Trimethylphosphine Oxide Complexes of Thorium and Uranium Tetranitrates; Crystal Structures of Ten- and Twelve-co-ordinate Complex Ions, Bis[trinitratotetrakis(trimethylphosphine oxide)thorium(IV)] Hexanitratothorate(IV) and Tetraphenylphosphonium Pentanitratobis(trimethylphosphine oxide)thorate(IV)

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The complexes $M(NO_3)_4\cdot xPMe_3O$ ($x = \frac{8}{3}$, M = Th; $x = \frac{10}{3}$, M = U), $[M(NO_3)_2(PMe_3O)_5][BPh_4]_2$ (M = Th or U), and $[PPh_4][Th(NO_3)_5(PMe_3O)_2]$ have been prepared and the formation of $[M(NO_3)_4\cdot 5PMe_3O]$ has been confirmed: their i.r. spectra are discussed. The crystal and molecular structures of $[Th(NO_3)_3(PMe_3O)_4]_2[Th(NO_3)_6]$ (1) and $[PPh_4][Th(NO_3)_5(PMe_3O)_2]$ (2) have been determined by the heavy-atom method from *X*-ray diffractometer data and refined by least squares to *R* 0.090 and 0.054 respectively. Crystal parameters are as follows: (1), monoclinic, space group *Pn*, *a* = 9.523(1), *b* = 14.507(2), *c* = 27.302(5) Å, β = 95.322(13)°, and *Z* = 2; (2), orthorhombic, space group *Pnma*, *a* = 24.626(6), *b* = 12.922(2), *c* = 12.777(2) Å, and *Z* = 4. The structure analyses are based on 5 131 (1) and 3 326 (2) intensities above background. Both crystals contain discrete ions. The co-ordination numbers for thorium in (1) are 10 (1 : 5 : 4 geometry) for the cation and 12 (icosahedron) for the anion, while in (2) the co-ordination number in the disordered anion is 12. The Th–O co-ordination distances are in the ranges: (1), 2.24—2.53 for the PMe_3O groups (average 2.34), 2.46—2.94 for the nitrate groups (average 2.61 Å); (2), 2.34—2.42 (average 2.38) and 2.52—2.75 (average 2.64 Å) respectively.

THE trimethylphosphine oxide complexes $M(NO_3)_4\cdot xPMe_3O$ ($x = 3$, $M = Th$,[1,2] U,[2] or Np;[1] $x = 4$, $M = Th$[1] or U;[1] $x = 5$, $M = Th$[2] or U[2]) have been reported earlier. Small ligands, such as SMe_2O, frequently give rise to a wide variety of complexes of differing stoicheiometry in the actinoid series,[3,4] and a re-examination of the $M(NO_3)_4$–PMe_3O systems for Th^{IV} and U^{IV} has led to the isolation of the new complexes reported in this paper, which also includes the structure of two of them.

EXPERIMENTAL

All the complexes were prepared and handled under dry-box conditions as described previously.[1] Thorium(IV) nitrate hydrate (B.D.H.) was used as supplied; $[PPh_4][NO_3]$ was prepared by metathesis of $[PPh_4]Br$ (E. Merck) with $Ag[NO_3]$ in ethanol. The compounds $Cs_2[U(NO_3)_6]$,[5] PMe_3O,[6] and $M(NO_3)_4\cdot 5PMe_3O$[2] were prepared by the published methods. Spectroscopic measurements and solvent drying were carried out as described previously.[1]

Preparations.—(*a*) $Th(NO_3)_4\cdot 2.67PMe_3O$. A solution of PMe_3O (4.5 mmol) in ethanol (10 cm^3) was added to a solution of hydrated thorium tetranitrate (1.5 mmol) in the same solvent; the resulting solution was evaporated to dryness and the *product* recrystallised from methyl cyanide–ethanol (1 : 2) and dried *in vacuo*, yield 48%, m.p. 278 ± 2° C.

(*b*) ' $Th(NO_3)_4\cdot 2.33PMe_3O$ '. As (*a*), but the ethanol solution was evaporated until crystals of the product separated. Yield 96%, m.p. 222 ± 1° C.

(*c*) $[PPh_4][Th(NO_3)_5(PMe_3O)_2]$. Solutions of $[PPh_4][NO_3]$ (1 mmol) and ' $Th(NO_3)_4\cdot 2.33PMe_3O$ ' (1.5 mmol) in acetone were mixed and evaporated slowly until crystals separated; the *product* was recrystallised from acetone–ethanol (1 : 1) and dried *in vacuo*, yield 80%, m.p. 180 ± 1 °C.

(*d*) $[Th(NO_3)_2(PMe_3O)_5][BPh_4]_2$. Sodium tetraphenylborate (1.5 mmol) in ethanol (10 cm^3) was added to $Th(NO_3)_4\cdot 5PMe_3O$ (0.5 mmol) in hot ethanol (10 cm^3). The filtrate from the cooled solution was evaporated to dryness *in vacuo*, and the *product* was recrystallised from methyl cyanide–ethanol (1 : 2) and dried *in vacuo*, yield 37%, m.p. 230 ± 2 °C.

(*e*) $U(NO_3)_4\cdot 3.33PMe_3O$. A solution of PMe_3O (1.5 mmol) in dichloromethane (10 cm^3) was added to $Cs_2[U(NO_3)_6]$ (0.5 mmol). The green filtrate was evaporated to dryness *in vacuo* and the *product* recrystallised from dichloromethane, then dried *in vacuo*, yield 27%, m.p. 197 ± 1 °C (decomp.).

(*f*) $[U(NO_3)_2(PMe_3O)_5][BPh_4]_2$. As (*e*) but in cold

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[1] K. W. Bagnall and M. W. Wakerley, *J.C.S. Dalton*, **1974**, 889.

[2] J. G. H. du Preez and C. P. J. van Vuuren, *J.C.S. Dalton*, **1975**, 1548.

[3] K. W. Bagnall, D. Brown, D. G. Holah, and F. Lux, *J. Chem. Soc.* (*A*), **1968**, 465.

[4] J. G. H. du Preez and M. L. Gibson, *J. Inorg. Nuclear Chem.*, **1974**, **36**, 1795.

[5] K. W. Bagnall, P. S. Robinson, and M. A. A. Stewart, *J. Chem. Soc.*, **1961**, 4060.

[6] A. B. Burge and W. E. McKee, *J. Amer. Chem. Soc.*, **1951**, **73**, 4590.

ethanol. The *product* precipitated in poor (*ca.* 10%) yield, m.p. 190 ± 1 °C (decomp.).

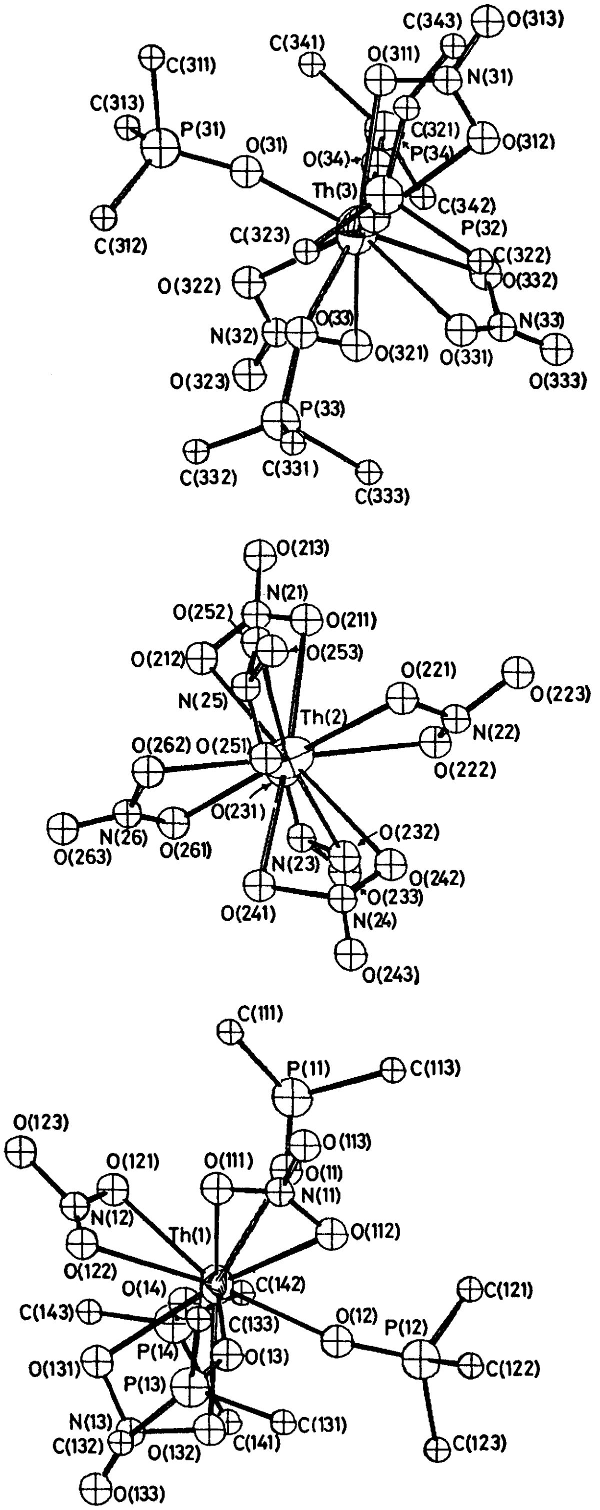

FIGURE 1 The individual ions of (1) showing the atomic numbering (viewed along *b*)

(*g*) 'Th(NO$_3$)$_4$·3.67PMe$_3$O.' See the Results section.

Thorium and uranium were determined as described previously;[7] C, H, and N were determined by combustion, using a Technicon analyser, and P by a published method.[8] The analytical results are summarised in Table 1.

X-*Ray Analysis*.—Both the products Th(NO$_3$)$_4$·2.67PMe$_3$O (1) and [PPh$_4$][Th(NO$_3$)$_5$(PMe$_3$O)$_2$] (2) were obtained as colourless prismatic crystals with pointed ends, and were mounted in Lindemann glass capillaries in a dry-box. The densities were determined by the flotation method. The crystal data are listed in Table 2. Data were collected with a Syntex $P2_1$ four-circle diffractometer using the θ—2θ scan technique with a graphite monochromator. Accurate cell constants were obtained by means of least-squares calculations based on the positions of 15 high-angle reflections. The systematic absences are: complex (1), $h0l$ for $h + l = 2n + 1$, indicating the space group Pn or $P2/n$; (2), $0kl$ for $k + l = 2n + 1$ and $hk0$ for $h = 2h + 1$, indicating either $Pnma$ or $Pn2_1a$.

For (1) the data were collected with Cu-K_α radiation to 2θ 130°. For (2), Mo-K_α radiation was employed to 2θ 55°. For both complexes, variable scan rates, between 1 and 29.3° min^{-1} in 2θ, depending on the intensity of a 2-s prescan, were used. For each complex, three standard reflections were measured at intervals of 100 reflections; no variation in their intensity was observed.

The data for both complexes were corrected for Lorentz and polarisation effects. Absorption corrections, calculated by the analytical method using program ABSCOR,[9] were also applied, and for (1), but not for (2), a secondary extinction correction was performed.

Structure Analyses.—Both structures were solved by standard Patterson and Fourier techniques. For (1) the analysis showed Pn to be the correct space group (nonstandard group of no. 7 Pc, with equivalent positions x, y, z and $\frac{1}{2} + x$, $-y$, $\frac{1}{2} + z$). There is a remarkable pseudosymmetry with the centre at Th(2) (see Figures 1 and 2), relating Th(1) and Th(3). However, refinement showed very clearly that the non-centric structure is correct; using only the Th atoms, R was 0.022 in Pn but 0.46 in $P2/n$. Blocked least-squares refinement (five blocks) with statistical weights, anisotropic temperature factors for the thorium atoms, and isotropic temperature factors for the light atoms gave a final value of R of 0.090. A number of atoms (especially carbon but also nitrogen and oxygen) showed very high thermal vibrations. This indicated some disorder at least in the PMe$_3$O groups, possibly also in some of the nitrate groups, and was supported by a Fourier map. It was very difficult, however, to locate some of the assumed disordered positions, and only one position with a population parameter of 1.0 was used for each of these atoms.

For (2) the correct space group was $Pnma$ (no. 62), with the molecules occupying four-fold special positions, with the thorium atom and 13 light atoms located in crystallographic mirror planes at $y = \pm 0.25$. Full-matrix least-squares refinement with unit weights and with isotropic temperature factors for all the atoms except Th (anisotropic) yielded a final value of R of 0.054. All the nitrate groups are disordered, with two positions for each of the bonding oxygens.

The atomic scattering-factor curves used were taken from ref. 10. Those for Th and P were corrected for anomalous

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[7] P. J. Alvey, K. W. Bagnall, D. Brown, and J. Edwards, *J.C.S. Dalton*, 1973, 2308.

[8] R. S. Young, 'Chemical Analysis in Extractive Metallurgy,' Griffin, London, 1971, p. 271.

[9] N. W. Alcock, in 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p.271.

[10] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

TABLE 1

Analytical results (%) *

Complex	M	C	H	N	P
' $Th(NO_3)_4 \cdot 3.67PMe_3O$ '	28.6 (28.4)	16.0 (16.2)	4.0 (4.0)	6.7 (6.9)	13.7 (13.9)
$Th(NO_3)_4 \cdot 2.67PMe_3O$	32.6 (32.0)	13.2 (13.2)	3.2 (3.4)	7.6 (7.7)	11.5 (11.4)
' $Th(NO_3)_4 \cdot 2.33PMe_3O$ '	33.5 (33.4)	12.9 (12.1)	3.3 (3.0)	8.2 (8.1)	10.5 (10.4)
$[PPh_4][Th(NO_3)_5(PMe_3O)_2]$	21.0 (21.8)	33.9 (33.8)	3.7 (3.6)	6.5 (6.6)	8.8 (8.7)
$[Th(NO_3)_2(PMe_3O)_5][BPh_4]_2$	16.0 (15.9)	51.6 (52.0)	6.0 (5.9)	1.9 (1.9)	10.8 (10.6)
$[U(NO_3)_2(PMe_3O)_5][BPh_4]_2$	16.2 (16.3)	52.6 (51.8)	6.8 (5.8)	1.9 (1.9)	10.6 (10.6)
$U(NO_3)_4 \cdot 3.33PMe_3O$	30.1 (30.0)	14.7 (15.2)	3.7 (3.8)	6.9 (6.8)	12.7 (13.1)

* Calculated values are given in parentheses.

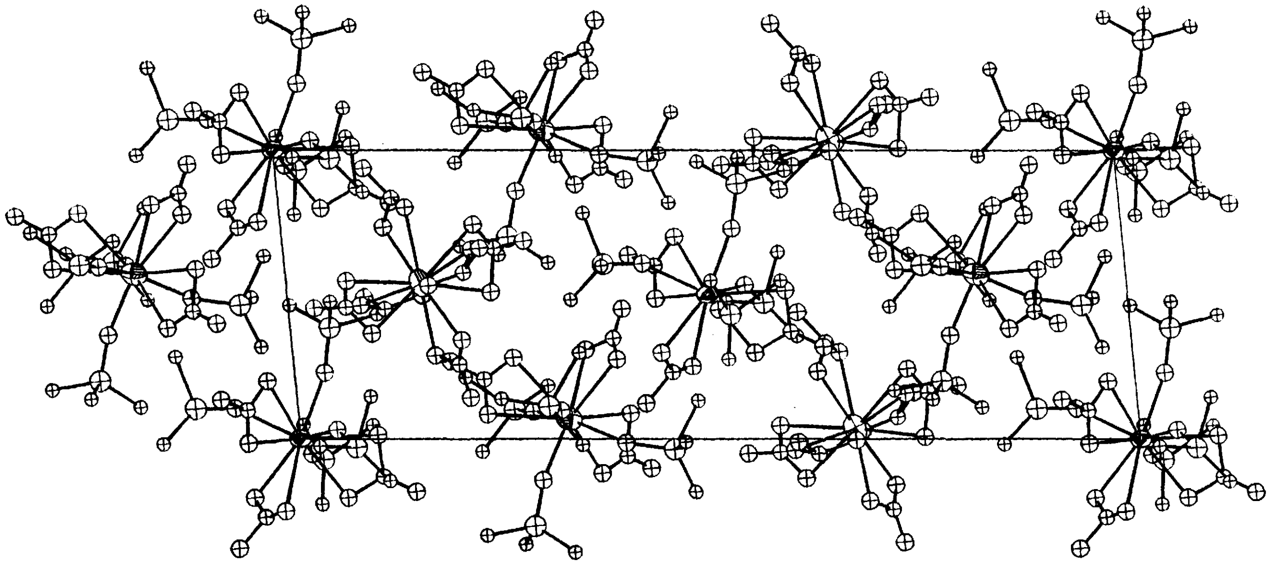

FIGURE 2 Unit cell of (1) (viewed along *b*)

TABLE 2

Crystal data

	Complex	
	(1)	(2)
Parameter	$C_{24}H_{72}N_{12}O_{44}P_8Th_3$	$C_{30}H_{29}N_5O_{17}P_3Th$
Crystal system	Monoclinic	Orthorhombic
Space group	*Pn* (no. 7)	*Pnma* (no. 62)
a/Å	9.523(1)	24.626(6)
b/Å	14.507(2)	12.922(2)
c/Å	27.302(5)	12.777(2)
α/°	90	90
β/°	95.322(13)	90
γ/°	90	90
U/Å^3	3 756(1)	4 066(1)
D_m/g cm^{-3}	1.93	1.75
D_c/g cm^{-3}	1.93	1.74
Z	2	4
F(000)	2 084	2 096
λ/Å	1.5418	0.71069
μ/cm^{-1}	141.6	43.9
Total reflections	7 093	4 783
Observed reflections $[(I)/\sigma(I) > 3\sigma]$	5 131	3 326

TABLE 3

Final atomic co-ordinates of (1) in fractions of cell edges, with standard deviation in parentheses

	x	*y*	*z*
Th(1)	0	−0.277 3(1)	0
Th(2)	−0.037 3(5)	−0.250 0(3)	0.339 5(1)
Th(3)	−0.069 7(2)	−0.224 0(2)	0.678 6(1)
P(11)	−0.104 1(17)	−0.367 8(10)	0.120 9(5)
P(12)	−0.384 4(17)	−0.315 5(12)	−0.047 3(6)
P(13)	0.028 7(12)	−0.049 6(7)	−0.066 0(4)
P(14)	0.070 4(19)	−0.526 8(11)	−0.025 3(6)
P(31)	0.300 9(16)	−0.183 6(11)	0.730 9(5)
P(32)	−0.111 5(18)	0.034 8(10)	0.701 1(6)
P(33)	0.036 5(27)	−0.137 6(16)	0.556 1(8)
P(34)	−0.100 8(15)	−0.454 6(9)	0.742 2(5)
O(11)	−0.106(5)	−0.344(4)	0.074(2)
O(12)	−0.229(4)	−0.306(3)	−0.036(1)
O(13)	−0.032(4)	−0.138(2)	−0.045(1)
O(14)	0.053(4)	−0.430(2)	−0.012(1)
O(31)	0.142(3)	−0.188(2)	0.716(1)
O(32)	−0.097(4)	−0.062(2)	0.687(1)
O(33)	0.014(3)	−0.157(2)	0.613(1)
O(34)	−0.094(3)	−0.356(2)	0.720(1)
O(111)	0.015(3)	−0.155(2)	0.062(1)
O(112)	−0.199(3)	−0.160(2)	0.033(1)
O(113)	−0.135(4)	−0.050(3)	0.090(1)
O(121)	0.203(4)	−0.311(3)	0.061(1)
O(122)	0.250(5)	−0.192(3)	0.026(1)
O(123)	0.378(7)	−0.253(4)	0.085(2)
O(131)	0.202(4)	−0.300(3)	−0.050(1)
O(132)	−0.014(5)	−0.302(3)	−0.093(2)
O(133)	0.182(6)	−0.331(4)	−0.132(2)
O(211)	−0.046(10)	−0.327(6)	0.428(3)
O(212)	0.136(4)	−0.337(3)	0.403(1)
O(213)	0.050(4)	−0.391(3)	0.469(1)

dispersion.[10] All the main calculations were carried out on a CDC 7600 computer, with the '*X*-Ray' system.[11] The final co-ordinates are in Tables 3 and 4, and bond lengths and angles are in Tables 5 and 6. Temperature factors and final structure factors are listed in Supplementary Publication No. SUP 22213 (51 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[11] J. M. Stewart, Technical Report TR-192, University of Maryland, 1972.

Table 3 (*Continued*)

	x	y	z
O(221)	−0.233(7)	−0.167(5)	0.378(2)
O(222)	−0.301(7)	−0.298(4)	0.350(2)
O(223)	−0.438(5)	−0.223(3)	0.395(2)
O(231)	−0.030(5)	−0.430(3)	0.331(1)
O(232)	−0.156(6)	−0.367(4)	0.276(2)
O(233)	−0.160(7)	−0.486(5)	0.266(2)
O(241)	−0.008(3)	−0.177(2)	0.257(1)
O(242)	−0.242(8)	−0.153(5)	0.271(2)
O(243)	−0.185(4)	−0.111(3)	0.213(1)
O(251)	0.003(4)	−0.076(2)	0.339(1)
O(252)	0.038(3)	−0.140(2)	0.413(1)
O(253)	0.011(4)	−0.003(3)	0.408(1)
O(261)	0.158(4)	−0.327(2)	0.297(1)
O(262)	0.213(3)	−0.199(2)	0.330(1)
O(263)	0.358(6)	−0.271(3)	0.293(2)
O(311)	−0.085(2)	−0.182(1)	0.775(1)
O(312)	−0.280(4)	−0.213(2)	0.738(1)
O(313)	−0.268(4)	−0.189(3)	0.813(1)
O(321)	−0.087(3)	−0.343(2)	0.605(1)
O(322)	0.118(5)	−0.336(3)	0.645(2)
O(323)	0.101(4)	−0.420(3)	0.586(1)
O(331)	−0.275(4)	−0.169(2)	0.615(1)
O(332)	−0.309(6)	−0.314(3)	0.651(2)
O(333)	−0.450(12)	−0.251(6)	0.603(4)
N(11)	−0.099(6)	−0.123(4)	0.060(2)
N(12)	0.270(4)	−0.230(2)	0.050(1)
N(13)	0.129(7)	−0.313(5)	−0.095(2)
N(21)	0.046(3)	−0.351(2)	0.431(1)
N(22)	−0.334(10)	−0.230(6)	0.365(3)
N(23)	−0.075(5)	−0.428(3)	0.288(1)
N(24)	−0.160(13)	−0.116(7)	0.249(4)
N(25)	0.051(5)	−0.069(3)	0.385(1)
N(26)	0.243(4)	−0.268(2)	0.303(1)
N(31)	−0.206(6)	−0.193(4)	0.775(2)
N(32)	0.060(6)	−0.367(3)	0.613(2)
N(33)	−0.348(4)	−0.227(2)	0.617(1)
C(111)	0.019(5)	−0.309(3)	0.163(2)
C(112)	−0.098(9)	−0.484(6)	0.123(3)
C(113)	−0.282(8)	−0.324(5)	0.139(3)
C(121)	−0.461(6)	−0.363(4)	−0.002(2)
C(122)	−0.475(6)	−0.199(3)	−0.051(2)
C(123)	−0.430(6)	−0.381(4)	−0.105(2)
C(131)	−0.146(13)	0.011(8)	−0.088(4)
C(132)	0.145(20)	−0.071(13)	−0.102(6)
C(133)	0.025(12)	0.050(9)	−0.022(4)
C(141)	−0.047(10)	−0.552(7)	−0.088(3)
C(142)	−0.048(10)	−0.627(6)	−0.005(3)
C(143)	0.225(14)	−0.566(9)	−0.018(5)
C(311)	0.333(7)	−0.130(5)	0.789(2)
C(312)	0.391(7)	−0.112(5)	0.686(2)
C(313)	0.364(8)	−0.298(5)	0.744(2)
C(321)	−0.138(21)	0.062(14)	0.757(7)
C(322)	−0.298(12)	0.065(8)	0.659(4)
C(323)	0.020(9)	0.100(5)	0.665(3)
C(331)	0.011(6)	−0.014(4)	0.542(2)
C(332)	0.183(7)	−0.160(5)	0.536(2)
C(333)	−0.132(9)	−0.179(7)	0.523(3)
C(341)	0.043(12)	−0.485(7)	0.785(4)
C(342)	−0.183(9)	−0.529(6)	0.700(3)
C(343)	−0.211(5)	−0.440(3)	0.797(2)

Table 4

Final atomic co-ordinates of (2) in fractions of cell edges, with standard deviations in parentheses

	x	y	z
Th	0.123 85(2)	0.25	0.102 64(4)
P(1)	0.395 0(2)	0.25	0.019 3(3)
P(2)	0.226 7(2)	0.25	0.324 6(4)
P(3)	−0.007 9(2)	0.25	−0.054 1(4)
O(2)	0.201 4(5)	0.25	0.219 1(9)
O(3)	0.047 0(5)	0.25	−0.004 9(10)
O(13)	0.163 3(4)	−0.057 6(9)	0.003 1(8)
O(23)	0.044 4(4)	0.040 8(8)	0.314 5(8)
O(33)	0.223 2(7)	0.25	−0.170 0(15)
O(11A)	0.164 6(6)	0.072 1(12)	0.124 9(11)
O(12A)	0.120 3(7)	0.087 7(14)	−0.018 9(13)
O(11B)	0.186 1(7)	0.077 1(14)	0.069 3(13)
O(12B)	0.099 6(7)	0.054 9(14)	0.029 8(14)
O(21A)	0.049 8(10)	0.119 4(21)	0.161 4(20)
O(22A)	0.101 4(7)	0.173 9(13)	0.285 1(13)
O(21B)	0.037 9(10)	0.154 5(20)	0.192 3(20)
O(22B)	0.115 6(6)	0.102 1(13)	0.246 7(12)
O(31A)	0.149 0(6)	0.209 2(11)	−0.092 0(12)
O(32A)	0.212 2(6)	0.283 5(11)	−0.002 4(11)
N(1)	0.149 4(5)	0.027 8(9)	0.033 4(9)
N(2)	0.065 2(4)	0.104 7(9)	0.254 8(8)
N(3)	0.195 4(6)	0.25	−0.089 6(12)
C(1)	0.299 5(7)	0.25	0.320 7(15)
C(2)	0.209 8(10)	0 132'7(21)	0.397 9(22)
C(3)	−0.060 4(13)	0.25	0.039 1(26)
C(4)	−0.017 8(9)	0.133 5(19)	−0.131 5(19)
C(11)	0.375 2(5)	0.137 8(8)	0.092 7(8)
C(12)	0.409 9(5)	0.103 3(10)	0.174 8(10)
C(13)	0.391 6(5)	0.022 8(11)	0.239 2(11)
C(14)	0.340 7(6)	−0.021 1(11)	0.224 5(11)
C(15)	0.306 8(6)	0.015 0(11)	0.146 3(11)
C(16)	0.323 6(5)	0.095 5(10)	0.080 4(9)
C(21)	0.467 0(7)	0.25	−0.006 0(13)
C(22)	0.493 1(6)	0.155 0(11)	−0.021 2(11)
C(23)	0.547 5(6)	0.155 4(13)	−0.054 2(13)
C(24)	0.573 9(10)	0.25	−0.073 3(19)
C(31)	0.363 4(6)	0.25	−0.108 9(13)
C(32)	0.354 2(5)	0.155 1(10)	−0.157 7(10)
C(33)	0.334 3(6)	0.155 3(12)	−0.262 2(11)
C(34)	0.324 8(9)	0.25	−0.309 9(17)

Table 5

Bong lengths (Å) and bond angles (°) in (1), with standard deviations in parentheses

(*a*) Bond lengths

	$i = 1$	$i = 3$
Th(*i*)–O(*i*1)	2.53(5)	2.24(3)
Th(*i*)–O(*i*2)	2.35(4)	2.38(3)
Th(*i*)–O(*i*3)	2.37(3)	2.25(3)
Th(*i*)–O(*i*4)	2.31(4)	2.25(3)
Th(*i*)–O(*i*11)	2.46(3)	2.71(2)
Th(*i*)–O(*i*12)	2.75(3)	2.70(3)
Th(*i*)–O(*i*21)	2.48(4)	2.64(3)
Th(*i*)–O(*i*22)	2.72(4)	2.64(4)
Th(*i*)–O(*i*31)	2.48(4)	2.61(3)
Th(*i*)–O(*i*32)	2.54(4)	2.67(5)
P(*i*1)–O(*i*1)	1.33(5)	1.53(3)
P(*i*1)–C(*i*11)	1.77(4)	1.78(7)
P(*i*1)–C(*i*12)	1.68(8)	1.87(7)
P(*i*1)–C(*i*13)	1.92(8)	1.78(7)
P(*i*2)–O(*i*2)	1.49(4)	1.47(4)
P(*i*2)–C(*i*21)	1.65(6)	1.61(20)
P(*i*2)–C(*i*22)	1.89(5)	2.07(11)
P(*i*2)–C(*i*23)	1.86(6)	1.91(8)
P(*i*3)–O(*i*3)	1.54(3)	1.61(4)
P(*i*3)–C(*i*31)	1.93(12)	1.84(6)
P(*i*3)–C(*i*32)	1.57(19)	1.58(8)
P(*i*3)–C(*i*33)	1.88(13)	1.86(9)
P(*i*4)–O(*i*4)	1.46(4)	1.56(3)
P(*i*4)–O(*i*41)	1.99(9)	1.78(10)
P(*i*4)–O(*i*42)	1.95(9)	1.70(9)
P(*i*4)–O(*i*43)	1.58(13)	1.92(5)
N(*i*1)–O(*i*11)	1.17(7)	1.16(6)

RESULTS AND DISCUSSION

The Complexes.—The formation of the reported[2] pentakis complexes, $M(NO_3)_4 \cdot 5PMe_3O$, in the presence of an excess of the ligand has been confirmed. Products with non-integral M : PMe_3O ratios were obtained by varying the preparative conditions, including the solvent, or mixture of solvents, used for recrystallisation. With a 1 : 3 mol ratio (M : ligand) in ethanol (Th) or dichloromethane (U) the products were of composition $Th(NO_3)_4 \cdot 2.67PMe_3O$ (after recrystallisation from MeCN) and $U(NO_3)_4 \cdot 3.33\ PMe_3O$. The former complex is analogous

TABLE 5 (*Continued*)

	i = 1	*i* = 3
N(*i*1)–O(*i*12)	1.27(6)	1.22(6)
N(*i*1)–O(*i*13)	1.41(7)	1.24(7)
N(*i*2)–O(*i*21)	1.38(5)	1.43(6)
N(*i*2)–O(*i*22)	0.86(5)	1.09(6)
N(*i*2)–O(*i*23)	1.38(7)	1.16(6)
N(*i*3)–O(*i*31)	1.37(7)	1.11(5)
N(*i*3)–O(*i*32)	1.37(9)	1.59(6)
N(*i*3)–O(*i*33)	1.21(9)	1.07(11)
Th(2)–O(211)	2.67(9)	
Th(2)–O(212)	2.60(4)	
Th(2)–O(221)	2.53(7)	
Th(2)–O(222)	2.65(6)	
Th(2)–O(231)	2.63(4)	
Th(2)–O(232)	2.60(5)	
Th(2)–O(241)	2.54(3)	
Th(2)–O(242)	2.94(7)	
Th(2)–O(251)	2.56(3)	
Th(2)–O(252)	2.60(3)	
Th(2)–O(261)	2.53(4)	
Th(2)–O(262)	2.53(3)	
N(21)–O(211)	0.94(10)	
N(21)–O(212)	1.23(5)	
N(21)–O(213)	1.19(5)	
N(22)–O(221)	1.35(11)	
N(22)–O(222)	1.12(11)	
N(22)–O(223)	1.36(11)	
N(23)–O(231)	1.20(6)	
N(23)–O(232)	1.20(7)	
N(23)–O(233)	1.28(8)	
N(24)–O(241)	1.70(12)	
N(24)–O(242)	1.14(14)	
N(24)–O(243)	1.00(11)	
N(25)–O(251)	1.32(5)	
N(25)–O(252)	1.29(5)	
N(25)–O(253)	1.29(6)	
N(26)–O(261)	1.17(5)	
N(26)–O(262)	1.29(4)	
N(26)–O(263)	1.15(7)	

(*b*) Bond angles

	i = 1	*i* = 3
O(*i*1)–Th(*i*)–O(*i*2)	81.2(13)	79.9(11)
O(*i*1)–Th(*i*)–O(*i*3)	134.4(14)	83.9(11)
O(*i*1)–Th(*i*)–O(*i*4)	81.3(15)	95.6(10)
O(*i*1)–Th(*i*)–O(*i*11)	74.1(13)	68.2(9)
O(*i*1)–Th(*i*)–O(*i*12)	68.9(13)	113.3(10)
O(*i*1)–Th(*i*)–O(*i*21)	74.5(13)	119.5(10)
O(*i*1)–Th(*i*)–O(*i*22)	111.6(13)	72.1(12)
O(*i*1)–Th(*i*)–O(*i*31)	140.6(14)	145.0(10)
O(*i*1)–Th(*i*)–O(*i*32)	138.6(15)	161.9(13)
O(*i*2)–Th(*i*)–O(*i*3)	81.7(12)	72.6(12)
O(*i*2)–Th(*i*)–O(*i*4)	88.9(13)	140.7(11)
O(*i*2)–Th(*i*)–O(*i*11)	114.3(12)	70.6(9)
O(*i*2)–Th(*i*)–O(*i*12)	66.7(10)	77.7(11)
O(*i*2)–Th(*i*)–O(*i*21)	152.2(12)	136.2(10)
O(*i*2)–Th(*i*)–O(*i*22)	161.3(12)	136.5(13)
O(*i*2)–Th(*i*)–O(*i*31)	118.8(13)	71.4(11)
O(*i*2)–Th(*i*)–O(*i*32)	66.0(14)	114.3(14)
O(*i*3)–Th(*i*)–O(*i*4)	140.0(12)	146.3(12)
O(*i*3)–Th(*i*)–O(*i*11)	75.2(10)	136.8(10)
O(*i*3)–Th(*i*)–O(*i*12)	65.5(10)	142.3(11)
O(*i*3)–Th(*i*)–O(*i*21)	125.2(12)	71.4(10)
O(*i*3)–Th(*i*)–O(*i*22)	79.7(12)	72.0(13)
O(*i*3)–Th(*i*)–O(*i*31)	84.1(12)	68.8(11)
O(*i*3)–Th(*i*)–O(*i*32)	66.8(13)	110.4(13)
O(*i*4)–Th(*i*)–O(*i*11)	142.4(11)	71.6(9)
O(*i*4)–Th(*i*)–O(*i*12)	143.5(11)	68.3(10)
O(*i*4)–Th(*i*)–O(*i*21)	74.5(12)	79.9(10)
O(*i*4)–Th(*i*)–O(*i*22)	106.0(13)	75.9(12)
O(*i*4)–Th(*i*)–O(*i*31)	66.6(14)	119.3(11)
O(*i*4)–Th(*i*)–O(*i*32)	73.8(14)	66.3(13)
O(*i*11)–Th(*i*)–O(*i*12)	47.7(10)	45.2(8)
O(*i*11)–Th(*i*)–O(*i*21)	71.7(11)	151.2(8)
O(*i*11)–Th(*i*)–O(*i*22)	59.7(12)	124.7(10)
O(*i*11)–Th(*i*)–O(*i*31)	118.7(12)	118.0(9)
O(*i*11)–Th(*i*)–O(*i*32)	141.7(13)	104.9(12)
O(*i*12)–Th(*i*)–O(*i*12)	115.0(10)	120.0(9)

TABLE 5 (*Continued*)

	i = 1	*i* = 3
O(*i*12)–Th(*i*)–O(*i*22)	104.3(11)	144.1(11)
O(*i*12)–Th(*i*)–O(*i*31)	148.6(11)	80.1(10)
O(*i*12)–Th(*i*)–O(*i*32)	115.7(12)	62.2(13)
O(*i*21)–Th(*i*)–O(*i*22)	45.9(12)	48.1(11)
O(*i*21)–Th(*i*)–O(*i*31)	75.3(13)	73.1(9)
O(*i*21)–Th(*i*)–O(*i*32)	127.2(14)	58.6(13)
O(*i*22)–Th(*i*)–O(*i*31)	60.1(13)	116.8(12)
O(*i*22)–Th(*i*)–O(*i*32)	106.8(14)	101.2(14)
O(*i*31)–Th(*i*)–O(*i*32)	53.7(14)	53.1(13)
O(*i*1)–P(*i*1)–C(*i*11)	116.9(27)	109.6(27)
O(*i*1)–P(*i*1)–C(*i*12)	107.0(36)	110.8(24)
O(*i*1)–P(*i*1)–C(*i*13)	103.4(31)	108.8(27)
C(*i*11)–P(*i*1)–C(*i*12)	115.6(31)	107.1(31)
C(*i*11)–P(*i*1)–C(*i*13)	102.6(27)	101.4(31)
C(*i*12)–P(*i*1)–C(*i*13)	110.4(38)	118.6(27)
O(*i*2)–P(*i*2)–C(*i*21)	113.1(24)	120.2(74)
O(*i*2)–P(*i*2)–C(*i*22)	111.2(23)	99.0(35)
O(*i*2)–P(*i*2)–C(*i*23)	111.4(25)	104.8(29)
C(*i*21)–P(*i*2)–C(*i*22)	100.7(26)	105.7(77)
C(*i*21)–P(*i*2)–C(*i*23)	110.0(27)	122.2(76)
C(*i*22)–P(*i*2)–C(*i*23)	109.9(24)	100.7(40)
O(*i*3)–P(*i*3)–C(*i*31)	98.5(37)	110.3(26)
O(*i*3)–P(*i*3)–C(*i*32)	112.0(69)	119.8(30)
O(*i*3)–P(*i*3)–C(*i*33)	112.6(41)	102.8(33)
C(*i*31)–P(*i*3)–C(*i*32)	122.4(72)	103.2(34)
C(*i*31)–P(*i*3)–C(*i*33)	77.4(49)	96.9(38)
C(*i*32)–P(*i*3)–C(*i*33)	126.7(77)	121.2(40)
O(*i*4)–P(*i*4)–C(*i*41)	109.2(32)	115.5(38)
O(*i*4)–P(*i*4)–C(*i*42)	124.0(33)	110.8(33)
O(*i*4)–P(*i*4)–C(*i*43)	116.2(50)	104.2(20)
C(*i*41)–P(*i*4)–C(*i*42)	79.5(37)	124.1(46)
C(*i*41)–P(*i*4)–C(*i*43)	119.0(53)	87.5(39)
C(*i*42)–P(*i*4)–C(*i*43)	104.5(55)	110.0(35)
O(*i*11)–N(*i*1)–O(*i*12)	120.7(48)	121.4(50)
O(*i*11)–N(*i*1)–O(*i*13)	122.1(47)	123.8(48)
O(*i*12)–N(*i*1)–O(*i*13)	116.6(48)	114.7(51)
O(*i*21)–N(*i*2)–O(*i*22)	128.8(46)	116.5(48)
O(*i*21)–N(*i*2)–O(*i*23)	89.0(36)	116.1(43)
O(*i*22)–N(*i*2)–O(*i*23)	141.3(54)	127.3(57)
O(*i*31)–N(*i*3)–O(*i*32)	111.7(53)	121.3(36)
O(*i*31)–N(*i*3)–O(*i*33)	124.3(63)	142.2(63)
O(*i*32)–N(*i*3)–O(*i*33)	124.0(58)	96.5(59)
Th(*i*)–O(*i*1)–P(*i*1)	153.8(30)	162.9(18)
Th(*i*)–O(*i*2)–P(*i*2)	165.4(23)	170.6(22)
Th(*i*)–O(*i*3)–P(*i*3)	150.0(20)	158.5(21)
Th(*i*)–O(*i*4)–P(*i*4)	171.2(23)	171.0(20)
Th(*i*)–O(*i*11)–N(*i*1)	104.2(31)	97.2(28)
Th(*i*)–O(*i*12)–N(*i*1)	86.9(29)	96.2(33)
Th(*i*)–O(*i*21)–N(*i*2)	92.1(22)	92.8(22)
Th(*i*)–O(*i*22)–N(*i*2)	92.4(38)	102.4(38)
Th(*i*)–O(*i*31)–N(*i*3)	98.7(36)	99.8(26)
Th(*i*)–O(*i*32)–N(*i*3)	95.8(34)	85.7(25)
O(211)–Th(2)–O(212)	42.9(22)	
O(211)–Th(2)–O(221)	74.8(25)	
O(211)–Th(2)–O(222)	71.4(24)	
O(211)–Th(2)–O(231)	70.8(21)	
O(211)–Th(2)–O(232)	106.4(22)	
O(211)–Th(2)–O(241)	175.4(21)	
O(211)–Th(2)–O(251)	116.0(21)	
O(211)–Th(2)–O(252)	65.8(20)	
O(211)–Th(2)–O(261)	108.2(22)	
O(211)–Th(2)–O(262)	108.7(21)	
O(212)–Th(2)–O(221)	113.8(16)	
O(212)–Th(2)–O(222)	110.4(16)	
O(212)–Th(2)–O(231)	63.6(12)	
O(212)–Th(2)–O(232)	109.5(14)	
O(212)–Th(2)–O(241)	132.7(11)	
O(212)–Th(2)–O(251)	113.6(11)	
O(212)–Th(2)–O(252)	71.1(10)	
O(212)–Th(2)–O(261)	68.9(11)	
O(212)–Th(2)–O(262)	70.2(11)	
O(221)–Th(2)–O(222)	48.5(21)	
O(221)–Th(2)–O(231)	122.8(18)	
O(221)–Th(2)–O(232)	107.3(19)	
O(221)–Th(2)–O(241)	108.6(16)	
O(221)–Th(2)–O(251)	69.3(17)	
O(221)–Th(2)–O(252)	63.3(16)	

TABLE 5 (*Continued*)

	$i = 1$
O(221)–Th(2)–O(261)	176.9(16)
O(221)–Th(2)–O(262)	129.8(17)
O(222)–Th(2)–O(231)	77.4(17)
O(222)–Th(2)–O(232)	63.0(18)
O(222)–Th(2)–O(241)	113.1(15)
O(222)–Th(2)–O(251)	113.8(16)
O(222)–Th(2)–O(252)	105.8(15)
O(222)–Th(2)–O(261)	132.6(16)
O(222)–Th(2)–O(262)	178.3(15)
O(231)–Th(2)–O(232)	46.0(14)
O(231)–Th(2)–O(241)	108.9(11)
O(231)–Th(2)–O(251)	167.9(13)
O(231)–Th(2)–O(252)	132.2(11)
O(231)–Th(2)–O(261)	59.6(13)
O(231)–Th(2)–O(262)	104.2(12)
O(232)–Th(2)–O(241)	75.7(13)
O(232)–Th(2)–O(251)	133.9(13)
O(232)–Th(2)–O(252)	168.6(14)
O(232)–Th(2)–O(261)	72.7(14)
O(232)–Th(2)–O(262)	118.5(14)
O(241)–Th(2)–O(251)	63.5(10)
O(241)–Th(2)–O(252)	112.7(9)
O(241)–Th(2)–O(261)	68.3(10)
O(241)–Th(2)–O(262)	66.9(9)
O(251)–Th(2)–O(252)	51.0(9)
O(251)–Th(2)–O(261)	108.4(12)
O(251)–Th(2)–O(262)	64.5(11)
O(252)–Th(2)–O(261)	117.1(10)
O(252)–Th(2)–O(262)	72.8(9)
O(261)–Th(2)–O(262)	49.0(10)
O(211)–N(21)–O(212)	125.1(63)
O(211)–N(21)–O(213)	102.9(64)
O(212)–N(21)–O(213)	131.9(34)
O(221)–N(22)–O(222)	118.7(87)
O(221)–N(22)–O(223)	108.9(68)
O(222)–N(22)–O(223)	121.9(82)
O(231)–N(23)–O(232)	116.3(46)
O(231)–N(23)–O(233)	126.4(50)
O(232)–N(23)–O(233)	89.9(48)
O(241)–N(24)–O(242)	108.2(84)
O(241)–N(24)–O(243)	106.3(91)
O(242)–N(24)–O(243)	115.5(112)
O(251)–N(25)–O(252)	116.6(35)
O(251)–N(25)–O(253)	115.9(37)
O(252)–N(25)–O(253)	108.6(36)
O(261)–N(26)–O(262)	116.4(36)
O(261)–N(26)–O(263)	127.6(41)
O(262)–N(26)–O(263)	115.1(38)
Th(2)–O(211)–N(21)	97.9(65)
Th(2)–O(212)–N(21)	93.7(23)
Th(2)–O(221)–N(22)	95.6(51)
Th(2)–O(222)–N(22)	95.8(60)
Th(2)–O(231)–N(23)	93.3(30)
Th(2)–O(232)–N(23)	94.3(33)
Th(2)–O(241)–N(24)	99.1(39)
Th(2)–O(251)–N(25)	96.3(24)
Th(2)–O(252)–N(25)	94.9(22)
Th(2)–O(261)–N(26)	98.7(26)
Th(2)–O(262)–N(26)	95.4(21)

to the previously reported[1] $M(NO_3)_4\cdot2.67PPr^n_3O$ (M = Th, U, or Np) tentatively formulated as $[M(NO_3)_3(PPr^n_3O)_4]_2[M(NO_3)_6]$. Additional thorium phases of composition $Th(NO_3)_4\cdot2.33PMe_3O$ and $Th(NO_3)_4\cdot3.67PMe_3O$ were also obtained, the former by slow evaporation of an ethanol solution of the components (Th : PMe_3O = 1 : 3) and the latter from an ethanolic solution of hydrated thorium tetranitrate and a nitromethane solution of the ligand (Th : PMe_3O = 4.3 : 1), followed by recrystallisation from ethanol–nitromethane–n-hexane–diethyl ether (1 : 1 : 2 : 10), but these two products could not be obtained reproducibly and are probably mixtures. Thus the crystal shown to be $Th(NO_3)_4\cdot2.67PMe_3O$ (1)

TABLE 6

Bond lengths (Å) and bond angles (°) in (2), with standard deviations in parentheses *

(*a*) Bond lengths

Th–O(2)	2.421(12)	N(2)–O(21A)	1.267(28)
Th–O(3)	2.339(13)	N(2)–O(22A)	1.321(20)
Th–O(11A)	2.524(15)	N(2)–O(21B)	1.226(28)
Th–O(12A)	2.611(18)	N(2)–O(22B)	1.246(18)
Th–O(11B)	2.743(18)	N(2)–O(23)	1.235(15)
Th–O(12B)	2.753(18)	N(3)–O(31A)	1.259(20)
Th–O(21A)	2.596(26)	N(3)–O(32A)	1.265(20)
Th–O(22A)	2.590(17)	N(3)–O(33)	1.235(24)
Th–O(21B)	2.705(25)	P(1)–C(11)	1.794(11)
Th–O(22B)	2.661(16)	P(1)–C(21)	1.802(18)
Th–O(31A)	2.617(15)	P(1)–C(31)	1.814(17)
Th–O(32A)	2.593(15)	C(11)–C(12)	1.425(17)
P(2)–O(2)	1.485(13)	C(11)–C(16)	1.392(17)
P(2)–C(1)	1.793(18)	C(12)–C(13)	1.401(19)
P(2)–C(2)	1.830(27)	C(13)–C(14)	1.389(19)
P(3)–O(3)	1.491(13)	C(14)–C(15)	1.383(20)
P(3)–C(3)	1.758(33)	C(15)–C(16)	1.401(19)
P(3)–C(4)	1.818(25)	C(21)–C(22)	1.399(17)
N(1)–O(11A)	1.355(19)	C(22)–C(23)	1.404(21)
N(1)–O(12A)	1.249(21)	C(23)–C(24)	1.406(21)
N(1)–O(11B)	1.197(21)	C(31)–C(32)	1.394(15)
N(1)–O(12B)	1.276(21)	C(32)–C(33)	1.422(19)
N(1)–O(13)	1.219(16)	C(33)–C(34)	1.387(18)

(*b*) Bond angles

O(2)–Th–O(3)	178.1(4)	O(22A)–Th–O(31A′)	169.3(5)
O(2)–Th–O(11A)	67.5(3)	O(22A)–Th–O(32A′)	125.6(5)
O(2)–Th–O(12A)	113.1(4)	O(21B)–Th–O(22B)	47.1(6)
O(2)–Th–O(11B)	69.8(4)	O(21B)–Th–O(31A)	119.7(6)
O(2)–Th–O(12B)	112.3(4)	O(21B)–Th–O(32A)	162.2(6)
O(2)–Th–O(21A)	112.1(6)	O(21B)–Th–O(11A′)	132.8(6)
O(2)–Th–O(22A)	67.4(5)	O(21B)–Th–O(12A′)	126.3(6)
O(2)–Th–O(21B)	110.9(6)	O(21B)–Th–O(11B′)	151.0(7)
O(2)–Th–O(22B)	68.6(4)	O(21B)–Th–O(12B′)	113.0(6)
O(2)–Th–O(31A)	113.4(4)	O(21B)–Th–O(21B′)	54.3(8)
O(2)–Th–O(32A)	69.9(4)	O(21B)–Th–O(22B′)	86.6(6)
O(3)–Th–O(11A)	112.8(3)	O(21B)–Th–O(31A′)	132.8(6)
O(3)–Th–O(12A)	67.9(4)	O(21B)–Th–O(32A′)	143.1(6)
O(3)–Th–O(11B)	111.2(4)	O(22B)–Th–O(31A)	122.1(5)
O(3)–Th–O(12B)	68.0(4)	O(22B)–Th–O(32A)	122.8(5)
O(3)–Th–O(21A)	66.5(6)	O(22B)–Th–O(11A′)	127.3(5)
O(3)–Th–O(22A)	110.9(5)	O(22B)–Th–O(12A′)	170.3(5)
O(3)–Th–O(21B)	67.4(6)	O(22B)–Th–O(11B′)	137.3(5)
O(3)–Th–O(22B)	110.2(4)	O(22B)–Th–O(12B′)	151.0(5)
O(3)–Th–O(31A)	68.5(4)	O(22B)–Th–O(21B)	88.6(6)
O(3)–Th–O(32A)	112.0(4)	O(22B)–Th–O(22B′)	91.8(5)
O(11A)–Th–O(12A)	49.4(5)	O(22B)–Th–O(31A′)	145.1(5)
O(11A)–Th–O(21A)	69.8(7)	O(22B)–Th–O(32A′)	107.6(5)
O(11A)–Th–O(22A)	68.8(5)	O(31A)–Th–O(32A)	48.9(5)
O(11A)–Th–O(21B)	81.2(6)	O(31A)–Th–O(11A′)	101.3(4)
O(11A)–Th–O(22B)	45.4(5)	O(31A)–Th–O)12A′)	66.7(5)
O(11A)–Th–O(31A)	80.2(4)	O(31A)–Th–O(11B′)	83.4(5)
O(11A)–Th–O(32A)	82.9(5)	O(31A)–Th–O(12B′)	85.1(5)
O(11A)–Th–O(11A′)	131.2(5)	O(31A)–Th–O(21A′)	124.9(6)
O(11A)–Th–O(12A′)	144.3(5)	O(31A)–Th–O(22A′)	169.3(5)
O(11A)–Th–O(21A′)	147.0(7)	O(31A)–Th–O(21B′)	132.8(6)
O(11A)–Th–O(22A′)	109.2(5)	O(31A)–Th–O(22B′)	145.1(5)
O(11A)–Th–O(21B′)	132.8(6)	O(32A)–Th–O(11A′)	64.7(5)
O(11A)–Th–O(22B′)	127.3(5)	O(32A)–Th–O(12A′)	65.6(5)
O(11A)–Th–O(31A′)	101.3(4)	O(32A)–Th–O(11B′)	46.7(5)
O(11A)–Th–O(32A′)	64.7(5)	O(32A)–Th–O(12B′)	81.6(5)
O(12A)–Th–O(21A)	68.1(7)	O(32A)–Th–O(21A′)	129.1(7)
O(12A)–Th–O(22A)	102.9(5)	O(32A)–Th–O(22A′)	125.6(5)
O(12A)–Th–O(21B)	81.9(7)	O(32A)–Th–O(21B′)	143.1(6)
O(12A)–Th–O(22B)	80.3(5)	O(32A)–Th–O(22B′)	107.6(5)
O(12A)–Th–O(31A)	44.0(5)	Th–O(2)–P(2)	152.7(8)
O(12A)–Th–O(32A)	81.6(5)	Th–O(3)–P(3)	169.0(8)
O(12A)–Th–O(11A′)	144.3(5)	O(2)–P(2)–C(1)	113.2(8)
O(12A)–Th–O(12A′)	106.9(5)	O(2)–P(2)–C(2)	111.7(9)
O(12A)–Th–O(21A′)	132.1(7)	C(1)–P(2)–C(2)	104.0(9)
O(12A)–Th–O(22A′)	146.4(5)	C(2)–P(2)–C(2′)	111.9(12)
O(12A)–Th–O(21B′)	126.3(7)	O(3)–P(3)–C(3)	112.4(12)
O(12A)–Th–O(22B′)	170.3(5)	O(3)–P(3)–C(4)	110.6(8)
O(12A)–Th–O(31A′)	66.7(5)	C(3)–P(3)–C(4′)	105.7(9)

Table 6 (*Continued*)

O(12A)–Th–O(32A)	65.6(5)	C(4)–P(3)–C(4)	111.8(11)
O(11B)–Th–O(12B)	47.4(5)	O(11A)–N(1)–O(12A)	111.0(13)
O(11B)–Th–O(21A)	84.7(7)	O(11A)–N(1)–O(13)	125.4(12)
O(11B)–Th–O(22A)	87.1(5)	O(12A)–N(1)–O(13)	123.5(13)
O(11B)–Th–O(21B)	97.6(7)	O(11B)–N(1)–O(12B)	126.4(15)
O(11B)–Th–O(22B)	64.2(5)	O(11B)–N(1)–O(13)	113.1(14)
O(11B)–Th–O(31A)	63.6(5)	O(12B)–N(1)–O(13)	120.5(13)
O(11B)–Th–O(32A)	65.6(5)	O(21A)–N(2)–O(22A)	112.1(16)
O(11B)–Th–O(11B′)	109.1(5)	O(21A)–N(2)–O(23)	123.9(15)
O(11B)–Th–O(12B′)	144.6(5)	O(22A)–N(2)–O(23)	123.5(12)
O(11B)–Th–O(21A′)	165.3(7)	O(21B)–N(2)–O(22B)	120.4(16)
O(11B)–Th–O(22A′)	124.6(5)	O(21B)–N(2)–O(23)	121.7(15)
O(11B)–Th–O(21B′)	151.0(7)	O(22B)–N(2)–O(23)	116.5(12)
O(11B)–Th–O(22B′)	137.3(5)	O(31A)–N(3)–O(32A)	117.5(15)
O(11B)–Th–O(31A′)	83.4(5)	O(31A)–N(3)–O(33)	118.9(15)
O(11B)–Th–O(32A′)	46.7(5)	O(32A)–N(3)–O(33)	123.5(15)
O(12B)–Th–O(21A)	49.5(7)	Th–O(11A)–N(1)	100.2(9)
O(12B)–Th–O(22A)	84.9(5)	Th–O(12A)–N(1)	99.2(11)
O(12B)–Th–O(21B)	63.6(7)	Th–O(11B)–N(1)	94.1(11)
O(12B)–Th–O(22B)	63.9(5)	Th–O(12B)–N(1)	91.8(10)
O(12B)–Th–O(31A)	63.0(5)	Th–O(21A)–N(2)	99.2(14)
O(12B)–Th–O(32A)	99.2(5)	Th–O(22A)–N(2)	97.9(10)
O(12B)–Th–O(11B′)	144.6(5)	Th–O(21B)–N(2)	94.9(14)
O(12B)–Th–O(12B′)	132.6(5)	Th–O(22B)–N(2)	96.6(10)
O(12B)–Th–O(21A′)	122.7(7)	Th–O(31A)–N(3)	96.2(10)
O(12B)–Th–O(22A′)	127.3(5)	Th–O(32A)–N(3)	97.1(10)
O(12B)–Th–O(21B′)	113.0(6)	C(11)–P(1)–C(21)	111.2(5)
O(12B)–Th–O(22B′)	151.0(5)	C(11)–P(1)–C(31)	110.8(5)
O(12B)–Th–O(31A′)	85.1(5)	C(11)–P(1)–C(11′)	107.8(5)
O(12B)–Th–O(32A′)	81.6(5)	C(21)–P(1)–C(31)	105.1(7)
O(21A)–Th–O(22A)	48.9(7)	P(1)–C(11)–C(12)	118.3(9)
O(21A)–Th–O(31A)	108.1(7)	P(1)–C(11)–C(16)	120.4(9)
O(21A)–Th–O(32A)	148.0(7)	C(12)–C(11)–C(16)	120.5(10)
O(21A)–Th–O(11A′)	147.0(7)	C(11)–C(12)–C(13)	118.2(11)
O(21A)–Th–O(12A′)	132.1(7)	C(12)–C(13)–C(14)	121.0(12)
O(21A)–Th–O(11B′)	165.3(7)	C(13)–C(14)–C(15)	120.3(13)
O(21A)–Th–O(12B′)	122.7(7)	C(14)–C(15)–C(16)	120.4(13)
O(21A)–Th–O(21A′)	81.1(8)	C(11)–C(16)–C(15)	119.6(11)
O(21A)–Th–O(22A′)	80.6(7)	P(1)–C(21)–C(22)	118.5(9)
O(21A)–Th–O(31A′)	124.9(6)	C(22)–C(21)–C(22′)	112.6(15)
O(21A)–Th–O(32A′)	129.1(7)	C(21)–C(22)–C(23)	118.5(14)
O(22A)–Th–O(31A)	146.1(5)	C(22)–C(23)–C(24)	119.8(16)
O(22A)–Th–O(32A)	135.1(5)	C(23)–C(24)–C(23′)	120.8(20)
O(22A)–Th–O(11A′)	109.2(5)	P(1)–C(31)–C(32)	118.3(8)
O(22A)–Th–O(12A′)	146.4(5)	C(32)–C(31)–C(32′)	123.2(14)
O(22A)–Th–O(11B′)	124.6(5)	C(31)–C(32)–C(33)	118.3(12)
O(22A)–Th–O(12B′)	127.3(5)	C(32)–C(33)–C(34)	118.2(14)
O(22A)–Th–O(21A′)	80.6(7)	C(33)–C(34)–C(33′)	123.8(18)
O(22A)–Th–O(22A′)	44.6(5)		

* Primed atoms are related to the corresponding unprimed atoms by the mirror plane at $y = 0.25$.

by the structure determination described in this paper was obtained from a preparation of analytical composition $Th(NO_3)_4 \cdot 2.33PMe_3O$. The variability of the results ($Th : PMe_3O = 1 : 3.84—4.2$) obtained in the attempted preparation of the previously reported [1] tetrakis complexes suggests that these may also be mixtures, presumably of the tris and pentakis PMe_3O complexes.

In order to investigate the nature of the pentakis complexes, which are known [2] to contain ionic nitrate groups, attempts were made to isolate the tetraphenylborates of the complex cations, a procedure which has been used to demonstrate the existence of the $[U(NO_3)_3\{P(NMe_2)_3O\}_4]^+$ ion.[12] Reaction of sodium tetraphenylborate with the pentakis complex (3 : 1 mol ratio) in ethanol (Th) or acetone (U) yielded the complexes $[M(NO_3)_2(PMe_3O)_5][BPh_4]_2$. The anionic complex $[Th(NO_3)_5(PMe_3O)_2]^-$ was also obtained as the salt from an acetone solution of '$Th(NO_3)_4 \cdot 2.33PMe_3O$' and $[PPh_4][NO_3]$, and its crystal structure has been determined. Direct preparation of $[Th(NO_3)_5(PMe_3O)_2]^-$ from hydrated thorium tetranitrate, PMe_3O, and $[PPh_4][NO_3]$ yielded precipitates of variable composition and the corresponding uranate(IV) complex could not be isolated.

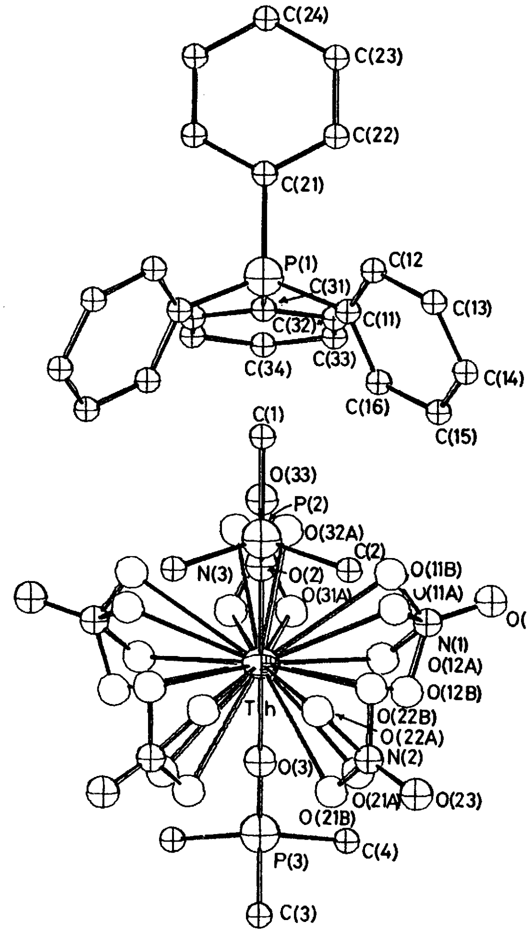

Figure 3 The individual ions of (2), showing the atomic numbering (viewed along *c*, with the mirror plane vertical)

The formation of these two ions may indicate that the tris complexes, $M(NO_3)_4 \cdot 3PMe_3O$, should be formulated as $[M(NO_3)_2(PMe_3O)_5][M(NO_3)_5(PMe_3O)_2]_2$, but crystals of these complexes suitable for *X*-ray studies could not be obtained.

Infrared Spectra.—The shifts in the P=O stretching frequencies in the i.r. spectra are given in Table 7. In each case non-bonded PMe_3O is absent, and the frequencies of the nitrate vibrations are consistent with the presence of bidentate nitrate groups, as found in earlier work with these systems.[1,2] The observed splitting of the ν_2 and ν_4 nitrate and ν(P=O) modes in the i.r. spectrum of $U(NO_3)_4 \cdot 3.33PMe_3O$ may indicate the presence of two uranium sites, but the presence of ionic nitrate makes it impossible to suggest any configuration without additional evidence.

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[12] J. G. H. du Preez and M. L. Gibson, *J. Inorg. Nuclear Chem.*, 1974, **36**, 81.

Crystal-structure Results.—The primary result of the structure determination is to confirm the chemical identification of the species as $[Th(NO_3)_3(PMe_3O)_4]_2$-$[Th(NO_3)_6]$ (1) (Figure 1) and $[PPh_4][Th(NO_3)_5(PMe_3O)_2]$ (2) (Figure 2). All the nitrate groups are bidentate, and the co-ordination numbers are therefore 10 for the cations of (1) and 12 for both anions. The packing of the crystals (Figures 3 and 4) appears to involve only electrostatic interactions between the pseudo-spherical ions.

The chief feature of interest is the geometries around the thorium atoms. Of the twelve-co-ordinate atoms one [Th(2) of complex (1), Figure 5] has the characteristic icosahedral geometry[13] with six bidentate nitrate groups as found in $[Ce(NO_3)_6]^{2-}$. Unfortunately, the disorder in the anion of (2) means that nothing useful can be said about its geometry. The two ten-co-ordinate cations in (1) are very similar (Figure 5). They can be described as 1 : 5 : 4 geometry [seen for Th(3) in Figure 5]. This has a closely planar base, but the atom in the 5 layer [O(332)] most nearly opposite one in the base is out of the plane. For Th(1) the corresponding base atoms are O(12), O(13), O(112), and O(132) and the apex is O(121). An alternative description is 1 : 6 : 3 geometry [seen for Th(1) in Figure 5]. This has a puckered 6 layer, with the nearly eclipsed atoms closer to the apex.

TABLE 7

Infrared spectra (cm^{-1})

Complex	Nitrate vibrations[a] ν_1	ν_4	ν_2	ν_3, ν_5	ν(P=O)	$\Delta\nu$(P=O)
'$Th(NO_3)_4 \cdot 3.67PMe_3O$'[b]	1 515w	1 295w	1 037s	743w, 710w	1 084m	79
$Th(NO_3)_4 \cdot 2.67PMe_3O$	1 495w, 1 515w, (1 548w)	1 300vw	1 037s	763m, 750w, 710w	1 091m	72
'$Th(NO_3)_4 \cdot 2.33PMe_3O$'	1 485w, 1 510w, (1 545w)	1 300vw	1 035s 1 031w	745w, 738w, 705w	1 087m	76
$[PPh_4][Th(NO_3)_5(PMe_3O)_2]$	1 520w	*c*	1 038s, 1 029m	756w, 708w	1 098m	65
$[Th(NO_3)_2(PMe_3O)_5][BPh_4]_2$	1 510w (1 559w)	1 310vw	1 031s	700w	1 075w	88
$[U(NO_3)_2(PMe_3O)_5][BPh_4]_2$	1 508w, 1 499w	1 310	1 033s	*c*	1 073m	90
$U(NO_3)_4 \cdot 3.33PMe_3O$[b]	1 515w	1 318w, 1 290w	1 036s, 1 028s	748w, 741w, 706w	1 094m, 1 077m	69, 86

[a] ν_6 was not clearly defined; assignments were made on the basis of bidentate NO_3 groups. [b] Ionic nitrate present (1 355 cm^{-1}). [c] Obscured by ligand or anion vibrations.

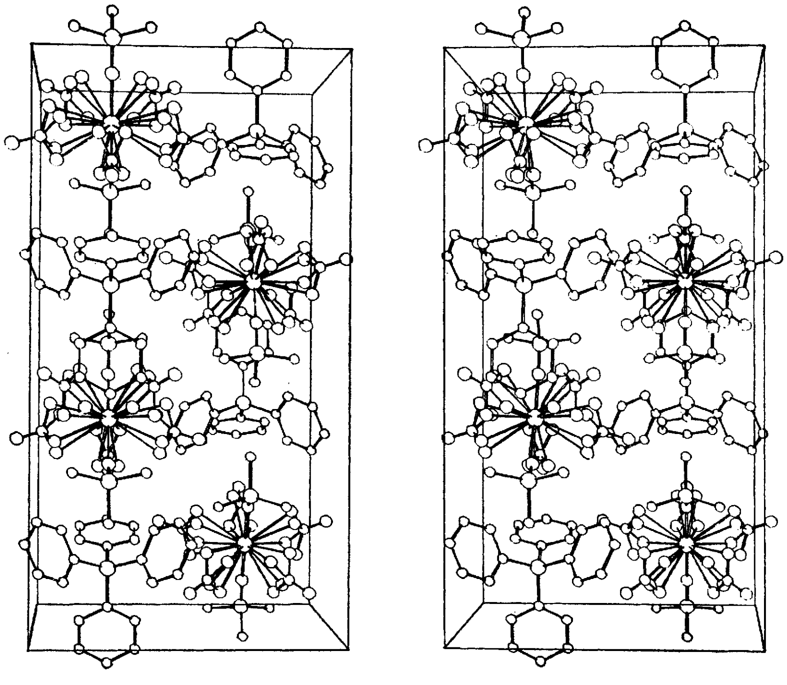

FIGURE 4 A stereoview of the unit cell of (2) (viewed along *c*)

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[13] A. Zalkin, J. D. Forester, and D. H. Templeton, *J. Chem. Phys.*, 1963, **39**, 2881.

This geometry for ten co-ordination has not been reported previously, and it seems that the geometry adopted depends critically on the types of ligands. Two complexes containing five bidentate ligands have bicapped square antiprisms [uranium tetrakis(acetoacetate)[14] and potassium thorium tetrakis(oxalate) tetrahydrate[15]]. Two complexes containing only two bidentate ligands have structures related to dodecahedra, with two of the eight positions replaced by the bidentate groups [(dimethyl sulphoxide)lanthanum nitrate[16] and lanthanum carbonate hydrate[17]]. In the present examples there are three bi- and four uni-dentate ligands. Three of the unidentate ligands form a triangle, with the fourth near one corner; this fourth ligand donor atom and its neighbour are two of the atoms in the 4 plane. Beyond this, it is not obvious why the observed grouping should be energetically favourable.

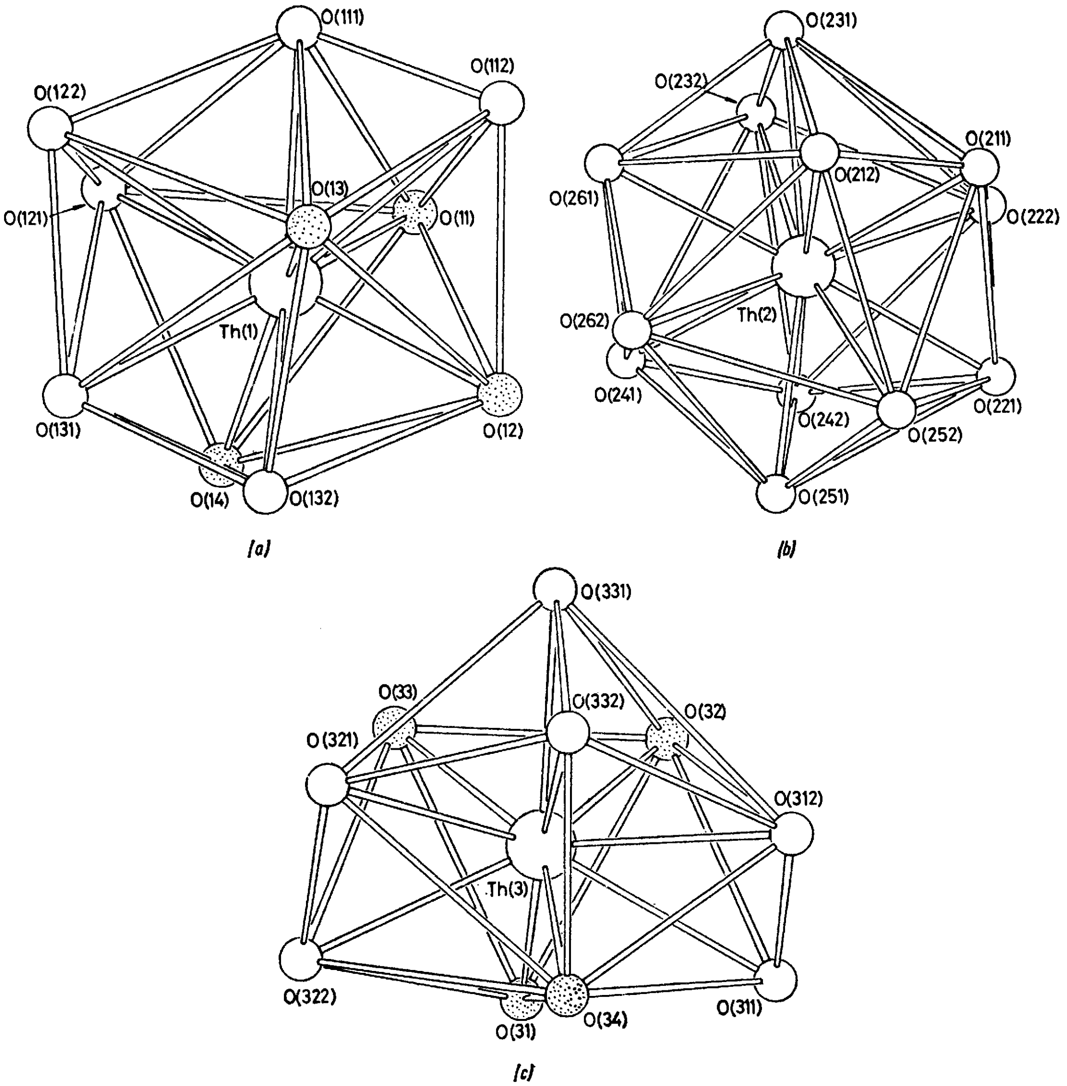

FIGURE 5 The co-ordination spheres of the three Th atoms in (1). The unidentate ligands are stippled

Within the rather limited accuracy, all the ligand groups have standard geometries. There are significant differences in the Th–O distances: Th–O(NO_3), average 2.61 and 2.64 Å; Th–O(PMe_3O), average 2.34 and 2.38 Å in (1) and (2) respectively. This contrast is similar to that in (dimethyl sulphoxide)lanthanum nitrate[16] [La–O(NO_3) 2.65, La–O(SMe_2O) 2.48 Å].

We thank Mr. M. A. Hart for the microanalyses (C, H, N, P, Th, and U), the Government of the People's Republic of China for support (to W. H.-Y.), and the S.R.C. for the diffractometer.

[7/1325 *Received, 22nd July,* 1977]

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[17] D. B. Shinn and H. A. Eick, *Inorg. Chem.*, 1968, **7**, 1340.