Actinide Structural Studies. Part 1. Crystal and Molecular Structures of Dinitratodioxobis(triphenylphosphine oxide)neptunium(VI), Dinitratodioxobis(triphenylphosphine oxide)uranium(VI), and Dichlorodioxo(triphenylphosphine oxide)neptunium(VI)

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The crystal structures of the title complexes, $[NpO_2(OPPh_3)_2(NO_3)_2]$ (1), $[UO_2(OPPh_3)_2(NO_3)_2]$ (2), and $[NpO_2(OPPh_3)_2Cl_2]$ (3), have been determined using *X*-ray diffraction methods. Compounds (1) and (2) are isomorphous and isostructural. Their crystals are monoclinic, space group $P2_1/c$, with hexagonal-bipyramidal co-ordination about the heavy atoms. The bidentate nitrate groups are *trans* to each other and bonded to the metal (M–O 2.52—2.54 Å), as are the triphenylphosphine oxide ligands (M–O 2.35—2.36 Å). The M–O bond lengths in the MO_2^{2+} cations (M = Np or U) are 1.739(10) and 1.764(9) Å respectively. Compound (3) is monoclinic, space group $P2_1$, and exhibits distorted octahedral co-ordination about neptunium, the *trans* ligands having Np–Cl lengths of 2.622(14) and 2.645(13) Å; for the triphenylphosphine oxide groups, Np–O lengths are 2.261(19) and 2.288(15) Å. The NpO_2^{2+} cation has Np–O bond lengths of 1.721(16) and 1.751(18) Å. Lattice parameters are: for (1) a = 11.038(5), b = 18.838(7), c = 10.897(4) Å, β = 128.27(3)°, and Z = 2; for (2), a = 11.043(1), b = 18.880(3), c = 10.870(2) Å, β = 128.17(1)°, and Z = 2; for (3), a = 10.757(4), b = 18.716(4), c = 10.734(3) Å, β = 124.05(2)°, and Z = 2. The structures have been refined to R values of 0.049 (1), 0.028 (2), and 0.042 (3) using respectively, 2 821, 2 638, and 2 063 observed diffractometer-measured intensities.

THE crystal structures of several uranyl(VI) complexes containing triphenylphosphine oxide (PPh_3O) have been examined.[1-3] As part of a study of neptunyl(VI) structural chemistry it was therefore of interest to examine complexes of this type in order to permit detailed comparison and identify changes consequent upon the change of actinide element. In this paper, the crystal structures of $[NpO_2(OPPh_3)_2(NO_3)_2]$ (1) and $[NpO_2(OPPh_3)_2Cl_2]$ (3) are compared with those of their uranyl(VI) analogues. The corresponding uranyl(VI) chloride complex, (4), has previously been examined,[1] but for the uranyl(VI) nitrate complex, (2), only the unit-cell constants have been reported;[4] this structure was therefore also determined.

EXPERIMENTAL

Preparation.—Complex (1) was prepared by adding freshly made solid $NpO_2(NO_3)_2 \cdot 6H_2O$ [5] (0.5 mmol) to an acetone solution (5 cm³) containing triphenylphosphine oxide (1 mmol). Crystals were obtained by evaporation from methanol. Complex (2) was prepared by adding a solution of PPh_3O (2 mmol) in methanol (10 cm³) to a solution of uranyl(VI) nitrate hexahydrate (0.86 mmol) in methanol (10 cm³). Crystals formed after *ca.* 24 h. Complex (3) was prepared by adding a solution of PPh_3O (0.36 mmol) in acetone (2 cm³) to a solution of hydrochloric acid (4 mol dm⁻³, 2 cm³) containing freshly ozonised Np^{VI} (0.12 mmol). Crystals grew at the interface between the two solutions.

Suitable crystals of (1)—(3) were mounted on quartz fibres with (1) and (3) encapsulated in Lindemann glass capillaries. Crystals of (1) and (3) were handled in a glove-box to afford protection from the α radiation of ^{237}Np.

Data Collection and Structural Refinement.—For crystal data see Table 1. Mo-K_α radiation (λ = 0.710 69 Å) was used throughout. Reflections were collected using a Syntex $P2_1$ automatic four-circle diffractometer, with the temperature controlled by the LT-1 attachment for (3). Accurate unit-cell parameters were obtained from least-squares calculations based on the positions of 15 reflections. Three standard reflections measured at intervals of every 100 reflections showed no significant change in intensity. The θ—2θ scan mode was used. The structures were solved using the heavy-atom technique.

For (1), a crystal of dimensions 1.1 × 0.3 × 0.3 mm was used, which gave transmission factors in the range 0.500—

TABLE 1

Comparative lattice parameters

Compound	(1) [a]	(2) [a]	(3) [a]	(4) [b]
Formula	$C_{36}H_{30}N_2NpO_{10}P_2$	$C_{36}H_{30}N_2O_{10}P_2U$	$C_{36}H_{30}Cl_2NpO_4P_2$	$C_{36}H_{30}Cl_2O_4P_2U$
M	949.6	950.6	896.5	897.5
System	Monoclinic	Monoclinic	Monoclinic	Triclinic
Temp., θ_c/°C	16	16	−100	Room temperature
Space group	$P2_1/c$	$P2_1/c$	$P2_1$	$P\bar{1}$
a/Å	11.038(5)	11.043(1)	10.757(4)	10.010 1(6)
b/Å	18.838(7)	18.880(3)	18.716(4)	10.258 9(9)
c/Å	10.897(4)	10.870(2)	10.734(3)	9.234 7(8)
α/°				110.093(6)
β/°	128.27(3)	128.17(1)	124.05(2)	92.129(6)
γ/°				78.384(6)
Z	2	2	2	1
U/Å³	1 778.8(13)	1 781.6(5)	1 790.7(8)	871.8
D_c/g cm⁻³	1.78	1.77	1.66	1.71
μ(Mo-K_α)/cm⁻¹	20.49	44.64	21.54	Uncorrected

[a] This paper. [b] Ref. 1.

TABLE 2

Atomic co-ordinates (× 10⁴), with standard deviations in parentheses for (1)

Atom	x	y	z
Np	0	5 000	5 000
P(1)	−3 146(3)	6 365(1)	3 625(3)
O(1)	−2 164(9)	5 757(4)	3 811(9)
O(2)	1 100(9)	5 682(4)	5 062(10)
O(3)	−1 635(11)	5 103(4)	2 065(10)
O(4)	87(11)	4 301(6)	3 078(11)
O(5)	−1 365(15)	4 478(7)	588(12)
N(1)	−965(12)	4 627(6)	1 856(12)
C(1)	−3 336(14)	6 191(6)	6 018(14)
C(2)	−4 084(17)	5 978(7)	6 592(16)
C(3)	−5 621(16)	5 763(7)	5 573(18)
C(4)	−6 431(15)	5 772(7)	4 039(15)
C(5)	−5 684(12)	5 975(6)	3 384(14)
C(6)	−4 150(12)	6 174(5)	4 393(12)
C(7)	−2 018(12)	7 163(5)	4 493(12)
C(8)	−2 362(14)	7 678(6)	5 160(14)
C(9)	−1 561(17)	8 303(7)	5 664(16)
C(10)	−409(16)	8 436(7)	5 520(16)
C(11)	−44(15)	7 914(8)	4 856(17)
C(12)	−871(14)	7 284(6)	4 366(15)
C(13)	−4 587(12)	6 556(5)	1 574(12)
C(14)	−5 465(15)	7 163(7)	1 097(14)
C(15)	−6 581(17)	7 301(8)	−538(17)
C(16)	−6 824(17)	6 803(8)	−1 598(16)
C(17)	−5 956(17)	6 189(8)	−1 107(16)
C(18)	−4 829(13)	6 061(7)	486(14)

0.673. The scan rate varied from 2.0 to 29.3° min^{-1}, depending on the intensity of a 2-s pre-scan, with a scan range about the $K_{\alpha1}$ and $K_{\alpha2}$ positions of $\pm 1.0°$. Of the 3 439 reflections collected in the range $0 \leqslant 2\theta \leqslant 50°$, 2 821 were considered observed $[I/\sigma(I) \geqslant 3.0]$, and used in the refinement. The systematic absences $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) indicated the space group $P2_1/c$, and the assumed value of Z required that the Np atoms were at special positions 1a, of symmetry $\bar{1}$. The remaining atoms, apart from hydrogen, were located on successive Fourier maps. The non-hydrogen atoms were refined with anisotropic temperature factors by least-squares methods. The weighting scheme $w = X \cdot Y$ was applied, where $X = 1.0$ or $(\sin\theta)/0.28$ for $\sin\theta \leqslant 0.28$, and $Y = 1.0$ or $50.0/F_o$ for $F_o \geqslant 50.0$. The final R value was 0.049. The final difference-Fourier map showed no peaks >3 e Å^{-3}, the strongest residuals being close to the Np atom.

TABLE 3

Atomic co-ordinates (× 10⁴), with standard deviations in parentheses for (2)

Atom	x	y	z
U	0	5 000	5 000
P(1)	−3 130(3)	6 370(1)	3 638(3)
O(1)	−2 143(8)	5 761(4)	3 836(9)
O(2)	1 142(9)	5 690(4)	5 112(11)
O(3)	−1 657(9)	5 093(5)	2 058(8)
O(4)	80(10)	4 307(5)	3 052(9)
O(5)	−1 351(13)	4 487(7)	591(12)
N(1)	−978(11)	4 626(6)	1 861(11)
C(1)	−3 300(12)	6 180(6)	6 077(12)
C(2)	−4 059(15)	5 979(8)	6 647(14)
C(3)	−5 611(17)	5 769(7)	5 614(20)
C(4)	−6 433(13)	5 773(8)	3 970(16)
C(5)	−5 653(13)	5 978(6)	3 448(14)
C(6)	−4 118(11)	6 183(5)	4 439(12)
C(7)	−2 013(9)	7 165(5)	4 510(9)
C(8)	−2 378(14)	7 681(6)	5 148(15)
C(9)	−1 524(16)	8 308(6)	5 726(17)
C(10)	−381(15)	8 430(7)	5 595(18)
C(11)	−24(17)	7 918(7)	4 900(19)
C(12)	−843(13)	7 288(6)	4 397(14)
C(13)	−4 560(11)	6 553(5)	1 616(11)
C(14)	−5 437(14)	7 171(7)	1 119(13)
C(15)	−6 584(16)	7 287(8)	−519(16)
C(16)	−6 820(16)	6 793(8)	−1 579(15)
C(17)	−5 964(16)	6 193(8)	−1 112(15)
C(18)	−4 823(13)	6 068(6)	501(13)

For (2), the crystal had dimensions 0.7 × 0.4 × 0.3 mm, with transmission factors between 0.403 and 0.535. The reflections were scanned at rates (2θ) between 1.0 and 29.3° min^{-1}, depending on the intensity of a 2-s pre-scan, and collected through the range $3 \leqslant 2\theta \leqslant 55°$. The scan range was $\pm 1.2°$ about the $K_{\alpha1}$ and $K_{\alpha2}$ positions. Of the 4 463 reflections collected, 2 638 were considered observed $[I/\sigma(I) \geqslant 3.0]$, and used in the refinement.

TABLE 4

Atomic co-ordinates (× 10⁴), with standard deviations in parentheses for (3)

Atom	x	y	z
Np	1 159.2(10)	2 500.0	3 488.2(7)
Cl(1)	2 942(11)	2 865(5)	2 654(9)
Cl(2)	−542(11)	2 058(4)	4 399(8)
P(1)	3 436(9)	848(3)	5 414(6)
P(2)	−1 611(9)	3 797(3)	705(6)
O(2)	2 699(19)	1 535(8)	4 628(17)
O(3)	84(29)	1 984(9)	1 858(21)
O(4)	−368(29)	3 429(10)	2 177(19)
O(5)	2 219(26)	3 019(10)	5 071(17)
C(1)	4 812(38)	454(20)	4 925(25)
C(2)	5 181(51)	1 056(24)	4 314(35)
C(3)	6 172(57)	851(29)	3 948(39)
C(4)	6 572(63)	112(39)	4 152(68)
C(5)	5 990(63)	−432(23)	4 832(42)
C(6)	5 384(66)	−155(47)	5 238(78)
C(7)	4 572(37)	972(12)	7 429(24)
C(8)	6 139(40)	952(18)	8 216(31)
C(9)	6 927(55)	1 132(18)	9 781(31)
C(10)	6 255(35)	1 292(14)	10 455(27)
C(11)	4 727(52)	1 246(16)	9 658(26)
C(12)	3 796(52)	1 125(12)	8 096(42)
C(13)	2 062(41)	178(18)	4 897(27)
C(14)	2 380(47)	−405(14)	5 844(28)
C(15)	1 176(55)	−941(16)	5 259(34)
C(16)	−160(40)	−849(15)	3 940(29)
C(17)	−382(49)	−252(22)	3 005(44)
C(18)	669(36)	251(15)	3 492(35)
C(19)	−1 154(33)	4 706(12)	671(25)
C(20)	−1 747(33)	5 080(13)	−674(23)
C(21)	−1 462(48)	5 797(16)	−636(32)
C(22)	−610(44)	6 146(16)	661(33)
C(23)	−68(46)	5 804(14)	2 022(37)
C(24)	−242(41)	5 080(16)	2 046(30)
C(25)	−1 920(54)	3 343(16)	−968(31)
C(26)	−3 422(46)	3 175(21)	−2 104(33)
C(27)	−3 625(66)	2 850(18)	−3 351(40)
C(28)	−2 429(54)	2 720(10)	−3 496(33)
C(29)	−931(50)	2 922(17)	−2 288(37)
C(30)	—658(56)	3 249(15)	—995(33)
C(31)	—3 135(39)	3 833(39)	714(37)
C(32)	—3 580(59)	3 206(18)	1 181(38)
C(33)	—4 898(74)	3 174(16)	1 114(44)
C(34)	—5 924(64)	3 720(14)	494(50)
C(35)	—5 628(56)	4 338(19)	3(33)
C(36)	—4 377(65)	4 361(16)	11(32)

The structure of (2) was refined starting from the atomic positions of the neptunyl(VI) analogue. All the non-hydrogen atoms were refined with anisotropic temperature factors to give a final R value of 0.028, with the same weighting scheme as for (1). The final difference-Fourier map showed no peaks >1 e Å^{-3}, the strongest peak being associated with ripples around the uranium atom.

For (3), a crystal of dimensions 0.83 × 0.14 × 0.33 mm was selected, with transmission factors in the range 0.651—0.882. The scan rate was varied from 2.0 to 29.3° min^{-1}, depending on the intensity of a 2-s pre-scan. The scan range about the $K_{\alpha1}$ and $K_{\alpha2}$ positions was ±1.2°. Of the 2 373 reflections collected, 2 063 were considered observed $[I/\sigma(I) \geqslant 3.0]$, and used in the refinement.

The systematic absences $0k0$ ($k \neq 2n$) indicated the space groups $P2_1/m$ or $P2_1$ for (3). The latter was chosen as it gave a reasonable site symmetry for Np with two molecules per unit cell. The positions of the neptunium atoms in the unit cell were found from a three-dimensional Patterson map. The remaining atoms, apart from hydrogen, were found through successive electron-density maps. The same weighting scheme was applied, with $X = 1.0$ or $(\sin\theta)/0.31$ for $\sin\theta \leqslant 0.31$ and $Y = 1.0$ or $65.0/F_o$ for $F_o \geqslant 65.0$. The final R value was 0.042. The final difference-Fourier map showed no peaks >3 e Å^{-3}.

Extinction corrections were not applied for any of the structures. The hydrogen atoms were generated in their calculated positions [refined only for (3)] with isotropic temperature factors, $B = 5.0$ Å^2, and included in final calculations. Lorentz, polarisation, and absorption corrections were applied, the last with the program ABSCOR.[6] The scattering factors [7] used were corrected for anomalous dispersion.[8] Computing was carried out with the 'X-RAY '76' system [9] on a Burroughs B6700 computer. Thermal parameters, observed and calculated structure factors, and hydrogen-atom co-ordinates are in Supplementary Publication No. SUP 23172 (65 pp.).*

The atomic co-ordinates for the structures are listed in Tables 2—4. Bond distances and angles are given in Tables 5 and 6. The least-squares planes for the phenyl rings and the equatorial ligand rings around the heavy

TABLE 5

Bond lengths (Å) and bond angles (°) with standard deviations in parentheses for $[MO_2(OPPh_3)_2(NO_3)_2]$ [M = Np (1) or U (2)]

(*a*) Bond lengths

(*i*) Around M	(1)	(2)
M–O(1)	2.633(8)	2.359(7)
M–O(2)	1.739(10)	1.764(9)
M–O(3)	2.525(9)	2.524(7)
M–O(4)	2.526(13)	2.536(11)
(*ii*) Nitrate groups		
N(1)–O(3)	1.270(18)	1.258(17)
N(1)–O(4)	1.258(12)	1.239(11)
N(1)–O(5)	1.195(19)	1.200(18)
(*iii*) Triphenylphosphine oxide groups		
P(1)–O(1)	1.502(9)	1.505(9)
P(1)–C(6)	1.791(17)	1.802(16)
P(1)–C(7)	1.801(10)	1.797(9)
P(1)–C(13)	1.803(10)	1.776(9)
C(6)–C(1)	1.404(18)	1.414(16)
C(1)–C(2)	1.369(29)	1.368(26)
C(2)–C(3)	1.393(19)	1.406(19)
C(3)–C(4)	1.321(22)	1.419(25)
C(4)–C(5)	1.436(27)	1.348(27)
C(5)–C(6)	1.382(15)	1.387(14)
C(7)–C(8)	1.398(21)	1.392(20)
C(8)–C(9)	1.367(18)	1.397(16)
C(9)–C(10)	1.396(30)	1.375(29)
C(10)–C(11)	1.419(26)	1.432(28)
C(11)–C(12)	1.387(19)	1.385(17)
C(12)–C(7)	1.375(25)	1.391(21)
C(13)–C(14)	1.376(17)	1.395(16)
C(14)–C(15)	1.429(17)	1.426(16)
C(15)–C(16)	1.379(25)	1.375(24)
C(16)–C(17)	1.382(22)	1.358(22)
C(17)–C(18)	1.394(16)	1.409(16)

TABLE 5 (*continued*)

(*b*) Bond angles

(*i*) Around M	(1)	(2)
O(1)–M–O(3)	64.7(4)	65.0(3)
O(3)–M–O(4)	49.8(3)	49.5(3)
O(4)–M–O(1)	66.1(3)	66.0(3)
O(2)–M–O(2)	180.0	180.0
O(2)–M–O(1)	91.4(4), 88.9(4)	91.4(3), 88.6(3)
O(2)–M–O(3)	94.2(4), 85.8(4)	92.1(4), 87.9(4)
O(2)–M–O(4)	91.9(5), 88.1(5)	92.6(5), 87.4(5)
(*ii*) Nitrate groups		
O(3)–N(1)–O(4)	114.4(13)	116.0(12)
O(4)–N(1)–O(5)	123.1(14)	121.8(13)
O(3)–N(1)–O(5)	122.3(10)	122.2(10)
(*iii*) Triphenylphosphine oxide groups		
O(1)–P(1)–C(6)	112.9(5)	112.5(5)
O(1)–P(1)–C(7)	111.0(5)	111.2(4)
O(1)–P(1)–C(13)	109.2(6)	109.7(5)
C(6)–P(1)–C(7)	110.4(6)	109.4(5)
C(7)–P(1)–C(13)	106.1(5)	106.6(4)
C(6)–P(1)–C(13)	107.0(6)	107.2(5)
C(6)–C(1)–C(2)	118.2(11)	118.5(10)
C(1)–C(2)–C(3)	120.2(15)	120.2(14)
C(2)–C(3)–C(4)	122.7(21)	121.2(20)
C(3)–C(4)–C(5)	119.1(13)	117.0(12)
C(4)–C(5)–C(6)	118.3(12)	123.0(13)
C(5)–C(6)–C(1)	121.4(15)	120.0(14)
C(12)–C(7)–C(8)	120.0(11)	119.8(10)
C(7)–C(8)–C(9)	119.4(17)	119.7(16)
C(8)–C(9)–C(10)	121.2(17)	120.1(16)
C(9)–C(10)–C(11)	119.9(13)	121.0(13)
C(10)–C(11)–C(12)	117.5(18)	117.7(19)
C(11)–C(12)–C(7)	122.1(15)	121.6(15)
C(18)–C(13)–C(14)	121.0(10)	119.3(9)
C(13)–C(14)–C(15)	119.0(14)	118.7(13)
C(14)–C(15)–C(16)	119.4(13)	120.3(13)
C(15)–C(16)–C(17)	121.1(12)	121.7(11)
C(16)–C(17)–C(18)	119.8(15)	119.0(15)
C(17)–C(18)–C(13)	119.6(12)	121.0(12)
M–O(1)–P(1)	159.1(4)	160.0(4)

TABLE 6

Bond lengths (Å) and bond angles (°) with standard deviations in parentheses for $[NpO_2(OPPh_3)_2Cl_2]$ (3)

(*a*) Bond lengths

(*i*) Around neptunium

Np–Cl(1)	2.622(14)	Np–O(3)	1.751(18)
Np–Cl(2)	2.645(13)	Np–O(4)	2.261(19)
Np–O(2)	2.288(15)	Np–O(5)	1.721(16)

(*ii*) Triphenylphosphine oxide groups

Group 1		Group 2	
P(1)–O(2)	1.50(1)	P(2)–O(4)	1.55(2)
P(1)–C(1)	1.97(4)	P(2)–C(19)	1.78(2)
P(1)–C(7)	1.81(2)	P(2)–C(25)	1.84(4)
P(1)–C(13)	1.77(4)	P(2)–C(31)	1.64(5)
C(1)–C(2)	1.47(6)	C(19)–C(20)	1.40(3)
C(2)–C(3)	1.38(9)	C(20)–C(21)	1.37(4)
C(3)–C(4)	1.43(9)	C(21)–C(22)	1.33(4)
C(4)–C(5)	1.57(10)	C(22)–C(23)	1.39(5)
C(5)–C(6)	1.10(12)	C(23)–C(24)	1.37(4)
C(6)–C(1)	1.25(9)	C(24)–C(19)	1.42(3)
C(7)–C(8)	1.40(5)	C(25)–C(26)	1.41(5)
C(8)–C(9)	1.43(4)	C(26)–C(27)	1.37(6)
C(9)–C(10)	1.30(7)	C(27)–C(28)	1.40(10)
C(10)–C(11)	1.37(6)	C(28)–C(29)	1.44(5)
C(11)–C(12)	1.41(4)	C(29)–C(30)	1.39(6)
C(12)–C(7)	1.40(7)	C(30)–C(25)	1.39(9)
C(13)–C(14)	1.40(4)	C(31)–C(32)	1.46(6)
C(14)–C(15)	1.47(6)	C(32)–C(33)	1.38(11)
C(15)–C(16)	1.35(4)	C(33)–C(34)	1.37(6)
C(16)–C(17)	1.43(5)	C(34)–C(35)	1.38(6)
C(17)–C(18)	1.33(5)	C(25)–C(36)	1.34(10)
C(18)–C(13)	1.42(3)	C(36)–C(31)	1.48(6)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 6 (*continued*)

(*b*) Bond angles

(*i*) Around neptunium

Cl(1)–Np–Cl(2)	176.4(3)	Cl(2)–Np–O(5)	91.4(10)
Cl(1)–Np–O(2)	86.5(6)	O(2)–Np–O(3)	88.5(7)
Cl(1)–Np–O(3)	90.1(11)	O(2)–Np–O(4)	174.9(8)
Cl(1)–Np–O(4)	90.1(9)	O(2)–Np–O(5)	92.1(7)
Cl(1)–Np–O(5)	89.0(10)	O(3)–Np–O(4)	87.7(8)
Cl(2)–Np–O(2)	89.9(6)	O(3)–Np–O(5)	178.9(11)
Cl(2)–Np–O(3)	89.5(11)	O(4)–Np–O(5)	91.7(8)
Cl(2)–Np–O(4)	93.4(9)		

(*ii*) Triphenylphosphine oxide

Group 1		Group 2	
O(2)–P(1)–C(1)	114(1)	O(4)–P(2)–C(19)	111(1)
O(2)–P(1)–C(7)	111(1)	O(4)–P(2)–C(25)	112(1)
O(2)–P(1)–C(13)	110(1)	O(4)–P(2)–C(31)	108(2)
C(1)–P(1)–C(7)	105(1)	C(19)–P(2)–C(25)	109(2)
C(1)–P(1)–C(13)	106(2)	C(19)–P(2)–C(31)	105(2)
C(7)–P(1)–C(13)	111(1)	C(25)–P(2)–C(31)	113(2)
C(1)–C(2)–C(3)	111(4)	C(19)–C(20)–C(21)	120(2)
C(2)–C(3)–C(4)	116(6)	C(20)–C(21)–C(22)	121(3)
C(3)–C(4)–C(5)	122(7)	C(21)–C(22)–C(23)	121(3)
C(4)–C(5)–C(6)	111(6)	C(22)–C(23)–C(24)	120(3)
C(5)–C(6)–C(1)	130(9)	C(23)–C(24)–C(19)	120(3)
C(6)–C(1)–C(2)	127(6)	C(24)–C(19)–C(20)	119(2)
P(1)–C(1)–C(2)	105(3)	P(2)–C(19)–C(20)	122(2)
P(1)–C(1)–C(6)	127(5)	P(2)–C(19)–C(24)	119(2)
C(7)–C(8)–C(9)	115(4)	C(25)–C(26)–C(27)	115(5)
C(8)–C(9)–C(10)	123(4)	C(26)–C(27)–C(28)	122(4)
C(9)–C(10)–C(11)	119(3)	C(27)–C(28)–C(29)	119(4)
C(10)–C(11)–C(12)	124(5)	C(28)–C(29)–C(30)	121(5)
C(11)–C(12)–C(7)	114(4)	C(29)–C(30)–C(25)	115(4)
C(12)–C(7)–C(8)	124(3)	C(30)–C(25)–C(26)	128(4)
P(1)–C(7)–C(8)	120(3)	P(2)–C(25)–C(26)	116(4)
P(1)–C(7)–C(12)	116(2)	P(2)–C(25)–C(30)	116(2)
C(13)–C(14)–C(15)	115(2)	C(21)–C(32)–C(33)	123(3)
C(14)–C(15)–C(16)	122(3)	C(32)–C(33)–C(34)	121(5)
C(15)–C(16)–C(17)	120(3)	C(33)–C(34)–C(35)	121(6)
C(16)–C(17)–C(18)	120(3)	C(34)–C(35)–C(36)	118(4)
C(17)–C(18)–C(13)	121(3)	C(35)–C(36)–C(31)	127(4)
C(18)–C(13)–C(14)	122(3)	C(36)–C(31)–C(32)	110(4)
P(1)–C(13)–C(14)	120(2)	P(2)–C(31)–C(32)	119(3)
P(1)–C(13)–C(18)	118(2)	P(2)–C(31)–C(36)	130(4)
Np–O(2)–P(1)	167(1)	Np–O(4)–P(2)	153(1)

TABLE 7

Deviations (Å) from mean planes for $[MO_2(OPPh_3)_2(NO_3)_2]$ [M = Np (1) or U (2)] *

Plane 1

	Deviation	
Atom	(1)	(2)
M	0.000	0.000
O(1)	±0.010	±0.083
O(3)	±0.112	±0.094
O(4)	±0.110	±0.092

Plane 2

	Deviation	
Atom	(1)	(2)
C(1)	0.014	−0.004
C(2)	0.001	0.006
C(3)	−0.017	−0.005
C(4)	0.017	0.001
C(5)	−0.001	0.000
C(6)	0.013	0.001

Plane 3

	Deviation	
Atom	(1)	(2)
C(7)	0.006	−0.007
C(8)	−0.001	0.019
C(9)	−0.004	−0.014
C(10)	0.004	−0.003
C(11)	0.001	0.015
C(12)	−0.006	−0.010

Plane 4

	Deviation	
Atom	(1)	(2)
C(13)	0.008	−0.004
C(14)	−0.019	0.001
C(15)	0.019	0.004
C(16)	−0.007	−0.007
C(17)	−0.004	0.003
C(18)	0.004	0.002

* All atoms are used in the calculation of the mean planes.

TABLE 8

Deviations (Å) from mean planes for $[NpO_2(OPPh_3)_2Cl_2]$ *

Plane 1

Atom	Deviation
Np	0.035
O(2)	−0.043
O(4)	−0.041
Cl(1)	0.026
Cl(2)	0.024

Plane 2

Atom	Deviation
C(1)	−0.046
C(2)	−0.017
C(3)	0.039
C(4)	−0.013
C(5)	−0.053
C(6)	0.090

Plane 3

Atom	Deviation
C(7)	0.015
C(8)	−0.024
C(9)	0.001
C(10)	0.034
C(11)	−0.045
C(12)	0.019

Plane 4

Atom	Deviation
C(13)	0.003
C(14)	0.003
C(15)	−0.020
C(16)	0.030
C(17)	−0.024
C(18)	0.008

Plane 5

Atom	Deviation
C(19)	−0.006
C(20)	−0.009
C(21)	−0.002
C(22)	0.028
C(23)	−0.044
C(24)	0.033

Plane 6

Atom	Deviation
C(25)	−0.014
C(26)	0.012
C(27)	−0.005
C(28)	0.000
C(29)	−0.001
C(30)	0.008

Plane 7

Atom	Deviation
C(31)	0.037
C(32)	−0.019
C(33)	0.006
C(34)	−0.010
C(35)	0.032
C(36)	−0.046

* All atoms are used in the calculation of the mean planes.

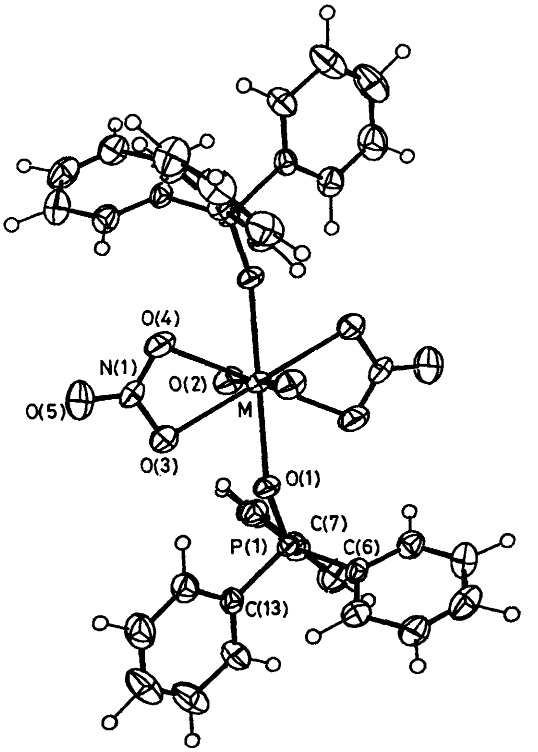

FIGURE 1 The $[MO_2(OPPh_3)_2(NO_3)_2]$ (M = U or Np) molecule, showing atomic numbering for the central atoms

atoms are given in Tables 7 and 8. The numbering schemes for $[MO_2(OPPh_3)_2(NO_3)_2]$ and $[NpO_2(OPPh_3)_2Cl_2]$ are shown in Figures 1 and 2 respectively.

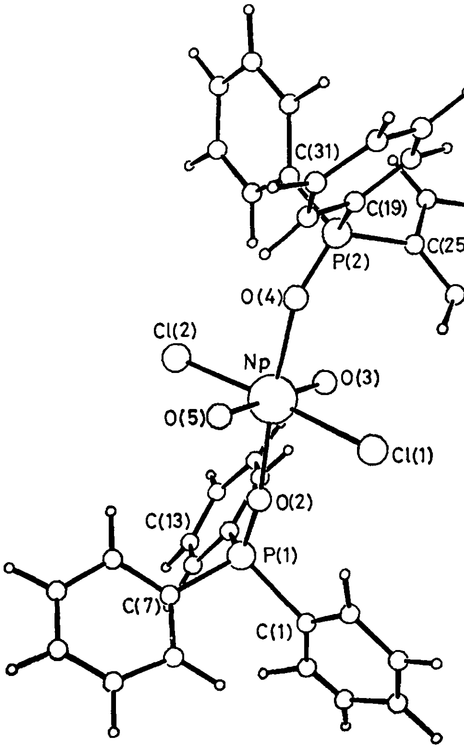

FIGURE 2 The $[NpO_2(OPPh_3)_2Cl_2]$ molecule, showing atomic numbering for the central atoms

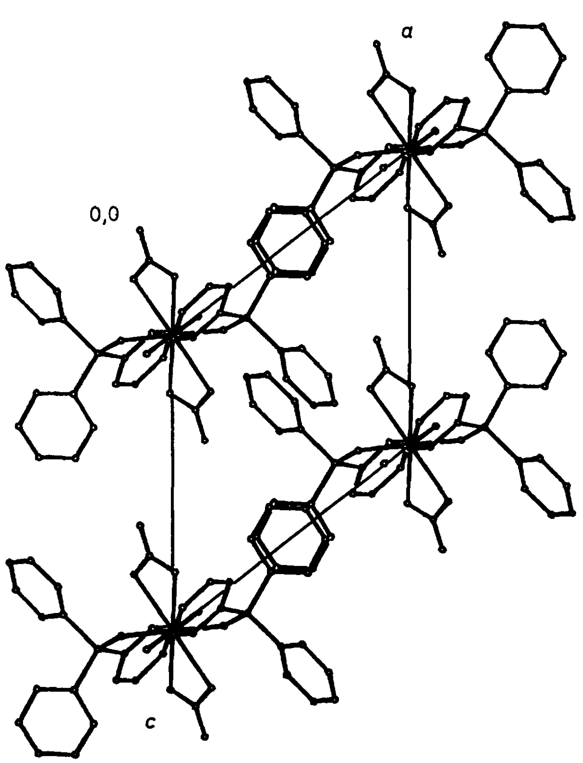

FIGURE 3 The packing of $[MO_2(OPPh_3)_2(NO_3)_2]$, viewed down the *b* axis

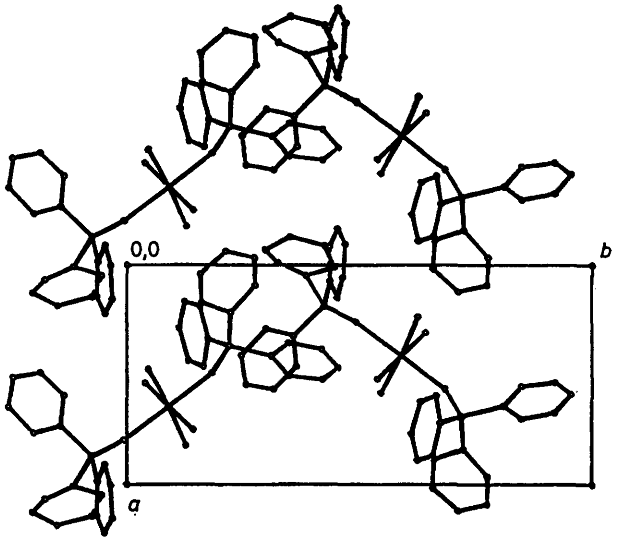

FIGURE 4 The packing of $[NpO_2(OPPh_3)_2Cl_2]$, viewed down the *c* axis

DISCUSSION

The complex $[NpO_2(OPPh_3)_2(NO_3)_2]$ (1) and the uranyl(VI) analogue, (2), are isostructural and isomorphous. Their co-ordination is shown in Figure 1, and the packing arrangement is illustrated in Figure 3. In each, the central metal atom is co-ordinated to eight oxygen atoms, at the vertices of a distorted hexagonal bipyramid.

Both chloride complexes are six-co-ordinate (Figure 2), with the $OPPh_3$ molecules *trans* to each other but, in contrast to the nitrate complexes, they crystallise in different space groups and exhibit some differences in phenyl-ring orientation. Views of the structure of $[NpO_2(OPPh_3)_2Cl_2]$ down the *c* and *b* axes are shown in Figures 4 and 5 respectively.

A detailed comparison between the U and Np environments shows small but consistent differences (Table 9). In the NpO_2^{2+} groups in (1) and (3) the separations of the oxygen atoms are almost exactly the same, although the Np–O bond lengths in (3) are different and lie either side of the value for (1). The U–O (UO_2^{2+}) bonds are longer than the Np–O (NpO_2^{2+}) bonds by 0.025 and 0.028 Å in the nitrate and the chloride complexes. The triphenylphosphine oxide ligands bond through oxygen to the metal at greater distances in (1) and (2) than in (3) and (4). This may be due to the increased crowding about the co-ordination sphere as the bidentate nitrate is substituted for chloride. When the M–O ($OPPh_3$) bond lengths of the uranyl(VI) complexes are compared with those of the neptunyl(VI) complexes, it is seen that they are very close in (1) and (2), but the $[MO_2(OPPh_3)_2Cl_2]$ structures show a greater difference. Again, the M–O (NO_3) bonds in (2) are only slightly longer than in (1) while the U–Cl bond lengths in (4) are longer than the mean for the Np–Cl bond lengths in (3).

A recent study [10] of the MO_2^{2+} systems indicates that the linear UO_2^{2+} cation contains a set of bonding mole-

TABLE 9

Comparative bond lengths (Å)

Compound	M–O ($OPPh_3$)	M–O (MO_2^{2+})	M–Cl	M–O (NO_3)
(1)[a] $[NpO_2(OPPh_3)_2(NO_3)_2]$	2.363(8)	1.739(10)		2.525(9) 2.526(13)
(2)[a] $[UO_2(OPPh_3)_2(NO_3)_2]$	2.359(7)	1.764(9)		2.524(7) 2.536(11)
(3)[a] $[NpO_2(OPPh_3)_2Cl_2]$	2.288(15) 2.261(19)	1.751(18) 1.721(16)	2.622(14) 2.645(13)	
(4)[b] $[UO_2(OPPh_3)_2Cl_2]$	2.300(8)	1.764(9)	2.645(5)	

[a] This paper. [b] Ref. 1.

cular orbitals formed through the combination of the 6*d* and 5*f* orbitals of uranium and the 2*p* orbitals of the oxygen atoms. The 12 valence electrons fill these completely to give two triple U–O bonds. The single 5*f* electron of NpO_2^{2+} occupies a non-bonding molecular orbital.[10] It should therefore affect neither the geometry nor the bond lengths of the MO_2^{2+} group. This suggests that the small consistent contraction from UO_2^{2+} to NpO_2^{2+} is due to a generalised ' actinide contraction ', and not to specific bonding effects. Its size is close to the differences between adjacent lanthanide and actinide 3+ ions at the beginning of each series, although these differences clearly cannot be compared directly to those for the 6+ oxidation state.

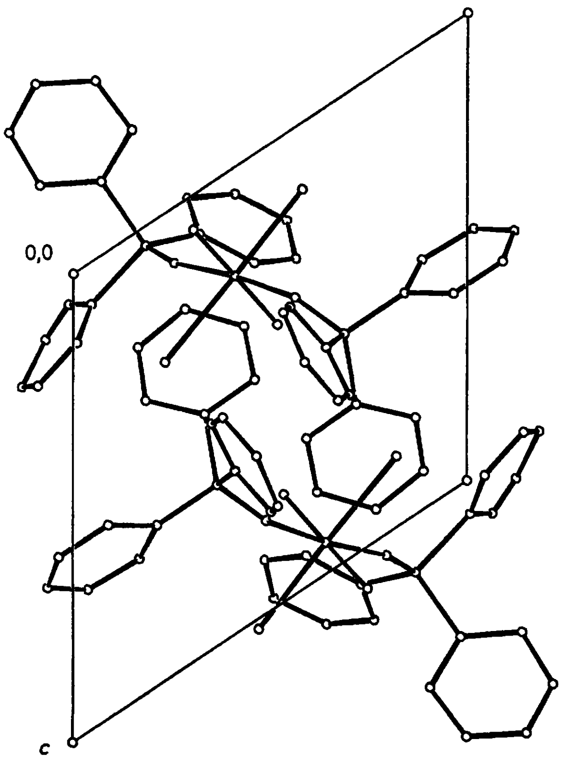

FIGURE 5 The packing of $[NpO_2(OPPh_3)_2Cl_2]$, viewed down the *b* axis

In the equatorial plane the shrinkage is essentially zero for (1) compared to (2). Between (3) and (4) it is 0.026 Å for M–O, and 0.011 Å for M–Cl (based on averaged distances). It is possible that the additional 5*f* electron in Np^{VI} has some antibonding character in the equatorial plane, but an alternative hypothesis is that the ' actinide contraction ' can be seen in (3) and (4), but that the six equatorial ligands in (1) and (2) have sufficient non-bonding ligand–ligand repulsion to prevent them moving in towards the Np atom. Evidence from the further structural studies now in progress should clarify this. Although the different space groups of (3) and (4) seem to have no effect on the immediate co-ordination spheres of the metal atom, they do produce different orientations of the phenyl rings, seen in the ring–ring dihedral angles (Table 10). It appears that favourable values of the angles lie near 90°, and one ligand in (3) achieves better values than those in (4) although the other is rather worse. Thus, there is likely to be little overall energy difference between the two forms. The unexpected difference in packing might arise from the size effect imposed by the radius of the metal atom, due to the actinide contraction.[11] This is responsible, for example, for the difference in the crystal systems of the tribromides of neptunium and plutonium.[12] Alternatively, the different methods used for recrystallisation of (3) and (4) could be responsible. In view of the smallness of the size change, and the absence of any change in the primary co-ordination sphere, it seems that dimorphism is more likely.

TABLE 10

Comparative interplane angles (°) of the phenyl rings in the triphenylphosphine oxide groups

Compound					
		(3)[a]			
		Group 1	Group 2		
(1)[a]	(2)[a]	[C(1)—C(18)]	[C(19)—C(36)]	(4)[b]	PPh_3O[c]
62.2	61.7	72.6	82.1	76.5	75.4
80.0	80.5	74.9	86.0	82.9	82.4
85.8	84.0	85.6	89.2	89.3	83.9

[a] This paper. [b] Ref. 1. [c] G. Bandoli, G. Bortolozzo, D. A. Clemente, U. Croatto, and C. Panattoni, *J. Chem. Soc. A*, 1970, 2778.

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