Synthetic, Spectroscopic and Structural Studies on Uranium and Thorium Complexes of Diphosphazane Dioxides†

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Co-ordination complexes of the diphosphazane dioxides $Ph_2P(O)N(Pr^i)P(O)Ph_2$ L^1, $Ph_2P(O)N(Pr^i)P(O)Ph(OC_6H_4Me\text{-}4)$ L^2 and $Ph_2P(O)N(Pr^i)P(O)(O_2C_{12}H_8)$ L^3 with UO_2^{2+} or Th^{4+} ions have been synthesised and characterised by IR and NMR spectroscopy. The structures of $[UO_2(NO_3)_2L^1]$ and $[Th(NO_3)_2L^1_3][Th(NO_3)_6]$ are established by X-ray crystallography. In the former, the uranyl ion is bonded to two bidentate nitrate groups and the two phosphoryl groups of the ligand L^1; the co-ordination polyhedron around the metal is a hexagonal bipyramid. The cationic moiety in the thorium complex contains three bidentate diphosphazane dioxide ligands and two bidentate nitrate groups around the ten-co-ordinated metal.

The fundamental co-ordination chemistry of lanthanides and actinides with ligands containing phosphoryl, carbonyl or *N*-oxide groups continues to attract considerable attention in view of its relevance to practical liquid–liquid extraction systems.[1-3] We have synthesised several new di- and tri-functional ligands containing the diphosphazane (P–N–P) framework.[4] The advantage of this type of ligand is that the substituents on the phosphorus and nitrogen atoms can be varied much more readily than with diphosphinoalkanes so that one can fine-tune the relative extraction efficacy of these ligands for various metal ions. Delpuech and co-workers[5-7] have studied the dynamic NMR spectra of uranyl perchlorate complexes containing the β-diphosphoramide $MeN[P(O)(NMe_2)_2]_2$ and have also reported the single-crystal structure of one of its complexes, *viz.* $[UO_2\{MeN[P(O)(NMe_2)_2]_2\}_2(EtOH)[ClO_4]_2$.[7] In this paper, we report the syntheses and spectroscopic and structural studies of UO_2^{2+} complexes of three new diphosphazane dioxides, $Ph_2P(O)N(Pr^i)P(O)Ph_2$ L^1, $Ph_2P(O)N(Pr^i)P(O)Ph(OC_6H_4\text{-}Me\text{-}4)$ L^2 and $Ph_2P(O)N(Pr^i)P(O)(O_2C_{12}H_8)$ L^3 and a Th^{4+} complex of L^1.

Experimental

All the solvents were purified by conventional procedures and distilled prior to use.[8] Uranyl and thorium nitrates (BDH, LR grade) were used as purchased. The diphosphazane dioxides, $Ph_2P(O)N(Pr^i)P(O)Ph_2$ L^1, $Ph_2P(O)N(Pr^i)P(O)Ph(OC_6H_4Me\text{-}4)$ L^2 and $Ph_2P(O)N(Pr^i)P(O)(O_2C_{12}H_8)$ L^3 were prepared by the oxidation of the corresponding phosphorus(III) diphosphazane precursors using aqueous hydrogen peroxide.[4] The ^1H and ^{31}P NMR spectra were recorded on a Bruker ACF200 spectrometer; $SiMe_4$ was used as an internal standard for the proton NMR and 85% H_3PO_4 as external standard for the ^{31}P NMR measurements. Infrared spectra were recorded using a BIO-RAD FTIR model FTS-7 spectrometer. Microanalyses were performed on a Heraeus CHN-O-Rapid elemental analyser. Melting points were determined on a Reichert-Kofler microheating stage fitted with a polarising microscope.

Syntheses.—$[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}]$ **1**. A solution of the diphosphazane dioxide L^1 (0.46 g, 9.96 × 10^{-4} mol) in dichloromethane (10 cm^3) was added to a solution of $UO_2(NO_3)_2\cdot 6H_2O$ (0.50 g, 9.96 × 10^{-4} mol) in ethanol (10 cm^3). The mixture was stirred for 10 min and concentrated to 10 cm^3 *in vacuo*. The resultant solution was cooled at 0 °C overnight to obtain a pale yellow crystalline solid. The solid was filtered off and washed with ethanol and dichloromethane to remove unreacted starting materials. The complex was insoluble in common organic solvents except dimethyl sulfoxide. Yield: 0.77 g (90 %).

$[UO_2Cl_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}]$ **2**. This complex was prepared by a similar procedure to that for complex **1** using the diphosphazane dioxide L^1 (0.46 g, 9.96 × 10^{-4} mol) and $UO_2Cl_2\cdot 6H_2O$ (0.45 g, 9.96 × 10^{-4} mol) as the metal precursor. Complex **2** was similarly insoluble in common organic solvents except dimethyl sulfoxide. Yield: 0.68 g (85 %).

$[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph(OC_6H_4Me\text{-}4)\}]$ **3**. The diphosphazane dioxide L^2 (0.20 g, 3.98 × 10^{-4} mol) in dichloromethane (10 cm^3) was added to a solution of $UO_2(NO_3)_2\cdot 6H_2O$ (0.20 g, 3.98 × 10^{-4} mol) in acetone (10 cm^3). The solution was stirred at room temperature for 1 h. Solvent was removed *in vacuo* and the resultant oil was dissolved in dichloromethane–diethyl ether (1 : 1) and cooled at 0 °C to obtain a microcrystalline solid. Yield: 0.26 g (75 %).

$[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)(O_2C_{12}H_8)\}]$ **4**. This complex was prepared by a similar procedure to that for complex **3** using L^3 (0.20 g, 3.98 × 10^{-4} mol) and $UO_2(NO_3)_2\cdot 6H_2O$ (0.20 g, 3.98 × 10^{-4} mol). Solvent was removed *in vacuo* and the residue extracted with acetone and crystallised from ethanol–diethyl ether (1 : 1) to obtain the title complex. Yield: 0.25 g (70%).

$[Th(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}_3][Th(NO_3)_6]$ **5**. A solution of the diphosphazane dioxide L^1 (0.12 g, 2.55 × 10^{-4} mol) in dichloromethane (15 cm^3) was added to a solution of $Th(NO_3)_4\cdot 6H_2O$ (0.10 g, 1.70 × 10^{-4} mol) in ethanol (10 cm^3). The mixture was evaporated slowly for one week under anhydrous conditions. A colourless crystalline solid was precipitated which was insoluble in all common organic solvents except dimethyl sulfoxide. Yield: 0.30 g (75 %).

Analytical and spectroscopic data are listed in Tables 1 and 2.

Crystal Structure Analyses of $[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}]$ **1** *and* $[Th(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}_3][Th(NO_3)_6]$ **5**.—A suitable crystal of each compound was glued to a glass fibre and coated with paraffin oil to protect it from air and moisture. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). Three reflections, monitored throughout the data collection showed no significant change in the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and IR spectroscopic data for the uranyl and thorium diphosphazane dioxide complexes **1**–**5**

				IR data[a] ($\tilde{\nu}$/cm^{-1})				Analyses (%)[b]		
	Compound	M.p./ °C	Colour	ν(UO_2)	ν(NO_3)	ν(PO)	Δν(PO)[c]	C	H	N
1	$[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}]$	200	Yellow	937	1439 1295	1164	40	37.5 (38.0)	3.3 (3.2)	4.6 (4.9)
2	$[UO_2Cl_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}]$	225	Pale yellow	927	—	1125	79	40.9 (40.5)	3.6 (3.4)	1.7 (1.8)
3	$[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph(OC_6H_4Me\text{-}4)\}]$	180	Yellow	936	1436 1283	1209 1186	42 23	37.9 (38.1)	3.5 (3.3)	4.5 (4.8)
4	$[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)(O_2C_{12}H_8)\}]$	190	Yellow	936	1435 1274	1196 1146	52 51	37.9 (36.7)	3.4 (2.9)	4.3 (4.8)
5	$[Th(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}_3][Th(NO_3)_6]$	205	Colourless	—	1437 1287	1134	70	41.8 (41.6)	3.6 (3.5)	6.7 (6.6)

[a] Recorded on KBr pellets. [b] Required values given in parentheses. [c] Δν(PO) = ν(PO)(ligand) − ν(PO)(complex)

Table 2 The ^1H and ^{31}P NMR spectroscopic data for L^1–L^3 [a] and the uranyl and thorium diphosphazane dioxide complexes **1**–**5**[b]

		^1H NMR			
	Compound	δ(Me)	δ(CH)	δ(Ph)	^{31}P NMR (δ)
	L^1	1.40 (d, 6.7)	3.73 (m)	7.3–7.8 (m)	28.0 (s)
	L^2	1.59 (d, 6.8), 1.40 (d, 6.8) 2.27 (s)[c]	4.02 (m)	7.0–7.9 (m)	30.2 (d, 11) 16.6 (d, 11)
	L^3	1.55 (d, 6.8)	4.21 (m)	7.1–7.5 (m)	31.8 (d, 14) 4.8 (d, 14)
1	$[UO_2(NO_3)_2L^1]$[d]	1.31 (d, 6.8)	3.67 (m)	6.9–8.3 (m)	35.1 (s)
2	$[UO_2Cl_2L^1]$[d]	1.30 (d, 6.6)	3.70 (m)	7.4–7.7 (m)	30.9 (s)
3	$[UO_2(NO_3)_2L^2]$[e]	1.1 (d, 6.9), 1.24 (d, 6.9) 2.30[c]	4.12 (m)	7.4–8.0 (m)	18.7 (br) 37.8 (br)
4	$[UO_2(NO_3)_2L^3]$[e]	1.05 (d, 6.7)	3.80 (m)	6.1–8.2 (m)	10.0 (d, 13) 46.3 (d, 13)
5	$[Th(NO_3)_2L^1{}_3][Th(NO_3)_6]$[d]	1.26 (d, 6.6)	3.60 (m)	7.4–7.7 (m)	30.0 (s)

[a] Data taken from ref. 4. [b] Coupling constants $^3J_{HH}$ and $^2J_{PP}$ in parentheses are in Hz. [c] Methyl group on the aryl ring. [d] Recorded in $(CD_3)_2SO$. [e] Recorded in $CDCl_3$.

intensities for both crystals. Data were corrected for Lorentz and polarisation effects and also for absorption by an empirical method using psi data[9] as well as by the DIFABS program.[10] The structures were solved by conventional Patterson and Fourier techniques and refined by a full-matrix least-squares treatment.[11,12] All the non-hydrogen atoms were refined anisotropically.

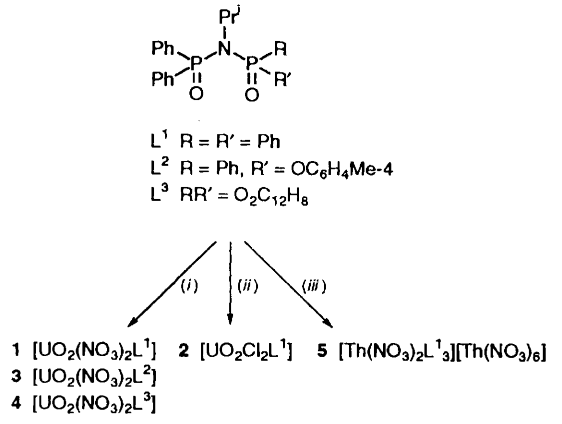
The data after absorption correction using the DIFABS program gave $R = 0.049$ and $R' = 0.056$ for complex **1** and $R = 0.049$ and $R' = 0.046$ for complex **5**. The residual peak heights near the heavy atom were small (1.2 e Å^{-3} for complex **1**, 1.5 e Å^{-3} for complex **5**). The data set after absorption correction by the empirical method of North *et al.*[9] showed higher R factors for both structures ($R = 0.068$, $R' = 0.078$ for complex **1** and $R = 0.058$, $R = 0.057$ for complex **5**). In addition the residual peak heights near the heavy atom were high (2.8 e Å^{-3} for complex **1**, 1.6 e Å^{-3} for complex **5**). Hence it was decided to use the data which had been corrected for absorption using the DIFABS program for further treatment. The hydrogen atoms were fixed at the geometrically calculated positions and included in the structure-factor calculations. The details pertaining to data collection and refinement are given in Table 3. Non-hydrogen atomic coordinates are listed in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Diphosphazane dioxides can be easily prepared by the oxidation of their corresponding phosphorus(III) diphosphazanes which are readily accessible from trivalent phosphorus-containing starting materials. The oxidation can be effected under mild conditions and this procedure is simpler than that reported for the preparation of the diphosphazane dioxides $RN[P(O)(NMe_2)_2]_2$ [R = Me, CH_2Ph, $(CH_2)_5Me$ or $(CH_2)_{11}Me$] from pentavalent phosphorus precursors; in particular this method obviates the need for the use of butyllithium.[13] Furthermore, the substituents on the phosphorus and nitrogen atoms can be altered much more easily than in the case of diphosphinoalkanes.

The synthesis of the complexes of L^1–L^3 with $UO_2{}^{2+}$ or Th^{4+} is shown in Scheme 1.



Scheme 1 (*i*) $UO_2(NO_3)_2$; (*ii*) UO_2Cl_2; (*iii*) $Th(NO_3)_4$

Table 3 Crystal data and details of the structure solution for $[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}]$ **1** and $[Th(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}_3][Th(NO_3)_6]$ **5**[a]

	1	**5**
Formula	$C_{27}H_{27}N_3O_{10}P_2U$	$C_{81}H_{81}N_{11}O_{30}P_6Th_2$
M	853.5	2338.5
Crystal size/mm	0.2 × 0.1 × 0.05	0.3 × 0.4 × 0.33
Colour	Pale yellow	Colourless
Space group	$P2_1/n$	$P2_1/c$
a/Å	11.789(3)	15.126(4)
b/Å	13.334(6)	31.319(5)
c/Å	21.585(4)	19.425(4)
β/°	95.33(2)	95.85(2)
U/Å^3	3378(6)	9154(18)
D_c/g cm^{-3}	1.68	1.70
F(000)	1624	4584
Scan technique	ω–2θ	ω
μ/cm^{-1}	61.31	38.62
Transmission factors	0.81–1.30	0.86–1.21
Total number of reflections	6839	16 299
Unique reflections	5913	14 335
Observed $[F_o > 5\sigma(F_o)]$ reflections	3976	7936
No. of parameters	388	1175
R^b	0.049	0.049
R'^c	0.056	0.046
g	0.004 621	0.002 106
Residual peak in final difference map/e Å^{-3}	1.2	1.5
$(\Delta/\sigma)_{max}$	0.06	0.12

[a] Data in common: monoclinic crystal system, $Z = 4$; $T = 20$ °C, $+h$, $+k$, $\pm l$ octants collected, 2–50° 2θ range, < 1% decay. [b] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1.0000/[\sigma^2(F) + gF^2]$.

Table 4 Non-hydrogen atomic coordinates for $[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}]$ **1**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
U	0.230 64(3)	0.279 61(3)	0.423 96(2)	C(21)	0.089 8(9)	0.345 5(8)	0.197 8(5)
O(1)	0.176 9(7)	0.155 6(6)	0.418 0(4)	C(22)	0.028 2(11)	0.324 9(11)	0.140 8(6)
O(2)	0.285 5(8)	0.402 7(6)	0.431 8(4)	C(23)	0.053 1(14)	0.376 0(14)	0.087 4(6)
N(2)	0.448 0(9)	0.202 8(10)	0.385 2(5)	C(24)	0.134 9(15)	0.450 5(14)	0.089 2(7)
O(3)	0.371 1(8)	0.237 7(8)	0.348 2(4)	C(25)	0.203 0(14)	0.472 6(10)	0.144 6(6)
O(4)	0.534 3(9)	0.170 1(11)	0.367 2(5)	C(26)	0.175 2(11)	0.419 6(9)	0.199 6(6)
O(5)	0.428 6(8)	0.204 6(8)	0.441 3(4)	C(31)	0.022 9(11)	0.517 5(10)	0.356 1(6)
N(3)	0.224 5(12)	0.264 6(9)	0.559 8(5)	C(32)	0.059 7(15)	0.567 2(10)	0.410 7(6)
O(6)	0.141 5(8)	0.295 8(7)	0.524 3(4)	C(33)	0.029 2(14)	0.562 1(11)	0.298 2(6)
O(7)	0.224 4(12)	0.256 1(10)	0.615 1(4)	C(34)	0.075 3(18)	0.657 5(15)	0.296 5(7)
O(8)	0.310 8(9)	0.247 1(9)	0.534 3(4)	C(35)	0.111 4(15)	0.710 5(10)	0.350 9(9)
O(9)	0.167 6(7)	0.311 5(6)	0.317 1(3)	C(36)	0.105 8(15)	0.664 5(13)	0.406 8(7)
O(10)	0.038 1(6)	0.334 6(6)	0.413 1(3)	C(41)	0.050 5(9)	0.156 0(9)	0.257 5(5)
P(1)	0.068 3(2)	0.288 4(2)	0.269 8(1)	C(42)	0.096 2(11)	0.111 4(11)	0.206 1(6)
P(2)	−0.036 4(3)	0.394 5(2)	0.365 7(1)	C(43)	0.082 7(14)	0.002 1(13)	0.202 8(9)
N(1)	−0.050 7(7)	0.333 0(7)	0.297 1(4)	C(44)	0.468 5(14)	0.451 1(13)	0.251 8(10)
C(11)	−0.173 8(10)	0.410 7(11)	0.393 3(5)	C(45)	0.506 8(12)	0.493 7(11)	0.205 2(9)
C(12)	−0.235 6(11)	0.497 3(11)	0.381 7(6)	C(46)	−0.002 5(10)	0.099 2(10)	0.300 8(7)
C(13)	−0.340 8(13)	0.506 2(15)	0.406 9(10)	C(51)	−0.158 3(10)	0.320 2(13)	0.252 9(6)
C(14)	−0.385 4(14)	0.429 3(20)	0.439 5(10)	C(52)	−0.254 4(12)	0.262 7(15)	0.279 6(8)
C(15)	−0.321 9(16)	0.345 9(20)	0.451 6(8)	C(53)	−0.196 4(14)	0.418 2(13)	0.222 9(7)
C(16)	−0.212 4(13)	0.332 7(14)	0.430 0(7)				

Uranyl Complexes of the Diphosphazane Dioxides L^1–L^3.—Treatment of $UO_2(NO_3)_2\cdot6H_2O$ with the diphosphazane dioxide $Ph_2P(O)N(Pr^i)P(O)Ph_2$ L^1, $Ph_2P(O)N(Pr^i)P(O)Ph(OC_6H_4Me\text{-}4)$ L^2 or $Ph_2P(O)N(Pr^i)P(O)(O_2C_{12}H_8)$ L^3 gives a yellow crystalline solid of composition $[UO_2(NO_3)_2L^1]$ **1**, $[UO_2(NO_3)_2L^2]$ **3** or $[UO_2(NO_3)_2L^3]$ **4**. Reaction of $UO_2Cl_2\cdot6H_2O$ with L^1 results in the ready formation of $[UO_2Cl_2L^1]$ **2**. For all these complexes the elemental analyses confirm the 1 : 1 ligand : metal stoichiometry. The infrared spectra show strong ν(PO) bands in the range 1125–1209 cm^{-1}. These bands are shifted towards lower wavenumbers in the complexes ($\Delta\delta$ = 40–79 cm^{-1}) compared to the free ligands, consistent with strong phosphoryl co-ordination to the uranyl ion. The IR spectra of the uranyl complexes **1**, **3** and **4** exhibit intense absorption bands between 1439–1435 and 1295–1274 cm^{-1} indicating the presence of bidentate chelated nitrate groups.[14] The asymmetric uranyl stretching frequency for these complexes **1**–**4** appears at 937, 927, 936 and 936 cm^{-1} respectively. The ^{1}H NMR spectra of **1**, **2** and **4** display a single resonance for the isopropyl methyl protons whereas for complex **3**, because of phosphorus chirality, two distinct resonances are observed. The isopropyl methine proton is observed as a multiplet for all these complexes (**1**–**4**). The ^{31}P NMR spectra show a single resonance for the complexes **1** and **2**; for complex **4** two doublets are observed because of the non-equivalence of the two phosphorus nuclei. The spectrum of complex **3** shows two broad peaks presumably because it is fluxional in solution. These ^{31}P resonances are shifted downfield compared to the chemical shifts of the free ligands (Table 2).

Table 5 Non-hydrogen atomic coordinates for [$Th(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}_3$][$Th(NO_3)_6$] **5**

Atom	*X/a*	*Y/b*	*Z/c*
Th(1)	1.004 04(3)	0.355 06(1)	0.189 44(2)
O(1)	0.884 9(4)	0.354 6(2)	0.095 3(3)
O(2)	0.895 8(5)	0.296 8(2)	0.194 1(3)
O(3)	0.897 8(5)	0.413 9(2)	0.200 3(4)
O(4)	1.062 4(5)	0.414 0(2)	0.258 8(4)
O(5)	1.163 1(5)	0.359 7(2)	0.198 2(4)
O(6)	1.077 7(4)	0.286 4(2)	0.186 3(4)
O(7)	1.061 2(5)	0.344 5(2)	0.070 4(4)
O(8)	1.034 3(5)	0.409 5(2)	0.100 3(4)
O(9)	1.070 7(8)	0.396 0(3)	−0.003 0(5)
O(10)	0.928 2(6)	0.355 3(3)	0.302 6(4)
O(11)	1.059 5(6)	0.329 2(2)	0.314 8(4)
O(12)	0.997 3(7)	0.346 8(3)	0.406 3(4)
N(4)	1.055 5(7)	0.383 7(3)	0.054 0(5)
N(5)	0.995 5(8)	0.342 9(3)	0.341 4(5)
P(1)	0.805 5(2)	0.335 2(1)	0.053 7(1)
N(1)	0.752 9(6)	0.301 7(3)	0.103 0(4)
C(1)	0.654 0(8)	0.289 2(4)	0.087 2(6)
C(2)	0.591 9(8)	0.322 6(4)	0.109 3(7)
C(3)	0.630 4(9)	0.274 0(4)	0.012 3(6)
P(2)	0.808 8(2)	0.275 6(1)	0.171 3(1)
P(3)	0.872 9(2)	0.453 9(1)	0.236 8(2)
N(2)	0.961 6(6)	0.478 1(3)	0.280 4(5)
C(28)	0.940 4(9)	0.519 1(4)	0.318 8(8)
C(29)	0.976 6(10)	0.558 9(4)	0.288 6(9)
C(30)	0.961 7(10)	0.516 6(5)	0.396 1(7)
P(4)	1.066 2(2)	0.460 8(1)	0.272 6(2)
P(5)	1.256 5(2)	0.341 9(1)	0.204 2(2)
N(3)	1.252 3(6)	0.288 8(3)	0.217 6(4)
C(55)	1.332 1(7)	0.262 1(4)	0.249 0(6)
C(56)	1.414 8(9)	0.269 4(4)	0.209 9(7)
C(57)	1.351 9(9)	0.268 0(4)	0.326 8(7)
P(6)	1.160 5(2)	0.259 5(1)	0.191 6(2)
C(4)	0.838 2(7)	0.309 0(4)	−0.019 9(5)
C(5)	0.845 0(8)	0.264 7(4)	−0.026 0(6)
C(6)	0.871 5(9)	0.244 8(5)	−0.083 1(7)
C(7)	0.897 8(9)	0.269 6(6)	−0.135 1(7)
C(8)	0.894 7(10)	0.314 1(6)	−0.133 1(7)
C(9)	0.864 3(9)	0.332 9(4)	−0.074 5(6)
C(10)	0.726 2(7)	0.376 8(3)	0.025 7(6)
C(11)	0.681 2(8)	0.378 2(4)	−0.039 7(6)
C(12)	0.619 4(9)	0.411 0(5)	−0.053 0(6)
C(13)	0.604 9(9)	0.441 4(4)	−0.005 4(8)
C(14)	0.652 7(9)	0.440 8(4)	0.061 2(7)
C(15)	0.713 9(8)	0.406 9(4)	0.076 3(6)
C(16)	0.830 0(8)	0.221 2(3)	0.146 2(6)
C(17)	0.916 9(9)	0.207 6(4)	0.159 2(7)
C(18)	0.939 4(9)	0.166 7(4)	0.137 3(10)
C(19)	0.875 3(11)	0.139 3(4)	0.107 7(9)
C(20)	0.788 5(10)	0.152 6(4)	0.098 6(7)
C(21)	0.765 0(8)	0.193 6(4)	0.117 9(7)
C(22)	0.737 4(7)	0.275 6(4)	0.238 8(5)
C(23)	0.692 7(9)	0.239 5(4)	0.260 1(6)
C(24)	0.639 3(9)	0.242 1(5)	0.312 4(6)
C(25)	0.630 9(9)	0.280 7(5)	0.345 9(7)
C(26)	0.672 7(10)	0.316 7(5)	0.326 3(7)
C(27)	0.727 2(8)	0.314 5(4)	0.273 5(6)
C(31)	0.826 4(8)	0.491 1(4)	0.172 3(6)
C(32)	0.858 6(8)	0.488 0(4)	0.107 2(6)
C(33)	0.830 7(11)	0.518 1(5)	0.056 9(7)
C(34)	0.772 3(12)	0.549 7(5)	0.068 8(8)
C(35)	0.739 0(10)	0.551 9(4)	0.131 7(9)
C(36)	0.767 3(9)	0.523 5(4)	0.185 3(7)
C(37)	0.796 5(8)	0.444 6(4)	0.299 9(6)
C(38)	0.708 6(9)	0.451 8(4)	0.289 2(8)
C(39)	0.652 7(11)	0.446 2(5)	0.340 0(11)
C(40)	0.688 3(13)	0.430 3(6)	0.405 1(10)
C(41)	0.776 6(12)	0.419 8(5)	0.415 4(7)
C(42)	0.831 7(9)	0.428 5(4)	0.364 5(6)
C(43)	1.129 3(7)	0.471 6(4)	0.351 5(6)
C(44)	1.123 7(10)	0.442 2(4)	0.405 9(7)
C(45)	1.172 4(12)	0.450 0(5)	0.470 2(8)
C(46)	1.228 2(12)	0.485 5(6)	0.478 5(8)
C(47)	1.231 8(10)	0.514 0(5)	0.425 5(7)
C(48)	1.186 7(9)	0.507 2(4)	0.362 2(6)
C(49)	1.116 0(9)	0.488 0(4)	0.204 4(6)
C(50)	1.205 4(9)	0.482 1(5)	0.200 2(7)
C(51)	1.243 7(10)	0.502 7(6)	0.146 3(9)
C(52)	1.192 9(16)	0.528 2(6)	0.099 4(9)
C(53)	1.104 1(14)	0.535 2(5)	0.105 3(8)
C(54)	1.066 4(10)	0.515 5(4)	0.157 7(7)
C(58)	1.319 0(8)	0.364 7(4)	0.277 4(7)
C(59)	1.277 3(9)	0.373 5(4)	0.334 7(7)
C(60)	1.324 5(12)	0.388 4(6)	0.397 2(8)
C(61)	1.413 2(13)	0.396 1(8)	0.395 8(14)
C(62)	1.456 0(12)	0.385 5(7)	0.343 6(14)
C(63)	1.412 1(9)	0.371 3(5)	0.280 0(8)
C(64)	1.309 1(8)	0.354 9(4)	0.127 0(6)
C(65)	1.351 7(10)	0.394 0(4)	0.124 5(8)
C(66)	1.391 7(11)	0.404 2(5)	0.066 5(9)
C(67)	1.386 0(11)	0.376 1(6)	0.011 1(8)
C(68)	1.345 4(10)	0.336 5(5)	0.013 2(8)
C(69)	1.305 4(9)	0.327 0(5)	0.072 8(6)
C(70)	1.171 8(7)	0.235 0(3)	0.108 7(6)
C(71)	1.245 7(8)	0.212 9(4)	0.094 7(6)
C(72)	1.251 0(9)	0.193 6(5)	0.030 3(7)
C(73)	1.181 1(10)	0.197 7(5)	−0.018 6(6)
C(74)	1.105 7(10)	0.219 8(5)	−0.005 7(6)
C(75)	1.101 6(8)	0.239 2(3)	0.057 1(6)
C(76)	1.156 1(7)	0.217 7(4)	0.255 1(6)
C(77)	1.172 0(9)	0.174 8(4)	0.239 1(7)
C(78)	1.167 3(11)	0.144 2(4)	0.291 1(7)
C(79)	1.144 0(9)	0.155 4(4)	0.354 5(7)
C(80)	1.126 9(9)	0.196 4(4)	0.369 4(7)
C(81)	1.132 9(9)	0.228 4(4)	0.319 2(7)
Th(2)	0.498 70(3)	0.094 28(1)	0.195 40(2)
O(13)	0.539 4(8)	0.083 6(5)	0.075 1(6)
O(14)	0.529 0(9)	0.024 8(4)	0.139 4(6)
O(15)	0.568 1(10)	0.019 4(6)	0.034 5(8)
O(16)	0.363 5(8)	0.067 1(4)	0.117 9(5)
O(17)	0.334 3(6)	0.104 4(3)	0.202 7(5)
O(18)	0.225 7(7)	0.080 4(4)	0.134 4(6)
O(19)	0.432 8(7)	0.150 5(4)	0.111 4(5)
O(20)	0.570 1(7)	0.159 6(3)	0.143 8(6)
O(21)	0.504 3(9)	0.206 4(4)	0.073 6(7)
O(22)	0.462 9(7)	0.164 8(3)	0.254 5(5)
O(23)	0.456 6(6)	0.108 3(3)	0.317 4(4)
O(24)	0.437 2(12)	0.171 0(4)	0.362 4(7)
O(25)	0.628 6(7)	0.123 6(3)	0.274 7(5)
O(26)	0.665 2(6)	0.083 6(3)	0.192 2(5)
O(27)	0.768 3(7)	0.109 4(4)	0.266 5(6)
O(28)	0.426 5(6)	0.030 2(3)	0.249 4(5)
O(29)	0.562 6(6)	0.039 3(3)	0.283 9(5)
O(30)	0.491 6(9)	−0.012 0(4)	0.326 0(6)
N(6)	0.546 4(11)	0.040 7(8)	0.084 8(11)
N(7)	0.305 0(8)	0.085 3(4)	0.150 2(7)
N(8)	0.502 8(11)	0.172 8(5)	0.109 0(8)
N(9)	0.451 7(9)	0.149 1(4)	0.312 3(7)
N(10)	0.691 4(7)	0.105 6(4)	0.246 4(7)
N(11)	0.493 8(9)	0.018 0(4)	0.288 0(6)

The structure of complex **1** has been determined by X-ray crystallography and reveals the chelating mode of binding of the diphosphazane dioxide to uranium. A perspective view is shown in Fig. 1. Selected bond distances and angles are given in Table 6. The dioxouranium group is linear [O(1)–U(1)–O(2) 178.6(4)°]; in addition to these two oxygen atoms the uranium is surrounded by six oxygen atoms provided by two bidentate nitrate groups and a bidentate diphosphazane dioxide ligand. The six oxygen atoms [O(3), O(5), O(6) and O(8)–O(10)] around the uranyl ion form a hexagon and are located respectively at 0.0105, 0.0779, −0.0121, −0.0954, −0.0563 and 0.0558 Å from the least-square plane. The co-ordination

Table 6 Selected bond distances (Å) and angles (°) in $[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}]$ **1** and $[Th(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}_3][Th(NO_3)_6]$ **5**

$[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}]$ **1**							
U(1)–O(1)	1.771(8)	U(1)–O(5)	2.535(10)	U(1)–O(9)	2.395(7)	O(10)–P(2)	1.513(7)
U(1)–O(2)	1.766(8)	U(1)–O(6)	2.503(9)	U(1)–O(10)	2.376(7)	P(1)–N(1)	1.680(9)
U(1)–O(3)	2.496(10)	U(1)–O(8)	2.517(9)	O(9)–P(1)	1.512(8)	P(2)–N(1)	1.687(9)
O(1)–U(1)–O(2)	178.6(4)	U(1)–O(5)–N(2)	96.5(7)	U(1)–O(9)–P(1)	140.0(4)	C(51)–N(1)–P(1)	114.5(7)
O(9)–U(1)–O(10)	69.0(3)	U(1)–O(6)–N(3)	97.7(8)	U(1)–O(10)–P(2)	136.0(4)	C(51)–N(1)–P(2)	127.8(7)
U(1)–O(3)–N(2)	98.7(7)	U(1)–O(8)–N(3)	97.9(8)	P(1)–N(1)–P(2)	117.5(5)		
$[Th(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}_3][Th(NO_3)_6]$ **5**							
Th(1)–O(1)	2.433(6)	Th(1)–O(7)	2.571(8)	O(3)–P(3)	1.506(8)	P(3)–N(2)	1.691(10)
Th(1)–O(2)	2.459(7)	Th(1)–O(8)	2.505(7)	O(4)–P(4)	1.490(7)	N(2)–P(4)	1.694(10)
Th(1)–O(3)	2.468(7)	Th(1)–O(10)	2.581(9)	O(5)–P(5)	1.512(8)	P(5)–N(3)	1.686(10)
Th(1)–O(4)	2.400(7)	Th(1)–O(11)	2.622(8)	O(6)–P(6)	1.504(7)	N(3)–P(6)	1.698(9)
Th(1)–O(5)	2.400(8)	O(1)–P(1)	1.506(6)	P(1)–N(1)	1.675(9)	Th(2)–O*	2.542(10)
Th(1)–O(6)	2.426(6)	O(2)–P(2)	1.500(8)	N(1)–P(2)	1.707(9)		
O(1)–Th(1)–O(2)	65.1(2)	Th(1)–O(3)–P(3)	149.0(5)	P(3)–N(2)–P(4)	120.8(6)	O(4)–P(4)–N(2)	108.2(5)
O(3)–Th(1)–O(4)	65.4(2)	Th(1)–O(4)–P(4)	149.6(5)	P(5)–N(3)–P(6)	122.0(6)	O(5)–P(5)–N(3)	109.0(4)
O(5)–Th(1)–O(6)	66.1(2)	Th(1)–O(5)–P(5)	154.9(4)	O(1)–P(1)–N(1)	110.2(4)	O(6)–P(6)–N(3)	111.6(4)
Th(1)–O(1)–P(1)	153.5(4)	Th(1)–O(6)–P(6)	151.2(4)	O(2)–P(2)–N(1)	111.6(4)		
Th(1)–O(2)–P(2)	152.2(4)	P(1)–N(1)–P(2)	121.2(6)	O(3)–P(3)–N(2)	112.6(5)		

* Average bond distance.

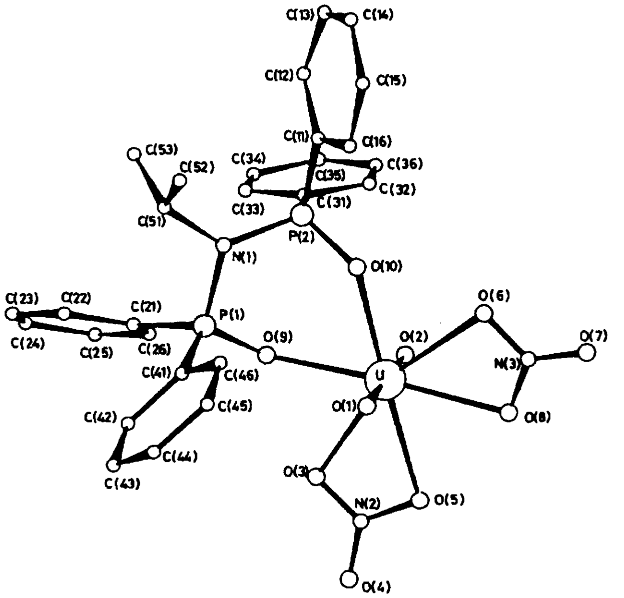


Fig. 1 A view of the molecular structure of $[UO_2(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}]$ **1**

polyhedron around uranium is a hexagonal bipyramid as found in other uranyl complexes, such as $[UO_2(NO_3)_2\{P(O)Ph_3\}_2]$,[15] $[UO_2(NO_3)_2\{Ph_2P(O)CH_2(CO)NEt_2\}]$,[16] $[UO_2(NO_3)_2\{(EtO)(Ph)P(O)CH_2(CO)NEt_2\}]$[16] and $[UO_2(NO_3)_2\{(Pr^iO)_2P(O)CH_2(CO)NEt_2\}]$.[17] The U–O(phosphoryl) [mean 2.386(7) Å] and the P=O [mean 1.513(8) Å] bond distances for complex **1** are comparable with the distances for $[UO_2\{MeN[P(O)(NMe_2)_2]_2\}_2(EtOH)][ClO_4]_2$[7] and other uranyl complexes listed above. The P(1), P(2), N(1), C(51) segment in complex **1** is planar. The nitrogen atom N(1) shows trigonal-planar geometry as the sum of all the angles around it is 359.8(6)°. The P(1)–N(1)–P(2) angle is 117.5(5)°. The dihedral angle between the P(1)–P(2)–O(9) and P(1)–P(2)–O(10) planes is 42.2(3)°. The co-ordinated $Ph_2P(O)N(Pr^i)P(O)Ph_2$ ligand adopts the *cis* geometry in contrast to the *trans* arrangement of phosphoryl groups found in several diphosphazane dioxides in the solid state.[4,7] The chelate ring O(9)–P(1)–N(1)–P(2)–O(10)–U(1) in complex **1** adopts a boat conformation whereas the analogous six-membered chelate ring in $[UO_2(NO_3)_2\{Ph_2P(O)CH_2(CO)NEt_2\}]$,[16] $[UO_2(NO_3)_2\{(EtO)(Ph)P(O)CH_2(CO)NEt_2\}]$[16] and $[UO_2(NO_3)_2\{(Pr^iO)_2P(O)CH_2(CO)NEt_2\}]$[17] assumes a nearly chair cyclohexane conformation. The ligand 'bite' angle [O(9)–U(1)–O(10) 69.0°] and the non-bonded 'bite' distance [O(9) ··· O(10) 2.70 Å] in complex **1** are the shortest observed among the uranyl complexes mentioned above.

Thorium Complex of the Diphosphazane Dioxide L^1.—Reaction of $Th(NO_3)_4{\cdot}6H_2O$ with the diphosphazane dioxide L^1 gives a colourless crystalline complex **5** of composition $Th(NO_3)_4{\cdot}1.5L^1$ irrespective of the metal-to-ligand ratio. This complex is insoluble in common organic solvents except dimethyl sulfoxide. The complex crystallises from the reaction mixture when the reaction is carried out under high dilution of the reactants. The infrared spectrum of the complex shows a strong intense ν(PO) band at 1134 cm^{-1} which is shifted to lower wavenumbers by 70 cm^{-1} from its value in the free ligand. This shift is indicative of co-ordination of the phosphoryl group to the metal. The ^1H NMR spectrum shows a doublet for the isopropyl methyl protons and a multiplet for the methine proton. The ^{31}P NMR spectrum shows a downfield shift of the phosphorus resonance compared to the free ligand as observed for the uranyl complex **1**.

The structure of complex **5** has been determined by X-ray crystallography. A perspective view of the structure is shown in Fig. 2. Selected structural data are given in Table 6. Three diphosphazane dioxide L^1 ligands are bonded to thorium in a bidentate chelating mode and the co-ordination polyhedron is completed by the chelation of two nitrate groups thus giving a ten-co-ordinated cationic $[Th(NO_3)_2L^1_3]^{2+}$ moiety. The co-ordination polyhedron around the metal cannot be fitted into any regular geometry for co-ordination number ten. The anionic moiety consists of $[Th(NO_3)_6]^{2-}$, in which twelve oxygen atoms surround the thorium ion in an icosahedral arrangement as found in $[Ce(NO_3)_6]^{2+}$ and in the trimethyl phosphine oxide complex, $[Th(NO_3)_3\{P(O)Me_3\}_4]_2[Th(NO_3)_6]$.[18] The structure of the cationic moiety in **5** is similar to that found in $[Th(NCS)_4\{(Me_2N)_2P(O)OP(O)(NMe_2)_2\}_2]$[19] and $[Th(NO_3)_4\{(EtO)_2P(O)CH_2C(O)NEt_2\}]$.[20] The average Th–O(phosphoryl) distances observed in these complexes are

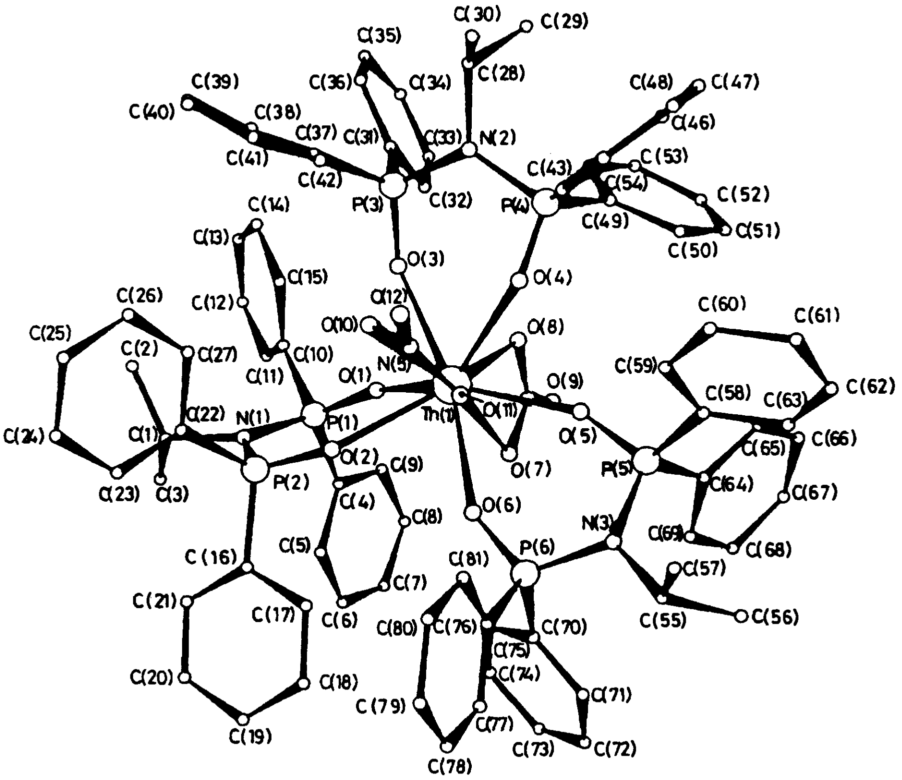


Fig. 2 A view of the cationic moiety, $[Th(NO_3)_2\{Ph_2P(O)N(Pr^i)P(O)Ph_2\}_3]^{2+}$, in **5**

close to each other but longer than those in $[Th(NO_3)_4\{P(O)Ph_3\}_2]$[21] and $[Th(NO_3)_3\{P(O)Me_3\}_4]_2[Th(NO_3)_6]$.[18] The diphosphazane dioxide ligand 'bite' angle (mean 65.5°) and non-bonded 'bite' distance (mean 2.631 Å) in complex **5** are smaller than the analogous values observed for $[Th(NCS)_4\{(Me_2N)_2P(O)OP(O)(NMe_2)_2\}_2]$[19] (2.76 Å) and $[Th(NO_3)_4\{(EtO)_2P(O)CH_2C(O)NEt_2\}]$ (2.80 Å).[20] It is worth noting that trimethylphosphine oxide replaces only one nitrate group from the thorium(IV) co-ordination sphere whereas in complex **5** the diphosphazane dioxide L^1 replaces two nitrate groups from the thorium(IV) cationic sphere. This difference may be attributed to the small 'bite' angle as well as the short O • • • O non-bonded 'bite' distances for the chelating ligand L^1. This may also be the reason for observing the maximum number of bidentate chelated ligands (three) in complex **5** compared to the complexes $[Th(NCS)_4\{(Me_2N)_2P(O)OP(O)(NMe_2)_2\}_2]$[19] and $[Th(NO_3)_4\{(EtO)_2P(O)CH_2C(O)NEt_2\}]$.[20]

The P–N–P unit and the isopropyl methine carbon atom [P(1), N(1), P(2), C(1); P(3), N(2), P(4), C(28) and P(5), N(3), P(6), C(55)] in complex **5** are coplanar. The nitrogen atoms N(1), N(2) and N(3) display planar geometry as the sum of the angles around each of these atoms is 359.9(7), 359.6(7)° and 359.9(7)° respectively. The P–N–P angles are close to each other (121 ± 1°) but are slightly higher than that observed for the uranyl complex **1** [117.5(5)°]. For complex **5**, the dihedral angles between the P(1)–P(2)–O(1) and P(1)–P(2)–O(2) planes in ligand 1, the P(3)–P(4)–O(3) and P(3)–P(4)–O(4) planes in ligand 2 and the P(5)–P(6)–O(5) and P(5)–P(6)–O(6) planes in ligand 3 are 8.8(3), 22.1(4) and 0.5(4)° respectively. The two P=O groups of each of the co-ordinated $Ph_2P(O)N(Pr^i)P(O)Ph_2$ ligands are essentially *cis* to each other, similar to the arrangement in the uranyl complex **1**.

Accessibility of a wide range of diphosphazane dioxide ligands opens up a systematic study of the co-ordination chemistry of f-block elements with this type of ligand. This approach can also be extended to the syntheses of diphosphazane dioxide bearing an additional nitrogen or *N*-oxide donor site and an investigation of their co-ordination complexes with f-block elements.

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