Triphenylphosphine Oxide Complexes of Actinide Tetrahalides. Crystal and Molecular Structure of *trans*-Tetrabromobis(triphenylphosphine oxide)-uranium(IV) †

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The crystal structure of the title compound has been determined from three-dimensional *X*-ray diffraction data. The compound crystallises in space group $P2_1$ with a = 12.073(6), b = 15.824(7), c = 10.162(5) Å, β = 100.3(1)°, and Z = 2. The structure was solved by Patterson and Fourier methods; full-matrix least-squares refinement based on 1 836 observed reflections gave a final R value of 0.054 (R' = 0.048). There is a distorted octahedral array of ligands around the uranium atom with the triphenylphosphine oxide (tppo) molecules co-ordinated in *trans* positions. The U–O distances are 2.21(3) and 2.24(2) Å, and the U–Br distances range from 2.758(5) to 2.800(5) Å. A new crystal modification of tetrachlorobis(triphenylphosphine oxide)uranium(IV), β-UCl_4·2tppo, is reported. The structural data are discussed in conjunction with i.r. results for this metastable phase, for α-UCl_4·2tppo, and for other actinide complexes of the type MX_4·2tppo (M = Th—Pu inclusive; X = Cl or Br). It is concluded that the β-phase is the *trans* isomer. Solid-state electronic spectra are reported for α- and β-UCl_4·2tppo and UBr_4·2tppo.

Few structural data are available for complexes of the type UX_4·2L (X = Cl or Br; L = oxygen donor ligand). In the compounds UCl_4·2OP(NMe_2)$_3$,[1,2] UBr_4·2OP(NMe_2)$_3$,[2] UCl_4·2OP(NMe_2)$_2$Ph,[3] UCl_4·2OC(CMe_3)(NMe_2),[4] and UCl_4·2OAsEt$_3$[5] the donor ligands are co-ordinated in *trans* positions, whilst in UCl_4·2tppo (tppo = triphenylphosphine oxide)[6] they are in *cis* positions in a distorted octahedral environment.

The i.r. spectra of samples of UCl_4·2tppo prepared at Manchester[7] and at Harwell[8] were recently compared and found to be different in the 1 000—1 100 cm^{-1} region. This observation, coupled with different literature assignments for the position of the P=O stretching vibration in this compound,[9—12] indicated the possible existence of two crystal modifications. *X*-Ray powder diffraction studies have now confirmed this, but all attempts to obtain single crystals of the second phase, β-UCl_4·2tppo, have yielded only the previously studied polymorph, now termed α-UCl_4·2tppo. The *X*-ray powder pattern of UBr_4·2tppo is very similar to that of β-UCl_4·2tppo and since, as discussed later (see Results and Discussion section), their i.r. spectra are almost identical in the 1 000—1 100 cm^{-1} region and quite different from the i.r. spectrum of α-UCl_4·2tppo, the structure of UBr_4·2tppo has been determined from three-dimensional *X*-ray data. The results are discussed in conjunction with the i.r. data, and solid-state electronic spectra are reported for α- and β-UCl_4·2tppo and UBr_4·2tppo.

Experimental

Preparation of the Complexes.—α-UCl_4·2tppo. Triphenylphosphine oxide (1.464 g, 5.26 mmol) dissolved in the minimum volume of tetrahydrofuran (thf) was added to a solution of UCl_4 (1.0 g, 2.63 mmol) in the same solvent. A pale green solid formed immediately and the mixture was stirred for 1—2 h. The product was isolated by centrifugation, washed with thf (2 × 5 cm^3) and then n-pentane (1 × 10 cm^3), and dried *in vacuo* (Found: C, 46.8; H, 3.4; Cl, 14.9; U, 25.2. UCl_4·2tppo requires C, 46.2; H, 3.2; Cl, 15.1; U, 25.4%).

β-UCl_4·2tppo. This was prepared on the same scale and in the same way as the α-phase but the reaction mixture was stirred for *only* 1—2 *min* prior to isolation and washing of the product as described above (Found: C, 45.9; H, 2.9; Cl, 15.2; U, 24.9%).

UBr_4·2tppo. The procedure described for α-UCl_4·2tppo was used for the preparation of the tetrabromo-analogue (UBr_4, 0.43 g; tppo, 0.47 g; thf, 10 cm^3). The product was dissolved in hot, anhydrous nitromethane and small, pale green crystals were obtained by allowing the solution to cool slowly in a nitrogen-filled glove box. They were isolated by decantation, washed with small volumes of thf and n-pentane, and allowed to dry in the box atmosphere (Found: C, 38.2; H, 2.8; Br, 28.2; U, 20.9. UBr_4·2tppo requires C, 38.7; H, 2.7; Br, 28.6; U, 21.3%).

Analysis.—Uranium was precipitated as the hydrous oxide and weighed as U_3O_8 after ignition at 750 °C. Chloride and bromide were precipitated and weighed as AgCl and AgBr respectively, or determined by potentiometric titration using silver nitrate. Carbon and hydrogen were determined by standard combustion methods.

Spectral Studies.—Infrared spectra were recorded using a PE 180 spectrometer, with samples mounted as mulls in Nujol between CsI (4 000—200 cm^{-1}) or silicon (300—50 cm^{-1}) plates. Electronic absorption spectra were recorded using a Cary 14 spectrophotometer, with samples mounted as mulls in Voltalef 901 fluorocarbon grease.

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† *Supplementary data available* (No. SUP 23461, 17 pp.): structure factors, thermal parameters, *X*-ray powder diffraction data, band positions of solid-state electronic spectra. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

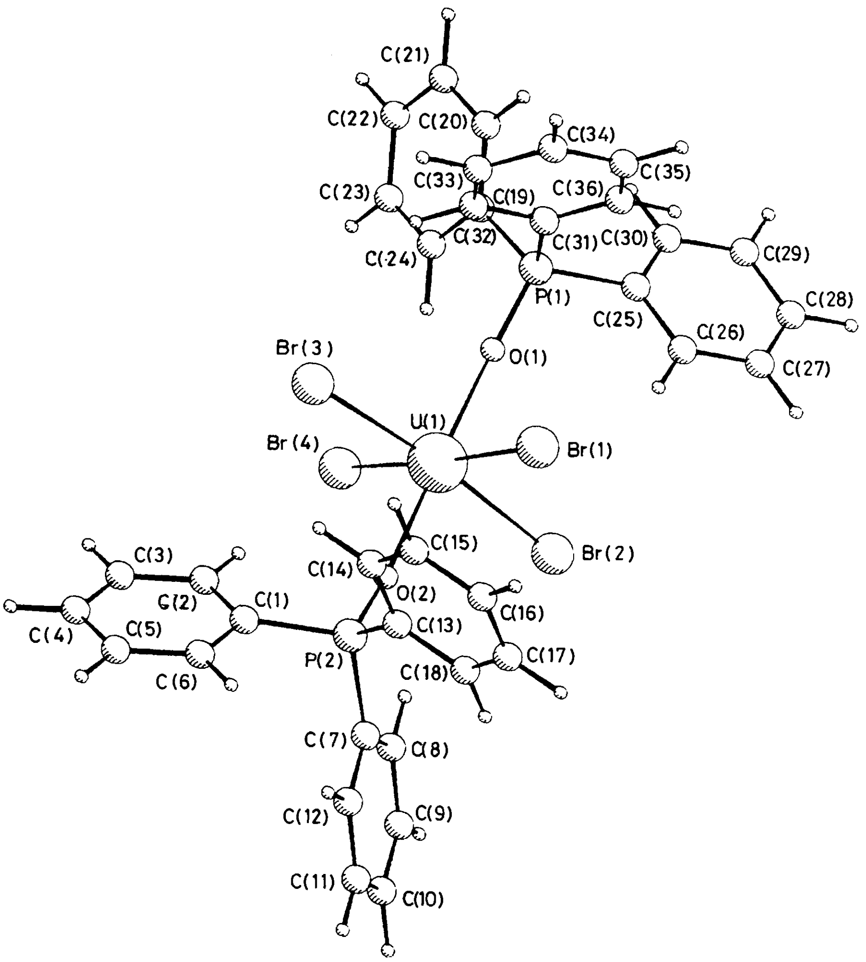

Figure 1. The UBr_4·2tppo molecule showing the atomic numbering scheme used

X-Ray Crystal Structure of UBr_4·2tppo.—*Data collection.* A single crystal of UBr_4·2tppo with dimensions *ca.* 0.1 × 0.1 × 0.2 mm was lodged in a glass capillary. Rotation and Weissenberg photographs indicated a monoclinic lattice. Intensity data were collected using a Philips PW 1 100 four-circle diffractometer in the range $6 < 2\theta < 50°$ with Mo-K_α radiation (graphite monochromator, θ—2θ scan mode, scan width 1.2°, and scan speed 0.03° s^{-1}). During the data collection two standard reflections were measured every 120 min to check the stability of the crystal and electronics. Using the criterion $I > 3\sigma(I)$ where $\sigma(I)$ is the estimated standard deviation derived from counting statistics, 1 836 of the 3 705 intensities recorded were deemed independent and observable and were used in the solution and refinement of the structure.

Corrections were made for Lorentz, polarization, and *X*-ray absorption effects.[13]

Crystal data. $C_{36}H_{30}Br_4O_2P_2U$, $M = 1\ 090.37$, Monoclinic, $a = 12.073(6)$, $b = 15.824(7)$, $c = 10.162(5)$ Å, $\beta = 100.3(1)°$, $U = 1\ 910.1$ Å^3, $D_c = 1.91$ g cm^{-3}, $Z = 2$, $F(000) = 1\ 048$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 82.6 cm^{-1}, space group $P2_1$ or $P2_1/m$ from systematically absent reflections ($0k0$, $k \neq 2n$); $P2_1$ was confirmed by the structure determination and refinement.

Structure determination. A three-dimensional Patterson map revealed the positions of the uranium atoms. These were consistent with the space groups $P2_1$ (general positions) and $P2_1/m$ with the uranium lying in the crystallographic mirror plane. Since the molecule itself could present a mirror plane with the tppo ligands in either *cis* or *trans* positions, the more symmetric space group $P2_1/m$ was initially considered. However, after the first difference-Fourier map calculated by subtracting the contribution of the uranium atoms, it became clear that this choice was incorrect. Thus, the Fourier peaks that could be attributed to the bromine atom positions were all doubled. After further calculation a choice of the Fourier peaks consistent with a model of the molecule having chemical meaning was possible, confirming the space group $P2_1$ and indicating the molecule had no crystallographic symmetry. The structure was refined by a full-matrix least-squares procedure. The function minimized was $\Sigma w||F_o| - |F_c||^2$ in which $w = 1.56/[\sigma^2(F_o) + 0.000\ 31\ F_o^2]$.

Isotropic refinement of this model without the hydrogen atom positions gave an *R* value of 0.095.

The scattering factors for uranium were taken from ref. 14, those for the non-hydrogen atoms from ref. 15, and those for the hydrogen atoms from ref. 16. Corrections for the real and imaginary parts of the anomalous dispersion were applied for U and Br.[17]

The refinement was carried out with the phenyl rings treated as rigid groups and restricted to their normal geometry (D_{6h} symmetry, C–C = 1.395 Å), using the group refinement procedure. Each ring was assigned six variable positional parameters and each ring carbon atom was assigned an individual isotropic thermal parameter. The atoms U, Br, O, and P were

Table 1. Atomic co-ordinates (× 10^4) for $UBr_4 \cdot 2tppo$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U(1)	2 448(1)	0	2 371(1)	C(33)	6 580(19)	1 730(15)	3 830(19)
Br(1)	2 688(4)	1 387(3)	4 042(4)	C(34)	6 899(19)	2 064(15)	5 112(19)
Br(2)	1 192(4)	−833(3)	3 996(4)	C(35)	6 698(19)	1 608(15)	6 221(19)
Br(3)	3 520(4)	878(3)	561(4)	C(36)	6 179(19)	818(15)	6 047(19)
Br(4)	2 349(4)	−1 425(3)	767(4)				
P(1)	5 197(8)	−533(6)	4 500(9)	H(2)	110	12	−119
P(2)	4(7)	1 142(6)	474(8)	H(3)	118	13	−348
O(1)	4 050(20)	−434(16)	3 582(19)	H(4)	33	123	−485
O(2)	836(17)	521(16)	1 216(19)	H(5)	−59	232	−393
C(1)	203(16)	1 219(11)	−1 202(18)	H(6)	−68	232	−164
C(2)	754(16)	568(11)	−1 748(18)				
C(3)	803(16)	570(11)	−3 109(18)	H(8)	−93	−43	115
C(4)	301(16)	1 225(11)	−3 924(18)	H(9)	−276	−96	101
C(5)	−251(16)	1 876(11)	−3 378(18)	H(10)	−432	−10	23
C(6)	−299(16)	1 873(11)	−2 016(18)	H(11)	−405	130	−41
C(7)	−1 400(15)	754(12)	454(19)	H(12)	−222	183	−27
C(8)	−1 559(15)	−77(12)	835(19)				
C(9)	−2 646(15)	−398(12)	750(19)	H(14)	145	255	36
C(10)	−3 574(15)	114(12)	284(19)	H(15)	178	381	158
C(11)	−3 415(15)	946(12)	−97(19)	H(16)	71	414	322
C(12)	−2 328(15)	1 266(12)	−12(19)	H(17)	−70	320	364
C(13)	180(16)	2 127(13)	1 268(18)	H(18)	−103	194	241
C(14)	1 017(16)	2 682(13)	1 020(18)				
C(15)	1 214(16)	3 431(13)	1 749(18)	H(20)	758	−79	468
C(16)	576(16)	3 625(13)	2 725(18)	H(21)	865	−177	374
C(17)	−261(16)	3 070(13)	2 972(18)	H(22)	776	−280	225
C(18)	−459(16)	2 321(13)	2 244(18)	H(23)	579	−283	170
C(19)	6 043(18)	−1 221(13)	3 754(20)	H(24)	471	−184	264
C(20)	7 215(18)	−1 199(13)	4 080(20)				
C(21)	7 856(18)	−1 787(13)	3 518(20)	H(26)	362	−16	623
C(22)	7 324(18)	−2 396(13)	2 631(20)	H(27)	332	−69	829
C(23)	6 152(18)	−2 417(13)	2 306(20)	H(28)	448	−177	936
C(24)	5 511(18)	−1 830(13)	2 867(20)	H(29)	595	−231	837
C(25)	4 961(17)	−913(12)	6 076(20)	H(30)	625	−177	631
C(26)	4 091(17)	−593(12)	6 666(20)				
C(27)	3 913(17)	−912(12)	7 891(20)	H(32)	584	71	278
C(28)	4 606(17)	−1 551(12)	8 526(20)	H(33)	672	204	308
C(29)	5 476(17)	−1 872(12)	7 935(20)	H(34)	725	260	523
C(30)	5 654(17)	−1 553(12)	6 710(20)	H(35)	692	184	709
C(31)	5 860(19)	484(15)	4 765(19)	H(36)	604	51	680
C(32)	6 061(19)	940(15)	3 656(19)				

allowed to vibrate anisotropically. Hydrogen-atom contributions were included as fixed atoms in calculated positions [d(C−H) = 0.95 Å and B_{iso} = 6 Å^2].

The final *R* value for the 1 836 reflections with $I > 3\sigma(I)$ was 0.054 (R' = 0.048).

Calculations were carried out on the CYBER computer of the Centro di Calcolo Interuniversitario Italia Nord Orientale with the SHELX 76 system of crystallographic programs.[18]

Results and Discussion

Structure of $UBr_4 \cdot 2tppo$.—The molecular structure and atomic nomenclature are illustrated in Figure 1. Final positional parameters are given in Table 1 and bond lengths and angles are listed in Table 2.

As shown in Figure 1, the uranium atom is six-co-ordinate with the neutral ligands in *trans* positions. The co-ordination octahedron is rather irregular. Thus, the four bromine atoms are situated alternately 0.11 Å above and below the best mean plane passing through them, the uranium atom lying in this plane. The oxygen and phosphorus atoms are roughly mirrored with respect to this plane but the phenyl rings are not, so the entire molecule is void of symmetry. The angles between the phenyl rings [C(1)—C(6), ring 1; C(7)—C(12), ring 2; C(13)—C(18), ring 3; C(19)—C(24), ring 4; C(25)—C(30), ring 5; and C(31)—C(36), ring 6] are: 1—2, 79; 1—3, 70; and 2—3, 67° in one tppo molecule and 4—5, 81; 4—6, 80; and 5—6, 77° in the second. The angles of the rings 1—6 with respect to the plane through the bromine atoms are, respectively, 55, 77, 18, 61, 64, and 26°.

A comparison of the bond distances and angles associated with the tppo molecules in α-$UCl_4 \cdot 2tppo$[6] and $UBr_4 \cdot 2tppo$ shows that there are no significant differences on changing from the *cis* to the *trans* arrangement of the ligands. The U−O distances are 2.21(3) and 2.24(2) Å for the *trans* compound and 2.24(1) Å for the *cis* compound; the O−P distances are, respectively, 1.52(3) Å (av.) and 1.524(7) Å, and the U−O−P angles are 164° (av.) and 165°. The U−Br distances in $UBr_4 \cdot 2tppo$ are close to those in $UBr_4 \cdot 2OP(NMe_2)_3$, 2.781 Å (av.).[2]

Figure 2 shows the molecular packing in $UBr_4 \cdot 2tppo$ viewed down *c*.

Structure of β-$UCl_4 \cdot 2tppo$.—The *X*-ray powder pattern of β-$UCl_4 \cdot 2tppo$ is quite distinct from that of the α-phase. Comparison of the former with the pattern of the tetrabromo-analogue (see SUP No. 23461) suggests that these two phases are isostructural although, perhaps not surprisingly in view of the large monoclinic unit cell, it is only the low-angle lines which can be clearly matched. No attempt has therefore been made to calculate a unit cell. However, even if the two are not

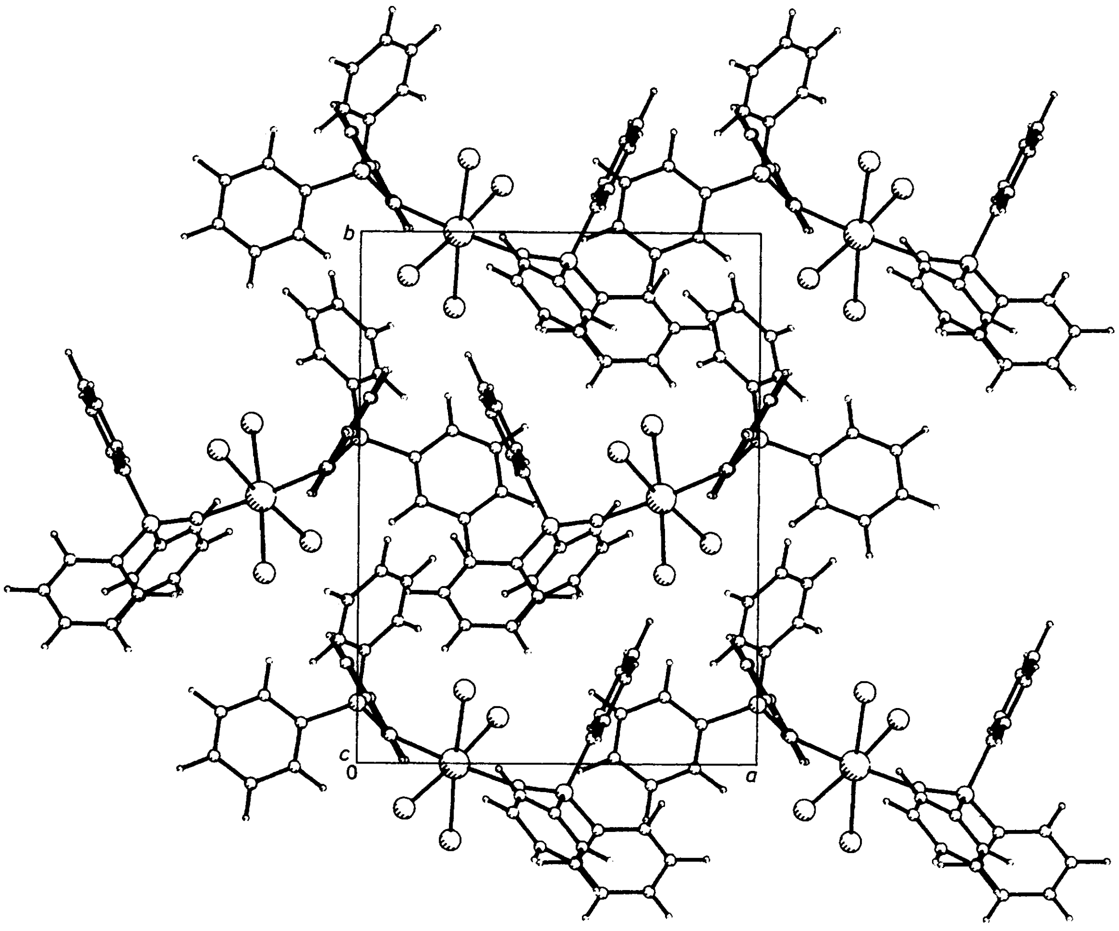

Figure 2. Packing of the UBr_4·2tppo molecules viewed down *c*

Table 2. Distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Uranium environment			
U-Br(1)	2.758(5)	Br(1)-U-Br(2)	91.2(2)
U-Br(2)	2.767(6)	Br(1)-U-Br(3)	90.0(2)
U-Br(3)	2.800(5)	Br(2)-U-Br(4)	89.6(2)
U-Br(4)	2.773(6)	Br(3)-U-Br(4)	89.7(2)
U-O(1)	2.21(3)	O(1)-U-O(2)	176(1)
U-O(2)	2.24(2)		
Br(1)-U-O(1)	85.4(8)	Br(1)-U-O(2)	90.9(6)
Br(2)-U-O(1)	92.2(6)	Br(2)-U-O(2)	88.3(7)
Br(3)-U-O(1)	93.4(6)	Br(3)-U-O(2)	86.2(7)
Br(4)-U-O(1)	90.9(8)	Br(4)-U-O(2)	92.8(6)
(*b*) Triphenylphosphine oxide			
P(2)-O(2)	1.51(3)	P(1)-O(1)	1.53(3)
P(2)-C(1)	1.77(2)	P(1)-C(19)	1.75(3)
P(2)-C(7)	1.80(2)	P(1)-C(25)	1.78(3)
P(2)-C(13)	1.75(2)	P(1)-C(31)	1.80(3)
U-O(2)-P(2)	160(2)	U-O(1)-P(1)	168(2)
O(2)-P(2)-C(1)	110(1)	O(1)-P(1)-C(19)	109(2)
O(2)-P(2)-C(7)	109(1)	O(1)-P(1)-C(25)	108(1)
O(2)-P(2)-C(13)	110(1)	O(1)-P(1)-C(31)	109(1)
C(1)-P(2)-C(13)	111(1)	C(19)-P(1)-C(31)	110(1)
C(1)-P(2)-C(7)	108(1)	C(19)-P(1)-C(25)	112(1)
C(7)-P(2)-C(13)	110(1)	C(25)-P(1)-C(31)	108(1)

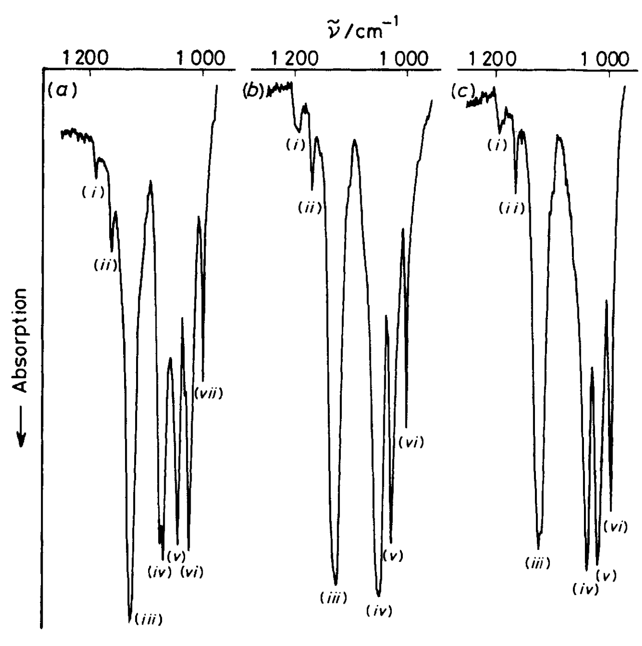

Figure 3. Infrared spectra (950—1 200 cm^{-1} only). (*a*) α-UCl_4·2tppo: (*i*) 1 186, (*ii*) 1 158, (*iii*) 1 120, (*iv*) 1 068, (*v*) 1 041, (*vi*) 1 022, and (*vii*) 998 cm^{-1}. (*b*) β-UCl_4·2tppo: (*i*) 1 185, (*ii*) 1 161, (*iii*) 1 121, (*iv*) 1 045, (*v*) 1 022, and (*vi*) 996 cm^{-1}. (*c*) UBr_4·2tppo: (*i*) 1 189, (*ii*) 1 160, (*iii*) 1 120, (*iv*) 1 035, (*v*) 1 016, and (*vi*) 993 cm^{-1}

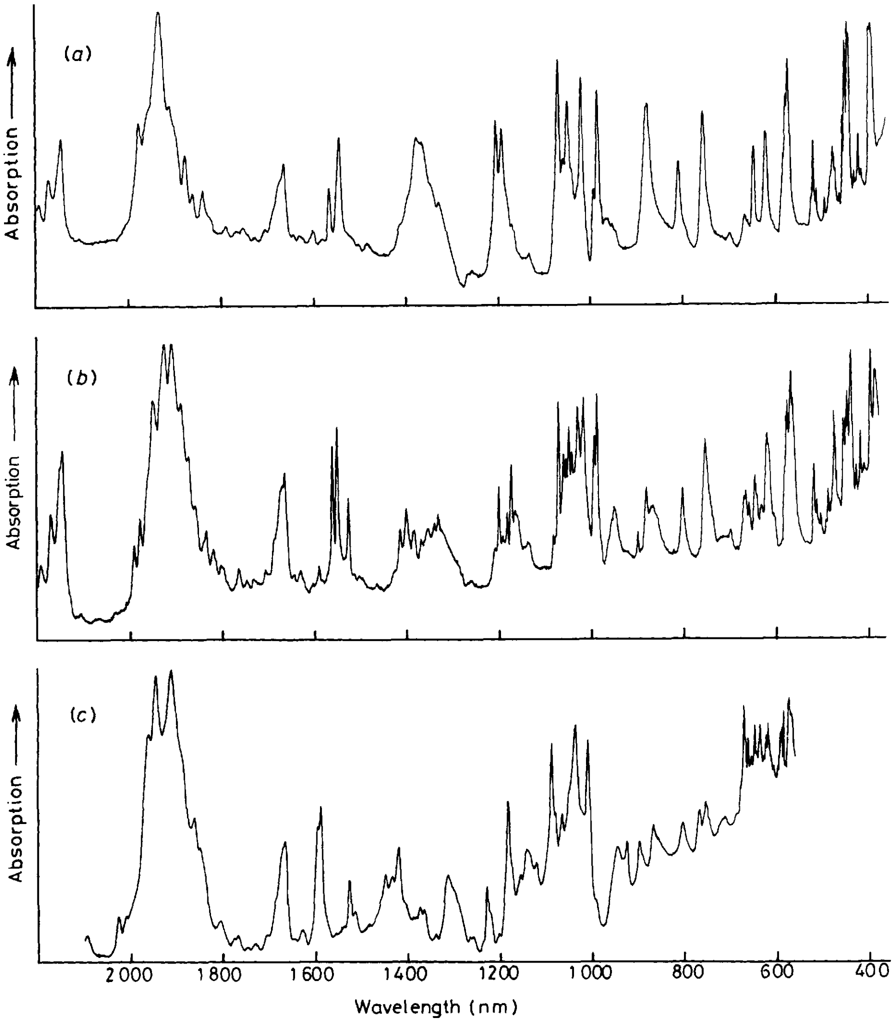

Figure 4. Solid-state electronic spectra (77 K) of (*a*) α-UCl_4·2tppo, (*b*) β-UCl_4·2tppo, and (*c*) UBr_4·2tppo

truly isostructural the i.r. evidence discussed in the next section points very strongly to the presence of *trans* tppo molecules in β-UCl_4·2tppo in contrast to the *cis* arrangement in α-UCl_4·2tppo.

Infrared Spectra.—The i.r. spectra recorded previously at Harwell for actinide tetrachloride complexes of the type MCl_4·2tppo (M = Th—Np inclusive) contained four bands between *ca.* 1 000 and 1 100 cm^{-1}, of which the highest frequency mode at *ca.* 1 070 cm^{-1} was assigned[8] to ν(P=O) following the earlier assignments of Gans and Smith[9] (1 070 cm^{-1}) for UCl_4·2tppo. Two of the remaining bands (at *ca.* 998 and 1 022 cm^{-1}) could be attributed to ligand modes but the origin of the fourth band, which appeared at *ca.* 1 040 cm^{-1}, was not established at that time. Subsequently a band at 1 043 cm^{-1} in the spectrum of the isostructural Pu analogue was assigned to ν(P=O) since the other bands in this region were relatively weak.[19] The position of the P=O stretching vibration of UCl_4·2tppo has been reported by others as 1 067[10] and 1 045 cm^{-1}.[11,12] No spectra have been published and it was not until a spectrum recorded at Manchester[7] was compared with those recorded at Harwell that it became apparent that the different assignments in the literature were possibly due to the existence of two different spectra, and probably two crystal modifications, for this compound. Thus the spectrum recorded by Tempest[7] contained only three bands between *ca.* 1 000 and 1 100 cm^{-1}, at 1 045, 1 025, and 995 cm^{-1} (*cf.* the spectra of MBr_4·2tppo discussed below). The different spectra recorded during the present study are illustrated in Figure 3.

Infrared spectra previously recorded for the actinide tetrabromide complexes MBr_4·2tppo (M = Th—Pu inclusive) also contained only three bands in the 1 000 to 1 100 cm^{-1} range and the ν(P=O) assignments (1 040—1 038 cm^{-1}) are therefore probably correct.[8] The spectrum of β-UCl_4·2tppo is almost identical with those of the tetrabromide complexes [Figure 3, ν(P=O) 1 045 cm^{-1}] and it is likely that in contrast to those in the α-modification, the tppo ligands are *trans* to each other. It now appears that the previous assignments for α-UCl_4·2tppo and other actinide tetrachloride complexes[8,19] require revision and that two ν(P=O) vibrations are observed for these complexes which contain *cis* tppo molecules. The new assignments are as follows, $ThCl_4$·2tppo, 1 070 and 1 046; $PaCl_4$·2tppo, 1 070 and 1 045; α-UCl_4·2tppo, 1 068 and 1 041; $NpCl_4$·2tppo, 1 068 and 1 040; and $PuCl_4$·2tppo, 1 071 and 1 043 cm^{-1}.

Electronic Spectra.—The solid-state transmission spectra of α- and β-UCl_4·2tppo and of UBr_4·2tppo are typical of those recorded for octahedral uranium(IV) complexes (see, for example, refs. 20 and 21). They are illustrated in Figure 4 and band positions are listed in SUP No. 23461. There is appreciably more vibronic structure in the spectrum of β-UCl_4·2tppo than in that of the α-modification. An explanation of this observation must await a detailed interpretation of the two spectra and assignment of the energy levels for the two phases.

Chemical Properties.—The phase β-UCl_4·2tppo is metastable, being readily converted to the α-phase at room temperature when left in contact with solvents in which it is slightly soluble, *e.g.* thf, nitromethane, dichloromethane, and methyl cyanide, and on recrystallisation from methyl cyanide. It is thus essential to isolate the product rapidly to avoid contamination by α-UCl_4·2tppo. It is perhaps significant that the other products for which ν(P=O) was previously reported at 1 045 cm^{-1} were also prepared either at room temperature [11] or at ice temperature [12] and were not recrystallised (see β-UCl_4·2tppo in the Experimental section) whilst products for which ν(P=O) was reported at *ca.* 1 070 cm^{-1} were recrystallised [8,9] or obtained from hot solution.[10]

The reason for the greater stability of α-UCl_4·2tppo is probably the strong graphite-type interaction between the phenyl groups of different molecules,[6] which results in a more stable crystal packing for the *cis* configuration of the triphenylphosphine oxide molecules.

Acknowledgements

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