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6. Scandium 1992

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CONTENTS

INTRODUCTION

This review surveys the coordination chemistry of scandium reported during the year 1992 and is similar in format to the corresponding review dealing with the 1991 literature [1]. The literature has been searched by using both *Current Contents* and *Chemical Abstracts*. Structural figures have been redrawn using coordinates taken from the Cambridge Crystallographic Data Base, implemented through the ETH, Zürich [2].

Organometallic complexes, with the exception of those containing borane-based ligands, have not been included. However, two discussions of the encapsulation of scandium clusters in fullerenes are noteworthy [3, 4].

6.1 EXTRACTION

Amongst a range of ions studied, scandium(III) ions have been extracted from aqueous medium to 1,1,2,2-tetrachlorodifluoroethane using as the extractant bis(2-ethylhexyl)hydrogen phosphate (HDEHP). The effects of the concentration of HDEHP and of pH on the extraction have been investigated [5]. The extraction of scandium(III) ions from 0.1 mol dm^{-3} aqueous sodium nitrate solution into tetrachloromethane using 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione (HA) has been studied; other metal ions included in the study are lanthanum(III), europium(III), lutetium(III) and indium(III). The studies have been carried out both the presence and the absence of Bu_4N^+ ions. For the scandium system, the presence of the Bu_4N^+ ions has little influence on the extraction. A value of $\log K_{ex3.0}$ of 22.3 $mol^{-2}\,dm^6$ has been determined where $K_{ex3.0}$ is defined according to equation (i) [6].

$$K_{ex3.0} = \frac{[ScA_3]_{org.}}{[Sc^{3+}][A^-]^3} \qquad \text{(i)}$$

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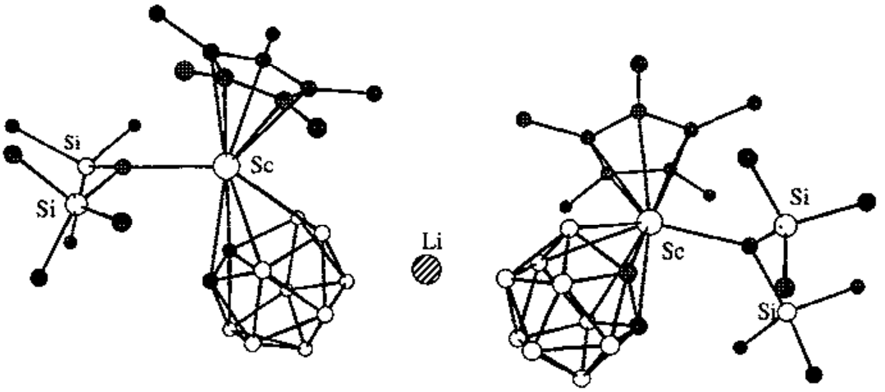
6.2 COMPLEXES WITH BORANE-BASED LIGANDS

The reactions of Na(η^5-C_5H_5) or Na(η^5-C_5H_4Me) with [Sc$(BH_4)_3$(thf)$_2$] lead to the formation of the complexes [Sc(BH_4)(η^5-C_5H_5)$_2$] or [Sc(BH_4)(η^5-C_5H_4Me)$_2$] respectively. Infrared data for these compounds have been reported [7].

The scandium carbaborane derivative [Li(thf)$_3$]Li[3-(η^5-C_5Me_5)-3-CH$(SiMe_3)_2$-3-Sc-1,2-$C_2B_9H_{11}$] has been structurally characterised. The $C_2B_9H_{11}$-unit is capped by a scandium-containing fragment and bond distances between the scandium centre and the carbaborane cage are Sc-B(av.) 2.556(14)Å and Sc-C(av.) = 2.576 (22)Å. Within the solid state structure, pairs of carbascandaborane clusters interact with a single Li^+ ion, (**1**), via three weak Li---B interactions per cage; the second Li^+ ion is coordinated by three thf molecules [8].



(**1**)

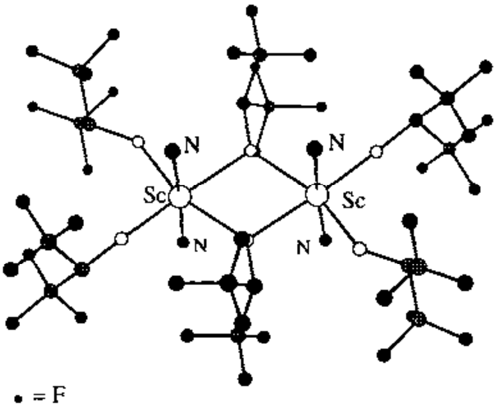
6.3 COMPLEXES WITH OXYGEN DONOR LIGANDS

In an *ab initio* theoretical study carried out with quasirelativistic pseudo-potentials and a flexible polarised basis set, the equilibrium structures of $[Sc(H_2O)_x]^{3+}$ (x = 1–3) and of $[Sc(NH_3)_x]^{3+}$ and $[Sc(HF)_x]^{3+}$ (x = 1–3) have been calculated. For the $[ScL_2]^{3+}$ complexes, a bent geometry is favoured, whilst for the $[ScL_3]^{3+}$ complexes, a pyramidal structure is preferred over a planar one. Energy barriers for going from bent to linear, and from pyramidal to planar geometries have been examined [9].

A method has been developed for determining hydrate numbers and has been exemplified with a study of scandium(III) sulfate. The enthalpy of solution of the hydrate has been estimated in the $Sc_2(SO_4)_3$–H_2O system and the solid phases are determined to be $Sc_2(SO_4)_3.6H_2O$, (273 to 295 K), $Sc_2(SO_4)_3.5H_2O$ (295 to 333 K) and $Sc_2(SO_4)_3.4H_2O$ (333 to 373 K). These new results are in contrast to previous data [10].

The alkali metal salts $M^I_3[M^{III}(OH)_6]$ in which M^I = K or Rb, and M^{III} = Sc or Cr, have been prepared and investigated by X-ray crystallography. Comparisons have been made between the structural parameters of the scandium(III) and chromium(III) complex ions [11].

The reactions of $[M\{N(SiMe_3)_2\}_3]$ (M = Sc, Y, La and Pr) with the alcohols ROH (R = $(CF_3)_2CH$, $(CF_3)Me_2C$ or $(CF_3)_2MeC$) in C_6H_6, thf or Et_2O lead to the formation of the complexes $[M(OR)_3(NH_3)_x]$ (x = 0–3 depending upon the reaction conditions), $[M(OR)_3(thf)_3]$ and $[M(OR)_3(Et_2O)_x]$ (x = 0.33–0.5). The compound $[\{Sc(OCH(CF_3)_2)_3(NH_3)_2\}_2]$ has been shown by crystallographic means to be possess the bridged dimeric structure (2). The dimer is centrosymmetric, with each scandium centre octahedrally coordinated; the two ammonia ligands per metal atom lie *trans* to one another. Selected distances are Sc-O(terminal) = 1.94(1)Å (av.), Sc-O(bridge) = 2.19(1)Å (av.), and Sc-N = 2.32(1)Å (av.) [12].

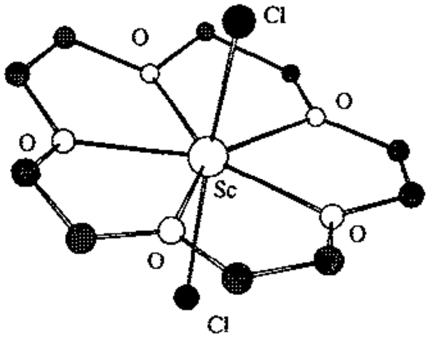


(2)

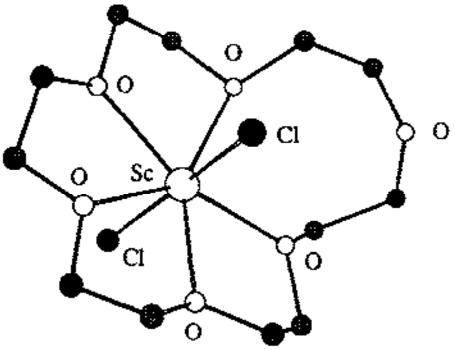
Scandium(III) complexes of 2-nitro, 3-nitro-, 4-nitro, 3,5-dinitro-, 2,4-dinitro-, 3,4-diaminobenzoic acids as well a range of chlorobenzoic acid derivatives have been the subjects of thermal decomposition studies [13-15]. The 2-nitro, 3-nitro-, 4-nitro, 3,5-dinitrobenzoic acid (HL) complexes have been shown to have a 1:3 (Sc:L) composition; infrared spectroscopic data are consistent with the bonding not being wholly ionic in character. Thermal decomposition is typically characterised by loss of water of crystallisation followed by transformation to Sc_2O_3.

Two complexes involving crown ether ligands have been prepared and crystallographically characterised by independent groups [16, 17]. Scandium(III) chloride reacts with 15-crown-5 (L) in acetonitrile to yield $[ScLCl_2]Cl$, [(3)]Cl, although if copper(II) chloride is present in the reaction mixture, the product is $[ScLCl_2]_2[CuCl_4]$. This salt can be obtained by treating [(3)]Cl with $CuCl_2$. The crystal structure of [(3)]Cl has been determined. The cation (3) contains a scandium(III) centre which is in a pentagonal bipyramidal environment, with the macrocyclic ligand lying in the equatorial plane [16]. This environment is reproduced in the cation $[ScL'Cl_2]^+$ (4) in which L' = 18-crown-6. The complex $[ScCl_2][SbCl_6]$ has been prepared by reacting $ScCl_3$ with $SbCl_5$, and the $[ScCl_2]^+$ ion has been stabilised by using the macrocyclic ligand L', thereby generating the complex $[ScL'Cl_2][SbCl_6]$. The crystal structure of $[(4)][SbCl_6]$ shows that in the complex cation, five of the six oxygen donor atoms in the 18-crown-6 ligand are involved in coordination to the scandium(III) centre (Sc-O = 2.190(5) to 2.229(5)Å in one of two independent molecules). For the *trans* chloride ligands, the angle Cl-Sc-Cl is 176.5(1)° [17].

The scandium(III) complexes [ScL_3Cl_3] and [$ScL_4(SCN)_3$] where L = phen-*N*-oxide have been synthesised and characterised by TG-DSC, infrared and fluorescence spectroscopies and molar conductance measurements [18].

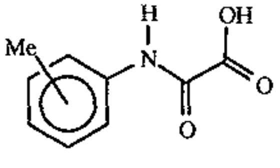


(3)



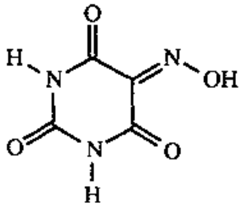
(4)

The oxamic acid derivatives (**5**) (HL) have been shown to be useful as analytical reagents in estimation amounts of scandium(III) ions by gravimetric methods. Complexes formed between scandium(III) ions and L^- have been prepared and characterised by elemental analysis, IR spectroscopy, and potentiometric and thermal methods. The experimental data are consistent with each L^- ligand functioning as an *O,O'*-donor; the complexes are stable up to 250°C [19]. The complexation of violuric acid (**6**) with scandium(III) ions has been investigated. Further work extends to yttrium(III) and lanthanum(III) complexes. The scandium(III) violurates (1:2, 1:3 and 2:3 complexes) are soluble in, for example, water, dilute mineral acids, methanol, acetone and dmf, but are insoluble in ethanol, chloroform and tetrachloromethane. They have been characterised by elemental analysis, IR and UV-VIS spectroscopies and molar conductivity measurements. The data indicate that in the 1:2 and 1:3 complexes, each violurate ion binds through the oximato *O*-atom and one other *O*-donor, whilst in the 2:3 complex, donation through a nitrogen atom is additionally involved. X-ray powder diffraction data have been reported for the 1:2 and 2:3 complexes. The UV-VIS spectroscopic data are consistent with octahedral scandium(III) environments in these species [20].



Me = 2- or 4-substituted

(**5**)

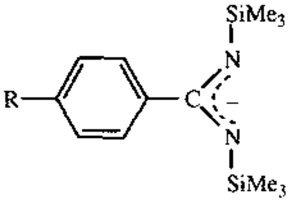


(**6**)

6.4 COMPLEXES WITH NITROGEN DONOR LIGANDS

Theoretical studies of a series of complexes including $[Sc(NH_3)_x]^{3+}$ ($x = 1$–3) were mentioned in section 6.3 [9].

Anhydrous scandium(III) chloride reacts with NaL ($L^- = (7)$) to give the complexes $[ScL_3]$. Related chemistry involving various lanthanoid trichlorides has also been investigated. The products have been characterised by elemental analysis, infrared, electronic and ^1H NMR spectroscopies and mass spectrometry. The results of the electronic spectroscopic work show that the *N*-silylated ligand results in unusually large crystal field splitting. The chelating nature of ligand L^- has been established from the results of the crystal structure determination of $[PrL_3]$ [21].



R = H, MeO, CF_3, Ph

(7)

The bis(phthalocyanine) complexes $[ScPc_2]$ and $[ScPc_2]^-$ have been included in an investigation of the cubic hyperpolarisability (γ) of series of $[MPc_2]$ and $[MPc_2]^-$ complexes (M = Sc, Y or lanthanoid). The method used was degenerate four-wave mixing (DFWM) at 1064 nm. The paper provides spectral data in the near-IR region for $[ScPc_2]$; the intervalence band is at 1190 nm. In non-linear optical studies, the phase conjugate signal has been measured as a function of laser intensity. The non-linear signal for $[ScPc_2]$ shows a deviation from cubic dependence at the highest pump intensities and this demonstrates the onset of saturation or else the presence of a competing non-linear process. An enhancement of γ is observed for the $[MPc_2]$ complexes when the probe wavelength begins to coincide with the intervalence transition of the complex. For M = Sc, the probe wavelength of 1064 nm is indeed close to the 1190 nm of the intervalence band, and, hence, of the complexes studied, $[ScPc_2]$ exhibits the largest value of γ [22]. Further work in this area has also been reported [23].

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