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5. Scandium

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CONTENTS

INTRODUCTION

This review covers the coordination chemistry of scandium for 1991 and follows the format of that for the 1990 literature [1]. The literature has been searched by use of *Currents Contents*. The Cambridge Crystallographic Data Base provided the coordinates for structure (**2**) which has been redrawn for this review.

5.1 SCANDIUM(III)

5.1.1 Complexes with halide and pseudo-halide ligands

The phase diagram for scandium(III) iodide-caesium iodide has been determined and the compounds Cs_3ScI_6 and $Cs_3Sc_2I_9$ are shown to be present. Raman spectra up to temperatures of 700°C have been measured and the temperature dependence of the spectra of polycrystalline samples of Cs_3ScI_6 and $Cs_3Sc_2I_9$ is reported. It is suggested that two predominantly ipnic species are in equilibrium in the melt, (equation (i)) [2].

$$[ScI_6]^{3-} \rightleftharpoons [ScI_4]^{-} + 2\,I^{-} \tag{i}$$

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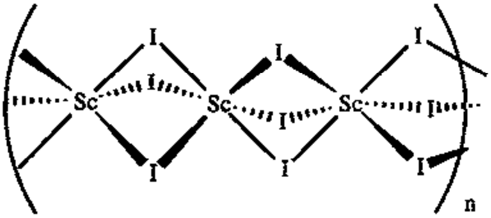
Reaction of scandium metal or scandium(III) iodide with lithium iodide or sodium iodide in a sealed tube at 750-850°C gives the paramagnetic lithium-containing phase $LiScI_3$ or sodium-containing phase $Na_{0.5}ScI_3$, respectively. Both have been structurally characterised. In $LiScI_3$, there are chains of confacial $ScI_{6/3}$ octahedra, (1), in which the Sc---Sc separation is 3.384 (1) Å. In $Na_{0.5}ScI_3$, the scandium atoms are paired within slightly distorted chains of confacial octahedra; the Sc---Sc distances are 3.278 (5) and 3.572 (5) Å [3]. The magnetic properties of the new phases are reported.



(1)

The reaction of hydrated scandium(III) chloride with Cl_2O_6 yields $Sc(ClO_4)_3.0.25Cl_2O_6$. At 95°C, this complex loses Cl_2O_6 and anhydrous scandium(III) perchlorate has been crystallised. The crystal structure shows features which are comparable with those of $Ga(ClO_4)_3$. The infrared and Raman spectroscopic data are consistent with the presence of bidentate ClO_4^- ligands [4].

5.1.2 Complexes with oxygen donor ligands

5.1.2.1 Alkoxide ligands

Developments during the decade 1980-1990 in the chemistry of alkoxide and aryloxide complexes of the lanthanide elements have been reviewed (137 references) [5].

Adducts of $Sc(silox)_3$ ($Hsilox = {}^tBu_3SiOH$) have been synthesised by the reactions shown in equations (ii) and (iii). Pyridine displaces thf from $Sc(silox)_3(thf)$ [6]; see also Section 5.1.3.

$$ScCl_3(thf)_3 + 3\,Na(silox) \longrightarrow Sc(silox)_3(thf) \quad \text{(ii)}$$

$$Sc\{N(SiMe_3)_2\}_3 + 5\ Hsilox \longrightarrow Sc(silox)_3(NH_3) \quad \text{(iii)}$$

5.1.2.2 Alcohols and ethers

The dinuclear complex $Sc_2(ClO_4)_6L_n.6H_2O$ in which $L = HO(CH_2CH_2O)_xCH_2CH_2OH$ ($x = 3$ and $n = 3$; $x = 1$ and $n = 5$) and the mononuclear complexes $Sc(ClO_4)_3L_2.3H_2O$ ($x = 2$) and

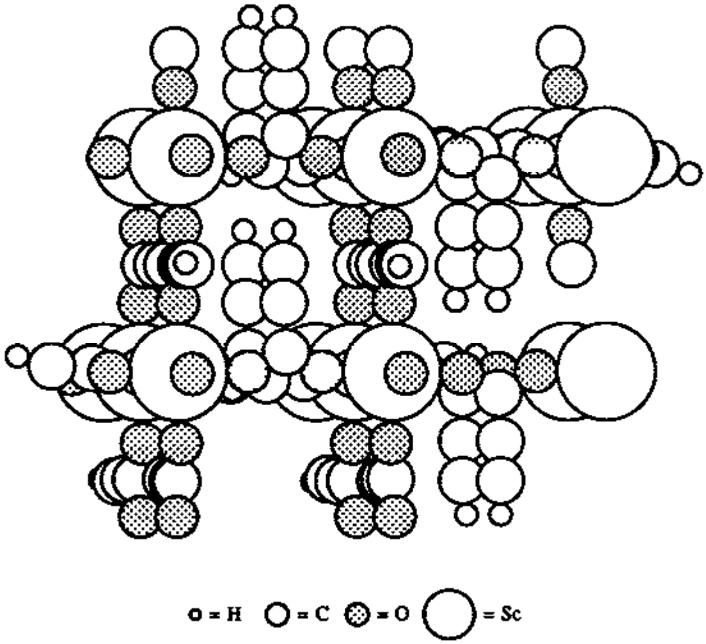
ScClL (x = 3 or 4) have been prepared and characterised by infrared and ^{1}H and ^{13}C NMR spectroscopy and TGA-DTA. It is concluded that the coordination number of the scandium centres is greater than six; comparisons are made between these new compounds and the yttrium and lanthanum analogues [7].

5.1.2.3 Ketone and β-diketonate ligands

The extraction of scandium(III) ions with Hacac in heptane has been investigated in the presence of 3,5-dichlorophenol (DCP). The effect of DCP has been interpreted after a detailed analysis of the extraction equilibria [8]. Extraction of scandium(III) ions by pyrazolone and some of its derivatives has been studied and is discuseed further in Section 5.1.3 [9].

5.1.2.4 Carboxylate ligands

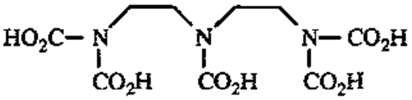
The crystal structure of *catena*(tris(μ-propynoato-*O,O'*)scandium), (2), has been determined. The compound was prepared by the addition of solid scandium(III) carbonate to aqueous propynoic acid followed by evaporation of the solution. In (2), the scandium centres are octahedrally coordinated; the propynoate ligands are in an *anti-anti* arrangement. The overall structure is an infinite, cubic three-dimensional coordination polymer which is unprecedented for a metal(III) carboxylate. Irradiation of (2) with ^{60}Co γ-rays causes a change from a crystalline sample to an amorphous solid [10].



(2)

A series of scandium(III) benzoates, Sc_xL_y, has been reported in which HL = 2,4-dinitrobenzoic acid, 3,5-dinitrobenzoic acid, 2,4-dichlorobenzoic acid, or 3,4-diaminobenzoic acid. The 2,4- and 3,5-dinitrobenzoate complexes were synthesised as hydroxy-salts with $x : y = 1 : 2$ and $1 : 1$, respectively. The 2,4-dichlorobenzoate and 3,4-diaminobenzoate complexes were isolated as oxy-salts with $x : y = 5 : 3$ and $4 : 6$, respectively. Infrared spectroscopic and X-ray diffraction data are presented for the new compounds. The interactions between scandium(III) and carboxylate *O*-donor centres exhibit ionic character [11].

The complex formation between scandium(III) ions and H_7L, (3), H_6L', (4), and H_5L'', (5) has been investigated by potentiometric methods. In aqueous KNO_3 (0.1 M), the complexes $[Sc(H_3L)]^-$, $[Sc(H_2L)]^{2-}$, $[Sc(HL)]^{3-}$, $[ScL]^{4-}$, $[Sc_2L]^-$ and $Sc_2(HL)$ are formed with (3). There is evidence for the formation of two hydroxy-species when scandium(III) ions react with (4). As anticipated, the tendency for the formation of protonated complexes increases with the number of carboxylate groups in the ligand. Stability constants for the new complexes have been determined and values of lg $K_{ScL}{}^{n-}$ are 20.99 for (5), 19.12 for (4), and 19.04 for (3). The isotachophoretic separation of the scandium(III) complexes is described [12].



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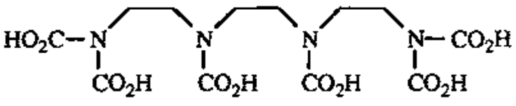

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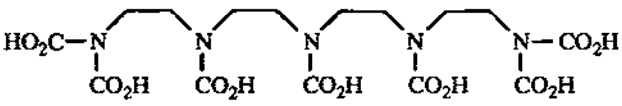


(5)

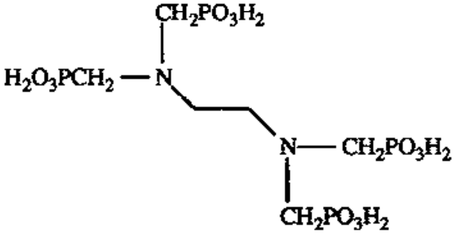
A new method for the extraction of scandium(III) ions from ascorbic acid at pH 6.0 has been detailed. The method involves the use of 0.1 M Aliquat 336S. (Aliquat 336S = $MeN[(CH_2)_7Me]_3Cl$ and is commercially available). The efficiency of extraction as a function of pH has been compared with five liquid anion exchangers in xylene and the separation of scandium(III) from various multimetal ion systems has also been monitored. These include iron(II)/scandium(III)/hafnium(IV), cerium(III)/scandium(III)/thorium(IV), cerium(III)/scandium(III)/uranium(VI), and aluminium(III)/scandium(III)/molybdenum(VI) [13].

5.1.2.5 *Phosphate and phosphonate ligands*

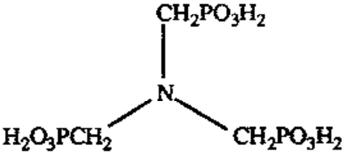
Structural data for the α- and γ-phases of $Li_3Sc_2(PO_4)_3$ have been collected by neutron diffraction and the structures refined. At 293 K, the α-phase is monoclinic and at 573 K, the γ-phase is orthorhombic [14].

An infrared and ^{31}P NMR spectroscopic investigation of solutions of the extracted complex ScL_3 has been reported where HL = di-(2-ethylhexyl)phosphoric acid. A range of concentrations of HL and L^- is covered. A polymeric complex has been characterised in which the acid residues of the ligands form bridging units between pairs of adjacent scandium atoms. In solutions in which the ratio [HL] : $[ScL_3] \geq 1$, the polymeric structure degrades and gives rise to complexes of formula ScH_3L_6 and $Sc_2H_4L_{10}$ [15].

Complex formation between the ligands H_8L, (6), and H_6L', (7), and scandium(III) ions (as well as yttrium and lanthanoid ions) has been studied by potentiometric methods at 298 K and an ionic strength of 0.1 M KNO_3. The protonation constants $K(MHL)$ and $K(MH_2L)$ for M = Sc deviate from those predicted based on a model using an ionic radius for Sc(III). Related studies for yttrium are outlined in the accompanying chapter of this issue of *Coord. Chem. Rev.*



(6)

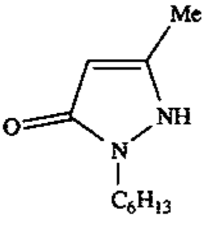


(7)

5.1.3 *Complexes with nitrogen donor ligands*

Adducts of the type $Sc(silox)_3L$ (Hsilox = $^tBu_3SiOH$) have been prepared (see Section 5.1.2.1). Related tantalum, titanium, and vanadium analogues have also been reported. For L = py, an attempt has been made to probe the electronic factors responsible for the preference of one of two observed coordination modes, viz. η^1-py-*N* versus η^2-py-*N,C* ligation [6].

The extraction of scandium(III) by the ligands 1-hexyl-3-methyl-5-pyrazolone, (**8**), 1-phenyl-3-methyl-5-pyrazolone, (**9**) or 1,1-bis(3-methyl-1-phenyl-2-pyrazolin-5-on-4-yl)heptane from aqueous trichloroacetate solutions has been studied in order to find the optimum conditions for metal extraction. A mechanism for the extraction process is proposed [9].



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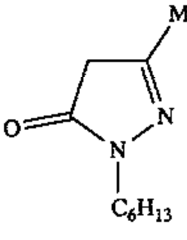
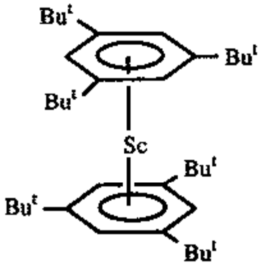


(9)

5.2 *SCANDIUM(I)/(0)*

Although organometallic in nature, the novel complexes (**10**) and (**11**) deserve a mention in this review. The cocondensation of scandium vapour with 1,3,5-tri-*t*-butylbenzene has yielded the first example of a scandium(0) complex, (**10**), which has been charaterised spectroscopically. The Raman and UV spectral data indicate the presence of the scandium(I) complex (**11**) [17].



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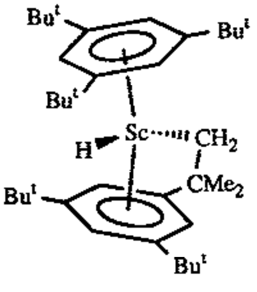

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