

1. SCANDIUM

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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_3 , Sc_5Cl_8 , and $\text{Sc}_7\text{Cl}_{10}$. 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.

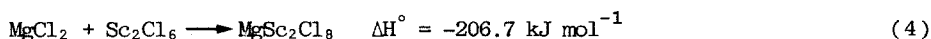
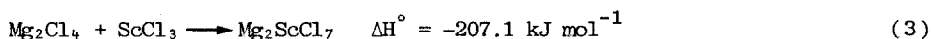
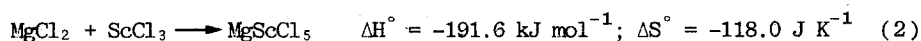
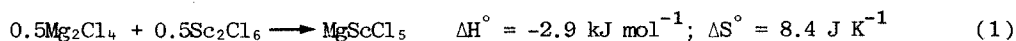
1.1 SCANDIUM(III)

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

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 $[\text{ScF}_n]^{(3-n)+}$ in aqueous solution have been measured in 0.5 M $\text{Na}[\text{ClO}_4]$ 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):



The gas phase complexes MScCl_5 have also been observed in the systems $\text{ScCl}_3/\text{MCl}_2$ ($\text{M} = \text{Ca}, \text{Sr}$ or Ba) [5].

The tetramethylene sulfoxide adduct $[\text{ScCl}_3(\text{C}_4\text{H}_8\text{SO})_3]$ has been prepared and characterised by chemical analysis, IR spectroscopy, conductance measurements, and X-ray powder patterns. The IR spectra indicate that the sulfoxide is coordinated to scandium *via* the oxygen atom [6]. Complex formation in MeCN solutions of ScCl_3 and $\text{ScCl}_3 + \text{K}[\text{NCS}]$ has been studied by ^{45}Sc NMR spectroscopy [7].

X-ray powder diffraction data indicate that $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ has the $\text{Cs}_3\text{Ti}_2\text{Cl}_9$ -type structure (space group $R\bar{3}c$, $a = 12.707(2) \text{ \AA}$, $c = 18.117(4) \text{ \AA}$) rather than the $\text{Cs}_3[\text{Cr}_2\text{Cl}_9]$ -type structure found for the other first-row transition metal compounds, $\text{Cs}_3[\text{M}_2\text{Cl}_9]$ ($\text{M} = \text{Ti}, \text{V}$, or Cr). The structure of $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ consists of close-packed ($\text{Cs} + 3\text{Cl}$) 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 $\{\text{Sc}_2\text{Cl}_9\}^{3-}$ groups that consist of two adjacent $\{\text{ScCl}_6\}^{3-}$ 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 $\text{Rb}_3\text{Sc}_2\text{I}_9$ (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 $\text{Cs}_2\text{LiScI}_6$ and $\text{Cs}_2\text{NaScI}_6$, which were prepared by heating mixtures of scandium metal, iodine, and the appropriate alkali metal iodides. $\text{Cs}_2\text{LiScI}_6$ has the trigonal $\text{Cs}_2\text{LiGaF}_6$ -type structure, while $\text{Cs}_2\text{NaScI}_6$ 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 ($[\text{Sc(III)}] = (4 \times 10^{-5})$ to 10^{-2} M ; $\text{pH} = 1.0$ 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 $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is $(1.0 \pm 0.1) \times 10^{-5}$ [11].

The kinetics of tetramethylurea (tmu) and *N,N*-dimethylacetamide (dma) ligand exchange on the hexa-coordinated ions $[\text{Sc}(\text{tmu})_6]^{3+}$ and $[\text{Sc}(\text{dma})_6]^{3+}$, 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, $\text{rate} = 6k_1[\{\text{Sc}(\text{tmu})_6\}^{3+}]$, whereas dma exchange occurs by both first- and second-order paths, $\text{rate} = 6(k_1 + k_2[\text{dma}])[\{\text{Sc}(\text{dma})_6\}^{3+}]$. Kinetic data are summarised in Table 1. The

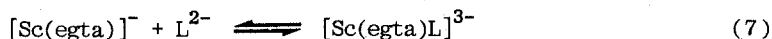
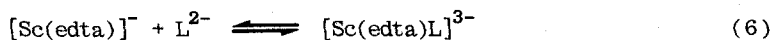
TABLE 1

Kinetic data for ligand exchange on $[\text{ScL}_6]^{3+}$ complexes

L	Solvent	$k_1(300 \text{ K})/\text{s}^{-1}$	$k_2(300 \text{ K})/\ell \text{ mol}^{-1} \text{ s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$
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

authors attribute the first-order path to a dissociative (D) mechanism involving formation of a five-coordinate $[\text{ScL}_5]^{3+}$ intermediate, and the second-order path, to an associative (A) mechanism involving production of a seven-coordinate $[\text{ScL}_7]^{3+}$ intermediate. The difference in mechanism for the tmu and dma complexes is probably due to the greater steric bulk of tmu, which favours the $[\text{Sc}(\text{tmu})_5]^{3+}$ intermediate over $[\text{Sc}(\text{tmu})_7]^{3+}$; in the case of the less crowded dma complexes, the $[\text{Sc}(\text{dma})_5]^{3+}$ and $[\text{Sc}(\text{dma})_7]^{3+}$ intermediates evidently have similar stabilities. NMR spectra of solutions of *N,N*-dimethylformamide and $[\text{Sc}(\text{dmf})_6][\text{ClO}_4]_3$ in CD_2Cl_2 at temperatures down to 180 K and of solutions of dimethylsulphoxide and $[\text{Sc}(\text{dmso})_6][\text{ClO}_4]_3$ in CD_3NO_2 at 245 K indicate that in these systems ligand exchange is fast on the NMR time scale [12].

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



5-Cl₃sal, or 3,5-Br₂sal) and egta is the ethyleneglycolbis(β-aminoethylether)tetraacetate(4-) anion. Measurements were made in 50% (v/v) ethanol-water at 25 °C and μ = 0.1 M (KNO₃); the results are summarised in Table 2.

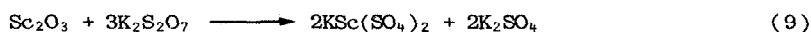
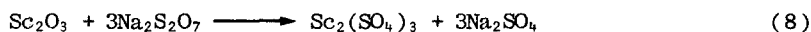
TABLE 2

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

L	Log K		
	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-Cl ₃ sal	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 Sc₂O₃ and alkali metal persulphates, M₂[S₂O₈] (M = Na or K), have been studied by DTA and X-ray diffraction techniques. Sc₂O₃ reacts with the thermally produced alkali metal pyrosulphates to give Sc₂(SO₄)₃ (when M = Na) or KSc(SO₄)₂ (when M = K), according to equations (8) or (9). Sc₂(SO₄)₃ is stable to 840 °C, at which



temperature it begins to decompose to Sc₂O₃ [16].

Sc(NH₄)(P₂O₇) has been prepared by heating Sc₂O₃ with [NH₄][H₂PO₄] 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 $\text{Sc}_2\text{Sb}_4\text{O}_9$ ($a = 10.051 \text{ \AA}$, $c = 8.544 \text{ \AA}$). 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 $210\text{--}380^\circ\text{C}$ produces H_2 , CO , CO_2 , Sc_2O_3 , and an intermediate product which is thought to be $\text{Sc}_2\text{O}_2(\text{CO}_3)$ 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 $\text{Sc}(\text{NO}_3)_3$ 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:

$(\text{ScOH})_2\text{V}_2\text{O}_7 \cdot 5.5\text{H}_2\text{O}$, $\text{Sc}_6\text{O}_4(\text{OH})_4\text{V}_{10}\text{O}_{28} \cdot 24\text{H}_2\text{O}$, and $\text{Sc}_5\text{O}_2(\text{OH})_5\text{V}_{10}\text{O}_{28} \cdot 25.5\text{H}_2\text{O}$ [20].

Vibrational spectra ($900\text{--}33 \text{ cm}^{-1}$ region) have been published for a number of scandium-containing mixed-metal oxides. The compounds studied include $\text{Sc}_6\text{WO}_{12}$ [21], LnScO_3 ($\text{Ln} = \text{La}$; Pr , Nd , Sm , Eu , Gd , Tb , Dy or Y) [22], BaSc_2O_4 , $\text{Ba}_2\text{Sc}_2\text{O}_5$, and $\text{Ba}_3\text{Sc}_4\text{O}_9$ [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 $\sim 780 \text{ cm}^{-1}$, Raman $\sim 760 \text{ cm}^{-1}$), 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 $\text{ScU}_5\text{S}_{17}$ has been prepared by heating a mixture of $16\text{UO}_2 + \text{Sc}_2\text{O}_3$ to 1300°C in a stream of hydrogen sulphide. $\text{ScU}_5\text{S}_{17}$ has a monoclinic structure, space group $B2/m$, in which the scandium atoms are octahedrally coordinated by four sulphur atoms at $2.529(6) \text{ \AA}$ and two sulphur atoms at $2.446(9) \text{ \AA}$; 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 $Prma$, 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 \AA (average = 2.77 \AA) [27].

1.1.6 Organometallic compounds

Mass spectra have been reported for tris(η^5 -cyclopentadienyl)scandium(III) and its alkyl-substituted derivatives $[(Rcp)_3Sc]$ ($R = Et, Pr, \text{ or } CHMe_2$). 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 $P6_3/mmc$, $a = 7.350(2) \text{ \AA}$, $c = 6.045(3) \text{ \AA}$). 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 nonstoichiometric 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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