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5. SCANDIUM

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CONTENTS

INTRODUCTION

The chemistry of scandium has attracted little attention during the past year. The importance of transition metal hydrides as energy storage systems and their potential catalytic applications has ensured some interest in scandium hydrides, and a number of studies of the radical ScX_2 (X = halide or pseudohalide) species have been described. This review covers the major journals through 1981, and coincides with the Chemical Abstracts coverage in volumes 94 and 95.

5.1 SCANDIUM(III)

5.1.1 Halides and halo-complexes

The equilibrium geometry of ScF_3 and $ScCl_3$ has been investigated using the CNDO/2 method, and it is proposed that the molecules adopt a trigonal planar (D_{3h}) configuration [1]. This agrees well with the results of the restricted Hartree-Fock calculations for ScF_3 described in last year's review [2]. The vapour pressure of ScF_3 has been determined in the temperature range 1159-1411 k using a calibrated Knudsen effusion mass spectrometer [3]. The thermodynamic quantities

$$\Delta H^{1275}_{vap}(ScF_3) = 340 \pm 2 \text{ kJ mol}^{-1}$$

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$$\Delta S_{vap}^{1275}(ScF_3) = 166.5 \pm 1.3 \text{ J K}^{-1}\text{mol}^{-1}$$

were reported.

A fluoride-selective ion electrode has been used in an investigation of the Sc^{3+}–F^- system, and stability constants for the binary complexes of $\log\beta_1 = 6.18$; $\log\beta_2 = 11.52$; $\log\beta_3 = 15.8$ have been derived [4]. Evidence was presented for the formation of polynuclear complex ions, possibly $[Sc_2F_3]^{3+}$. From a study of the equilibrium

$$[ScF_4]^- + AlF_3 \rightleftharpoons [AlF_4]^- + ScF_3$$

a value of

$$\Delta H_f^{298}([ScF_4]^-) = -2012.5 \pm 12.6 \text{ kJ mol}^{-1}$$

has been proposed [5]. The reaction of $ScCl_3$ with K[SCN] in acetonitrile is reported to yield the complex $K_3[Sc(SCN)_6]$ [6].

5.1.2 Complexes with S- and O-bonded ligands

The I.R. transmission spectrum of the mixed oxide $YScO_3$ has been reported [7]. A neutron diffraction study of the related compound, $CeScS_3$, has also been reported [8]. The disordered γ, δ and cubic phases of the ZrO_2–Sc_2O_3 system have been investigated by Raman spectroscopy [9]. An X-ray diffraction study of the compound $Sc_3Sb_5O_{12}$ (from Sc_2O_3 + Sb_2O_3) has also been described [10].

The compound $M_3Sc(SO_4)_3$ (M = K, Rb or Cs) is obtained on heating a stoichiometric mixture of M_2SO_4 with $Sc_2(SO_4)_3$ for 250-300 h at 600°C [11]. A closely related compound $K_3Sc(VO_4)_2$ is obtained on heating an intimate mixture of Sc_2O_3, V_2O_5 and K_2CO_3 to 400-500°C [12]. A number of tripolyphosphate complexes have been characterised in the $Sc(NO_3)_3$–$Na_5P_3O_{10}$–H_2O system [13]. The $Sc_2(SO_4)_3$-urea-H_2O system has been investigated, and the compounds $Sc_2(SO_4)_3.10L$, $Sc_2(SO_4)_3.5L$ and $Sc_2(SO_4)_3.2L$-$4H_2O$ (L = urea) have been characterised as components [14]. This study was conducted at 0 °C, but an earlier study at 30 °C had reached the same conclusions [15]. The species $[ScL_6]^{3+}$ are formed from the reaction of anhydrous $Sc[ClO_4]_3$ with L in triethylorthoformate (L = *N*-methylacetamide, *N,N*-dimethylacetamide, *N*-phenylacetamide, *N*-methylformamide, *N,N*-dimethylformamide, *N,N*-diethylformamide or *N,N*-dibutylformamide) have been investigated by ^1H NMR spectroscopy. It was possible to follow the ligand exchange reactions with *N*-methylacetamide, *N,N*-dimethylacetamide, *N,N*-diethylacetamide and

N-phenylacetamide by ^1H NMR spectroscopy (90 MHz) although with the other ligands, exchange was fast upon the NMR timescale [16].

The stability constants for the formation of scandium(III) complexes of a range of C_2-C_7 aliphatic and substituted benzoic acids have been reported [17]. A ^1H NMR study of the water molecules in crystalline hydrated scandium(III) oxalates $Sc(ox)_3.5.4H_2O$ and $Sc(ox)_3.2H_2O$ has been described [18]. A review (in Russian) dealing with the thermal decomposition of lanthanide, yttrium and scandium oxalates and carbonates has been published [19]. Studies on scandium(III) complexes of phthallic, isophthallic, terephthallic, fumaric, maleic and succinic acids have been described [20,21]. A number of other complexes with substituted salicylic acids [22,23], glycine, iminodiacetic acid [24], edta [23] and tetrahydroxy-4-benzoquinone [25,26] have also been reported.

5.1.3 Organometallic compounds

The reaction of $ScCl_3$ with lithium 1,2-bis-(trimethylsilyl)cyclopentadienide ($Li(R_2cp)$) in thf at 20 °C leads to the formation of the complex $[Sc\{\eta\text{-}(R_2cp)\}_2(\mu\text{-}Cl)_2Li(thf)_2]$. This complex is isostructural with the corresponding neodymium complex, the structure of which is shown in Fig. 1 [27]. The complex contains the novel $\{Sc(\mu\text{-}Cl)_2Li\}$ unit, which it is suggested may occur widely in lanthanide complexes. Heating the above complex to 140–150 °C results in the formation of the complex $[\{Sc(R_2cp)_2Cl\}_2]$, which is also formed upon attempted sublimation of the binuclear scandium-lithium complex [28]. The scandium complex is isostructural with $[\{Pr(R_2cp)_2Cl\}_2]$, the structure of which has been reported and is shown in Fig. 2. The dominant feature is the central $\{Sc(\mu\text{-}Cl)_2Sc\}$ ring, with $r(Sc\text{-}Cl) = 2.58, 2.51$ Å, $Cl\text{-}\hat{Sc}\text{-}Cl' = 79°$ and $Sc\text{-}\hat{Cl}\text{-}Sc = 101°$.

5.2 SCANDIUM(II)

5.2.1 Halides and halo-complexes

The radical species ScX_2 (X = Cl, Br and CN) have been identified by EPR spectroscopy as products of the co-deposition of scandium and X_2 in an argon matrix at 14 K (see Table 1) [29]. It is suggested that the chemiluminescence observed in the reaction of scandium atoms with halogen molecules arises from an excited ScX_2^* species, and not from the ScX^* compounds previously suggested [30,31]. The proposed reaction scheme is:

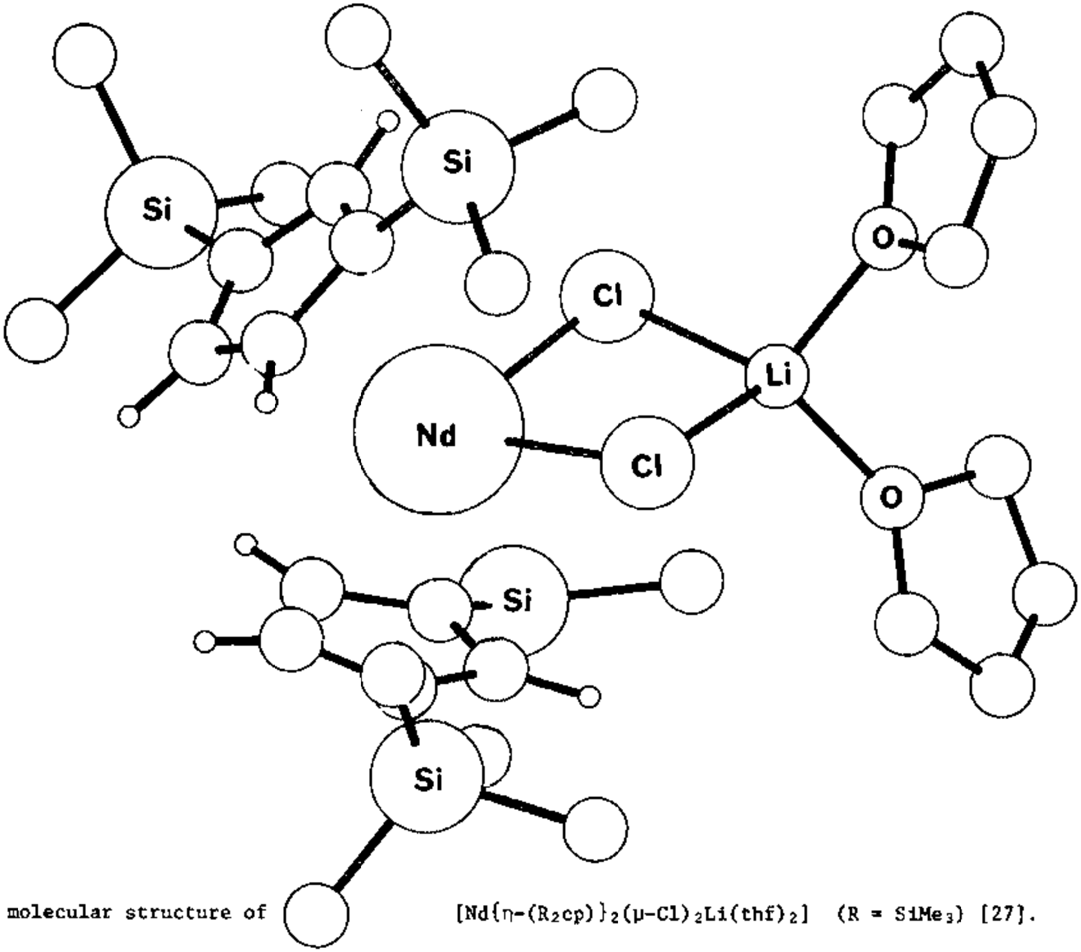

Fig. 1: The molecular structure of [Nd{η-(R$_2$cp)}$_2$(μ-Cl)$_2$Li(thf)$_2$] (R = SiMe$_3$) [27].

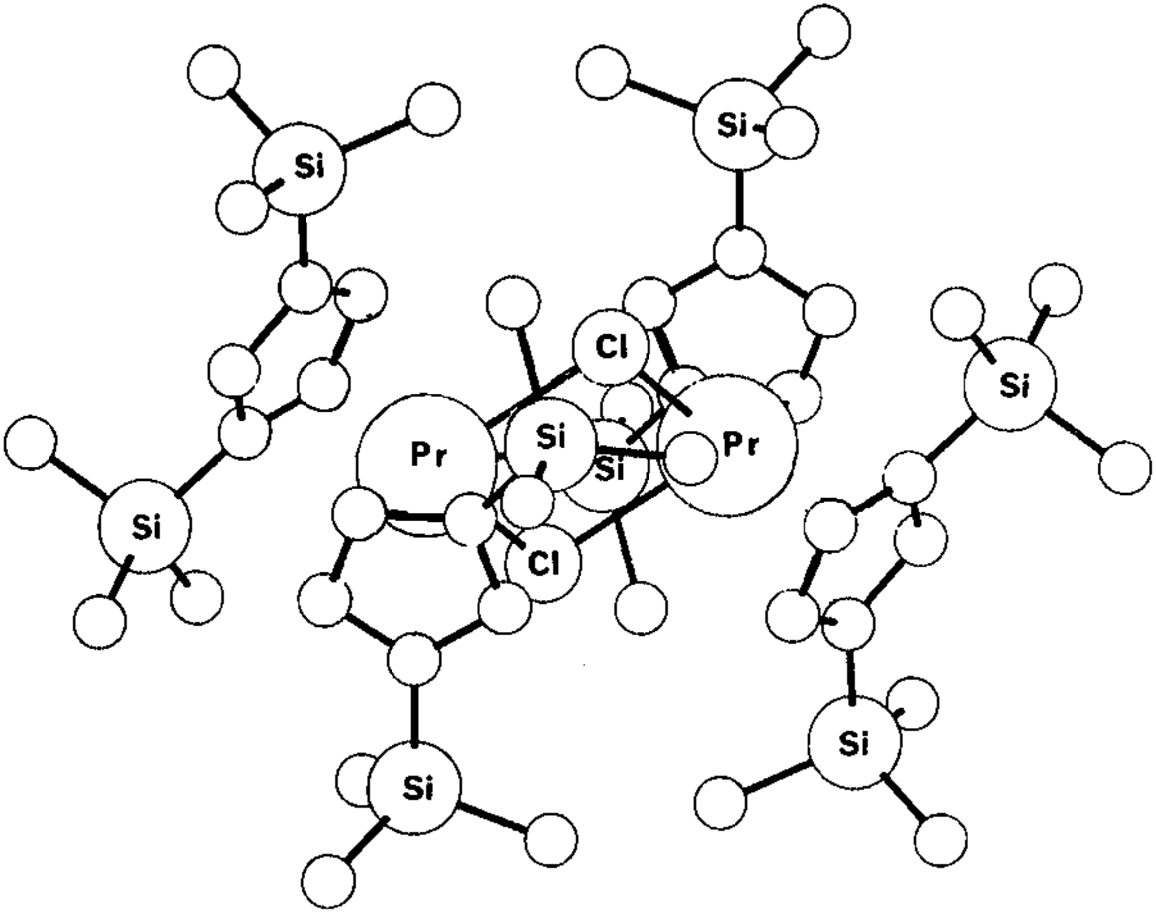

Fig. 2: The molecular structure of $[Pr_2(R_2cp)_4Cl_2]$ (R = $SiMe_3$) [28].

$$Sc + X_2 \longrightarrow ScX^{\dagger} + X$$

$$ScX^{\dagger} + X_2 \longrightarrow ScX_2{}^{*} + X$$

$$ScX_2{}^{*} \longrightarrow ScX_2 + h\nu$$

Although $ScCl_2$ and $ScBr_2$ are not isolable species at room temperature, the derivatives $MScX_3$ (M = Cs or Rb; X = Cl or Br) are readily prepared from the reaction of $M_3Sc_2X_9$ with Sc at 750 °C, and $CsScI_3$ from the reaction of CsI_3 with Sc under similar conditions [32].

5.2.2 *Hydrides and other ligands*

The radical ScH_2 species has been generated from $ScH_{1.98}$, and an EPR investigation of the matrix isolated compound has been reported [33]. A ^{1}H and ^{45}Sc NMR investigation of $ScH_{1.98}$ has been reported, and the results shown to be consistent with a fluorite structure. A Knight shift for ^{45}Sc of 0.055% and a $^{45}Sc\,T_1$, of 0.21 sec are all consistent with a low value of electron d states at the Fermi level [34]. A mass spectrometric investigation into the ScH molecule has been reported, and a value for $\Delta H_{\mathrm{dissoc}}$(ScH) of 199±8 kJ mol^{-1} obtained [35].

The magnetic susceptibilities of the compounds ScS, ScSe and ScTe have been determined. χ(ScS) is temperature independent, whereas χ(ScSe) decreases and χ(ScTe) increases as the temperature rises, over the temperature range 290–700 K [36].

The molecules ScC_2, ScC_3, ScC_4, ScC_5 and ScC_6 have been identified by Knudsen effusion mass spectrometry and the ΔH_f values for the reactions determined [37].

$$Sc(g) + nC(s) \longrightarrow ScC_n$$

n	ΔH_f (kJ mol^{-1})
2	237.1±3.2
3	355.0±2.3
4	390.1±3.8
5	416.6±2.5
6	490.6±3.8

TABLE 1

EPR data for ScX_2

Compound	g	$A\,^{45}Sc$ (MHz)	A other (MHz)	Ref.
$ScCl_2$	1.983	200		[29]
$ScBr_2$	1.970	197	^{79}Br, 22	[29]
$Sc(CN)_2$	1.980	201		[29]
ScH_2	1.980	212		
	1.987	128	^{1}H, 12	[33]

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