3. Scandium 1993

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CONTENTS

INTRODUCTION

This review surveys the coordination chemistry of scandium reported during the year 1993 and follows a similar format to the 1992 review [1]. The literature has been searched by using *Current Contents* and the Cambridge Crystallographic Data Base. Structural figures have been redrawn using coordinates taken from the latter, implemented through the ETH, Zürich [2]. Organometallic complexes have, in general, been excluded, although in section 3.2 some fullerene chemistry is described.

A review which includes discussions of zero oxidation state scandium compounds has appeared [3].

3.1 SOLID STATE COMPOUNDS

The reaction of elemental scandium with Sc_2O_3 and iodine in the solid state has been studied by DTA. The product is ScOI, and the structure of this compound has been determined by X-ray crystallography [4]. The crystal structure of $CsScS_3$ has also been elucidated [5].

3.2 FULLERENE DERIVATIVES

Members of a series of endohedral scandafullerenes have been characterised by mass spectrometric and ESR spectral data. In the same study, Shinohara *et al.* have shown that $Sc@C_{82}$ can be separated from $Sc_3@C_{82}$ by using liquid chromatography with an ethanol-deactivated silica-gel column [6]. The same workers have reported that $Sc_2@C_{74}$, $Sc_2@C_{82}$ and $Sc_2@C_{84}$ may be isolated from soot by arc-burning with Sc_2O_3. Mass spectrometric and UV-VIS absorption results have been described [7].

3.3 COMPLEXES WITH CARBABORANE LIGANDS

The reactions of $Na_2[C_2B_9H_{11}]$ with $[Cp^*ScCl_2]_x$, or $C_2B_9H_{13}$ with $[Cp^*ScMe_2]_x$ (both in thf) lead to $[Cp^*ScC_2B_9H_{11}(thf)_3]$. When treated with $Li[CH(SiMe_3)_2]$, this product gives $[Cp^*(C_2B_9H_{11})Sc\{CH(SiMe_3)_2\}]Li(thf)_3$ and $[Cp^*(C_2B_9H_{11})Sc\{CH(SiMe_3)_2\}_2Li]Li(thf)_3$, an X-ray structural determination of which has been carried out. After reaction with dihydrogen, the relatively unreactive complex $[Cp^*(C_2B_9H_{11})ScH]_2[Li(thf)_n]_2$ forms, which, after recrystallisation from toluene yields $[Cp^*(C_2B_9H_{11})ScH]_2[Li(thf)_2].{}^3/_2C_6H_5Me$ in which the two anionic units are connected by bridging hydrogen atoms. The applications of such scandium(III) derivatives as α-alkene polymerisation catalysts have been addressed [8].

3.4 COMPLEXES WITH HALIDE LIGANDS

The single crystal structure of distrontium scandium heptafluoride has been determined, and the scandium centres are observed to be 7-coordinate. The luminescence spectrum of chromium(III)-doped Sr_2ScF_7 exhibits a broad emission band between 740 and 940 nm with a maximum at 844 nm [9].

3.5 COMPLEXES WITH GROUP 16 DONOR LIGANDS

Bond dissociation enthalpy data have been detailed for the processes given in equations (i) and (ii); these occur via charge stripping of ions produced by fast atom bombardment. The enthalpies of reaction for (i) and (ii) are effectively the same (4.9 ± 0.3 and 4.7 ± 0.3 eV, respectively) [10]. The gas-phase reactions of methanol and Sc^+ ions have been studied using FT-ion cyclotron resonance mass spectrometry. The exothermic processes that take place result in the formation of $[ScOH]^+$, $[ScOMe]^+$, $[ScO]^+$ and $[Sc(OCH_2)]^{2+}$ with further reactions giving $[Sc(OMe)_2(MeOH)_n]^+$ as the final product. Estimates have been made of the Sc–O bond energies [11].

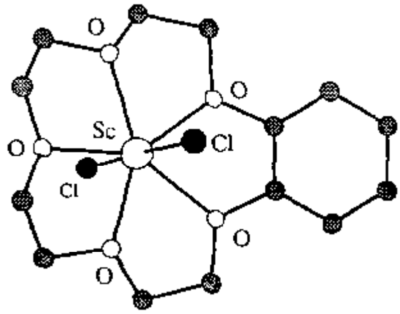
$$[Sc(OH)]^{2+} \rightarrow Sc^+ + OH^+ \qquad (i)$$

$$[Sc(OH)]^{2+} \rightarrow Sc^{2+} + OH \qquad (ii)$$

Scandium(III) acetate and its deuterated analogue have been the subjects of a ^{45}Sc NMR spectroscopic investigation, and the first- and second-order quadrupolar shifts over the temperatures range 4–300 K have been studied in relation to structural phase transitions. The transition temperature of $Sc(CD_3O_2)_3$ is 158 K as opposed to 167 K for $Sc(CH_3O_2)_3$. Below these temperatures, two sets of first-order quadrupolar shifts which correspond to the two scandium ion sites observed in the crystal are observed [12].

Other scandium(III) carboxylate complexes that have been studied this year include derivatives of methylbenzoic and methoxybenzoic acids [13]. In addition, scandium(III) triflate has been shown to be effective as a Lewis acid catalyst in Diels-Alder reactions. It may be used in aqueous or organic media, and can be recovered and reused. The catalyst is prepared from the reaction of Sc_2O_3 and triflic acid (≈50% TfOH/water) at 100°C [14]. Further work has demonstrated the catalytic applications of $Sc(OTf)_3$ in aldol and Michael addition reactions of silyl enolates with aldehydes, acetals and α,β-unsaturated ketones [15].

The reactions of scandium(III) chloride with the crown ethers 18-crown-6, benzo-15-crown-5 and 15-crown-5 (L) and $SbCl_5$ lead to the formation of $[ScCl_2L][SbCl_6]$. With 12-crown-4 in the presence of acetonitrile, the complex $[ScCl_2(12\text{-crown-4})(MeCN)][SbCl_6]$ has been isolated. Spectroscopic characterisation (^1H and ^{13}C NMR) has been complemented by an X-ray crystallographic studies of $[ScCl_2(15\text{-crown-5})][SbCl_6]$ and $[ScCl_2(\text{benzo-15-crown-5})][SbCl_6]$; in the complex cation $[ScCl_2(\text{benzo-15-crown-5})]^+$, (1), the $ScCl_2$-unit is approximately linear (av. Sc–Cl 2.395 Å) and the O_5-donor set lies in a close to planar array around the scandium(III) centre (Sc–O = 2.166 to 2.223(4) Å) [16].



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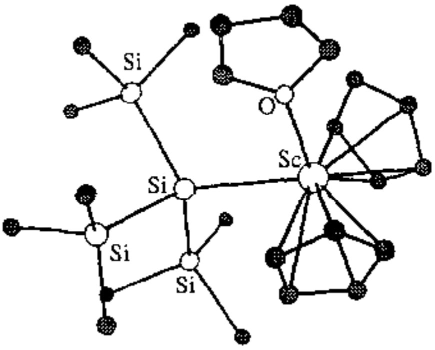

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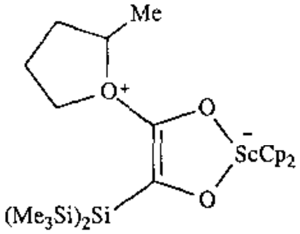

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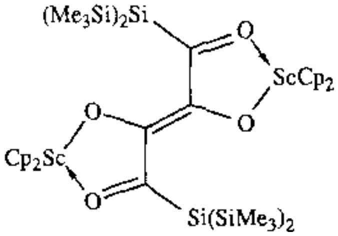


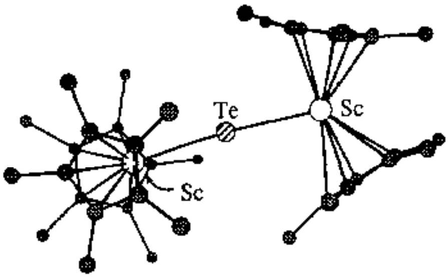
(4)

The preparations of the scandium(III) complexes in the series $[Cp_2Sc(thf)ER_3)]$ (ER_3 = $Si(SiMe_3)_3$, $Si(SiMe_3)_2Ph$, Si^tBuPh_2, $SiPh_3$ or $Ge(SiMe_3)_3$) from $[\{Cp_2ScCl\}_2]$ have been described. Of these, $[Cp_2Sc(thf)\{Si(SiMe_3)_3\}]$ (2) has been crystallographically characterised; the distances Sc-O and Sc-Si are 2.216(3) and 2.863(2)Å, respectively. For ER_3 = $Si(SiMe_3)_3$, Si^tBuPh_2 and $Ge(SiMe_3)_3$, reactions with CO give the scandoxyketenes $[(Cp_2ScO)(R_3E)C{=}C{=}O]$

which have been trapped as adducts, for example complex (3). In non-polar solvents, the carbonylation of [$Cp_2Sc(thf)ER_3$)] for ER_3 = $Si(SiMe_3)_3$, Si^tBuPh_2 and $Ge(SiMe_3)_3$, gives enedione diolates such as compound (4). The chemistry of the new species has been explored in detail, with complex characterisation involving the use of IR and ^1H, ^{13}C and ^{29}Si spectroscopies and mass spectrometry [17].

A hydroxy-bridged porphyrin complex of scandium(III) is described in section 3.6.

When elemental tellurium or $^nBu_3P$=Te react with [$Cp^*{}_2ScR$] (R = CH_2Ph or CH_2SiMe_3), the products are [Cp*ScTeR]. These alkyl complexes are thermally unstable with respect to the elimination of R_2Te and thereby give the tellurium bridged species (5). The elimination or R_2Te can be reversed by irradiating (5). A crystal structure determination of (5) shows that the environment about the Te centre is close to linear (∠Sc-Te-Sc = 172.07°) and the Sc-Te bond lengths are 2.7528(12)Å; these data are consistent with delocalised Sc-Te-Sc π-bonding. Proton NMR spectroscopic data are presented and in the UV-VIS spectrum, compound (5) exhibits absorbances at 297 (ε = 13 500), 383 (ε = 15 300) and 447 nm (ε = 5 500) [18].



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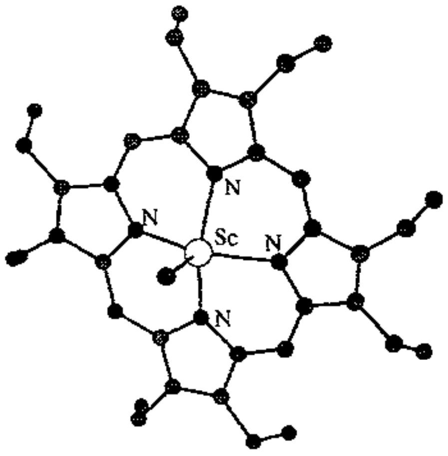
3.4 COMPLEXES WITH GROUP 15 DONOR LIGANDS

When treated with [Li_2(OEP)$(thf)_2$], the complex [$ScCl_3(thf)_3$] yields [Sc(OEP)Cl] which can be used as a precursor to a wide range of scandium(III) octaethylporphyrin derivatives including both σ- and π-bonded species. These products include [Sc(OEP)(OTf)], [Sc(OEP)(O^tBu)], [Sc(OEP)Me], [Sc(OEP){$CH(SiMe_3)_2$}], [Sc(OEP){$N(SiMe_3)_2$}] and [Sc(OEP)(η^5-C_9H_7)] and they have typically been characterised by IR, ^1H NMR and UV-VIS spectroscopies. The single crystal structures of [Sc(OEP)Me].CH_2Cl_2, (4).CH_2Cl_2, [Sc(OEP){$CH(SiMe_3)_2$}] and the indenyl derivative [Sc(OEP)(η^5-C_9H_7)] have been determined. Upon hydrolysis, each of the new complexes is transformed into the hydroxy-bridged compound [{Sc(OEP)}$_2$(μ-OH)$_2$] (5), the crystal structure of which has been elucidated. The two porphyrin ligands are eclipsed and each scandium(III) centre lies out of the plane of the *N*4-donor set. The average Sc–O bond distance is 2.078(2)Å and the angle Sc-O-Sc is 109.89(7)° [19].

The reaction of [$Sc(O_3SCF_3)_3$] with Li[$C(PMe_2)_2SiMe_3$] yields the scandium(III) complex [ScL_3] where HL = $Me_2PCH(SiMe_3)PMe_2P$. In [ScL_3], the ligand is tridentate acting in a *P,P',C*-mode [20].



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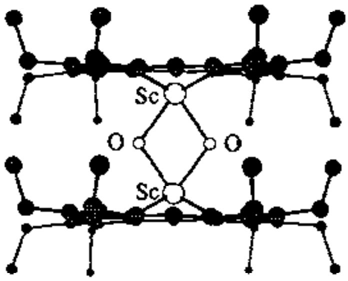

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