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6. SCANDIUM

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CONTENTS

INTRODUCTION

The chemistry of scandium continues to attract little attention. As in previous years, scandium hydrides have been of some interest as components of energy storage systems. This review covers the major journals through 1982, and coincides with Chemical Abstracts coverage in volumes 95 and 96. The format closely resembles that adopted in the review of the 1981 literature [1].

6.1 SCANDIUM(III)

6.1.1Halides and halo-complexes

Burgess and Kijowski have produced an excellent review concerned with the solution thermochemistry of scandium(III) and other lanthanide halides [2]. The solubility and thermochemical properties of the anhydrous and solvated ScX_3 (X = halide) species in a range of solvents are comprehensively reviewed. In addition, the available preparative routes to the anhydrous and solvated species are critically evaluated. This review must provide an essential starting point for anyone with interests in the solution chemistry of scandium. These same authors have also reported accurately redetermined enthalpies of solution for scandium(III) halides in a variety of solvents [3].

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	Solvent	ΔH (kJ mol^{-1}, 298.2 K)
For $ScCl_3$	H_2O	-205.1±1.7
	MeOH	-155.4±1.9
	dmso	-160.5±1.9
For ScI_3	H_2O	-261.3±2.7
	MeOH	-217.2±2.0
	dmso	-393.0±1.1

Equilibrium geometries and potential constants have been determined for scandium(III) halides [4]; in general the results correlate well with those reported previously [5].

Mass spectroscopic and thermochemical investigations of the mixed scandium(III) chloride-aluminium chloride system have been described [6]. The dimerisation of $ScCl_3$ (to Sc_2Cl_6) is exothermic ($\Delta H = -23.8$ kJ mol^{-1}), and the gas phase reaction of Sc_2Cl_6 with Al_2Cl_6 produces the heteronuclear system:

$$Sc_2Cl_6 + Al_2Cl_6 \rightleftharpoons 2ScAlCl_6$$

Mass spectroscopy has also been used in the determination of the enthalpy of formation of the tetrafluoroscandate(III) ion [7].

The extraction of scandium(III) from halide rich medium by arsine oxides has been investigated [8]. In a series of arsine oxides, the efficiency of extraction was found to be:

$$Ph_3AsO > Ph_2RAsO > PhR_2AsO > R_3AsO$$

$$R = n\text{-}C_8H_{17}$$

In each case, the extracted species was of the stoichiometry, $\{Sc(OH)Cl_2.2L\}$.

6.1.2 Complexes with S- and O- bonded ligands

A considerable number of mixed oxides have been characterised structurally of thermochemically. A crystallographic investigation has described the unit cell dimensions for the pyroxenes in the binary system $NaCrSi_2O_6$-$NaScSi_2O_6$ at 50 kbar pressure [9]. The ternary systems CaO-SrO-Sc_2O_3 and BaO-SrO-Sc_2O_3 have also been studied; novel components include $(Ca,Sr)Sc_2O_4$, $(Sr,Ba)_3Sc_4O_9$ and $Ba_x(Ca_{2x}Sc_{2-x})Sc_6O_{12}$ [10]. The structural characterisation of the species

Ho_2ScNbO_7 and Sm_2ScTaO_7 has also been reported [11]. Related species, including $LaScO_3$ and La_2ScNbO_7, are present in the $LaNbO_4$-$LaScO_3$-$La_2Ti_2O_7$ pseudoternary system [12]. Conductivity studies of the $Sc(NO_3)_3$-Na_3O_4 system have indicated that novel compounds of the type $3Sc_2O_3.2V_2O_5.nH_2O$ are formed [13].

The oxidation of cyclohexene by active oxygen over scandium oxide has been studied [14]. The thermal decomposition of scandium peroxides has also been investigated [15].

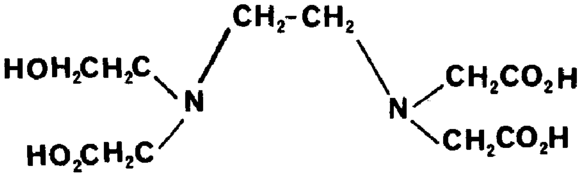
Powder neutron diffraction studies of the compounds $CaSc_2S_4$, $SrSc_2S_4$ and $PbSc_2S_4$ have been reported; these are fully consistent with a calcium ferrate, $CaFe_2O_4$ type structure [16].

The solution chemistry of scandium(III) has not been widely investigated, although a review (with twenty five references) covering the extraction and chemistry of scandium has appeared [17].

The formation of polynuclear iron(III) hydroxo complexes has been shown to be inhibited by the presence of scandium(III) or chromium(III) aquo complexes; the role of these ions in basic solutions containing iron(III) is discussed [18]. The behaviour of scandium(III) in trace amounts in solutions containing sulphate and/or citrate over the pH range 1.0-12.0 has been studied [19].

Scandium(III) complexes with alkanedicarboxylates (malonate, succinate, glutarate, adipate, pimelate, suberate, azeleate and sebacate) have been described; in each case, neutral hydrated complexes are formed [20]. On heating, the complexes initially dehydrate, and then, on further heating to 763-978 K, decompose to leave Sc_2O_3.

A study of the exchange of labelled $[^{46}Sc(H_2O)_6]^{3+}$ with the complex [ScL]

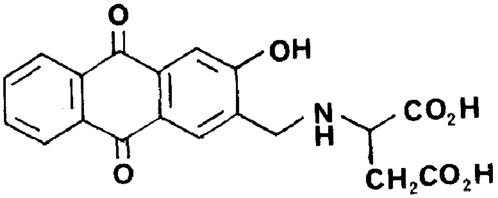


(1)

(L = 1) has been described. The rate of exchange is given by:

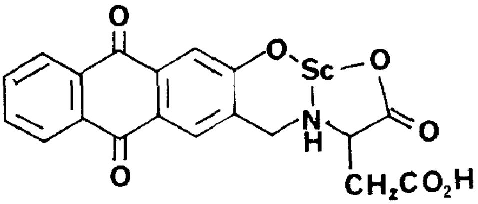
$$\rho = k_f[H^+][ScL][Sc^{3+}(aq)]/[Sc^{3+}(aq)] - k_r[H^+][ScL]$$

where k_f = 750 and k_r = 746 . This is consistent with a pathway in which the rate determining step is dissociation of a protonated carboxylate ligand from the complex, followed by competition of $[H_nL]^{(3-n)-}$ for all of the free Sc^{3+}(aq) in solution [21]. Activation parameters were also reported, and shown to be consistent with the proposed mechanism. A 1:1 complex with alixarin (2)



(2)

has been characterised [22]. The complex is red (λ_{max} = 510 nm) and is thought to possess structure **3**.



(3)

The extraction of scandium by 8-hydroxyquinoline has also been studied [23].

A study of scandium phosphites present in the $Sc_2(HPO_3)_3$-H_3PO_3-H_2O system has revealed the presence of species of stoichiometry $Sc_2(HPO_3)_3.nH_2O$, $ScH_3P_2O_6.nH_2O$ and $ScH_6P_3O_9.nH_2O$ [24].

A structural study of the scandium phosphate prepared by the reaction of Sc_2O_3 with phosphoric acid has been reported [25].

A scandium complex with methylphenylphosphonate has been reported; the compound $[ScL_3]$ (HL = MePhP(O)OH) has been characterised [26].

The reaction of scandium(III) chloride with trialkyl phosphates, $(RO)_3PO$ (R = n-butyl or ethyl), in acetonitrile has been investigated by ^{45}Sc NMR; all the possible octahedral species, $[ScCl_{6-x}L_x]^{(x-3)-}$ are present in solution [27].

6.2 MISCELLANEOUS COMPLEXES

A study of the flourite form of ScH_2 has been reported [28]. A full MCSCF/CI theoretical study of ScH has been completed; the lowest six states arise from the $^2D(4s^23d^1)$ atomic configuration, with the $^2\Sigma^+$ as the ground state [29].

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