Coordination Chemistry Reviews, 62 (1985) 131—143
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

4. SCANDIUM

EDWIN C. CONSTABLE

CONTENTS

INTRODUCTION

This year has seen something of a resurgence of interest in the coordination chemistry of scandium. This review covers the major journals through 1983, and coincides with the Chemical Abstracts coverage in volumes 97, 98 and 99. The format closely resembles that presented in previous reviews in this journal [1]. I should like to thank Dr Paul Raithby for his help in obtaining data from the Cambridge Crystallographic Data Centre.

The chemistry of scandium has been reviewed in the section of the 1982 Annual reports dealing with scandium, yttrium, the lanthanides and the actinides [2]. A review has also appeared on the subject of scandium complexonates [3].

4.1 SCANDIUM(III)

4.1.1 Halides and halo-complexes

A thermal analytical study of the scandium(III) fluoride system has been reported; the phase diagram shows no evidence for an α-UO_3 phase [4]. A number of theoretical studies of scandium(III) halides have been completed. A study of XY_3 molecules, including some scandium(III) halides, has given a set of kinetic force constants and compliance constants [5]. A related study of planar (D_{3h}) XY_3 species, including scandium(III) fluoride, chloride, bromide

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and iodide, has reported Coriolis constants $[\zeta ij]$ [6].

The transport of scandium(III) fluoride through silicon(IV) chloride or germanium(IV) chloride has been investigated [7]. The method results in the growth of good scandium(III) fluoride crystals, and the transport reactions appear to be of the type:

$$4ScF_3(s) + 3MCl_4(g) \rightleftharpoons 4ScCl_3(g) + 3MF_4(g)$$
$$4ScF_3(s) + 3MCl_4(g) \rightleftharpoons 2Sc_2Cl_6(g) + 3MF_4(g)$$

$$M = Si \text{ or } Ge$$

The quasi-binary Rb_3ScCl_6-Cs_3ScCl_6 section in the RbCl-$ScCl_3$-CsCl system has been studied, and shown to consist of a continuous series of solid solutions [8]. X-Ray powder patterns indicate that the compound $TlScF_6$, present in the TlF_3-ScF_3 system, is isostructural with vanadium(III) fluoride [9]. A statistical distribution of the thallium(III) and scandium(III) ions in the lattice is postulated. A single crystal X-ray study of scandium(III) fluoride was also described in this investigation.

The PbF_2-ScF_3 system has also been investigated in the composition region $Pb_{1-x}Sc_xF_{2+x}$ ($0 \leq x \leq 0.17$) at 830 K [10]. Only a solid solution is present in the disordered fluorite phase, in contrast to the related PbF_2-InF_3 system. The unit-cell dimensions of the novel complexes Ag_2MScF_7 (M = Mg, Mn, Co, Ni or Zn) have been published [11].

A method for the preparation of $[Sc(thf)_3Cl_3]$ has been published in Inorganic Syntheses [12]. The reaction of $[Sc(H_2O)_6]Cl_3$ with a mixture of thionyl chloride and tetrahydrofuran results in good yields, according to the equation:

$$[Sc(H_2O)_6]Cl_3 + 6SOCl_2 + 3thf \rightarrow [Sc(thf)_3Cl_3] + 6SO_2 + 12HCl$$

The thf ligands are bonded to the metal through oxygen, as expected. The complexes $[Sc(thf)_3X_3]$ (X = Cl or Br) have also been prepared by the reaction of elemental scandium with mercury(II) chloride or bromide in thf [13].

The reaction of scandium(III) fluoride with hydrazine has been investigated [14]. A slow reaction occurs with 100% liquid hydrazine (96 h at 50°C) to give $[ScF_3(N_2H_4)]$. This complex is stable in dry air, but hydrolyses to produce hydrazinium tetrafluoroscandate(III), $[N_2H_5][ScF_4]$. The product of reaction of $[ScF_3(N_2H_4)]$ with 5% aqueous hydrofluoric acid is $(N_2H_5)_2(ScF_4)_2.HF.H_2O$. On heating, $[ScF_3(N_2H_4)]$ decomposes to give anhydrous scandium(III) fluoride. In contrast, the reaction of scandium(III) fluoride with 80% hydrazine hydrate produces $[N_2H_5][Sc(OH)F_3]$. These results may be compared with the lack of reactivity that scandium(III) fluoride exhibits towards ammonia.

The solution properties of scandium(III) halides have been the subject of a number of investigations, and it is apparent that aqueous solutions of scandium(III) chloride contain a number of complex species. The thermodynamic and kinetic parameters associated with the solution of scandium(III) oxide in hydrochloric acid have been determined [15]. The value of $\Delta H^{\dagger}$ varies from 1420 cal mol^{-1} at 25°C to 4932 cal mol^{-1} at 75°C. The solution properties are consistent with the presence of a number of solution species, including polynuclear complexes. A ^{45}Sc NMR study of aqueous solutions of scandium(III) chloride is also consistent with the presence of a number of chloro-complexes [16]. A more detailed investigation of the ^{45}Sc NMR properties of aqueous scandium(III) chloride solutions has also been reported [17]. In acidic (hydrochloric acid) medium, it was shown that the chemical shift (δ w.r.t. 0.11 molal scandium(III) chloride in 1.0 molal hydrochloric acid), line-width at half height and T_1 relaxation time were all dependent upon chloride ion concentration. In basic solutions (14 molal sodium hydroxide), there was little dependence upon chloride ion concentration, and the major solution species was $[Sc(OH)_4]^-$. The solutions showed a considerable solvent isotope effect on changing from water to deuterium oxide. For a 0.11 molal solution of scandium(III) chloride in 0.05 molal hydrochloric acid, a T_1 of 7.2±0.3 ms was determined.

The solvent extraction of scandium(III) from chloride-rich medium has been studied. When di-n-butyl sulphoxide or butyl benzyl sulphoxide are used, the extracted species are of the type $\{ScCl_3.nL\}$ (L = $n\text{-}Bu_2SO$ or $n\text{-}BuSOCH_2Ph$) [18]. In each case, the sulphoxide is thought to coordinate to the metal ion through the oxygen atom. Extraction from hydrochloric acid by tri-n-butyl phosphate has also been investigated, and a thermodynamic extraction constant for the process of $K = 2.5\pm0.2 \times 10^{-3}$ determined [19].

A localised molecular orbital study of a number of scandium(III) halo-complexes has been reported; the basis set for scandium was obtained from *ab initio* atomic SCF calculations on the ^2D ground state. Standard bond distances for Sc-F and Sc-Cl of 3.810 and 4.590 atomic units respectively were used. Complexes for which calculations were reported included $[(H_3N)_5ScF]^{2+}$ and $[(H_3N)_5ScCl]^{2+}$ [20].

4.1.2 Complexes with oxygen and sulphur donor ligands

A detailed study of the properties of scandium(III) in aqueous solution has been reported by Sylva [21]. The system was investigated in 0.10 mol dm^{-3} aqueous potassium nitrate solution at 25°C in the pH range 3.695 to 5.097, over a concentration range 0.211×10^{-3} mol dm^{-3} to 2.11×10^{-3} mol dm^{-3}. The data was fully consistent with a series of hydrolytic equilibria producing polynuclear hydroxoscandium(III) species; the only solution species present were $[Sc(H_2O)_5(OH)]^{2+}$, $[Sc_2(H_2O)_n(OH)_2]^{4+}$ and $[Sc_3(H_2O)_m(OH)_5]^{4+}$. It was only necessary to implicate these species in solution equilibria, and no further improvement was obtained using models containing $[Sc(OH)_2]^+$, $[Sc_2(OH)_3]^{3+}$, $[Sc_3(OH)_4]^{5+}$, $[Sc_4(OH)_6]^{6+}$, $[Sc_4(OH)_7]^{5+}$, $[Sc_5(OH)_8]^{7+}$ or $[Sc_5(OH)_9]^{6+}$. Equilibrium constants for the formation of the three solution species were determined:

Species	$-\lg \beta$
$[Sc(OH)]^{2+}$	4.840
$[Sc_2(OH)_2]^{4+}$	6.096
$[Sc_3(OH)_5]^{4+}$	17.567

Aqueous solutions of scandium(III) sulphate and scandium(III) chloride have been studied by ^{45}Sc NMR techniques [17]. In strongly alkaline solution, the predominant species present is $[Sc(OH)_4]^-$. Related ^{45}Sc NMR studies of aqueous scandium(III) nitrate, scandium(III) chloride and scandium(III) perchlorate, have revealed that the anions may coordinate to the metal in each case [16].

The solubility of scandium(III) nitrate in water over the temperature range 0 - 60°C has been studied [22]. Studies of the related ternary systems $Sc(NO_3)_3$-H_2O-HNO_3, $Sc(NO_3)_3$-H_2O-urea and $Sc(NO_3)_3$-H_2O-organic solvent have also been investigated at 25°C or 30°C [22]. The interaction of iron(III) with scandium(III) in alkaline medium at 22±2°C, $i = 2(NaClO_4)$ has been studied; polyheteronuclear hydroxo-bridged complexes are formed [23].

Structural studies of the hexahydroxyscandate(III) species $Sr_3[Sc(OH)_6]_2$ and $Ca_3[Sc(OH)_6]_2$ have been reported; the compounds dehydrate on warming, to yield $Sr_3Sc_2O_6$ or $Ca_3Sc_2O_6$ respectively [24]. Scandium(III) oxide dissolves in aqueous pertechnic acid to give solutions from which $Sc(TcO_4)_3.3H_2O$ may be isolated. On heating, this compound undergoes sequential dehydration to yield $Sc(TcO_4)_3.H_2O$ and finally $Sc(TcO_4)_3$ [25]. In contrast, $Sc(ReO_4)_3$ decomposes to yield Sc_2O_3 and Re_2O_7 upon strong heating [26]. A structural study of $BaSc_2O_4$ has been reported; the compound forms pseudo-orthorhombic crystals [27].

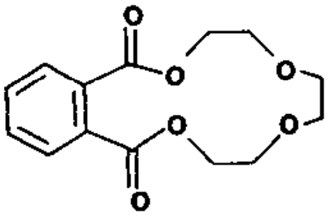
The reaction of $[Sc(H_2O)_5(OH)]^{2+}$ with hydrochloric acid solutions of H_2TiO_3 has been shown to yield $ScTi(OH)O_3.H_2O$ in the pH range 2 - 4.3; at pH > 4.3, scandium(III) hydroxide is precipitated [28]. The initial products from heating $ScTi(OH)O_3.H_2O$ are scandium(III) oxide, titanium(IV) oxide and water, although further heating results in the formation of Sc_2TiO_5 [28].

The thermal decomposition of $Sc(H_2PO_4)_3$ has been investigated at 543 K and 663 K. At 543 K decomposition to $ScH_2P_3O_{10}$ commences, although this phase is best obtained pure after heating to 623 K for 16 h. At a temperature of 673 K, the compound $Sc_4(P_4O_{12})_3$ (m.p. 1013 K) is formed, whereas at temperatures in excess of 1013 K, $[\{Sc(PO_3)_3\}_n]$ is obtained [29].

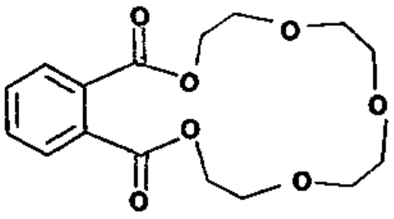
A high-temperature X-ray diffraction study of the complexes $MSc(SO_4)_2$ (M = K, Rb or Cs) has been completed [30]. The compounds $M_3Sc(SO_4)_3$ (M = K, Rb or Cs) have also been described [30].

Sulphoxide complexes, $ScCl_3.nL$ (L = $n-Bu_2SO$ or $n-BuSOCH_2Ph$) are implicated in the extraction of scandium from chloride-rich media by these ligands [18]. The complexes $[Sc(thf)_3X_3]$ (X = Cl or Br) have been mentioned earlier [12,13].

The macrocyclic ligands **1** and **2** are formed by the reaction of phthalic anhydride with the triethylene glycol and tetraethylene glycol respectively;



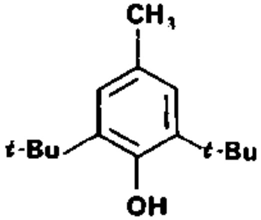
(1)



(2)

they have been shown to react with solutions of scandium(III) nitrate in thf to form the complexes $ScL(NO_3)_3.H_2O$ (L = **1** or **2**) [31].

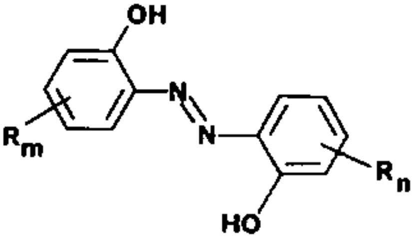
Low coordination numbers are unusual for scandium(III) complexes, although it is now apparent that a judicious choice of ligands facilitates their preparation. Lappert has reported the use of 2,6-bis(*tert*-butyl)-4-methylphenol (3) as a sterically hindering ligand for the preparation of such species. The complex $[ScL_3]$ (HL = 3) may be prepared by the reaction of $[Sc\{N(SiMe_3)_2\}_3]$ with HL or by the reaction of $ScCl_3$ with NaL. The complex reacts with NaL. The complex reacts with monodentate ligands such as thf or



(3)

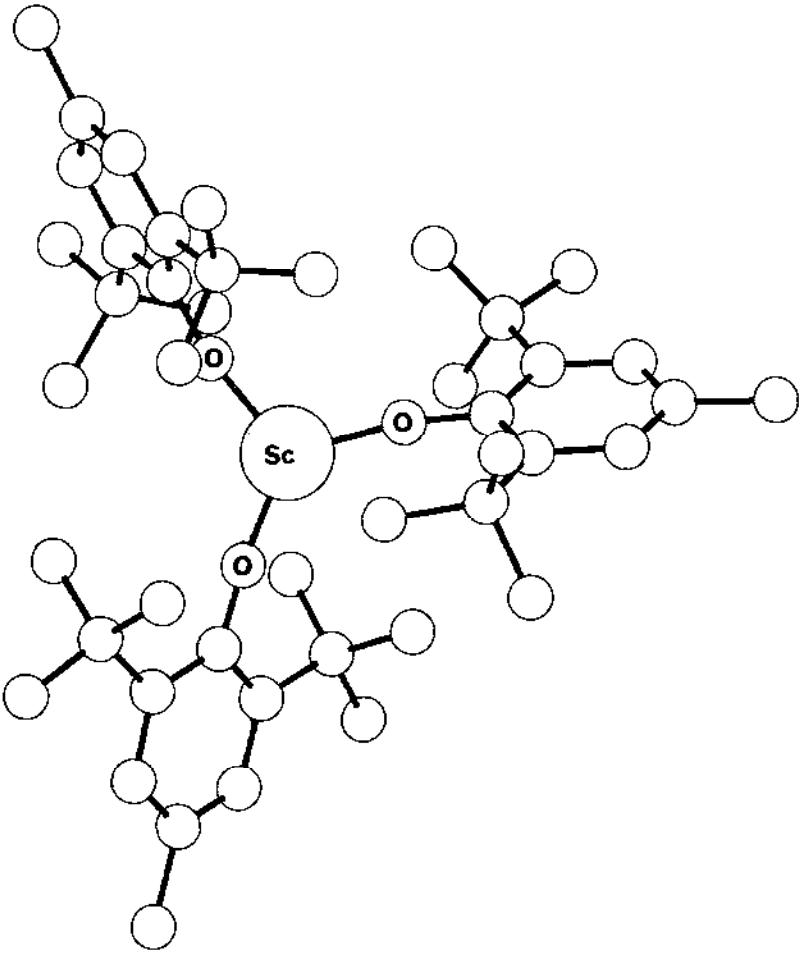
triphenylphosphine oxide to yield $[ScL_3(thf)]$ or $[ScL_3(Ph_3PO)]$ respectively, in a reaction which may be reversed upon heating *in vacuo*. These adducts, $[ScL_3L']$ (HL = 3; L' = thf or Ph_3PO) may also be prepared directly from scandium(III) chloride in the presence of NaL and L'. The binuclear complex $[L_2Sc(\mu\text{-}L)_2Na(thf)_2]$ has been isolated as a by-product from these reactions; upon heating *in vacuo*, it decomposes to yield $[ScL_3]$. A single crystal structural analysis of the complex $[ScL_3]$ has been reported, and the complex shown to possess the structure shown in **4** [32]. The scandium is in a trigonal planar environment (deviation of the metal from the O_3 plane, ~0.13 Å), with $\angle_{ave}$ O-Sc-O 119.5° and $\angle_{ave}$ Sc-O-C 168.4°. The Sc-O bond distances are in the range 1.854-1.889 Å.

A large number of 1:1 complexes of scandium(III) with a series of substituted 2,2'-dihydroxyarylazocompounds (5) have been reported. The



(5)

complexes are coloured (λ_{max} 515-570 nm), and exhibit interesting solution equilibria. The complexes may exist as $[ScL]^+$ (H_2L = 5) or $[Sc(HL)]^{2+}$ (H_2L =

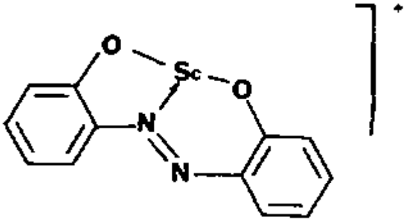


(4)

5); the former complex is thought to possess structure **(6)**, whilst the latter exists as the tautomeric system ($7 \rightleftarrows 8$) [33].

The kinetics of the interaction of scandium(III) with arsenazo III **(9)** has been investigated over the pH range 0.5 - 0.9, at 25°C [34]; a 1:1 complex is formed in the rate determining step, with the rate given by:

$$\rho = k_1[\mathrm{Sc}^{3+}][\mathrm{L}]/[\mathrm{H}^+]$$



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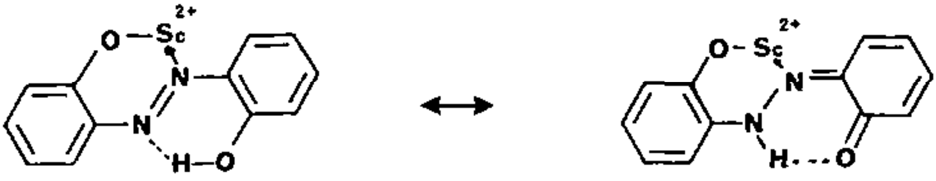

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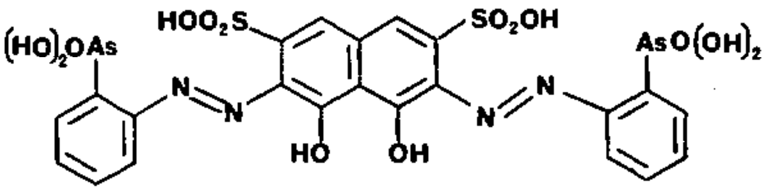
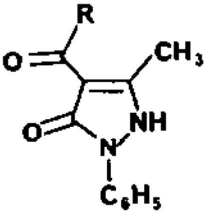


(9)

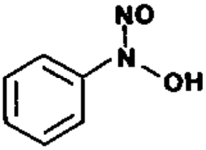
Molecular orbital calculations dealing with the complexes $[(NH_3)_5Sc(H_2O)]^{3+}$ (Sc-N, 4.118 atomic units; Sc-O, 3.940 atomic units) and $[Sc(NH_3)_6]^{3+}$ have been reported [20].

The extraction of scandium(III) from aqueous solution by a synergic process involving benzene solutions of tri-n-octylphosphine oxide and 4-acyl-3-methyl-1-phenylpyrazol-5(1*H*)-ones (**10**) has been investigated [35].



(10)

An electrochemical study of the Sc^{3+}-NH_4Cl-cupferron-diphenylguanidine quaternary system has been reported [36]. The complex which is formed is of the type, $[ScCl_2LL']$ (HL = cupferron (**11**); L' = PhNHC(=NH)NHPh) is formed, with $\beta = 1.22 \times 10^7$.

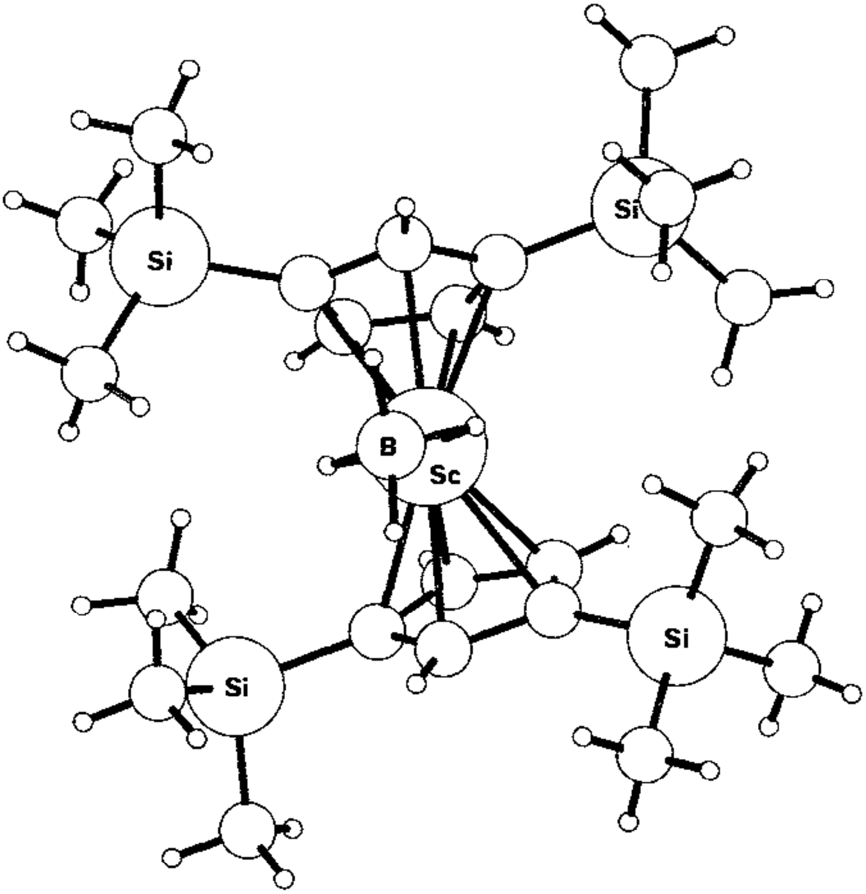


(11)

Alloys of the composition $Sm_{1-x}Sc_xS$ ($0 \le x \le 0.40$) have been studied [37].

4.1.3 Organometallic complexes

Molecular orbital studies of the complexes $[Sc(NH_3)_5(CH_3)]^{2+}$ and $[Sc(NH_3)_5H]^{2+}$ have been reported [20]. The complex $[Sc(\eta\text{-}L)_2(BH_4)]$ (HL = 1,3-$C_5H_4(SiMe_3)_2$) is unique amongst related lanthanide complexes in not forming a



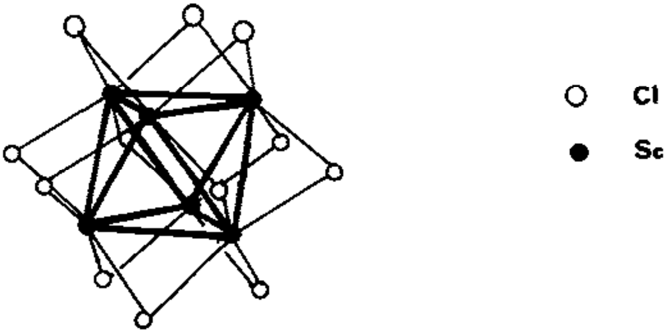
(12)

thf adduct [38]. The compound has been shown to possess the structure (12), in which the borohydride acts as a bidentate ligand bonded to the scandium through two bridging hydrogen atoms (Sc-H, 2.03 Å; Sc-C, 2.457-2.498 Å; B-H_{bridge}, 1.19 Å; B-H_{term}, 1.19 Å; Sc...B, 2.252 Å; $\angle H_b$-Sc-H_b, 55°; $\angle H_b$-B-H_b, 105°; $\angle H_t$-B-H_t, 128°). Variable temperature ^{11}B NMR studies revealed that a novel exchange process, by which the terminal and bridging hydrides are interconverted is operative.

4.2 SCANDIUM(I)

A low resolution *ab initio* study of scandium(I) fluoride has been reported [39]. The GVB/CI technique was used, and the ground state shown to be $^1\Sigma^+$. Calculated ground state equilibrium distances, Sc-F, 1.811 Å and stretching frequencies, ν_{Sc-F}, 742.3 cm^{-1} correspond reasonably well with the experimental values of 1.787 Å and 735.6 cm^{-1} respectively. The lowest thirty states were also studied. The bonding in the compound corresponds to an ionic system, $Sc^+...F^-$ [39]. An MRD/CI study of the low energy levels of scandium(I) hydride has also been described [40].

Low valent scandium chlorides may be prepared by the reaction of scandium(III) chloride with scandium metal. Previously characterised species include Sc_5Cl_8 [41], Sc_7Cl_{10} [42] and ScCl [43], which exhibit unusual structural features. A new member of this series, Sc_7Cl_{12} has now been structurally characterised. It is best formulated $Sc(Sc_6Cl_{12})$ (**13**). It may be regarded as a cubic close packed system of octahedral $[Sc_6Cl_{12}]^{3-}$ clusters with scandium cations occupying the octahedral sites. The metal-metal distances in the cluster are in the range 3.201-3.230 Å [44].



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