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# 1. SCANDIUM

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## CONTENTS

## INTRODUCTION

Scandium chemistry continues to be a relatively unexplored area, and only a small number of papers on scandium have been published during 1980. Nevertheless, two review articles have appeared. Komissarova [1] has summarised the chemistry of the $Sc^{3+}$ ion in aqueous solution, focussing on hydration, hydrolysis, polymerisation, and complex formation processes as a function of the scandium concentration, the pH of the medium, and the nature of the ligands. Corbett [2] has reviewed the structural chemistry of reduced binary halides of early transition metals, including such compounds as $ScCl$, $Sc_5Cl_8$, and $Sc_7Cl_{10}$. These compounds exhibit structures in which halide-capped metal octahedra are condensed into infinite chains, double chains, or double metal layers.

The present review covers the major journals for the 1980 calendar year and the lesser known and/or foreign journals for the period covered by Chemical Abstracts, Volume 91, Number 21 through Volume 93, Number 18.

## 1.1 SCANDIUM(III)

### *1.1.1 Halides and halo-complexes*

The new ternary fluorides $Ag_3ScF_6$ and $AgScF_4$ have been prepared by heating AgF and $ScF_3$ at elevated temperatures. $Ag_3ScF_6$ has a monoclinic structure of

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the $Na_3AlF_6$ type, while $AgScF_4$ has a monoclinic structure which is of a new, unknown structure type [3]. Stability constants for the formation of the fluoride complexes $[ScF_n]^{(3-n)+}$ in aqueous solution have been measured in 0.5 *M* $Na[ClO_4]$ at 25 °C; values of $\log\beta_n$ are 6.18±0.02, 11.52±0.05, and 15.8±0.4 for $n = 1, 2,$ and 3, respectively [4].

Gas phase equilibria in mixtures of $ScCl_3$ and $MgCl_2$ have been studied by mass spectrometric measurements on gases emerging from Knudsen cells. The following thermodynamic data have been obtained for reactions (1)-(4):

$$0.5Mg_2Cl_4 + 0.5Sc_2Cl_6 \longrightarrow MgScCl_5 \quad \Delta H^\circ = -2.9\ \text{kJ mol}^{-1};\ \Delta S^\circ = 8.4\ \text{J K}^{-1} \tag{1}$$

$$MgCl_2 + ScCl_3 \longrightarrow MgScCl_5 \quad \Delta H^\circ = -191.6\ \text{kJ mol}^{-1};\ \Delta S^\circ = -118.0\ \text{J K}^{-1} \tag{2}$$

$$Mg_2Cl_4 + ScCl_3 \longrightarrow Mg_2ScCl_7 \quad \Delta H^\circ = -207.1\ \text{kJ mol}^{-1} \tag{3}$$

$$MgCl_2 + Sc_2Cl_6 \longrightarrow MgSc_2Cl_8 \quad \Delta H^\circ = -206.7\ \text{kJ mol}^{-1} \tag{4}$$

The gas phase complexes $MScCl_5$ have also been observed in the systems $ScCl_3/MCl_2$ (M = Ca, Sr or Ba) [5].

The tetramethylene sulphoxide adduct $[ScCl_3(C_4H_8SO)_3]$ has been prepared and characterised by chemical analysis, IR spectroscopy, conductance measurements, and X-ray powder patterns. The IR spectra indicate that the sulphoxide is coordinated to scandium *via* the oxygen atom [6]. Complex formation in MeCN solutions of $ScCl_3$ and $ScCl_3$ + K[NCS] has been studied by $^{45}Sc$ NMR spectroscopy [7].

X-ray powder diffraction data indicate that $Cs_3Sc_2Cl_9$ has the $Cs_3Tl_2Cl_9$-type structure (space group $R\bar{3}c$, $a$ = 12.707(2) Å, $c$ = 18.117(4) Å) rather than the $Cs_3[Cr_2Cl_9]$-type structure found for the other first-row transition metal compounds, $Cs_3[M_2Cl_9]$ (M = Ti, V, or Cr). The structure of $Cs_3Sc_2Cl_9$ consists of close-packed (Cs + 3Cl) layers perpendicular to the $c$ axis with the $Sc^{3+}$ ions in octahedral sites that lie in chains parallel to $c$. Every third octahedral site is vacant, resulting in $\{Sc_2Cl_9\}^{3-}$ groups that consist of two adjacent $\{ScCl_6\}^{3-}$ octahedra which share a common face [8].

The reaction of $ScI_3$ with alkali metal iodides has been studied by differential thermal analysis. One compound, $K_3ScI_6$ (m.p. 556 °C), has been detected in the $ScI_3$-KI system, and two compounds, $Rb_3ScI_6$ (m.p. 602 °C) and $Rb_3Sc_2I_9$ (m.p. 611 °C), have been identified in the $ScI_3$-RbI system [9]. Among the first examples of iodo elpasolites are the new compounds $Cs_2LiScI_6$ and $Cs_2NaScI_6$, which were prepared by heating mixtures of scandium metal, iodine, and the appropriate alkali metal iodides. $Cs_2LiScI_6$ has the trigonal $Cs_2LiGaF_6$-type structure, while $Cs_2NaScI_6$ has the cubic $K_2NaAlF_6$-type structure [10].

### *1.1.2 Complexes with O-donor ligands*

The hydrolysis of $Sc^{3+}$ ions in aqueous solution ([Sc(III)] = (4 x $10^{-5}$) to $10^{-2}$ *M*; pH = 1.0 to 5.9), leading to formation of mononuclear and polynuclear hydroxo complexes, has been studied by ion exchange, dialysis, and spectrophotometry. The first hydrolysis constant of $[Sc(H_2O)_6]^{3+}$ is (1.0±0.1) x $10^{-5}$ [11].

The kinetics of tetramethylurea (tmu) and *N,N*-dimethylacetamide (dma) ligand exchange on the hexa-coordinated ions $[Sc(tmu)_6]^{3+}$ and $[Sc(dma)_6]^{3+}$, respectively, in $CD_3NO_2$ and $CD_3CN$ have been studied by NMR line-broadening techniques. In both solvents, tmu exchange follows a first-order rate law, rate = $6k_1[\{Sc(tmu)_6\}^{3+}]$, whereas dma exchange occurs by both first- and second-order paths, rate = $6(k_1 + k_2[dma])[\{Sc(dma)_6\}^{3+}]$. Kinetic data are summarised in Table 1. The authors attribute the first-order path to a dissociative (D) mechanism involving formation of a five-coordinate $[ScL_5]^{3+}$ intermediate, and the second-order path, to an associative (A) mechanism involving production of a seven-coordinate $[ScL_7]^{3+}$ intermediate. The difference in mechanism for the tmu and dma complexes is probably due to the greater steric bulk of tmu, which favours the $[Sc(tmu)_5]^{3+}$ intermediate over $[Sc(tmu)_7]^{3+}$; in the case of the less crowded dma complexes, the $[Sc(dma)_5]^{3+}$ and $[Sc(dma)_7]^{3+}$ intermediates evidently have similar stabilities. NMR spectra of solutions of *N,N*-dimethylformamide and $[Sc(dmf)_6][ClO_4]_3$ in $CD_2Cl_2$ at temperatures down to 180 K and of solutions of dimethylsulphoxide and $[Sc(dmso)_6][ClO_4]_3$ in $CD_3NO_2$ at 245 K indicate that in these systems ligand exchange is fast on the NMR time scale [12].

**TABLE 1**

**Kinetic data for ligand exchange on $[ScL_6]^{3+}$ complexes**

| L | Solvent | $k_1$(300 K)/$s^{-1}$ | $k_2$(300 K)/$\ell$ $mol^{-1}$ $s^{-1}$ | $\Delta H^{\ddagger}$/kJ $mol^{-1}$ | $\Delta S^{\ddagger}$/J $K^{-1}$ $mol^{-1}$ |
|---|---|---|---|---|---|
| tmu | $CD_3NO_2$ | 0.26±0.03 | | 91.2±2.3 | 47.8±6.7 |
| | $CD_3CN$ | 1.08±0.05 | | 68.6±1.3 | -15.7±3.8 |
| dma | $CD_3NO_2$ | 4.6 ±0.3 | | 30.3±2.0 | -132 ±6 |
| | $CD_3NO_2$ | | 112±3 | 26.0±0.6 | -119 ±2 |
| | $CD_3CN$ | 6.7 ±4.2 | | 28.3±5.5 | -135 ±26 |
| | $CD_3CN$ | | 199±19 | 29.0±1.0 | -104 ±4 |

Pandey *et al.* [13-15] have measured equilibrium constants for formation of the binary and ternary chelate complexes $[ScL]^{+}$, $[Sc(edta)L]^{3-}$, and $[Sc(egta)L]^{3-}$ (eqns. (5)-(7)), where L is a substituted salicylate ligand (3-Mesal, 4-Mesal,

$$Sc^{3+} + L^{2-} \rightleftharpoons ScL^{+} \qquad (5)$$

$$[Sc(edta)]^{-} + L^{2-} \rightleftharpoons [Sc(edta)L]^{3-} \qquad (6)$$

$$[Sc(egta)]^{-} + L^{2-} \rightleftharpoons [Sc(egta)L]^{3-} \qquad (7)$$

5-Clsal, or 3,5-$Br_2$sal) and egta is the ethyleneglycolbis(β-aminoethylether)tetraacetate(4-) anion. Measurements were made in 50% (v/v) ethanol-water at 25 °C and $\mu = 0.1$ *M* ($KNO_3$); the results are summarised in Table 2.

**TABLE 2**

**Equilibrium data for the formation of some binary and ternary scandium(III) chelate complexes, as defined by equations (5)-(7)**

| | Log K | | |
|---|---|---|---|
| L | Equation (5) | Equation (6) | Equation (7) |
| 4-Mesal | 10.41±0.04 | 6.10±0.07 | 5.83±0.01 |
| 3-Mesal | 10.11±0.06 | 5.95±0.01 | 5.72±0.01 |
| 3,5-$Br_2$sal | 9.68±0.01 | 5.78±0.02 | 5.54±0.02 |
| 5-Clsal | 9.07±0.03 | 5.34±0.02 | 5.21±0.02 |

### *1.1.3 Oxyanion salts and mixed-metal oxides*

The reactions which occur upon heating mixtures of $Sc_2O_3$ and alkali metal persulphates, $M_2[S_2O_8]$ (M = Na or K), have been studied by DTA and X-ray diffraction techniques. $Sc_2O_3$ reacts with the thermally produced alkali metal pyrosulphates to give $Sc_2(SO_4)_3$ (when M = Na) or $KSc(SO_4)_2$ (when M = K), according to equations (8) or (9)). $Sc_2(SO_4)_3$ is stable to 840 °C, at which temperature it begins to decompose to $Sc_2O_3$ [16].

$$Sc_2O_3 + 3Na_2S_2O_7 \longrightarrow Sc_2(SO_4)_3 + 3Na_2SO_4 \qquad (8)$$

$$Sc_2O_3 + 3K_2S_2O_7 \longrightarrow 2KSc(SO_4)_2 + 2K_2SO_4 \qquad (9)$$

$Sc(NH_4)(P_2O_7)$ has been prepared by heating $Sc_2O_3$ with $[NH_4][H_2PO_4]$ at 250-270 °C; it decomposes at 400-780 °C with stepwise loss of ammonia and water [17]. Coprecipitation of Sc(III) and Sb(III) hydroxides, followed by annealing the mixture at 700-750 °C under argon, produces a pure tetragonal phase of composition $Sc_2Sb_4O_9$ ($a$ = 10.051 Å, $c$ = 8.544 Å). Above 800 °C in an inert atmosphere, this compound decomposes to $Sc_2O_3$ and $Sb_2O_3$ [18]. Thermal decomposition of scandium formate in a flowing dinitrogen atmosphere at 210-380 °C produces $H_2$, CO, $CO_2$, $Sc_2O_3$, and an intermediate product which is thought to be $Sc_2O_2(CO_3)$ on the basis of IR evidence. The intermediate product decomposes between 380 and 1000 °C to $Sc_2O_3$ and $CO_2$ [19].

The composition of hydrated scandium vanadates(V), obtained by mixing $Sc(NO_3)_3$ and $Na_3VO_4$ solutions, has been investigated as a function of the pH of the $Na_3VO_4$ solution, the temperature of the synthesis, and the vanadium:scandium ratio. The following compounds were isolated and characterised by chemical analysis, IR and broad-line $^1H$ NMR spectroscopy, and thermogravimetric analysis: $(ScOH)_2V_2O_7.5.5H_2O$, $Sc_6O_4(OH)_4V_{10}O_{28}.24H_2O$, and $Sc_5O_2(OH)_5V_{10}O_{28}.25.5H_2O$ [20].

Vibrational spectra (900-33 $cm^{-1}$ region) have been published for a number of scandium-containing mixed-metal oxides. The compounds studied include $Sc_6WO_{12}$ [21], $LnScO_3$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy or Y) [22], $BaSc_2O_4$, $Ba_2Sc_2O_5$, and $Ba_3Sc_4O_9$ [23]. In several cases the spectra have been assigned and force fields have been determined on the basis of theoretical calculation. $BaSc_2O_4$ exhibits an anomalously high-frequency Sc-O stretching band (IR ~780 $cm^{-1}$, Raman ~760 $cm^{-1}$), which has been interpreted in terms of the presence of five-coordinate scandium [23]. Raman spectra have been reported for single crystals of $Sc_2O_3$ [24].

### *1.1.4 Sulphides*

The compound $ScU_8S_{17}$ has been prepared by heating a mixture of $16UO_2 + Sc_2O_3$ to 1300 °C in a stream of hydrogen sulphide. $ScU_8S_{17}$ has a monoclinic structure, space group $B2/m$, in which the scandium atoms are octahedrally coordinated by four sulphur atoms at 2.529(6) Å and two sulphur atoms at 2.446(9) Å; the three sites occupied by uranium are octacoordinated [25].

### *1.1.5 Phosphides and Arsenides*

X-ray powder diffraction studies of the Sc-P and Sc-As system have revealed the existence of several new scandium phosphide and arsenide phases. Two new phases of composition $Sc_3P_2$ have been identified; both are orthorhombic, space group $Pnma$, but one is isostructural with $Hf_3P_2$ while the other is isostructural with $Cr_3C_2$. The corresponding $Sc_3As_2$ polymorphs have also been identified, along with a new phase of composition $Sc_5As_3$, which is isostructural with $Yb_5Sb_3$ [26]. X-ray powder profile refinement of the structure of $Sc_3As_2$ ($Hf_3P_2$-type polymorph) indicates that the As atoms are surrounded by seven scandium atoms at distances ranging from 2.655 to 2.847 Å (average = 2.77 Å) [27].

### *1.1.6 Organometallic compounds*

Mass spectra have been reported for tris($\eta^5$-cyclopentadienyl)scandium(III) and its alkyl-substituted derivatives [$(Rcp)_3Sc$] (R = Et, Pr, or $CHMe_2$). All of these compounds form fairly stable molecular ions, but the relative intensity of the molecular ion peak decreases with an increase in the number of carbon atoms in the alkyl substituent owing to rearrangements involving loss of ethene or propene [28].

## 1.2 SCANDIUM(II)

Reduction of $Cs_3Sc_2Cl_9$ with scandium metal at 695–700 °C affords the blue scandium(II) compound $CsScCl_3$, which has the $CsNiCl_3$ structure (hexagonal perovskite, space group $P6_3/mmc$, $a$ = 7.350(2) Å, $c$ = 6.045(3) Å). The structure of $CsScCl_3$ is closely related to that of $Cs_3Sc_2Cl_9$ ($CsSc_{0.67}Cl_3$), in that both compounds contain hexagonal close-packed (Sc + 3Cl) layers, but the octahedral scandium sites, which are one-third vacant in $CsSc_{0.67}Cl_3$, are completely filled in $CsScCl_3$. The close relationship between the two structures permits preparation of nonstoicheiometric compounds of the type $CsSc_xCl_3$ ($0.67 \leq x \leq 1.00$) in which the octahedral scandium sites are partially occupied. The question of whether the scandium vacancies are ordered or disordered has been investigated by X-ray methods [8].

## 1.3 SCANDIUM(I)

Band calculations on ScCl are in accord with $d$-band metallic properties [29,30]. This compound has a structure in which two close-packed layers of scandium atoms are sandwiched between close-packed layers of chlorine atoms. The ClScScCl sandwiches stack along the (001) direction of the trigonal crystal [31].

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