Structure and Stereochemistry in *f*-Block Complexes of High Co-ordination Number. Part 3.* The [M(bidentate ligand)$_2$(unidentate ligand)$_4$] System: Crystal Structures of Tetrakis(isothiocyanato)-bis(octamethylpyrophosphoramide-*OO''*)uranium(IV) and Tetrachlorobis(octamethylpyrophosphoramide-*OO''*)thorium(IV)†

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The crystal structures of octamethylpyrophosphoramide (ompp) adducts of uranium(IV) thiocyanate and thorium(IV) chloride have been determined and the complexes shown to be [U(NCS)$_4$(ompp)$_2$] (1) and [ThCl$_4$(ompp)$_2$] (2). The structures were refined by least squares to residuals of 0.043 [(1), 2 926 ' observed ' reflections] and 0.060 [(2), 2 209 ' observed ' reflections] for *X*-ray diffraction data measured at 295 K. For (1), crystals are orthorhombic, space group *Fdd*2, with unit-cell dimensions a = 44.26(2), b = 20.69(1), c = 9.110(5) Å, and Z = 8; for (2), crystals are monoclinic, space group $P2_1/n$, with unit-cell dimensions a = 18.714(7), b = 10.883(3), c = 18.999(7) Å, β = 105.01(3)°, and Z = 4. In each case the metal atom is eight-co-ordinated by the four unidentate ligands and a pair of bidentate octamethylpyrophosphoramide ligands. In (1) the metal atom lies on a crystallographic two-fold axis; U–N are 2.423(9) and 2.466(10) Å and U–O 2.297(6) and 2.414(7) Å. In (2) the molecule has no crystallographically imposed symmetry and Th–O range between 2.412(16) and 2.455(16) Å and Th–Cl between 2.725(8) and 2.763(7) Å. The two compounds are two different structural isomers of the system [M(bidentate ligand)$_2$(unidentate ligand)$_4$]. The stereochemistry about the metal atom in (1) is square antiprismatic, whereas in (2) it is dodecahedral.

For complexes in which the central atom is eight-co-ordinate, electron-pair repulsion calculations suggest that an unusually rich variety of stereoisomers may be obtained in the system containing four identical unidentate ligands and two symmetrical identical bidentate ligands. With values of the normalised bite from 1.20 to 1.25, which are appropriate for bidentate ligands fitting along various edges of a square antiprism or a dodecahedron, seven isomers have been located as potential-energy minima (Figure 1).[1,2] Each of these stereochemistries distorts as the normalised bite is decreased; for example, isomer (I) changes smoothly to a dodecahedron with the bidentate ligands spanning the two A–A edges and the four unidentate ligands occupying the B sites. On the other hand, isomer (II) distorts towards a dodecahedron where one trapezoid is formed from the two bidentate ligands and the other from the four unidentate ligands.

The relative stabilities of these isomers is a function of the normalised bite of the bidentate ligands. For example at b = 1.1—1.2 isomers (II), (IV), and (VI) are stabilised with the bidentate ligands spanning the square edges of a square antiprism.

The relative stabilities are also predicted to be critically dependent upon the choice of uni- and bi-dentate ligands. For unidentate ligands with short effective bond lengths such as halide, R(X$^-$/uncharged ligand) < 1.0, it is isomer (I) which is stabilised relative to all other isomers. All compounds containing four halide ions are of the type [M(pdma)$_2$X$_4$]$^{x\pm}$, where pdma = *o*-C$_6$H$_4$(AsMe$_2$)$_2$ and X = Cl or Br,[3] and are isomer (I) as predicted, and the experimental bond angles may be fitted against those calculated to yield R(X$^-$/pdma) ≈ 0.7 (repulsion exponent[2] n = 6). The thiocyanato-complexes [M(bipy)$_2$(NCS)$_4$], where bipy = 2,2'-bipyridyl and M = Zr or Nb,[4] are also of isomer (I), but the bond-angle fitting procedure yields R(NCS$^-$/bipy) ≈ 1.0 (n = 6). This high value for R(NCS$^-$/uncharged ligand) is also found for [U(NCS)$_4$-{OP(NMe$_2$)$_3$}$_4$][5] and suggests that it may be possible to isolate a thiocyanate with a different structure to the corresponding halide. In this paper the structures of [U(NCS)$_4$-(ompp)$_2$] (1) and [ThCl$_4$(ompp)$_2$] (2), where ompp is octamethylpyrophosphoramide, (Me$_2$N)$_2$P(O)OP(O)(NMe$_2$)$_2$, are reported.

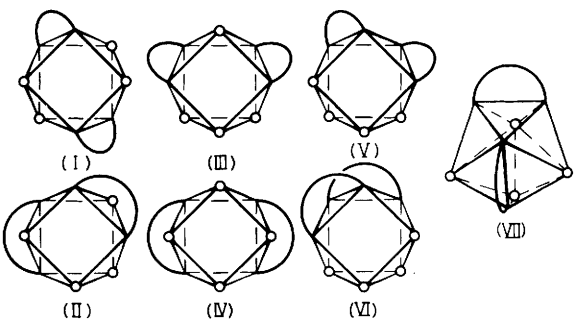

Figure 1. Stereochemistries for [M(bidentate ligand)$_2$(unidentate ligand)$_4$]

Experimental

Bis(octamethylpyrophosphoramide)tetrathiocyanatouranium(IV).—The preparation of this compound has been described in the literature.[6]

In the present preparation, octamethylpyrophosphoramide (0.2 cm^3, 0.8 mmol) was added to a solution of uranium tetrachloride (0.14 g, 0.4 mmol) in acetone (25 cm^3). A solution of potassium thiocyanate (0.16 g, 1.6 mmol) in acetone (10 cm^3) was added. The precipitated potassium chloride was filtered off, and the solution evaporated to a small volume; an equal volume of ethyl acetate was added and the solution allowed to evaporate, giving green crystals. All processes were carried out under a nitrogen atmosphere; once dry, the crystals were stable in air and a capillary was not used for the *X*-ray work.

* Part 2 is ref. 5.

† *Supplementary data available* (No. SUP 23490, 31 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

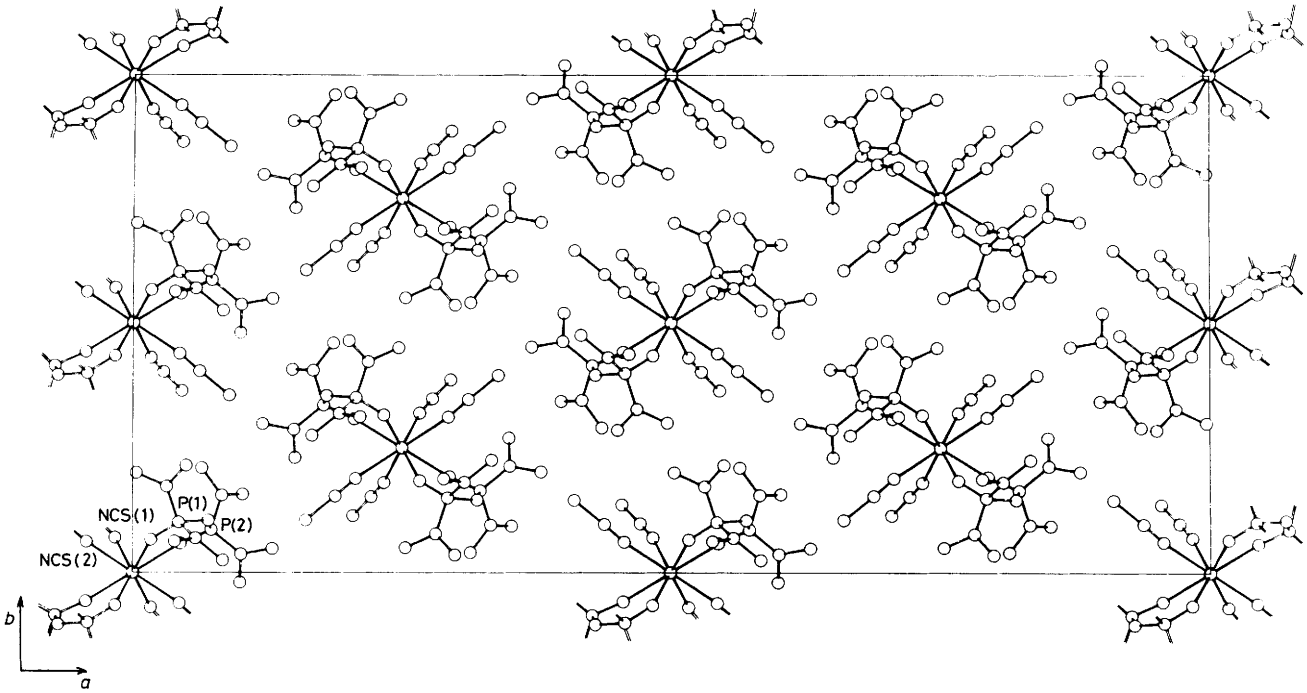

Figure 2. Unit-cell contents of complex (1) projected down *c*, showing non-hydrogen atoms and ligand labelling

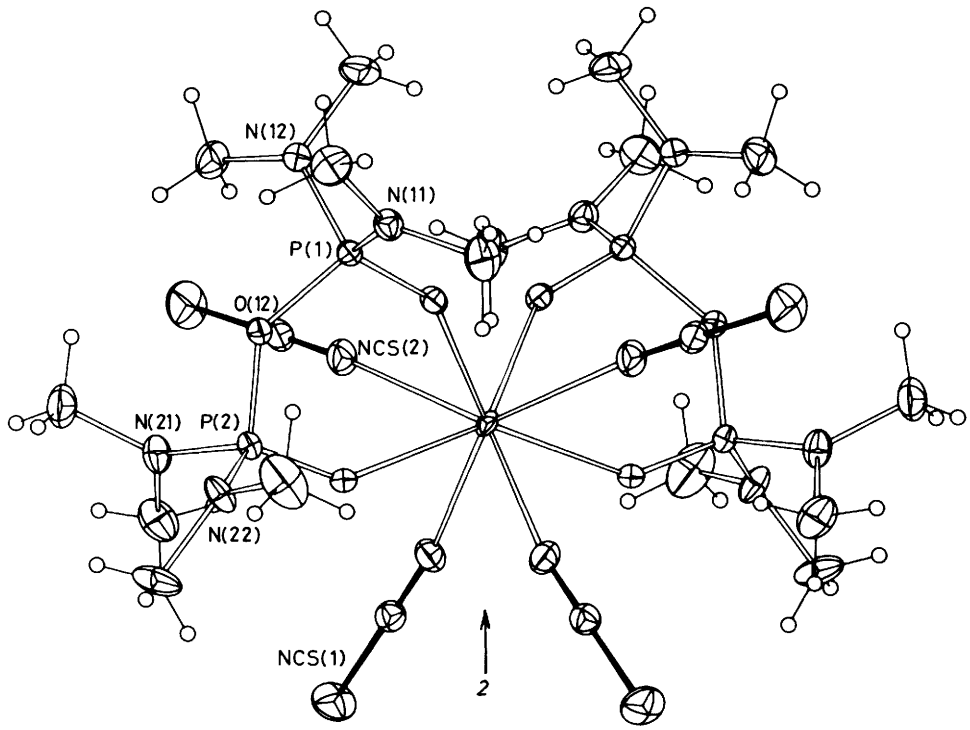

Figure 3. Projection of the molecule of complex (1) onto the plane defined by N(1,2), O(1′,2′)

Tetrachlorobis(octamethylpyrophosphoramide)thorium(IV).—The preparation of this compound has been described in the literature.[7]

Octamethylpyrophosphoramide (0.6 cm^3, 2.4 mmol) was added to a solution of thorium tetrachloride (0.3 g, 0.8 mmol) in acetone (50 cm^3). The mixture was heated to 50 °C for 1 h and allowed to cool to room temperature, depositing colourless crystals. Exposure to the air for several hours causes the crystals to become opaque; accordingly, after carrying out the above procedures under nitrogen, crystals for *X*-ray work were mounted in capillaries.

Crystallography.—General procedural details are given in ref. 8.

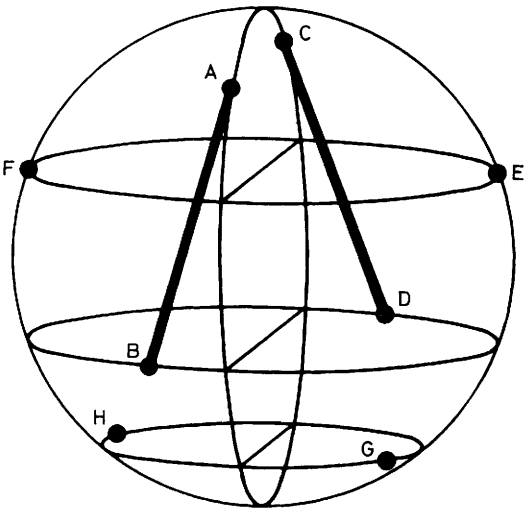

Figure 4. General stereochemistry for isomer (II) of [M(bidentate ligand)$_2$(unidentate ligand)$_4$]

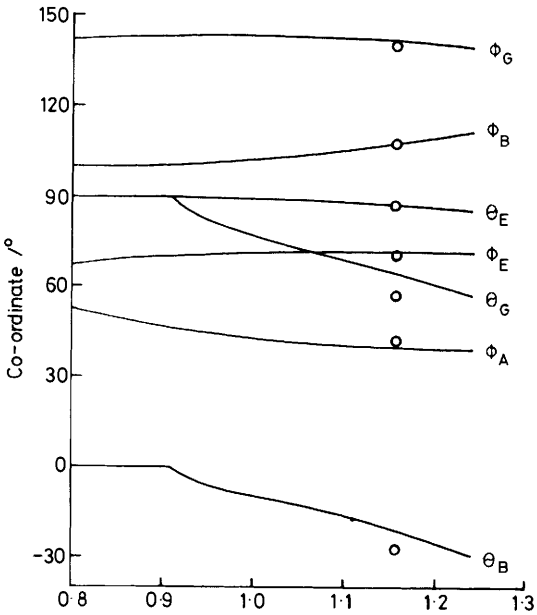

Figure 5. Angular co-ordinates (°) for isomer (II) of [M(bidentate ligand)$_2$(unidentate ligand)$_4$] as a function of b (n = 6). Open circles indicate parameters for [U(NCS)$_4$(ompp)$_2$]

Crystal data. (1), $C_{20}H_{48}N_{12}O_6P_4S_4U$, M = 1 042.9, Orthorhombic, space group $Fdd2$ (C_{2v}^{19}, no. 43), a = 44.26(2), b = 20.69(1), c = 9.110(5) Å, U = 8 342(5) Å^3, Z = 8, D_c = 1.66 g cm^{-3}, $F(000)$ = 4 128, μ_{Mo} = 41.2 cm^{-1}. Specimen size: trapezoidal prism, 0.35 × (0.25, 0.18) × 0.13 mm; $2\theta_{max.}$ = 70°, N = 4 841, N_o = 2 926, R = 0.043, R' = 0.044.

(2), $C_{16}H_{48}Cl_4N_8O_6P_4Th$, M = 946.4, Monoclinic, space group $P2_1/n$ [C_{2h}^5, no. 14 (variant)], a = 18.714(7), b = 10.883(3), c = 18.999(7) Å, β = 105.01(3)°, U = 3 737(3) Å^3, Z = 4, D_c = 1.68 g cm^{-3}, $F(000)$ = 2 248, μ_{Mo} = 43.2 cm^{-1}. Specimen size: prism, 0.30 × 0.20 × 0.15 Å; $2\theta_{max.}$ = 40°, N = 3 585, N_o = 2 209, R = 0.060, R' = 0.069.

Abnormal features: (2). A number of attempts to measure data on this complex resulted in crystal decomposition after a small number of hours exposure to X-rays, in spite of the crystal being sealed in a capillary. Accordingly, a successful attempt was made to measure data very rapidly, in successive 5° shells in 2θ using the maximum scan rate (30° min^{-1}) available on the diffractometer. In this way, over a 12 h period, 3 585 reflections were measured to $2\theta_{max.}$ = 40°, involving exposure of the crystal to the X-rays for only 1.8 h; the relatively minor decomposition evidenced in the standards was corrected for by appropriate scaling. Isotropic thermal parameters only were refined for the peripheral ligand atoms.

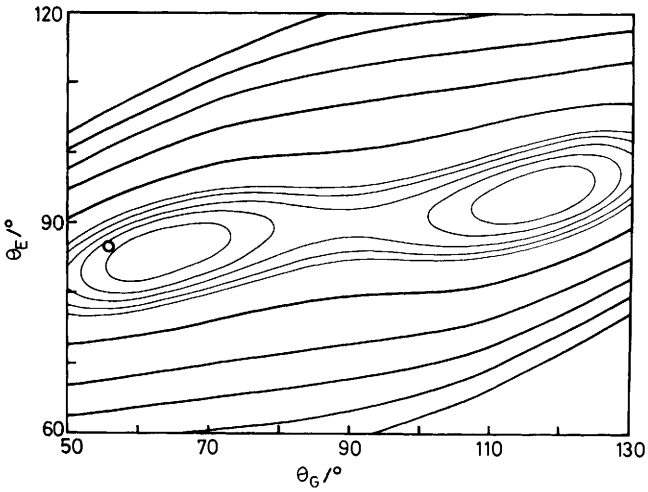

Figure 6. Projection of the potential-energy surface for isomer (II) of [M(bidentate ligand)$_2$(unidentate ligand)$_4$] onto the θ_G–θ_E plane. The five faint contour lines are for successive 0.02 increments above the minima and the five heavy contour lines are for successive 0.2 increments above the minima (n = 6, b = 1.16). The location of [U(NCS)$_4$(ompp)$_2$] is indicated

Discussion

Complex (1).—The unit-cell contents of this complex are depicted in Figure 2; the stoicheiometry defined by the structure determination is consistent with the formulation [U(NCS)$_4$(ompp)$_2$] as expected. The crystal array is of high symmetry (space group $Fdd2$) and the molecules lie on crystallographic special positions of symmetry 2, so that one half of the molecule only comprises the asymmetric unit. A projection of the molecule in Figure 3 shows the disposition of the two-fold axis relative to the ligand array about the metal.

Figure 3 shows that the stereochemistry about the uranium atom conforms to that of the square-antiprismatic isomer (II), constituting the first well defined example of this type. {However, a similar stereochemistry is found in [Er(HOCH$_2$CO$_2$)$_2$(H$_2$O)$_4$][Er(HOCH$_2$CO$_2$)$_4$],[9] containing unsymmetrical bidentate ligands.} The general stereochemistry for isomer (II) of [M(bidentate ligand)$_2$(unidentate ligand)$_4$] is shown in Figure 4. Angular co-ordinates are defined relative to the two-fold axis passing through the midpoint of AC, and with θ_A = 0 and θ_C = 180°.

With a normalised bite of the bidentate ligand of b = 1.19, the stereochemistry is square antiprismatic with ABGE and CDHF as the two square faces. Repulsion-energy calculations show that, as the size of the normalised bite is decreased, θ_B approaches 0° and θ_G approaches 90° with the formation of a dodecahedron comprising one trapezoid formed by the two bidentate ligands and the other trapezoid formed by the four unidentate ligands. The variation of angular parameters with b is shown in Figure 5, calculated using n = 6 in the repulsion law. The angular parameters for [U(NCS)$_4$(ompp)$_2$], where

Table 1. Non-hydrogen atom co-ordinates for complex (1)

Atom	*x*	*y*	*z*
U	0	0	½
Thiocyanate groups			
N(1)	0.016 6(2)	−0.069 7(4)	0.302 1(10)
C(1)	0.028 4(2)	−0.098 2(4)	0.211 0(11)
S(1)	0.045 33(8)	−0.136 0(1)	0.083 0(4)
N(2)	0.043 3(2)	−0.061 4(5)	0.598 0(14)
C(2)	0.061 9(2)	−0.096 7(5)	0.630 0(12)
S(2)	0.089 53(9)	−0.144 9(2)	0.674 8(5)
Octamethylpyrophosphoramide ligands			
O(12)	0.070 1(1)	0.104 6(7)	0.643 0(6)
P(1)	0.042 59(4)	0.100 78(9)	0.757 3(3)
O(1)	0.016 8(1)	0.065 8(3)	0.686 1(6)
N(11)	0.031 5(2)	0.172 4(3)	0.801 6(9)
C(111)	0.003 2(2)	0.200 2(5)	0.752 1(18)
C(112)	0.049 4(3)	0.214 6(6)	0.892 4(15)
N(12)	0.058 2(2)	0.069 0(4)	0.900 5(9)
C(121)	0.083 5(3)	0.024 7(6)	0.896 1(15)
C(122)	0.038 9(3)	0.062 5(6)	1.030 6(12)
P(2)	0.072 89(5)	0.085 87(10)	0.472 4(2)
O(2)	0.044 2(1)	0.058 2(3)	0.418 5(8)
N(21)	0.100 5(2)	0.036 8(4)	0.458 9(10)
C(211)	0.099 6(3)	−0.019 6(6)	0.358 8(17)
C(212)	0.129 5(2)	0.048 2(6)	0.531 2(17)
N(22)	0.082 6(2)	0.154 8(4)	0.402 0(10)
C(221)	0.102 0(3)	0.156 7(5)	0.273 8(13)
C(222)	0.063 9(3)	0.209 8(6)	0.422 0(21)

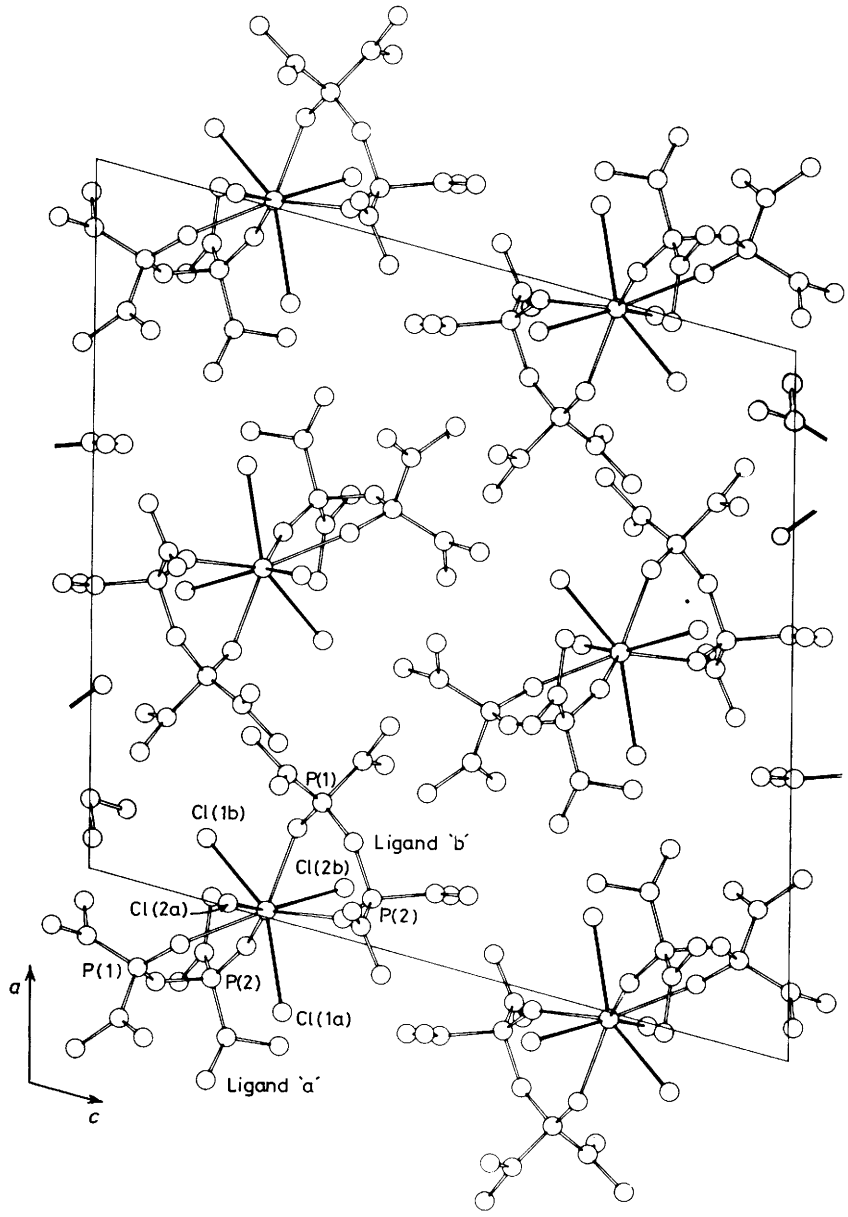

Figure 7. Unit-cell contents of complex (2) projected down *b*, showing non-hydrogen atoms and ligand labelling

Table 2. Uranium environment of complex (1). Entries in the first row are the metal–ligand distances (Å); the remaining entries are the angles (°) subtended by the two appropriate ligands. Primed atoms are generated by the intramolecular two-fold rotor $\bar{x},\bar{y},z$

	N(1)	N(2)	O(1)	O(2)
r(U–L)	2.423(9)	2.466(10)	2.297(6)	2.414(7)
N(2)	74.1(3)			
O(1)	143.5(2)	77.7(3)		
O(2)	79.8(3)	74.9(3)	70.7(2)	
N(1′)	83.9(3)	144.3(3)	107.1(2)	73.7(2)
N(2′)	144.3(3)	137.5(4)	71.2(3)	118.9(3)
O(1′)	107.1(2)	71.2(3)	84.9(2)	141.7(2)
O(2′)	73.7(2)	118.9(3)	141.7(2)	144.2(2)

b = 1.16, are also marked in Figure 5, the main discrepancy between experimental and calculated values being the low values of θ_B and θ_G.

The potential-energy surface projected onto θ_G–θ_E is shown in Figure 6, calculated for b = 1.16. The square-antiprismatic structure corresponding to the minimum at θ_G = 63.6° and θ_E = 86.2° is readily distorted by decreasing or increasing θ_G corresponding to creasing the square faces across the AG and CH diagonals, or across the BE and DF diagonals, respectively. The two minima at θ_G = 63.6°, θ_E = 86.2° and at θ_G = 116.4°, θ_E = 93.8° corresponding to the two different optical isomers are connected *via* the saddle at $\theta_G = \theta_E$ = 90° corresponding to the dodecahedron with one trapezoid formed by the bidentate ligands and the other trapezoid by the uniden-

Table 3. Atom co-ordinates for complex (2)

Atom	x	y	z	x	y	z
Th	0.009 82(5)	0.062 86(9)	0.254 96(5)			
	Ligand 'a'			Ligand 'b'		
Cl(1)	−0.128 0(3)	0.033 0(7)	0.279 5(4)	0.088 8(4)	0.167 1(7)	0.168 5(4)
Cl(2)	0.005 3(4)	−0.171 8(6)	0.200 1(4)	0.072 2(4)	0.224 4(7)	0.366 1(4)
O(12)	−0.135 5(8)	0.271 5(15)	0.097 3(8)	0.140 3(9)	−0.200 2(17)	0.378 5(9)
P(1)	−0.122 7(4)	0.133 5(9)	0.071 2(4)	0.183 5(4)	−0.115 6(8)	0.333 6(4)
O(1)	−0.072 7(8)	0.063 9(16)	0.131 8(7)	0.138 4(8)	−0.006 5(17)	0.298 4(9)
N(11)	−0.202 1(10)	0.066 2(22)	0.045 5(10)	0.209 9(10)	−0.214 2(20)	0.283 0(10)
C(111)	−0.262(2)	0.112(3)	−0.017(2)	0.250(2)	−0.167(3)	0.231(2)
C(112)	−0.220(2)	−0.047(3)	0.081(2)	0.191(2)	−0.339(4)	0.272(2)
N(12)	−0.097 8(10)	0.164 7(20)	−0.002 5(10)	0.257 6(11)	−0.050 1(26)	0.390 6(12)
C(121)	−0.096(1)	0.059(3)	−0.054(1)	0.260(2)	0.069(3)	0.422(2)
C(122)	−0.048(2)	0.268(3)	−0.007(2)	0.317(2)	−0.142(3)	0.429(2)
P(2)	−0.108 2(4)	0.333 9(7)	0.177 3(4)	0.067 7(4)	−0.169 1(8)	0.405 8(4)
O(2)	−0.048 9(10)	0.260 5(14)	0.226 8(9)	0.027 4(8)	−0.065 4(18)	0.364 4(8)
N(21)	−0.185 9(12)	0.352 2(24)	0.199 7(12)	0.099 7(20)	−0.128 2(33)	0.495 4(13)
C(211)	−0.254(2)	0.282(3)	0.171(2)	0.103(3)	−0.003(5)	0.517(3)
C(212)	−0.177(2)	0.403(4)	0.275(2)	0.110(3)	−0.218(6)	0.543(3)
N(22)	−0.074 8(15)	0.469 4(18)	0.166 5(11)	0.023 7(15)	−0.304 9(29)	0.390 5(21)
C(221)	0.008(2)	0.484(3)	0.177(2)	0.042(3)	−0.413(6)	0.378(3)
C(222)	−0.127(2)	0.568(4)	0.132(2)	−0.037(4)	−0.302(7)	0.420(4)

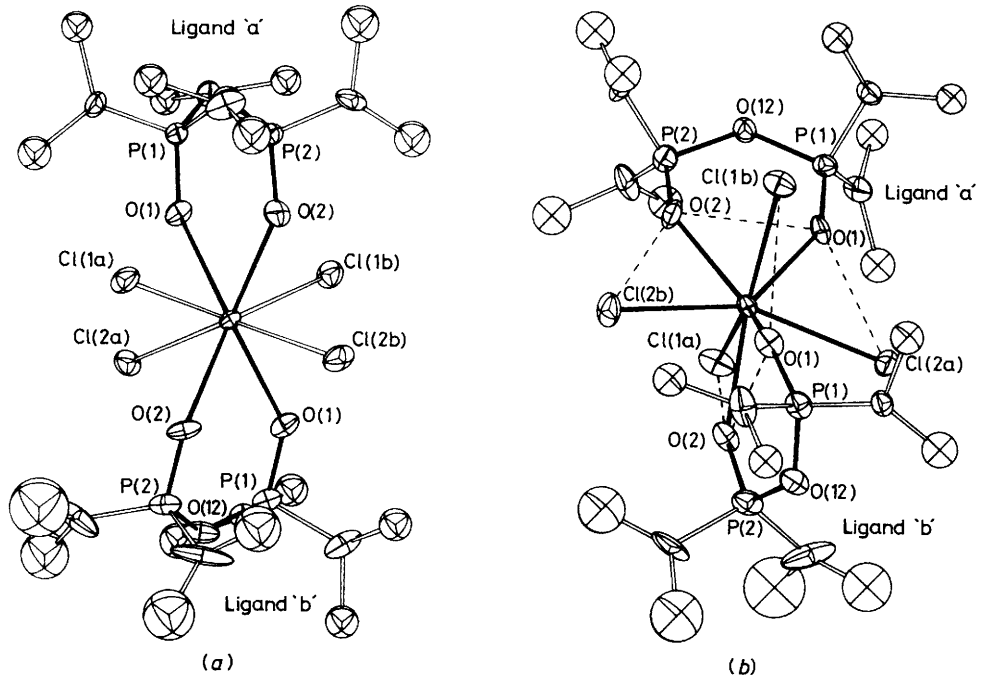

Figure 8. Projections of the molecule of complex (2): (*a*) down a pseudo-two-fold axis; (*b*) normal to one of the trapezoidal planes

Table 4. Thorium environment of complex (2). Entries in the first column are the metal–ligand distances (Å); the remaining entries are the angles (°) subtended by the two appropriate ligands

	r(Th–L)	O(2a)	O(1b)	O(2b)	Cl(1a)	Cl(2a)	Cl(1b)	Cl(2b)
O(1a)	2.45(1)	69.2(5)	130.1(6)	136.5(5)	77.0(4)	72.1(4)	74.2(4)	139.9(4)
O(2a)	2.41(2)		134.5(6)	130.5(6)	75.6(5)	140.9(4)	77.4(5)	71.4(4)
O(1b)	2.45(2)			68.6(5)	141.8(5)	76.9(4)	72.1(4)	75.8(4)
O(2b)	2.45(2)				73.5(4)	77.1(4)	140.6(4)	77.1(4)
Cl(1a)	2.756(7)					90.9(2)	145.9(2)	100.0(2)
Cl(2a)	2.752(7)						97.3(2)	147.7(2)
Cl(1b)	2.725(8)							90.4(2)
Cl(2b)	2.763(7)							

Table 5. Ligand geometries (non-hydrogen atoms) of complex (1); distances in Å, angles in degrees

N(1)–C(1)	1.14(1)	N(2)–C(2)	1.14(1)	C(1)–S(1)	1.59(1)	C(2)–S(2)	1.63(1)
U–N(1)–C(1)	170.0(7)	U–N(2)–C(2)	170.0(10)	N(1)–C(1)–S(1)	178.4(9)	N(2)–C(2)–S(2)	177.6(10)
P(1)–O(12)	1.605(6)	P(2)–O(12)	1.606(6)	N(11)–C(111)	1.45(1)	N(21)–C(211)	1.48(2)
P(1)–O(1)	1.500(6)	P(2)–O(2)	1.478(7)	N(11)–C(112)	1.44(1)	N(21)–C(212)	1.46(1)
P(1)–N(11)	1.612(7)	P(2)–N(21)	1.593(8)	N(12)–C(121)	1.45(1)	N(22)–C(221)	1.45(2)
P(1)–N(12)	1.616(8)	P(2)–N(22)	1.622(8)	N(12)–C(122)	1.47(1)	N(22)–C(222)	1.42(2)
P(1)–O(12)–P(2)	132.4(4)	O(12)–P(2)–O(2)	110.5(4)	P(1)–N(11)–C(111)	123.3(7)	P(2)–N(21)–C(211)	122.0(7)
O(12)–P(1)–O(1)	108.7(3)	O(12)–P(2)–N(21)	106.7(4)	P(1)–N(11)–C(112)	122.3(7)	P(2)–N(21)–C(212)	122.4(8)
O(12)–P(1)–N(11)	110.4(4)	O(12)–P(2)–N(22)	101.0(4)	C(111)–N(11)–C(112)	114.4(8)	C(211)–N(21)–C(212)	115.3(9)
O(12)–P(1)–N(12)	102.7(4)	O(2)–P(2)–N(21)	112.7(4)	P(1)–N(12)–C(121)	124.4(7)	P(2)–N(22)–C(221)	119.9(7)
O(1)–P(1)–N(11)	108.7(4)	O(2)–P(2)–N(22)	115.9(4)	P(1)–N(12)–C(122)	116.2(7)	P(2)–N(22)–C(222)	120.0(8)
O(1)–P(1)–N(12)	118.6(4)	N(21)–P(2)–N(22)	109.1(4)	C(121)–N(12)–C(122)	114.5(9)	C(221)–N(22)–C(222)	115.3(10)
N(11)–P(1)–N(12)	107.5(4)						

Table 6. Ligand least-squares planes for complexes (1) and (2) defined by the P_2O_3 skeleton of the chelate rings and given in the form $pX + qY + rZ = s$ where the right-hand orthogonal Å frame (X,Y,Z) is defined with X parallel to a and Z in the ac plane; σ (defining atoms) and atom deviations, δ, are given in Å. Also given are ligand O · · · O distances, M–O distances (Å), and M–O–P angles (°)

	Complex (1)	Complex (2) Ligand a	Complex (2) Ligand b
10^4p	−3 431	8 769	2 715
10^4q	9 030	3 436	5 489
10^4r	−2 587	−3 360	7 906
s	−0.601	−2.283	4.592
σ	0.04	0.08	0.07
δ[O(1)]	−0.04	−0.05	0.00
δ[P(1)]	0.05	0.02	0.04
δ[O(12)]	−0.03	0.05	−0.09
δ[P(2)]	−0.02	−0.10	0.09
δ[O(2)]	0.03	0.08	−0.04
δ[N(11)]	1.45	−1.27	−1.08
δ[N(12)]	−1.11	1.32	1.56
δ[N(21)]	−1.32	−1.54	1.67
δ[N(22)]	1.29	1.07	−1.15
δ(M)	−0.58	0.01	−0.81
O · · · O	2.728(9)	2.76(2)	2.76(2)
M–O	2.297(6)	2.45(1)	2.45(2)
	2.414(7)	2.41(2)	2.45(2)
M–O–P	148.3(4)	149(1)	141(1)
	142.0(4)	147(1)	146(1)

tate ligands. The structural parameters for $[U(NCS)_4(ompp)_2]$ are also marked in Figure 6, and as is usually observed they lie within the first one or two contours, approximately 0.03 energy units above the minimum.

These small angular distortions in $[U(NCS)_4(ompp)_2]$ result in fairly large differences in the individual atom repulsion-energy coefficients, Y_i. Using the experimental angular parameters and effective bond-length ratios of all metal–ligand bonds equal to unity, the calculations show that the A end of the bidentate ligand is subject to less repulsion than the B end, and the thiocyanate group in the E site is subject to more repulsion than that in the G site: $Y_A/Y_B = 0.898$, $Y_E/Y_G = 1.124$ ($n = 6$). The relative bond lengths observed are in agreement with these predictions: $(U–O_A)/(U–O_B) = 0.95$ and $(U–N_E)/(U–N_G) = 1.02$.

These structural conclusions are unchanged for small differences in $R(NCS^-/ompp)$.

Atomic co-ordinates are given in Table 1, the uranium environment in Table 2.

Complex (2).—The unit-cell contents of this complex are depicted in Figure 7; the stoicheiometry defined by the structure determination is consistent with the formulation $[ThCl_4(ompp)_2]$ as expected. There is no crystallographic symmetry inherent in the molecule, one of which comprises the asymmetric unit.

Consideration of the stereochemistry about the metal atom shows it to be the dodecahedral form of isomer (I), in which all chlorine atoms occupy the B sites [rather than the dodecahedron (VII) in which one occupies an A site]. 'Dodecahedral' and 'square-antiprism' projections are displayed in Figure 8 and corresponding planes have been calculated. For the 'square antiprism,' the planes are O(1a,1b), Cl(2a,1b) (deviations: 0.39, 0.38, −0.38, and −0.40 Å) and O(2a,2b), Cl(1a,2b) (deviations: −0.39, −0.36, 0.38, and 0.38 Å) (dihedral angle 1.2°), while for the dodecahedron the planes are O(1,2a), Cl(2a,b) (deviations: 0.12, −0.12, −0.06, and 0.06 Å) and O(1,2b), Cl(1a,b) (deviations: −0.07, 0.07, −0.04, and 0.04 Å) (dihedral angle 87.9°). For either configuration all distances

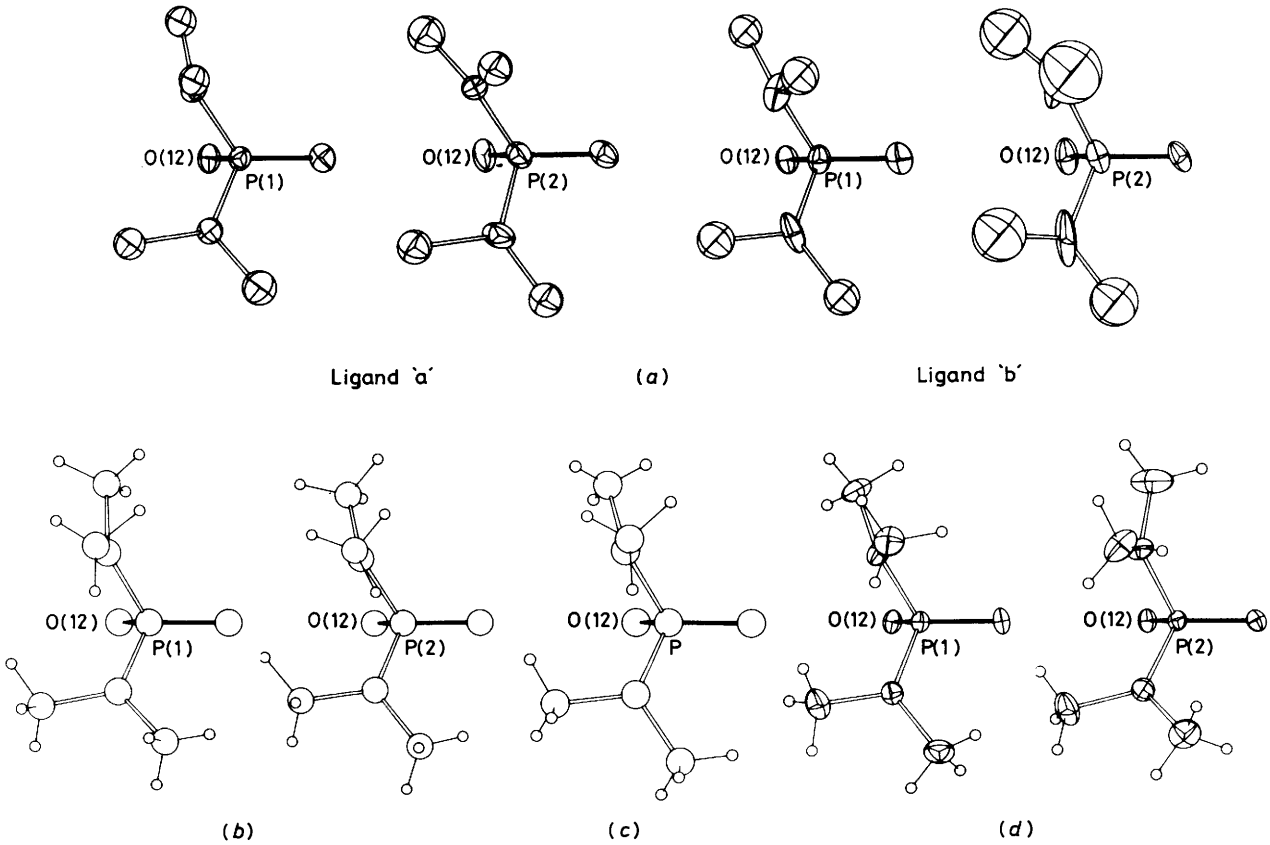

Figure 9. Projection of the phosphorus environment for each of the phosphorus atoms in (*a*) $[ThCl_4L_2]$, (*b*) $[CuL_2]^{2+}$,[9] (*c*) $[CuL_3]^{2+}$,[10] and (*d*) $[U(NCS)_4L_2]$ (L = ompp). Projection is along the P–P line in each case. The 'a' and 'b' type NMe_2 substituents on P lie below and above the median plane respectively

from the metal to ligands of the same type should be equivalent; observed values range from 2.41(2) to 2.45(2) Å for Th–O and 2.725(8)—2.763(7) Å for Th–Cl. Bond angles can be fitted against those calculated to yield $R(Cl^-/ompp) \approx 0.9$ ($n = 6$).

Atom co-ordinates are given in Table 3, the thorium environment in Table 4.

The Ligands.—In view of the limited range of detailed data previously available on octamethylpyrophosphoramide complexes,[10,11] the reasonable precision of determination of the ligand geometry (Table 5) in the present uranium structure (1) renders comparison useful, particularly in regard of angular geometry and ligand conformation. In both compounds the P_2O_3 skeleton of the chelate ring is tolerably close to planarity (Table 6), but the deviations of the metal atoms from the plane vary considerably and show no apparent dependence on the metal–oxygen distance or the O · · · O bite distance of the ligand. In $[Mg,Co,Cu(ompp)_3]^{2+}$ (ref. 10) and $[Cu(ompp)_2]^{2+}$,[11] ligand puckering is similarly quite small as is the metal atom deviation, except in the latter complex in which it is 0.30 Å; for these complexes, ligand O · · · O distances are 2.81, 2.89, 2.88, and 2.75 Å respectively, while mean M–O distances are 2.06, 2 09, 2.07, and 1.94 Å. Although it has been previously observed that 'the two dimethylamino-groups on a particular phosphorus atom are staggered with respect to each other thus avoiding any non-bonding interactions,' previous examples have probably been insufficient confidently to establish a trend. The projections of the NMe_2 substituent dispositions relative to the P_2O_3 plane are shown in Figure 9 (projection along P · · · P) and clearly establish two different substituent types

Table 7. Octamethylpyrophosphoramide geometrical parameters. Type 'a' and 'b' substituents are defined in Figure 9; σ is the estimated standard deviation (Å) for a plane defined by PNC_2. The complexes $[M(ompp)_3]$ (M = Mg, Co, or Cu) are isostructural and only that of magnesium is quoted as typical. The oxygen atom bound to the metal is denoted O

Compound	Phosphorus and substituent	σ	Angle/° O–P–N	Angle/° O(12)–P–N
$[Mg(ompp)_3]^{2+}$ [a]	a		110.6(3)	108.6(3)
	b		118.5(3)	101.0(2)
$[Cu(ompp)_2]^{2+}$ [b]	P(1): a	0.00	111.5(1)	108.5(1)
	b		117.9(1)	100.7(1)
	P(2): a	0.00	110.2(1)	109.2(1)
	b		119.7(1)	100.4(1)
$[U(NCS)_4(ompp)_2]$ [c]	P(1): a	0.00	108.7(4)	110.4(4)
	b	0.10	118.6(4)	102.7(4)
	P(2): a	0.03	112.7(4)	106.7(4)
	b	0.10	115.9(4)	101.0(4)
$[ThCl_4(ompp)_2]$ [c]	P(1a): a	0.01	110(1)	108(1)
	b	0.10	121(1)	100(1)
	P(2a): a	0.05	108(1)	107(1)
	b	0.10	118(1)	102(1)
	P(1b): a	0.04	103(1)	110(1)
	b	0.08	119(1)	102(1)
	P(2b): a	0.03	109(1)	105(1)
	b	0.08	115(1)	100(1)

[a] Ref. 10. [b] Ref. 9. [c] This work.

which we term ' a ' and ' b ' which appear pairwise in a seemingly preferred orientation; within a given ligand, the dispositions appear to be coupled so that above the P_2O_3 plane an ab pair is observed with a ba pair below. No significant variations in bond lengths appear to occur between the two substituent types. Significant perturbations are observed, however, in respect of angular geometry, particularly at the phosphorus atoms (Table 7). In type ' a ' substituents the nitrogen atom and its immediately adjoining substituent atoms lie close to coplanarity, while the two O–P–N angles are equal and approximately 110°. In type ' b ' substituents, the nitrogen atom, relative to its neighbouring atoms, is appreciably pyramidal, with the two O–P–N angles unequal and deviating appreciably on either side of 110°.

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