

1. SCANDIUM

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INTRODUCTION

As usual, relatively little work has been done on scandium during the past year. Among the more interesting developments are the use of scandium(III) as a template for synthesis of a complex with a 14-membered hexaaza macrocyclic ligand, the synthesis of novel alkyl-bridged heterometallic complexes of the type $[(\eta-C_5H_5)_2Sc(\mu-R)_2AlR_2]$, NMR kinetic studies of ligand exchange on $[ScL_6]^{3+}$ complexes (L = trimethylphosphate or dimethylmethylphosphonate), and an EPR study of the ScF_2 molecule. In addition, there has been a number of studies of scandium halides and halo-complexes, oxoanion salts, and metal chelates, especially chelates that contain bidentate O-donor ligands. This review covers the major journals for the 1979 calendar year and the lesser known and/or foreign journals for the period covered by Chemical Abstracts, Volume 90, Number 1 to Volume 91, Number 20.

1.1 SCANDIUM(III)

1.1.1 Halides and halo-complexes

Quantum mechanical calculations of the ab initio restricted-Hartree–Fock type have been carried out on first-row transition metal trifluorides, where the metal varies from scandium to nickel [1]. The equilibrium geometry of ScF_3 was found to be trigonal planar (D_{3h} symmetry) with an Sc–F distance of 1.88 Å; population analysis indicated that the bonds are about 63% ionic.

TABLE 1

Thermodynamic data at 298 K for formation of gas-phase complexes of the type $MScCl_4$ ($M = Li, Na, K, Rb, \text{ or } Cs$)

Reaction	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{J mol}^{-1} \text{ K}^{-1}$	Ref.
$0.5 \text{ Li}_2\text{Cl}_2 + 0.5 \text{ Sc}_2\text{Cl}_6 \rightarrow \text{LiScCl}_4$	-32.6	-3.8	4
$0.5 \text{ Na}_2\text{Cl}_2 + 0.5 \text{ Sc}_2\text{Cl}_6 \rightarrow \text{NaScCl}_4$	-41.4	-8.4	5
$0.5 \text{ K}_2\text{Cl}_2 + 0.5 \text{ Sc}_2\text{Cl}_6 \rightarrow \text{KScCl}_4$	-46.9	+3.8	6
$0.5 \text{ Rb}_2\text{Cl}_2 + 0.5 \text{ Sc}_2\text{Cl}_6 \rightarrow \text{RbScCl}_4$	-45.2	-2.5	7
$0.5 \text{ Cs}_2\text{Cl}_2 + 0.5 \text{ Sc}_2\text{Cl}_6 \rightarrow \text{CsScCl}_4$	-47.7	+3.3	8
$\text{LiCl} + \text{ScCl}_3 \rightarrow \text{LiScCl}_4$	-237.2	-146.9	4
$\text{NaCl} + \text{ScCl}_3 \rightarrow \text{NaScCl}_4$	-242.7	-149.4	5
$2 \text{ ScCl}_3 \rightarrow \text{Sc}_2\text{Cl}_6$	-200.0	-139.7	4

Electron diffraction values for the $\text{Sc}-\text{F}$ bond distance are in the range 1.91–1.93 Å [2,3], but there is disagreement as to whether the experimental geometry of ScF_3 is planar or pyramidal [1–3].

Gas phase equilibria in mixtures of ScCl_3 and alkali metal chlorides have been studied by mass spectroscopic measurements on the gases emerging from Knudsen cells [4–8]. The thermodynamic data obtained are summarized in Table 1.

A series of hexachlorometallate compounds of the type $\text{Cs}_2\text{LiM}^{\text{III}}\text{Cl}_6$ ($M^{\text{III}} = \text{Sc}, \text{Y}, \text{La}-\text{Nd}, \text{Sm}-\text{Lu}, \text{V}, \text{Cr or In}$) has been prepared by evaporation of concentrated hydrochloric acid solutions that contain a 2 : 1 : 1 ratio of Cs^+ , Li^+ and M^{3+} [9]. These compounds have cubic or hexagonal structures, depending on the ionic radius of the M^{3+} cation. $\text{Cs}_2\text{LiScCl}_6$ is isostructural with $\text{Cs}_2\text{NaCrF}_6$ [10], and therefore the crystals are expected to contain $\{\text{ScCl}_6\}$ octahedra with shared faces.

1.1.2 Complexes with O-bonded ligands

Most of the papers that have appeared in this area report studies of oxo-anion salts and complexes with bidentate chelating ligands. Additional papers include a broad-line ^1H NMR investigation of scandium peroxide compounds [11] and a single-crystal X-ray study of scandium dioxide sulphide, $\text{Sc}_2\text{O}_2\text{S}$ [12]. The scandium atom in $\text{Sc}_2\text{O}_2\text{S}$ is surrounded by three sulphur atoms at 2.708(1) Å, three oxygen atoms at 2.096(1) Å, and one oxygen atom at 2.167(4) Å; the coordination polyhedron is a C_{3v} monocapped octahedron.

The constitution and thermal decomposition of complex selenites of scandium and alkali metals, $M\text{Sc}(\text{SeO}_3)_2 \cdot n \text{H}_2\text{O}$ ($M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{ or } \text{Cs}$), have been characterized by a variety of physical methods. Empirical formulae of these compounds show a slight excess of selenite and a slight deficiency of alkali metal, e.g. $\text{Na}_{0.9}\text{ScH}_{0.5}(\text{SeO}_3)_{2.2} \cdot 1.9 \text{H}_2\text{O}$. IR and broadline ^1H NMR spectra suggest that the excess selenite is present as $[\text{HSeO}_3]^-$ ions [13].

The composition and properties of scandium orthophosphates, obtained by reaction of scandium chloride, phosphoric acid, and aqueous ammonia, have been studied as a function of pH of the reaction medium and thermal treatment of the products [14]. The complex scandium silicates and germanates, $\text{Pb}_2\text{Sc}_2\text{Si}_2\text{O}_9$ and $\text{Pb}_2\text{Sc}_2\text{Ge}_2\text{O}_9$, have been prepared by solid state reactions at 820–900°C. X-ray powder patterns show that these compounds are orthorhombic and isostructural with kentrolite $\text{Pb}_2\text{Mn}_2\text{Si}_2\text{O}_9$; IR and Raman spectra reveal the presence of pyrosilicate (Si_2O_7) and pyrogermanate (Ge_2O_7) groups [15].

Scandium carboxylates of the type $[\text{Sc}(\text{O}_2\text{CR})_3]$ ($\text{R} = \text{Et}, \text{Pr}, \text{CMe}_2\text{H}$ or C_7H_{15}) have been prepared by heating scandium ethanoate with the appropriate carboxylic acid at $\sim 80^\circ\text{C}$ under 10 torr. A small ($\sim 70\text{ cm}^{-1}$) difference between the asymmetric and symmetric $\text{C}=\text{O}$ stretching frequencies in these compounds indicates that the carboxylate ligands are bidentate and suggests coordination number six for the scandium atom. The caprylate derivative, $[\text{Sc}(\text{O}_2\text{CC}_7\text{H}_{15})_3]$, is monomeric in refluxing benzene [16].

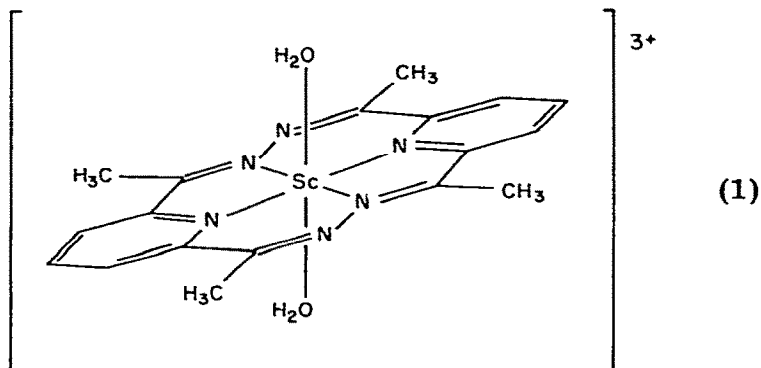
A solvent extraction study has established that at concentrations of 10^{-5} – 10^{-3} M , scandium forms mononuclear salicylate complexes $[\text{Sc}(\text{Hsal})_3]$ (at $\text{pH} \leq 4$) and $[\text{Sc}(\text{OH})(\text{Hsal})_2]$ (at $\text{pH} > 4$). Stability constants, β_n , for $[\text{Sc}(\text{Hsal})_n]^{(3-n)+}$ in aqueous solution are $\beta_1 = (3 \pm 1) \times 10^2$, $\beta_2 = (5.0 \pm 0.6) \times 10^4$, and $\beta_3 = (5.3 \pm 0.3) \times 10^6$ [17].

Negative ion mass spectra have been reported for several tris(dipivaloyl-methanato)metal(III) complexes, including $[\text{Sc}(\text{dpm})_3]$. Consistent with the availability of energetically accessible, unoccupied metal d orbitals, 99% of the total negative ion current is carried by the molecular ion $[\text{Sc}(\text{dpm})_3]^-$ [18]. There has been considerable interest in the vapour pressures of scandium tris(β -diketonates) because of the importance of volatile β -diketonate chelates in gas chromatographic analyses. Vapour pressure data and thermodynamic quantities for vapourization of $[\text{Sc}(\text{RCOCHCOR}')_3]$ ($\text{R}, \text{R}' = \text{Me}, \text{Me}; \text{Me}, \text{CF}_3$; or CF_3, CF_3) have been reported but, unfortunately, the two papers that have appeared on this subject [19,20] are in serious disagreement at points where they overlap. Tris(3-mesitylacetylacetonato)scandium(III) has been prepared and its NMR spectrum reported in connection with a study of the magnetic anisotropy in metal β -diketonate chelate rings [21].

1.1.3 Complexes with polydentate chelating ligands

The first example of the use of the $\text{Sc}(\text{III})$ ion as a template for synthesis of a macrocyclic compound has been reported by Radecka-Paryzek [22]. Condensation of 2,6-diacetylpyridine with hydrazine in ethanol in the presence of $\text{Sc}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ affords a solid compound formulated, on the basis of spectral and thermogravimetric analysis data, as $[\text{Sc}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{H}_2\text{O})_2][\text{ClO}_4]_3 \cdot 4\text{H}_2\text{O}$. The $[\text{Sc}(\text{C}_{18}\text{H}_{18}\text{N}_6)(\text{H}_2\text{O})_2]^{3+}$ cation (1) is believed to have an octahedral structure with the $\text{Sc}(\text{III})$ ion bound to four nitrogen atoms of

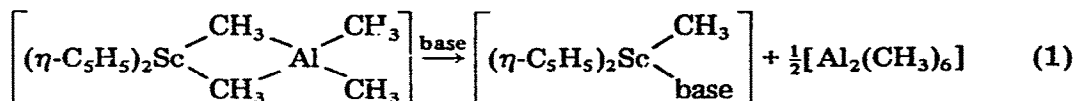
the 14-membered hexaaza macrocyclic ligand in the equatorial plane, and two water molecules in axial positions.



Scandium, yttrium, and rare earth complexes of the type $KM\{(\text{HOCH}_2\text{CH}_2)\text{-N}(\text{CH}_2\text{COO})_2\}_2 \cdot n \text{H}_2\text{O}$ have been synthesized by reaction of aqueous suspensions of stoichiometric amounts of freshly precipitated $M(\text{OH})_3$, β -hydroxyiminodiethanoic acid, and KOH [23]. The scandium compound was isolated as the tetrahydrate. On the basis of previous work, the β -hydroxyiminodiethanoate ion is assumed to act as a tetradentate ligand.

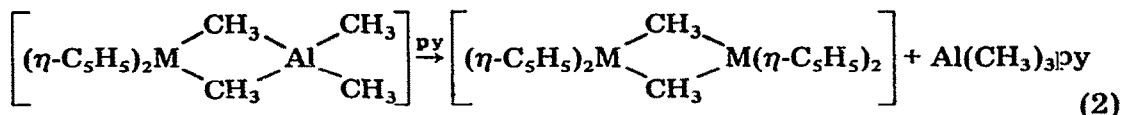
1.1.4 Organometallic compounds

Novel crystalline complexes of the type $[(\eta\text{-C}_5\text{H}_5)_2\text{M}(\mu\text{-R})_2\text{AlR}_2]$ ($\text{M} = \text{Sc}$, Y , or rare earth; $\text{R} = \text{Me}$ or Et) have been prepared by reaction $[\{\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{-Cl}\}_2]$ with $\text{Li}[\text{AlR}_4]$ in toluene [24]. A di- μ -alkyl bridged structure is indicated by bands at 1250 and 1235 cm^{-1} in the IR spectra of the methyl derivatives, by ^1H and ^{13}C NMR spectra of the scandium and yttrium compounds, and by a single-crystal X-ray study of $[(\eta\text{-C}_5\text{H}_5)_2\text{Yb}(\mu\text{-CH}_3)_2\text{Al}(\text{CH}_3)_2]$. NMR spectra of the $[(\eta\text{-C}_5\text{H}_5)_2\text{Sc}(\mu\text{-R})_2\text{AlR}_2]$ complexes exhibit two distinct alkyl resonances at room temperature, but exchange of bridging and terminal alkyl groups in the methyl derivative becomes fast on the NMR time scale at temperatures above 100°C. The yttrium analogues are fluxional at room temperature, but not at -45°C. The X-ray study reveals an approximately tetrahedral environment about the Yb and Al atoms in $[(\eta\text{-C}_5\text{H}_5)_2\text{Yb}(\mu\text{-CH}_3)_2\text{Al}(\text{CH}_3)_2]$; the $\text{Yb}(\mu\text{-CH}_3)_2\text{Al}$ unit is strikingly similar to the $\text{Al}(\mu\text{-CH}_3)_2\text{Al}$ unit in $[\text{Al}_2(\text{CH}_3)_6]$. Reaction of $[(\eta\text{-C}_5\text{H}_5)_2\text{Sc}(\mu\text{-CH}_3)_2\text{Al}(\text{CH}_3)_2]$ with the Lewis bases pyridine or tetrahydrofuran cleaves the di- μ -methyl-heterometallic bridges to give $[(\eta\text{-C}_5\text{H}_5)_2\text{Sc}(\text{CH}_3)(\text{base})]$ plus $[\text{Al}_2(\text{CH}_3)_6]$ (reaction (1)) [25].



In contrast, the analogous $[(\eta\text{-C}_5\text{H}_5)_2\text{M}(\mu\text{-CH}_3)_2\text{Al}(\text{CH}_3)_2]$ ($\text{M} = \text{Y}$, Dy - Yb)

complexes react with pyridine to give $\text{Al}(\text{CH}_3)_3\text{py}$ and the homometallic methyl-bridged complexes $[\{\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2\}_2]$ (reaction (2)). It appears



from reactions (1) and (2) that Lewis acidity increases in the order:
rare earth $\sim \text{Y} < \text{Al} < \text{Sc}$.

1.1.5 Kinetic studies of ligand exchange

The exchange of trimethylphosphate (tmp) and dimethylmethylphosphonate (dmmp) ligands on the hexa-coordinated ions $[\text{Sc}(\text{tmp})_6]^{3+}$ and $[\text{Sc}(\text{dmmp})_6]^{3+}$, respectively, has been studied by NMR line-broadening techniques [26,27]. The rate of ligand exchange is given by: exchange rate = $6k_{\text{ex}}[\text{ScL}_6^{3+}]$, where the rate constant $k_{\text{ex}} = \tau_c^{-1}$ depends on both the nature of the ligand L (tmp or dmmp) and the solvent (CD_3CN or CD_3NO_2); τ_c is the mean lifetime of the ligand in a coordinated site. In general, first- and second-order pathways may contribute to the exchange process: $k_{\text{ex}} = k_1 + k_2[\text{L}]$. The general case is exemplified by ligand exchange on $[\text{Sc}(\text{dmmp})_6]^{3+}$ in CD_3CN . For $[\text{Sc}(\text{tmp})_6]^{3+}$ in CD_3CN , only the first-order pathway is important: $k_{\text{ex}} = k_1$. In CD_3NO_2 , both $[\text{Sc}(\text{dmmp})_6]^{3+}$ and $[\text{Sc}(\text{tmp})_6]^{3+}$ undergo ligand exchange by the second-order path: $k_{\text{ex}} = k_2[\text{L}]$. The mechanistic implications of these rate laws have been discussed in terms of dissociative, dissociative interchange, and associative mechanisms. The authors attribute the k_1 path to a dissociative process involving formation of $[\text{ScL}_5]^{3+}$ as a reactive intermediate; for the k_2 path, they favour an associative mechanism involving formation of a $[\text{ScL}_7]^{3+}$ transition state. Evidently, five- and seven-coordinate scandium(III) species are of similar stability and the choice of mechanism depends on the nature of the ligand and solvent.

1.2 SCANDIUM(II)

The radical molecule ScF_2 has been produced at ~ 2000 K by heating a mixture of scandium metal and excess ScF_3 , and it has been studied by EPR at 12 K in argon or xenon matrices [28]. Observed ^{45}Sc and ^{19}F hyperfine splittings of 220 and 28 MHz, respectively, imply that the unpaired electron has $\sim 4\%$ scandium 4s character and less than 1% ^{19}F character (2s and 2p). Thus ScF_2 is highly ionic and $\text{F}^-\text{Sc}^{2+}\text{F}^-$ appears to be a reasonable approximation to the electronic structure. The observed g value of 1.995(1) is not consistent with a $^2\Delta$ ground state, and therefore ScF_2 must be bent. The unpaired electron probably occupies (primarily) the d_{xy} orbital, which is slightly stabilized relative to the $d_{x^2-y^2}$ orbital for a bent structure.

A method has been developed for growing ScH_2 crystals by vapour phase

deposition [29]. Nucleation and growth of ScH_2 occur on molybdenum metal when ScCl_3 vapour and an excess of reducing agent (Na or Mg) are mixed in a stream of dihydrogen gas at atmospheric pressure and temperatures of 800–970°C. The ScH_2 deposits as black crystals which have a cubic unit cell with lattice parameter $a = 4.785(1)$ Å.

The synthesis has been achieved, and the structure determined, of a new compound which is not easily classified in terms of formal oxidation states. The ternary boride ScIr_3B_4 has been prepared from the elements at 1100°C [30]. It has a hexagonal structure, space group $P6_3/m$, with $a = 7.576(2)$ Å and $c = 3.442(1)$ Å. Refinement of X-ray powder diffraction data indicates that the Sc atom is surrounded by a trigonal prism of six Ir atoms at 2.894 Å, with three more Ir atoms at 3.121 Å; Sc—B distances are 2.585 and 2.569 Å.

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