandium μ-tellurides (selenides) according to the scheme below:

$$Cp_2^*Sc{-}R \underset{\text{hexane}}{\overset{E}{\rightarrow}} Cp_2^*Sc{-}E{-}R \underset{-\,ER_2}{\overset{DH}{\rightarrow}} Cp_2^*Sc{-}E{-}ScCp_2^* \ (E = Se \text{ and } Te)$$

Examples include: $Cp_2^*Sc–Te–CH_2C_6H_5$ (**A**) [18], $Cp_2^*Sc–Te–ScCp_2^*$ (**B**) [18,19] (see Fig. 1), $Cp_2^*Sc–Se–ScCp_2^*$ (**C**) [18] and $DpSc(PMe_3)–Te–Sc(PMe_3)Dp$ (**D**) [20], where $Dp = Me_2Si[(^tBu)C_5H_3]_2$. With non-controversial binding of Cp* groups to the metal the real interest surrounds the nature of the metal–metal bonding which features a near linear Sc–E–Sc arrangement in all cases e.g. 172.07(5)° (**B**), 173.74(10)° (**C**) and 180.0° (**D**). Whereas the Sc–E bond distances (mean) Sc–Te 2.7528(12) Å (**B**), Sc–Se 2.5425(16) Å (**C**) and Sc–Te 2.875(5) Å (**D**) are shorter than the respective calculated single bond values, the actual extent of multiple π-bonding present in each individual case is open to discussion.

3. Coordination number 4

The first reported four-coordinate scandium compound appeared in 1973. In an attempt to explore the covalent nature of the Sc–C bond in organometallic systems, Atwood and Smith [21] synthesised Cp_3Sc whose structure consists of Cp_2Sc units bridged by further cyclopentadienyl groups to form a polymeric array. Each metal is formally bound to two of the ligands in the expected penta-hapto fashion and to two others via an η^1-link. Thus the structure reveals both bridging and terminal Sc–Cp interactions; the average Sc–C bond length to the η^5-bonded rings of 2.494(5) Å is predictably shorter than the bridging Sc–C(η^1) bond lengths of 2.574(4) Å.

Structural characterisation of $[Cp_2ScCl]_2$ [22] revealed a di-μ-chloro bridged dimer with two Cp groups per metal atom bound in the expected penta-hapto fashion: the Sc–C bond length mean 2.46(1) Å is very slightly shorter than the analogous value in the tricyclopentadienyl species and this is attributed either to reduced steric bulk around the scandium and/or to the greater electronegativity of the chlorine which can remove electron density from the metal centre. Within the bridging $[Sc_2Cl_2]$ unit the Sc–Cl distance is mean 2.575(4) Å (see Fig. 2).

Bottomley et al. [23] reported a synthesis of tricyclopentadienyl scandium which produced an interesting by-product. Their utilisation of molten Cp_2Mg in conjunction with scandium trifluoride afforded the expected product along with $[(\eta^5\text{-}Cp)_2ScF]_3$, a trimeric moiety. The structure of the latter compound shows a planar, six-membered $(ScF)_3$ ring with an average F–Sc–F angle of 86.5(3)°: this compares to the analogous $[Cp^*_2UCl]_3$ trimer [24] in which the Cl–U–Cl bond angle was noted at 84.5(3)°. The mean Sc–F bond length of 2.046(8) Å compares closely with the value of 2.012(5) Å calculated for ScF_3 itself.

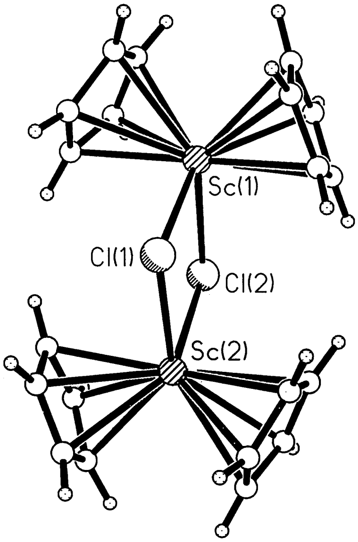


Fig. 2.

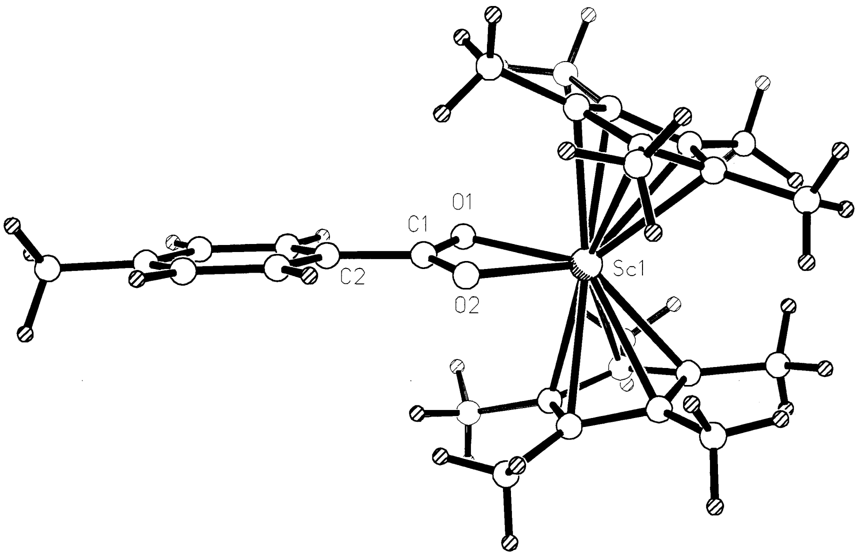


Fig. 3.

In 1983, Lappert et al. [25] examined a range of lanthanide and pre-lanthanide tetrahydroborate complexes, $Ln\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}_2(BH_4)(THF)_n$, to determine the nature of the BH_4^- anion coordination. For Ln = Sc, the IR evidence pointed towards bidentate coordination to the metal, an observation validated by X-ray crystallography. A four-coordinate scandium centre was revealed for the complex, with the structure containing a crystallographic 2-fold axis passing through the Sc and B atoms. The Sc–H bond length of 2.03(4) Å, coupled with the Sc···B interaction of 2.52(3) Å, provided corroborative evidence for the bidentate coordination of the anion.

The reaction of $Cp_2^*ScCH_3$ with pyridine led to the release of methane and the generation of $Cp_2^*Sc(\eta^2\text{-}(CN)C_5H_4N)$, a four-coordinate scandium complex [11]. Treatment of $Cp_2^*ScCH_3$ with $CpCo(CO)_2$ provided a convenient route to the 'scandoxycarbene' complex $CpCo(CO)=C(CH_3)OScCp_2^*$ where a μ^2,η^1,η^1-carbonyl ligand was shown to be present in addition to the bridging scandoxycarbene unit between two metal centres [26]. The Sc–O bond length in the scandoxycarbene unit appears at 2.067(2) Å, while the C–O bond itself has a length of 1.268(4) Å: clearly this exhibits a lower bond order than the μ^2,η^1,η^1-carbonyl which has an inherent C–O distance of 1.202(4) Å.

Reaction of $Cp_2^*Sc\text{-}C_6H_4\text{-}p\text{-}CH_3$ and CO_2 provided the four-coordinate complex $Cp_2^*Sc(O_2C)C_6H_4CH_3$ [27] (bidentate carboxylate attachment) following direct carbon dioxide insertion into the Sc–C bond (see Fig. 3).

Direct addition of anhydrous hydrazine to $Cp_2^*ScCH_3$ afforded $Cp_2^*ScN(H)NH_2$, an unsubstituted hydrazido(1 −) complex. Subsequent addition of acetonitrile to the resulting complex led to immediate generation of the heterometallacyclic product $Cp_2^*ScN(H)C(CH_3)NNH_2$. The near-equivalence of the Sc–N bond lengths (2.277(4), 2.155(4) Å), coupled with the planarity of the five-membered ScNCNN ring, points towards resonance stabilisation [28].

Interest in the cyclo-octatetraene derivatives of scandium was aroused by the isolation of $[Sc_2(\eta\text{-}C_8H_6\{1,4\text{-}(SiMe_3)_2\})_2(\mu\text{-}Cl)_2(\mu\text{-}THF)]$ from the reaction between scandium trichloride tris-THF and the dilithiated cyclo-octatetraene derivative [29]. The X-ray crystal structure clearly reveals the dimeric nature of the complex which features a bridging THF ligand, only the second reported example at the time. The 'semi-bridging' nature of the THF ligand, as reflected in the irregular Sc–O bond lengths, 2.324(7), 3.056(9) Å possibly also accounts for the asymmetry in the chloride bridging of the core (Sc_2Cl_2) unit Sc–Cl 2.518(3), 2.590(3) Å.

The reactivity of d^0 M–Si bonds towards unsaturated species has been explored by Tilley et al. [30]. Reaction of $Cp_2Sc[Si(SiMe_3)_3](THF)$ with two equivalents of CN(Xyl), where $Xyl = 2,6\text{-}Me_2C_6H_3$, and subsequent rearrangement afforded a four-coordinate scandium complex featuring a five-membered cyclic N_2-donor system. The basic 'Cp_2N_2' coordination sphere of the metal atom includes a Sc–N dative bonding interaction (2.324(8) Å) in addition to the Sc–N single bond (2.133(7) Å). Reaction of $Cp_2Sc[Si(SiMe_3)_3](THF)$ with CO_2 readily occurred to yield a dimeric silanecarboxylate complex, $[Cp_2Sc(\mu\text{-}O_2CSi(SiMe_3)_3)]_2$ [31]. Clearly the Sc–Si link afforded an invaluable reactive centre for the activation of carbon dioxide and isonitriles; Tilley's group also showed the bond to be reactive towards ethylene and organic carbonyls. The crystal structure of the scandium silyl precursor itself was determined in 1993 [32].

The complex $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}(PMe_3)Sc(\mu\text{-}H)]_2$ [33] was shown to be a double hydrogen-bridged dimer; the importance of this system was highlighted by its utilisation in the catalysis of α-olefin regiospecific polymerisation. The most notable structural feature of the compound is the elongated Sc–P bond at 2.996(1) Å, indicating the fragility of the linkage; this was verified by ^{31}P-NMR studies which confirmed rapid dissociation of the PMe_3 group. Reaction of this complex with two equivalents of ethylene yielded an unusual ethylene-bridged dimer, $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}\ (PMe_3)Sc]_2(\mu^2,\eta^2,\eta^2\text{-}C_2H_4)$ [34]. In this system the Sc–P bond now exists at 2.825(3) Å, a significant shortening on its precursor, although the PMe_3 dissociation was still shown to be rapid. The C–C bond length 1.433(12) Å of the olefin bridge is intermediate between 'single' and 'double' bond dimensions, ca. transition metal olefin complexes with sp^2 hybridisation of the μ-ethylene carbons. The product of the reaction between propene and $[(Cp^*SiNR)(PMe_3)Sc(\mu\text{-}H)]_2$, where $Cp^*SiNR = \{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}$ is the phosphine-free compound $[(Cp^*SiNR)Sc]_2(\mu\text{-}CH_2CH_2CH_3)_2$ [34] which is a dimeric entity in which the two scandium fragments are linked by μ-alkyl bridges, giving two three-centre two-electron bonds. A centre of inversion relates the two halves of the molecule.

The diprotonic cyclopentadienylamino ligand $Cp(H)^{NMe}SiN(H)R$, where $SiNR = -SiMe_2N^tBu$ and $NMe = 3\text{-}CH_2CH_2NMe_2$ as a pendant amine donor, reacts with $Sc(CH_2SiMe_3)_3 \cdot 2THF$ (as generated in situ) to provide the scandium alkyl compound $[(Cp^{NMe}SiNR)Sc(CH_2SiMe_3)]$ (**A**) [35] accompanied by alkylsilane elimination (2Me_4Si). The resulting scandium centre is pseudotetrahedral with four different substituents and the reaction was 100% diastereoselective for the (1*S*)–(R_{Sc})/(1*R*)–(S_{Sc}) pair of enantiomers. Treatment of product (**A**) with dihydrogen results in hydrogenolysis of the Sc–C bond with Me_4Si elimination and formation of the dimeric scandium hydride $[(Cp^{NMe}SiNR)Sc(\mu\text{-}H)]_2$ of which the symmetric (C_i) 1*R*-*trans*-1*S* diastereomer was characterised crystallographically.

4. Coordination number 5

An important aspect of metallo-porphyrin chemistry relates to the size comparability between metal ion(s) and the ligand 'cavity' dimensions. For the porphyrin ligand OEP (OEP = octaethylporphyrin) the central 'hole' is ideally suited to metal ions of radii 0.60–0.65 Å for coordination directly within the N_4 plane; smaller metal ions can also feasibly be accommodated via ring deformation [36]. In the specific case of scandium, entrapment directly within the cavity is precluded (on size considerations, r = 0.68 Å) hence the metal atom sits atop the nitrogen plane, with further coordinating ligands forced into adopting a *cis*-configuration.

Typically for the five-coordinate (OEP)$ScCH_3$ [37] (see Fig. 4) the metal is located at a distance of 0.66 Å from the N_4 plane. In the case of (OEP)$ScCH(SiMe_3)_2$ the metal atom now resides 0.71 Å out of the N_4 plane [37]; in a similar vein (OEP)$Sc(\eta^5\text{-}C_5H_5)$ [38], where the Cp ring attachment is regular penta-hapto, has the metal located at a distance 0.80 Å from the mean N_4 ring of the porphyrin. For the indenylide analogue (OEP)$Sc(\eta^5\text{-}C_9H_7)$ [37] the metal

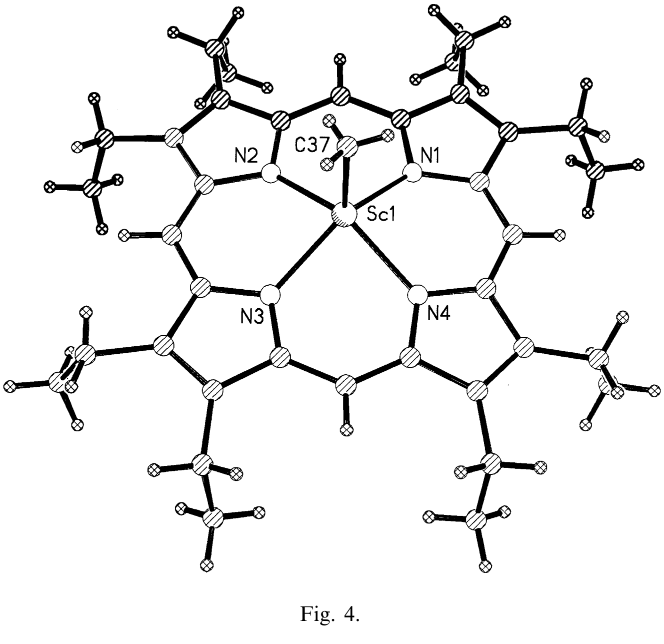


Fig. 4.

separation from the N_4 plane is 0.78 Å but in this case the scandium atom is dislocated from the midpoint of the C_5 ring of the indenyl ligand as a result of pronounced ligand tilting.

Two further scandium–porphyrin structures have been reported: $ClSc(TTP)\cdot 2(C_{10}H_7Cl)$ where TTP = *meso*-tetratolylporphyrin [39] is formally a 10-electron species in which the metal atom resides out of the ligand cavity, 0.68 Å above the N_4 plane. The square pyramidal geometry observed was, at the time, the first reported instance for scandium. The Sc–Cl bond is unusually short at 2.32(1) Å; this can be contrasted with both a terminal Sc–Cl bond length mean 2.414(4) Å in the six-coordinate $ScCl_3(THF)_3$ [40] and the enhanced Sc–Cl bridging bonds in $[Cp_2ScCl]_2$ [22] mean 2.575(4) Å. Again the μ-oxo-bridged dimer $O[Sc(TTP)]_2\cdot 6THF$ [39] shows the metal at a distance of 0.82 Å out of the N_4 plane with Sc–N mean 2.20(3) Å. The bridging unit deviates from linearity with Sc–O–Sc 110(3)°.

A recent approach to scandium phosphine complexes utilises the 'mixed' terdentate system $(^iPr_2PCH_2SiMe_2)_2N^-[L]$ which combines a central amido (hard) anchor and two adjacent phosphine (soft) centres [41]. Reaction of Li[L] with $ScCl_3(THF)_3$ produces the monosolvate $ScCl_2(L)\cdot THF$ which is a convenient precursor to stable five-coordinate bis(hydrocarbyl) scandium complexes of the type $ScR_2(L)$. The crystal structures for $R = C_2H_5$ and CH_2SiMe_3 reveal a distorted trigonal bipyramidal metal geometry in which the two phosphorus atoms occupy the axial positions e.g. for $R = C_2H_5$, Sc–P 2.779(2) Å, P–Sc–P 166.95(4)°; for $R = CH_2SiMe_3$, Sc–P 2.794(2) Å P–Sc–P 154.92(6)°. Whereas these dialkyl complexes can be considered as coordinatively unsaturated (formal 12 e^- species) there is no evidence for agostic interactions involving C–H bonds of the substituted R groups.

5. Coordination number 6

In 1968, Guseinova et al. [42] reported the preliminary structure of $Sc(HCOO)_3$; although the rather high value of $R = 0.205$ reflected the instability of the crystals and precluded further refinement, a six-coordinate geometry was noted. Surprisingly, it took over 20 years before the refined structure of this compound was reported by Hasek and co-workers [43]. In essence the structure consists of a polymeric framework in which each metal atom is octahedrally bound to three symmetrically independent oxygens and three centrosymmetric analogues: thus the formate anions act as bridging groups with Sc–O mean 2.082 Å.

Melson et al. [44] have determined the structure of tris(acetylacetonato)scandium, and comment on the considerable distortion from regular octahedral geometry to a trigonal antiprism. The intrachelate O–O 'bite' of 2.715(5) Å in the scandium moiety is comparable to known values for $M(acac)_3$ species. The Sc–O bond length of 2.070(9) Å allowed Melson to calculate the effective ionic radius of six-coordinate scandium; a value of 0.68 Å was afforded from application of the Lingafelter-Braun approach. Melson compared this value with the previously reported Pauling radius of scandium (0.81 Å), concluding that the latter value was applicable for

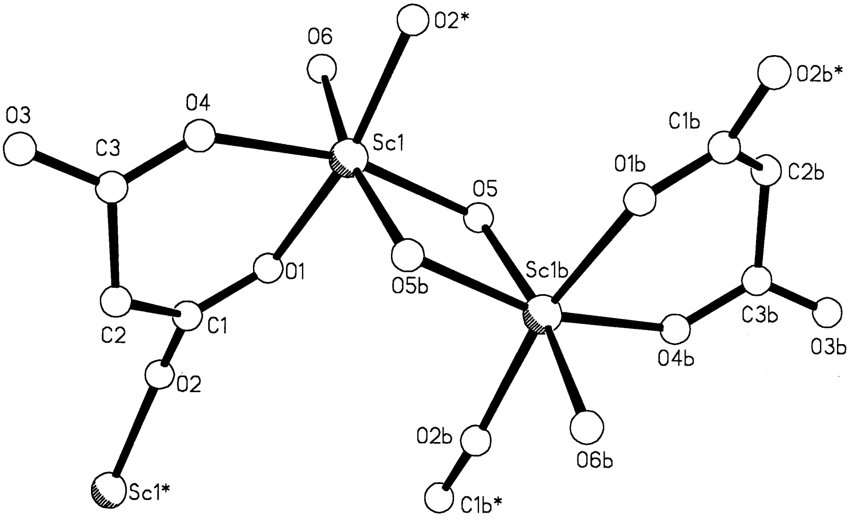


Fig. 5.

those complexes revealing ionic character. He surmised that his newly-calculated figure of 0.68 Å was the ideal value for scandium in complexes exhibiting predominantly covalent interactions and is the figure quoted religiously to this day. Melson's subsequent structural determination of tris(tropolonato)scandium(III) [45] allowed comparisons with both the tris(acetylacetonato) compound and the stereochemical models proposed by Kepert [46]. The latter concluded that the geometries around the metal ions in $[M(bidentate)_3]^{n+}$ complexes depended to a great degree on the ligand 'twist angle', Φ. For values around 0° trigonal prismatic geometry should result, while an angle of Φ approaching 60° would theoretically lead to the adoption of the trigonal antiprism form. The structure of $Sc(trop)_3$ provided a Φ value of 33° which appears intermediate between the two forms, but is the closest noted to prismatic for the $M(trop)_3$ systems. The metal is of course d^0 here, hence there are no electronic factors to outweigh the ligand influence and hence Kepert's model is followed. In the acac analogue, the flexibility of the ligand and the twist angle of 60° lead to the antiprismatic form.

The structure of $[Sc(OH)(C_3H_2O_4)\cdot 2H_2O]$ [47] (see Fig. 5) revealed an octahedral environment around each metal centre comprising two oxygen atoms from a malonate ligand (bidentate chelate), two bound water molecules and two bridging (μ^2-OH) units. The octahedra are bound in pairs by the bridging hydroxo groups, giving a Sc···Sc separation of 3.27 Å. These octahedra are further linked into infinite chains by carboxylate bridges. Additionally, hydrogen bonds are apparent between these infinite chains, rendering a highly complex structure overall.

The six-coordinate $ScCl_3(THF)_3$ [40] is confirmed as the *mer*-isomer with O–Sc–O interbond angles ranging from 82.9(3) to 96.7(2)° and Sc–Cl mean 2.414 Å. Similarly, the structure of $ScCl_3(H_2O)_3$ again shows *mer*-octahedral geometry, with Sc–Cl 2.413(6)–2.419(5) Å, Sc–O mean 2.122(9) Å and O–Sc–O mean 88(2)° [48].

In 1984 Fuchs and Strähle [49] reported the structure of the scandium(III) acetate $Sc(CH_3COO)_3$; each metal atom exhibits a compressed octahedral geometry with three bridging acetato groups per metal linking the atoms into a linear chain. Within the crystal lattice the polymeric complex links are arranged in a hexagonal close-packed array. Not unexpectedly, the structure of $[Sc(ClCH_2COO)_3]_n$ [50] reveals a similar polymeric array. Each metal is octahedrally-coordinated to six different anions, with adjacent metal atoms bound by three bridging carboxylate links. The mean Sc–O bond length of 2.075 Å is close to the figure of 2.084 Å in the non-substituted acetate complex previously discussed.

The crystal structure of the six-coordinate *p*-toluenesulphonate derivative $[Sc(C_7H_7SO_3)_2(H_2O)_4](C_7H_7SO_3)\cdot 2H_2O$ [51] shows an octahedral metal geometry comprising two oxygen atoms (*cis*) from unidentate sulphonate groups and four oxygen atoms from individual water molecules. The M–O bonds to the sulphonate are noticeably shorter at 2.044 Å than the corresponding M–O(H_2O) interactions at 2.117 Å. A degree of steric hindrance can also be observed within the molecule: although the value of 147.2(2)° for one of the Sc–O–S bond angles is analogous with that observed in many of the lanthanide sulphonates, the second Sc–O–S angle of 175.6(2)° reveals the steric interaction between the two ligands.

For $[Sc_2(O_2NC_6H_4SO_3)_4(OH)_2(H_2O)_2]_n$ [52] (see Fig. 6) an infinite chain structure was observed, with each unit of the polymeric complex containing two octahedral scandium centres comprising four oxygen atoms from the sulphonate ligands with two *trans* sites filled by oxygens from either the hydroxide or water ligands. The bidentate bridging mode of the two sulphonate groups between metal pair units was clearly evident.

The coordination environment around each metal is in reality highly disparate. One of the scandium centres in each pair reveals 'normal' coordination with six regular Sc–O bonds providing an average length of 2.055 Å. This is a marked

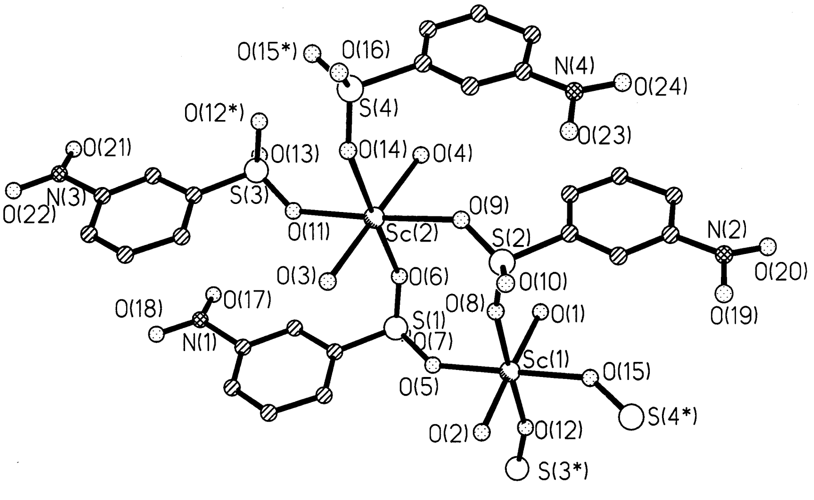


Fig. 6.

contrast to the second metal site which can be summarily considered as the metal trapped within a cage of six oxygen atoms; the enhanced mean Sc–O bond length of 2.412 Å clearly shows this. These two types of metal centre alternate along the regular polymeric structure.

The reaction of $Sc(OH)_3$ with aqueous picric acid yielded an aqueous picrate solution which crystallised as $[Sc(pic)_2(OH_2)_4](pic)(Hpic)\cdot \sim 8.2H_2O$ [53]. The structure of the cation revealed the scandium to be six-coordinate with the two picrate ligands bound in a *trans* manner; distinct deviations from idealised octahedral geometry are manifest, with the tetraoxo array of water oxygen atoms showing *cis* angles of 84.2(3)° and 97.2(3)°; the distortions are explicable in terms of the stereochemical bulk of the picrate groups.

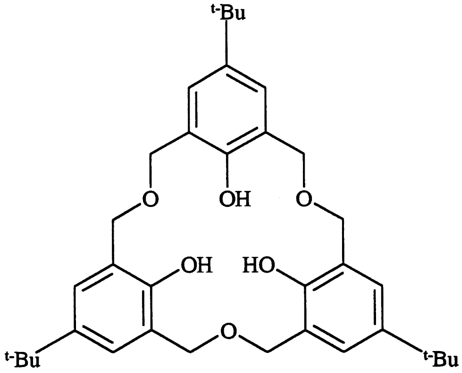
The reaction between $Sc\{N(SiMe_3)_2\}_3$ and excess $(CF_3)_2CHOH$ afforded the complex $[Sc\{OCH(CF_3)_2\}_3(NH_3)_2]_2$ [54], a dimeric species in which the fluorinated (hfib) ligands exhibit both terminal and bridging character. The terminal hfib ligands act as weak π-donors to the d^0 metal, hence a *cis* geometry is preferential, and the $Sc–O_{(terminal)}$ bond length 1.94 Å clearly reveals the influence of the additional π-bond overlap. In contrast the Sc–O bond length for the bridging hfib groups is much longer at 2.19(1) Å.

The six-coordinate complex, $[(OEP)Sc(\mu\text{-}OH)]_2$ [37], the product of hydrolysis of any (OEP)ScX species, shows (OEP)Sc fragments bridged by two μ-OH groups, with an average Sc–O bond length of 2.078(2) Å and a bond angle of 109.89(7)° for the Sc–O–Sc bridge. Here the metal atoms reside at a distance of 0.84 Å from the N_4 plane of the porphyrin rings, Sc–N mean 2.203(2) Å while the two porphyrin rings adopt an eclipsed conformation.

In the case of the phosphane complex $Sc[C(PMe_2)_2SiMe_3]_3$ [55] ligand binding is intermediate between σ-chelation and π-type coordination and the resulting metal geometry approximates to trigonal prismatic with respect to the phosphorus atoms Sc–P mean 2.617 Å. With the ScP_2 plane at an angle of 121° to the CP_2 plane there is evidence for a 'folding' of the four membered ScPCP chelate ring which can be attributed to an interaction between the carbanion and the metal d-orbitals. Steric hindrance, however, restricts the closest approach of the planar carbanionic carbon atoms to the metal centre to Sc···C 2.908 Å.

In 1994, Fjellvåg and Karen [56] published the results of powder neutron diffraction studies on the parent scandium trichloride: MCl_3 species are known to exhibit a varied range of structures, including a cubic close-packed array, 'YCl_3-type', and a hexagonal close-packed derivative, BI_3-type'. It emerges that $ScCl_3$ adopts the latter type wherein the scandium atoms regularly occupy one-third of the octahedral holes within the hexagonally close-packed array of chlorine atoms. The structure can best be regarded as layers comprising $ScCl_6$ octahedra sharing three edges. The Sc–Cl bond lengths are considered equivalent, although very slight discrepancies are observed between the upper and lower halves of the octahedra (2.515(8) and 2.528(8) Å, respectively). Poppelmeier and Corbett [57] previously reported the structures of a number of 'reduced' scandium chlorides such as Sc_5Cl_8 and Sc_7Cl_{10}. A variety of structural forms were observed, with one prevailing trend: as the number of M–M bonding interactions increased, so the M–Cl bond strength decreased and hence the bond lengthened. Thus the $ScCl_6$ octahedra in Sc_5Cl_8 reveal bond lengths longer than $ScCl_3$, at 2.538 and 2.563 Å, while the 'isolated' metal atoms in Sc_7Cl_{10} show a shorter, stronger M–Cl bond of length 2.502 Å. A brief overview of the structures reveals that Sc_5Cl_8 contains two types of infinite chains, one with $ScCl_6$ octahedra and the other comprising edge-sharing scandium octahedra. The Sc_7Cl_{10} structure contains the isolated metal atoms previously mentioned in addition to infinite double chains comprising edge-sharing Sc octahedra. High temperature treatment of $BaCl_2$:$ScCl_3$ (1:1) provides colourless crystals of $Ba_2Cl[ScCl_6]$ whose structure consists of isolated $[ScCl_6]^{3-}$ octahedra, Sc–Cl 2.42–2.52 Å, and accompanying Ba^{2+} cations with one 'lonesome' chloride ion [58].

The reaction of *p*-*tert*-butyloxacalix[3]arene(LH_3) and $Sc(OTf)_3$ (OTf = trifluoromethane sulphonate) in a DMSO/acetone mixture in the presence of Et_3N as a proton scavenger produces colourless crystals of $[Sc_2L_2(DMSO)_2]\cdot 2DMSO\cdot acetone$ [59].



(LH_3)

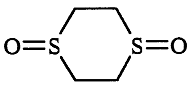
The structure is dimeric with a $Sc_2(\mu\text{-}O)_2$ core unit and features scandium centres with distorted octahedral metal geometry. Each calixarene ligand acts as an 8-e^- trianion following proton loss (× 3) and provides one bridging aryloxide and two terminal aryloxide linkages together with one backbone ether linkage interaction. $Sc-O_{(bridge)}$ 2.101(8), 2.150(8) Å, $Sc-O_{(aryloxide)}$ 1.979(8), 1.960(8) Å and $Sc-O_{(ether)}$ 2.535(8), $Sc-O_{(DMSO)}$ 2.055(8) Å. The sixth coordination site is occupied by a unidentate dmso ligand.

Addition of $Sc_2(SO_4)_3$ and $(NH_3OH)_2SO_4$ in aqueous solution results in the formation of the hydroxylammonium scandium sulphate $Sc(NH_3OH)(S0_4)_2\cdot 1.5H_2O$ [60].

Each metal centre of the chain structure is octahedrally-coordinated by five oxygen atoms from sulphate groups and one water molecule; $Sc-O_{(sulphate)}$ 2.026(2)–2.104(2), $Sc-O_{(water)}$ 2.130(2) Å. The coordinated water molecule is hydrogen bonded to sulphate ions and further hydrogen bonding exists between the chains and hydroxylammonium cations and the lattice water molecules.

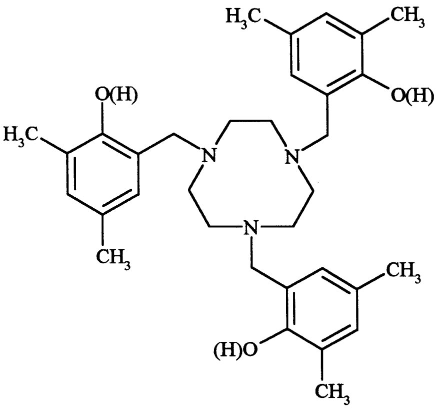
The reaction of aqueous scandium perchlorate and glycine leads to the formation of the six-coordinate complex $[Sc_2(glycine)_6(ClO_4)_6]_n$ [61]. The amino acid binds solely through oxygen atoms of carboxylic groups and the complex has an infinite chain structure built from dimeric units e.g. each pair of scandium atoms is linked by three bridging carboxylate groups from three separate glycine molecules. The non-bonding distance between metal atoms is 4.519 Å and mean Sc–O 2.066 Å.

A new picrate derivative $[Sc_6(pic)_6(L)_3(OH)_{10}(H_2O)_2](pic)_2(H_2O)_{10}$ has been described involving variable metal coordination. The disulphone, (L), acts as a bridging molecule between centrosymmetric hexameric clusters involving two scandium(III) centres with coordination seven and four scandium(III) centres with six coordination [62].

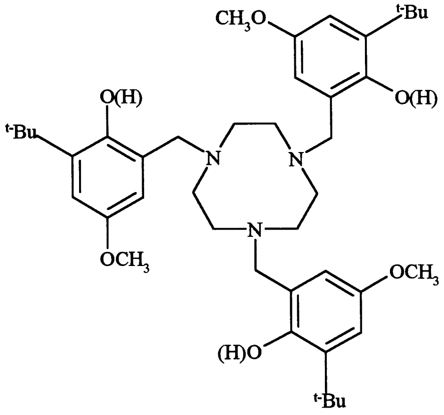


(L)

Reaction of $[PhC(NSiMe_3)_2]Li(TMEDA)$ (TMEDA = N′,N′,N‴,N‴-tetramethylethylenediamine) with $ScCl_3(THF)_3$ in THF provides $[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}Cl)_2Li(TMEDA)$ [63] which features a six-coordinate (essentially octahedral) scandium centre as part of a planar $Sc(\mu\text{-}Cl)_2Li$ core unit with the lithium further coordinated to the bidentate TMEDA ligand. Sc–Cl 2.529(3)–2.560(3), Sc–N 2.168(5)–2.230(5) Å. Further reaction of this product with dihydrogen at room temperature in hexane gives the dimeric scandium hydride $\{[PhC(NSiMe_3)_2]_2Sc(\mu\text{-}H)\}_2$ in which each scandium centre is six-coordinate with a distorted octahedral arrangement Sc–H 1.92(3), 1.87(3), 2.00(3) 1.98(3) Å.



($L^{Me}H_3$)



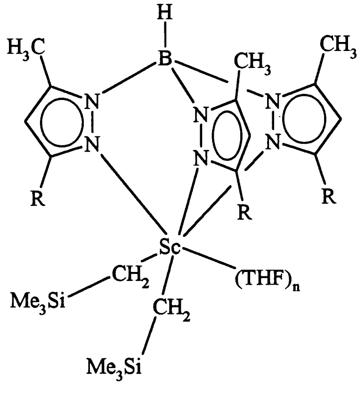
($L^{OMe}H_3$)

The azamacrocycles 1,4,7-tris(3,5-dimethyl-2-hydroxy-benzyl)-1,4,7-triazacyclononane ($L^{Me}H_3$) and 1,4,7-tris(3-*t*-butyl-5-methoxy-2-hydroxy-benzyl)-1,4,7-triazacyclononane ($L^{OMe}H_3$) form six-coordinate neutral complexes with Sc(III) of the type [$ScL^{Me}\cdot 2MeCN$] (**A**) and [ScL^{OMe}] (**B**) [64]. Each ligand shows *fac*-octahedral binding via three *N*-donor sites of the ring in combination with three anionic *O*-donor sites of the attached arms following proton loss. Bond dimensions (**A**) Sc–O 1.969(5), 1.965(8), 1.979(7), Sc–N 2.339(8), 2.351(6), 2.328(9) Å; (**B**) Sc–O 1.977(2), 1.977(2), 1.960(2), Sc–N 2.354(2), 2.365(2), 2.412(2) Å. The unsubstituted parent ligand 1,4,7-trimethyl-1,4,7-triazacycloazanonane (L) reacts with $ScCl_3(THF)_3$ in acetonitrile to provide the neutral six-coordinate complex $ScCl_3(L)$ in which the ligand binding is terdentate *N*-donor (η^3-mode) resulting in a half-sandwich structure [65].

The six-coordinate tris(dibenzoylmethanato-*O*,*O*′) scandium compound shows regular octahedral metal geometry [66].

A structurally characterised example of the hexaaquascandium(III) cation [67] is provided by the trimellitate salt $[Sc(H_2O)_6]^{3+}[C_9H_3O_6]^{3-}$ where $C_9H_3O_6$ = 1,2,4-benzenetricarboxylate anion.

More recently, treatment of $Sc(CH_2SiMe_3)_3(THF)_3$, as generated in situ from $ScCl_3(THF)_3$ (1 mol) and $Li(CH_2SiMe_3)$ (3 mol), and the tris(pyrazolylborate) ligand (L^1) provides the six-coordinate bis-trimethylsilyl complex $(L^1)Sc(CH_2SiMe_3)_2(THF)$ (**A**) following alkane elimination. The formally 12-electron metal centre shows some distortion from the ideal octahedral geometry Sc–N 2.318(12), 2.273(13), 2.372(12), Sc–C 2.253(13), 2.250(14), Sc–O_{THF} 2.206(10) Å (interestingly the reaction with the related tris(pyrazolylborate) ligand (L^2), where a trio of methyl groups are replaced by *t*-butyl groups, results in the five-coordinate compound $(L^2)Sc(CH_2SiMe_3)_2$ (**B**). In this case the enhanced steric requirements of the ligand preclude coordination of the solvent (THF) molecule(s) and the metal exhibits trigonal bipyramidal geometry) [68].



Compound (A) with n = 1: this features ligand L^1 where R = CH_3.
Compound (B) with n = 0: this features ligand L^2 where R = *t*-Bu.

6. Coordination number 7

The structure of $[\{(H_2O)_5Sc\}(OH)_2\{Sc(H_2O)_5\}](C_6H_5SO_3)_4 \cdot 4H_2O$ [69] features a di-μ-hydroxo bridged dimeric framework in which each metal centre is seven-coordinate with a distorted pentagonal bipyramidal geometry. The axial $Sc–O_{(water)}$ bond length mean 2.148(6) Å is predictably shorter than that of the more hindered equatorial water ligands Sc–O mean 2.228(4) Å. The two hydroxo links also bind equatorially Sc–O mean 2.070 Å. For the related $[Sc(OH)(H_2O)_5]_2X_4 \cdot 2H_2O$ (X = Cl, Br) [70] the dimeric 4 + cationic unit is identical with $Sc–O_{(water)}$ mean 2.187 Å for the chloride species and mean 2.179 Å in the bromide analogue. The $Sc–O_{(hydroxide)}$ bond lengths of 2.067 Å and 2.062 Å in the chloride and bromide complexes, respectively, compare favourably to the value of 2.070 Å observed in the sulphonate noted above [69]. The halide anions participate in the formation of a hydrogen bond network which links the discrete units into a 3D array.

Treatment of hydrated scandium nitrate with the pentadentate ligand 2,6-diacetylpyridinebissemicarbazone (dapsc) provides the seven-coordinate $[Sc(OH_2)_2(dapsc)]^{3+}$ [71] terpositive cation; two nitrate anions and a hydroxide ion balance the charge on the complex. An interesting feature of the structure is that the two water ligands reside in a *trans* conformation, sited axially above and below the Sc(dapsc) plane, Sc–O mean 2.110 Å.

Recent interest in the macrocyclic chemistry of scandium has focused on crown ether complexation of scandium(III) both for neutral and cationic species. The synthetic approach exploits halide abstraction from $ScCl_3$ (using $SbCl_5$ in acetonitrile solution) to provide the anhydrous $ScCl^{2+}$, (possibly $ScCl^{2+}$) and Sc^{3+} cations which can be stabilised in situ by complexation with a suitable crown ether. In the first example using 18-crown-6, the ionic compound $[ScCl_2(18\text{-crown-}6)][SbCl_6]$ was obtained [72]. The cation has a threaded structure such that the metal resides directly within the ring cavity but is only directly bonded to five of the crown oxygens Sc–O 2.190(5)–2.229(5) mean 2.210 Å (see Fig. 7). The resulting seven-coordinate metal geometry is ca. pentagonal bipyramidal leaving the sixth and remaining ring oxygen well outside the equatorial ScO_5 plane (+ 1.3015 Å) and clearly not involved in the metal coordination Sc···O 4.137(5) Å.

Coincidentally Strel'tsova et al. [73] described two similar examples, viz. $[ScCl_2(15\text{-crown-}5)]Cl$ and $[ScCl_2(15\text{-crown-}5)]_2[CuCl_4]$, which again feature a linear $ScCl_2^+$ unit inserted directly into the crown cavity but with a regular pentagonal bipyramidal geometry reflecting total involvement of the oxacrown oxygen atoms. For the latter compound Cl–Sc–Cl lies at 179.8(4)° with Sc–O mean 2.125(2) Å. Equally the structure of the related $[ScCl_2(\text{benzo-}15\text{-crown-}5)][SbCl_6]$ shows all the ring oxygen atoms coordinated to the metal centre in a regular and symmetrical equatorial girdle Sc–O mean 2.188 Å [74]. The benzo group is clearly tilted (24.9°) from the equatorial ScO_5 plane (see Fig. 8).

This preference for seven-coordinate pentagonal bipyramidal geometry featuring a threaded $ScCl_2^+$ unit and an equatorial array of five ring oxygen atoms

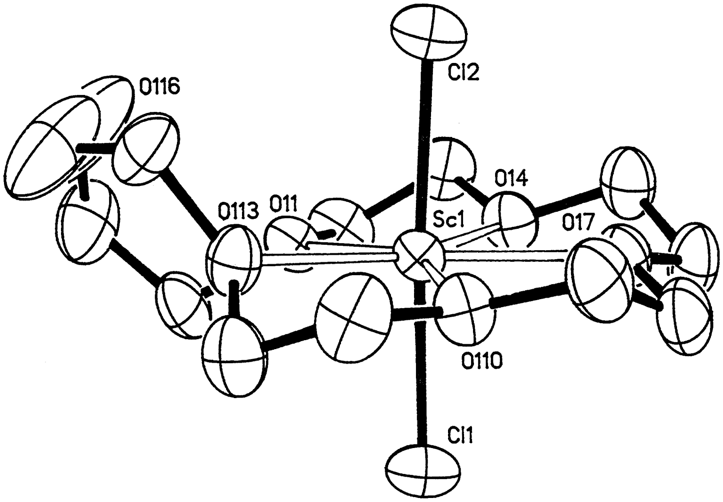


Fig. 7.

continues for the larger crowns. Reaction of $ScCl_3(THF)_3$ (1 mol) with dibenzo-24-crown-8 (1 mol) in the presence of $SbCl_5$ (1 mol) in acetonitrile afforded $[ScCl_2(crown)(H_2O)][SbCl_6]\cdot 2MeCN$ [75]. In this case the equatorial array of five oxygen atoms comprises four of the ring oxygen donors together with a stray water molecule. The $Sc–O_{(crown)}$ bond distances mean 2.25 Å compare closely with those observed in the 18-crown-6 (mean 2.210 Å) and 15-crown-5 (mean 2.125 Å) analogues. The $Sc–O_{(water)}$ bond is the shortest observed, at 2.130(8) Å. As it turns out the presence of the water impurity, most probably introduced during recrystallisation, is fortuitous since collective binding of five oxygen

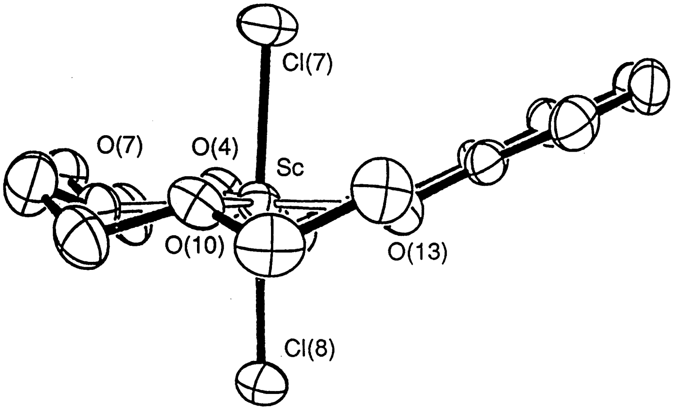


Fig. 8.

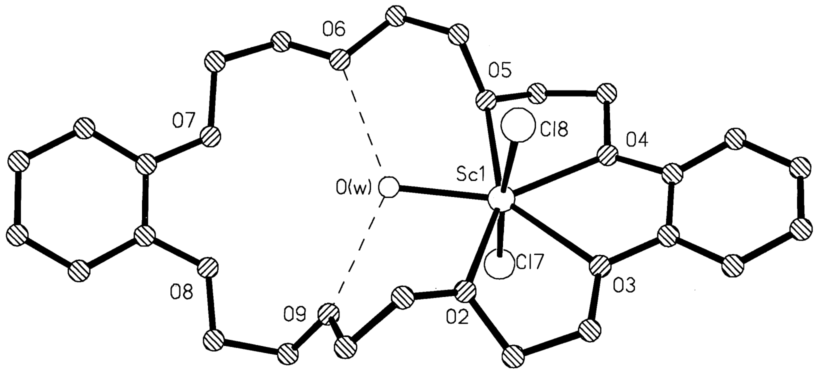


Fig. 9.

atoms from the ring would entail savage distortion. Moreover, the coordinated water molecule is ideally located to allow stabilisation via intramolecular hydrogen bonding with two of the remaining crown oxygen atoms $O_{(water)}\cdots O_{(crown)}$ 2.65, 2.75 Å. The central $ScCl^{2+}$ unit is essentially linear Cl–Sc–Cl 173.8(2)°, Sc–Cl mean 2.932(4) Å (see Fig. 9).

The structure of $[ScCl_2(dibenzo\text{-}30\text{-}crown\text{-}10)(H_2O)_2][SbCl_6]$ MeCN H_2O [75] is no less remarkable (see Fig. 10). The coordination geometry around the metal is again pentagonal bipyramidal, with the equatorial array consisting of three oxygen atoms from the crown and two oxygen atoms from coordinated water molecules. The aqueous ligands again prove to be perfectly located to allow hydrogen bonding

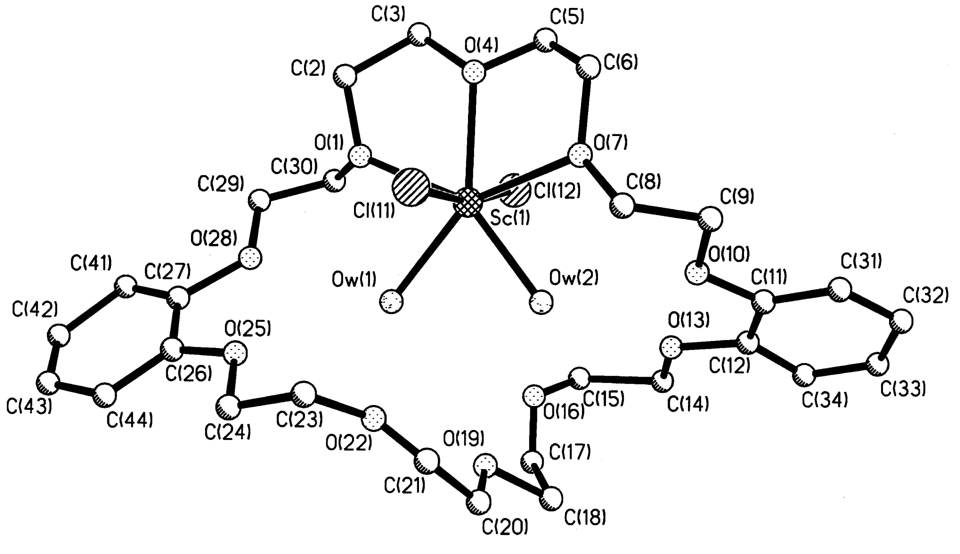


Fig. 10.

with the non-coordinating oxygen atoms on the macrocycle; interestingly one of the water ligands shows hydrogen bonds to three crown oxygen atoms while the second is involved in four such stabilising interactions. The Sc–$O_{(crown)}$ bond lengths mean 2.253(8) Å are similar to those observed in the smaller crowns, while the Sc–$O_{(water)}$ bond lengths 2.160(8), 2.148(9) Å compare favourably to that observed in the dibenzo-24-crown-8 example.

Although these 'restricted coordination' crown ether complexes are prototypical for scandium, there are equivalent lanthanide(III) species, notably $[M(NCS)_3(dibenzo\text{-}30\text{-}crown\text{-}10)(H_2O)_2]$ M = Gd and Dy [76], where the respective metal atom is bound 'off-centre' to three crown donor sites with a total coordination number of eight.

Direct treatment of aqueous scandium chloride and picolinic acid produced colourless crystals of $[Sc(C_5H_4NCO_2)_2(OH)H_2O)]_2 \cdot 4H_2O$ [77]. The structure features a dimeric $[Sc\text{-}\mu(OH)]_2$ unit with hydroxide bridges; each metal centre is bonded to an individual water molecule and two picolinato anions resulting in a seven-coordinate metal geometry. Sc–$O_{(bridge\ hydroxide)}$ 2.063(2), 2.080(1) Å Sc–$O_{(carboxylic)}$ 2.176(1), 2.156(1) Å, Sc–$O_{(water)}$ 2.175(2) Å, Sc–N 2.405(1), 2.407(1) Å.

7. Coordination number 8

An eight-coordinate zircon-type structure has been reported for scandium orthovanadate with the trivalent metal atoms each bound to eight neighbouring oxygen atoms Sc–O mean 2.23 Å [78].

Hansson [79] and Watanabe and Nagashima [80] have reported (independently) the structure of tetraaquo-tris-oxalato discandium(III) dihydrate, $Sc_2(C_2O_4)_3 \cdot 6H_2O$ which consists of scandium-oxalate layers, with each metal atom assuming distorted dodecahedral geometry; six of the coordination sites are filled by three bidentate oxalate chelates, with the coordination number raised to eight by the presence of two binding water molecules per metal. The Sc–$O_{(ligand)}$ bond lengths range from 2.184(6) to 2.259(6) Å, mean 2.236(6) Å.

Two groups published ScL_4 structures, for L = the tropolonato ligand, $C_7H_5O_2^-$. Each group obtained a crystalline material which was characterised as $[HScL_4]_2$, a hydrogen-bonded acid dimer species. Einstein's [81] group discovered the metal to be eight-coordinate, bound to the four bidentate ligands with Sc–O bond lengths ranging from 2.161(3) to 2.310(3) Å. Two of the tropolonato groups assume symmetrical coordination to the metal with the remaining ligands asymmetrically bound: this discrepancy was attributed to differing levels of hydrogen bonding involvement (see Fig. 11).

The structure reported by Melson et al. [82] has near-identical bond lengths and although the shape parameter calculations are not conclusive a dodecahedral metal geometry was favoured, over square antiprismatic, based on the stereochemical requirements of the ligand.

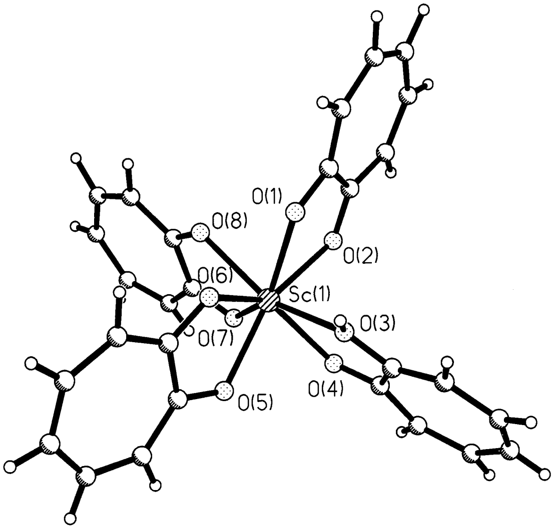


Fig. 11.

A further example of M(bidentate)$_4$ complexation is provided by $Sc(OC(O)NHNH_2)_4$ [83] which exhibits mixed *O*/*N*-donation, with a coordination geometry again close to dodecahedral, Sc–O mean 2.164 Å, Sc–N mean 2.382 Å. Tan et al. [84] report the structure of $Sc(NO_3)_3(H_2O)_2$(benzo-15-crown-5) featuring the crown ether as lattice solvate. Each nitrate group is bidentate and, together with the two water molecules, the metal coordination geometry approximates to dodecahedral.

A unique example of two eight-coordinate scandium moieties within the same structure has appeared in the Russian literature viz. $[Sc(C_2H_3O_3)_2(H_2O)_4][Sc(C_2H_3O_3)_4]$ [85]: the anion incorporates four bidentate hydroxyacetato ligands and the accompanying cation has the scandium bonded to two hydroxyacetato ligands, with four water molecules completing the coordination sphere.

Elucidation of the crystal structure of $Sc(NO_3)_2(OC(NH_2)_2)_4$ [86] revealed a distorted dodecahedral array, with $Sc–O_{(nitrate)}$ mean 2.228 Å.

Another example of an eight-coordinate complex is provided by $[Sc_2(NO_3)_2(\mu\text{-}OH)_2(bpce)_2][NO_3]_2 \cdot 2MeCN$ [87], where bpce = 1,2-bis(pyridine-α-carbaldimino) ethane. The centrosymmetric dimeric structure has two bridging hydroxy groups and features each scandium centre as eight-coordinate with distorted dodecahedral geometry based on an approximately coplanar array of the two hydroxy and two nitrate oxygen atoms perpendicular to the coplanar bpce ligand. The short Sc–O bond lengths, 2.053 and 2.089 Å, and the asymmetry of the bridging hydroxy links are seen to provide a compromise between the unfavourable O–O interelectronic repulsion and the corresponding loss in Sc–O bond energy. The tetradentate *N*-donor ligand has Sc–N distances ranging from 2.341 to 2.403 Å.

Total halide abstraction from $ScCl_3$ by judicious use of $SbCl_5$ in tandem with $SbCl_3$ in acetonitrile solution in the presence of 12-crown-4 results in the formation of $[Sc(12\text{-crown-}4)_2][SbCl_6][Sb_2Cl_8(MeCN)_2]\cdot 2MeCN$ [88]. The anhydrous Sc^{3+} cation is sandwiched by two crown ligands, with each oxacrown providing four oxygen donor sites, and assumes distorted square antiprismatic geometry of ca. D_4 symmetry, Sc–O 2.160(8)–2.274(9) Å mean 2.218(8) Å. The two crown rings are essentially parallel with an angle of interaction 0.27° and adopt a staggered conformation, so as to minimise interligand repulsions (see Fig. 12). The accompanying centrosymmetric halogen-bridged counteranion $[Sb_2Cl_8(MeCN)_2]$ represents a rare example of a discrete dimeric $[SbCl_4]_2$ structural unit; presumably the presence of coordinated acetonitrile ligands effectively blocks any further oligomerisation.

8. Coordination number 9

The structure of the hydrated scandium nitrate $[Sc(NO_3)_3(H_2O)_3]$ molecule which co-crystallises with 18-crown-6 [89] reveals a nine-coordinate oxygen environment for the metal, with each nitrate ligand attached in bidentate fashion and with three water molecules completing the coordination sphere $Sc–O_{(nitrate)}$ mean 2.295 Å and $Sc–O_{(water)}$ mean 2.215 Å. The crown ether is merely held in lose association to the metal by secondary hydrogen bonding of the type $O_{crown}\cdots H_2O–Sc$ (see Fig. 13).

In the related $Sc(NO_3)_3(terpy)$ [87] the scandium atom is essentially coplanar with the three nitrogen atoms of the terpyridyl ligand, but one of the nitrate anions is bound asymmetrically with one Sc–O bond enhanced by 0.248 Å from its partner.

Nine-fold coordination is found in $[NO]_2^+[Sc(NO_3)_5]^{2-}$ [90] which features a mononuclear anion in which the metal is bonded to four bidentate (OO) and one monodentate (O) nitrate groups.

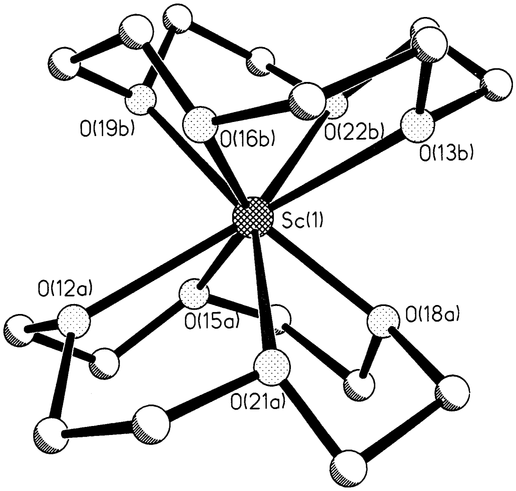


Fig. 12.

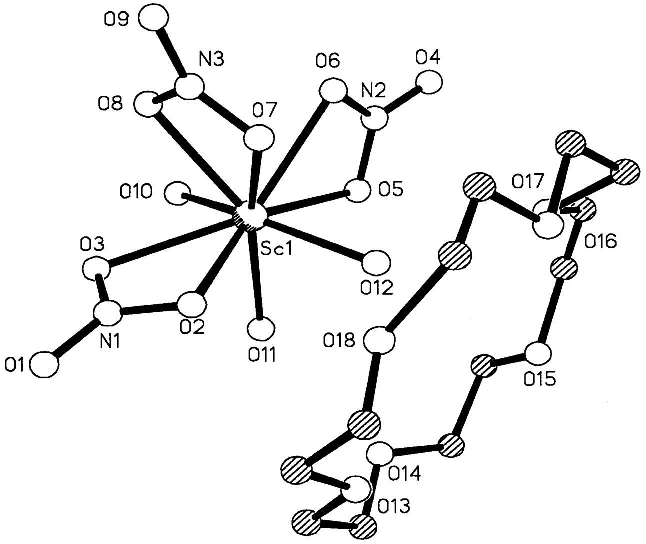

O9
N3
O6
O4
O8
O7
N2
O10
O5
O17
O3
Sc1
O16
O12
O2
O11
N1
O18
O1
O15
O14
O13

Fig. 13.

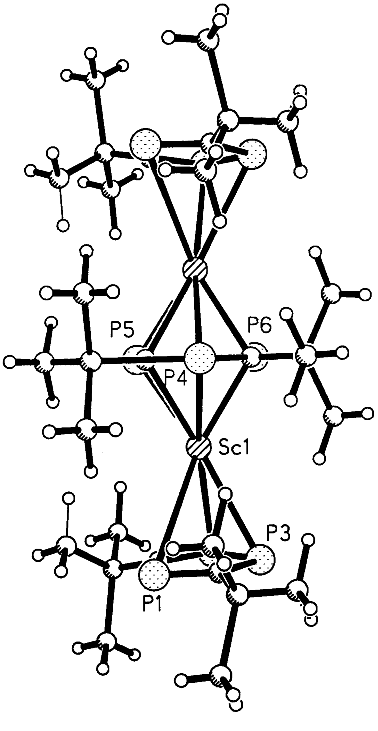

P5
P6
P4
Sc1
P3
P1

Fig. 14.

9. Addendum

Recent studies by Cloke and Nixon et al. have established the existence of lower valence scandium species: co-condensation of electron beam vaporised scandium with an excess of ^{t}Bu–C≡P at 77 K produces a dark brown matrix which affords two products viz. purple $[Sc(\eta^5\text{-}P_2C_3^tBu_3)_2]$ (**A**) [91] and green $[(\eta^5\text{-}P_3C_2^tBu_2)Sc(\mu,\eta^6{:}\eta^6\text{-}P_3C_3^tBu_3)\ Sc(\eta^5\text{-}P_3C_2^tBu_2)$ (**B**) [92]. Although there is no X-ray structural data for (**A**), magnetic and spectroscopic (UV–vis, EPR) measurements point to a metallocene structure based on Sc(II)(d^1). Identification of (**B**) as the first example of a formal Sc(I)(d^2) complex derives from magnetic, spectroscopic (UV–vis, EPR) measurements and an X-ray crystallographic determination reveals a triple-decker structure (see Fig. 14).

Acknowledgements

The authors would like to thank the University of Warwick (PRM) and the EPSRC/Alpha-Fry Metals Ltd., Croydon, Surrey (DRA) for postgraduate studentships.

References

[1] R. Astbury, Proc. R. Soc. London Ser. A 112 (1926) 448.

[2] We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory(a) for access to the Cambridge Structural Database(b). (a) D.A. Fletcher, R.F. McMeeking, D. Parkin, J. Chem. Inf. Comput. Sci. 36 (1996) 746–749. (b) F.H. Allen, O. Kennard, Chem. Des. Autom. News 8 (1993) 31–37.

[3] G.A. Melson, R.W. Stotz, Coord. Chem. Rev. 7 (1971) 133.

[4] F.G.N. Cloke, Chem. Soc. Rev. 22 (1993) 17.

[5] (a) R.C. Fay, Coord. Chem. Rev. 37 (1981) 1; 45 (1982) 1. (b) E.C. Constable, Coord. Chem. Rev. 57 (1984) 229; 62 (1985) 131; 71 (1986) 383. (c) C.E. Housecroft, Coord. Chem. Rev. 124 (1993) 41; 127 (1994) 131; 142 (1995) 147; 146 (1995) 37; 152 (1996) 467; 164 (1997) 183.

[6] R.D. Shannon, Acta Crystallogr. Sect. A 32 (1976) 751.

[7] L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, NY, 1960.

[8] P.B. Hitchcock, M.F. Lappert, A. Singh, J. Chem. Soc. Chem Commun. (1983) 1499.

[9] E.C. Alyea, D.C. Bradley, R.G. Copperthwaite, J. Chem. Soc. Dalton Trans. (1972) 1580.

[10] J.S. Ghotra, M.B. Hursthouse, A.J. Welch, J. Chem. Soc. Chem Commun. (1973) 669.

[11] M.E. Thompson, S.M. Baxter, A.R Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.

[12] (a) W.E. Piers, P.J. Shapiro, E.E. Bunel, J.E. Bercaw, Synlett (1990) 74. (b) B.J. Burger, M.E. Thompson, W.D. Cotter, J.E. Bercaw, J. Am. Chem. Soc. 112 (1990) 1566.

[13] M.A. St Clair, W.P. Schaefer, J.E. Bercaw, Organometallics 10 (1991) 525.

[14] S. Hajela, W.P. Schaefer, J.E. Bercaw, Acta Crystallogr. Sect. C 48 (1992) 1771.

[15] G.C. Bazan, W.P. Schaefer, J.E. Bercaw, Organometallics 12 (1993) 2126.

[16] R.E. Marsh, W.P. Schaefer, G.C. Bazan, J.E. Bercaw, Acta Crystallogr. Sect. C 48 (1992) 1416.

[17] W.P. Schaefer, R.D. Kohn, J.E. Bercaw, Acta Crystallogr. Sect C 48 (1992) 251.

[18] W.E. Piers, D.J. Parks, L.R MacGillivray, M. Zaworotko, Organometallics 13 (1994) 4547.

[19] W.E. Piers, L.R MacGillivray, M. Zaworotko, Organometallics 12 (1993) 4723.

[20] W.E. Piers, G. Ferguson, J.F. Gallagher, Inorg. Chem. 33 (1994) 3784.
[21] J.L. Atwood, K.D. Smith, J. Am. Chem. Soc. 95 (1973) 1488.
[22] J.L. Atwood, K.D. Smith, J. Chem. Soc. Dalton Trans. (1973) 2487.
[23] F. Bottomley, D.E. Paez, P.S. White, J. Organomet. Chem. 291 (1985) 35.
[24] J.M. Manriquez, P.J. Fagan, T.J. Marks, S.H. Vollmer, C.S. Day, V.W. Day, J. Am. Chem. Soc. 101 (1979) 5075.
[25] M.F. Lappert, A. Singh, J.L. Atwood, W.E. Hunter, J. Chem. Soc. Chem. Commun. (1983) 206.
[26] M.A. St Clair, B.D. Santarsiero, J.E. Bercaw, Organometallics 8 (1989) 17.
[27] M.A. St Clair, B.D. Santarsiero, Acta Crystallogr. Sect. C 45 (1989) 850.
[28] P.J. Shapiro, L.M. Henling, R.E. Marsh, J.E. Bercaw, Inorg. Chem. 29 (1990) 4560.
[29] N.C. Burton, F.G.N. Cloke, P.B. Hitchcock, H.C. de Lemos, A.A. Sameh, J. Chem. Soc. Chem. Commun (1989) 1462.
[30] B.K Campion, R.H. Heyn, T.D. Tilley, J. Am. Chem. Soc. 112 (1990) 2011.
[31] B.K Campion, R.H. Heyn, T.D. Tilley, Inorg. Chem. 29 (1990) 4355.
[32] B.K Campion, R.H. Heyn, T.D. Tilley, Organometallics 12 (1993) 2584.
[33] P.J. Shapiro, E.E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867.
[34] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623.
[35] Y. Mu, W.E. Piers, D.C. MacQuarrie, M.J. Zaworotko, V.G. Young, Organometallics 15 (1996) 2720.
[36] D. Dolphin, The Porphyrins, vols. 1–4, Academic Press, New York, 1978.
[37] J. Arnold, C.G. Hoffman, D.Y. Dawson, F.J. Hollander, Organometallics 12 (1993) 3645.
[38] J. Arnold, C.G. Hoffman, J. Am. Chem. Soc. 112 (1990) 8620.
[39] M.G. Sewchok, R.C. Haushalter, J.S. Merola, Inorg. Chim. Acta 144 (1988) 47.
[40] J.L. Atwood, K.D. Smith, J. Chem. Soc. Dalton Trans. (1974) 921.
[41] M.D. Fryzuk, G. Giesbrecht, S.J. Rettig, Organometallics 15 (1996) 3329.
[42] (a) M.K Guseinova, A.S. Antsishkina, M.A. Porai-Koshits, Zh Strukt. Khim. 9 (1968) 1040. (b) M.K Guseinova, A.S. Antsishkina, M.A. Porai-Koshits, J. Struct. Chem. (USSR) 9 (1968) 926.
[43] J. Hasek, J. Ondracek, P. Karen, J. Bauer, Collect. Czech. Chem. Commun. 55 (1990) 426.
[44] T.J. Anderson, M.A. Neuman, G.A. Melson, Inorg. Chem. 12 (1973) 927.
[45] T.J. Anderson, M.A. Neuman, G.A. Melson, Inorg. Chem. 13 (1974) 158.
[46] D.L. Kepert, Inorg. Chem. 11 (1972) 1561.
[47] E. Hansson, Acta Chem. Scand. 27 (1973) 2841.
[48] G.R Willey, P.R Meehan, M.D. Rudd, M.G.B. Drew, J. Chem. Soc. Dalton Trans. (1995) 3173.
[49] R. Fuchs, J. Strähle, Z. Naturforsch. Teil B 39 (1984) 1662.
[50] Y. Sugita, Y. Ohki, Y. Suzuki, A. Ouchi, Bull. Chem. Soc. Jpn. 60 (1987) 3441.
[51] Y. Ohki, Y. Suzuki, T. Takeuchi, A. Ouchi, Bull. Chem. Soc. Jpn. 61 (1988) 393.
[52] Y. Tateyama, Y. Ohki, Y. Suzuki, A. Ouchi, Bull. Chem. Soc. Jpn. 61 (1988) 2214.
[53] J.M. Harrowfield, B.W. Skelton, A.H. White, Aust. J. Chem. 47 (1994) 397.
[54] D. C. Bradley, H. Chudzynska, M.E. Hammond, M.B. Hursthouse, M. Motevalli, W. Ruowen, Polyhedron 11 (1992) 375.
[55] (a) H.H. Karsch, G. Ferazin, O. Steigelmann, H. Kooijman, W. Hiller, Angew. Chem. Int. Ed. Engl. 32 (1993) 1739. (b) H.H. Karsch, G. Ferazin, H. Kooijman, O. Steigelmann, A. Schier, P. Bissinger, W. Hiller, J. Organomet. Chem. 482 (1994) 151.
[56] H. Fjellvåg, P. Karen, Acta Chem. Scand. 48 (1994) 294.
[57] K.R. Poppelmeir, J.D. Corbett, Inorg. Chem. 16 (1977) 294, 1107. See also: J. Am. Chem. Soc. 100 (1978) 5039.
[58] S. Masselmann, G. Mayer, Z. Anorg. Allg. Chem. 624 (1998) 551.
[59] C.E. Daitch, P.D. Hampton, E.N. Duesler, Inorg. Chem. 34 (1995) 5641.
[60] A. Mirceva, L. Golic, Acta Crystallogr. Sect. C 51 (1995) 175.
[61] C.H. Yan, Y.W. Zhang, B. Li, T.Z. Jin, G.X. Xu, Polyhedron 15 (1996) 2895.
[62] J.D. Ayala, G. Vicentini, G. Bombieri, J. Alloy. Compd. 225 (1995) 357.
[63] J.R Hagadorn, J. Arnold, Organometallics 15 (1996) 984.

[64] B. Adam, E. Bill, E. Bothe, B. Goerdt, G. Haselhorst, K Hildenbrand, A. Sokolowski, S. Steenken, T. Weyhermuller, K Wieghardt, Chem. Eur. J. 3 (1997) 308.
[65] S. Hajela, W.P. Schaefer, J.E. Bercaw, J. Organomet. Chem. 532 (1997) 45.
[66] E.G. Zaitseva, I.A. Baidina, P.A. Stabnikov, S.V. Borisov, I.K Igumenov, Zh. Strukt. Khim. 31 (1990) 184.
[67] E. Kalalova, J. Bauer, Vysk. Skoly. Chem. Techn. Pr. 19 (1975) 41.
[68] J. Blackwell, C. Lehr, Y. Sun, W.E. Piers, S.D. Pearce-Batchilder, M.J. Zaworotko, V.G. Young Jr., Can. J. Chem. 75 (1997) 702.
[69] F. Matsumoto, Y. Ohki, Y. Suzuki, O. Ouchi, Bull. Chem. Soc. Jpn. 62 (1989) 2081.
[70] N.B. Ilyukhin, S.P. Petrosyants, Russ. J. Inorg. Chem. 39 (1994) 1449.
[71] D.D. McRitchie, R.C. Palenik, G.J. Palenik, Inorg. Chim. Acta 20 (1976) L27.
[72] G.R Willey, M.T. Lakin, N.W. Alcock, J. Chem. Soc. Chem. Commun. (1992) 1619.
[73] (a) N.R Strel'tsova, V.K Bel'skii, B.M. Bulychev, O.K. Kireeva, Zh. Neorg. Khim. 37 (1992) 1822. (b) N.R Strel'tsova, V.K Bel'skii, B.M. Bulychev, O.K. Kireeva, Russ. J. Inorg. Chem. 37 (1992) 934.
[74] G.R Willey, M.T. Lakin, N.W. Alcock, J. Chem. Soc. Dalton Trans. (1993) 3407.
[75] G.R Willey, P.R Meehan, M.D. Rudd, M.G.B. Drew, J. Chem. Soc. Dalton Trans. (1995) 811.
[76] (a) M = Gd; S. Yang, G. Wang, H.G. Wang, X.K Yao, Polyhedron 10 (1991) 1889. (b) M = Dy; S. Yang, Z.H. Yiang, D. Liao, G. Wang, R. Wang, H.G. Wang, X.K. Yao, J. Incl. Phenom. 15 (1993) 159.
[77] J.F. Ma, Z.S. Jin, J.Z. Ni, Polyhedron 14 (1995) 563.
[78] W.O. Milligan, L.W. Vernon, J. Phys. Chem. 56 (1952) 145.
[79] E. Hansson, Acta Chem. Scand. 26 (1972) 1337.
[80] M. Watanabe, K Nagashima, J. Inorg. Nucl. Chem. 33 (1971) 3604.
[81] A.R. Davis, F.W.B. Einstein, Inorg. Chem. 13 (1974) 1880.
[82] T.J. Anderson, M.A. Neuman, G.A. Melson, Inorg. Chem. 13 (1974) 1884.
[83] B. Barlic, L. Golic, F. Lazarini, Acta Crystallogr. Sect. C 3 (1974) 407.
[84] M.Y. Tan, X.M. Gan, N. Tang, J.P. Zou, Goadeng Xuexino Huaxue Xuebao (Chem. J. Chin. Univ.) 9 (1988) 1217.
[85] L.M. Dikareva, A.S. Antsyshkina, M.A. Porai-Koshits, V.N. Ostrikova, I.V. Arkhangel'skii, A.Z. Zamanov, Dokl. Akad. Nauk. Az. SSR 34 (1978) 41.
[86] V.I. Kuskov, E.N. Treushnikov, N.V. Belov, Kristallografiya 23 (1978) 1196.
[87] A.M. Arif, F.A. Hart, M.B. Hursthouse, M. Thornton-Pett, W. Zhu, J. Chem. Soc. Dalton Trans. (1984) 2449.
[88] G.R Willey, P.R Meehan, M.G.B. Drew, Polyhedron 15 (1996) 1397.
[89] Z.-S. Jin, Y.-S. Liu, S.-G. Zhang, F.-L. Yu, J.-Z. Ni, Huaxue Xueboo (Acta Chim. Sin.) (Chin.) 45 (1987) 1048.
[90] C.C. Addison, A.J. Greenwood, M.J. Haley, N. Logan, J. Chem. Soc. Chem. Commun. (1978) 580.
[91] P.L. Arnold, F.G.N. Cloke, J.F. Nixon, Chem. Commun. (1998) 797.
[92] P.L. Arnold, F.G.N. Cloke, P.B. Hitchcock, J.F. Nixon, J. Am. Chem. Soc. 118 (1996) 7630.