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Uranyl polyhalides. Molecular structure of $[UO_2(OAsPh_3)_4](Br_3)_2$ and $[UO_2(OPPh_3)_4](I_3)_2$

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Abstract

Uranyl trihalides of general formula $[UO_2L_4](X_3)_2$ (L = hexamethylphosphoramide (HMPA), triphenylphosphine oxide ($OPPh_3$), triphenylarsine oxide ($OAsPh_3$); X = Br, I), along with some other higher polyiodides, have been prepared by reacting $UO_2X_2 \cdot nH_2O$ with X_2 and L in methanol or acetonitrile. The molecular structures of $[UO_2(OAsPh_3)_4](Br_3)_2$ and $[UO_2(OPPh_3)_4](I_3)_2$ have been established by X-ray diffraction analysis. ^{31}P NMR spectra are consistent with the existence of conformational isomers in solution for cations bearing HMPA and $OPPh_3$.

Keywords: Actinides; Dioxouranium(VI) polyhalides; Uranyl polyhalides; Polybromides; Polyiodides

1. Introduction

There is current interest on anhydrous uranyl complexes because of the scarcity of studies to explore the potentially unique properties of these products [1–4]. Cationic uranyl species of this nature are of particular interest with regard to luminiscence phenomena since most of this kind of studies has been carried out on uranyl salts in aqueous media.

The synthesis of a number of anhydrous compounds involving uranyl cations has been reported [5], although the species structurally characterized to date circumscribe to $[UO_2(DMF)_5](BF_4)_2$ [6], $[UO_2(DMSO)_5](BF_4)_2$ [7], and $[UO_2(HMPA)_4](A)_2$ (A = I_3 [8], IO_4 [9], BrO_4 [9], ClO_4 [10]). The usual route to prepare cationic species consists of reacting the appropriate halocomplex with soluble salts of low coordinating anions, traditionally perchlorate, in excess of the parent neutral ligand and in aprotic solvents. Similarly, the simplest rational route to polyhalides consists of treating the halides with excess halogen. The scarcity of simple procedures to prepare anhydrous uranyl halocomplexes is presumably responsible for the low number of anhydrous cationic uranyl complexes that have been fully characterized.

Recently we reported the synthesis of a few anhydrous uranyl bromocomplexes from hydrated uranyl bromide [4]. Here we report a facile synthesis for some uranyl polyhalides along with the structural characterization of $[UO_2(OAsPh_3)_4](Br_3)_2$ and $[UO_2(OPPh_3)_4](I_3)_2$.

2. Experimental

2.1. General procedures and measurements

Unless otherwise specified all operations were carried out in air. Diethyl ether was distilled over Na-benzophenone ketyl prior to use. All other reagents were commercial products and were used without further purification. Elemental analyses (C, H, N) were performed on a LECO CHNS-932 analyzer (Module VTF-900 for O). Uranium was determined by gravimetry as uranyl oxinate. IR spectra as KBr pellets were recorded on a Nicolet Impact 410 (Software OMNIC for Windows) spectrometer. NMR spectra were recorded on a Varian

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Unity Inova-400 spectrometer (400 MHz for ^{1}H and 161.92 MHz for ^{31}P). Chemical shifts are relative to TMS (^{1}H), or external 85% H_3PO_4 (^{31}P), with downfield values reported as positive. Coupling constants J are given in Hertz.

2.2. Preparation of the complexes

2.2.1. Preparation of $UO_2Br_2 \cdot xH_2O$

Uranyl acetate was quantitatively transformed to uranyl bromide as follows: $UO_2(CH_3CO_2)_2 \cdot 2H_2O$ (0.5 g, 1.18 mmol) was dissolved in a mixture of methanol (5 ml) and 47% hydrobromic acid (2 ml). The solution was concentrated to dryness in a bath at approx. 100 °C leading to an orange residue of composition $UO_2Br_2 \cdot xH_2O$ $(2 < x < 3)$.

2.2.2. Preparation of $[UO_2L_4](Br_3)_2$ (L = HMPA, $OPPh_3$, $OAsPh_3$)

The orange residue above obtained (ca. 1.15 mmol of $UO_2Br_2 \cdot xH_2O$) was dissolved in methanol (2 ml) and 0.5 g (3.13 mmol) of Br_2 was added with stirring. Then a solution of L (6.27 mmol) in methanol (15 ml) was added. After stirring the resulting mixture for 10 min at room temperature (r.t.), the orange microcrystalline precipitate was filtered, washed with diethyl ether (3 × 2 ml), and dried under vacuum.

2.2.2.1. $[UO_2(HMPA)_4](Br_3)_2$. Yield 1.477 g (85.5%). IR (cm^{-1}): ν(U=O) 917; ν(P=O) 1068. *Anal.* Found: C, 19.47; H, 4.70; N, 11.65; U, 16.01. Calc. for $C_{24}H_{72}Br_6N_{12}O_6P_4U$: C, 19.66; H, 4.95; N, 11.46; U, 16.23%.

2.2.2.2. $[UO_2(OPPh_3)_4](Br_3)_2$. Yield 1.623 g (75.8%). IR (cm^{-1}): ν(U=O) 925; ν(P=O) 1050. *Anal.* Found: C, 44.05; H, 3.15; U, 12.55. Calc. for $C_{72}H_{60}Br_6O_6P_4U$: C, 46.43; H, 3.25; U, 12.78%.

2.2.2.3. $[UO_2(OAsPh_3)_4](Br_3)_2$. Yield 2.27 g (94.4%). IR (cm^{-1}): ν(U=O) 901; ν(As=O) 840, 858. *Anal.* Found: C, 41.62; H, 2.94; U, 11.81. Calc. for $C_{72}H_{60}As_4Br_6O_6U$: C, 42.43; H, 2.97; U, 11.68%.

2.2.3. Preparation of a solution of UO_2I_2 in acetonitrile

Uranyl acetate was quantitatively transformed to $UO_2Cl_2 \cdot xH_2O$ by heating to dryness a solution of $UO_2(CH_3CO_2)_2 \cdot 2H_2O$ (0.5 g, 1.18 mmol) in a mixture of methanol (5 ml) and 35% hydrochloric acid (2 ml). The resulting $UO_2Cl_2 \cdot xH_2O$ was dissolved in acetonitrile (2 ml) and then a solution of 1.4 g (6.6 mmol) of NaI in acetonitrile (6 ml) was added. After stirring the mixture for 10 min the NaCl precipitated was filtered and washed with acetonitrile (2 × 1 ml). The clear red filtrate, consisting of a solution of UO_2I_2 and NaI in acetonitrile with some residual water, was used to prepare the polyiodides.

2.2.4. Preparation of $[UO_2L_4](I_3)_2$ (L = HMPA, $OPPh_3$, $OAsPh_3$)

The solution above prepared, containing about 1.15 mmol of UO_2I_2 in 10 ml of acetonitrile was treated with 1.21 g (4.76 mmol) of I_2 dissolved in 15 ml of acetonitrile. Then, 5 mmol of L in acetonitrile (15 ml) was added. After stirring the resulting mixture for 10 min the brown microcrystalline precipitate was filtered, washed with diethyl ether (3 × 2 ml) and dried under vacuum.

2.2.4.1. $[UO_2(HMPA)_4](I_3)_2$. Yield 1.858 g (90.06%). IR (cm^{-1}): ν(U=O) 917; ν(P=O) 1072. *Anal.* Found: C, 16.31; H, 4.02; N, 9.71; U, 13.39. Calc. for $C_{24}H_{72}I_6N_{12}O_6P_4U$: C, 16.49; H, 4.15; N, 9.61; U, 13.62%.

2.2.4.2. $[UO_2(OPPh_3)_4](I_3)_2$. Yield 1.75 g (69.14%). IR (cm^{-1}): ν(U=O) 920; ν(P=O) 1065. *Anal.* Found: C, 39.95; H, 2.83; U, 11.22. Calc. for $C_{72}H_{60}I_6O_6P_4U$: C, 40.32; H, 2.82; U, 11.10%.

2.2.4.3. $[UO_2(OAsPh_3)_4](I_3)_2$. Yield 2.588 g (93.42%). IR (cm^{-1}): ν(U=O) 890; ν(As=O) 850. *Anal.* Found: C, 36.76; H, 2.59; U, 10.08. Calc. for $C_{72}H_{60}As_4I_6O_6U$: C, 37.27; H, 2.61; U, 10.26%.

2.2.5. Preparation of $[UO_2L_4](I_7)_2$ (L = HMPA, $OPPh_3$, $OAsPh_3$)

A solution of UO_2I_2 in acetonitrile containing about 1.15 mmol of UO_2I_2 was treated successively with 16 g (18.9 mmol) of I_2 in acetonitrile (20 ml) and 5 mmol of L in acetonitrile (15 ml) at r.t. After stirring the resulting mixture for 10 min, the microcrystalline precipitate was filtered and dried under vacuum.

2.2.5.1. $[UO_2(HMPA)_4](I_7)_2$. Yield 2.941 g (90.19%). Blue black. IR (cm^{-1}): ν(U=O) 922; ν(P=O) 1065. *Anal.* Found: C, 10.96; H, 2.85; N, 6.72; U, 8.57. Calc. for $C_{24}H_{72}I_{14}N_{12}O_6P_4U$: C, 10.43; H, 2.63; N, 6.08; U, 8.61%.

2.2.5.2. $[UO_2(OPPh_3)_4](I_7)_2$. Yield 3.178 g (85.22%). Blue black. IR (cm^{-1}): ν(U=O) 918; ν(P=O) 1054. *Anal.* Found: C, 27.19; H, 1.87; U, 7.66. Calc. for $C_{72}H_{60}I_{14}O_6P_4U$: C, 27.37; H, 1.91; U, 7.53%.

2.2.5.3. $[UO_2(OAsPh_3)_4](I_7)_2$. Yield 3.784 g (96.138%). Brown black. IR (cm^{-1}): ν(U=O) 898; ν(As=O) 850, 858. *Anal.* Found: C, 39.38; H, 2.85; U, 7.07. Calc. for $C_{72}H_{60}As_4I_{14}O_6U$: C, 25.93; H, 1.81; U, 7.14%.

2.3. Crystal-structure determinations

Suitable single crystals were grown at r.t. by slow evaporation of saturated solutions in acetonitrile. Crystal data for $[UO_2(OAsPh_3)_4](Br_3)_2$: monoclinic, $P2_1/n$, $a = 9.383(1)$, $b = 15.150(1)$, $c = 26.358(1)$ Å, $\alpha = 90°$, $\beta = 94.668(1)°$, $\gamma = 90°$, $V = 3734.8(1)$ Å^3, $Z = 2$. Crystal data for $[UO_2(OPPh_3)_4](I_3)_2$: monoclinic, $P2_1/n$, $a = 9.407(1)$, $b = 15.739(1)$, $c = 26.189(1)$ Å, $\alpha = 90°$, $\beta = 98.366(1)°$, $\gamma = 90°$, $V = 3836.4(1)$ Å^3, $Z = 2$.

Crystals of $[UO_2(OAsPh_3)_4](Br_3)_2$ (block, orange, dimensions $0.50 \times 0.15 \times 0.10$ mm) and for $[UO_2(OPPh_3)_4](I_3)$ (block, orange, dimensions $0.20 \times 0.10 \times 0.05$ mm) were used for the structure determination. X-ray data were collected using a Bruker SMART CCD area detector single-crystal diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) by the phi-omega scan method. A total of 1271 frames of intensity data were collected for each compound. The first 50 frames were recollected at the end of data collection to monitor for decay. The integration processes yield a total 25 322 for $[UO_2(OAsPh_3)_4](Br_3)_2$ and 20 468 for $[UO_2(OPPh_3)_4](I_3)$, of which 9182 and 6782, respectively, were independent. Absorption corrections were applied using SADABS program (maximum and minimum transmission coefficients 0.5334 and 0.1235 for $[UO_2(OAsPh_3)_4](Br_3)_2$; and 0.8004 and 0.4559 for $[UO_2(OPPh_3)_4](I_3)$). The structures were solved using the Bruker SHELXTL-PC software by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in the riding mode. For $[UO_2(OAsPh_3)_4](Br_3)_2$ convergence was reached at a final $R_1 = 0.0440$ [for $I > 2\sigma(I)$], $wR_2 = 0.0910$ (for all data), 403 parameters, with allowance for the thermal anisotropy for all non-hydrogen atoms. Residual electron densities extremes were 1.253 and -0.919 e Å^{-3} and the goodness-of-fit on F^2 was 1.047 for all observed reflections. For $[UO_2(OPPh_3)_4](I_3)$ convergence was reached at a final $R_1 = 0.0553$ [for $I > 2\sigma(I)$], $wR_2 = 0.1204$ (for all data), 403 parameters, with allowance for the thermal anisotropy for all non-hydrogen atoms. Residual electron densities extremes were 1.476 and -1.622 e Å^{-3} and the goodness-of-fit on F^2 was 1.031 for all observed reflections. Crystal data and details on the data collection and refinement are given in the supplementary material.

3. Results and discussion

3.1. Synthesis and characterization of the complexes

The first evidence of the facile formation of uranyl tribromide complexes was obtained during the preparation of addition compounds of UO_2Br_2 (**4**). Thus, when 30% H_2O_2 was added to a solution consisting of UO_2Br_2, HBr, CH_3OH and $AsPh_3$ a product consistent with the formulation $[UO_2(OAsPh_3)_4](Br_3)_2$ was obtained. This was attributed to the simultaneous formation of $OAsPh_3$ and Br_2, and the subsequent rearrangement of the species in solution to form the tribromide complex. Following a more rational procedure—treatment of a solution of $UO_2Br_2 \cdot xH_2O$ in CH_3OH with Br_2 and then with $OAsPh_3$—we were able to prepare the same product in good yield. The tribromides containing $OPPh_3$ and HMPA were similarly isolated. The addition of bromine to the solution of uranyl bromide prior to the organic ligand is advisable. This way the precipitation of neutral $UO_2Br_2L_2$ adducts is avoided. However, to minimize side reactions of bromine with the organic ligands these should be added soon after the addition of bromine is completed.

In a similar manner a number of polyiodides can be easily isolated. The ability of iodide ions to form triiodides but also higher polyiodides allowed the isolation of a variety of compounds with the same uranyl cation and variable amount of iodine. Among them only the triiodides and ‘heptaiodides’ could be prepared in an accurate and reproducible manner. The triiodides could be obtained even with a significant excess of iodine above the stoichiometric. In this regard it is to note that the starting UO_2I_2 solution is rich in NaI so that a considerable excess of iodine is required to form species beyond I_3^-; and also that neither NaI nor NaI_n lead to precipitation with the organic ligands in these conditions. The ‘heptaiodides’ are formed with a large excess of iodine and likely they are authentic heptaiodides having in mind that the anion I_7^- is well known in many compounds [11]; however, at present we have been unable to obtain crystals of quality for the structural characterization.

All compounds are insoluble in water and diethyl ether, somewhat soluble in acetone and methanol, and very soluble in dimethyl formamide and dimethyl sulfoxide. Care should be exercised in the washing of the precipitates with diethyl ether, and in drying by pumping, as the halogen is easily removed from the polyhalide ions. They decompose before melting with liberation of the halogen.

The IR spectra of the compounds in the region 4000–400 cm^{-1} characterize by a strong band around 900 cm^{-1} characteristic for $\nu_{as}(UO_2)$ along with several bands attributable to the organic ligand. It is to note that $\nu_{as}(UO_2)$ shifts slight but regularly to lower energies, for each set of compounds with the same anion, in the sequence $OPPh_3 > HMPA > OAsPh_3$. This suggests that the basicity of the ligands [12] plays same role (*cis*-effect) on the strength of the U–O multiple bond, the more basic the ligand ($OAsPh_3$) the lower $\nu_{as}(UO_2)$. However, the nature of the anion also affects the position of this band as for compounds with the

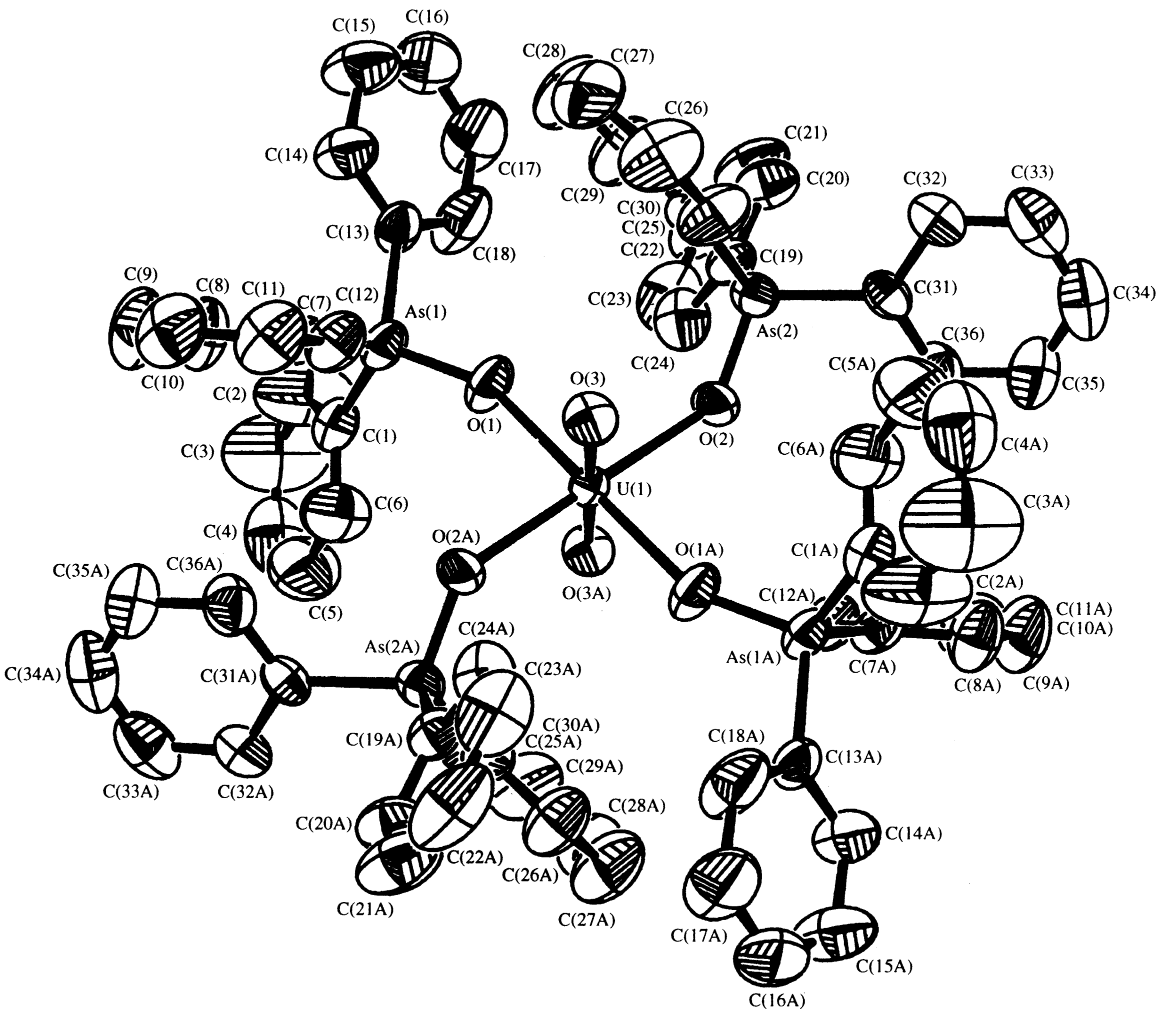

Fig. 1. Molecular structure and atom-labeling scheme for $[UO_2(OAsPh_3)_4](Br_3)_2$, (50% probability ellipsoids); hydrogen atoms are omitted.

same cation $\nu_{as}(UO_2)$ are only occasionally coincident. The bands assigned to $\nu(O{=}P)$ and $\nu(O{=}As)$ occur at lower frequencies in the complexes than in the free ligands as expected [13]. In this regard, it is worth noting that we have obtained products of composition $[UO_2(OAsPh_3)_4](Br_3)_2$ with three slightly different IR spectra (data reported in the experimental part belong to the product structurally characterized). This suggests the existence of conformational isomers for the cation, what can be extended to the other cations having in mind the steric requirements of these ligands and the precedent for all *trans*-$[UO_2Cl_2(OPPh_3)_2]$ [14].

Full characterization of the complexes through NMR is difficult. ^{31}P NMR spectra show that in solvents in which they are more soluble, DMF and DMSO, the ligands $OPPh_3$ and HMPA are totally displaced from the coordination sphere of uranium. The same occurs in methanol, despite the tribromides are prepared in this solvent. In acetone-d_6, at 20 °C, the ^{1}H NMR spectrum of $[UO_2(HMPA)_4](Br_3)_2$ shows two signals at $\delta = 2.92$ and 2.78 ppm (d, $J_{P\text{–}H} = 9.8$ Hz, intensity ratio = 5/6) that shift at $\delta = 2.88$ and 2.66 ppm (d, $J_{P\text{–}H} = 9.8$ Hz, intensity ratio = 3/2) at -70 °C. The ^{31}P NMR spectrum shows a broad signal at $\delta = 35.6$ ppm at 20 °C, and two signals at $\delta = 35.5$ and 29.7 ppm at -70 °C, far from the position for the free ligand ($\delta = 25.1$ ppm at 20 °C). Similar superior complexity was observed in the NMR of the other HMPA and $OPPh_3$ compounds. These findings are also consistent with the existence of conformational isomers for the cations in solution. However, this assumption should be regarded with caution as the polyhalide ions react with the solvent, and the reaction by-products may react with the cationic complexes.

3.2. Molecular structures

The molecular structures for the cations in $[UO_2(OAsPh_3)_4](Br_3)_2$ (**1**) and $[UO_2(OPPh_3)_4](I_3)_2$ (**2**) are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are listed in Table 1.

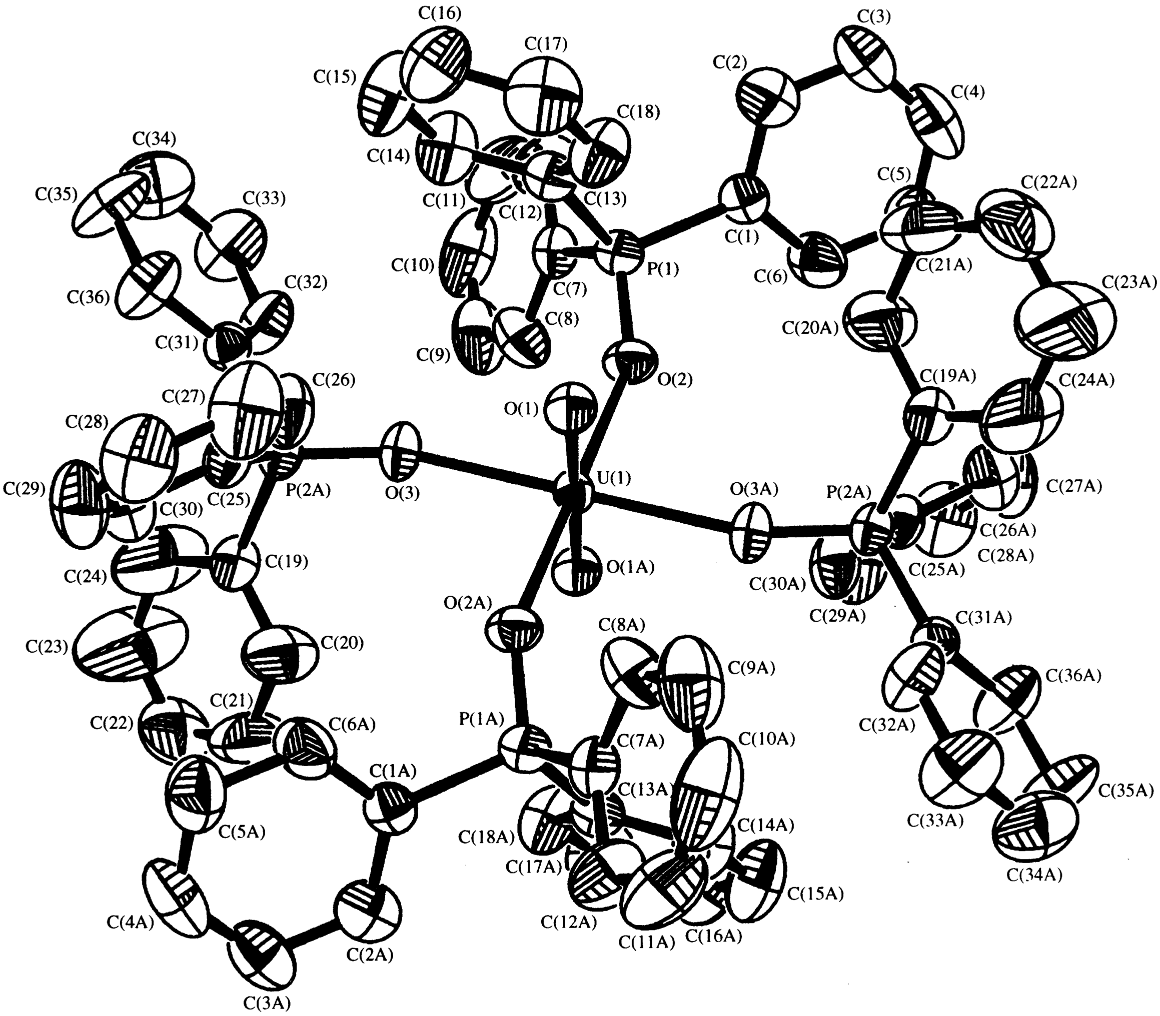

Fig. 2. Molecular structure and atom-labeling scheme for $[UO_2(OPPh_3)_4](I_3)_2$, (50% probability ellipsoids); hydrogen atoms are omitted.

Table 1
Selected bond lengths (Å) and angles (°) for $[UO_2(OAsPh_3)_4](Br_3)_2$ and $[UO_2(OPPh_3)_4](I_3)_2$

$[UO_2(OAsPh_3)_4](Br_3)_2$ (**1**)		$[UO_2(OPPh_3)_4](I_3)_2$ (**2**)	
Bond lengths			
U(1)–O(3)	1.772(3)	U(1)–O(1)	1.753(5)
U(1)–O(1)	2.265(3)	U(1)–O(2)	2.302(6)
U(1)–O(2)	2.284(3)	U(1)–O(3)	2.308(5)
As(1)–O(1)	1.670(3)	P(2)–O(3)	1.513(6)
As(2)–O(2)	1.678(3)	P(1)–O(2)	1.521(6)
Br(2)–Br(3)	2.531(2)	I(1)–I(2)	2.919(13)
Br(1)–Br(2)	2.550(2)	I(2)–I(3)	2.901(13)
Bond angles			
O(3)–U(1)–O(3)	180.0(3)	O(1)–U(1)–O(1)	180.0(5)
O(3)–U(1)–O(1)	89.78(16)	O(1)–U(1)–O(2)	90.9(2)
O(1)–U(1)–O(2)	89.49(13)	O(2)–U(1)–O(3)	90.8(2)
As(1)–O(1)–U(1)	154.2(2)	U(1)–O(3)–P(2)	159.2(4)
As(2)–O(2)–U(1)	140.4(2)	U(1)–O(2)–P(1)	146.9(4)
Br(3)–Br(2)–Br(1)	179.06(6)	I(3)–I(2)–I(1)	179.75(5)

As expected, the uranium is coordinated in a pseudo-octahedral fashion by two *trans*-oxo and four O-donor ligands in the equatorial plane. Comparison with related complexes is difficult, as these are the unique uranyl tribromides structurally identified, and only one uranyl triiodide has been fully characterized [8]. In **1** there are three couples of identical U-ligand distances associated to each pair of *trans*-ligands. In **2** the four U–O distances in the equatorial plane are virtually identical. The trihalide ions in **1** and **2** are almost linear and symmetrical, with distances and angles in the range of other trihalides [11].

The distances U–O(oxo) in **1** (1.772) and **2** (1.753) are typical for uranyl compounds [15]. The somewhat larger distance in **1** might be derived from the superior basicity of $OAsPh_3$ respect to $OPPh_3$. This may cause reduction in π-donation from the oxo ligands to the uranium with concomitant decreasing in the strength of the bonds within the uranyl entity. Consistent with this assumption are the distances U–O(P,As), shorter in **1** than in **2**, and the position of $\nu_{as}(UO_2)$ before commented. The existence of two pairs of slightly different distances in **1** may be due only to packing forces. Indeed, several uranyl complexes of composition UO_2L_4 as for example $[UO_2Br_4]^{2-}$ in $(NMe_4)_2[UO_2Br_4]$ [16] and $[UO_2(HMPA)_4]^{2+}$ in $[UO_2(HMPA)_4](ClO_4)_2$ [10] display two and four different U–L distances, respectively, despite the counterions possess high symmetry. It is to note that the mean U–O(P) distance in **2**, 2.305, is slightly superior to that in the closely related $[UO_2(HMPA)_4](I_3)_2$, 2.292 [8], as expected from the lower basicity of $OPPh_3$ with regard to HMPA.

The angles O(oxo)–U–O(oxo), O(oxo)–U–O(P,As) and O(P,As)–U–O(P,As) are close to 180°, 90° and 90°, respectively, in both cations. In **1** the angles U–O–As, 154.2° and 140.4°, are identical for each pair of *trans*-ligands, both within the wide range of values found in UO_2–$OAsPh_3$ complexes [4,17–19]. The same is applicable to the angles U–O–P in **2**, 146.0° and 159.2°, also in the range of other UO_2–$OPPh_3$ complexes (for example in $[UO_2(NCS)_2(OPPh_3)_2(Me_2CO)]$ the angles are 143.3° and 163.3° [20]).

Finally, the orientation of the equatorial ligands is similar in both complexes. The cations are centrosymmetric with regard to the $UO_2(OX)_4$ (X = P, As) group. Two of opposite X atoms are oriented toward the bisection of adjacent O(oxo)–U–O(X) angles while the other two X atoms lye close to the equatorial plane (dihedral angles for As(2)–O(2)–U(1)–O(3) = 42.92°, for As(1)–O(1)–U(1)–O(2) = 5.57°, for P(1)–O(2)–U(1)–O(1) = 43.13°, for P(2)–O(3)–U(1)–O(2) = 7.29°). We believe there are several possible conformations of similar energy for the group $U(OX)_4$ (square planar UO_4, non-linear U–O–X). The adoption of a particular conformation is likely determined by packing forces. However, the steric demand of these ligands may lead to restraints in free rotation and consequently to the existence of stable conformers for these cations no only as solid salts but also in solution. Studies to get further insight on this possibility are in progress with salts involving anions more stable than polyhalides.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 186697 and 186698 for $[UO_2(OAsPh_3)_4][Br_3]_2$ and $[UO_2(OPPh_3)_4][I_3]_2$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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