Structure and Bonding in Octahedral Uranium(IV) Complexes of the Type UX_4·2L (X = Halogen, L = Unidentate, Neutral Oxygen Donor). Part 2.[1] The Crystal Structures of Tetrachlorobis[tris(pyrrolidinyl)phosphine oxide]-, Tetrachlorobis(di-isobutyl sulphoxide)-, and Tetrabromobis(triphenylarsine oxide)-uranium(IV)†

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The crystal structures of three complexes of uranium(IV) halides, UCl_4·2tprpo (**1**), UCl_4·2dibso (**2**), and UBr_4·2tpao (**3**) [tprpo = tris(pyrrolidinyl)phosphine oxide, dibso = di-isobutyl sulphoxide, and tpao = triphenylarsine oxide], have been determined from three-dimensional *X*-ray diffraction data, and refined by full-matrix least-squares methods. For (**1**) the crystals are monoclinic, space group $C2/c$ (final R = 0.046), for (**2**) monoclinic, space group $P2_1/c$ (final R = 0.047), and for (**3**) monoclinic, space group $P2_1$ (final R = 0.080). In each complex the uranium co-ordination is octahedral, with slight displacements (0.1 Å) of the bromine atoms in (**3**) from their mean plane. The molecules in (**1**) and (**2**) have inversion symmetry. Compound (**3**) is isomorphous with the triphenylphosphine oxide analogue, UBr_4·2tppo; the molecule is devoid of symmetry and adopts the same conformation as in the isomorph. The U–Cl distances are 2.620(4) Å in (**1**) and 2.605(3) Å in (**2**), while U–Br is 2.803(7) Å in (**3**); U–O is 2.233(7) Å in (**1**), 2.248(7) Å in (**2**), and 2.12(3) Å in (**3**). The U–X (X = halogen) and U–O bond lengths obtained in this work and in Part 1 of this series are compared with other estimates of these bonds in similar complexes. It is found (*i*) that the inverse relationship between the bond-length changes δ(U–X) and δ(U–O) previously noted for complexes containing the UO_2X_4 chromophore ('axial–equatorial effect') is maintained in the complexes studied here, thereby providing further evidence for the ligand–ligand repulsion effects which dominate the (largely ionic) bonding in such complexes, and (*ii*) that the data, when grouped according to generic ligand type, lend support for the donor-strength sequence As=O > P=O > S=O > C=O based on chemical evidence.

The aim and scope of this investigation are given in Part 1 of this series.

Experimental

Samples of crystalline material were kindly provided by Professor Jan du Preez, Uranium Research Institute, University of Port Elizabeth. The methods of preparation have been published elsewhere: UCl_4·2dibso,[2] UBr_4·2tpao[3]; that of UCl_4·2tprpo was the same as for UCl_4·2tdpo[4]; dibso = di-isobutyl sulphoxide, tpao = triphenylarsine oxide, tprpo = tris(pyrrolidinyl)phosphine oxide, and tdpo = tris(dimethylamido)phosphine oxide.

Crystallography.—General procedural details are given in ref. 1.

Crystal data. $C_{24}H_{48}Cl_4N_6O_2P_2U$, M = 894.5, monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), a = 17.026(8), b = 11.713(5), c = 18.209(9) Å, β = 109.20(2)°, U = 3 429(5) Å^3, D_m = 1.74, Z = 4, D_c = 1.73 g cm^{-3}, $F(000)$ = 1 759.9, μ = 49.2 cm^{-1}, crystal radius = 0.07(1) mm, μr = 0.34.

$C_{16}H_{36}Cl_4O_2S_2U$, M = 704.4, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 10.101(5), b = 10.426(5), c = 13.292(6) Å, β = 106.36(2)°, U = 1 343 Å^3, D_m = 1.74, Z = 2, D_c = 1.74 g cm^{-3}, $F(000)$ = 679.9, μ = 63.0 cm^{-1}, crystal radius = 0.10(1) mm, μr = 0.63.

$C_{36}H_{30}As_2Br_4O_2U$, M = 1 202.1, monoclinic, space group $P2_1$ (C^2_2, no. 4), a = 10.243(5), b = 15.970(8), c = 12.186(6) Å, β = 100.94(2)°, U = 1 935 Å^3, D_m = 2.21, Z = 2, D_c = 2.18 g cm^{-3}, $F(000)$ = 1 119.9, μ = 127 cm^{-1}, prismatic crystal 0.075(5) × 0.10(5) × 0.10(5) mm.

Special features. UCl_4·2tprpo. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final refinement 11 structure factors suspected of systematic errors were omitted. Final residuals were: R = 0.046, R' = 0.036 (with 10^4g = 5.17), for N_r = 1 707 (N = 2 306).

UCl_4·2dibso. All non-hydrogen atoms were refined with anisotropic thermal parameters. Final residuals were: R = 0.047, R' = 0.040 (with 10^4g = 2.23), for N_r = 1 838 (N = 2 830).

UBr_4·2tpao. Attempts to grind spherical crystals for data collection resulted in the formation of tarry decomposition products on the surface, and a small prismatic specimen was therefore used; absorption corrections were not applied. Because of severe distortion during refinement, the phenyl rings were constrained throughout as rigid bodies with artificially calculated hydrogen co-ordinates; some of the (isotropic) carbon thermal parameters also had to be tied together. Only the heavier atoms (U, Br, As) were refined with anisotropic thermal parameters. Final values of the residuals were: R = 0.080, R' = 0.069 (with 10^4g = 8.01), for N_r = 1 864 (N = 2 761). A few difference peaks of about 2 e Å^{-3} in the vicinity of the uranium atom revealed the presence of small residual errors due to absorption (ref. 5).

Results and Discussion

Tetrachlorobis[tris(pyrrolidinyl)phosphine oxide]uranium(IV).—The atomic co-ordinates of the asymmetric unit are

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

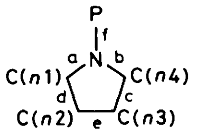
Table 1. Atomic co-ordinates (× 10^4) of non-hydrogen atoms in $UCl_4{\cdot}2tprpo$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U	2 500(−)	2 500(−)	5 000(−)	N(2)	3 106(4)	−900(6)	6 133(4)
Cl(1)	1 093(2)	2 814(3)	5 264(2)	C(21)	3 047(8)	−2 073(9)	6 412(8)
Cl(2)	1 818(2)	862(3)	4 015(2)	C(22)	3 749(12)	−2 688(2)	6 298(13)
O	2 863(3)	1 225(4)	5 965(3)	C(23)	4 020(10)	−2 072(10)	5 736(10)
P	2 840(2)	237(2)	6 495(1)	C(24)	3 723(9)	−859(9)	5 724(9)
N(1)	1 934(4)	−55(6)	6 556(4)	N(3)	3 449(4)	582(6)	7 345(4)
C(11)	1 589(8)	641(10)	7 072(6)	C(31)	3 791(8)	1 733(10)	7 577(6)
C(12)	708(8)	166(14)	6 858(9)	C(32)	4 418(9)	1 542(12)	8 383(8)
C(13)	463(8)	−75(13)	6 018(8)	C(33)	4 064(10)	597(14)	8 721(6)
C(14)	1 248(5)	−516(11)	5 900(6)	C(34)	3 696(9)	−183(11)	8 035(6)

Table 2. Distances (Å) and angles (°), with standard deviations in parentheses, for $UCl_4{\cdot}2tprpo$

Uranium environment			
U-Cl(1)	2.620(4)	O-U-Cl(1)	89.0(2)
U-Cl(2)	2.621(4)	O-U-Cl(2)	89.7(2)
U-O	2.233(7)	Cl(1)-U-Cl(2)	90.2(1)
U-O-P	162.5(5)		
Phosphorus environment			
P-O	1.515(7)	O-P-N(2)	107.5(4)
P-N(1)	1.617(9)	O-P-N(3)	106.2(4)
P-N(2)	1.616(8)	N(1)-P-N(2)	104.7(5)
P-N(3)	1.606(8)	N(2)-P-N(3)	114.9(5)
O-P-N(1)	115.5(4)	N(1)-P-N(3)	108.4(5)

Table 3. Ring geometries in $UCl_4{\cdot}tprpo$; distances (Å) with σ in parentheses; bond angles (°) have σ = 0.8—1.5°; means, *m*, given as *m* ± *d*(σ), where *d* is the mean deviation from *m*; data in square brackets from uranyl complex (see text)



	a	b	c	d	e
Ring (1)	1.503(17)	1.472(13)	1.511(19)	1.475(21)	1.525(19)
Ring (2)	1.480(14)	1.475(21)	1.506(17)	1.448(30)	1.468(26)
Ring (3)	1.474(14)	1.488(15)	1.509(18)	1.486(22)	1.520(17)

N-C	1.482 ± 0.009(15)	[1.475 ± 0.006(12)]
C-C	1.494 ± 0.022(22)	[1.483 ± 0.020(19)]

	a—b	b—c	a—d	c—e	d—e	a—f	b—f
Ring (1)	109.6	101.4	105.2	104.6	104.7	120.4	122.9
Ring (2)	110.1	104.9	104.7	109.4	108.6	124.5	121.4
Ring (3)	109.6	111.0	105.0	102.9	105.0	125.1	125.2

C-N-C	109.8 ± 0.23(1.0)	[110.5 ± 1.0(1.0)]
N-C-C	104.1 ± 1.2(1.0)	[104.3 ± 0.2(1.0)]
C-C-C	105.5 ± 1.6(1.0)	[106.8 ± 1.8(1.0)]
P-N-C	123.3 ± 1.7(0.8)	[122.1 ± 0.9(0.7)]

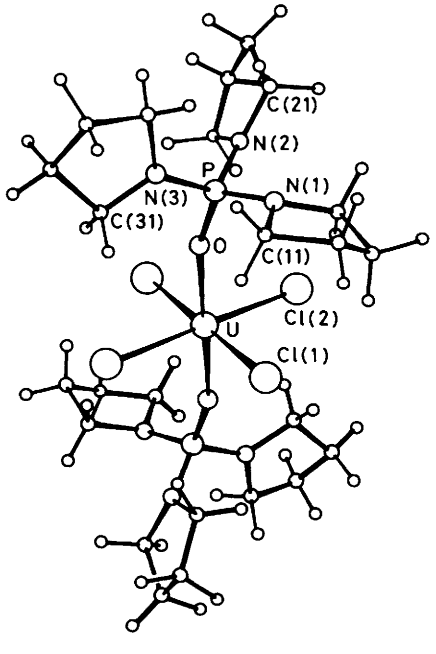


Figure 1. Perspective view of the $UCl_4{\cdot}2tprpo$ molecule, showing the atomic numbering scheme of the asymmetric unit

given in Table 1, and bond lengths and angles in Tables 2 and 3. The molecular structure and atom numbering are illustrated in Figure 1.

The molecule possesses inversion symmetry and the co-ordination of the uranium environment is octahedral, with no close non-bonded contacts to disturb the planarity of the UCl_4 moiety. The P–O and P–N bond lengths are similar to those [1.50(1), 1.62(1) Å, respectively] found for oxide tdpo in, *e.g.*, $UCl_4{\cdot}2tdpo$.[6] Since no structural data on the tprpo ligand are available in the literature, its geometry is presented in some detail, and compared with data obtained by us[7] on a uranyl complex containing the same ligand, $[UO_2(NO_3)_2(tprpo)_2]$ (Table 3). It is interesting that, despite differences in the co-ordination environment and uranium valence state, the main structural features of the ligand are very similar in both complexes. The pyrrolidinyl rings display similar puckering, with deviations of the ring atoms from their mean planes ranging from 0.1 to 0.3 Å. The nitrogen atoms adopt a flattened pyramidal configuration, except in ring 3, where N(3) is coplanar with its bonded neighbours (Table 4). The variability in torsion angles reveals that the ring conformations are somewhat flexible in the free molecule; this was also noted for the uranyl complex.

Tetrachlorobis(di-isobutyl sulphoxide)uranium(IV).—The atomic co-ordinates in the asymmetric unit are listed in Table 5, and bond lengths and angles in Table 6. The molecular structure and atom numbering are illustrated in Figure 2.

The molecule of this complex also possesses inversion symmetry about the uranium atom. The geometry of the isobutyl substituents is unremarkable, with normal bond lengths and angles. The short non-bonded contacts between the sulphur atom and the methylene hydrogen atoms (Table 7), whose co-ordinates are approximately fixed by the conform-

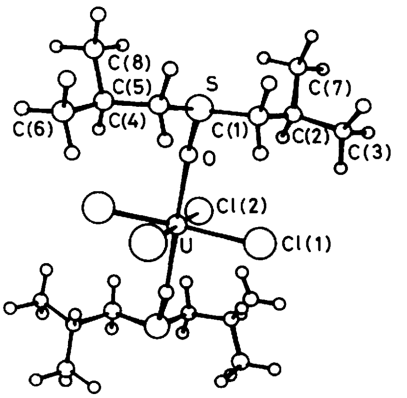


Figure 2. Perspective view of the UCl_4·2dibso molecule, showing the atomic numbering scheme in the asymmetric unit

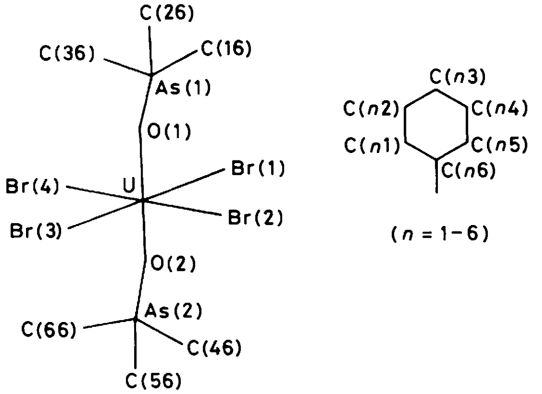


Figure 3. Atomic numbering scheme used for UBr_4·2tpao

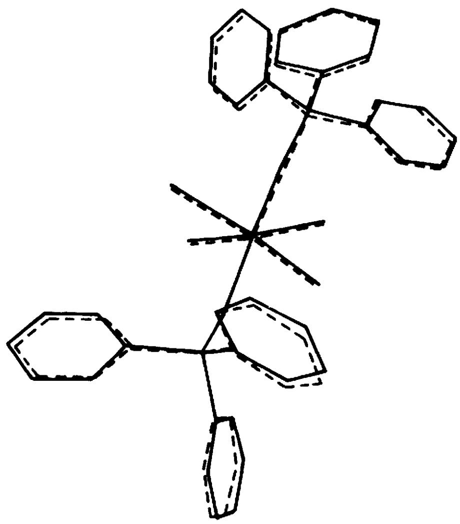


Figure 4. Schematic comparison of the conformations of UBr_4·2tpao (solid lines) and UBr_4·2tppo[8] (dashed lines)

Table 4. Coplanarity of the pyrrolidinyl nitrogen atoms and their bonded partners in UCl_4·2tprpo. Deviations from least-squares mean planes are given in Å; ⟨σ⟩ is the mean e.s.d. of the planar deviations in each case

Ring					⟨σ⟩
(1)	P 0.060,	N(1) −0.177,	C(11) 0.057,	C(14) 0.061	0.021
(2)	P 0.045,	N(2) −0.134,	C(21) 0.049,	C(24) 0.043	0.023
(3)	P −0.011,	N(3) 0.030,	C(31) −0.010,	C(34) −0.010	0.020

Table 5. Atomic co-ordinates (× 10^4) of non-hydrogen atoms in UCl_4·2dibso

Atom	x	y	z
U	0(−)	0(−)	0(−)
S	843(3)	160(3)	−2 540(2)
Cl(1)	2 243(3)	1 335(3)	779(2)
Cl(2)	1 299(3)	2 099(3)	736(2)
O	551(6)	−264(6)	−1 512(4)
C(1)	2 204(11)	1 278(12)	−2 148(9)
C(2)	3 600(11)	642(13)	−1 659(9)
C(3)	4 629(15)	1 677(17)	−1 163(13)
C(4)	−539(10)	1 194(12)	−3 148(8)
C(5)	−1 924(12)	480(12)	−3 521(9)
C(6)	−3 057(13)	1 496(18)	−3 794(13)
C(7)	4 082(14)	−109(18)	−2 479(13)
C(8)	−1 939(17)	−381(14)	−4 477(12)

Table 6. Distances (Å) and angles (°), with standard deviations in parentheses, for UCl_4·2dibso

Uranium environment			
U–Cl(1)	2.612(3)	O–U–Cl(1)	90.8(2)
U–Cl(2)	2.598(3)	O–U–Cl(2)	90.4(2)
U–O	2.248(7)	Cl(1)–U–Cl(2)	90.6(1)
U–O–S	156.1(5)		
Di-isobutyl sulphoxide			
S–O	1.542(8)	C(1)–C(2)–C(3)	108(1)
S–C(1)	1.766(12)	C(1)–C(2)–C(7)	111(1)
S–C(4)	1.769(11)	C(3)–C(2)–C(7)	111(1)
C(1)–C(2)	1.53(2)	C(4)–C(5)–C(6)	107(1)
C(2)–C(3)	1.51(2)	C(4)–C(5)–C(8)	110(1)
C(2)–C(7)	1.53(2)	C(6)–C(5)–C(8)	112(1)
C(4)–C(5)	1.54(2)	S–C(1)–C(2)	112.8(9)
C(5)–C(6)	1.53(2)	S–C(4)–C(5)	112.4(8)
C(5)–C(8)	1.55(2)		

Table 7. Short non-bonded contacts (Å) in UCl_4·2dibso (σ = 0.01 Å)

S···C(2)	2.75	S···H(11)	2.35
S···C(5)	2.75	S···H(12)	2.35
O···C(1)	2.62	S···H(41)	2.35
O···C(4)	2.63	S···H(42)	2.35
C(1)···C(4)	2.72		

ation of the carbon chain, reveal a crowded arrangement in which the hydrogen atoms straddle the sulphur atom. Further evidence of rigidity is provided by the close contacts between the sulphur atom and its next-nearest carbon neighbours. Together with the symmetry in torsion angles on both sides of the sulphur atom [S–C(1)–C(2)–C(3) and S–C(4)–C(5)–C(6) are −169(1) and 167(1)°, respectively, while S–C(1)–C(2)–C(4) and S–C(1)–C(2)–C(8) are 69(1) and −70(1)°] this suggests the possibility of mirror symmetry. However, closer investigation revealed that such symmetry is only approximate. (It is not possible for the molecule as a whole, since the plane containing the S–O–U–O–S chain neither bisects the angle between, nor does it coincide with, two U–Cl bond vectors.) The C_2S=O group is pyramidal, as expected; no meaningful comparisons are available, since the data on uranium-co-ordinated S=O ligands

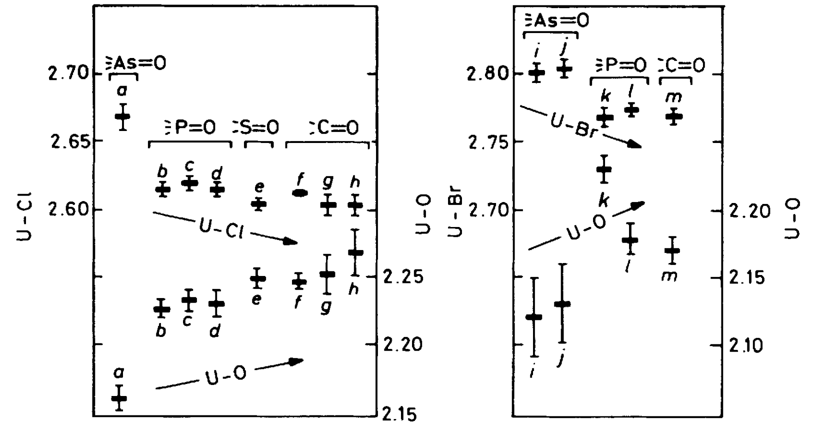


Figure 5. Bond-length trends (Å) as function of the generic type of oxygen-donor ligand, L, in UX_4·2L (X = Cl or Br) complexes; alphabetic symbols refer to Table 11

Table 8. Atomic co-ordinates (× 10^4) of non-hydrogen atoms in UBr_4·2tpao

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U	2 626(2)	0(–)	2 567(2)	C(33)	2 240(29)	3 755(22)	4 275(26)
Br(1)	4 232(5)	–1 442(3)	2 687(5)	C(34)	1 965(29)	3 220(22)	5 115(26)
Br(2)	4 425(5)	885(3)	1 484(4)	C(35)	2 708(29)	2 484(22)	5 384(26)
Br(3)	948(5)	1 404(3)	2 304(5)	C(36)	3 724(29)	2 281(22)	4 813(26)
Br(4)	1 002(5)	–839(3)	3 821(5)	C(41)	–1 758(30)	–599(18)	947(25)
As(1)	4 549(4)	1 193(3)	5 030(3)	C(42)	–2 986(30)	–901(18)	1 110(25)
As(2)	436(4)	–537(3)	–229(3)	C(43)	–3 634(30)	–1 538(18)	420(25)
O(1)	3 644(30)	491(22)	4 115(25)	C(44)	–3 055(30)	–1 872(18)	–432(25)
O(2)	1 473(34)	–390(22)	1 012(28)	C(45)	–1 826(30)	–1 569(18)	–596(25)
C(11)	5 008(30)	1 317(17)	7 429(29)	C(46)	–1 178(30)	–933(18)	94(25)
C(12)	5 008(30)	983(17)	8 488(29)	C(51)	2 148(30)	–1 861(21)	–578(18)
C(13)	4 574(30)	155(17)	8 597(29)	C(52)	2 731(30)	–2 423(21)	–1 225(18)
C(14)	4 140(30)	–337(17)	7 647(29)	C(53)	2 389(30)	–2 391(21)	–2 387(18)
C(15)	4 141(30)	–2(17)	6 588(29)	C(54)	1 463(30)	–1 798(21)	–2 904(18)
C(16)	4 575(30)	826(17)	6 479(29)	C(55)	879(30)	–1 236(21)	–2 257(18)
C(21)	6 817(28)	629(18)	4 186(24)	C(56)	1 221(30)	–1 268(21)	–1 093(18)
C(22)	8 166(28)	629(18)	4 133(24)	C(61)	–1 147(34)	950(24)	–1 204(29)
C(23)	9 003(28)	1 253(18)	4 689(24)	C(62)	–1 244(34)	1 761(24)	–1 667(29)
C(24)	8 492(28)	1 878(18)	5 298(24)	C(63)	–101(34)	2 183(24)	–1 831(29)
C(25)	7 143(28)	1 878(18)	5 351(24)	C(64)	1 140(34)	1 795(24)	–1 533(29)
C(26)	6 306(28)	1 254(18)	4 795(24)	C(65)	1 236(34)	984(24)	–1 071(29)
C(31)	3 999(29)	2 814(22)	3 973(26)	C(66)	93(34)	562(24)	–906(29)
C(32)	3 256(29)	3 552(22)	3 704(26)				

Table 9. Uranium and arsenic environments in UBr_4·2tpao, bond lengths in Å and angles in °, with estimated standard deviations in parentheses

(*a*) Uranium environment

U–Br(1)	2.795(6)	Br(1)–U–Br(3)	176.2(2)	Br(2)–U–O(1)	88.9(9)
U–Br(2)	2.831(7)	Br(1)–U–Br(4)	89.5(2)	Br(2)–U–O(2)	91.6(9)
U–Br(3)	2.797(8)	Br(2)–U–Br(3)	89.7(2)	Br(3)–U–O(1)	90.0(9)
U–Br(4)	2.787(6)	Br(2)–U–Br(4)	174.8(2)	Br(3)–U–O(2)	84.3(9)
U–O(1)	2.121(30)	Br(3)–U–Br(4)	91.2(2)	Br(4)–U–O(1)	86.1(8)
U–O(2)	2.126(32)	Br(1)–U–O(1)	93.8(9)	Br(4)–U–O(2)	93.6(9)
Br(1)–U–Br(2)	89.9(2)	Br(1)–U–O(2)	91.9(9)	O(1)–U–O(2)	174(1)

(*b*) As(1) environment

As(1)–O(1)	1.713(32)	O(1)–As(1)–C(16)	109(1)	C(16)–As(1)–C(36)	110(1)
As(1)–C(16)	1.854(37)	O(1)–As(1)–C(26)	110(1)	C(26)–As(1)–C(36)	110(1)
As(1)–C(26)	1.878(31)	O(1)–As(1)–C(36)	109(1)	U–O(1)–As(1)	158(2)
As(1)–C(36)	1.910(37)	C(16)–As(1)–C(26)	109(1)		

(*c*) As(2) environment

As(2)–O(2)	1.692(32)	O(2)–As(2)–C(46)	107(1)	C(46)–As(2)–C(66)	107(1)
As(2)–C(46)	1.878(33)	O(2)–As(2)–C(56)	109(1)	C(56)–As(2)–C(66)	113(1)
As(2)–C(56)	1.846(31)	O(2)–As(2)–C(66)	107(1)	U–O(2)–As(2)	170(2)
As(2)–C(66)	1.925(37)	C(46)–As(2)–C(56)	114(1)		

Table 10. Short non-bonded intramolecular contacts (Å) in $UBr_4 \cdot 2tpao$

As(1)···H(15)	2.84(3)	As(2)···H(45)	2.88(3)
As(1)···H(21)	2.98(3)	As(2)···H(51)	2.93(3)
As(1)···H(25)	2.93(3)	As(2)···H(55)	2.94(3)
As(1)···H(31)	2.99(3)	As(2)···H(65)	2.83(3)
As(1)···H(35)	2.97(3)	O(1)···H(15)	2.51(5)

Table 11. Comparison of U–X, U–O bond lengths (Å) and U–O–Y (Y = As, P, S, or C) bond angles (°) in uranium complexes of the type $UX_4 \cdot 2L$ (L = *trans*-co-ordinated ligand); alphabetic symbols refer to Figure 5 and data sources (below)

Complex		U–X	U–O	U–O–Y
$[UCl_4(Et_3AsO)_2]$	*a*	2.67(1)	2.16(1)	162.5(5)
$[UCl_4\{Ph(Me_2N)_2PO\}_2]$	*b*	2.616(4)	2.226(6)	159.8(4)
$[UCl_4(tprpo)_2]$	*c*	2.620(4)	2.233(7)	162.5(5)
$[UCl_4\{(Me_2N)_3PO\}_2]$	*d*	2.615(5)	2.23(1)	163.1(6)
$[UCl_4(dibso)_2]$	*e*	2.605(3)	2.248(7)	156.1(5)
$[UCl_4\{(Me_3C)(Me_2N)$-$CO\}_2]$	*f*	2.612(2)	2.246(5)	165.2(5)
α-$[UCl_4\{(PhMeN)_2CO\}_2]$	*g*	2.604(8)	2.252(14)	165(1), 164(1)
β-$[UCl_4\{(PhMeN)_2CO\}_2]$	*h*	2.606(8)	2.268(18)	152(2), 163(2)
$[UBr_4(tpao)_2]$	*i*	2.803(7)	2.12(3)	158(2), 170(2)
$[UBr_4\{Ph_2(Ph_2AsC_2H_4)$-$AsO\}_2]$	*j*	2.809(4)	2.13(3)	171.8(1)
$[UBr_4(tppo)_2]$	*k*	2.774(6)	2.23(1)	160(2), 168(2)
$[UBr_4(tdpo)_2]$	*l*	2.779(3)	2.18(1)	166(1)
$[UBr_4\{(PhMeN)_2CO\}_2]$	*m*	2.771(3)	2.217(10)	180(–)

[a] Ref. 10. [b] M. R. Caira and L. R. Nassimbeni, *J. Inorg. Nucl. Chem.*, 1977, **39**, 455. [c,e,i] This work. [d,l] Ref. 6. [f] G. Bombieri, F. Benetollo, and G. de Paoli, *Acta Crystallogr., Sect. C*, 1983, **39**, 1353. [g,h,m] This work and ref. 1. [j] Ref. 11. [k] Ref. 8.

in the literature are restricted to dimethyl sulphoxide, with low precision in the reported bond lengths.

Tetrabromobis(triphenylarsine oxide)uranium(IV).—Atomic co-ordinates are listed in Table 8 and the atomic numbering scheme is shown in Figure 3; selected bond lengths and angles are given in Table 9, short, non-bonded contacts in Table 10.

This structure is isomorphous with that of tetrabromobis-(triphenylphosphine oxide)uranium(IV);[8] however, the assignment of non-unique axes and choice of enantiomer are the opposite to those reported for the tppo complex, since the similarity was only discovered in the later stages of structural analysis. If allowance is made for this, the unit-cell parameters and atomic co-ordinates agree closely, as do the molecular conformations (Figure 4). Hamilton's[9] R ratio based on a refinement with an enantiomorphic co-ordinate set ($R_g = 0.077$ for $N_p = 146$, as against $R_g = 0.074$ originally) gave no statistically significant preference for either, so that the absolute configuration remains undetermined. The As–O bond length found here is in better agreement with the value of [1.71(1) Å] reported for $[UCl_4(Et_3AsO)_2]$ [10] than the values of 1.64(1) Å in $[UBr_4\{Ph_2As(O)CH_2CH_2AsPh_2\}_2]$ [11] (**I**) and 1.65(4) Å in $[UO_2(NO_3)_2(tpao)]$ [12] (**II**). On the other hand, the As–C-(phenyl) bond length [mean 1.88(4) Å] is closer to that in (**I**) [1.87(5) Å] than in (**II**) [1.96(3) Å]. The bromine atoms are displaced alternately from their mean plane as in the dimethyldiphenylurea complexes and in $UBr_4 \cdot 2tppo$, the deviations being of the same magnitude (*ca.* 0.1 Å) as in the latter.

The results of this study have considerably extended the number and variety of structural data on the octahedral complexes formed between uranium tetrahalides and large, unidentate oxygen-donor ligands. Bond-length information is now to hand for six distinct types of chloro and five types of bromo complex, and involves donor ligands terminating in As=O, P=O, S=O, and C=O. Data on the U–X and U–O bond lengths appear in Table 11 and in Figure 5. From these the following conclusions relevant to the objectives of this study[1] may be drawn. First, in going from donor-ligand types As=O to C=O, the same inverse relationship between the U–O and U–X bond lengths exists for both chloro and bromo complexes: as the former distance increases, so the latter decreases. These observations confirm similar trends noted previously[13] for complexes containing the UO_2X_4 chromophore with *trans*-substituted oxygen. Secondly, for each halogen the data may be grouped according to generic ligand type (As=O, P=O, S=O, and C=O), each with very similar bond lengths, although those for S=O and C=O ligands do not differ appreciably. Thirdly, the ranges over which the bond lengths change for the same span in ligand type are narrower for the bromo complexes. This is understandable in view of the greater difference in oxygen–halogen electronegativity for the bromo (as against the chloro) complexes; the uranium bonds more strongly to oxygen in these compounds (mean U–O 2.18 Å in $UBr_4 \cdot 2L$, 2.23 Å in $UCl_4 \cdot 2L$), and donor-strength variations are less influential because the U–O bonding distance is evidently nearing its minimum value for U^{IV}. We conclude that the structural information available points to a donor-strength sequence: As=O > P=O > S=O ~ C=O and thus confirms the chemical evidence[1] for such a sequence.

A further parameter of interest, the U–O–Y angle, is listed in Table 11; it rather variable in the solid state, displaying large differences even in the same molecule. However, most values (12 out of 17 available estimates) lie in the range 160—170°, mean 164.1 ± 2.8°, evidently the 'natural' preferred angle, due to the spatial distribution of charge density from the oxygen lone-pair orbitals. Also, the fact that this angle rarely opens out to greater than 170° reveals preference for a value appreciably less than 180°. On the other hand, the wide variations that occur imply a low angular deformation energy, less than the gain in lattice energy achieved by a molecular conformation which permits more efficient packing.

The structure of the *cis* isomer of $[UCl_4(tppo)_2]$ [14] is also of interest. Even though it constitutes a unique exception among the otherwise *trans*-substituted $UX_4 \cdot 2L$ complexes discussed above, the observed bond lengths [U–Cl 2.609(3) and 2.626(3), U–O 2.242(7) Å] deserve some comment. The U–O and shorter U–Cl bonds, lying in the 'equatorial' plane, have lengths similar to those observed in *trans* complexes involving Cl and other P=O ligands (Table 11). The two 'axial' U–Cl bonds are longer, which one would expect if these atoms experienced repulsion by the equatorial ligands. Presumably the complementary axial–equatorial bond-length effect is operative even if the oxygen atoms in the UO_2X_4 chromophore are *cis*-substituted.

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