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The chemistry of uranium
Part 41*. Complexes of uranium tetrahalide, with emphasis on iodide, and triphenylphosphine oxide, tris(dimethylamino)phosphine oxide or tris(pyrrolidinyl)phosphine oxide. Crystal structure of tetrabromobis[tris(pyrrolidinyl)phosphine oxide]uranium(IV)

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Abstract

The complexes $UI_4(tppo)_2$ (tppo = triphenylphosphine oxide), $UI_4(tdpo)_2$ (tdpo = tris(dimethylamino)phosphine oxide) and $UI_4(tpyrpo)_2$ (tpyrpo = tris(pyrrolidinyl)phosphine oxide) have been prepared and IR and electronic spectra of both the solid and solutions are reported for them. The crystal structure of $UBr_4(tpyrpo)_2$ has been determined by X-ray crystallography. The compound is monoclinic, space group *C2/c*, with $a = 17.226(5)$, $b = 11.883(5)$, $c = 18.372(5)$ Å, $\beta = 109.30(3)°$; $D_c = 2.005(5)$ g cm^{-3}. There are four molecules in the unit cell and the uranium atoms, which are *trans*-octahedrally surrounded by meridional bromide ions and apical oxygen atoms of the tpyrpo ligands, are in special positions on inversion centres. Selected bond lengths are: U–Br 2.775(2) Å, U–O 2.22(1) Å, P–O 1.52(1) Å, P–N 1.62(1) Å. The relative donor strengths of the three phosphine oxide ligands towards the uranium tetrahalides, as obtained from crystallographic data, are discussed. The preparation and characterization of the less common $[UX_3L_3]$ complexes, where X = Cl, Br, I; Y = I, Ph_4B; L = tdpo, tpyrpo and $[UI(tdpo)_5]I_3$ is discussed. Six coordinate chromophores are assigned to these complexes.

Introduction

Uranium(IV) iodide reacts with the bulky oxygen donor ligand triphenylarsine oxide (tpao) to undergo a completely unexpected reaction. At −20 °C the solid green *trans*-octahedral $UI_4(tpao)_2$ complex similar to the chloro and bromo analogues, was isolated. However, at room temperature a red complex with the same empirical formula but an autoionized structure, viz. $[UI_2(tpao)_4][UI_6]$ [2] was isolated. The isolation of this extraordinary product has aroused a new interest in the halogen complexes of uranium(IV), especially those containing both iodide and strong oxygen donor ligands. This interest was further amplified by the fact that the relatively weak uranium–iodine interaction leads to increased ionization of iodide and hence to the formation of unusual cationic coordination compounds. Complexes of bulky ligands which will form six coordinated complexes are of special interest since these can readily be characterized by their electronic spectra in the 1900 nm region [3]. In order to gain a greater insight into these phenomena a comprehensive investigation was initiated to systematically study the differences between the uranium(IV) iodide complexes and the corresponding chloro and bromo analogues. There were two objectives, firstly, to collect more structural data; the now well known tetragonal distortion [4–6] observed in complexes of the type UX_4L_2 (where X = Cl, Br, I; L = a very strong bulky donor ligand) being of special interest. This objective

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proved to be elusive. The structures of numerous uranium(IV) chloride complexes and some of the uranium(IV) bromide compounds are known but successful single crystal structure on uranium(IV) iodide complexes are almost non-existent. A variety of uranium(IV) iodide complexes of neutral ligands selected for this study were isolated in crystalline form but none were sufficiently stable to allow the collection of reliable X-ray data. However, the crystal structure of $UBr_4(tpyrpo)_2$ was successfully completed. The second objective was to investigate the formation of complexes of the type $[UX_{(4-x)}L_{(2+x)}]$ where $x=0$–4. Some of the results for the complexes obtained when using the ligands tris(pyrrolidinyl)phosphine oxide (tpyrpo) with a D_N of 47.2 [7], tris(dimethylamino)phosphine oxide (tdpo) with a D_N 38.8 [8] and triphenylphosphine oxide (tppo) are discussed here. The latter ligand was of special interest in view of the reported oxidation of uranium(IV) iodide by tppo in non-aqueous solvents [9]. The results include a description of the properties of the complexes of the form UI_4L_2, a discussion of the apparent donor strengths of the ligands as obtained from structural studies and the results of studies of solutions of uranium(IV) in the presence of an excess of ligand. The latter work lead to the isolation of novel six coordinated uranium(IV) complexes of the form $[UX_3L_3]Y$ where X = Cl, Br, I; Y = I, Ph_4B; L = tdpo, tpyrpo.

Results and discussion

Yellow–green complexes of the type UI_4L_2 were isolated with all three ligands. These complexes resembled the well-studied chloro and bromo analogues in many respects and were indefinitely stable in a dry nitrogen or argon atmosphere. However, they were much more hygroscopic and hydrolyzed within minutes upon exposure to the humid laboratory atmosphere. All three complexes were sparingly soluble in methyl cyanide, but $UI_4(tppo)_2$ was found to decompose in hot methyl cyanide solutions. This was due to the oxidation of the uranium(IV) by tppo as suggested previously [9].

The IR spectra of solid $UI_4(tdpo)_2$ and $UI_4(tpyrpo)_2$ were similar to those of their chloro and bromo analogues. The IR spectrum of $UI_4(tppo)_2$ shows only three absorption bands in the region 1000–1100 cm^{-1} which was similar to the spectra of *trans*-$UCl_4(tppo)_2$ and *trans*-$UBr_4(tppo)_2$ [10]. A large shift in the $\nu(P-O)$ absorption band, Table 1, was observed indicating strong coordination of the ligands. The solid reflectance electronic spectra of the UI_4L_2 complexes resemble those recorded for other six coordinated uranium(IV) complexes and were similar to those of the analogous chloro and bromo complexes. The positions of the two most prominent bands in each of these spectra are reported in Table 2 together with those of the corresponding bands found in the spectra of the chloro and bromo analogues and in the UX_6^{2-} complexes. In view of the similarity between the electronic and IR spectra of the UI_4L_2 complexes and those of the analogous *trans*-octahedral chloro and bromo complexes, a *trans*-octahedral coordination sphere was assigned to all three of the iodide complexes.

A comparison of the thermal decomposition studies performed on these complexes in a non-static and dry nitrogen atmosphere with those of the chloro and bromo analogues indicate that the UX_4L_2 complexes, where X = Cl, Br, I; L = tdpo and tpyrpo, were of comparable stability, all decomposing in the range 240–290 °C. Solid $UI_4(tppo)_2$ was considerably less stable than $UBr_4(tppo)_2$, the former starting to decompose at ±130 °C whereas the latter started to decompose only at ±250 °C. It appeared that the decomposition of $UI_4(tppo)_2$ also was the result of the oxidation of UI_4 by tppo. Evidence for this was the formation of triphenylphosphine oxide upon heating solid $UI_4(tppo)_2$ for several hours at 130 °C under a stream of dry nitrogen. The presence of triphenylphosphine oxide was confirmed by thin layer chromatography and hplc techniques. The relatively large difference in the thermal stabilities between the uranium tetraiodide complexes of tppo with respect to the corresponding tdpo and tpyrpo complexes is probably related to the greater polarizability of the P=O bond in tpyrpo and tdpo [11, 12].

The molecular structure and atomic numbering scheme is shown in Fig. 1. Final positional parameters are given in Table 3 and bond lengths and angles are listed in Table 4. It may be seen from Fig. 1 that the uranium atom is six coordinated with the neutral ligands in *trans* positions. The structure is isomorphous with that of tetrachlorobis-[tris(pyrrolidinyl)phosphine oxide]uranium(IV) reported recently [5]. The crystal structures of all the UX_4L_2 compounds (X = Cl, Br; L = tppo, tdpo, tpyrpo) are now known and the most important bond lengths in these compounds are compared in Table 5. The various bond lengths compare favourably with each other for a certain halide and again confirm the now well observed tetragonal distortion in going from UCl_4L_2 to UBr_4L_2, L being kept the same [4–6]. The crystallographic data given in Table 5, especially those for the bromo compounds, seems to suggest a donor strength order for these three ligands tppo ≈ tpyrpo < tdpo, i.e. in the order of decreasing U–O bond length and increasing U–Br bond length. In a recent publication [14] the donor

TABLE 1. Analytical and physical data of complexes

Compound	Analytical data (%)					IR data (cm^{-1})		Conductivity Λ_{500} ($S\ cm^2\ mol^{-1}$)
	U	X	C	N	H	ν(P−O)	$\Delta\nu$(P−O)	
$UCl_4(tdpo)_2$	32.1(32.24)	19.1(19.20)	19.3(19.52)	11.1(11.38)	4.8(4.91)	1036	172	17.8
$UBr_4(tdpo)_2$	25.7(25.98)	34.7(34.89)	15.6(15.73)	9.0(9.17)	3.8(3.96)	1018	190	27.5
$UI_4(tdpo)_2$	21.2(21.56)	45.6(45.98)	13.1(13.05)	7.5(7.61)	3.2(3.30)	998	210	62.2
$UCl_4(tppo)_2$	25.2(24.41)	15.1(15.14)	46.0(46.17)		3.1(3.22)	1045	143	
$UBr_4(tppo)_2$	21.2(21.36)	28.5(28.68)	38.7(38.80)		2.8(2.71)	1038	150	
$UI_4(tppo)_2$	18.0(18.22)	38.5(38.86)	33.3(33.10)		2.4(2.32)	1015	173	
$UI_4(tppo)_4$	12.6(12.81)	27.1(27.31)	46.3(46.52)		3.2(3.25)	–	–	
$UCl_4(tprpo)_2$	26.5(26.61)	15.7(15.85)	32.1(32.22)	9.3(9.39)	5.5(5.40)	1044	136	18.6
$UBr_4(tprpo)_2$	22.1(22.19)	29.7(29.80)	26.8(26.88)	7.6(7.83)	4.4(4.51)	1017	163	28.3
$UI_4(tprpo)_2$	18.7(18.89)	40.0(40.28)	22.5(22.87)	6.5(6.67)	3.8(3.84)	982	198	74.2
$UI_4(tpyrpo)_4$	13.2(13.41)	28.2(28.60)	32.2(32.48)	9.4(9.47)	5.4(5.45)	998	182	–
$[UCl_3(tprpo(_3][Ph_4B]$	16.4(16.58)	7.4(7.41)	50.2(50.2)	8.8(8.78)	6.5(6.46)	1012	168	92.7
$[UBr_3(tdpo)_3][Ph_4B]$	17.7(17.84)	17.7(17.96)	37.7(37.80)	9.3(9.45)	5.4(5.60)	1010	198	98.3
$UI_4(tdpo)_3$	18.4(18.55)	39.4(39.56)	16.6(16.85)	9.8(9.82)	4.1(4.25)	~990	–	134.6
$UI_4(tdpo)_4$	16.0(16.28)	34.5(34.71)	19.6(19.71)	11.2(11.49)	4.8(4.96)			
$UI_4(tdpo)_4(ea)$	15.1(15.35)	32.5(32.74)	21.4(21.70)	10.6(10.84)	5.3(5.20)			
$UI_4(tdpo)_5$	14.4(14.50)	30.6(30.92)	21.7(21.95)	12.5(12.80)	5.4(5.53)			
$UClI_3(tdpo)_4(Bz))$	16.1(16.43)	26.1(26.27)(I)	24.7(24.87)	11.4(11.60)	5.5(5.43)			
$UClI_3(tdpo)_4(ea)$	16.1(16.31)	26.0(26.09)(I)	22.8(23.05)	11.3(11.52)	5.3(5.53)			

TABLE 2. Wavelengths (nm) of the two major bands in the solid reflectance electronic spectra of uranium(IV) halo complexes

Compound	X					
	Cl		Br^-		I^-	
UX_6^{2-}	1075	1980	1100	2050	1140	2165
$UX_4(tppo)_2$	1050	1932	1060	1938	1065	1045
$UX_4(tdpo)_2$	1030	1910	1040	1912	1050	1910
$UX_4(tprpo)_2$	1030	1898	1035	1898	1045	1885

strength for these three ligands, obtained from a comparison of the crystallographic data of $U(NO_3)_4L_2$ (L = tppo, tdpo and tpyrpo), were given as tppo > tdpo > tpyrpo. These two sets of donor strength orders derived from solid state crystallographic data are clearly in contradiction with the donor strength order, tppo < tdpo < tpyrpo, obtained from a detailed solution study [15] of the donor strengths of a variety of neutral oxygen donor ligands towards uranium as well as the donor numbers of tdpo and tpyrpo, viz. D_N 47.25 and D_N 38.86. It is, therefore, obvious that solid state crystallographic data alone cannot be used to infer donor strength of ligands towards metal ions as bond distances will not only depend upon the donor strength of a particular ligand, but also on the donor strengths and stereochemical requirements of ligands already coordinated to the metal ion. This is illustrated by the two observations discussed below.

A careful investigation of the IR spectra for the three UX_4L_2 complexes (X = Cl, Br, I; L = tdpo, tpyrpo) (Figs. 2 and 3) reveals an interesting phenomenon in the region 700–800 cm^{-1}. (The absorption band in free tdpo in this region has been ascribed to the asymmetric PN vibration [16]). For the three tdpo complexes, the features remain practically identical on going from $UC1_4L_2$ to UI_4L_2, but for the tpyrpo complexes a change in the relative intensities of the two absorptions can clearly be seen on going from UBr_4L_2 to UI_4L_2. We presently believe that this change in the IR spectra reflects a change in the configuration of the substituent nitrogen atoms. In both $UC1_4(tpyrpo)_2$ and $UBr_4(tpyrpo)_2$ two nitrogen atoms in the tpyrpo ligand adopt a flattened pyramidal configuration [5] while the third is coplanar

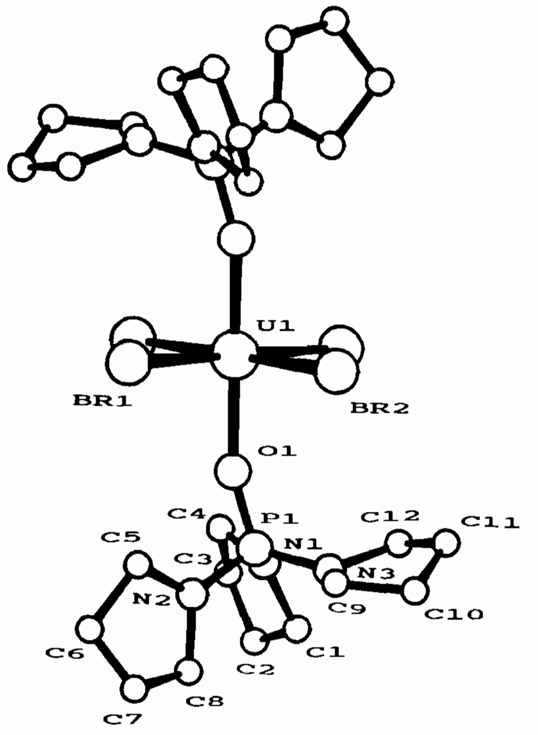

Fig. 1. A perspective view and atomic numbering scheme of the UBr_4tpyrpo$_2$ complex.

TABLE 3. Atomic coordinates for UBr_4(tppo)$_2$ with e.s.d.s in parentheses

Atom	*x/a*	*y/b*	*z/c*
U1	0.2500(0)	0.2500(0)	0.0000(0)
Br1	0.1780(1)	0.0781(1)	−0.1022(1)
Br2	0.3975(1)	0.2133(1)	−0.0265(1)
P1	0.2185(2)	0.4709(3)	−0.1486(2)
O1	0.2158(6)	0.3759(8)	−0.0945(5)
N1	0.1908(8)	0.5833(11)	−0.1145(8)
C1	0.1977(13)	0.6994(15)	−0.1430(13)
C2	0.1234(17)	0.7563(22)	−0.1375(19)
C3	0.1017(17)	0.7001(19)	−0.0770(17)
C4	0.1298(14)	0.5820(17)	−0.0743(13)
N2	0.1579(8)	0.4344(12)	−0.2331(7)
C5	0.1251(14)	0.3220(17)	−0.2536(11)
C6	0.0636(17)	0.3416(21)	−0.3339(12)
C7	0.0964(16)	0.4301(22)	−0.3671(11)
C8	0.1343(13)	0.5107(18)	−0.2996(10)
N3	0.3076(8)	0.4992(11)	−0.1557(8)
C9	0.3427(11)	0.4314(16)	−0.2043(10)
C10	0.4295(12)	0.4781(23)	−0.1841(12)
C11	0.4524(12)	0.5069(20)	−0.1035(13)
C12	0.3757(11)	0.5479(17)	−0.0903(10)

TABLE 4. Selected interatomic distances (Å) and angles (°) with e.s.d.s in parentheses

U(1)–Br(1)	2.775(2)	N(2)–C(5)	1.48(2)
U(1)–Br(2)	2.774(2)	N(2)–C(8)	1.48(2)
U(1)–O(1)	2.22(1)	C(5)–C(6)	1.55(3)
P(1)–O(1)	1.52(1)	C(6)–C(7)	1.46(4)
P(1)–N(1)	1.61(1)	C(7)–C(8)	1.57(3)
P(1)–N(2)	1.62(1)	N(3)–C(9)	1.48(2)
P(1)–N(3)	1.62(1)	N(3)–C(12)	1.51(2)
N(1)–C(1)	1.51(2)	C(9)–C(10)	1.55(3)
N(1)–C(4)	1.49(2)	C(10)–C(11)	1.47(3)
C(1)–C(2)	1.51(3)	C(11)–C(12)	1.52(3)
C(2)–C(3)	1.50(4)	C(3)–C(4)	1.51(3)
Br(1)–U(1)–Br(2)	89.8(1)	C(1)–N(1)–C(4)	111(1)
Br(1)–U(1)–O(1)	91.3(3)	N(1)–C(1)–C(2)	102(2)
Br(2)–U(1)–O(1)	89.5(3)	N(1)–C(4)–C(3)	104(2)
U(1)–O(1)–P(1)	163.3(7)	C(1)–C(2)–C(3)	106(2)
O(1)–P(1)–N(1)	106.6(6)	C(2)–C(3)–C(4)	106(2)
O(1)–P(1)–N(2)	106.5(7)	C(5)–N(2)–C(8)	114(2)
O(1)–P(1)–N(3)	116.4(7)	N(2)–C(5)–C(6)	101(2)
N(1)–P(1)–N(2)	114.5(8)	N(2)–C(8)–C(7)	101(2)
N(1)–P(1)–N(3)	105.7(8)	C(5)–C(6)–C(7)	105(2)
N(2)–P(1)–N(3)	107.4(8)	C(6)–C(7)–C(8)	104(2)
P(1)–N(1)–C(1)	124(1)	C(9)–N(3)–C(12)	111(1)
P(1)–N(1)–C(4)	122(1)	N(3)–C(9)–C(10)	102(2)
P(1)–N(2)–C(5)	124(1)	N(3)–C(12)–C(11)	103(2)
P(1)–N(3)–C(9)	121(1)	C(9)–C(10)–C(11)	104(2)
P(1)–N(3)–C(12)	121(1)	C(10)–C(11)–C(12)	106(2)

TABLE 5. Selected bond distances of UX_4L_2 complexes (Å)

Compound	U–X	U–O	P=O	Reference
UCl_4(tppo)$_2$	2.626(3)			
	2.609(3)	2.242(7)	1.524(7)	13
UCl_4(tdpo)$_2$	2.615(5)	2.23(1)	1.50(1)	4
UCl_4(tpyrpo)$_2$	2.620(4)	2.233(7)	1.515(7)	5
UBr_4(tppo)$_2$	2.774(6)	2.23(1)	1.52(3)	10
UBr_4(tdpo)$_2$	2.779(3)	2.18(1)	1.53(1)	4
UBr_4(tpyrpo)$_2$	2.775(2)	2.22(1)	1.52(1)	

with its bonded neighbours. The adoption of these configurations is to be expected in view of oxygen and nitrogen lone pair repulsions and interpyrrolidine ring repulsions. Changing the bromine atoms to the large iodine atoms, apparently forces one of the pyramidal nitrogen atoms to change configuration, thus allowing somewhat closer approach of the tpyrpo ligand to the uranium(IV) centre. This seems to be in agreement with the relatively large increase in ν(P = O) on going from UBr_4(tpyrpo)$_2$ to UI_4(tpyrpo)$_2$ (see Table 1). It is also of interest to note that the spectrum of UBr_4(tpyrpo)$_2$ in CH_2Cl_2 solution has the intensities of the two absorptions in the 700–800 cm^{-1} region inverted and is similar to that of solid UI_4(tpyrpo)$_2$. No crystals of UI_4(tpyrpo)$_2$ suitable for complete X-ray analysis could be isolated by us to confirm the above. The second observation is that when UI_4 is reacted with a total of four or more equivalents of tdpo and tpyrpo in the absence of a

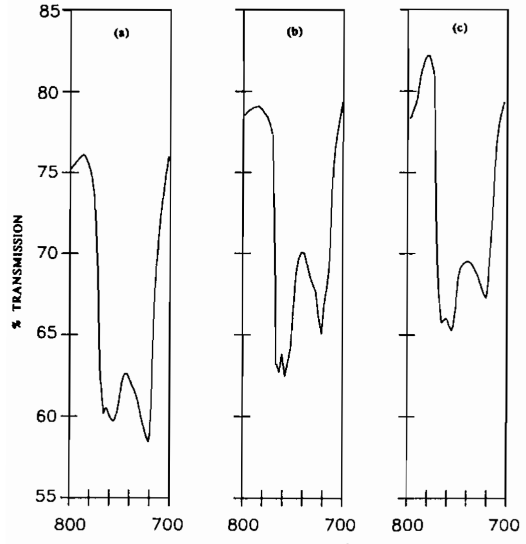

Fig. 2. IR spectra of UX_4tdpo_2 complexes in the 700–800 cm^{-1} region: X = Cl (a); Br (b); I (c).

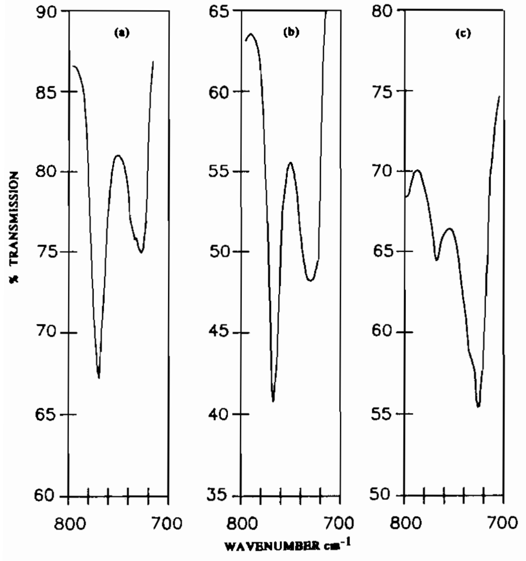

Fig. 3. IR spectra of $UX_4tpyrpo_2$ complexes in the 700–800 cm^{-1} region: X = Cl (a); Br (b); I (c).

large, non-coordinating anion such as Ph_4B, $UI_4(tpyrpo)_4$ but not $UI_4(tdpo)_4$ can be isolated. In the case of tdpo, solids of the type $UI_4(tdpo)_4$ and $UI_4(tdpo)_4(ea)$ (ea = ethyl acetate) (when ea is added to the reaction mixture) were found to precipitate. The $UI_4(tdpo)_4$ complex could, however, be prepared by desolvating the ethyl acetate adduct under vacuum at 80 °C for *c.* 4 h. The solid reflectance spectra recorded for the complexes $UI_4(tdpo)_5$ and $UI_4(tdpo)_4(ea)$ are typical of spectra recorded for other six coordinated uranium(IV) complexes. In addition, the IR spectra of these compounds in the solid state confirm the absence of any features due to either non-coordinated tdpo or ea and it would, therefore, appear that these two compounds exist in the form $[UXL_5]X_3$. It is of interest to note that a similar behaviour was observed for the mixed halo complex $UClI_3(tdpo)_4$ which crystallizes with one benzene molecule in its lattice. The solid reflectance electronic spectrum of this complex is again typical of six coordinated uranium(IV), suggesting $[UClI(tdpo)_4]I_2$ coordination. When this complex is stirred over ea for 10 min, a white powdery solid, $UClI_3(tdpo)_4(ea)$ is obtained. The IR spectrum of this complex confirms the presence of coordinated ethyl acetate and the solid reflectance spectrum, which is practically identical to that of the $UClI_3(tdpo)_4$ complex, clearly indicates a blue shift in the origin of the charge transfer bands to ~350 nm, thus confirming the absence of U–I interaction. The above differences observed in the behaviour of tdpo and tpyrpo would appear to be stereochemically related. As the relatively large iodides (2.5 Å) [17] are replaced by relatively small oxygen atoms (1.40 Å) [17] on going from UI_4L_2 to $[UI_2L]^{2+}$, etc. first order steric effects [18] decrease and stability of the solid complexes depends more on second order steric effects. The tdpo ligand apparently provides less second order stereochemicaly crunching and, therefore, readily incorporates a fifth ligand, such as tdpo or ea or another molecule, e.g. benzene to form either a compound of the type $[UIL_5]I_3$ or a clathrate.

Solution studies

The conductometric titrations of $UX_4(tdpo)_2$ (X = Cl, Br and I) with tdpo are shown in Fig. 4 and the spectrophotometric titrations of UI_4L_2 with tdpo and tpyrpo are shown in Figs. 5 and 6, respectively. The results of both the conductometric and spectrophotometric titrations showed that very little chloride can be replaced by tpdo in acetonitrile

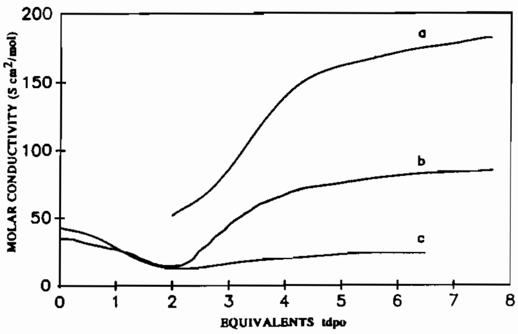

Fig. 4. Conductometric titration curves for UCl_4 (c), UBr_4mecn_4 (b) and $UI_4(tdpo)_2$ (a), with tdpo in mecn solution.

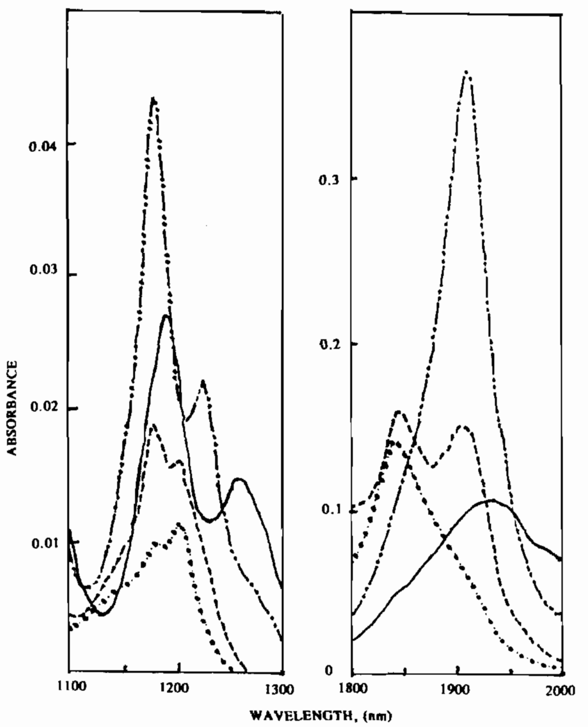

Fig. 5. Spectrophotometric titration of UI_4tdpo_2 with tdpo (L) in CH_2Cl_2 solution. UI_4:L mole ratio 2(——); 3(– – · · – –); 4(– – –); 5(· · · ·).

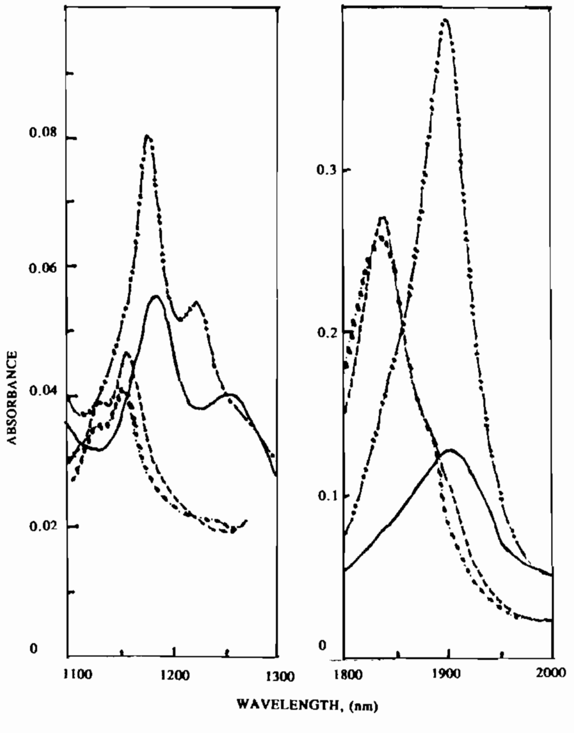

Fig. 6. Spectrophotometric titration of $UI_4tpyrpo_2$ with tpyrpo (L) in CH_2Cl_2 solution. UI_4:L mole ratio 2(——); 3(– – · · – –); 4(– – –); 5(· · · ·).

and dichloromethane solutions whereas tpyrpo is capable of replacing up to one equivalent of chloride in the presence of an excess of tpyrpo. Bromide and iodide are replaced with increasing ease by both tdpo and tpyrpo from the complexes UBr_4L_2 and UI_4L_2, respectively. IR studies indicate that very little, if any, free ligand is present in solutions up to a U:L mole ratio of 1:4. The nature of the UV–Vis spectra obtained during the spectrophotometric investigation, closely resembles UV–Vis spectra of six coordinated uranium(IV) complexes and, therefore, suggests that the species formed in solution (up to a U:L mole ratio of 1:4) are mainly six coordinated. This is to be cxpected in view of the size of the ligands studied. Plots of absorbance versus equivalents ligand added, indicate that the major species formed in solution for the UI_4 system are UI_4L_3 and UI_4L_4.

Complexes of the type UX_4L_3 and $[UX_3L_3][Ph_4B]$

Only one complex of the type UX_4L_3, viz. $UI_4(tdpo)_3$, could be isolated. In the presence of the large, non-coordinating anion, tetraphenylborate, and by removing one halogen through precipitation, either as NaX or AgX, both $[UCl_3(tpyrpo)_3][Ph_4B]$ and $[UBr_3(tdpo)_3][Ph_4B]$ could be isolated. The solid reflectance electronic spectra of the $[UX_3L_3][Ph_4B]$ and UI_4L_3 complexes are very similar to the spectra recorded for the corresponding UX_4L_2 complexes. All the major bands in these spectra show a slight blue shift due to the replacement of anionic ligand. The UV–Vis spectra of the $[UX_3L_3][Ph_4B]$ complexes in CH_2Cl_2 are practically identical to those of the solid complexes (the non-coordinating anion Ph_4B minimizing reactions like $[UX_3L_3]X \Leftrightarrow UX_4L_2 + L$ and $2[UX_3L_3]X \Leftrightarrow UX_4L_2 + [UX_2L_4]2X$) thus confirming the blue shift in the major absorption bands and the absence of features due to the UX_4L_2 and $[UX_2L_4]X_2$ species. The molar conductivities of $UI_4(tdpo)_3$, $[UCl_3(tpyrpo)_3][Ph_4B]$ and $[UBr_3(tdpo)_3][Ph_4B]$ are all in the range 85–100 S cm^2 mol^{-1} which is in the region expected for a 1:1 electrolyte. In addition, the IR spectra of the solid complexes confirm the absence of non-coordinated ligand and the absorption bands of the tetraphenylborate ion in these complexes are practically identical to those in the sodium salt, confirming the non-coordinating nature of this ion. The above results, therefore, strongly suggest that these complexes are of the form $[UX_3L_3]^+$. This assignment appears to be in agreement with thc relativcly high ϵ_m values of the major absorption bands of these complexes in CH_2Cl_2 solution compared to the corresponding bands in the symmetrical $UX_6{}^{2-}$, UCl_4L_2 and $[UX_2L_4]^{2+}$ complexes. Complexes of the type MX_4L_3

(X = Cl and Br; L = neutral oxygen donor ligand) are well known for thorium(IV), e.g. $ThBr_4(tdpo)_3$ [16], $ThCl_4(dedmu)_3$ [19] (dedmu = *N*,*N*′-diethyl-*N*,*N*′-dimethylurea) and $ThCl_4(ddu)_3$ [19] (ddu = *N*,*N*′-dimethyl-*N*,*N*′-diphenylurea), but such complexes are not commonly found for uranium(IV). Examples of such complexes are UCl_4L_3 (L = dimethyl sulfoxide [20], diethyl sulfoxide, di-(1-naphthyl) sulfoxide [21]) and $UBr_4(ea)_3$ [22]. None of these complexes are expected to have an ionized structure of the type $[UX_3L_3]^+$ in view of the relatively weak donor strengths of C=O and S=O donor ligands. Although the dimethyl sulfoxide compound has been shown to have the auto-ionized structure, $[UCl_2(dmso)_6][UCl_6]$ [23], no evidence for a similar type of structure could be found for the compounds under discussion. The IR spectra of the complexes, $[UX_3L_3]^+$, do not reveal much about the coordination in these complexes. Both in the solid state and in CH_2Cl_2 solution, there are some overlap of the P=O and symmetric NC2 stretching frequencies which prevents accurate determination of the positions of these frequencies. Approximate mean values are reported in Table 1 and a comparison with the corresponding UX_4L_2 complexes would suggest a somewhat stronger U–O interaction in the $[UX_3L_3]^+$ complexes.

In conclusion, it would appear that the formation of this type of complex is dependent on both the donor strength and stereochemistry of the ligand as well as the relative stability of the $[UX_2L_4]^{2+}$ entity. Thus, tdpo, being too weak a donor, does not give $[UCl_4L_3]^+$, but both $[UBr_3L_3][Ph_4B]$ and UI_4L_3. Tpyrpo, on the other hand, gives $[UCl_3L_3][Ph_4B]$, but neither $[UBr_3L_3][Ph_4B]$ nor $[UI_3L_3]Y$, ($Y = I^-$ or Ph_4B^-). In both the latter two cases, $[UBr_2L_4]Y_2$ or $[UI_2L_4]Y_2$ (Y = I or Ph_4B) are formed preferentially. In the case of tppo only UI_4tppo_4 could be prepared.

Experimental

All the complexes were prepared and handled in a dry nitrogen atmosphere, either in Schlenk tubes or in a dry box.

Materials

Uranium tetrachloride [24], $UBr_4(mecn)_4$ (mecn = methyl cyanide) [25] and a uranium tetraiodide stock solution [26] were prepared as previously described. The ligands were obtained as follows: tppo (Merck) was recrystallized from dry ethyl acetate and dried *in vacuo*; tdpo (BDH Ltd) was dried over activated 3 Å molecular sieves for 48 h before use and tpyrpo was prepared as described elsewhere [27]. All solvents used were dried over activated molecular sieves and distilled in a N_2 atmosphere before use.

Instrumental

IR studies

IR spectra of the solids were recorded on a Beckman 4250 (4000–200 cm^{-1}) instrument, as nujol mulls mounted between CsI cells. Solution spectra were recorded in CH_2Cl_2 using KBr liquid cells.

Electronic spectra

Electronic spectra, of the solids, were recorded at room temperature with samples mounted as mulls, in fluorinated carbon, between glass plates on a Beckman DK2A spectrophotometer. Spectra of solutions were recorded in CH_2Cl_2 on a Perkin-Elmer 330 UV–Vis spectrophotometer.

Spectrophotometric titrations were carried out by adding aliquots of the ligand (in the appropriate solvent) to a solution of the metal complex in the same solvent. A 1 cm^3 microsyringe (Hamilton Co., accuracy $\leqslant \pm 1\%$) was used for the addition of the ligand. Preparation and transfer of solutions were carried out in an inert nitrogen atmosphere using freshly distilled solvents. The stoichiometries of complexes formed in solution were obtained from plots of absorbance versus equivalents of ligand added.

Thermogravimetric analysis

A Perkin-Elmer TGS-2 thermobalance was used as described previously [28]. Nitrogen was used as a carrier gas and a constant heating rate of 5 °C/min was used.

Conductivity measurements

Conductivity of 0.003 M solutions (in acetone) of the metal complexes were recorded using a Philips PW 9505 conductivity meter and a Philips PW 9510 conductivity cell. Solutions of the uranium(IV) complexes were prepared in a nitrogen atmosphere dry box using freshly distilled solvents. These solutions were transferred to a Metrohm EH 876-20 titration vessel (with thermostatic jacket) in which a slight positive nitrogen pressure (flow rate ≈ 15 cm^3/min) was maintained. All conductometric measurements and titrations were performed at 20 °C (±0.1 °C).

Analytical

Uranium was precipitated as the hydrous oxide from aqueous solutions by aqueous NH_3 and determined as U_3O_8 after ignition at 750 °C. Halide was determined by potentiometric titration after the removal of uranium by precipitation. Analytical results are given in Table 1.

Crystallography

A well-formed crystal of maximum dimension 0.2 mm was used for the X-ray work. Crystal data are: $C_{24}H_{48}Br_4N_6O_2P_2U$, formula weight = 1072, $a = 17.226(5)$, $b = 11.883(5)$, $c = 18.372(5)$ Å, $\beta = 109.30(3)°$, $V = 3549$ Å [5], $D_c = 2.005(5)$ g/cm^3 for $Z = 4$, μ(MoKα) 106 cm^{-1}, monoclinic space group C_2/c. The intensities of 3375 reflections were measured up to $\Theta = 25°$ on a Philips four-cycle diffractometer by the $\Theta/2\Theta$ technique using graphite monochromatized Mo Kα radiation. The compound was stable under irradiation. The intensities were corrected for the Lorentz and polarization factors and for absorption [29]. A total of 2325 independent reflections with $I > 3\sigma(I)$ was used in subsequent calculations.

The structure was solved by standard methods and refined to the conventional R factor of 0.067. At this stage the maximum shift on the refined parameters was 0.03σ on the coordinates and 0.05σ on the thermal parameters. The quantity minimized in the refinement was ΣwF^2 with $w = 1$. Scattering factors for U and Br [30] were corrected for anomalous dispersion, while those for C, N, O and P were supplied internally by SHELX [31].

Final atomic parameters and selected bond lengths and angles are reported in Tables 3 and 4.

Preparation of complexes

The complexes $UX_4(tdpo)_2$ and $UX_4(tpyrpo)_2$ (X = Cl and Br) were all prepared as described previously [15].

UI_4L_2 complexes (L = tppo, tdpo, tpyrpo)

These complexes were all prepared as follows. An appropriate amount of UI_4 stock solution, containing 1–1.5 mmol uranium, in a Schlenk tube was diluted to ~50 cm^3 with dry, oxygen-free mecn and two equivalents of ligand, dissolved in ~20 cm^3 of mecn, were added slowly and with stirring. For tppo, precipitation was almost immediate whereas for tdpo and tpyrpo, cooling to −18 °C results in the formation of the crystalline product. The solid complexes were washed with ethyl acetate (2×5 cm^3), followed by isopentane and dried *in vacuo.*

$[UCl_3(tpyrpo)_3][Ph_4B]$ and $[UBr_3(tdpo)_3][Ph_4B]$

$[UBr_3(tdpo)_3][Ph_4B]$: 0.8 g (0.87 mmol) of $UBr_4(tdpo)_2$ was suspended in 30 cm^3 acetonitrile and 2 equiv. (1.75 mmol; 0.31 g) of tdpo added. The mixture was stirred until no more solid material could be detected in solution. One equiv. of $NaPBh_4$ (0.87 mmol), 0.3 g) (dissolved in a minimum volume of acetonitrile) was added while stirring. Solid NaBr was removed by filtration in a nitrogen atmosphere and the volume of the reaction mixture reduced to ≈30 cm^3 by vacuum evaporation. Cooling to −18 °C resulted in the formation of a pale green solid which was washed with ethyl acetate (2×) followed by petroleum ether and dried in vacuo. $[UCl_3(tpyrpo)_3][Ph_4B]$ was prepared in an analogous way.

$UI_4(tdpo)_3$

0.8 g (0.72 mmol) of $UI_4(tdpo)_2$ was suspended in ≈30 cm^3 CH_2Cl_2 and 1 equiv. of tdpo, (0.72 mmol, 0.13 g) in CH_2Cl_2, was added. The mixture was stirred until no more solid material could be detected. The volume of the reaction mixture was then reduced by vacuum evaporation until a pale green solid started to form. The solid was washed with petroleum ether and dried *in vacuo.*

$UI_4(tdpo)_5$

This was prepared as described for $UI_4(tdpo)_3$ but adding an additional 3 equiv. of tdpo (2.16 mmol, 0.38 g) instead.

$UI_4(tdpo)_4(ea)$

0.5 g (0.32 mmol) of $UI_4(tdpo)_5$ was stirred over ethyl acetate for several hours in a nitrogen atmosphere. The solid material was then washed with petroleum ether and dried *in vacuo.*

$UI_4(tdpo)_4$

This was prepared by heating $UI_4(tdpo)_4(ea)$ at 80 °C for ~4 h in vacuo.

$UClI_3(tdpo)_4(Bz)$ (Bz = benzene)

0.8 g (1.1 mmol of $UCl_4(tdpo)_2$ was suspended in 50 cm^3 acetonitrile and an additional 2 equiv. of tdpo (2.2 mmol, 0.39 g) and 4 equiv. of NaI (4.3 mmol, 0.65 g) were added. The mixture was refluxed under nitrogen for 2 h and the solid NaCl formed was removed by filtration. Addition of benzene results in the formation of a pale green solid which was washed with benzene and dried *in vacuo.*

$UClI_3(tdpo)_4(ea)$ was prepared by stirring $UClI_3(tdpo)_4(Bz)$ over ea for 10 min. The resultant white solid was washed with petroleum ether and dried *in vacuo.*

UI_4L_4 (L = tppo and tpyrpo)

~0.5 of the UI_4L_2 complex was suspended in ~15 cm^3 of mecn and an additional 2 equiv. of ligand dissolved in ~10 cm^3 mecn, added. The mixtures were stirred until no more solid material could be detected in the solution. Addition of a 2:1 mixture of ea and isopentane (dropwise) results in the precipitation of yellowish solids. These were washed with isopentane and dried *in vacuo*.

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