The Chemistry of Uranium. Part 42.[1] Cationic Uranium(IV) Complexes $UX_2L_4Y_2$ (X = Cl, Br or I; Y = ClO_4 or BPh_4; L = bulky strong neutral O-donor Ligand) and $[U(ClO_4)_4(OAsPh_3)_4]$: Crystal Structures of $[UX_2L_4][BPh_4]_2$ (L = tris(pyrrolidine-1-yl)phosphine oxide, X = Br or I)†

Jan G. H. du Preez,[*,a] **Leon Gouws,**[a] **Hans Rohwer,**[a] **Bernardus J. A. M. van Brecht,**[a] **Ben Zeelie,**[a] **Umberto Casellato**[b] **and Rodolfo Graziani**[c]

[a] *Uranium Chemistry Research Unit, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, South Africa*

[b] *Instituto di chimica e Tecnologia dei Radioelementi del C.N.R., Area di Recerca, Corso Stati Uniti, 35100 Padua, Italy*

[c] *Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Universita di Padova, Via Marzolo 4, 35100 Padua, Italy*

Solid complexes of the type $[UX_2L_4(ClO_4)_2]$ [X = Cl or Br; L = triphenylphosphine oxide (tppo), tris(dimethylamino)phosphine oxide (tdpo), tris(pyrrolidin-1-yl)phosphine oxide (tpyrpo) or triphenylarsine oxide (tpao)] were isolated and characterized. All formed six-co-ordinated doubly charged cationic complexes in polar non-aqueous solvents. The major bands around 1900 nm in the electronic spectra were shifted towards higher energy as the donor strength of L increased and could be used to identify the different species. Spectrophotometric titrations of solutions of $[UX_2(ClO_4)_2]$ with L in acetone indicated disproportionation, resulting in the formation of $[UX_4L_2]$ and $[U(ClO_4)_4L_n]$ moieties with n varying from 0 to 5. Differences between the chloro and bromo systems were identified. Spectral studies on solutions of $[U(ClO_4)_4(tpao)_n]$ when $n < 2$ suggested the presence of both mono- and bi-dentate perchlorato groups. The complex $[U(ClO_4)_4(tpao)_4]$, which has unusual perchlorate co-ordination, was isolated as a surprisingly stable solid. The structures of the isomorphous pair $[UX_2(tpyrpo)_4][BPh_4]_2$ (X = Br or I) were determined by X-ray crystallography. The compounds are monoclinic, space group $P2_1/c$, with a = 28.120(5), b = 15.998(4), c = 22.010(5) Å and β = 98.01(3) for the bromide and a = 28.172(5), b = 16.007(6), c = 22.059(5) Å and β = 97.91(3) for the iodide. The structural details of the compounds were comparable. The uranium atoms have *trans*-octahedral co-ordination spheres with mean bond lengths U–Br 2.775, U–I 2.980, U–O 2.230 Å (bromide) and 2.216 Å (iodide).

Previous studies on UX_4 complexes mainly concentrated on the preparation and characterization of solid species of the type UX_4L_n (X = Cl or Br; L = neutral oxygen-donor ligand and n = 2–8).[2–4] The most common and well studied amongst these are six-co-ordinated UX_4L_2 species.[5–7] We have illustrated[8] that electronic spectra in the region of 1900 nm can be applied to identify the latter compounds in the solid state as well as in their non-aqueous solutions. The changes in the intensity of the bands were recently utilized as the basis for spectrophotometric titrations of UCl_4 with chloride ions in a non-aqueous solution. The resulting data could be used qualitatively as well as quantitatively to describe the formation of the species $[UCl_5(solv)]^-$ and $[UCl_6]^{2-}$ (solv = solvent).[9] In the light of the success achieved in the above work it was decided to study the solution behaviour of UX_2Y_2 systems when these are treated with monodentate neutral ligands by incremental addition of the latter in non-aqueous solution and applying spectrophotometric and conductometric monitoring techniques [X = Cl or Br; Y = a weakly co-ordinating anionic ligand, *viz.* ClO_4^-; and L = bulky neutral ligands of varying donor strengths, *viz.* triphenylphosphine oxide (tppo), tris(dimethylamino)phosphine oxide (tdpo), tris(pyrrolidin-1-yl)phosphine oxide (tpyrpo) and triphenylarsine oxide (tpao)].

The aim of this work was to identify the different complex uranium(IV) species which are present in significant amounts at each stage of the titration with L. This should clearly illustrate, first, how the dominant species is a function of the donor strength of both the anionic and the neutral ligands and, secondly, the relationship between species in solution and the solids which precipitate from the solutions. The spectral properties and structure of solids having the cation $[UX_2L_4]^{2+}$ are of particular interest since these compounds can be regarded as having the 'symmetry inverse' of the UX_4L_2 compounds for the same X and L ligands. The latter compounds revealed tetragonal distortions (U–X bond lengthening and U–O bond shortening) when the donor strength of L was increased for the same X.[10] Additional U–O bond shortening could be expected for the cationic species. It was also necessary to study aspects of the $U(ClO_4)_4$ system in order to determine to what extent perchlorate is non-co-ordinating under the conditions employed.

Experimental

Preparations.—The starting materials UCl_4, $[UBr_4(MeCN)_4]$, $[UI_4(MeCN)_4]$ and the complexes UX_4L_2 (X = Cl

---

† Dibromo- and diiodo-tetrakis[tris(pyrrolidin-1-yl)phosphine oxide-κ*O*]uranium(IV) bis(tetraphenylborate).

Supplementary data available: see Instrucrions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

or Br; L = tpao, tpyrpo, tdpo, or tppo) were prepared as previously described.[11,12]

Stock solutions of $UX_2(ClO_4)_2$ (X = Cl or Br) were prepared by dissolving *ca.* 1.5 g of the uranium tetrahalide, UCl_4 or $[UBr_4(MeCN)_4]$, in dry acetone (30 cm^3). This solution was analysed and 2 mol of anhydrous silver perchlorate were added for every mol of uranium in the residual solution. The mixture was stirred for 15 min and then centrifuged in a sealed tube to separate the silver halide. Analyses verified that the uranium to halide mol ratio was 1:2 (solution A). These operations were performed in dry nitrogen atmospheres. Solutions of $U(ClO_4)_4L_2$ were prepared by suspending *ca.* 1.5 g of the corresponding UX_4L_2 complex in dichloromethane (30 cm^3) in a Schlenk vessel. Four mol of anhydrous silver perchlorate per mol of uranium were added. After vigorous stirring for 1.5 h the silver halide precipitate was separated from the resultant blue-green $U(ClO_4)_4L_2$ solution (solution B) as described above. This solution was stored under nitrogen and was surprisingly stable for several days at room temperature.

The $UX_2L_4(ClO_4)_2$ complexes (X = Cl or Br; L = tpao, tpyrpo, tdpo, or tppo) were prepared by addition of the corresponding ligand, dissolved in dry acetone, to solution A (20 cm^3) in a Schlenk vessel. The mixture was continually stirred and flushed with pure nitrogen. The addition was continued until a uranium to ligand mol ratio of 1:4 was reached. Precipitation occurred after the addition of dry diethyl ether (5 cm^3) followed by cooling to −18 °C. The complexes were filtered off, dried in a vacuum and analysed. The complexes $[U(ClO_4)_4(tpao)_4]$ and $[U(ClO_4)_4(tdpo)_5]$ were prepared by the addition of either tpao (2 mmol) or tdpo (3 mmol), dissolved in dichloromethane, to aliquots (20 cm^3) of solution B. The complexes were isolated as described above. The preparations of $[UX_2(tpyrpo)_4][BPh_4]_2$ (X = Br or I) were performed in Schlenk tubes flushed with nitrogen. Approximately 1 g of $[UX_4(MeCN)_4]$ (X = Br or I), which was previously analysed, was suspended in dry methyl cyanide. The ligand tpyrpo and sodium tetraphenylborate were added so that the U:tpyrpo:BPh_4 mol ratio was 1:5:2. The suspensions were well shaken, centrifuged and the resultant clear green-brown solutions decanted from the sodium halide precipitate. Upon cooling the solutions to −18 °C large pale green-brown air-stable crystals were formed. These were first washed with ethyl acetate (2 × 5 cm^3), subsequently with light petroleum (1 × 5 cm^3) and then dried *in vacuo* before analysis.

Analysis.—The perchlorate was analysed by potentiometric titration on a Metrohm E536 potentiograph fitted with an Orion perchlorate-sensitive indicator electrode. Tetraphenylarsonium chloride solution, standardized with a standard perchloric acid solution, was used as precipitant. All the other analytical methods and instruments used have been described previously.[12] The analytical, conductivity, and spectral data are summarized in Table 1.

Spectrophotometric and Conductometric titrations.—Spectrophotometric titrations were performed in a Metrohm EA 880–150 titration vessel at 25 °C and under a nitrogen atmosphere. The vessel was connected to a 1 cm flow cell inside either a Beckman Acta MVII or a DK2A spectrophotometer. Solution A was used to prepare standard 0.005 mol dm^{-3} uranium(IV) solutions. These were titrated with 0.25 mol dm^{-3} ligand solutions dissolved in acetone. Spectra were recorded after the addition of each mole fraction. Conductometric titrations were done in an analogous manner. The spectrophotometers and flow cell were replaced by a Philips PW 9509 digital conductivity meter and a PW 9512/60 conductivity cell.

Crystal-structure Determinations of $[UX_2(tpyrpo)_4][BPh_4]_2$ (X = Br *or* I).—*Crystal data.* $C_{96}H_{136}B_2Br_2N_{12}O_4P_4U$ **1**, *M* = 2063.3, monoclinic, space group $P2_1/c$, *a* = 28.120(5), *b* = 15.998(4), *c* = 22.010(5) Å, β = 98.01(3)°, *U* = 9805 $Å^3$, D_m = 1.40 g cm^{-3}, *Z* = 4, *Dc* = 1.40 g cm^{-3}, μ(Mo-Kα) = 30.7 cm^{-1}, *F*(000) = 4240.

$C_{96}H_{136}B_2I_2N_{12}O_4P_4U$ **2**, *M* = 2157.3, monoclinic, space group $P2_1/c$, *a* = 28.172(5), *b* = 16.007(6), *c* = 22.059(5) Å, β = 97.91(3)°, *U* = 9853 $Å^3$, D_m = 1.45 g cm^{-3}, *Z* = 4, D_c = 1.46 g cm^{-3} μ(Mo-Kα) = 28.1 cm^{-1}, *F*(000) = 4384.

Data collection and processing. Reflection intensities were measured on a Philips four-circle diffractometer using the θ–2θ scan technique, θ_{max} = 25°, with graphite-monochromated Mo-Kα radiation. The bromine compound was stable but the iodine compound decomposed upon irradiation with X-rays when exposed to the atmosphere. This compound was then sealed in a glass capillary under nitrogen. No deterioration was observed under these conditions. The number of recorded reflections were 11 857 (**1**) and 13 728 (**2**) while the numbers of observed reflections were 5582 (**1**) and 6928 (**2**); the criterion for considering a reflection observed was $I > 3\sigma(I)$. The intensities were corrected for absorption,[13] Lorentz, and polarization effects. The data were collected on parallelepiped crystals of dimension less than 0.2 mm. The bromide structure **1** was solved by Patterson and conventional Fourier techniques. Since the two compounds are isomorphous and isostructural, the structure of **1** was successfully used as the starting point for the refinement of the iodine compound. Full-matrix least-squares refinement was performed with the uranium, bromine or iodine, phosphorus, oxygen, and boron atoms treated anisotropically. The hydrogen-atom positions could not be located on the difference maps and were not included in the calculations. The refinements converged with *R* = 0.063 (**1**) and 0.069 (**2**) while using unit weights. At convergence the shift in the refined parameters was less than 0.025, while Fourier difference synthesis indicated only small residual electron density around the heavy-atom positions. All calculations were performed using SHELX and PARST[14] while the molecular structure of **1** was prepared with PLUTO.[14] The final atomic coordinates are given in Table 2, selected bond lengths and bond angles in Table 3.

Additional material for both structures available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Perchlorate Complexes.—The $[UY_4(tpao)_4]$ (Y = ClO_4 in subsequent discussion) and $[UY_4(tdpo)_5]$ complexes were slightly hygroscopic but indefinitely stable in a dry nitrogen atmosphere. Both are very soluble in dichloromethane but only sparingly soluble in acetone. The infrared spectrum of solid $[UY_4(tpao)_4]$ indicates that all four of the tpao ligands are strongly bonded to the uranium (Table 1). Evidence for both monodentate perchlorate co-ordination, bands at 1084, 982, 923 and 900 cm^{-1}, and bidentate perchlorate co-ordination, bands at 1258 and 1206 cm^{-1},[15] is found (Table 1). Infrared spectra of solutions of UY_4 in dichloromethane and containing 2, 3 and 4 mol of tpao per mol of uranium are portrayed in Fig. 1. These clearly indicate that the broad unsymmetrical complex absorption band, in the vicinity of 1100 cm^{-1}, gradually becomes symmetrical as the amount of the co-ordinated perchlorate decreases. At a UY_4:tpao mol ratio of 1:4 the solution spectrum suggests a large amount of ionic perchlorate with little evidence of covalent perchlorate. The solution spectrum of $[UY_4(tpao)_4]$ is therefore different to that of its solid. The infrared spectrum of solid $[UY_4(tdpo)_5]$ is difficult to interpret in the region 900–1200 cm^{-1} due to overlap of ν(P=O), ν(P–N), and ν(Cl–O) vibration bands. However, the symmetrical band at 622 cm^{-1} is indicative of ionic perchlorate. The apparent absence of a band in the region corresponding to ν(P=O) for the free ligand indicates that all the tdpo ligands are co-ordinated. The infrared spectrum changes significantly upon dissolution of this complex in dichloromethane when evidence for both free tdpo and co-ordinated perchlorate appears. The

Table 1 Selected spectral, conductance, and analytical data

	Infrared (cm^{-1})			Analysis[c] (%)			
Compound	Shift in ν(M=O)[a]	Perchlorate ν(Cl–O)	Electronic (nm)[b]	U	X	ClO_4	Λ_M[d]/S cm^2 mol^{-1}
$[U(ClO_4)_4(tpao)_4]$	69	1258, 1206, 1084, 982, 923, 900, 620		12.3 (12.4)		20.7 (20.7)	
$[U(ClO_4)_4(tdpo)_5]$	174	1100, 622		15.4 (15.5)		25.7 (26.0)	—
$[UCl_2(tpao)_4(ClO_4)_2]$	33	1095, 630	1820 (40)	13.2 (13.2)	3.95 (3.95)	10.9 (11.1)	138
$[UBr_2(tpao)_4(ClO_4)_2]$	48	1092, 625	1795 (41)	12.5 (12.6)	8.30 (8.45)	10.6 (10.5)	139
$[UCl_2(tpyrpo)_4(ClO_4)_2]$	155	1100, 625	1870 (59)	15.4 (15.3)	4.70 (4.60)	12.6 (12.9)	139
$[UBr_2(tpyrpo)_4(ClO_4)_2]$	160	1092, 620	1860 (60)	14.5 (14.6)	9.85 (9.85)	12.2 (12.2)	140
$[UCl_2(tdpo)_4(ClO_4)_2]$	169	1100, 625	1860 (40)	19.4 (19.4)	6.60 (5.80)	16.3 (16.2)	140
$[UBr_2(tdpo)_4(ClO_4)_2]$	175	1097, 622	1850 (41)	18.1 (18.1)	12.0 (12.2)	15.2 (15.1)	141
$[UCl_2(tppo)_4(ClO_4)_2]$	150	1095, 625	1875 (41)	14.5 (14.7)	4.20 (4.35)	11.8 (12.3)	141
$[UBr_2(tppo)_4(ClO_4)_2]$	152	1095, 622	1870 (41)	13.9 (13.9)	9.20 (9.35)	11.5 (11.6)	144
$[UBr_2(tpyrpo)_4][BPh_4]_2$	168	—	1865 (60)				147
$[UI_2(tpyrpo)_4][BPh_4]_2$	170	—	1875 (60)				150

[a] Shifts in ν(P=O) and ν(As=O) bands upon co-ordination when compared to the free ligand. [b] The position of the major band from the region of the electron spectrum diagnostic for six-co-ordination. The molar absorptivity (dm^3 mol^{-1} cm^{-1}) of the bond in dichloromethane solution is given in parentheses. [c] Calculated values are given in parentheses. [d] Conductivities of 0.003 mol dm^{-3} solutions in acetone.

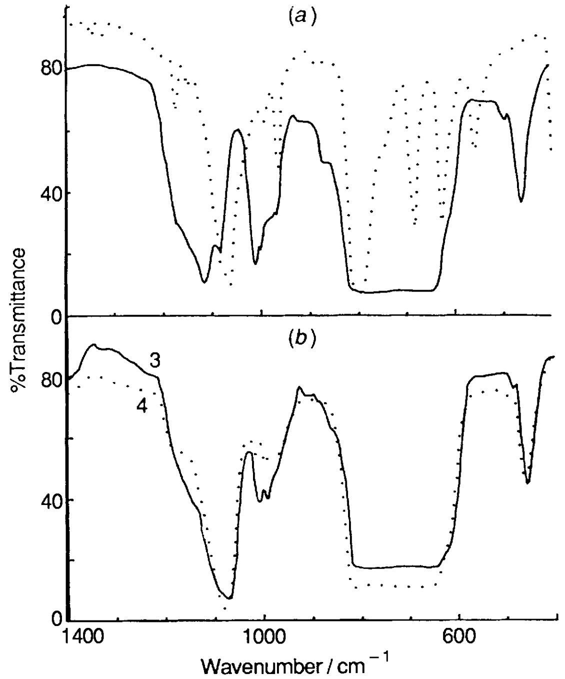

Fig. 1 Infrared solution spectra of $[U(ClO_4)_4]$ in the presence of *n* mol equivalents of tpao in dichloromethane (*a*) *n* = 2 and (*b*) *n* = 3 or 4. The dotted curve in (*a*) is the spectrum of $[UCl_2(tpao)_4(ClO_4)_2]$ in a KBr pellet

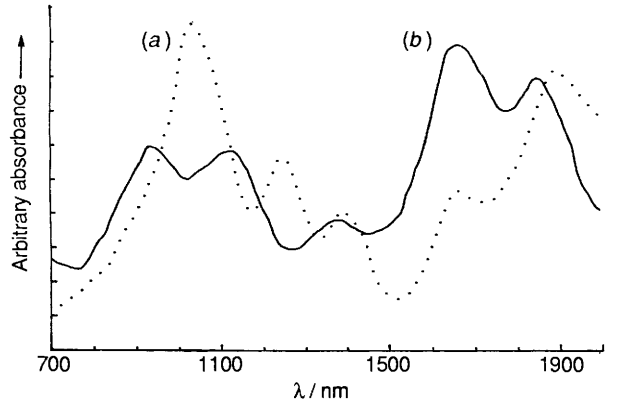

Fig. 2 Solid reflectance electronic spectra of $[U(ClO_4)_4(tpao)_4]$(*a*) and $[U(ClO_4)_4(tdpo)_5]$ (*b*)

electronic spectra of both solid $[UY_4(tpao)_4]$ and $[UY_4(tdpo)_5]$, Fig. 2, are uncharacteristic of either six- (one major band in the 1700–2000 nm region) or seven- and eight-co-ordinated (no significant bands in the same region) uranium(IV) species having oxygen-donor ligands. There is insufficient evidence to propose a structue for these chromophores. The spectra of both complexes dissolved in dichloromethane are typical of six-co-ordinated uranium(IV) chromophores, *viz.* single major bands at 1900 and 1890 nm for $[UY_4(tpao)_4]$ and $[UY_4(tdpo)_5]$ respectively. The infrared spectrum of the tdpo complex, dissolved in dichloromethane, reveals the presence of free ligand. The above spectral evidence indicates that although the stoichiometry of the solid complexes $[UY_4(tpao)_4]$ and $[UY_4(tdpo)_5]$ are different, the major species in solution are analogous.

$UX_2L_4Y_2$ *Complexes.—General behaviour.* All these complexes are slightly hygroscopic but indefinitely stable in a dry nitrogen atmosphere at room temperature. Thermal degradation studies indicate that gradual decomposition under nitrogen only starts at *ca.* 450 °C. The infrared spectra of the solid complexes contain symmetrical bands at 1100 and 625 cm^{-1} indicating the presence of unco-ordinated perchlorate ions. Shifts to lower energy in the ν(P=O) and ν(As=O) bands of the neutral ligands indicate co-ordination of these ligands. The shifts are larger for the bromo than for the corresponding chloro complexes. The solid reflectance electronic spectra of the complexes are all typical of six-co-ordinated uranium(IV) in that they have one major band in the 1800–2000 nm region and one in the region of 1000 nm (typical examples are depicted in Fig. 3). When the positions of the bands in the 1750–2050 nm range of the electronic spectra of these cationic uranium complexes, Table 1, and of the corresponding UCl_4L_2 complexes[1] are considered, certain trends are evident. The bands in the spectra of UCl_4L_2 compounds shift to higher wavelength (lower energy) as L is substituted in the order of increasing donor strength of the neutral ligands, *viz.* tppo, tdpo, tpyrpo, and tpao. Similar shifts are obtained for corresponding bromide and iodide compounds and when comparing the UCl_4L_2 and $[UCl_2L_4]^{2+}$ complexes, for the same L.

tpao *Complexes.* Solutions of UX_2Y_2 in acetone were titrated by the incremental addition of tpao to obtain specific U:L mol ratios.* The progress of the reactions was followed by

---

* 'Mol ratio of *x*' will be used for a U:L mol ratio of 1:*x* for the rest of the discussion (*x* = 0,1,2, *etc.*).

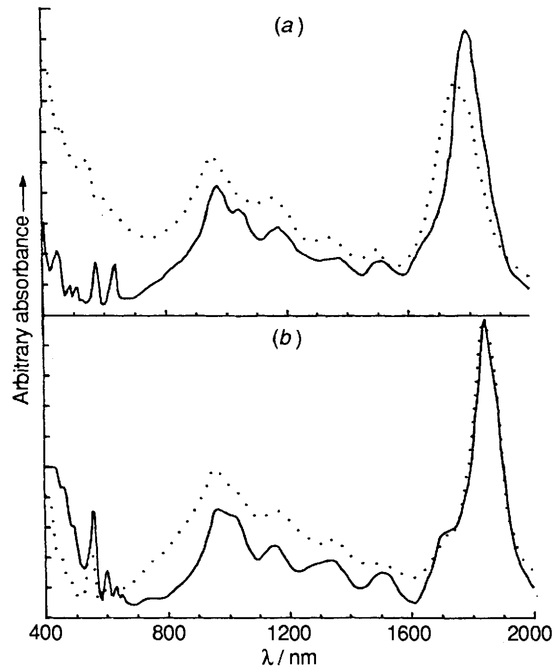

Fig. 3 Solid reflectance electronic spectra of (*a*) $[\mathrm{UCl_2(tpao)_4(ClO_4)_2}]$ (——) and $[\mathrm{UBr_2(tpao)_4(ClO_4)_2}]$ (····), (*b*) $[\mathrm{UCl_2(tpyrpo)_4(ClO_4)_2}]$ (——) and $[\mathrm{UBr_2(tpyrpo)_4(ClO_4)_2}]$ (····)

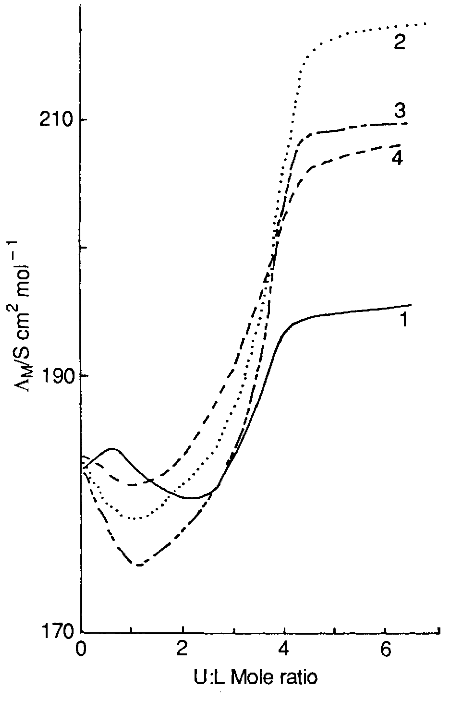

Fig. 4 Molar conductivities of 0.0035 mol dm^{-3} acetone solutions of $[\mathrm{UCl_2(ClO_4)_2}]$ as a function U:L mol ratio for L = tpao (1), tpyrpo (2), tdpo (3), and tppo (4)

monitoring conductance and spectral changes in these solutions. The conductometric results are portrayed in Fig. 4.

Chloro-complexes. The results obtained for X = Cl are represented in Scheme 1. The supporting evidence for the conclusion regarding a specific compound is indicated by an italic letter symbol directly below the compound (see Fig. 5 for spectral results).

Bromo-complexes. In order to interpret the spectra for the bromo systems it was necessary to study the $[\mathrm{UBr_4(tpao)}_n]$ system first. A $[\mathrm{UBr_4(tpao)_2}]$ solution in dichloromethane was

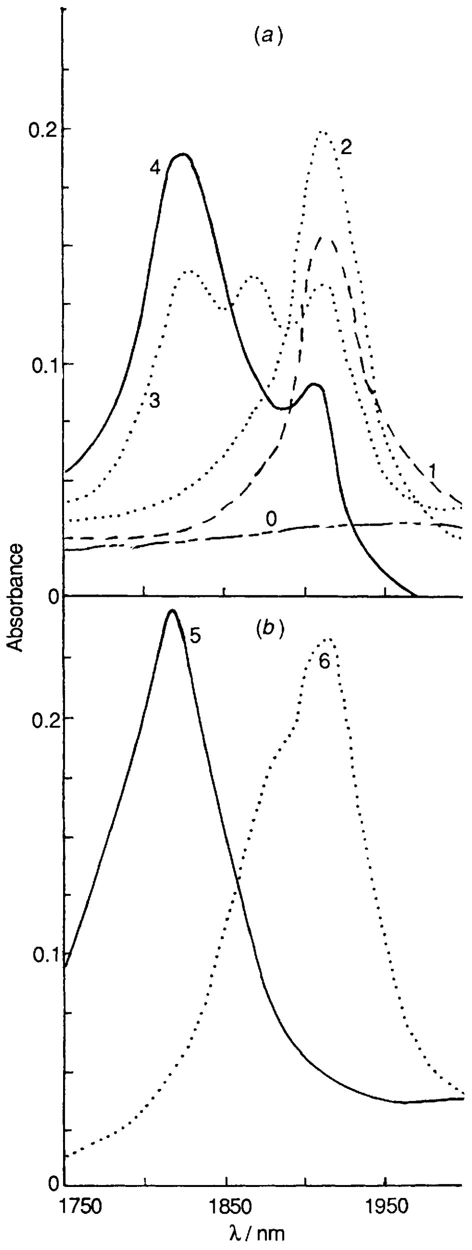

Fig. 5 (*a*) Electronic spectra of 0.004 mol dm^{-3} acetone solutions of $[\mathrm{UCl_2(ClO_4)_2}]$ having U:tpao mol ratios of 0, 1, 2, 3 and 4:1. The numbers on the curves indicate the mol ratio. (*b*) Spectra of $[\mathrm{UCl_2(tpao)_4(ClO_4)_2}]$ (5) and $[\mathrm{UCl_4(tpao)_2}]$ (6) in dichloromethane

$$\underset{(a)}{\mathrm{UCl_2Y_2(solv)}_x} \xrightarrow{2\mathrm{L}} \underset{(b),(c)}{\mathrm{UCl_4L_2}} + \underset{(a),(d)}{\mathrm{UY_4L_2(solv)}_y} \xrightarrow{\mathrm{L}} \underset{(b)}{\mathrm{UCl_4L_2}} +$$

$$\underset{(e),(f)}{[\mathrm{UCl_3L_3}]\mathrm{Y}} + \underset{(f),(g)}{\mathrm{UCl_2L_4Y_2}} + \underset{(a)}{\mathrm{UClL}_n\mathrm{(solv)}_n\mathrm{Y}} \text{ and/or}$$

$$\mathrm{UY_4L}_n\mathrm{(solv)}_x \xrightarrow{\mathrm{L}} \underset{(g),(i)}{\mathrm{UCl_2L_4Y_2}} + \underset{(b)}{\mathrm{UCl_4L_2}} + \underset{(h)}{\mathrm{UY_4L}_n\mathrm{(solv)}_x}$$

Scheme 1 (*a*) Higher than six-co-ordinated species present since no absorption band found in region of 1900 nm but a major band around 1200 nm; (*b*) band at 1910 nm [compare Fig. 5(*b*)]; (*c*) relative decrease in conductivity (Fig. 4) due to formation of non-electrolyte; (*d*) has low conductivity since it contains either co-ordinated or strongly ion-paired Y (Fig. 4, minimum in conductivity at this point); (*e*) band at 1860 nm; (*f*) assists in increase in conductivity by replacement of Y (Fig. 4); (*g*) band at 1820 nm [compare Fig. 5(*b*)]; (*h*) $\mathrm{UY_4L}_n$ species do not have bands indicating six-co-ordination even in a titration of $\mathrm{UY_4}$ *vs.* L, up to a mol ratio of 4 when precipitation starts; (*i*) major species formed at mol ratio 4 (see end-point in conductometric titration, Fig. 4)

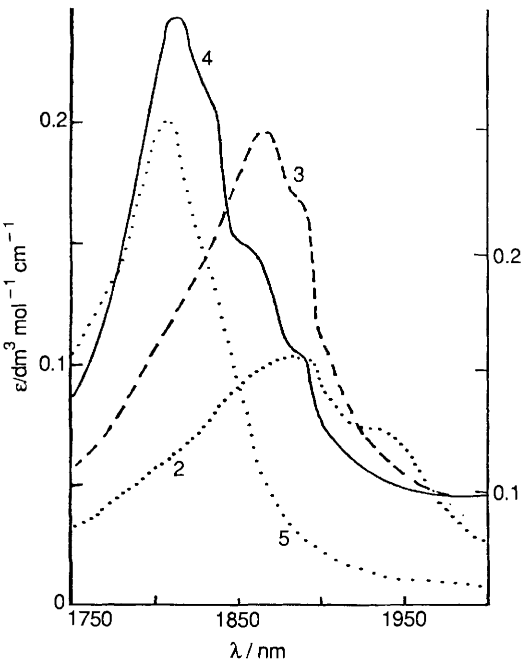

Fig. 6 Electronic spectra of 0.0038 mol dm^{-3} solutions of UBr_4 in acetone having U : tpao mol ratios of 2, 3 and 4 : 1. The numbers on the curves indicate the mol ratio. Curve 5 is the spectrum of $[UBr_2(tpao)_4(ClO_4)_2]$ in dichloromethane. The right ordinate refers to curve 5

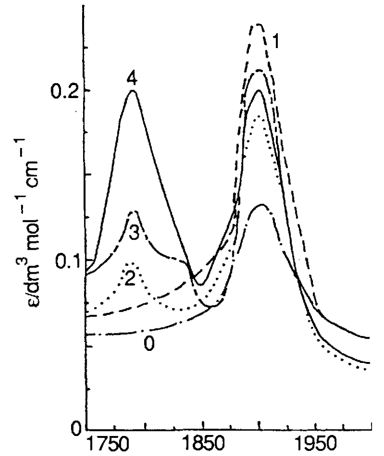

Fig. 7 Electronic spectra of 0.0038 mol dm^{-3} solutions of $[UBr_2(ClO_4)_2]$ in acetone having U : tpao mol ratios of 0, 1, 2, 3 and 4 : 1. The numbers on the curves indicate the mol ratios

titrated with tpao and the spectra recorded (Fig. 6). All the bands thus obtained have some low-symmetry character which could be ascribed to disproportionation. The bands at 1900, 1860 and 1820 nm may be assigned to $[UBr_4L_2]$, $[UBr_3L_3]^+$ and $[UBr_2L_4]^{2+}$ respectively; the last band corresponds closely to that found at 1810 nm in the spectrum of $[UBr_2L_4]Y_2$. If the spectra portrayed in Fig. 7 are interpreted in an analogous manner to those in Fig. 6, the conclusion is reached that the bromo system differs from the chloro in that only six-coordinated species, namely $[UBr_4L_2]$ and $[UBr_2L_4]^{2+}$, dominate throughout. Some small amounts of the former compound precipitates in the 1 to 2 mol ratio region. This redissolves upon addition of further ligand. At a mol ratio of 3 there is an indication (a shoulder at 1820 nm) that a small amount of $[UBr_3L_3]^+$ is present. The conductometric behaviours of the chloro and bromo systems are very similar.

P=O *Complexes*. The conductometric, Figs 4 and 8, and spectrophotometric results obtained from the study of UX_2Y_2 and tdpo, tpyrpo and tppo indicated that the behaviour of these

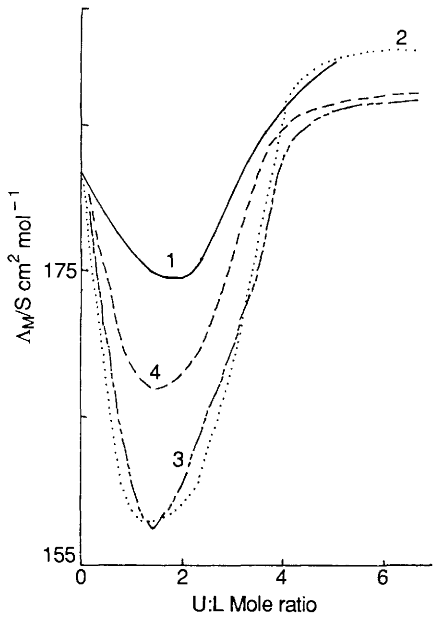

Fig. 8 Plots of molar conductivity *vs* mol ratio for 0.0035 mol dm^{-3} solutions of $[UBr_2(ClO_4)_2]$ in acetone titrated with tpao (1), tpyrpo (2), tdpo (3) and tppo (4)

ligands is similar. It was therefore decided to perform a detailed study on the tdpo–UX_2Y_2 system only.

The results obtained for X = Cl are represented in Scheme 2. See Fig. 9 for the spectral results.

$$\underset{(a)}{UCl_2Y_2(solv)_2} \xrightarrow{L} \underset{(b)\text{–}(d)}{UCl_4L_2} + \underset{(a)}{UY_4(solv)_x} \xrightarrow{2L} \underset{(b)}{UCl_4L_2} +$$

$$\underset{(e),(f)}{UY_4L_4} \xrightarrow{L} \underset{(g)}{[UCl_2L_4]Y_2} + \underset{(e)}{UY_4L_4} + \underset{(h)}{UCl_4L_2}$$

Scheme 2 (*a*) No band around 1900 nm, but bands around 1200 nm; (*b*) band at 1910 nm, compare Fig. 9(*b*); (*c*) slight turbidity due to precipitation of UCl_4L_2 in conductometric titration; (*d*) decrease in conductivity due to formation of non-electrolyte (Fig. 4); (*e*) band at ≈ 1880 nm, compare Fig. 9(*b*); (*f*) two isosbestic points (1840 and 1950 nm) observed in spectra of mol ratios 1 to 3 suggesting only the presence of two species; (*g*) shoulder at ≈ 1860 nm [compare Fig. 9 (*b*)]; (*h*) broad band around 1900 nm suggests the presence of some UCl_4L_2 (1910 nm)

Even at a mol ratio of 5 all three species are still present. This tendency to disproportionate is also suggested by the broadness of the absorption band at 1900 nm for UCl_4L_2 [Fig. 9(*b*)].

In order to interpret the spectral behaviour of the bromo system it is necessary first to investigate the reaction between UBr_4 and tdpo in dichloromethane. The results of a spectrophotometric titration in this solvent are given in Fig. 10. The broadness of the band attributed to $[UBr_4(tdpo)_2]$ suggests that some disproportionation to $[UBr_3(tdpo)_3]^+$ and $[UBr_5(tdpo)]^-$ occurs. Upon addition of excess of tdpo more of the cationic species forms; compare curve 5 in Fig. 10, *i.e.* 5 with 1. Upon addition of tdpo to UBr_2Y_2 in acetone solution it appears that the major species which initially forms is $[UBr_3(tdpo)_3]^+$; this is postulated as a result of the presence of a band at 1910 nm, Fig. 11. The conductivity also decreases up to a mol ratio of 1.5, Fig. 8. The formation of $[UBr_3(tdpo)_3]^+$ increases up to a mol ratio of 2, after which the concentration of the doubly charged cationic species rapidly increases. Spectral evidence for this is the appearance of a band at 1850 nm, curves 3, 4 and 5 in Fig. 11.

Solid Complexes.—The above study on solutions of uranium(IV) in the presence of various ligands and anions resulted in the identification of numerous cationic complexes on

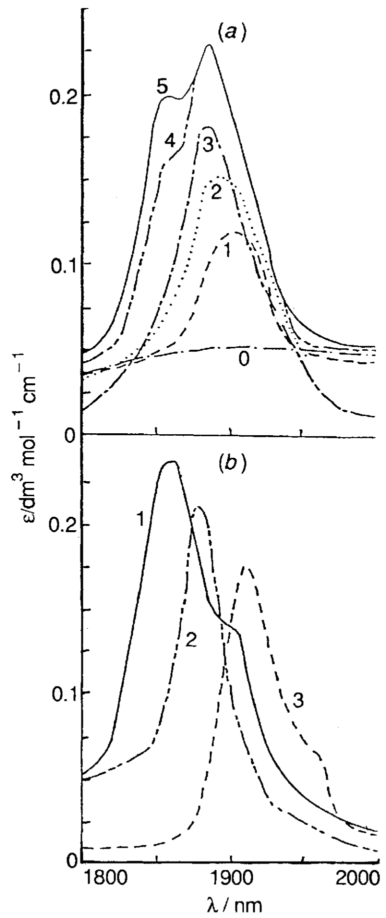

Fig. 9 Electronic spectra of 0.004 mol dm^{-3} solutions of (*a*) [$UCl_2(ClO_4)_2$] in acetone having U : tdpo mol ratios of 1, 2, 3, 4 and 5 numbers on the curves indicate the mol ratios) and (*b*) [$UCl_2(tdpo)_4$-$(ClO_4)_2$] (1), [$U(ClO_4)_4(tdpo)_5$] (2), both in acetone, and [UCl_4-$(tdpo)_2$] (3) in dichloromethane

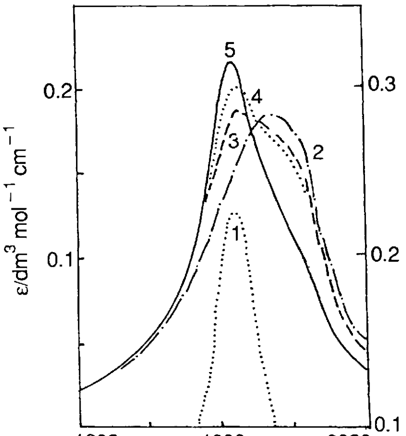

Fig. 10 Electronic spectra of 0.004 mol dm^{-3} solutions of [UBr_4-$(tdpo)_2$] in acetone titrated with tdpo dissolved in dichloromethane. The numbers on the curves indicate the U:tdpo mol ratios. The electronic spectrum of a solution of [$UBr_3(tdpo)_3$]BPh_4 in dichloromethane is given as curve 1. The right ordinate refers to the latter spectrum

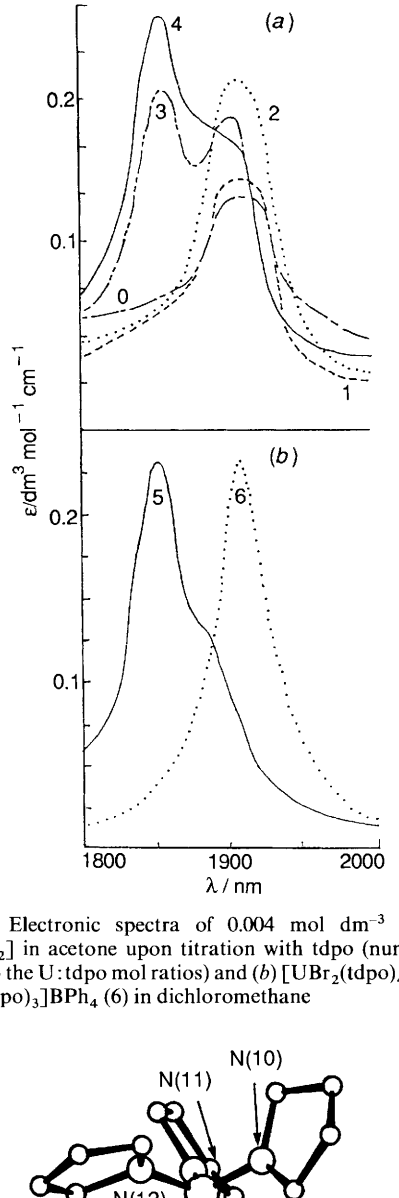

Fig. 11 (*a*) Electronic spectra of 0.004 mol dm^{-3} solutions of [$UBr_2(ClO_4)_2$] in acetone upon titration with tdpo (numbers on the curves refer to the U : tdpo mol ratios) and (*b*) [$UBr_2(tdpo)_4(ClO_4)_2$] (5) and [$UBr_3(tdpo)_3$]BPh_4 (6) in dichloromethane

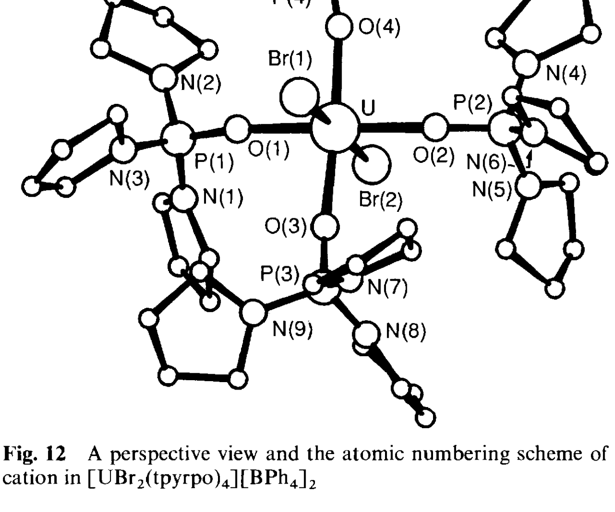

Fig. 12 A perspective view and the atomic numbering scheme of the cation in [$UBr_2(tpyrpo)_4$][BPh_4]$_2$

the basis of spectral evidence. Attempts were made to isolate some of these complexes from solution by the addition of the large anion tetraphenylborate. The solid compound could then be analysed and characterized and its structure determined unequivocally by X-ray techniques. This would then provide additional evidence for the above conclusions. This was achieved for the isostructural pair of compounds [$UBr_2(tpyrpo)_4$][BPh_4]$_2$ and [$UI_2(tpyrpo)_4$][BPh_4]$_2$. Although the iodo complexes of uranium(IV) are discussed elsewhere,[1] it is convenient to discuss the two structures together.

Table 2 Fractional atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for $[UBr_2(tpyrpo)_4][BPh_4]_2$ and $[UI_2(tpyrpo)_2][BPh_4]_2$

	$[UBr_2(tpyrpo)_4][BPh_4]_2$			$[UI_2(tpyrpo)_2][BPh_4]_2$		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
U	2 426(0)	3 161(0)	8 882(0)	2 428(0)	3 180(0)	8 883(0)
X(1)	1 958(1)	3 174(2)	7 683(1)	1 934(1)	3 168(1)	7 590(1)
X(2)	2 851(1)	3 097(2)	10 095(1)	2 865(1)	3 113(2)	10 191(1)
O(1)	2 993(4)	2 311(7)	8 629(6)	3 000(4)	2 348(7)	8 650(5)
O(2)	1 899(4)	4 029(7)	9 227(5)	1 908(4)	4 057(7)	9 229(5)
O(3)	1 976(4)	2 044(7)	9 014(5)	1 979(4)	2 067(7)	9 018(5)
O(4)	2 854(4)	4 251(7)	8 644(5)	2 852(4)	4 255(7)	8 641(5)
P(1)	3 407(2)	1 701(3)	8 637(2)	3 414(1)	1 732(3)	8 644(2)
P(2)	1 654(2)	4 621(3)	9 632(2)	1 649(1)	4 644(3)	9 618(2)
P(3)	1 579(2)	1 400(3)	8 987(2)	1 579(1)	1 425(3)	8 986(2)
P(4)	3 129(2)	4 889(3)	8 311(2)	3 132(1)	4 908(3)	8 311(2)
N(1)	3 458(5)	1 130(9)	9 248(7)	3 454(5)	1 173(10)	9 252(7)
N(2)	3 896(5)	2 212(9)	8 623(6)	3 900(5)	2 253(9)	8 623(6)
N(3)	3 295(5)	1 125(11)	8 032(8)	3 305(6)	1 151(9)	8 040(7)
N(4)	1 972(6)	5 470(10)	9 728(7)	1 941(6)	5 508(10)	9 694(7)
N(5)	1 619(5)	4 236(10)	10 301(7)	1 608(5)	4 235(9)	10 280(7)
N(6)	1 122(5)	4 824(9)	9 285(7)	1 115(5)	4 823(9)	9 286(7)
N(7)	1 098(5)	1 710(9)	8 560(7)	1 104(5)	1 725(9)	8 572(6)
N(8)	1 456(5)	1 266(9)	9 656(7)	1 455(6)	1 261(10)	9 660(7)
N(9)	1 764(5)	529(9)	8 728(7)	1 765(5)	555(9)	8 725(6)
N(10)	2 808(5)	5 732(9)	8 248(7)	2 798(5)	5 740(9)	8 238(7)
N(11)	3 657(5)	5 043(9)	8 721(7)	3 649(6)	5 069(10)	8 718(7)
N(12)	3 224(5)	4 603(9)	7 624(7)	3 246(6)	4 601(10)	7 641(7)
C(1)	3 036(9)	720(16)	9 450(12)	3 048(9)	729(16)	9 458(12)
C(2)	3 226(10)	284(18)	10 051(13)	3 223(10)	274(17)	10 017(12)
C(3)	3 749(11)	381(19)	10 116(13)	3 758(10)	332(18)	10 080(12)
C(4)	3 911(8)	902(14)	9 652(11)	3 904(8)	982(15)	9 662(10)
C(5)	4 071(8)	2 891(13)	9 060(9)	4 066(8)	2 914(13)	9 079(10)
C(6)	4 642(8)	2 855(14)	9 069(11)	4 633(9)	2 865(15)	9 119(11)
C(7)	4 662(8)	2 641(15)	8 438(11)	4 685(9)	2 677(16)	8 469(11)
C(8)	4 262(7)	1 986(13)	8 215(9)	4 271(7)	2 024(14)	8 244(9)
C(9)	3 085(8)	1 429(15)	7 420(11)	3 097(7)	1 462(13)	7 436(10)
C(10)	3 000(9)	602(16)	7 044(11)	3 006(9)	642(16)	7 092(11)
C(11)	3 270(9)	−34(17)	7 389(13)	3 282(10)	−7(18)	7 418(13)
C(12)	3 489(8)	245(14)	8 008(10)	3 518(8)	299(14)	8 019(10)
C(13)	2 512(8)	5 480(14)	9 888(10)	2 508(8)	5 519(15)	9 850(10)
C(14)	2 596(11)	6 433(19)	10 001(13)	2 578(11)	6 486(18)	9 936(13)
C(15)	2 164(9)	6 900(18)	9 773(11)	2 133(9)	6 957(17)	9 760(11)
C(16)	1 739(9)	6 344(16)	9 825(12)	1 724(8)	6 338(15)	9 801(11)
C(17)	1 436(7)	3 381(14)	10 353(10)	1 411(7)	3 395(13)	10 337(9)
C(18)	1 363(12)	3 385(23)	11 066(16)	1 325(11)	3 419(20)	11 033(14)
C(19)	1 666(12)	3 965(22)	11 341(16)	1 659(11)	3 976(21)	11 354(15)
C(20)	1 785(9)	4 617(18)	10 904(13)	1 799(9)	4 637(17)	10 880(12)
C(21)	700(8)	5 022(14)	9 634(11)	697(9)	5 032(15)	9 613(11)
C(22)	286(9)	5 062(16)	9 108(12)	300(10)	5 023(17)	9 102(13)
C(23)	494(9)	5 297(16)	8 547(12)	482(9)	5 309(17)	8 527(12)
C(24)	1 016(7)	5 009(13)	8 635(10)	1 012(7)	4 987(13)	8 621(9)
C(25)	882(9)	1 338(17)	7 969(12)	863(9)	1 340(17)	8 011(12)
C(26)	482(9)	1 909(19)	7 737(11)	453(9)	1 901(19)	7 758(11)
C(27)	568(9)	2 728(16)	8 073(12)	535(9)	2 677(17)	8 052(11)
C(28)	867(8)	2 538(14)	8 675(10)	880(8)	2 549(14)	8 668(10)
C(29)	949(9)	1 001(17)	9 809(13)	978(9)	1 038(16)	9 848(12)
C(30)	1 086(12)	906(21)	10 469(17)	1 082(11)	952(20)	10 513(15)
C(31)	1 570(10)	1 049(17)	10 772(12)	1 572(10)	1 076(17)	10 759(12)
C(32)	1 833(8)	1 121(14)	10 193(10)	1 835(8)	1 138(14)	10 185(10)
C(33)	2 027(7)	500(12)	8 184(9)	2 036(7)	523(12)	8 172(8)
C(34)	1 966(10)	−436(19)	7 978(13)	1 973(9)	−402(18)	8 004(13)
C(35)	1 887(9)	−875(17)	8 539(12)	1 902(10)	−861(18)	8 535(13)
C(36)	1 580(8)	−309(15)	8 882(11)	1 592(8)	−279(15)	8 883(11)
C(37)	3 022(8)	6 570(14)	8 111(10)	3 004(8)	6 578(14)	8 102(11)
C(38)	2 587(9)	7 120(15)	8 075(11)	2 580(9)	7 154(15)	8 062(10)
C(39)	2 140(8)	6 588(14)	7 881(11)	2 139(9)	6 603(15)	7 866(11)
C(40)	2 279(7)	5 704(12)	8 144(9)	2 270(7)	5 719(13)	8 112(9)
C(41)	4 114(9)	5 354(16)	8 467(12)	4 093(9)	5 384(16)	8 483(11)
C(42)	4 446(11)	5 494(19)	9 046(14)	4 435(11)	5 529(19)	9 031(14)
C(43)	4 238(9)	5 205(15)	9 614(11)	4 236(9)	5 244(16)	9 596(12)
C(44)	3 707(8)	5 120(14)	9 409(10)	3 696(9)	5 173(16)	9 402(11)
C(45)	3 503(9)	3 796(15)	7 528(11)	3 499(8)	3 799(15)	7 553(10)
C(46)	3 309(10)	3 567(19)	6 855(14)	3 338(11)	3 588(11)	6 865(15)
C(47)	3 010(13)	4 222(24)	6 606(17)	3 007(14)	4 237(15)	6 626(18)
C(48)	2 927(9)	4 863(16)	7 070(12)	2 956(9)	4 881(17)	7 088(12)
B(1)	9 002(7)	2 051(13)	8 857(9)	9 004(7)	2 037(14)	8 881(9)

Table 2 (*continued*)

	$[UBr_2(tpyrpo)_4][BPh_4]_2$			$[UI_2(tpyrpo)_2][BPh_4]_2$		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
C(49)	9 185(4)	1 089(6)	8 638(6)	9 209(4)	1 089(6)	8 667(6)
C(50)	8 905(4)	608(6)	8 197(6)	8 942(4)	610(6)	8 214(6)
C(51)	9 082(4)	−144(6)	8 000(6)	9 127(4)	−139(6)	8 026(6)
C(52)	9 540(4)	−416(6)	8 245(6)	9 579(4)	−411(6)	8 291(6)
C(53)	9 821(4)	65(6)	8 687(6)	9 846(4)	67(6)	8 644(6)
C(54)	9 644(4)	817(6)	8 883(6)	9 661(4)	818(6)	8 932(6)
C(55)	9 129(4)	2 771(8)	8 360(6)	9 134(5)	2 763(7)	8 385(6)
C(56)	9 227(4)	2 561(8)	7 775(6)	9 225(5)	2 542(7)	7 801(5)
C(57)	9 343(4)	3 184(8)	7 377(6)	9 335(5)	3 158(7)	7 395(5)
C(58)	9 361(4)	4 018(8)	7 565(6)	9 353(5)	3 995(7)	7 573(5)
C(59)	9 263(4)	4 228(8)	8 151(6)	9 261(5)	4 216(7)	8 157(5)
C(60)	9 147(4)	3 604(8)	8 548(6)	9 151(5)	3 600(7)	8 563(5)
C(61)	8 392(3)	1 993(9)	8 837(6)	8 402(3)	1 972(8)	8 853(6)
C(62)	8 083(3)	2 626(9)	8 589(6)	8 093(3)	2 611(8)	8 617(6)
C(63)	7 590(3)	2 555(9)	8 601(6)	7 602(3)	2 537(8)	8 632(6)
C(64)	7 406(3)	1 850(9)	8 860(6)	7 419(3)	1 825(8)	8 881(6)
C(65)	7 715(3)	1 217(9)	9 107(6)	7 727(3)	1 187(8)	9 117(6)
C(66)	8 208(3)	1 288(9)	9 096(6)	8 219(3)	1 260(8)	9 102(6)
C(67)	9 262(4)	2 259(8)	9 575(4)	9 265(4)	2 264(8)	9 589(4)
C(68)	9 719(4)	2 617(8)	9 651(4)	9 715(4)	2 645(8)	9 671(4)
C(69)	9 974(4)	2 708(8)	10 238(4)	9 967(4)	2 732(8)	10 258(4)
C(70)	9 773(4)	2 441(8)	10 749(4)	9 769(4)	2 437(8)	10 763(4)
C(71)	9 316(4)	2 084(8)	10 673(4)	9 319(4)	2 056(8)	10 682(4)
C(72)	9 061(4)	1 992(8)	8 086(4)	9 068(4)	1 969(8)	10 094(4)
B(2)	4 705(7)	8 276(16)	8 360(11)	4 683(6)	8 300(14)	8 354(9)
C(73)	5 148(4)	7 562(7)	8 448(6)	5 110(4)	7 572(8)	8 422(6)
C(74)	5 527(4)	7 677(7)	8 922(6)	5 489(4)	7 664(8)	8 892(6)
C(75)	5 876(4)	7 059(7)	9 049(6)	5 834(4)	7 038(8)	9 008(6)
C(76)	5 848(4)	6 327(7)	8 701(6)	5 802(4)	6 320(8)	8 647(6)
C(77)	5 469(4)	6 213(7)	8 227(6)	5 423(4)	6 228(8)	8 172(6)
C(78)	5 119(4)	6 830(7)	8 101(6)	5 077(4)	6 854(8)	8 060(6)
C(79)	4 320(3)	8 091(8)	8 882(5)	4 294(4)	8 124(8)	8 865(5)
C(80)	4 492(3)	7 770(8)	9 460(5)	4 472(4)	7 807(8)	9 441(5)
C(81)	4 182(3)	7 672(8)	9 897(5)	4 167(4)	7 701(8)	9 882(5)
C(82)	3 699(3)	7 894(8)	9 756(5)	3 683(4)	7 912(8)	9 748(5)
C(83)	3 527(3)	8 215(8)	9 178(5)	3 505(4)	8 229(8)	9 172(5)
C(84)	3 838(3)	8 313(8)	8 741(5)	3 810(4)	8 335(8)	8 731(5)
C(85)	4 389(4)	8 255(9)	7 648(4)	4 370(4)	8 280(8)	7 638(4)
C(86)	4 095(4)	7 563(9)	7 494(4)	4 076(4)	7 588(8)	7 489(4)
C(87)	3 839(4)	7 492(9)	6 906(4)	3 820(4)	7 515(8)	6 904(4)
C(88)	3 878(4)	8 113(9)	6 471(4)	3 858(4)	8 133(8)	6 467(4)
C(89)	4 173(4)	8 805(9)	6 624(4)	4 153(4)	8 824(8)	6 616(4)
C(90)	4 428(4)	8 876(9)	7 212(4)	4 409(4)	8 898(8)	7 202(4)
C(91)	4 964(4)	9 221(6)	8 520(5)	4 950(4)	9 232(6)	8 510(5)
C(92)	5 301(4)	9 489(6)	8 154(5)	5 285(4)	9 499(6)	8 141(5)
C(93)	5 540(4)	10 246(6)	8 280(5)	5 527(4)	10 253(6)	8 266(5)
C(94)	5 443(4)	10 735(6)	8 773(5)	5 434(4)	10 740(6)	8 761(5)
C(95)	5 106(4)	10 467(6)	9 139(5)	5 100(4)	10 473(6)	9 131(5)
C(96)	4 866(4)	9 710(6)	9 013(5)	4 858(4)	9 719(6)	9 005(5)

The structural arrangement of the cation together with the adopted atom numbering are depicted in Fig. 12. Selected interatomic distances and angles are given in Table 3. The uranium atom is in a six-co-ordinate *trans*-octahedral environment with small distortions from the idealized geometry. The X(1)–U–X(2) axes show little deviation from linearity and the four oxygen atoms of each complex are displaced by ±0.11 Å in slightly staggered configurations from the mean equatorial planes. The mean U–Br distance of 2.775 Å compares well with values of 2.774(6) Å in $[UBr_4(tppo)_2]$,[16] 2.779(3) Å in $[UBr_4(tdpo)_2]$,[1] 2.779(3) Å in $[UBr_4\{(PhMeN)_2CO\}_2]$[17] and 2.784(6) Å in $[UBr_4(tmu)_2]$ (tmu = tetramethylurea).[18] The mean U–I bond distance of 2.980 Å can only be compared with a mean value of 3.011 Å found in $[UI_4(tmu)_2]$.[12] The small disparity in these bond distances can readily be ascribed to the different nature of the co-ordination spheres in the two complexes. The difference between the U–Br and U–I bond distances in the two $[UX_2(tpyrpo)_4][BPh_4]_2$ complexes is 0.23 Å. This compares favourably with the difference of 0.21 Å found in the $[UX_4(tmu)_2]$ complexes. These values are intermediate between the differences in the covalent, ionic and atomic radii for these two halogen atoms which are 0.20, 0.24 and 0.25 Å respectively. The four U–O bond distances in the iodine structure fall in a range from 2.20 to 2.24 Å with a mean value of 2.216 Å. The mean of the U–O bonds for the bromine structure is 2.230 Å. Comparison of these values with that of 2.233(7) Å found in the $[UCl_4(tpyrpo)_2]$ complex[17] confirms that the average U–O bond distances become slightly longer as the halide is changed from iodide to bromide to chloride. This is in agreement with the change in magnitude in the shift in ν(P=O) absorption band in the infrared spectra of the corresponding complexes. Although the mean P–N bond lengths show a reverse order, the difference is not significant if experimental error is considered. These trends can readily be rationalized in terms of the pattern of Lewis acidity exhibited by the uranium(IV) halides, *viz.* iodide > bromide > chloride. The

Table 3 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for $[UBr_2(tpyrpo)_4][BPh_4]_2$ **1** and $[UI_2(tpyrpo)_4][BPh_4]_2$ **2**

	1	**2**		**1**	**2**
U–X(1)	2.780(2)	2.988(2)	P(1)–N(2)	1.604(15)	1.607(15)
U–X(2)	2.771(2)	2.971(2)	P(1)–N(3)	1.614(18)	1.616(16)
U–O(1)	2.225(12)	2.203(12)	P(2)–N(4)	1.624(17)	1.605(17)
U–O(2)	2.239(12)	2.235(12)	P(2)–N(5)	1.612(16)	1.616(16)
U–O(3)	2.232(11)	2.227(11)	P(2)–N(6)	1.615(15)	1.602(14)
U–O(4)	2.223(11)	2.200(11)	P(3)–N(7)	1.614(15)	1.583(14)
O(1)–P(1)	1.517(13)	1.527(12)	P(3)–N(8)	1.573(17)	1.592(17)
O(2)–P(2)	1.529(13)	1.523(12)	P(3)–N(9)	1.619(16)	1.620(15)
O(3)–P(3)	1.514(12)	1.518(12)	P(4)–N(10)	1.618(15)	1.624(15)
O(4)–P(4)	1.528(13)	1.549(12)	P(4)–N(11)	1.645(14)	1.619(16)
P(1)–N(1)	1.616(16)	1.600(16)	P(4)–N(12)	1.637(16)	1.628(17)
O(3)–U–O(4)	173.9(4)	173.7(4)	N(2)–P(1)–N(3)	110.2(8)	109.8(8)
O(2)–U–O(4)	90.0(4)	89.7(4)	N(1)–P(1)–N(3)	110.4(9)	110.5(8)
O(2)–U–O(3)	92.2(4)	92.7(4)	N(1)–P(1)–N(2)	109.1(8)	110.7(8)
O(1)–U–O(4)	89.4(4)	88.7(4)	O(2)–P(2)–N(6)	108.2(7)	110.2(7)
O(1)–U–O(3)	89.0(4)	89.7(4)	O(2)–P(2)–N(5)	112.7(8)	110.9(7)
O(1)–U–O(2)	174.4(4)	172.8(4)	O(2)–P(2)–N(4)	108.0(8)	108.2(8)
X(2)–U–O(4)	94.7(3)	95.6(3)	N(5)–P(2)–N(6)	109.8(8)	107.7(8)
X(2)–U–O(3)	91.2(3)	90.4(3)	N(4)–P(2)–N(6)	110.5(8)	109.1(8)
X(2)–U–O(2)	85.0(3)	83.9(3)	N(4)–P(2)–N(5)	107.7(8)	110.8(8)
X(2)–U–O(1)	89.5(3)	89.3(3)	O(3)–P(3)–N(9)	109.2(7)	108.9(7)
X(1)–U–O(4)	88.3(3)	88.3(3)	O(3)–P(3)–N(8)	108.2(8)	109.0(7)
X(1)–U–O(3)	85.9(3)	85.7(3)	O(3)–P(3)–N(7)	111.6(7)	112.5(7)
X(1)–U–O(2)	94.0(3)	95.1(3)	N(8)–P(3)–N(9)	109.6(8)	108.2(8)
X(1)–U–O(1)	91.6(3)	91.8(3)	N(7)–P(3)–N(9)	110.1(8)	110.2(7)
X(1)–U–X(2)	176.9(1)	176.0(1)	N(7)–P(3)–N(8)	108.1(8)	108.0(8)
U–O(1)–P(1)	165.0(8)	167.0(7)	O(4)–P(4)–N(12)	114.5(7)	113.5(7)
U–O(2)–P(2)	162.8(7)	164.9(7)	O(4)–P(4)–N(11)	108.4(7)	108.9(7)
U–O(3)–P(3)	165.5(7)	164.9(7)	O(4)–P(4)–N(10)	106.5(7)	105.9(7)
U–O(4)–P(4)	164.6(7)	165.7(7)	N(11)–P(4)–N(12)	107.3(8)	105.9(8)
O(1)–P(1)–N(3)	107.2(8)	108.7(7)	N(10)–P(4)–N(12)	108.3(8)	110.0(8)
O(1)–P(1)–N(2)	109.3(7)	108.5(7)	N(10)–P(4)–N(11)	111.9(8)	112.8(8)
O(1)–P(1)–N(1)	110.6(8)	108.6(7)			

structural details concerning the tpyrpo ligands in the two complexes described here are in good agreement with each other as well as with the parameters for $[UCl_4(tpyrpo)_2]$. The pyrrolidinyl rings are puckered in a similar manner to that described in $[UCl_4(tpyrpo)_2]$. The nitrogen, phosphorus and adjacent carbon atoms are generally coplanar but a number of rings show considerable deviations. This results in different P–N bond lengths and strengths. The infrared spectra of uranium(IV) complexes containing tpyrpo usually show unsymmetrical or even split ν(P–N) absorption bands. This phenomenon may be explained in terms of these deviations.

Acknowledgements

The authors acknowledge the financial assistance received from the Foundation for Research and Development and the University of Port Elizabeth.

References

1 Part 41, J. G. H. du Preez, H. E. Rohwer, B. J. A. M. van Brect, B. Zeelie, U. Casellato and R. Graziani, *Inorg. Chim. Acta*, in the press.

2 K. W. Bagnall, *Coord. Chem. Rev.*, 1967, **2**, 145; *Comprehensive Inorganic Chemistry*, Pergamon, New York, 1973, vol. 5, p. 151.

3 D. Brown, *International Revue of Science*, ed. K. W. Bagnall, M. T. P. and Butterworths, London, 1972, ch. 3.

4 K. W. Bagnall, *Comprehensive Co-ordination Chemistry*, Pergamon, Oxford, 1987, vol. 3, p. 1129.

5 K. W. Bagnall, D. Brown, P. J. Jones and J. G. H. du Preez, *J. Chem. Soc. A*, 1966, 737.

6 B. C. Lane and L. M. Venanzi, *Inorg. Chim. Acta*, 1969, **3**, 239.

7 J. G. H. du Preez, B. J. Gellatly and M. L. Gibson, *J. Chem. Soc., Dalton Trans.*, 1977, 1062.

8 J. G. H. du Preez and B. Zeelie, *Inorg. Chim. Acta*, 1987, **139**, 105.

9 J. G. H. du Preez, D. R. Groot and H. E. Rohwer, *S. Afr. Sci. J.*, 1991, **35**, 173.

10 J. G. H. du Preez, B. J. Gellatly, G. Jackson, L. R. Nassimbeni and A. L. Rodgers, *Inorg. Chim. Acta*, 1978, **27**, 181.

11 J. G. H. du Preez and B. Zeelie, *Inorg. Chim. Acta*, 1986, **118**, L25.

12 J. G. H. du Preez, B. Zeelie, U. Casellato and R. Graziani, *Inorg. Chim. Acta*, 1987, **129**, 289.

13 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

14 G. M. Sheldrick, SHELX 76, Program for crystal structure determinations, University of Cambridge, 1976; M. Nardelli, *Comput. Chem.*, 1983, **7**, 96; S. Motherwell, PLUTO 78, Program for plotting molecular and crystal packing diagrams, University of Cambridge, 1978.

15 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

16 G. Bombieri, F. Benetollo, K. W. Bagnall and M. J. Plews, *J. Chem. Soc., Dalton Trans.*, 1983, 343.

17 J. F. de Wet and M. R. Caira, *J. Chem. Soc., Dalton Trans.*, 1986, 2043 and refs. therein.

18 J. G. H. du Preez, B. Zeelie, U. Casellato and R. Graziani, *Inorg. Chim. Acta*, 1986, 122, 119.

Received 23*rd November* 1990; *Paper* 0/05285J