The Complex Chemistry of Scandium. Part 1. Preparation and Properties of some Scandium(III) Complexes of Polyamines. *X*-Ray Crystal Structures of Tri(nitrato-*OO'*)(2,2':6',2''-terpyridyl-*NN'N''*)scandium(III) and [1,2-bis(pyridine-α-carbaldimino)ethane-*NN'N''N'''*]-di-μ-hydroxo-di(nitrato-*OO'*)discandium(III) Dinitrate Bis(acetonitrile) *

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The complexes $Sc(NO_3)_3$(terpy), $Sc(NO_3)_3$(terpy)(H_2O), $ScCl_3$(tpta), $Sc(NO_3)_3$(bpce)$(H_2O)_2$, and $Sc(NO_3)_2(OH)$(bpce) have been prepared and characterised [terpy = 2,2':6',2''-terpyridyl, tpta = 2,4,6-tris(α-pyridyl)-1,3,5-triazine, and bpce = 1,2-bis(pyridine-α-carbaldimino)ethane]. Single-crystal *X*-ray structure determinations show that $Sc(NO_3)_3$(terpy) is monomeric, [$Sc(NO_3)_3$(terpy)], and nine-co-ordinated, while $Sc(NO_3)_2(OH)$(bpce) is dimeric, [$Sc_2(NO_3)_2(\mu\text{-}OH)_2$(bpca)$_2$][$NO_3$]$_2$, with hydroxo-bridges, each Sc ion being eight-co-ordinated.

Despite significant recent work, the complex chemistry of scandium remains insufficiently investigated. This situation is probably partially caused by the very high price of the metal, but perhaps also there is a feeling that its chemistry, with only one stable oxidation state, is likely to be comparatively featureless. However, scandium(III) is the only stable ion of its outer-electronic configuration and bonding type, size, and charge in the Periodic Table and is therefore well worth detailed investigation.

The following is a brief account of the co-ordination chemistry of this little studied element. Its ionic radius (0.81 Å, Pauling) is on the borderline between six-co-ordination and higher co-ordination numbers. In those *X*-ray crystal structures which are known, Sc^{3+} is predominantly six-co-ordinate, as in [Sc(acac)$_3$],[1] [$ScCl_3$(thf)$_3$],[2] [Sc(trop)$_3$],[3] and [Sc(mal)(OH)(H_2O)]·H_2O [4] (acac = acetylacetonate, thf = tetrahydrofuran, trop = tropolonate, and mal = malonate). However, a co-ordination number of seven occurs in [ScL(H_2O)$_2$][OH][NO_3]$_2$,[5] where L is C_5H_3*N*(CMe=*N*NHC*O*NH$_2$)$_2$-2,6, Sc^{3+} being co-ordinated by three N and two O atoms (italicised) from the quinquedentate ligand and by two water molecules. Eight-fold co-ordination occurs in [Sc(trop)$_3$(Htrop)] [6] and in Sc_2(oxa)$_3$(H_2O)$_4$·2H_2O (oxa = oxalate).[7] The only nine-co-ordinate complex known before this present report is apparently [NO]$_2$[$Sc(NO_3)_5$] which contains four bidentate and one monodentate nitrate ions.[8] In contrast, scandium will, with bulky ligands, adopt a co-ordination number of only three, which is observed [9] in [Sc{N(SiMe$_3$)$_2$}$_3$].

Scandium(III) is also capable of forming organometallic compounds. Thus $Sc(C_5H_5)_3$ forms a polymeric structure [10] rather similar to the corresponding lanthanide structures, where each Sc atom is co-ordinated to two η^5 and two σ ligands. $Sc(C_5H_5)_3$ has been isolated;[11] its structure is unknown but presumably must include Sc–C bonds.

Kinetic studies (in CD_3CN) using n.m.r. line-shape methods [12] show a fairly rapid exchange of [Sc{OP(OMe)$_3$}$_6$]$^{3+}$ with added ligand ($\Delta H^\ddagger = 29.8$ kJ mol^{-1}, $\Delta S^\ddagger = -111$ J K^{-1} mol^{-1}), supporting the theoretical viewpoint that as a d^0 ion, Sc^{3+} should form labile complexes.

In this present work, we have sought to extend the chemistry of Sc^{3+} in its reactions with uncharged nitrogen-donor ligands. Our experience with the related but larger lanthanide ions suggested that an extensive chemistry of amine complexes should exist, particularly for chelate ligands. The isolation of the substituted pyridine complex mentioned above also supports this view.

Experimental

Trinitrato(2,2':6',2''-*terpyridyl*)*scandium*(III), (1).—$Sc(NO_3)_3$·6H_2O (0.246 g, 0.727 mmol) in acetonitrile (20 cm^3) was treated with 2,2':6',2''-terpyridyl (terpy) (0.203 g, 0.727 × 1.2 mmol) in acetonitrile (20 cm^3), both solutions being almost boiling. The mixture was boiled under reflux for 30 min and allowed to cool overnight. The product, golden needles, was collected by filtration, washed twice with acetonitrile, and dried (at 15 mmHg) at room temperature (Found: C, 39.0; H, 2.3; N, 17.95; Sc, 9.6. $C_{15}H_{11}N_6O_9Sc$ requires C, 38.8; H, 2.4; N, 18.1; Sc, 9.7%) (yield, 79%). An analogous preparative procedure but without reflux gave golden needles of similar appearance, but which were the monohydrate, $Sc(NO_3)_3$(terpy)(H_2O) (2) (Found: C, 37.35; H, 2.6; N, 17.3; Sc, 9.3. $C_{15}H_{13}N_6O_{10}Sc$ requires C, 37.4; H, 2.7; N, 17.4; Sc, 9.3%). The complexes are stable in air but decompose above 250 °C. They are insoluble in non-plolar organic solvents, but dissolve in Me_2SO and dissolve sparingly in hot $MeNO_2$. They readily dissolve in water, but the ligand separates out from the solution.

Trichloro[2,4,6-*tris*(α-*pyridyl*)-1,3,5-*triazine*]*scandium*(III), (3).—This preparation was carried out under a N_2 atmosphere. Anhydrous $ScCl_3$ was obtained by dehydration of $ScCl_3$·6H_2O by $SOCl_2$. $ScCl_3$ (0.0945 g, 0.625 mmol) in dry acetonitrile (15 cm^3) was treated with 2,4,6-tris(α-pyridyl)-1,3,5-triazine (tpta) (0.235 g, 0.625 × 1.2 mmol) in acetonitrile (20 cm^3), both solutions being almost boiling. A pale yellow precipitate formed immediately. The mixture was boiled under reflux for 1 h, and the product collected by filtration, washed twice with acetonitrile and dried (at 0.005 mmHg) at 60 °C (Found: C, 46.5; H, 2.75; Cl, 22.3; N, 18.1. $C_{18}H_{12}Cl_3N_6Sc$ requires C, 46.6; H, 2.6; Cl, 22.9; N, 18.1%) (yield, 93%). The complex is stable in air and is unaffected at 300 °C. It is moderately soluble in methanol ($\Lambda_m = 15.3$ ohm^{-1} cm^2 mol^{-1}) and sparingly soluble in hot $MeNO_2$. On dissolution in water, the tpta ligand dissociates. Attempts to prepare a nitrato-complex by a method analogous to that used for complex (1) gave only impure products.

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* *Supplementary data available* (No. SUP 23962, 25 pp.): thermal parameters, H-atom co-ordinates, full bond distances and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: mmHg ≈ 13.6 × 9.8 Pa.

Table 1. Fractional atomic co-ordinates for $[Sc(NO_3)_3(terpy)]$ (1)

Atom	x	y	z
Sc	2 621(1)	3 467	2 947(1)
N(1)	4 292(4)	3 540(2)	1 936(3)
C(11)	5 096(5)	2 902(3)	1 761(4)
C(12)	6 351(5)	2 971(3)	1 367(4)
C(13)	6 786(5)	3 731(3)	1 144(4)
C(14)	5 948(5)	4 391(3)	1 296(4)
C(15)	4 694(5)	4 278(3)	1 684(3)
N(2)	2 636(4)	4 748(2)	2 320(3)
C(21)	3 701(5)	4 951(3)	1 831(3)
C(22)	3 784(6)	5 729(3)	1 467(4)
C(23)	2 704(6)	6 293(3)	1 552(4)
C(24)	1 585(6)	6 087(3)	2 012(4)
C(25)	1 597(5)	5 306(2)	2 416(3)
N(3)	659(4)	4 237(2)	3 274(3)
C(31)	495(5)	5 021(3)	2 960(3)
C(32)	−624(6)	5 523(3)	3 161(4)
C(33)	−1 612(6)	5 207(4)	3 678(4)
C(34)	−1 450(5)	4 419(4)	3 986(4)
C(35)	−297(5)	3 950(3)	3 781(4)
O(11)	3 878(4)	2 316(2)	3 640(3)
O(12)	1 485(4)	2 463(2)	3 580(3)
O(13)	2 748(4)	1 352(2)	4 256(3)
N(11)	2 722(4)	2 012(2)	3 853(3)
O(21)	5 004(4)	3 919(2)	3 975(3)
O(22)	3 340(4)	3 717(2)	4 755(3)
O(23)	5 688(4)	4 104(2)	5 675(3)
N(21)	4 729(4)	3 925(2)	4 840(3)
O(31)	573(4)	3 465(2)	1 459(3)
O(32)	1 829(4)	2 370(2)	1 602(3)
O(33)	−477(4)	2 476(2)	414(3)
N(31)	604(4)	2 768(2)	1 148(3)

Table 2. Fractional atomic co-ordinates for $[Sc_2(NO_3)_2(\mu\text{-}OH)_2(bpce)_2][NO_3]_2\cdot 2MeCN$ (5)

Atom	x	y	z
Sc	4 183	−578(1)	4 405(1)
C(1)	3 385(3)	277(4)	6 803(3)
C(2)	2 899(3)	904(5)	7 521(4)
C(3)	2 414(3)	1 886(6)	7 089(5)
C(4)	2 428(3)	2 207(5)	5 958(5)
C(5)	2 929(2)	1 558(4)	5 290(3)
N(1)	3 404(2)	582(3)	5 699(2)
C(6)	2 997(2)	1 846(4)	4 093(4)
N(2)	3 471(2)	1 191(3)	3 544(2)
C(7)	3 567(3)	1 480(5)	2 342(3)
C(8)	3 617(3)	158(5)	1 738(4)
N(3)	4 125(2)	−726(3)	2 427(3)
C(9)	4 558(3)	−1 533(5)	1 946(4)
C(10)	5 005(2)	−2 491(4)	2 650(3)
C(11)	5 460(3)	−3 455(5)	2 190(5)
C(12)	5 831(3)	−4 382(6)	2 905(6)
C(13)	5 752(3)	−4 276(5)	4 043(5)
C(14)	5 292(3)	−3 276(4)	4 448(4)
N(4)	4 914(2)	−2 388(3)	3 778(3)
O(1)	5 075(1)	696(3)	4 164(2)
N(1a)	3 057(2)	−2 382(3)	4 786(3)
O(1a)	2 527(2)	−3 104(4)	4 987(3)
O(2a)	3 665(2)	−2 363(3)	5 388(2)
O(3a)	3 030(2)	−1 565(3)	3 960(2)
N(1b)	4 507(2)	−2 121(5)	8 718(3)
O(1b)	4 253(3)	−1 029(4)	9 011(3)
O(2b)	4 621(2)	−2 382(3)	7 718(3)
O(3b)	4 594(3)	−3 029(4)	9 422(3)
C(1c)	3 812(4)	4 746(8)	1 016(5)
C(2c)	3 626(4)	4 973(6)	2 189(7)
N(1c)	3 473(4)	5 140(7)	3 092(6)

[1,2-*Bis*(*pyridine-α-carbaldimino*)*ethane*]*trinitratoscandium*(III) *Dihydrate*, (4).—$Sc(NO_3)_3\cdot 6H_2O$ (0.266 g, 0.785 mmol) in acetonitrile (20 cm^3) was treated with 1,2-bis(pyridine-α-carbaldimino)ethane (bpce) (0.187 g, 0.785 mmol) in acetonitrile (20 cm^3), both solutions being almost boiling. Some very finely divided pale yellow material was immediately formed, but on allowing to stand overnight, pale yellow crystals were deposited. These were collected, being carefully separated from the powdery material, washed twice with acetonitrile, and dried (at 15 mmHg) at room temperature (Found: C, 32.7; H, 3.15; N, 18.9; Sc, 9.5. $C_{14}H_{18}N_7O_{11}Sc$ requires C, 33.3; H, 3.6; N, 19.4; Sc, 8.9%). The complex is stable in air and is unaffected at 250 °C. It is soluble in Me_2SO (Λ_m = 72.7 ohm^{-1} cm^2 mol^{-1}) and the bpce ligand dissociates on dissolution in water. The use of smaller quantities of reagents in more dilute solution at room temperature gave, on allowing to stand, a few crystals of bis[1,2-bis(pyridine-α-carbaldimino)ethane]-di-μ-hydroxo-dinitratodiscandium dinitrate bis(acetonitrile), complex (5), which were characterised by *X*-ray diffraction as described below.

X-*Ray Crystallography*.—*Complex* $[Sc(NO_3)_3(terpy)]$ (1): *crystal data*. $C_{15}H_{11}N_6O_9Sc$, $M = 464.3$, monoclinic, space group $P2_1/c$, $a = 8.982(1)$, $b = 16.486(2)$, $c = 13.272(2)$ Å, $\beta = 108.40(1)°$, $U = 1\,864.82$ Å^3, $D_m = 1.69$, $Z = 4$, $D_c = 1.66$ g cm^{-3}, $F(000) = 932$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 4.02$ cm^{-1}. Intensity data were recorded on a Nonius CAD-4 diffractometer and the structure solved and refined by standard methods. The final R value was 0.0426 for 3 272 data with $I > 3\sigma(I)$. Final atomic co-ordinates are given in Table 1.

Complex $[Sc_2(NO_3)_2(\mu\text{-}OH)_2(bpce)_2][NO_3]_2\cdot 2MeCN$ (5): *crystal data*. $C_{32}H_{36}N_{14}O_{14}Sc_2$, $M = 930.7$, monoclinic, space group $P2_1/n$, $a = 17.658(2)$, $b = 9.937(2)$, $c = 11.827(1)$ Å, $\beta = 92.96(1)°$, $U = 2\,068.7$ Å^3, $Z = 2$, $D_c = 1.50$ g cm^{-3}, $F(000) = 948$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 13.23$ cm^{-1}. The final R value was 0.0449 for 3 523 recorded and 2 156 observed reflections having $I > 3\sigma(I)$. Other details of the procedure are as for complex (1). Final atomic co-ordinates are given in Table 2.

Spectra.—I.r. spectra were obtained using a Perkin-Elmer 577 spectrophotometer, KBr or CsI plates, and Nujol or hexachlorobutadiene mulls. Proton n.m.r. spectra were obtained using a Bruker WP-80 instrument at 30 °C.

Results

Infrared Spectra.—Complex $[Sc(NO_3)_3(terpy)]$ (1) shows bands characteristic of co-ordinated terpyridyl and co-ordinated nitrate. Most terpyridyl bands are shifted to higher wavenumber (free ligand wavenumbers in parentheses): CH stretch, 3 105 (3 050); ring stretch, 1 602, 1 576, 1 561 (1 583, 1 562); CH deformation, 781 (771), 668, 658, 648 cm^{-1} (660, 635). Nitrate bands: A_1 1 510, 1 502; B_2 1 304; A_1 1 020; and B_1 812 cm^{-1}. Complex (2) shows a very similar spectrum but including water bands at 3 340 and 1 660 cm^{-1}, and a weak to medium absorption around 1 397 cm^{-1}.

$ScCl_3$(tpta) (3) shows bands characteristic [13] of co-ordinated α-substituted pyridine but also shows residual bands of unco-ordinated pyridine groups (free ligand wavenumbers in parentheses): ring stretch, 1 555, 1 522 (1 524); CH deformation, 1 010, 994 (994); 780, 762 (733); 680, 670 cm^{-1} (670).

$Sc(NO_3)_3(bpce)(H_2O)_2$ (4) shows side-chain C=N stretching at 1 661 cm^{-1} (1 648 in the free ligand) and ring stretching at 1 600 and 1 570 cm^{-1} (1 586, 1 565). The nitrate bands occur at 1 500, 1 295, 1 015, and 810 cm^{-1}. This spectrum is rather complex and no further certain correlations between peaks of the free and co-ordinated ligands can be made.

All the complexes show absorption in the region of 300 cm^{-1} [complex (1): 355, 326, 295, and 280; complex (3): 425, 405, 364, and 320; complex (4): 349, 315, and 290 cm^{-1}]. It is possible that these are due to Sc–N stretching modes although they seem too low in frequency for such an assignment.

^{1}H *N.M.R. Spectra.*—Resonance positions (τ) for the complexes are as follows (free ligand positions in parentheses). Complex (1) (solvent CD_3NO_2): $H^{3,3''}$, ~3.3 (3.20); $H^{4,4''}$, 3.51 (3.89); $H^{5,5''}$, 4.01 (4.41); $H^{6,6''}$, 2.91 (3.11); $H^{3',5'}$, ~3.3 (3.36); and $H^{4'}$, ~3.3 (3.75). Complex (3) (CD_3OD): H^3, 0.75 (0.90); H^4, 1.60 (1.83); H^5, 2.05 (2.25); and H^6, 0.97 (0.90). Complex (4) [$(CD_3)_2SO$]: H_2O, 6.58; CH_2, 6.00 (6.01); CH, 1.60 (1.61); H^3, 2.05 (2.10); H^4, 2.14 (2.17); H^5, 2.52 (2.58); and H^6, 1.39 (1.39).

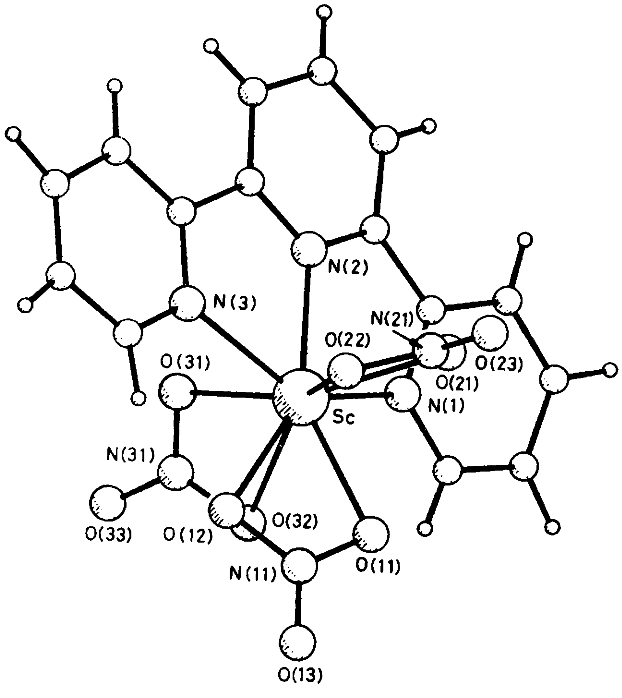

Figure 1. Molecular structure of [Sc(NO$_3$)$_3$(terpy)] (1) showing the atom-numbering scheme

Discussion

Structures and Properties.—(*a*) [Sc(NO$_3$)$_3$(terpy)] (1). This is a nine-co-ordinate complex and is thus apparently only the second known for Sc^{3+} with so high a co-ordination. A general view of the structure of the complex is shown (Figure 1) together with the packing arrangement (Figure 2). There is no semi-regular co-ordination polyhedron. The scandium ion is essentially co-planar with the terpy ligand, the six oxygen atoms from the three bidentate nitrate ligands being arranged in a necessarily unsymmetrical manner in the remaining unused part of the co-ordination sphere so that ligand–ligand interactions are minimised. The interligand distances within the co-ordination sphere which are smaller than 3 Å are shown in Table 3 together with the corresponding interbond angles (interligand distances are defined as the interatomic distances between pairs of ligand atoms which are directly bonded to scandium). Nitrate 1 [N(11), O(11), O(12), and O(13)] has five contacts in the region 2.743—2.865 Å, all to oxygen; nitrate 2 [N(21), O(21), O(22), and O(23)] has three contacts to oxygen (2.800—2.865 Å) and three to nitrogen (2.651—2.875 Å), while nitrate 3 [N(31), O(31), O(32), and O(33)] has only two contacts to oxygen (2.743 and 2.751 Å)

Table 3. Interatomic distances (Å) and angles (°) in [Sc(NO$_3$)$_3$(terpy)] (1)

(*i*) Distances from Sc

N(1), 2.311; N(2), 2.272; N(3), 2.322; O(11), 2.250; O(12), 2.242; O(21), 2.271; O(22), 2.317; O(31), 2.234; O(32), 2.482

(*ii*) Interligand atom distances (and ligand–Sc–ligand angles)

N(1)–N(2), 2.630 (70.1); N(1)–O(21), 2.651 (70.7); N(1)–O(32), 2.863 (73.3); N(2)–N(3), 2.624 (69.7); N(2)–O(21), 2.875 (78.5); N(2)–O(31), 2.806 (77.0); N(3)–O(22), 2.722 (71.9); N(3)–O(31), 2.704 (72.8); O(11)–O(12), 2.140 (56.9); O(11)–O(21), 2.814 (77.0); O(11)–O(22), 2.865 (77.7); O(11)–O(32), 2.751 (70.9); O(12)–O(22), 2.800 (75.8); O(12)–O(32), 2.743 (70.8); O(21)–O(22), 2.096 (54.4); O(31)–O(32), 2.105 (52.7)

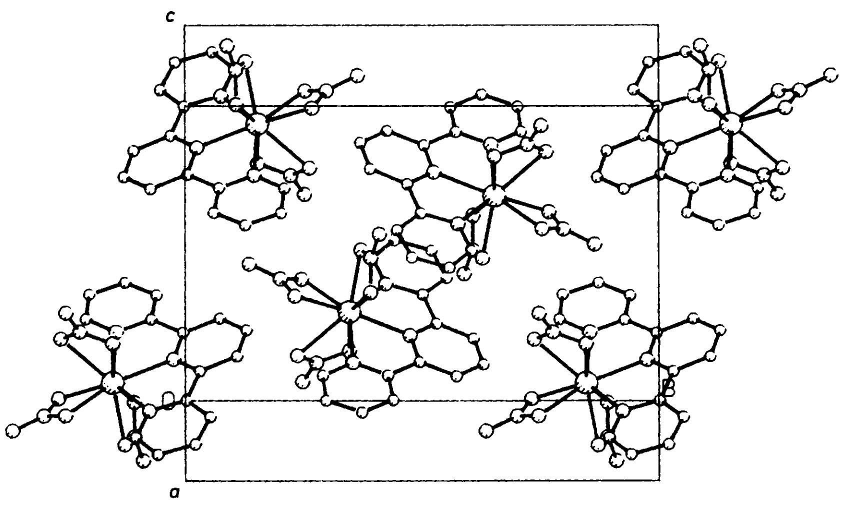

Figure 2. Packing diagram of the crystal structure of [Sc(NO$_3$)$_3$(terpy)] (1)

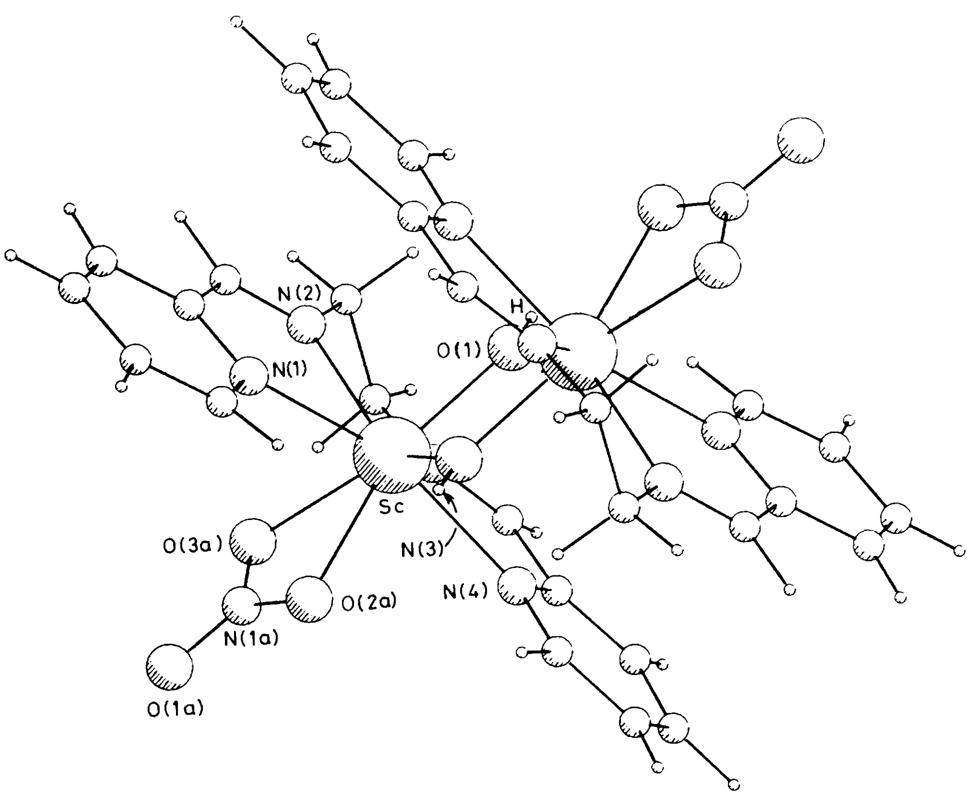

Figure 3. Structure of the cation $[Sc_2(NO_3)_2(\mu\text{-}OH)_2(bpce)_2]^{2+}$ of (5) showing the atom-numbering scheme

and three to nitrogen (2.704—2.863 Å). Of all these, the only one below 2.7 Å is the N(1)–O(21) interaction at 2.651 Å, a close approach which is perhaps caused by the somewhat inflexible coplanar nature of the terpyridyl ligand. The N(1)–N(2) and N(2)–N(3) distances are slightly shorter at 2.630 and 2.624 Å but these contacts occur within the semi-rigid organic framework.

The scandium–ligand interatomic distances are also shown in Table 3. The unsymmetrical co-ordination of nitrate 3 is noteworthy; it has one interatomic distance 0.248 Å longer than the other. Excluding Sc–O(32), the mean Sc–O distance is 2.263 Å and the mean Sc–N distance is 2.302 Å. Taking the ligand radii to be 1.40 and 1.43 Å for O and N respectively, this gives an ionic radius for nine-co-ordinate Sc^{3+} of *ca.* 0.867 Å. The very long Sc–O(32) distance suggests that the very considerable interligand repulsion which is evident in this compound falls little short of being sufficient to expel O(32) from the co-ordination sphere, giving two bidentate and one monodentate nitrato-groups and an eight-co-ordinate complex. This localisation of the effects of interligand repulsion at only one metal–ligand position in a high co-ordination number complex is noteworthy; a rather similar example occurs[14] in $[Nd(NO_3)_3(18\text{-crown-}6)]$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane) where only two of the Nd–O(crown) bonds are long compared with the other 10 Nd–O bonds, presumably as the result of increased interligand repulsion in the Nd complex, as compared with the corresponding La complex[15] which has all 12 La–O bonds of similar length. It is noteworthy that in $[Sc(NO_3)_3(terpy)]$ (1) all three nitrate ions are significantly distorted, presumably by interligand repulsion. Thus the interbond angles between N and the two-co-ordinated O are only 113.8, 113.0, and 115.9° for nitrates 1, 2, and 3 respectively.

Complex (1) is a non-electrolyte in nitromethane, and in CD_3NO_2 the average downfield shift in the ^1H n.m.r. spectrum, caused by the inductive deshielding effect of co-ordination, is 0.21 p.p.m. The electronic spectrum in nitromethane shows absorptions at 368 (ε = 27) and 385 nm (ε = 26 dm^3 mol^{-1} cm^{-1}) compared with the free terpyridyl ligand which absorbs at 368 nm only (ε = 14 dm^3 mol^{-1} cm^{-1}). These facts are consistent with the complex maintaining its integrity in nitromethane solution; although partial dissociation of the terpyridyl with rapid exchange cannot be ruled out it is extremely unlikely.[16]

(*b*) $[Sc_2(NO_3)_2(\mu\text{-}OH)_2(bpce)_2][NO_3]_2\cdot 2MeCN$ (5). This is a centrosymmetric dimeric complex with two bridging hydroxy groups, the scandium ions being eight-co-ordinate. Each bpce ligand is approximately coplanar, while the two hydroxy and two nitrate oxygen atoms which are co-ordinated to one particular scandium ion form a very approximate co-planar system which is perpendicular to the plane of the tetramine. The effect of this is to produce a distorted dodecahedral co-ordination. The structure of the complex cation is shown (Figure 3), together with the packing arrangement (Figure 4).

Interligand distances which are equal to or less than 3.0 Å, and the corresponding interbond angles, are shown in Table 4, together with the scandium–ligand atom distances. The four Sc–N distances, 2.341—2.403 Å, are somewhat greater than the two Sc–O(nitrate) distances at 2.333 and 2.295 Å. The two Sc–OH distances are notably short at 2.053 and 2.089 Å; this observation is considered again below.

The interligand distances fall into three groups (*a*) unconstrained N–O and O–O contacts, in the range 3.013—2.803 Å, (*b*) N–N contacts, at 2.618—2.644 Å, and (*c*) O(nitrate)–O(nitrate) at 2.132 Å and O(hydroxide)–O(hydroxide) at 2.439 Å. The unconstrained contacts in group (*a*) are

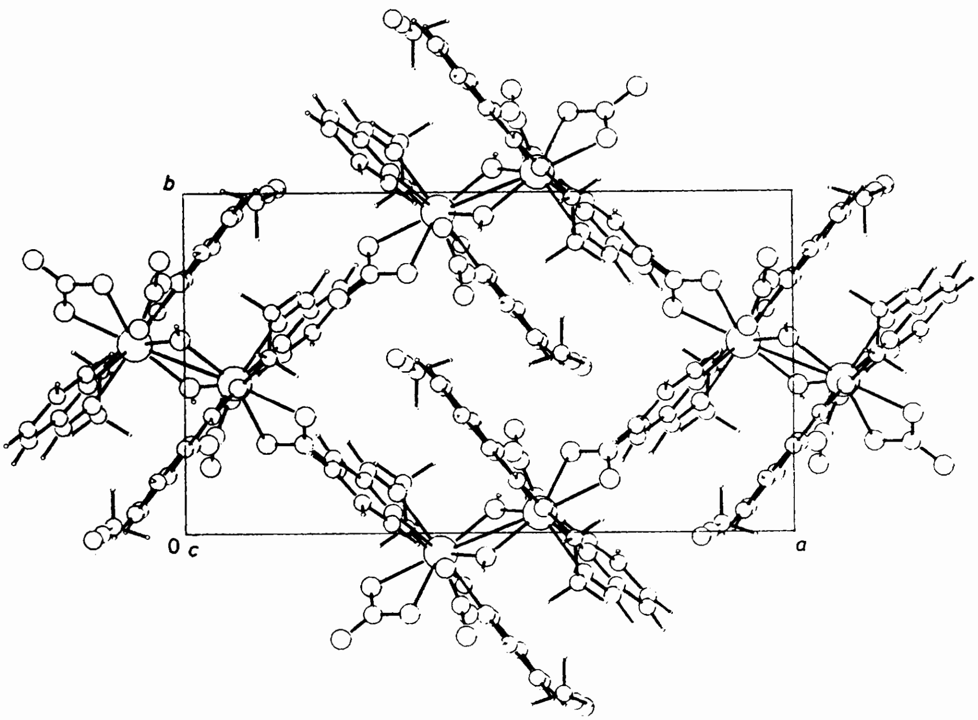

Figure 4. Packing diagram of the crystal structure of $[Sc_2(NO_3)_2(\mu\text{-}OH)_2(bpce)_2][NO_3]_2\cdot2MeCN$ (5)

Table 4. Interatomic distances (Å) and angles (°) in $[Sc_2(NO_3)_2(\mu\text{-}OH)_2(bpce)_2]^{2+}$, the cation of (5)

(*i*) Distances from Sc

N(1), 2.403; N(2), 2.360; N(3), 2.341; N(4), 2.357; O(1), 2.053; O(1′), 2.089; O(2a), 2.333; and O(3a), 2.295

(*ii*) Interligand atom distances (and ligand–Sc–ligand angles)

N(1)–N(2), 2.629 (67.0); N(1)–O(2a), 2.987 (78.2); N(1)–O(3a), 3.013 (79.7); N(2)–N(3), 2.618 (67.7); N(2)–O(1), 2.929 (82.9); N(2)–O(3a), 2.896 (76.9); N(3)–N(4), (68.5); N(3)–O(1), 2.944 (83.9); N(3)–O(3a), 2.843 (75.6); N(4)–O(1′), 2.958 (83.2); N(4)–O(2a), 2.987 (79.2); O(1)–O(1′), 2.439 (72.2); O(1′)–O(2a), 2.803 (78.5); and O(2a)–O(3a), 2.132 (54.8)

(*iii*) Bridging system

Sc–O–H = 124.32 and 127.67°
Sc–O–Sc = 107.84° O–H = 0.782 Å

distinctly longer than for the nine-co-ordinate $[Sc(NO_3)_3(terpy)]$ (1), as might be expected. Group (*b*) are somewhat smaller than group (*a*) owing to the constraining effect of the bpce ligand configuration, while the O(nitrate)–O(nitrate) distance is similar to the values for the terpyridyl complex (1). However, the distance of 2.439 Å is very remarkable in the case of the interbridging hydroxide interaction. This distance is 0.364 Å less than the next largest unconstrained distance, and 0.212 Å less than any unconstrained interaction in the nine-co-ordinate terpyridyl complex (1). When considered together with the very short Sc–OH distances, there must be a strong suggestion of a pronounced covalent contribution to bonding in the $Sc(\mu\text{-}OH)_2Sc$ system. The $Sc(\mu\text{-}OH)_2Sc$ system has idealised local symmetry D_{2h}, and the Sc–Sc distance (3.347 Å) is too great for direct metal–metal interaction. If we consider the bonding system arising out of an sd_{z^2} hybrid from each Sc and two sp^2 hybrids from each O, all lying in the ScO_2Sc plane, the two low-energy bonding orbitals would be A_g and B_{1u} and two non-bonding orbitals of B_{1g} and B_{1u} symmetry are available. If this system is occupied by the four lone-pair sp^2 electrons from the two O atoms, the bonding interaction would be expected to lead to a shortening of the O–O distance. The very slight asymmetry of the bridge, with Sc–O = 2.053 and 2.089 Å, doubtless provides a balance between reduction of unfavourable O–O interelectronic repulsion and loss of Sc–O bond energy.

Structures of complexes (2), (3), *and* (4). For these complexes no *X*-ray data are available, and the possible structures must be discussed on a basis of their stoicheiometry, from general properties and spectra, and by analogy with similar compounds where these are known.

For $Sc(NO_3)_3(terpy)(H_2O)$ (2) it is reasonable to assume a monomeric structure as more than sufficient ligands are present to satisfy the highest known co-ordination number (9) of scandium. The most likely formulation is probably simply $[Sc(NO_3)_3(terpy)]\cdot H_2O$, because $[Sc(NO_3)_2(terpy)(H_2O)]NO_3$ which would be at first sight an attractive possibility where the interligand repulsion has been reduced compared with $[Sc(NO_3)_3(terpy)]$ (1), is ruled out by the absence of i.r. bands at 1 362, 1 348, and 830 cm^{-1} due to ionic nitrate. In $[Sc(NO_3)_3(terpy)]\cdot H_2O$ it is quite possible that one nitrato-group could be monodentate but the distinction between monodentate and bidentate nitrate cannot be firmly made on infrared evidence alone.[17]

In the case of $ScCl_3(tpta)$ (3), it is likely that the formulation $[ScCl_3(tpta)]$, with six-co-ordinate Sc, is correct. As in the complex $YCl_3(tpta)(H_2O)_2$, the i.r. spectrum suggests [13] that one pyridyl nitrogen atom of the ligand remains unco-ordinated, the triazine being co-ordinated by three atoms in a similar manner to terpyridyl. Although six-co-ordination is rather low for scandium, the presence of three fairly large chloride ligands should render it stable, but the possibility of chloro-bridging cannot be dismissed. In methanolic solution, the complex is a non-conductor, co-ordination of chloride ion being maintained. The ^1H n.m.r. spectrum in CD_3OD at 23 °C shows an average downfield shift, due to the inductive effect of co-ordination, of 0.13 p.p.m. compared with the free triazine. The n.m.r. peaks are very considerably broadened and there is no definite indication of peaks assignable to the single uncomplexed pyridine ring. It thus appears that in methanol there is exchange between the two complexed and the single uncomplexed pyridine rings. Whether this takes place by intramolecular, dissociative intermolecular, or interactive intramolecular means is uncertain.

The dihydrate $Sc(NO_3)_3(bpce)(H_2O)_2$ (4) cannot be 12-co-ordinate and it remains to suggest which ligands are unco-ordinated. The nitrate i.r. region is somewhat obscured by ligand vibrations, but ionic nitrate seems to be absent. If this is so, and assuming the powerful tetradentate bpce is fully co-ordinated, the constitution must be $[Sc(NO_3)_3(bpce)]\cdot 2H_2O$ with one or with two nitrato-groups monodentate. The complex is rather insoluble and could only be studied in solution in Me_2SO, in which the conductivity and ^1H n.m.r. spectrum (average shift 0.03 p.p.m. downfield relative to the free tetramine) indicate dissociation of both bpce and nitrate ion.

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