Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam – Printed in the Netherlands

THE COORDINATION CHEMISTRY OF SCANDIUM

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(Received December 8th, 1970)

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A INTRODUCTION

Scandium has been known for almost one hundred years, although its chemistry, and in particular its coordination chemistry, has been little studied The lack of attention has probably been due to the difficulty, until recently, of obtaining a pure source of scandium, although the metal and the oxide are now commercially available in high purity

Scandium is the first member of the 3*d* transition series and has a ground state electronic configuration of [Ar] $3d^1 4s^2$

Vickery[1] has reviewed the chemistry of scandium up to 1960, his monograph being mainly concerned with analytical procedures and the chemistry of trivalent scandium salts. Most of the chemistry of scandium so far reported has been derived in connection with studies on the lanthanides[2], but in the past few years interest in the coordination chemistry of scandium has increased

This review is concerned with the coordination chemistry of scandium, and is discussed in sections involving ligands with different donor atoms.

B COMPLEXES WITH OXYGEN DONOR LIGANDS

(i) Neutral oxygen donor ligands

A great deal of the early work on complex formation of lanthanides and scandium involved partition between aqueous and organic phases In those few cases where solid complexes were isolated, these were found to be relatively unstable species, or often highly solvated, particularly when the ligand employed was unidentate For scandium, the chemistry of which is similar to that of the lanthanides in many aspects[2], it is expected that the most stable complexes will be formed with oxygen donor ligands

TABLE 1

Scandium halide and thiocyanate complexes with neutral oxygen donor ligands

Complex	Ligand (L)	Ref
$ScCl_3(L)_6$	Urea	37
$ScBr_3(L)_6$	dmso, urea	9, 38
$ScCl_3(L)_4$	dmso, urea	9, 38
$ScCl_3(L)_3$	Dioxan, benzaldehyde, hexamethylphosphoramide, tributylphosphate, trimorpholinophosphine oxide and thf	29–31, 39–41
$Sc(NCS)_3(L)_3$	dmso, dmf, Ph_3PO, Ph_3AsO, pyNO, 2-picNO, 3-picNO, 4-picNO, and lutNO	3
$ScCl_3(L)_2$	Dioxan, acetone, thf, dmf, and ethylacetate	39, 42
$ScCl_3(L)$	Acetophenone, benzophenone	39

Only a few complexes of scandium(III) with neutral oxygen donor ligands have been characterized (see Tables 1 and 2) with most of these appearing in the literature only recently Crawford and Melson[3] have recently reported complexes of general formula

TABLE 2

Scandium perchlorate, tetrahydroborate, and nitrate complexes with neutral oxygen donor ligands

Complex	Ligand (L)	Ref
$Sc(ClO_4)_3(L)_6$	dmso, dmf, dma, pyNO, 2-picNO, urea hexamethylphosphoramide, and thioxane oxide	9, 14, 26, 30, 38
$Sc(NO_3)_3(L)_6$	Urea	38
$Sc(ClO_4)_3(L)_4$	Ph_3PO	32
$Sc(ClO_4)_3(L)_4\ 7H_2O$	Dioxan	43
$Sc(ClO_4)_3(L)_3$	$bipyO_2$, dpO_2, and daO_2	32
$Sc(BH_4)_3(L)$	thf	44

Abbreviations dpO_2 = 1,2-bis(diphenylphosphinyl)ethane, daO_2 = 1,2-bis(diphenylarsinyl)ethane, $bipyO_2$ = 2,2′-bipyridyl-1,1′-dioxide, dma = dimethylacetamide

$Sc(NCS)_3L_3$ where L is dimethylsulfoxide, *N,N*-dimethylformamide, triphenylphosphine and arsine oxides, pyridine-*N*-oxide, 2-, 3-, and 4-picoline-*N*-oxides, and 2,6-lutidine-*N*-oxide The observed frequencies for the characteristic vibrations of the thiocyanate group in these complexes indicate the presence of nitrogen coordinated thiocyanate in all the compounds[4-8] The conductance of the complexes in acetone indicate slight ionization with the exception of $Sc(NCS)_3(Ph_3AsO)_3$ which is considerably more dissociated into ionic species than the others In chloroform, however, $Sc(NCS)_3(Ph_3AsO)_3$ and the other complexes that were sufficiently soluble to enable conductance measurements to be made, were not ionized It can, therefore be concluded that the complexes are neutral, six-coordinate species with both ligand and thiocyanate coordinated and can thus be formulated $[Sc(NCS)_3L_3]$

For $[Sc(NCS)_3(dmso)_3]$, $\nu(S{=}O)$ is decreased from the free ligand value on coordination This coupled with the observation that the asymmetric $\nu(C{-}S)$ mode of dimethylsulfoxide is increased on coordination confirms that coordination is through the oxygen atom[9-13] The complexes $[Sc(NCS)_3(dmf)_3]$, and those containing pyridine-*N*-oxide and its alkyl substituted derivatives all show a decrease in $\nu(X{-}O)$ relative to the free ligand value, indicating oxygen coordination[13-22] The $\nu(As{-}O)$ mode in $[Sc(NCS)_3(Ph_3AsO)_3]$ is at a higher frequency than in the free ligand, however, it has been found that on coordination $\nu(As{-}O)$ may increase[23,24], or decrease[25] in frequency depending on the magnitude of the coupling between the As–O and M–O bonds

The use of an anion that has non- or very weak coordinating properties, such as the perchlorate ion, might be expected to bring out the maximum coordination number of a metal ion in its complexes with various ligands Recent studies with lanthanide perchlorates and oxygen donor ligands have shown that the coordination number varies with ionic size, values from six to nine being reported[10,11,13,26-28] This variation has been considered to be a necessary consequence of the different crystal radii of the lanthanide species

On the other hand, ligands such as hexamethylphosphoramide[29,30] and trimorpholinophosphine oxide[31] exhibit a constant coordination number (apparently six) for all the lanthanides, scandium, and yttrium. In the former case this is attributed to the steric bulk of the ligand preventing the metal ions from achieving their maximum coordination number, however, in the latter case effects other than steric hinderance are reported to be involved.

In view of the smaller size of scandium(III) compared with any of the trivalent lanthanide ions, it is expected to exhibit a maximum coordination number on the low end of the range observed for the lanthanides Crawford and Melson[32] have reported the characterization of several complexes with scandium(III) perchlorate of general formula $Sc(ClO_4)_3L_6$ (L = dimethylsulfoxide, *N,N*-dimethylformamide, pyridine-*N*-oxide, and 2-, 3-, and 4-picoline-*N*-oxides), $Sc(ClO_4)_3L_4$ (L = triphenylphosphine oxide), and $Sc(ClO_4)_3L_3$ [L = 2,2′-bipyridyl-1,1′-dioxide, 2,2-bis(diphenylphosphinyl) ethane, and 1,2-bis-(diphenylarsinyl) ethane] The characteristic perchlorate absorptions indicate that with the exception of $Sc(Ph_3PO)_4(ClO_4)_3$ all complexes contain ionic perchlorate with T_d symmetry[33] The infrared mull spectrum of $Sc(Ph_3PO)_4(ClO_4)_3$ exhibits a complex series of bands in the regions of perchlorate absorption. It is concluded that in this complex, coordination of some of the perchlorate ions takes place[34] In solution, the infrared spectrum is different and closely resembles those found for the complexes containing only ionic perchlorate, thus solvolysis of the coordinated perchlorate must take place. This is consistent with the observation that this complex behaves as a 3 1 electrolyte in solution All the other complexes reported also behaves as 3 1 electrolytes, therefore, the coordination number suggested by the vibrational spectra and conductivity data for these complexes is six In $Sc(Ph_3PO)_4(ClO_4)_3$ unidentate coordination of two perchlorate ions in addition to the four triphenyl phosphine oxide ligands would satisfy this coordination number

Edwards et al [26] observed a coordination number of six for scandium(III) in their study of complexes of transition and non-transition metal ions with thioxane oxide Yttrium(III) and cerium(III) exhibited coordination numbers of nine with this ligand The fact that similar ligands only result in six-coordinate complexes with scandium(III), even when a large excess of ligand is employed, can be attributed to the smaller ionic size of the scandium(III) ion

If the oxygen donor ligands are considered as single particles then the idealized symmetry for the $[ScL_6]^{3+}$ cation will be O_h, and one infrared active, Raman-inactive scandium–oxygen stretching mode (F_{1u}) is expected Crawford and Melson [32] observed an infrared-active, Raman-inactive band in the region of 450 cm^{-1} which they assigned to the scandium–oxygen stretching mode Earlier, Kutek and Petru [9] erroneously assigned a band in this region of the infrared spectrum of $Sc(dmso)_6(ClO_4)_3$ to a perchlorate mode

A lowering of the symmetry from O_h will give rise to differences in the vibrational spectra associated with scandium–oxygen modes A recent study [35] of dimethylsulfoxide complexes $[M(dmso)_6]^{n+}$ has led to the conclusion that the point group symmetry of the cation is either D_{3d} or S_6 depending on the configuration of the ligand Both symmetries predict two infrared-active, Raman-inactive ν(M–O) vibrations For $[Sc(dmso)_6](ClO_4)_3$ the broad asymmetric absorption band in the infrared spectrum at ca 450 cm^{-1} is assigned to ν(Sc–O) [32] This band is probably composite in nature and a consideration of ν(Sc–O) alone does not provide conclusive evidence for deviation of the cation from O_h symmetry However, the infrared and Raman active symmetric and antisymmetric CSO deformations, assigned to bands at 384 and 333 cm^{-1} in the free ligand are shifted to 357 and 336 cm^{-1} in the complex Thus $[\delta'(CSO) - \delta''(CSO)]$ decreases from 51 cm^{-1} in the free ligand [36] to 21 cm^{-1} in the complex cation This behavior has been attributed [35] to the existence of an S_6 point group for $[M(dmso)_6]^{n+}$ Similar deviations from O_h symmetry are to be expected in the other complexes containing $[ScL_6]^{3+}$ cations

The observed decrease of ν(S=O) on coordination in $[Sc(NCS)_3(dmso)_3]$ [3] and $[Sc(dmso)_6](ClO_4)_3$ [32], (50–60 cm^{-1}) is comparable to that found for dimethylsulfoxide complexes of the lanthanides, but less than with tervalent transition metal ions, where shifts up to 120 cm^{-1} are observed [12] The observed decrease of 30–40 cm^{-1} in ν(N–O) for $[Sc(bipyO_2)_3](ClO_4)_3$ [32] from 1255 cm^{-1} in the free ligand also closely resembles those found for lanthanide complexes [28]. A similar observation was reported by Donoghue et al [29,31] in their investigation of complexes of scandium(III) and the tervalent lanthanides with hexamethylphosphoramide and trimorpholinophosphine oxide In general, for the vibrational data currently available, the order of metal–ligand interaction is transition metal(III) > scandium(III) > lanthanide(III). Scandium(III) will form stronger complexes than the lanthanides due to its smaller ionic size and thus greater polarizing ability, but weaker complexes than tervalent transition metals because of its slightly larger size

(ii) β-Diketonates

Among the oxygen donor ligands, those containing the carbonyl group offer a potential site of coordination. The β-diketones which predominantly exist as enolic tautomers have a replaceable hydrogen atom and react with tervalent metal ions such as scandium(III) to form neutral tris-bidentate complexes. A number of complexes of scandium(III) with various β-diketones have been prepared (Table 3). In general, as will be pointed out later, these complexes have properties more closely related to those of the 3*d* transition metal β-diketonates than those of the lanthanide compounds.

TABLE 3

β-Diketonate complexes of scandium(III)

Complex	Melting point (°C)	Ref
$Sc(acac)_3$	187–190	49, 54, 60, 66, 69, 70
$Sc(tfaa)_3 \cdot 3H_2O$	124–126	49
$Sc(hfaa)_3$	116–117	49
$Sc(dpm)_3$	152–156	49, 65
$Sc(bza)_3$	205	71
$Sc(dbm)_3$	248	71, 72
$Sc(tta)_3$	147–149	71–73
$Sc(Br\text{-}acac)_3$	180 dec	66
$M[Sc(hfaa)_4]$ (M = K, Rb, Cs)	227, 231 and 240, respectively	74
$Sc(acac)_3 \cdot 2CHCl_3$		56
$Sc(acac)_3 \cdot 2CH_2Br_2$		56
$Sc(tta)_3$ phen	213	73
$Sc(tta)_3$ bipy	179	73

Abbreviations: tfaa = trifluoroacetylacetone, hfaa = hexafluoroacetylacetone, dpm = dipivaloylmethane, bza = benzoylacetone, dbm = dibenzoylmethane, tta = 2-thenoyltrifluoroacetone, phen = 1,10-phenanthroline, bipy = 2,2′-bipyridyl, acac = acetylacetone, Br-acac = γ-bromoacetylacetone.

The acetylacetonate of scandium(III), $Sc(acac)_3$, like those of the tervalent 3*d* transition metal ions, is thermally stable and sublimable. A heat of sublimation for $Sc(acac)_3$ of 23.8 kcal mole^{-1} has been reported by Melia and Merrifield[45,46]. This is comparable to the heats of sublimation of the isomorphous iron(III) and vanadium(III) compounds[46–48] of 23.6 and 24.6 kcal mole^{-1}, respectively. The lanthanide chelates of acetylacetone are not volatile and decompose on heating. Berg and Acosta[49] have attributed this lack of volatility to the fact that only hydrates of the lanthanide chelates are formed which decompose on heating in vacuo to form basic polymeric compounds. The anhydrous complexes of scandium, yttrium, and the lanthanides with hexafluoroacetylacetone and dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione) are all thermally stable and volatile, and are utilized in the separation of mixtures. It was noted that the volatility of these chelates increased with a decrease in the ionic size of the central metal ion.

The acetylacetonates of the lanthanides form unstable addition compounds with bases such as ammonia and organic amines and exist as both monomers and dimers in non-aqueous solvents[50–53], whereas scandium acetylacetonate neither combines with ammonia nor exhibits association in solvents such as chloroform or benzene[54]. Dimeric acetylacetonate species of scandium and other 3*d* transition metals have been detected in the mass spectra of their vapors[55], and addition compounds of scandium acetylacetonate with chloroform and dibromomethane have been reported by Clark et al [56] The strength of the bonds binding the halomethane molecules in these compounds, however, is rather small (from 3 to 5 kcal mole^{-1}) and is of the order of a dipole–dipole interaction The bonding is attributed to hydrogen bonding of the halomethane to the carbonyl oxygens of the acetylacetone rather than to coordination to the central metal ion. This was supported by preliminary NMR studies Kononenko et al [73] have reported adducts of the type $Sc(tta)_3$ L (L = phen and bipy) where they suggest that the amine is coordinated, however they offer no evidence to support this

A comparison of the first formation constants (K_1) for the acetylacetonates of scandium(III), yttrium(III) and lanthanum(III) shows a regular decrease in going from scandium to lanthanum[57], a reflection on the increasing size of the central metal ion Log K_1 for the lanthanide chelates[2,57] varies from 6 2 to 5 0 whereas that for the scandium compound is approximately 8[57 58] (log K_1 for the isomorphous iron(III) compound is 9 3)

Attempts to correlate stability constants with variations in the carbonyl stretching frequency of β-diketonates have met with varying degrees of success (see, for example, ref 59) This is in part due to confusion in the assignment of the carbonyl stretching frequency[60–63] Some researchers assign the highest frequency band in the 1600 cm^{-1} region of the infrared spectrum to the C=C stretching mode of the chelate ring whereas others assign it to the carbonyl stretching mode The latter assignment appears to be the one that is presently accepted, however in either case, the correlation is at best only qualitative For reports of infrared as well as electronic spectral data on various β-diketonates of scandium consult the references cited in Table 3

The results of an X-ray analysis of Fe(acac)$_3$ by Roof[47] led to the conclusions (1) that the six-membered chelate ring is planar with C_{2v} symmetry, and (2) that the ring C–C and C–O bonds are intermediate between single and double bond distances (1 39 Å and 1 28 Å respectively) These results provide strong evidence for the existence of resonance in the chelate ring and Calvin and Wilson[64] have suggested that the M–O bond is part of this resonance system i e , benzenoid resonance The C–H stretching mode of the ring proton moves to slightly higher frequency on chelation and lies somewhat toward the aromatic side lending support to benzenoid resonance. However, the NMR spectrum of Sc(dpm)$_3$ [65] has an absorption attributed to the ring proton at 4 22τ whereas aromatic protons absorb at approximately 2 65–2 85τ Also in an NMR study of several diamagnetic acetylacetonates by Holm and Cotton[66], a chemical shift of only +0 70 ppm (relative to pure water) was observed for the ring proton of scandium acetylacetonate No large positive shift of the order of +2.50 ppm observed for benzene protons was found, but they conclude that this does not preclude benzenoid resonance since little is known concerning proton shifts in heteroaromatic rings

The reactions that metal acetylacetonates undergo have also been cited as evidence for aromatic character[67], however, Kluiber[68] has noted that the ring bromination of Cr(acac)$_3$ proceeds without any ring cleavage and that there is no significant decrease in reactivity of the γ-carbon on complexation. Presumably, scandium acetylacetonate and the other chelates studied react similarly. On the basis of this experimental evidence he concludes, assuming electrophilic substitution, little if any aromatic character exists Thus, an enolate type resonance is probably sufficient to account for the structural features and reactivity of the chelate ring

(iii) Carboxylates

In general, when carboxylate ions are added to an aqueous scandium solution, a sparingly soluble salt is precipitated, however the use of carboxylates such as the oxalate for gravimetric analytical procedures is unsuitable since in the presence of an excess of the anion, soluble complexes are formed. Normal carboxylate salts are difficult to obtain due to the ease of hydrolysis of the scandium ion, thus basic or oxysalts, which will not be discussed in this section, are often isolated

Head and Holley[75] have reported the preparation of scandium formate by extraction of the hydroxide in a Soxhlet apparatus with aqueous formic acid solution On heating, they found that the compound decomposes directly to the oxide, unlike the decomposition of the formates of lanthanum and cerium which pass through an intermediate of the type M_2O_3 6CO[76] An X-ray diffraction study of scandium formate[77] indicates that its crystal structure is monoclinic, space group $P2_1/c$, with a = 10 316 ± 0 001 Å, b = 6 622 ± 0 0006 Å, and c = 8 940 ± 0 001 Å The scandium ions are six-coordinate in a polymeric framework with the formate ions acting as bridging groups The formate ions in the plane are bonded with a syn—anti configuration and those joining the planar layers have an anti—anti configuration This polymeric layer-like or framework structure is a common feature in the formates of transition metals

The triacetate can be prepared by the reaction of scandium chloride[39] or nitrate[78] with acetic anhydride The mono- and trichloroacetate analogs are prepared by reaction of the hydroxide (or hydrated oxide) with the corresponding acid[79,80] The infrared spectrum of the triacetate from 3400 to 600 cm^{-1} has been measured by Grigorev and Maksimov[78] They assume that the scandium ion has a coordination number of six with each acetate ion functioning as a bidentate ligand, i e D_3 symmetry They interpret their results to indicate that the bonding in scandium acetate is more covalent than in the corresponding lanthanum and cerium salts, and that the symmetry of the molecule is distorted somewhat from D_3 toward C_3.

Scandium oxalate can be precipitated from solutions of scandium salts by the addition of oxalic acid, but precipitation is never complete due to formation of complexes Vickery's experiments[81] with ion-exchange resins give evidence for the formation of complex anions containing scandium and oxalate ions in the ratios of 1 2 8 at pH 6 1 and 1 1 32 at pH 8, and spectrophotometric measurements by Dubovenko[82] show the presence of $Sc(C_2O_4)^+$ and $Sc(C_2O_4)_2^-$ ions at a pH of approximately 2 and 5, respectively. Ivanov-Emin and Gridasova[83] noted that in systems with potassium, rubidium, cesium, and ammonium oxalates raising the Sc^{3+} to $C_2O_4{}^{2-}$ ratio to 1 2 produced sparingly soluble dioxalatoscandates, however, a further increase in the alkali metal oxalate concentration gave readily soluble trioxalatoscandates

Sterba-Bohm and Skramovsky[84] have reported the isolation of the sodium, potassium and ammonium dioxalatoscandates, $MSc(C_2O_4)_2$ $2H_2O$, with the rubidium and cesium analogs being reported by Ivanov-Emin et al.[85]. On heating, these compounds lose two molecules of water to form the anhydrous species[86]. Although the stoichiometry of the anhydrous compounds indicates a coordination number of four for scandium, it is unlikely that this is the case, in view of its strong tendency toward six coordination Possible support for this supposition can be found in the results obtained with the dioxalate compounds of titanium, $MTi(C_2O_4)_2$ $2H_2O$ ($M = K$, Rb or NH_4) Recent infrared evidence[87] suggests that, although the water molecules are not bound to the metal, the complexes behave as though they are oxalate bridged polymers with the metal atom in an octahedral environment

Wirth[88] has reported the isolation of the trisoxalatoscandates of sodium, potassium, and ammonium, however, in the case of the ammonium species, Sterba-Bohm and Skramovsky[84] found that only the dioxalato compound could be isolated Both the sodium and potassium compounds are isolated as hydrates, $Na_3Sc(C_2O_4)_3$ $6H_2O$ and $K_3Sc(C_2O_4)_3$ $4H_2O$ The sodium compound loses two moles of water on drying over $CaCl_2$[85] and both compounds are completely dehydrated on heating[86]

The addition of oxalic acid to a solution containing scandium ions results in the precipitation of $Sc_2(C_2O_4)_3$ nH_2O The degree of hydration of this precipitate has been the subject of much disagreement in the literature with values for n of 1–6, 10, 12, and 18 being reported[75,81,84,89–97] Sterba-Bohm and Skramovsky[84] have observed that minor quantities of alien ions grossly affect the nature of the precipitated oxalate, and Vickery[81] found that the moist oxalate readily absorbs ammonia and carbon dioxide These observations could account for the various degrees of hydration reported since many of the products reported were dried in air and the scandium employed by several of the early workers was contaminated with thorium Vickery, by carrying out all operations in an inert atmosphere, isolated the 3-, 6- and 18-hydrate Klein and Bernays[95] have also isolated the hexahydrate by drying the precipitated oxalate over anhydrous calcium chloride in a desiccator

The infrared spectra of the hydrated bis- and trisoxalatoscandates cited above, and the trihydrate of scandium oxalate have been measured by Gridosova et al [98]. They note that the frequencies and intensities of the absorption bands in the infrared spectra of these compounds are quite similar and agree closely with those observed in the spectra of simple alkali metal oxalates (i e , they are ionic salts), however, the electronic spectra of these compounds indicated that the bonding has some covalent character

Several other carboxylates of scandium such as the lactate[99], malonate and succinate[100,101], malate[102], gluconate[103], trimellitate[104], and mellitate[105] have been reported, however, these reports include very limited amounts of physical data and no conclusions with regard to their coordination chemistry are given.

(iv) Alcoholates

Scandium chloride is much more soluble in alcohols than are yttrium and the tripositive rare earth metal chlorides[106] Kirmse[107] in a study of the solubility of scandium chloride in a series of straight-chain alcohols (methanol–nonanol) reported that the solubility corresponded to six molecules of the alcohol being associated with each molecule of the halide. The solid adducts isolated from these solutions (denoted by brackets in Table 4) contain less alcohol. Funk and Koehler[39] have shown that the presence of a base such as ammonia in alcoholic solutions of scandium chloride leads to the formation of the corresponding alkoxide

TABLE 4

Alcohol adducts of general formula $ScX_3 \cdot nROH$

ROH	*n*	X	Ref
Methanol	4, (3), 2	Cl	107, 108
Methanol	5,4	Br	108
Ethanol	3 5 (3), 2	Cl	107, 108
Ethanol	4 3	Br	108
Ethanol	3	SCN	109
1-Propanol	(4), 3,2	Cl	107, 108
2-Propanol	1	Cl	108
1-Butanol	(3), 2	Cl	107, 108
1-Pentanol	(4), 3, 2	Cl	107, 108
1-Hexanol	(3), 2	Cl	107, 108
1-Heptanol	(4) 3	Cl	107
1-Octanol	(4), 3	Cl	107
1-Nonanol	(3)	Cl	107
Benzyl alcohol	3, 2	Cl	108
Allyl alcohol	4, 2	Cl	108
Cyclohexanol	2	Cl	108

A variety of alcohol adducts have also been prepared by the reaction of scandium chloride or bromide with alcohol vapors[108] The reported adducts were determined from the isothermal decomposition of the alcohol-saturated halide at varying pressures. Since little more than analytical data are given in all cases cited, no conclusions with regard to coordination number or symmetry of "complexes" formed can be given A comprehensive list of the reported alcohol adducts is given in Table 4

(v) Hydroxoscandates

The addition of hydroxyl ions to solutions of simple scandium salts precipitates the white, gelatinous hydroxide. Ivanov-Emin and Ostroumov[110] reported that the precipitation incidence of scandium hydroxide takes place at a pH of 4 8—4 9 Vickery[111] later confirmed this observation and reported that the solubility of the hydroxide is pH-dependent in the alkaline region, an indication of its amphoteric properties Sterba-Bohm[112] first detected this amphoteric behavior during studies on the separation of tungsten from scandium, and later he and Melichar[113] isolated the compound $K_2[Sc(OH)_5H_2O] \cdot 3H_2O$ from a solution of scandium hydroxide in potassium hydroxide Ivanov-Emin et al[114] reported the isolation of an identical compound during studies on the solubility of scandium hydroxide in potassium hydroxide solutions and concluded that its infrared spectrum was consistent with the proposed structure

Several other hydroxoscandates have been isolated in recent years. Ivanov-Emin and Ostroumov[115] reported the separation of $Na_3[Sc(OH)_6]\ 2H_2O$ from an aqueous solution o scandium and sodium hydroxides This compound which readily absorbs carbon dioxide and water crystallizes as plates belonging to the orthorhombic system Ivanov-Emin and Nisel'son[116] reported that this compound loses water of crystallization at 100–120° and decomposes to the tetrahydroxoscandate and alkali at a slightly higher temperature At 256° decomposition of the tetrahydroxo species to sodium metascandate, $NaScO_2$, begins and is complete at 300° They also reported the thermal decomposition of the potassium analog, and observed it to be similar to that of the sodium compound.

The anhydrous analogs of the above hexahydroxoscandates have been prepared[117] by the reaction of anhydrous scandium chloride with alkali in absolute methanol These compounds are identical with those obtained from the dehydration of the hydrated species as inferred from their infrared spectra

Some alkaline earth hydroxoscandates isolated from the reaction of sodium hydroxoscandate with the appropriate alkaline earth hydroxide in aqueous solution have also been reported[118] Chemical analysis of the compounds indicated the following compositions $Ca_3[Sc(OH)_6]_2$ $Ca[Sc(OH)_4]_2\ 2H_2O$ $Sr[Sc(OH)_4]_2\ 2H_2O$, and $Ba_3[Sc(OH)_6]_2$ These hydroxo salts are white crystalline powders which are stable when stored in a desiccator over potassium hydroxide

The existence of the tetrahydroxoscandate of barium is inferred from the thermogravimetric analysis of the hexahydroxo species The thermal stability of the alkaline earth hydroxoscandates was found to increase from calcium to barium and comparison of the alkali and alkaline earth hydroxoscandates shows that the former are much more stable

The infrared spectra of the alkaline earth hydroxoscandates are similar to those obtained for the sodium and potassium analogs Both show a broad band in the region 3100–3500 cm^{-1}, an intense band in the range 850–1150 cm^{-1}, and a second broad band centered at ca 450 cm^{-1} Arkhangel'skii et al [119], from a study of several hydroxo compounds of scandium, have assigned bands observed at 3250 cm^{-1} and 932 cm^{-1} to stretching and bending modes associated with the hydroxyl groups, respectively An absorption band observed at 460–470 cm^{-1} was assigned to the Sc–O stretching mode Similar assignments can be made for the bands observed in the infrared spectra of hydroxoscandates

Due to the great tendency for the Sc^{3+} ion to form six-coordinate species, the $[Sc(OH)_6]^{3-}$ ion present in the above compounds, undoubtedly contains each hydroxyl ion as a unidentate ligand Water present in the hydrated hexahydroxoscandates would be water of crystallization and not coordinated water, however, in the case of species containing the $[Sc(OH)_4]^-$ group, six coordination is probably achieved through coordination of the two water molecules present in these compounds This can neither be verified nor discounted on the basis of published data

As observed in other six-coordinate scandium compounds the $[Sc(OH)_6]^{3-}$ ion is probably distorted from pure octahedral symmetry with this distortion giving rise to the observed broadness of the infrared band assigned to the Sc—O stretching mode This supposition is supported by the observations of Sipachev and Grigor'ev[120] in their studies of the infrared and Raman spectra of the hexaquocation of scandium

Although the chemistry of scandium is quite generally parallel to that of the rare earth elements[121], the isolation of compounds like $Na_3[Sc(OH)_6]$ indicates the amphoteric behavior of its hydroxide Yttrium and the rare earth metal hydroxides are much less acidic[122]

C COMPLEXES WITH NITROGEN DONOR LIGANDS

(i) *Ammonia*

In 1955, Vickery[111] attributed the incomplete precipitation of scandium hydroxide by ammonium hydroxide to the formation in solution of hexamminoscandium(III) ions $[Sc(NH_3)_6]^{3+}$ rather than to the presence of carbonates in the ammonia solution as suggested by Fischer and Bock[123] The absorption of ammonia by scandium oxalate trihydrate or hexahydrate at 25° leads to the formation of the anhydrous compound $[Sc(NH_3)_6]_2(C_2O_4)_3$, also proposed to contain scandium(III) ions[81] If the oxalate 18-hydrate is used, a dodecahydrate, $[Sc(NH_3)_6]_2(C_2O_4)_3$ $12H_2O$ is obtained Replacement of six-coordinated water molecules by ammonia was proposed to account for this behavior No absorption of ammonia was observed under anhydrous conditions, although an exothermic reaction was initiated when water was introduced into the system The reaction of anhydrous scandium acetate with liquid ammonia in a sealed ampoule at room temperature followed by volatilization of excess ammonia, however, leads to the isolation of a compound with composition $2[Sc(OOCCH_3)_3]$ $3NH_3$ for which a polymeric structure was suggested[124] The reaction of scandium halides with ammonia have been studied in more detail particularly by Russian workers Although anhydrous ScF_3 does not react with dry gaseous ammonia, the action of ammonia at 6–7 atm pressure on ScF_3 $0\ 25H_2O$ gives a product containing 6 28% NH_3 corresponding to a composition ScF_3 $0\ 4NH_3$[125] Part of this ammonia is lost in air but when heated at 105°, anhydrous scandium fluoride is obtained In contrast to the unreactivity of the fluoride, a compound of composition $ScCl_3$ $5\ 75NH_3$ was proposed as the product from the reaction of anhydrous scandium chloride and liquid ammonia[126] No further investigations of this compound have been made however Tananaev and Orlovskii[127] showed that anhydrous scandium chloride bromide and iodide all absorb ammonia to give products containing between 7 and 8 molecules of ammonia per scandium halide The behavior of the chloride and bromide derivatives in the presence or absence of moisture was described and the thermal stability of the products with all three halides investigated in a dry argon atmosphere[128] (Fig 1)

A study of the infrared spectra (2000–400 cm^{-1}) of some of the chloride and bromide compounds has been made[129] By comparison of the spectra of deuterated and non-deuterated ScX_3 $5NH_3$, ScX_3 $4NH_3$ and ScX_3 $2NH_3$ (X = Cl, Br) it was concluded that these compounds contain coordinated ammonia Assuming a coordination number of six for scandium, the formulas $[Sc(NH_3)_5X]X_2$ and *trans*-$[Sc(NH_3)_4X_2]X$ were assigned to the species containing five and four ammonia molecules, respectively The compounds $ScX_3.2NH_3$ may be di- or polymeric with halogen bridges. Recently, bands in the region 380–430 cm^{-1} have been observed in the spectrum of $ScCl_3$ $5NH_3$ and assigned to Sc–N stretching vibrations[130] A detailed study of the infrared spectra of the above complexes, particularly in the far infrared region should enable more definite conclusions concerning their structures to be drawn The "hydrated" compounds were shown not to contain

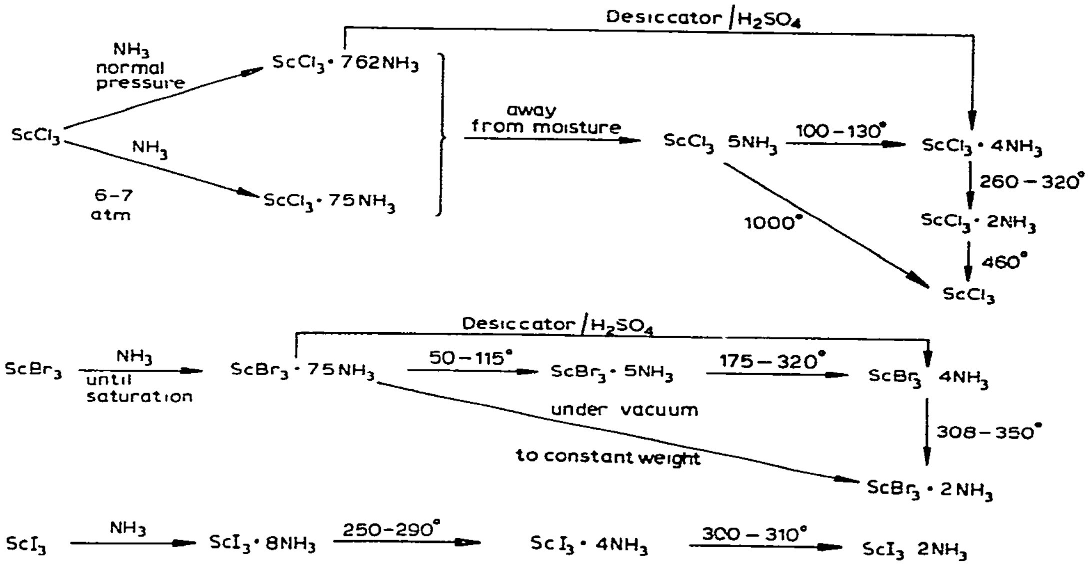

Fig 1 Ammonia adducts of scandium(III)

coordinated ammonia, but to be a mixture of scandium hydroxide and ammonium halide, indicating hydrolysis of the ammine complexes takes place readily in air[127] Saturation of hydrated scandium chloride with ammonia also gives a similar mixture, with uncoordinated ammonia In the light of these results, it appears doubtful that the $[Sc(NH_3)_6]^{3+}$ ion can exist in basic aqueous solution as suggested by Vickery[111]

The determination of ammonia pressure at 25°enabled the heats of formation of $ScCl_3$ $5NH_3$ and $ScCl_3$ $4NH_3$ to be calculated[131] (17 2 and 18 2 kcal $mole^{-1}$ respectively) The heat of dissociation for the reaction

$$ScCl_3\ 5NH_3 \rightleftharpoons ScCl_3\ 4NH_3 + NH_3$$

was estimated to be 13 2 kcal $mole^{-1}$ Isotherms for the decomposition of $ScCl_3$ 7 $78NH_3$ and $ScBr_3$ 7 58 NH_3 suggest the existence of compounds ScX_3 $7NH_3$ (X = Cl, Br) not detected by thermogravimetric analysis

(ii) Primary, secondary and tertiary amines

Several compounds have been obtained from the reaction of anhydrous scandium halides with primary, secondary and tertiary amines, but little physical data have been obtained on these species and no conclusions have been drawn concerning their structure The reported compounds are summarized in Table 5 Firsova et al[37] measured the infrared spectra of some of the compounds For those with primary amines, a decrease in both $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ of the ligand was observed suggesting coordination through the nitrogen atom However, with $(CH_3)_2NH$, $H_2\overline{C(CH_2)_4N}H$ and $(C_2H_5)_2NH$, $\nu(NH)$ was found to increase and with $(CH_3)_3N$ a rise of 31 cm^{-1} was observed for $\nu(C-N)$ In the

TABLE 5

Complexes of scandium halides with primary, secondary and tertiary amines

Amine ligand (L)	Formula of complex*	Ref
$C_2H_5NH_2$	$ScCl_3$ 2L	132
n-$C_3H_7NH_2$	$ScCl_3$ 3L	132
n-$C_4H_9NH_2$	$ScCl_3$ 2L	132
i-$C_5H_{11}NH_2$	$ScCl_3$ 3L	37
$C_6H_5NH_2$	$ScCl_3$ 2L and $ScCl_3$ 3L	37
$C_6H_5CH_2NH_2$	$ScCl_3$ 2L and $ScCl_3$ 5L	37
2-Napthyl NH_2	$ScCl_3$ 2L and $ScCl_3$ 3L	37
$NH_2(CH_2)_2NH_2$	$ScCl_3$ 3L	133
$NH_2(CH_2)_2NH_2$	$ScCl_3$ 2L and $ScCl_3$ 5L	134
$(CH_3)_2NH$	$ScCl_3$ 2L	132
$(CH_3)_2NH$	$ScCl_3$ 3L	37
$(C_2H_5)_2NH$	$ScCl_3$.3L	37, 132
$(C_2H_5)_2NH$	ScX_3 4L	133
$(i\text{-}C_3H_7)_2NH$	ScX_3 L	133
$(n\text{-}C_4H_9)_2NH$	$ScCl_3$ 3L	132
$(n\text{-}C_5H_{11})_2NH$	$ScCl_3$ 3L	132
$H_2\overline{C(CH_2)_4N}H$	ScX_3 4L	135, 136
$H_2\overline{C(CH_2)_4N}H$	$ScCl_3$ 3L	37
$(C_2H_5)_3N$	ScX_3 L	37, 132 134

*X = Cl, Br

latter compound, a band assigned to ν(N—H) must arise from impurity in both the ligand and scandium adduct The products of the reaction between ethylenediamine and scandium chloride depend on the conditions under which the reaction is carried out If anhydrous $ScCl_3$ and anhydrous ethylenediamine are mixed in a 1 6 ratio, a white powder of indefinite composition is obtained[134] Heating this product to 150° or maintaining a temperature of 120° for fifteen hours removes excess ethylenediamine and $ScCl_3(en)_2$ is obtained. With diethyl ether as solvent, $ScCl_3(en)_5$ can be isolated, which when heated to 150° also results in $ScCl_3(en)_2$ Thermogravimetric analysis failed to detect any intermediate species in this transition The insolubility of $ScCl_3(en)_2$ in organic solvents did not allow conductance studies to be made, but this species may exist as $[Sc(en)_2Cl_2]Cl$, analogous to the compounds containing *o*-phenanthroline and 2,2'-bipyridyl In absolute ethanol $ScCl_3(en)_3$ is obtained[133], while in aqueous solution, hydrolysis takes place and scandium hydroxide is precipitated[134]. Further investigations of the physical and chemical properties of the amine compounds should establish the type of coordination involved

Petru and Jost[135] reported that when anhydrous scandium chloride or bromide is placed in a desiccator in pyridine vapor, absorption of the amine by the halide takes place and $ScCl_3$ 2py and $ScBr_3$ 3py (py = pyridine) are obtained after pumping excess pyridine out of the desiccator The formulae proposed are based on the increase in weight of the halide only No absorption of pyridine was found when ScF_3 was used In anhydrous acetone the reaction between $ScCl_3$ and pyridine resulted in a compound of uncertain composition[136], although when scandium chloride is heated in an excess of pyridine for 1 h under anhydrous conditions and benzene or ether added, colorless plates of composition $ScCl_3$ 3py are obtained[37]

Recently, Greenwood and Tranter[137] carried out a much more thorough investigation of the products from the reactions between anhydrous scandium chloride or bromide and pyridine By dissolving the anhydrous halides in boiling pyridine, ScX_3 4py (X = Cl, Br) are obtained as white crystalline products after concentration of the filtered solution The infrared spectra of these compounds suggest the presence of both coordinated and uncoordinated pyridine Exposure to a vacuum causes one molecule of pyridine to be lost, the species ScX_3 3py obtained no longer exhibiting bands due to uncoordinated pyridine The formulae $[py_3ScX_3]$ py were suggested for the tetrapyridine compounds The chloro complex is a weak electrolyte in nitromethane, but the bromo species behaves as a 1 1 or an ion paired 1 2 electrolyte, suggesting the latter complex has a different structure The far infrared spectrum is also more simple for the bromo than for the chloro compound Similar data obtained for ScX_3 3py lead to the suggestion that the chloride has a hexacoordinated C_{3v} structure, 1 2,3-py_3ScCl_3, while the bromide has a distorted tetrahedral structure $[py_3ScBr]^{2+}(Br^-)_2$

The tetrapyridine complexes are thus derived from the above species by the addition of one uncoordinated pyridine molecule In the far infrared spectra of the complexes bands in the region 260–280 cm^{-1} are assigned to ν(Sc–N) with ν(Sc–Cl) and ν(Sc–Br) being assigned between 300–350 cm^{-1} and 266–268 cm^{-1}, respectively Compounds of the type ScX_3 2py reported by Petru and Jost[135] could not be isolated, although evidence for their formation was indicated by thermogravimetric analysis of the above compounds at high heating rates Firsova et al [37] suggested from infrared studies that in $ScCl_3$ 2-ampy, (2-ampy = 2-aminopyridine) coordination was through the nitrogen atom of the pyridine ring In the quinoline complex $ScCl_3$ quin and $ScCl_3$ 3 amquin coordination again is through the heterocyclic nitrogen atom in each case

In 1961, the compounds $ScCl_3$ 3phen, $ScCl_3$ 2bipy and $ScCl_3$ 2(4,4′-bipy) were prepared and shown to be 1 3 electrolytes in water[138] The infrared spectra of $ScCl_3$ 2bipy H_2O and $ScCl_3$ 2phen $4H_2O$ were measured as part of a study of the complexes formed between hydrated rare earth chlorides and bipyridyl and *o*-phenanthroline[139] The ν(Sc–N) vibrations assigned in the region of 280 cm^{-1} are considerably higher than found for the complexes with the rare earths, reflecting the greater polarizing power of the scandium ion No evidence was found for ν(Sc–Cl) vibrations, it being concluded that the metal–chloride link in these complexes is ionic and that some coordination of water molecules takes place

The anhydrous complexes $ScCl_3$ 2bipy and $ScCl_3$ 2phen were obtained from tetrahydrofuran solution by the reaction of anhydrous scandium chloride with the ligands in large excess[140] No evidence for the formation of $ScCl_3$ 3ligand was obtained The complexes behave as 1 1 electrolytes with strong ion-pairing in acetonitrile or nitromethane solution, similar to the corresponding titanium(III) species[141] From investigations of the infrared spectra, particularly in the far infrared region, the structures *cis*-$[Sc(bipy)_2Cl_2]Cl$ and *cis*-$[Sc(phen)_2Cl_2]Cl$ were assigned A series of thiocyanate derivatives were also obtained and characterized by infrared and conductivity measurements[140,142] The tris ligand complexes were assigned structures $[Sc(bipy)_3](NCS)_3$ and $[Sc(phen)_3](NCS)_3$ with the bis ligand species $[Sc(bipy)_2(NCS)_2]NCS$ and $[Sc(phen)_2(NCS)_2]NCS$ both being obtained as *cis* and *trans* isomers The thiocyanate ion is bonded to scandium through the nitrogen atom, $\nu(Sc-NCS)$ being assigned between 300 and 325 cm^{-1}. The positions of $\nu(Sc-Cl)$ and $\nu(Sc-NCS)$ are lower than those reported for $\nu(V-Cl)$ and $\nu(Cr-NCS)$, indicating a weaker bond for the scandium complexes The positions of $\nu(Sc-N_{ligand})$ are similar to those discussed earlier The ability of the scandium ion to form *cis* and *trans* isomers is surprising in view of the expected lability of the ion and further investigations of these systems are in progress Recently, Russian authors have reported the isolation of *trans*-$[Sc(ligand)_2(NCS)_2]NCS$, (ligand = bipy or phen) from anhydrous alcoholic solution[143] and a compound $Sc_2(C_2O_4)_3 \cdot 2phen$ containing both coordinated oxalate and phenanthroline[144]

One of the few paramagnetic compounds of scandium was obtained by Herzog et al [145] in 1961 by the treatment of scandium chloride and bipyridyl in tetrahydrofuran with dilithiumbipyridyl The black crystals of composition $Sc(bipy)_3$ have a room temperature magnetic moment of 1 99 Bohr magnetons, indicating the presence of 1 unpaired electron The compound is oxidized by three equivalents of iodine and it was suggested that it contains scandium in a zero oxidation state Although little further work has been carried out on this interesting compound, similar species with other metal ions have been investigated in some detail X-ray structural investigation of the isomorphous compounds $Ti(bipy)_3$, $V(bipy)_3$ and $Cr(Bipy)_3$ indicate trigonally distorted octahedral structures, the distortion increasing in the order $Cr < V < Ti$, i e , with increasing size of the central metal atom[146] The effect of this distortion is to split the t_{2g} orbitals of the metal into $a_1 + e$ If the metals are assigned zero oxidation states and there is an appreciable separation between the a_1 and e orbitals, the magnetic moments observed for these species including scandium, may be accounted for There has been considerable discussion where the electrons in these "electron rich" compounds are located From measurements of the absorption spectra of some neutral bipyridyl compounds[147], it was suggested that for lanthanide derivatives, the electrons are mainly associated with the ligand, but for the Ti, V and Cr compounds, the spectra are dependent on the metal and some delocalization of the electrons onto the metal takes place For the iron compound, $Fe(bipy)_3$ the absorption spectra and ESR measurements appeared to lead to conflicting results, although it was still concluded that the compound contains iron in a zero oxidation state and neutral bipyridyl ligands[148] Lack of information on the scandium complex does not enable any conclusions to be drawn as to whether the species is $Sc(bipy)_3$, $Sc^{3+}(bipy^-)_3$, or whether an "intermediate" situation exists. A corresponding phenanthroline derivative $Sc(phen)_3$ is obtained by the reduction of $[Sc(phen)_2Cl_2]Cl$ by dilithium benzophenone in tetrahydrofuran solution[149] Like the bipyridyl compound, $Sc(phen)_3$ has a magnetic moment corresponding to one unpaired electron and is non-conducting in tetrahydrofuran

A series of isothiocyanato complexes of scandium $M_3[Sc(NCS)_6] \cdot nH_2O$ has been reported, first in 1927[150] and again more recently[151,152] From the positions of $\nu(C{\equiv}N)$ and $\nu(C-S)$, coordination through the nitrogen atom was established Attempts to isolate scandium thiocyanate have been unsuccessful and lead to solvated, hydroxy[153] or ill-defined products[3] The conditions of the extraction of scandium by thiocyanate ion have been known for some time[154] and various equilibria have been suggested[155,156] although the species extracted by ether from acidic or aqueous solution is not the simple thiocyanate $Sc(NCS)_3$ but probably an acidic, hydrated or hydroxy species[3] Scandium can also be extracted from aqueous thiocyanate solutions into chloroform or dichloroethane containing nitrogen donor ligands[157,158] The species $LH^+[Sc(NCS)_4L_2]$, (L = collidine) can be isolated from chloroform when collidine is used as the ligand With phenanthroline, a complex containing two moles of ligand is proposed as the species in the organic layer Scandium forms complexes containing three molecules of methyl, propyl or hexyl diantipyrinylmethanes at pH 2 The extraction of these species by chloroform from a thiocyanate system is specific for scandium[159]

Anhydrous scandium chloride is slightly soluble in acetonitrile and benzonitrile and the adducts $ScCl_3$ $3CH_3CN$ and $ScCl_3$ $3C_6H_5CN$ have been isolated from the solutions[39,42] Presumably the nitriles are coordinated to scandium through the nitrogen atom

Other complexes with nitrogen donors that have been investigated include a series of Schiff bases for which luminescent reactions were studied [160] and two brief reports on phthalocyanine compounds [161,162]. Extended Huckel calculations on ScOH porphin have suggested the compound should be stable but have an unusual visible–ultraviolet spectrum[163] Its synthesis has not yet been reported, however

D NITROGEN AND OXYGEN DONORS

The use of 8-hydroxyquinoline (HQ) for the gravimetric determination of scandium has been known for several years although the composition of the precipitate has been the subject of much discussion

Pokras and Bernays[164] found that the compound ScQ_3HQ was precipitated from aqueous solutions at pH 7 5 Attempts to remove the "extra" molecule of HQ by heating ScQ_3 HQ were not successful and no discontinuity corresponding to ScQ_3 was observed In benzene and toluene, the compound was completely dissociated into ScQ_3 and HQ, suggesting only weak forces were holding the extra HQ molecule[165] In ethyl alcohol, Moeller and Ramaniah suggested deviations from Beer's law were due to hydrolysis of ScQ_3 HQ to give ScQ_3 and HQ[166] Much of the early work on the complexation of scandium by HQ has been summarized in more recent papers[167,168] Cardwell and Magee[167] confirmed the composition of the precipitate from solutions of pH 6 5 as ScQ_3 HQ, but at pH 8 8, the compound $(ScQ_3)_2HQ$ was isolated Again thermogravimetric studies did not indicate a constant weight level corresponding to ScQ_3 occurred in either case The compound ScQ_3 3HQ was prepared by a solid phase reaction at 100–110° between ScQ_3 HQ and HQ On heating, HQ was lost to give a constant weight level corresponding to ScQ_3 HQ, which then behaved in a similar manner to the above two compounds.

Petronio and Ohnesorge[168], however suggest that the species precipitated from aqueous solution under the conditions used by Pokras and Bernays[164] is the unsolvated ScQ_3 Solutions of this compound in ethyl alcohol do not obey Beer's law in the near ultraviolet region and an equilibrium between a bis and tris species was proposed $\log K_3$ for the formation of ScQ_3 was estimated to be 9

If the precipitated compound is indeed the unsolvated species ScQ_3, the thermogravimetric data can be understood and the low results often obtained for the gravimetric determination of scandium by 8-hydroxyquinoline explained

If crystals of the precipitated compound can be obtained, an X-ray structure determination should finally resolve the question of its structure and enable the behavior in solution to be understood.

When 8-hydroxyquinoline and "scandium thiocyanate" ethereal solutions are mixed in a molar ratio of 4:1, a yellow precipitate corresponding to ScQ_2NCS is obtained[149]. Infrared spectra show that the thiocyanate is terminally nitrogen bonded, the spectrum remaining almost unchanged in tetrahydrofuran solution. The compound is non-conducting in THF and nitromethane, but weakly conducting in acetonitrile and *N,N*-dimethylformamide. Molecular weight measurements could not be obtained in THF, although in DMF, in which some ionization takes place, the data suggest the presence of a polymeric species. If the thiocyanate is bound only through the nitrogen atom, the scandium may be five-coordinate.

Three different complexes of scandium with the iminodiacetate ion, $[NH(CH_2COO^-)_2]$, ida, have been isolated, $[Sc(ida)]Cl\cdot 2H_2O$, $[Sc_2(ida)_3]\cdot H_2O$ and $K[Sc(ida)_2]\cdot 3H_2O$ depending on the reaction conditions[169,170,171]. All three species may be completely dehydrated by heating between 100 and 280°C. Infrared spectra of the hydrated, dehydrated and deuterated compounds have been measured and the conclusion was reached that in all the compounds the Sc–O bond is "ionic" and the Sc–N bond covalent. The strength of the Sc–N bond is suggested to decrease in the order $[Sc(ida)Cl > Sc_2(ida)_3 > K[Sc(ida)_2]$. No suggestions as to the structures of the compounds were put forward, however.

The stability constant, K, of the 1:1 complex of scandium with ethylenediaminetetraacetic acid, has been measured by a polyarographic technique[172], $K = 23.1 \pm 0.15$ at 20°C and $\mu = 0.1$. This value is greater than that found for the corresponding complex with yttrium (18.09 ± 0.04), lanthanum (15.50 ± 0.05) or lutetium (19.83 ± 0.07) but less than that with indium (24.95 ± 0.1) or ferric ion (25.1 ± 0.1), a correlation closely following changes in ionic size of the cations[173].

The $K[M(EDTA)]\cdot nH_2O$, M = Sc, Y, La and Lu have recently been reported, although no values for n were given[174]. The rate of ligand exchange for each species was measured by line broadening of the ^1H NMR spectrum of the ligand and the order $Sc < Lu < Y < La$ was found, which exactly reflects the decreasing values of K noted above.

A spectrophotometric study of complex formation between scandium, yttrium and lanthanum with diethylenetriaminepentaacetic acid[175] showed that stability constants for the 1:1 complexes decreased in the order $Sc > Y > La$ ($\log K_{Sc} = 26.28 \pm 0.37$, $\log K_Y = 21.95 \pm 0.03$, $\log K_{La} = 19.23 \pm 0.03$), again reflecting the increase in cationic size from scandium to lanthanum.

Amino acids are potentially capable of complex formation through both the nitrogen of the amine group and the oxygen of the carboxyl group, or through the carboxyl group only, depending on the pH at which the reaction takes place. At pH 6, $Sc(OH)_3$ does not dissolve in solutions of aminoacids and no compounds were synthesized in which both nitrogen and oxygen donor atoms are coordinated[176]. In weakly acidic solutions, however, several compounds containing scandium-oxygen bonds only were isolated: $ScGlut(GlutH)\cdot 3H_2O$, $Sc_2(Glut)(GlutH)_4\cdot 5H_2O$ ($GlutH_2$ = glutamic acid), $Sc_2(SO_4)_3(GlH)_4\cdot 5H_2O$ (GlH = glycine), $Sc_2(SO_4)_3(AlnH)_4$, (AlnH = alanine), $Sc_2(SO_4)_3(AmH)_3$, (AmH = aminobutyric acid), $Sc_2(SO_4)_3(NorH)_3$, (NorH = norleucine) and $Sc(SO_4)(GlutH)\cdot 2H_2O$.

If sulfuric acid is added to aqueous solutions of these compounds, or the reactions are carried out in dilute sulfuric acid, the amino acids are protonated and exist as cations with the scandium as a complex sulfate.

Pyramidone (pd)* reacts with scandium chloride, the complex $[Sc(pd)_4][B(C_6H_5)_4]_3$ being isolated on addition of sodium tetraphenylborate[177]. Infrared and ^1H NMR data suggest that the ligand is coordinated to scandium through the carbonyl oxygen and exocyclic tertiary nitrogen atom, making the scandium eight-coordinated Similar complexes were obtained with yttrium and some lanthanides The ability of scandium to form eight-coordinate species is not very great due to its relatively small size compared with the lanthanides, although some examples are known

E HALIDE COMPLEXES

The ability of the scandium ion to form complexes with fluoride ion has been known for many years Meyer[93] in 1914 isolated the colorless crystalline species $M_3[ScF_6]$, ($M = NH_4^+, Na^+, K^+$) by treatment of aqueous scandium solutions with ammonium, sodium or potassium fluoride Later, Sterba-Bohm[178] suggested the species $(NH_4)_2ScF_5$ and NH_4ScF_4 are intermediates in the decomposition of ammonium hexafluoroscandate to scandium fluoride in aqueous solution An X-ray diffraction study of $(NH_4)_3ScF_6$ showed that two modifications exist, an α form, found at high temperatures, of cubic symmetry and isostructural with $(NH_4)_3FeF_6$ and a β form of tetragonal symmetry which is the low temperature form[179] The thermal degradation of β-$(NH_4)_3ScF_6$ was studied by Hajek[180] who found that between 260 and 350°C the compound decomposed to give impure NH_4ScF_4 which in turn decomposed to ScF_3 between 350 and 440° All three compounds were proposed to contain ScF_6 octahedra, with NH_4ScF_4 containing four bridging fluoride ions Similar data for the thermal decomposition of $(NH_4)_3ScF_6$ were reported by Ivanov-Emin et al [181] These authors also investigated the solubility of ammonium hexafluoroscandate in ammonium fluoride solutions In solutions of high ammonium fluoride concentration $(NH_4)_3ScF_6$ is the stable species, but as the concentration is decreased, decomposition takes place and NH_4ScF_4 is obtained, indeed the latter compound may be prepared by dissolving $(NH_4)_3ScF_6$ in water and stirring for 48 h during which time crystals of ammonium tetrafluoroscandate separate from solution No species corresponding to $(NH_4)_2ScF_5$ or $(NH_4)_3Sc_2F_9$ described by Sterba-Bohm[178] were detected

Kury et al.[182] studied the complexing of scandium by fluoride ion in aqueous solution The data obtained were interpreted by assuming the presence of species ScF^{2+}, ScF_2^+, $ScF_3(aq)$ and ScF_4^- Equilibrium constants for the formation of these species were measured and the heat and entropy changes accompanying the reactions were calculated (see Table 6) The scandium complexes are more stable than the corresponding fluoride

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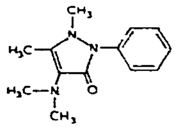
* Pyramidone =



complexes of Al^{III} or Fe^{III}, this greater stability arising from a more negative enthalpy term rather than from an entropy effect. Some possible explanations for this stability were put forward by these authors although none of them is really satisfying. Distribution diagrams for the fluoride complexing of scandium have been published using the above stability constant data[183].

TABLE 6

Halide complexing of scandium (III) in aqueous solution[182,192]

Reaction*	$K^{298}_{(\mu = 0)}$	$\Delta H^{298}_{(\mu = 0.5)}$ (kcal mole^{-1})	$\Delta S^{298}_{(\mu = 0.5)}$ (e.u.)
$Sc^{3+} + F^- \rightleftharpoons ScF^{2+}$	1.2×10^7	0.3	29 ± 3
$ScF^{2+} + F^- \rightleftharpoons ScF_2^+$	6.4×10^5	−1.5	19 ± 3
$ScF_2^+ + F^- \rightleftharpoons ScF_3(aq)$	3.0×10^4	−0.8	16 ± 4
$ScF_3(aq) + F^- \rightleftharpoons ScF_4^-$	7×10^2		
$Sc^{3+} + Cl^- \rightleftharpoons ScCl^{2+}$	90	−1.5	0 ± 2
$ScCl^{2+} + Cl^- \rightleftharpoons ScCl_2^+$	37	−1.7	−1 ± 4
$Sc^{3+} + Br^- \rightleftharpoons ScBr^{2+}$	120	−0.5	4 ± 2
$ScBr^{2+} + Br^- \rightleftharpoons ScBr_2^+$	10	−0.6	0 ± 2

*Coordinated water neglected

The work of Meyer[93] has recently been repeated and for the addition of ammonium, sodium or potassium fluoride to scandium solutions, the successive complexation by fluoride ions was again suggested[184,185]. The species $ScF_3 \cdot 0.16H_2O$, $NaScF_4 \cdot H_2O$, $KScF_4 \cdot 0.1H_2O$, M_3ScF_6 ($M = NH_4^+, Na^+$) and $K_{2.5}ScF_{5.5} \cdot 0.2H_2O$ were isolated from the solutions. $(NH_4)_3ScF_6$ was shown to be a 3:1 electrolyte in water and to decompose at pH 7.5–7.7 to give a precipitate of ScF_3. The Raman spectrum of $(NH_4)_3ScF_6$ has been reported[186], the $[ScF_6]^{3-}$ ion assignments were made on the basis of O_h symmetry A_{1g}, 504 cm^{-1}, E_g, 370 cm^{-1}, F_{2g}, 240 cm^{-1}. The spectrum is very similar to that of $[InF_6]^{3-}$, $[AlF_6]^{3-}$, $[GaF_6]^{3-}$ and $[FeF_6]^{3-}$.

Several visual–thermal analysis studies on alkali metal fluoride-scandium fluoride systems have been made[187,188]. The species detected in these systems are $MScF_4$ ($M = Li^+$, Na^+) and the cryolite type M_3ScF_6 ($M = Na^+, K^+, Rb^+, Cs^+$). For the latter group of complexes, as the alkali metal ionic radius increases, so does the stability of the complex, a conclusion reached by comparison of the differences between the melting points of the complex and that of the corresponding alkali metal fluoride. The sodium fluoride–scandium fluoride system has been studied in more detail by Thoma and Karraker[189]. They also observed two complexes being formed, $NaScF_4$ and Na_3ScF_6. The former complex possesses hexagonal symmetry with $a = 12.97$, $c = 9.27$ Å while the latter exists in both a high-temperature (α) and a low-temperature (β) form, the transition occurring at 680°C. β-Na_3ScF_6 is monoclinic, space group $P2_1/n$, with $a = 5.60$, $b = 5.81$, $c = 8.12$ Å and $\beta = 90°45'$. Na_3ScF_6 is similar to Na_3AlF_6 in its crystal symmetry, both species crystallizing from melts and inverting to monoclinic low temperature forms The scandium species resembles its aluminum analog rather than corresponding trivalent lanthanide species due to the similar polarizabilities of Sc^{3+} and Al^{3+}

The compound Cs_2KScF_6 is prepared from Sc_2O_3, CsCl and KCl in a stream of fluorine at 500° (ref 190) It crystallizes in a cubic form, a = 9 32 Å, isomorphous with K_2NaCrF_6 The solid state reaction between ScF_3, NaF and MgF_2 at 830° for 24 h in argon results in Na_2MgScF_7 which crystallizes in the orthorhombic form isomorphous with Na_2MgAlF_7[191]

The complexing of scandium by chloride ion in aqueous solution was studied initially by Paul[192] in 1962 The data he obtained for the formation of the species $ScCl^{2+}$ and $ScCl_2^+$ are presented in Table 6 Later investigations[193–195] also indicated the presence of the above species although the stability constants derived differ considerably from those determined by Paul The reasons for this discrepancy are not understood Scandium is slightly adsorbed by an anion exchange column from 7–12 M hydrochloric acid indicating the presence of an anionic species at high chloride concentration[196]. In high concentrations of hydrochloric acid, $ScCl_4^-$ has been suggested to be the anionic species, in 2–8 M HCl, $ScCl^{2+}$ and $ScCl_2^+$ are present and in very dilute HCl, $Sc(OH)^{2+}$ is the main species[194]

The stability constants, ΔH and ΔS values for complexing of scandium by bromide ion are listed in Table 6 from the study by Paul[192] As was the case for the chloride ion, other authors have proposed substantially different values for the stability constants of the $ScBr^{2+}$ and $ScBr_2^+$ ions[197]. It is interesting to compare the data of Paul for complexing of scandium by fluoride, chloride and bromide ions The fluoride complexes are much more stable than the corresponding chloride and bromide species, although the first chloride complex is less stable than the first bromide complex Comparison of these data with those for the corresponding indium halide species[198] shows that the fluoride complexes of scandium are more stable than those of indium, although for the chloride and bromide species, the reverse is true Indium(III) and scandium(III) have almost identical ionic radii[173]

Several studies of phase diagrams involving alkali metal chlorides and bromides with scandium chloride and bromide have been carried out over the last few years[199–206] Two general types of complex halide species are formed

M_3ScCl_6 M = Li[199,200], Na[199–201], K[200,202,203], Rb[200 203], Cs[200,203,204]
M_3ScBr_6 M = Na[205], K[205], Rb[206], Cs[206]
$M_3Sc_2Cl_9$ M = K[200], Rb[203], Cs[203,204]
$M_3Sc_2Br_9$ M = Na[205], K[205], Rb[206], Cs[206]

In the formation of these species, scandium(III) closely resembles titanium(III), vanadium(III) and chromium(III)[207]. They are probably isomorphous species containing octahedral arrangements of halide ions, the $Sc_2X_9^{3-}$ ions consisting of two halide octahedra sharing a common face Two forms of Li_3ScCl_6 were detected, the $\alpha \rightarrow \beta$ conversion taking place at 470°C[199] The energy of transfer from $ScCl_6^{3-}$ to $Sc_2Cl_9^{3-}$ has been estimated to be 36.2 kcal $mole^{-1}$, 37 5 kcal $mole^{-1}$ and 39 7 kcal $mole^{-1}$ for the potassium rubidium and cesium derivatives, respectively[208] K_2ScCl_5 has also been detected[202,203] although no corresponding species with other alkali metal halides or with the bromide ion is known

Recently, $Cs_2NaScCl_6$ has been isolated by evaporation to dryness of a hot aqueous HCl solution of the appropriate cations[209] The scandium(III) ion is no doubt octahedrally surrounded by six chloride ions and the X-ray powder pattern has been indexed on the basis of a face centered cubic structure

F MISCELLANEOUS COMPLEXES

Interaction of diisopropylmethylphosphonate with hydrated scandium chloride at 50–60°C leads to the formation of tris(isopropoxymethylphosphonato) scandium(III), Sc(imp)$_3$, with simultaneous evolution of isopropyl chloride[210] The general insolubility of the complex is interpreted as being indicative of a polynuclear configuration involving phosphonate bridges A distorted octahedral symmetry is assigned to the scandium ion on the basis of the general similarity of the compounds X-ray powder pattern with other M(imp)$_3$ complexes

A crystalline precipitate slowly separates from an aqueous solution of tropolone and scandium nitrate which is an acid of the type HSc(trop)$_4$ [211] Dissolution of this acid in a hot methanol–chloroform mixture and subsequent concentration of the solution yields the tristropolonate of scandium, Sc(trop)$_3$ This complex has a distinctly different lattice from those of the larger rare earth ions which have a polymeric structure, as judged by X-ray powder data, infrared spectra, and its greater solubility The tristropolonate of scandium is soluble in chloroform and is isomorphous with Fe(trop)$_3$ Although trivalent scandium is significantly smaller than any of the rare earth ions it is alleged to form an eight-coordinate species with tropolone by reaction of the tris species with sodium tropolonate in polar media The X-ray powder pattern of the tetrakis compound. NaSc(trop)$_4$, shows it to be isomorphous with the rare earth analogs which are known to form eight-coordinate species

The compounds $ScCl_3$ dppe and $ScBr_3$ 1 5 dppe have been isolated from the reaction of 1,2-bis(diphenylphosphine)ethane, (dppe), with scandium chloride and bromide, respectively[137]. A band at 303 cm^{-1} in both compounds was assigned to ν(Sc–P), with ν(Sc–Cl) at 317 cm^{-1} and ν(Sc–Br) at 275 cm^{-1}

The chloride species behaves as a weak 1 1 electrolyte in nitromethane whereas the bromide is a strong 1 1 electrolyte or an ion paired 1 2 electrolyte Molecular weight measurements in nitromethane indicated a degree of association of 4 5 monomer units for the chloride while the apparent molecular weight of the bromide increased over a period of two weeks It was suggested that the polymers contain tetrahedrally coordinated scandium and may be written $[-CH_2PPh_2ScCl_2Ph_2PCH_2-]_n^{n+}$ nCl$^-$ and $[-CH_2PPh_2ScBr(Ph_2PCH_2-)_2]_n^{2n+}$ 2nBr$^-$

Complexes of scandium with sulfur donor ligands have not been investigated until recently, although it was reported[212] in 1960 that scandium is precipitated by sodium mercaptobenzothiazolate. $NaC_7H_4NS_2$,at pH 5 5–6 as the basic salt $Sc(C_7H_4NS_2)_2OH$ Using $Na_2[S_2C_2(CN)_2]$, sodium maleonitriledithiolate, the complex $[(nC_3H_7)_4N][Sc(S_2C_2(CN)_2)_3]$ has been isolated[213] This compound undoubtedly contains strong scandium–sulfur bonds since it is obtained in an unsolvated form from aqueous ethanol solution

Complexes of the lanthanides with the *N,N*-diethyldithiocarbamate ion (dtc$^-$) of general formulae Ln(dtc)$_3$ and [NEt$_4$] [Ln(dtc)$_4$] have been reported[214] In view of the apparent stability of the above scandium compound, complexes with dithiocarbamate ions and other sulfur donor ligands should also be capable of isolation

Scandium tris(cyclopentadienide), Sc(C$_5$H$_5$)$_3$ has been known for several years and may be prepared from the chloride and sodium cyclopentadienide[215,216] or the fluoride and magnesium cyclopentadienide[217] The compound is straw-colored, has a melting point of 240°C, and sublimes at 200–250° under vacuum The near infrared reflection spectrum between 4,000 and 10,000 cm^{-1} has been measured[218] It has been suggested that the bonding between scandium and the cyclopentadiene rings is purely ionic in nature[215,216,219] Mass spectral measurements on some lanthanide triscyclopentadienide complexes have recently been reported[220] From the abundances of various ions it was concluded that the species are ionic in nature The crystal structure of one of the compounds for which the mass spectrum was measured, viz tris (cyclopentadienyl)samarium(III) has recently been reported[221] It was concluded, in conflict with the above suggestion, that the Sm–C bond has only about 37% partial ionic character The cyclopentadienyl rings have a definite preferred orientation about the Sm^{III}, as expected if the bond has a large amount of covalent character In view of the smaller ionic radius of scandium(III) compared to samarium(III), Sc(C$_5$H$_5$)$_3$ may be expected to have considerable covalent character

Triphenyl scandium, Sc(C$_6$H$_5$)$_3$ and tri(phenylacetylide) scandium, Sc(C≡CC$_6$H$_5$)$_3$ have been reported[222,223] although the nature of the bonding in these compounds is not known Scandium chloride has also been reported to form addition compounds with olefins[224] and ethylene polymerization has been observed using scandium species as catalysts[225]

G SUMMARY

This review has discussed the coordination chemistry of scandium, most of which has been reported during the last few years

It is apparent that when comparisons are made between scandium and the lanthanides or early members of the *3d* transition elements, the size of the scandium ion is important in determining the stoichiometry and relative stability of the species formed Scandium has a strong preference for a coordination number of six, with an octahedral or distorted octahedral stereochemistry However, compounds with unusual stoichiometries that cannot readily be rationalized on the basis of six coordination may contain the scandium ion in different stereochemical environments

The next few years will undoubtedly see a large increase in the number of scandium complexes synthesized, however, the need for physical measurements and structural characterization of existing species is acute in order to resolve questions of stereochemistry, mode of bonding and stability

In view of the importance of early transition elements as catalysts in many industrial processes, polymerization, oligomerization, hydrogeneration etc , the synthesis of species containing scandium in oxidation states other than three and also the field of organoscandium chemistry should receive increasing attention

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