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Co-ordination Chemistry of Scandium. Part III.¹ Complexes of Scandium(III) Perchlorate with Uni- and Bi-dentate Oxygen Donor Ligands

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Complexes of the type $[ScL_6](ClO_4)_3 \{L = dimethyl sulphoxide. MN-dimethylformamide, pyridine N-oxide, 2-, 3-, and 4-picoline N-oxides, <math>\frac{1}{2}(2.2'-bipyridyl 1,1'-dioxide), \frac{1}{2}[1,2-bis-(diphenylphosphinylethane)], \frac{1}{2}[1,2-bis-(diphenylphosphinylethane]$ have been isolated. With triphenylphosphine oxide, $ScL_4(ClO_4)_3$ is obtained. Complexes have been characterized by i.r. and Raman spectroscopy and conductance measurements. I.r. spectral data indicate distortion of the $[ScL_6]^{3+}$ cations from O_h symmetry, and co-ordination of the perchlorate ion in the triphenylphosphine oxide complex.

WE have recently reported several scandium(III) thiocyanate and chloride complexes with neutral oxygen and nitrogen donor ligands in which scandium(III) exhibits a co-ordination number of six.^{1,2} Competition between ligand and anion for co-ordination sites leads to both being co-ordinated in many of these complexes. The use of an anion that has non- or very weak co-ordinating properties towards scandium(III) might be expected to bring out the maximum co-ordination number for

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scandium(III) in its complexes with various ligands. Kutek has described complexes of scandium(III) perchlorate which contain six molecules of unidentate oxygen donor ligands.^{3,4}

Recent studies with lanthanide perchlorates and

¹ Part II, N. P. Crawford and G. A. Melson, J. Chem. Soc. (A), 1969, 1049.

² N. P. Crawford and G. A. Melson, *J. Chem. Soc.* (A), 1969, 427.

³ F. Kutek, Coll. Czech. Chem. Comm., 1967, 32, 3767.

⁴ F. Kutek and F. Petru, Coll. Czech. Chem. Comm., 1968, **33**, 296.

oxygen donor ligands have shown that the co-ordination number of the lanthanide is dependent on ionic size, values from six to eight being reported.⁵⁻⁹ In view of the smaller size of scandium(III) compared with any of the trivalent lanthanide ions, it was of interest to determine the co-ordination number of scandium(III) in products obtained from the reaction of scandium(III) perchlorate and various neutral oxygen-donor ligands.

EXPERIMENTAL

Materials.—Scandium(III) perchlorate heptahydrate was prepared by reaction of perchloric acid with an excess of scandium oxide.¹⁰ (>99.8% Sc₂O₃, Koch-Light and Johnson Matthey). 2,2'-Bipyridyl 1,1'-dioxide and 1,2-bis-(diphenylphosphinyl)ethane were prepared by literature methods.^{11,12} 1,2-bis(diphenylarsinyl)ethane was obtained by the addition of a slight excess of 30% hydrogen peroxide to 1,2-bis(diphenylarsino)ethane dissolved in the minimum quantity of acetone; addition of ether to the solution gave the white product, m.p. 105°. Hexakis-(NN-dimethylformamide)scandium(III) perchlorate was prepared as previously described.³

All other materials used were as reported earlier.¹

Preparation of Complexes.—All reactions were carried out under anhydrous conditions due to the hygroscopic nature of the products.

Hexakis(dimethyl sulphoxide)scandium(III) Perchlorate.— Methanolic solutions of scandium(III) perchlorate (1 mol.) and dimethyl sulphoxide (dmso) (8 mol.) when mixed gave a white precipitate which was collected, washed with methanol, and dried *in vacuo* over $Mg(ClO_4)_2$ [Found: C, 18·1; H, 4·2; S, 23·9; Sc, 5·5. Sc(dmso)₆(ClO₄)₃ requires C, 17·8; H, 4·4; S, 23·7; Sc, 5·5%].

Hexakis(pyridine N-oxide)scandium(III) Perchlorate.—A solution of pyridine N-oxide (pyNO) (8 mol.) in ethanol was added to a methanolic solution of scandium(III) perchlorate (1 mol.). The mixture was set aside in an ice-water bath for 1 hr., the white crystalline complex was filtered off, recrystallised from ethanol, and dried as previously described [Found: C, 40·1; H, 3·5; N, 9·1; Sc, 5·1. Sc(PyNO)₆-(ClO₄)₃ requires C, 39·5; H, 3·3; N, 9·2; Sc, 5·9%].

Hexakis-(2-picoline N-oxide)scandium(III) Perchlorate.— Methanolic solutions of 2-picoline N-oxide (2-picNO) (8 mol.) and scandium(III) perchlorate (1 mol.) were mixed; addition of ether to the solution gave a white precipitate.

Similarly, scandium(III) perchlorate reacted with 3-picoline N-oxide (3-picNO) and 4-picoline N-oxide (4-picNO) to give white precipitates [Found: C, 42.6; H, 4.1; N, 8.6; Sc, 4.6; for Sc(2-picNO)₆(ClO₄)₃. Found: C, 43.7; H, 4.3; N, 8.6; Sc, 4.5; for Sc(3-picNO)₆(ClO₄)₃. Found: C, 42.8; H, 4.2; N, 7.9; Sc, 4.6; for Sc(4-picNO)₆(ClO₄)₃. Required for all three compounds C, 43.3; H, 4.2; N, 8.4; Sc, 4.5%].

Bisperchloratotetrakis(triphenylphosphine oxide)scandium-(III) Perchlorate.—An ethanolic solution containing scandium(III) perchlorate (1 mol.) and triphenylphosphine oxide (Ph₃PO) (8 mol.) was heated under reflux for 24 hr. On evaporation of the solution to low bulk the complex separated as white crystals; these were filtered off and dried as previously [Found: C, 59.4; H, 4.3; Sc, 3.2. $Sc(Ph_3PO)_4$ -(ClO_4)₃ requires C, 59.3; H, 4.1; Sc, 3.1%].

Tris-(2,2'-bipyridyl 1,1'-dioxide)scandium(III) Perchlorate. —Ethanolic solutions of scandium(III) perchlorate (1 mol.) and 2,2'-bipyridyl 1,1'-dioxide (bipyO₂) (4 mol.) when mixed gave a white precipitate which was collected, washed with ethanol, and dried [Found: C, 39.8; H, 2.8; N, 9.4; Sc, 5.2. Sc(bipyO₂)₃(ClO₄)₃ requires C, 39.6; H, 2.6; N, 9.2; Sc, 5.0%].

Tris-[1,2-bis(diphenylphosphinyl)ethane]scandium(III) Perchlorate.—This complex was obtained as a white powder with conditions similar to those described above [Found: C, 56.7; H, 4.5; Sc, 2.9. $Sc(dpO_2)_3(ClO_4)_3$ requires C, 57.25; H, 4.4; Sc, 2.8%].

Tris-[1,2-bis(diphenylarsinyl)ethane]scandium(III) Perchlorate.—This complex was obtained in a similar manner to that described above [Found: C, 49.2; H, 4.2; Sc, 2.4. $Sc(daO_2)_3(ClO_4)_3$ requires C, 49.3; H, 3.8; Sc, 2.4%].

Analyses.—Scandium was determined by titration with EDTA at pH 10 with Eriochrome Black T as indicator.¹³ All other elements were determined by the microanalytical department of the University of Strathclyde. Samples were heated at 100° to constant weight prior to analysis.

Physical Measurements.—I.r. and conductance techniques were the same as those described earlier.² Raman spectra were obtained with a Cary model 81 Raman spectrometer with a helium-laser source.

RESULTS AND DISCUSSION.

The complexes isolated from the reaction of hydrated scandium perchlorate with various oxygen donor ligands are recorded in Table 1, together with some of the characteristic absorptions of the ligands and perchlorate anion. In spite of using the hydrated perchlorate, anhydrous complexes were obtained, provided the procedures for isolation and purification of solid products were carried out under anhydrous conditions with carefully dried solvents. Triphenylarsine oxide and 2,6-lutidine N-oxide yield hydrated species under similar experimental conditions and are not discussed further.

For the complexes involving unidentate ligands, the position of v(X=O) (X = S, C, or N) decreases in frequency relative to the free ligand value, indicating coordination of the ligand through the oxygen atom to scandium. The magnitude of this decrease, and thus the strength of the scandium(III)-ligand interaction, is similar to that found in lanthanide complexes, but less than in complexes of tervalent transition-metal ions involving these ligands.¹⁴ This conclusion is in agreement with our earlier investigations with scandium(III) thiocyanate complexes and these ligands.¹ No definite assignment can be made for v(P=O) in Sc(Ph₃PO)₄-

¹⁴ See ref. 1 for relevant references.

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&</sup>lt;sup>13</sup> L. Wunsch, Coll. Czech. Chem. Comm., 1955, 20, 1107.

(ClO₄)₃ due to absorptions associated with the perchlorate ion.

The observed decrease of 30-40 cm.⁻¹ in v(N=O) for $Sc(bipyO_2)_3(ClO_4)_3$ from 1255 cm.⁻¹ in the free ligand closely resembles those found for lanthanide complexes.⁹ is thus not associated with the perchlorate ion. However, our observed Raman-active, i.r.-inactive band at 474 cm.⁻¹ is assigned to v_2 of the perchlorate ion.

The i.r. spectrum of Sc(Ph₃PO)₄(ClO₄)₃ exhibits a complex series of bands in the regions of perchlorate

Table	1
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Characteristic infrared absorptions and Raman shifts for the complexes.*

	Ligand		Perchlorate		
Compound	ν (X=O)	ν ₁	ν ₂	ν ₃	v ₄
$Sc(dmso)_{\epsilon}(ClO_{\epsilon})_{3}$	1010sh, 995s	936m †	474m †	1100sbr	626m
$Sc(dmf)_{a}(ClO_{a})_{a}$	1670s, 1620s	a	a	1090sbr	626s
$Sc(pyNO)_{\epsilon}(ClO_{\epsilon})_{3}$	1240s, 1223s	930m †	476m †	1100sbr	625s
$Sc(2-picNO)_{a}(ClO_{a})_{3}$	1245s, 1224s	935m †	472m †	1084bsr	622m
$Sc(3-picNO)_{a}(ClO_{a})_{3}$	1275s, 1262sh	935m †	472m †	1090sbr	625m
$Sc(4-picNO)_{4}(ClO_{4})_{3}$	1222s, 1210s	928m †	475m †	1085sbr	619m
$Sc(bipyO_2)_3(ClO_4)_3$	1225s, 1210sh	a	a	1090sbr	625m
$Sc(dpO_2)_3(ClO_4)_3$	1146sh, 1131s	a	а	1090sbr	625m
$Sc(daO_{2})_{3}(ClO_{4})_{3}$	888sh, 872s	a	a	1085 sbr	623m
$Sc(Ph_3PO)_4(ClO_4)_3$	b	930s,† 905s	458m †	1190s	650m
		895s	445m	1082s, 1068s	623s •
				1022s, 1015s	610s
				994s	
		-		1085sbr	624m ď
				1098sbr	625m •
				1090sbr	622m ^f

* All values in cm.⁻¹. † Observed in Raman spectrum only.

• Raman spectra not well defined. • Obscured by perchlorate absorptions. • Assignment of perchlorate absorption in 1100 cm.⁻¹ region complicated by ν (P=O). • MeCN solution. • MeNO₂ solution. • NN-dimethylformamide.

s = strong; m = medium; br = broad; sh = shoulder.

In $Sc(dpO_2)_3(ClO_4)_3$, the two v(P=O) absorption bands are $ca. 40 \text{ cm}.^{-1}$ lower than those of the free ligand (1184 and 1173 cm.⁻¹). This decrease is similar in magnitude to that found for triphenylphosphine oxide (Ph₃PO) on co-ordination in Sc(Ph₃PO)₃(NCS)₃.¹ The conclusion reached earlier concerning the strength of the scandiumligand interaction for unidentate ligands are also applicable for these two bidentate ligands.

However, for $Sc(daO_2)_3(ClO_4)_3$, the positions of v(As=O) in the complex are very similar to those of the free ligand (885 and 865 cm.⁻¹). The increase in v(As=O)on co-ordination of triphenylarsine oxide to scandium(III) has been attributed to the decrease in As-O d_{π} - p_{π} bonding being more than offset by an increase in σ -bonding arising from coupling between As-O and Sc-O.¹ Presumably on co-ordination of daO₂, these opposing effects are of similar magnitude so that v(As=O) appears unchanged from free ligand to complex.

The characteristic perchlorate absorptions listed in Table 1 indicate that with the exception of Sc(Ph₃PO)₄- $(ClO_4)_3$ all complexes contain ionic perchlorate with T_d symmetry.¹⁵ For the four normal modes expected, v_1 and v_2 are Raman-active, and v_3 and v_4 , i.r.-active. Kutek and Petru assigned a band at 455 cm.⁻¹ in the i.r. spectrum of $Sc(dmso)_6(ClO_4)_3$ to a perchlorate mode.⁴ We have also observed a band in the region of 450 cm.⁻¹ in the i.r. spectrum of this compound, but it is absent in the Raman spectrum (see Figure). This band is assigned to an i.r.-active scandium-oxygen stretching mode and

absorption. We conclude that in this complex coordination of some of the perchlorate ions take place.¹⁶ In solution, the i.r. spectrum is different and closely



I.r. (A) and Raman (B) spectra of dimethyl sulphoxide (---) and $Sc(dmso)_{6}(ClO_{4})_{3}$ (-----) between 500 and 200 cm.⁻¹

resembles those found for the complexes containing only ionic perchlorate. Thus, solvolysis of the coordinated perchlorate must take place. This is conconsistent with the observation that in these solvents,

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W. C. Jones and W. E. Bull, J. Chem. Soc. (A), 1968, 1849.

 $Sc(Ph_3PO)_4(ClO_4)_3$ has a molar conductance characteristic of a 3:1 electrolyte. All the other complexes reported also behave as 3:1 electrolytes in acetonitrile, nitromethane, and NN-dimethylformamide solutions.^{7,17,18} (Table 2). The co-ordination number

TABLE 2 Molar conductances of the perchlorate complexes (10⁻³M-solutions)

	$\Lambda_m \text{ (ohm}^{-1} \text{ cm}^2)$			
Complex	CH ₃ CN	CH_3NO_2	DMF	
$Sc(dmso)_{6}(ClO_{4})_{3}$	440	235	201	
$Sc(dmf)_6(ClO_4)_3$	452	241	208	
$Sc(pyNO)_6(ClO_4)_3$	415	228	204	
$Sc(2-picNO)_6(ClO_4)_3$	400	225	201	
$Sc(3-picNO)_6(ClO_4)_3$	416	231	202	
$Sc(4-picNO)_{6}(ClO_{4})_{3}$	412	231	201	
$Sc(bipyO_{2})_{3}(ClO_{4})_{3}$	440	216	205	
$Sc(dpO_{a})_{a}(ClO_{4})_{a}$	491	242	206	
$Sc(daO_a)_a(ClO_A)_a$	482	248	210	
$Sc(Ph_3PO)_4(ClO_4)_3$	480	210	192	

suggested by the vibrational spectra and conductivity data for the scandium(III) complexes is thus six. In $Sc(Ph_3PO)_4(ClO_4)_3$ monodentate co-ordination of two perchlorate ions in addition to the four triphenylphosphine oxide ligands would satisfy this co-ordination number. The i.r. spectrum in the perchlorate region is thus complicated by the presence of both ionic and coordinated perchlorate and it is not possible to differentiate between unidentate (C_{3v}) and bidentate (C_{2v}) co-ordination.

Indium(III), which has a similar ionic radius to scandium(III), also forms a complex of the type In- $(Ph_3PO)_4(ClO_4)_3$ with triphenylphosphine oxide.¹⁹ However, the indium complex does not contain co-ordinated perchlorate, and a co-ordination number of four is suggested. With neutral oxygen donor ligands, tervalent lanthanide perchlorates form complexes with coordination numbers as high as eight.⁵⁻⁹ The fact that similar ligands only result in six co-ordinate 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 [ScL₆]³⁺ cation will be O_h , and one i.r.-active, Raman-inactive scandium-oxygen stretching mode (F_{1u}) is expected. However, if the symmetry of the ligand is considered, the symmetry of the cation will be lower than O_h and differences in vibrational spectra associated with scandium-oxygen modes will arise. A recent study of dimethyl sulphoxide complexes $[M(dmso)_6]^{n+}$, has led to the conclusion that the point group of the cation is either D_{3d} or S_6 depending on the configuration of the ligand.²⁰ Both symmetries predict two i.r.-active, Raman-inactive v(M-O) vibrations. The i.r. and Raman 17 C. P. Prabhakaran and C. C. Patel, J. Inorg. Nuclear Chem.,

J. Chem. Soc. (A), 1970

spectra of $Sc(dmso)_6(ClO_4)_3$ in the 500–200 cm.⁻¹ region are illustrated in the Figure. The broad, asymmetric absorption band in the i.r. spectrum at ca. 450 cm.⁻¹, absent in the Raman spectrum is assigned to v(Sc-O). This band is probably composite in nature, and a consideration of v(Sc-O) alone does not provide conclusive evidence for deviation of the cation from O_h symmetry. However, the i.r. and Raman active 'symmetric' and 'antisymmetric' CSO deformations, assigned to bands at 384 and 333 cm.⁻¹ in the free ligand ²¹ 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 to 21 cm.⁻¹ in the complex cation. This behaviour has been attributed ²⁰ to the existence of an S_6 point group for $[M(dmso)_6]^{n+}$ where the plane of symmetry of dmso is no longer a symmetry element of the point group as a whole, and uncoupling of the two CSO deformations occurs.

The position of v(Sc-O) is considerably lower than is observed for $\nu(Cr-O)$ in $Cr(dmso)_6(ClO_4)_3$, (529 cm.⁻¹),²⁰ again indicating much weaker co-ordination of the ligand to scandium(III). The absorption band observed in the i.r. spectrum of Sc(dmso)₆(ClO₄)₃ at 277 cm.⁻¹ may arise from an Sc-O-S angle deformation, while the Raman-active, i.r.-inactive band at 474 cm.⁻¹ is assigned to v_2 of the perchlorate ion.

Similar deviations from O_h symmetry are to be expected in the other complexes containing $[ScL_{6}]^{3+}$ cations. The presence of two v(Sc-O) modes supports this conclusion (Table 3). For the complexes containing pyridine N-oxide and its methyl substituted derivatives. the positions of absorption (364-385 cm.⁻¹) are lower than those observed 2^{2} for $[M(pyNO)_{6}]^{3+}$ $(M = Cr^{III},$ Fe^{III}, and Al^{III}).

The spectrum of $Sc(Ph_3PO)_4(ClO_4)_3$ exhibits a weak absorption band at 420 cm.⁻¹ which does not appear in the spectrum of the free ligand. However, bands are also observed in this region for PhaPO complexes of Zn^{II}, Tl^{III},²³ In^{III},²⁴ and Sn^{IV}.²⁵ Since it is unlikely that $\nu(M-O)$ occurs at the same frequency for all these metal ions, v(Sc-O) probably occurs at lower wavenumbers. Four strong bands are observed in the 270-320 cm.⁻¹ region, no absorptions occurring between 320 and 420 cm.⁻¹. It is, however, impossible to make definite assignments for v(Sc-O) arising from the ligand due to possible ligand absorptions and perchlorate interaction. Sc(Ph₃PO)₃(NCS)₃ also has absorptions in this region, but bands due to v(Sc-N) from the co-ordinated thiocyanate ion are also expected. Similarly, assignments of v(Sc-O) in Sc(dpO₂)₃(ClO₄)₃ and Sc(daO₂)₃- $(ClO_4)_3$ cannot be made conclusively either although possible positions are reported in Table 3.

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^{1961, 17, 134.}

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²⁵ J. P. Clark, V. M. Langford, and C. J. Wilkins, J. Chem.

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Scandium(III)–oxygen stretching modes in perchlorate and thiocyanate complexes with oxygen donor ligands.*					
Perchlorates	v(ScO)	Thiocyanates	ν (Sc-O)		
$\begin{array}{l} \operatorname{Sc}(\operatorname{dmso})_{\mathfrak{s}}\operatorname{ClO}_{4})_{3} & & \\ \operatorname{Sc}(\operatorname{dmf})_{\mathfrak{e}}(\operatorname{ClO}_{4})_{3} & & \\ \operatorname{Sc}(\operatorname{pyNO})_{\mathfrak{s}}(\operatorname{ClO}_{4})_{3} & & \\ \operatorname{Sc}(2\operatorname{-picNO})_{\mathfrak{s}}(\operatorname{ClO}_{4})_{3} & & \\ \operatorname{Sc}(3\operatorname{-picNO})_{\mathfrak{s}}(\operatorname{ClO}_{4})_{3} & & \\ \operatorname{Sc}(4\operatorname{-picNO})_{\mathfrak{s}}(\operatorname{ClO}_{4})_{3} & & \\ \operatorname{Sc}(4\operatorname{-picNO})_{\mathfrak{s}}(\operatorname{ClO}_{4})_{3} & & \\ \end{array}$	450sbr 420sh, 395m 382m, 364m 385s, 374s 380s, 364s 378m, 365m	$\begin{array}{l} & Sc(dmso)_{3}(NCS)_{3} \\ & Sc(dmf)_{3}(NCS)_{3} \\ & Sc(pyNO)_{3}(NCS)_{3} \\ & Sc(2-picNO)_{3}(NCS)_{3} \\ & Sc(3-picNO)_{3}(NCS)_{3} \\ & Sc(4-picNO)_{3}(NCS)_{3} \\ & Sc(4-picNO)_{3}(NCS)_{3} \\ & \end{array}$	445sbr, 420sh 420s, 395m, 373m 370s, 350s 389m, 372s 387m, 352s 390s, 374		
	315s, 303s 279s, 270s?	$Sc(htNO)_{36}NCS)_3$ $Sc(Ph_3PO)_3(NCS)_3$ $Sc(Ph_3AsO)_3(NCS)_3$	383s, 365s 324s, 312s 284s? 418sh, 406m 390m?		
$\begin{array}{llllllllllllllllllllllllllllllllllll$	388m, 373m 322s, 288s? 420sh, 396m?				

TABLE 3

* All values in cm.-1.

Two bands assigned to v(Sc-O) in $Sc(bipyO_2)_3(ClO_4)_3$ occur at higher frequencies than those found in the eightco-ordinate lanthanide complexes,⁹ suggesting a stronger metal-ligand interaction, although the difference in coordination number between the species could affect the strength of the interaction.

The relative positions of v(M-O) (where M is scandium, a lanthanide, or a transition-metal in the tervalent state) for complexes of similar molecular formula will provide a better foundation for discussion of the strengths of metal-ligand interaction than shifts in v(X=O) associated with the ligand alone. 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.

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