The Chemistry of Uranium. Part 18.[†] Arsine Oxide and Phosphine Oxide Complexes of Uranium Tetrahalides

By **Jan G. H. du Preez,*** **Barry J. Gellatly,** and **Marjorie L. Gibson,** Uranium Chemistry Research Unit, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, South Africa

A comparative study has been made between various arsine oxide and phosphine oxide complexes of uranium tetrahalides both in acetone solution and in the solid state. Conductimetric, potentiometric, and spectrophotometric methods have been used in solution, spectroscopic and structural methods on solids. The significantly greater ionising power of arsine oxide ligands is indicated and is discussed together with the structural differences between arsine oxide and phosphine oxide complexes of the type $UCl_4\cdot2L$ and $UX_4\cdot6L$ [X = Cl and Br; L = AsR_3O, PR_3O, or $P(NMe_2)_3O$; R = Me, Et, or Ph].

A NUMBER of phosphine oxide and arsine oxide complexes of uranium tetrachloride and tetrabromide have previously been investigated.[1-7] These studies have consisted mainly of the preparation and characterisation of solid complexes, and little or no solution chemistry has been reported. Although phosphine and arsine oxides appear to be very similar in their donor properties (*e.g.* stoicheiometries and general features of solid complexes, *viz.* $UCl_4\cdot2L$ [5] and $CoCl_2\cdot2L$ [8,9]), some differences are known (*e.g.* UCl_5 forms [10] a 1 : 1 complex with

---

[†] Part 17 is ref. 14.

[1] P. Gans and B. C. Smith, *J. Chem. Soc.*, 1964, 4172.

[2] K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc.* (*A*), 1966, 737.

[3] D. Brown, J. Hill, and C. E. F. Rickard, *J. Chem. Soc.* (*A*), 1970, 497.

[4] P. Day and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 197.

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

[6] B. C. Smith and M. A. Wassef, *J. Chem. Soc.* (*A*), 1968, 1817.

[7] Z. M. S. Al-Kazzaz, K. W. Bagnall, and D. Brown, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1493.

[8] A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc.* (*A*), 1968, 2039.

[9] A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc.* (*A*), 1968, 987.

[10] K. W. Bagnall, D. Brown, and J. G. H. du Preez, *J. Chem. Soc.*, 1965, 5217.

triphenylphosphine oxide but chlorinates [11] triphenylarsine oxide).

The results of recent conductimetric [12] and potentiometric [13] studies of the donor strength of neutral ligands towards certain Lewis acids in acetone point to more significant differences in donor properties than previously anticipated. Furthermore, an attempt [14] to describe uranium(IV)–ligand interaction theoretically, using an ionic model, stressed the need for more experimental information. A more detailed comparative study of these properties for a number of phosphine and arsine oxide ligands was therefore undertaken, both in solution and the solid state.

The R groups in the PR_3O and AsR_3O ligands were varied systematically: R = methyl (tmpo, tmao), ethyl (tepo, teao), phenyl (tppo, tpao), and dimethylamino (tdpo). Using these ligands, a number of new complexes, as well as known complexes, of the uranium tetrahalides UX_4 (X = Cl, Br, or I) and thorium tetrachloride have been prepared. The solid complexes were studied by diffuse-reflectance spectral and magnetic-susceptibility methods. Conductimetric, potentiometric, and spectrophotometric titrations were performed in acetone solution. (Although UCl_4 and UBr_4 were mainly used as Lewis acids, some studies were also carried out using UI_4 and $ThCl_4$.)

EXPERIMENTAL

All the hygroscopic materials were handled in a dry-nitrogen-atmosphere box. Uranium tetrachloride,[15] $UBr_4\cdot4MeCN$,[16] and $UI_4\cdot8cpl$ (ref. 17, cpl = ε-caprolactam) were prepared as previously. Commercial triphenylphosphine oxide (tppo), triphenylarsine oxide (tpao), tris(dimethylamino)phosphine oxide (tdpo), and tetra-n-butylammonium chloride and bromide were used as supplied. Trimethylphosphine oxide [9] (tmpo), triethylphosphine oxide [18] (tepo), trimethylarsine oxide [19] (tmao), and triethylarsine oxide [19] (teao) were prepared by standard procedures and sublimed *in vacuo*. Pro Analysi grade acetone (E. Merck) was deoxygenated with dry nitrogen before use. Standard solutions of UCl_4 and UBr_4 in acetone were prepared by dissolving the tetrahalides in deoxygenated acetone, filtering off any insoluble material, and making up to a known volume. The solutions were then analysed for U^{IV} and halide ion. Fresh solutions were prepared each day. The ligand solutions were prepared by dissolving the ligand in acetone and then diluting to the required concentration.

$MX_4\cdot2L$.—Uranium (or thorium) tetrachloride or $UBr_4\cdot4MeCN$ (*ca.* 2 g) was dissolved in ice-cold acetone (*ca.* 20 cm^3) and allowed to stand for 10 min. Any solid impurities were filtered off and the solution of 2 equivalents of ligand in acetone was added dropwise with stirring. The solid product was filtered off, washed with acetone, and dried *in vacuo*.

$MX_4\cdot4L$ *and* $MX_4\cdot6L$.—Uranium (or thorium) tetrachloride, $UBr_4\cdot4MeCN$, or $UI_4\cdot8cpl$ (*ca.* 2 g) was dissolved in ice-cold acetone (*ca.* 20 cm^3) and allowed to stand for 10 min. Any solid impurities were filtered off and the solution was added dropwise to a stirred solution of either 4 or 6 equivalents of ligand in acetone. The solid product was washed with acetone and dried *in vacuo*.

Uranium(IV) [20] and thorium(IV) [21] were determined by published methods. Chloride, bromide, and iodide were determined potentiometrically. Conductimetric and potentiometric titrations were performed as previously described.[12,13] Electronic spectra of solutions were recorded on a Beckman Acta M(VII) spectrophotometer in 0.5-, 1-, or 4-cm silica cells. Electronic spectra of solids were obtained at room temperature on a Beckman DK-2A instrument by diffuse reflectance. Infrared spectra were recorded, using Perkin-Elmer 457 (250—4 000 cm^{-1}) and 180 (150—400 cm^{-1}) instruments, as Nujol mulls mounted between KBr or Polythene plates. Variable-temperature magnetic-susceptibility measurements were made as described earlier.[22]

RESULTS AND DISCUSSION

The molar conductances of 0.001 mol dm^{-3} solutions of UCl_4 and UBr_4 in acetone are 24 and 32 S cm^2 mol^{-1} respectively. The 'free'-halide concentrations determined for the same solutions are 1×10^{-11} and 7×10^{-5} mol dm^{-3} respectively. Thus the conductance of the UBr_4 solution can be ascribed to ionised halide but the conductance of the UCl_4 solution cannot. For UCl_4, the conductance is most likely due to autoionisation [Scheme, path (*c*)]. The electronic spectra of UCl_4 and UBr_4 in acetone suggest that there is a mixture of six- and higher-co-ordinate species present, with the six-co-ordinated species being far more important in the UBr_4 than in the UCl_4 solution. The peak for six-co-ordination at *ca.* 2 000 nm is relatively higher than that for eight-co-ordination at *ca.* 1 150 nm for UBr_4 than UCl_4 [see absorption maxima in the vicinity of 650, 1 150, and 2 000 nm for curve (——), Figures 1(*a*) and 2(*a*)]. Although the species present in these solutions cannot be determined conclusively, the above experimental results can be explained in terms of the simultaneous equilibria in the Scheme.

Therefore, for UCl_4 in acetone, the important species are $UCl_4\cdot4Me_2CO$ (b_0) and $[UCl_3(OCMe_2)_5][UX_5(OCMe_2)]$ (c_1), with $UCl_4\cdot2Me_2CO$ (b_1) and $[UCl_3(OCMe_2)_5]Cl$ (a_1) being present in only very small concentrations. For UBr_4 in acetone, $UBr_4\cdot4Me_2CO$ (b_0), $UBr_4\cdot2Me_2CO$ (b_1), and $[UBr_3(OCMe_2)_5]Br$ (a_1) are the most important species with $[UBr_3(OCMe_2)_5][UBr_5(OCMe_2)]$ (c_1) present in only small concentrations.

---

[11] K. W. Bagnall, J. G. H. du Preez, and B. J. Gellatly, unpublished work.

[12] J. G. H. du Preez, R. A. Edge, M. L. Gibson, H. E. Rohwer, and C. P. J. van Vuuren, *J. S. African Chem. Inst.*, 1976, **29**, 15.

[13] J. G. H. du Preez, B. J. Gellatly, M. L. Gibson, D. R. Groot, and H. E. Rohwer, *J. S. African Chem. Inst.*, 1976, **29**, 105.

[14] J. G. H. du Preez, P. L. Gellatly, and H. E. Rohwer, *J. Inorg. Nuclear Chem.*, 1977, in the press.

[15] J. A. Hermann and J. F. Suttle, *Inorg. Synth.*, 1957, **5**, 143.

[16] J. G. H. du Preez, M. L. Gibson, and C. P. J. van Vuuren, *J. S. African Chem. Inst.*, 1971, **24**, 135.

[17] J. G. H. du Preez and M. L. Gibson, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1771.

[18] A. B. Burge and W. E. McKee, *J. Amer. Chem. Soc.*, 1951, **73**, 4590.

[19] A. Merijanian and R. A. Zingaro, *Inorg. Chem.*, 1966, **5**, 187.

[20] K. W. Bagnall, A. M. Deane, T. L. Markin, P. S. Robinson, and M. A. A. Stewart, *J. Chem. Soc.*, 1961, 1611.

[21] F. J. Welcher, 'The Analytical Uses of Ethylenediaminetetra-acetic Acid,' Van Nostrand, New York, 1958, ch. 10, p. 199.

[22] R. Colton, A.E.R.E. Report, 1963, R–4186.

The reactions of phosphine and arsine oxide complexes with these acetone solutions are now investigated and compared with those of other oxygen-donor ligands. Mutual differences amongst P=O and As=O ligands themselves are stated and discussed.

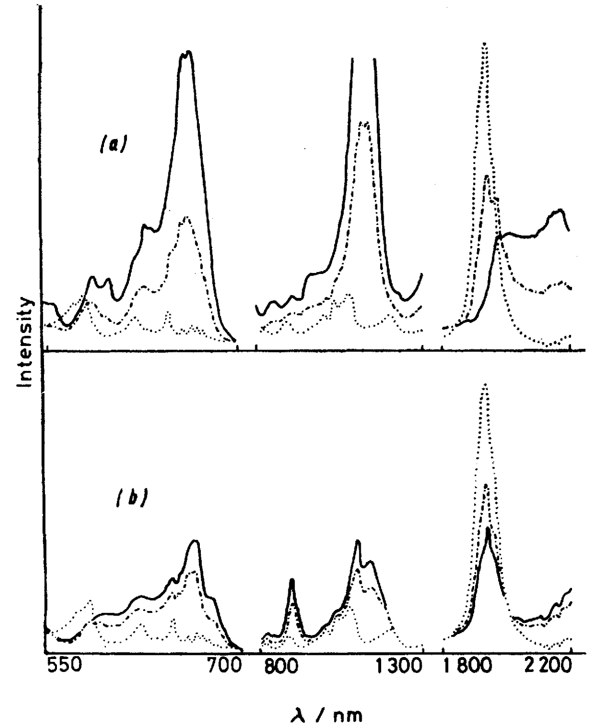


FIGURE 1 Spectrophotometric-titration curves of UCl_4 with tepo in acetone solution. tepo : UCl_4 = (*a*) 0 (——), 1 : 1 (—·—), 2 : 1 (····); (*b*) 6 : 1 (——), 4 : 1 (—·—), 2 : 1 (····)

Uranium Tetrachloride.—The conductimetric-titration curves showed sharp end-points at uranium : ligand ratios of 1 : 2. In the case of the smaller ligands (*i.e.* tmpo, tepo, tmao, and teao) there are indications of initial enhanced autoionisation (relative initial increase in conductivity followed by a decrease). After a mol ratio of 1 : 2, there were considerable increases in conductivity for the arsine oxide ligands, moderate increases for the smaller phosphine oxide ligands, and hardly any for the large phosphine oxide ligands, *e.g.* tdpo and tppo.

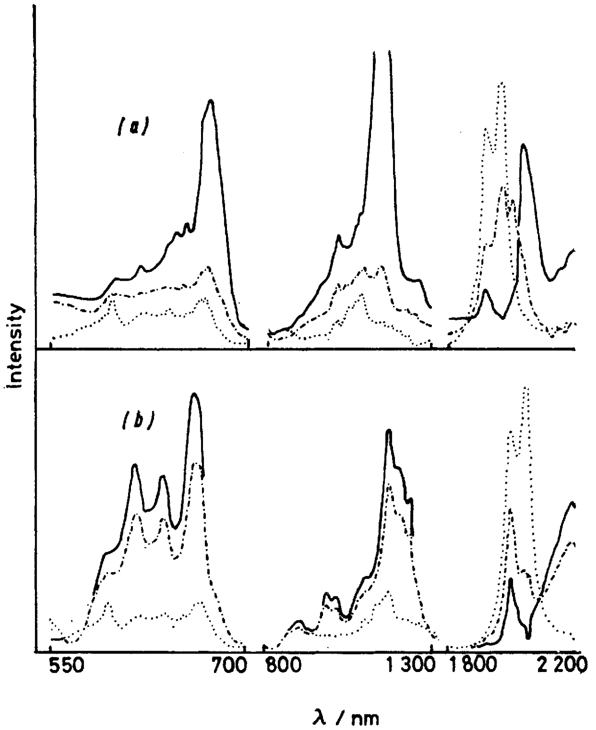
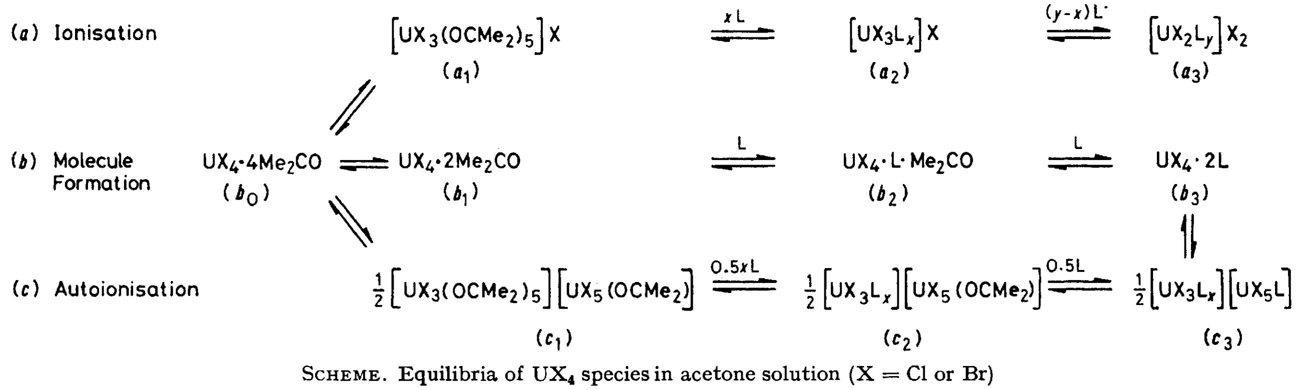


FIGURE 2 Spectrophotometric-titration curves of UBr_4 with tepo in acetone solution. tepo : UBr_4 = (*a*) 0 (——), 1 : 1 (—·—), 2 : 1 (····); (*b*) 5 : 1 (——), 3 : 1 (—·—), 2 : 1 (····)



SCHEME. Equilibria of UX_4 species in acetone solution (X = Cl or Br)

Similar solid uranium(IV) halide complexes to (b_0) and (b_1) are known, *i.e.* UCl_4·4cpl (J. G. H. du Preez, M. L. Gibson, and P. J. Steenkamp, *J. Inorg. Nuclear Chem.*, 1974, **36**, 579) and UCl_4·2tmu [tmu = tetramethylurea; K. W. Bagnall, J. G. H. du Preez, and M. L. Gibson, *J. Chem. Soc.* (*A*), 1971, 2124]. The thorium(IV) analogue of species (a_1) is known, $[ThCl_3(dmso)_5]Cl$ (dmso = dimethyl sulphoxide; P. J. Alvey, K. W. Bagnall, D. Brown, and J. Edwards, *J.C.S. Dalton*, 1973, 2308). The existence of $[UX_5(OCMe_2)]^-$ in species (c_1) and (c_2) has already been proposed (J. G. H. du Preez, R. A. Edge, M. L. Gibson, H. E. Rohwer, and C. P. J. van Vuuren, *Inorg. Chim. Acta*, 1974, **10**, 27). x = 3—5, y = 4—6.

In the spectrophotometric titrations of all these ligands, dramatic reductions in the absorptions of the peaks at 675 and 1 150 nm and corresponding increases in the peak at 2 000 nm occurred until a mol ratio of *ca.* 1 : 1.5 had been reached. In the region between 1 : 1.5 and 1 : 2 mol ratio more gradual similar changes occurred (see Figure 1 for tepo). This corresponds to the formation of six-co-ordinate uranium(IV) species. Little or no changes occurred after this ratio for the larger ligands. These spectrophotometric results therefore suggest that a greater amount of six-co-ordinate uranium(IV) species already exist, at a mol ratio of 1 : 1.5, than would be expected if only six-co-ordinated $UCl_4\cdot 2L$ is formed, indicating the presence of six-co-ordinate species like $[UCl_5(OCMe_2)]^-$ containing no Group 5 ligands. For the smaller ligands (tmpo and tepo), small changes occurred in the 675 and 1 150 nm regions after mol ratios of 1 : 2. Sizeable reductions, however, occurred in the 2 000 nm region suggesting that considerable amounts of higher-co-ordinate species form. The reductions in the absorption of the peaks at 2 000 nm were not accompanied by pronounced increases in absorption of the common solution spectra of the eight-co-ordinate species. In addition, these spectra are very similar to the solid-reflectance spectrum of $UCl_4\cdot 6$tmpo which was shown to be seven-co-ordinate.[23] In the light of this similarity and the fact that even the smaller P=O ligands are relatively large, seven-co-ordinate uranium(IV) is here strongly suspected (Figures 1 and 2).

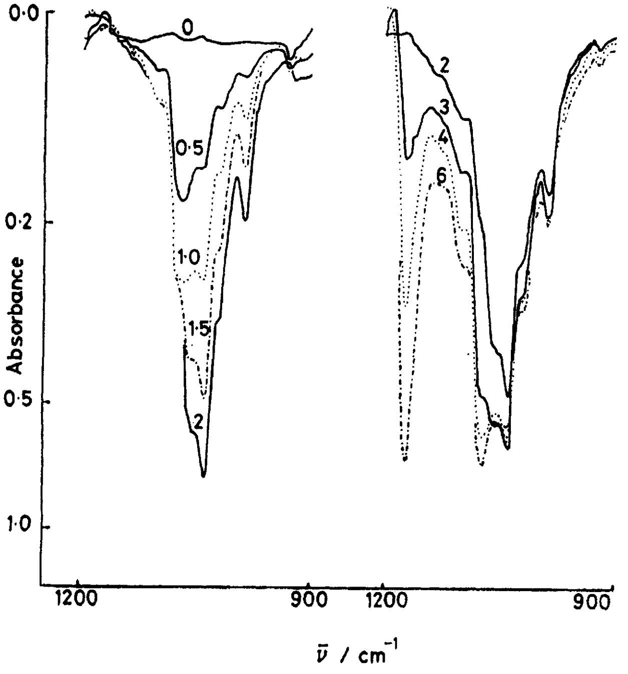


FIGURE 3 Infrared spectrophotometric-titration curves of UCl_4 with tepo. Numbers on curves indicate tepo : UCl_4 ratio

The potentiometric-titration curves indicate that a relatively large increase in chloride-ion concentration only occurs at, or after, a mol ratio of 1 : 2 has been reached. After this mol ratio there were considerable increases in the 'free'-chloride-ion concentration for arsine oxide ligands, moderate increases for the smaller phosphine oxide ligands (tmpo and tepo), and hardly any for the large phosphine oxide ligands (tdpo and tppo).

When acetone solutions of UCl_4 were titrated stepwise with tepo and followed by i.r. spectroscopy in the 800—1 200 cm^{-1} region, three major peaks were obtained in each case (see Figure 3). After addition of 0.5 equivalent of tepo, a peak ascribed to bound ligand appeared at 1 070 cm^{-1} having a shoulder at 1 040 cm^{-1}. On addition of more ligand the relative intensities of these peaks changed. They were equally strong at 1 equivalent of tepo and the peak at 1 040 cm^{-1} became stronger up to 2 equivalents of tepo. After this point the shoulder at *ca.* 1 040 cm^{-1} gradually became more pronounced again, but apparently shifted to a slightly higher wavenumber and at the same time a free-ligand peak at 1 172 gradually increased in intensity.

The above experimental data can best be interpreted, in our opinion, in the following way. In the 0—2 : 1 mol ratio region, apart from species in equilibria in acetone solution, the formation of $UCl_4\cdot 2L$ molecules can take place mainly *via* two paths: first, through solvent replacement in the neutral solvated species (b_1) and (b_2), and, secondly, through stepwise replacement in the autoionised species (c_1). At a UCl_4 : L mol ratio of 1 : 2 both paths result in maximum formation of $UCl_4\cdot 2L$. For the larger ligands tdpo, tppo, tpao, *etc.*, the first path is more important. For the smaller ligands, tmpo, tepo, tmao, *etc.*, although the first path must still be regarded as an important one, the second path plays a significant role. {Conductimetric and i.r. spectroscopic results, the latter only for tepo, suggest enhanced autoionisation: the i.r. peaks at 1 070 and 1 040 cm^{-1} can be ascribed to $[UCl_3(\text{tepo})_x]^+$ and $UCl_4\cdot 2$tepo species respectively (x = 3 or 4).} The formation of mainly six-co-ordinate species of U^{IV} even before a UCl_4 : L ratio of 1 : 2 (*ca.* 1 : 1.5) can be readily interpreted in terms of the formation of species (b_2) and (b_3) [path (b)] and (c_2) [path (c)]. Although the third possible path, namely ionisation through stepwise replacement of acetone, is unimportant in this region, it has been shown that a significant relative increase in Cl^- concentration already occurs just after a mol ratio of *ca.* 1.5 : 1 in the case of the stronger ligands, *i.e.* As=O and tmpo.[13] The fact that this significant increase in the degree of ionisation corresponds with the formation of six-co-ordinate species suggests that an enhanced degree of co-ordinate saturation of U^{IV} has been reached with the formation of these species. A much more prominent relative increase occurs at or immediately after a mol ratio of 1 : 2. For the weaker ligands, significantly increased ionisation only occurs gradually after a mol ratio of 1 : 2 (tdpo and tppo).

At a mol ratio of 1 : 2 the six-co-ordinate molecular species $UCl_4\cdot 2L$ is the dominant species in solution for all the ligands but relatively more important in the case of the larger ones. After a mol ratio of 1 : 2 most of the species remain six-co-ordinate, except in the cases of tmpo and tepo (already discussed).

Uranium Tetrabromide.—The reactions of UBr_4 with

---

[23] G. Bombieri and D. Brown, *J.C.S. Dalton*, 1976, 735.

these ligands are very similar to those of UCl_4. There is a relatively stronger molecule formation up to a 1 : 2 ratio, especially with larger ligands. The potentiometric-titration curves of, for example, tmpo and teao indicate a decrease in bromide-ion concentration up to a mol ratio of 1 : 2. In general, the degree of ionisation is always higher than for UCl_4 and autoionisation is less important, mainly as a result of the considerably lower formation constant of $[UBr_5L]^-$ species. The results of the i.r. spectrophotometric titration of UBr_4 with tepo in acetone solution are in agreement with this. The absorption of the peak at 1 068 cm^{-1} {1 070 cm^{-1} for the chloro-analogue and ascribed to the presence of $[UCl_3(tepo)_x]^+$} was significantly higher than that at 1 032 cm^{-1} (1 040 cm^{-1} for the chloro-analogue and ascribed to the presence of UCl_4·2tepo). The free-ligand peak at 1 172 cm^{-1} was much less pronounced and the bound tepo peak at 1 068 cm^{-1} more prominent on addition of excess of tepo than in the analogous situation for UCl_4.

TABLE

Physical and analytical data for the complexes

Compound	Colour	Analysis (%) M Found	M Calc.	X Found	X Calc.	I.r. spectra (cm^{-1}) ν(E=O)	ν(M–X)
tmpo						1 163	
UCl_4·2tmpo [a]	Pale green	42.3	42.2	25.2	25.2	1 040	252
UBr_4·2tmpo	Pale green	32.0	32.1	42.6	43.1	1 031	175
UCl_4·6tmpo [a]	Green	25.3	25.5	15.2	15.2	1 055	
UBr_4·6tmpo	Green	21.5	21.4	29.0	28.8	1 055	
tmao						870	
UCl_4·2tmao	Pale green	36.2	36.5	21.7	21.8	807	235
UBr_4·2tmao	Pale green	28.8	28.7	38.1	38.5	787	163
UCl_4·6tmao	Very pale green	20.1	19.9	11.9	11.9	831	
UBr_4·6tmao	Off white	17.7	17.3	23.6	23.3	832	
UI_4·6tmao	Off white	15.6	15.2	31.9	32.5	831	[b]
$ThCl_4$·6tmao	White	18.9	19.5	11.2	11.9		
tepo						1 167	
UCl_4·2tepo [a]	Green	36.3	36.7	21.8	21.9	1 025	253
UBr_4·2tepo [a]	Blue-green	28.9	28.8	38.7	38.7	1 010	175
teao						879	
UCl_4·2teao [a]	Green-blue	32.3	32.3	19.2	19.3	805	238
UBr_4·2teao [a]	Green	26.1	26.0	35.0	35.0	800	615
UCl_4·4teao	Very pale green	21.7	21.8	13.0	13.0	815	223
UBr_4·6teao	Very pale green	14.8	14.6	19.7	19.7	814	
UI_4·6teao	Very pale green	12.8	13.1	28.3	28.0	815	[b]
$ThCl_4$·6teao	White	15.8	16.1	9.9	9.8	840	
tppo						1 185	
UCl_4·2tppo [a]	Blue-green	25.4	25.4	15.1	15.1	1 045	257
UBr_4·2tppo [a]	Blue-green	21.3	21.4	28.6	28.7	1 030	189
tpao						880	
UCl_4·2tpao [a]	Blue-green	23.1	23.2	13.7	13.8	839	245
UBr_4·2tpao [a]	Blue-green	19.7	19.8	26.5	26.6	824	172
UBr_4·4tpao [a]	Blue-green	12.8	12.9	17.5	17.3	831	
$ThCl_4$·4tpao	White	14.1	14.0	8.4	8.5	858	
tdpo						1 208	
UCl_4·2tdpo [a]	Blue-green	32.3	32.3	19.2	19.2	1 035	259
UBr_4·2tdpo [a]	Green	26.1	26.0	34.9	34.9	1 017	180

[a] Prepared previously. [b] Not within the measured experimental range.

Since these ligands are all strong to very strong, solvent is replaced readily and stable complexes form which normally precipitated during solution studies, sometimes even in very dilute solution (tmao, teao, tmpo, *etc.*). Their strong ionising nature (smaller ligands) leads to the precipitation of various cationic species with high lattice energies, the natures of which are very concentration dependent since a number can coexist. Normally the higher the cationic charge the higher the lattice energy.[14]

Solid-state Chemistry.—The important results which emerge from the solution studies are: (*i*) the formation of UX_4·2L species with all the ligands studied; (*ii*) the possibility of ionisation and formation of cationic species with the stronger ligands; and (*iii*) the great variety of species simultaneously present in solution. As expected, these trends are seen in the solid complexes obtained from such solutions. The solid compounds investigated are listed in the Table. Many complexes of the type UX_4·2L (X = Cl or Br) are known.[1-7] We have now prepared UBr_4·2tmpo, UCl_4·2tmao, and UBr_4·2tmao. Thus, even with the wide range of size and ligand strength, all the ligands in the series form UX_4·2L complexes. The reactivity towards water seems to be determined by the size of the ligand. With the smallest ligands, tmpo and tmao, the complexes are very hygroscopic, whereas those with the largest, tppo and tpao, are virtually insoluble in water. The tmpo and tmao complexes are also solvoscopic. All the complexes are gradually oxidised on prolonged exposure to air.

By using an excess of ligand (>6L) we prepared complexes of the type UX_4·6L (X = Cl, Br, or I) with the ligands tmao, tmpo, and teao (with two exceptions) (Table). The complex of UCl_4 with teao has a stoicheiometry of $UCl_4{\cdot}4teao$ and on repeated attempts the products from the reaction of UI_4 with tmpo gave analyses corresponding to $UI_4{\cdot}6$—8tmpo.* The electronic spectra obtained for the $UX_4{\cdot}2L$ complexes closely resemble that of $[UCl_6]^{2-}$. It appears that this type of spectrum is characteristic of six-co-ordinate U^{IV}, and to a great extent independent of the arrangement of the six ligands around the uranium. A change in co-ordination number, however, has a significant effect on the electronic spectrum. The solid-state spectra of $UCl_4{\cdot}6tmpo$, $UBr_4{\cdot}6tmpo$, $UCl_4{\cdot}6tmao$, $UBr_4{\cdot}6tmao$, and $UI_4{\cdot}6tmao$ are shown in Figure 4. The shapes of the first three spectra are closely related whereas the other two are typical of six-co-ordinate U^{IV}. Whereas the magnetic susceptibility of $UCl_4{\cdot}6tmpo$ is slightly temperature dependent in the range 90—300 K, those of $UBr_4{\cdot}6tmpo$ and $UCl_4{\cdot}6tmao$ are temperature independent.[24]

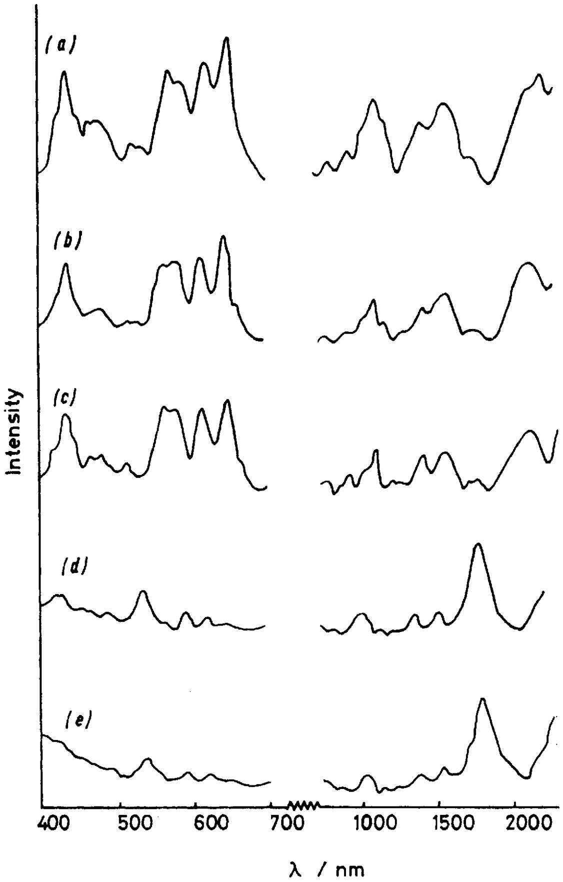


FIGURE 4 Solid-reflectance spectra of (a) $UCl_4{\cdot}6tmpo$, (b) $UBr_4{\cdot}6tmpo$, (c) $UCl_4{\cdot}6tmao$, (d) $UBr_4{\cdot}6tmao$, (e) $UI_4{\cdot}6tmao$

The structure of $UCl_4{\cdot}6tmpo$ has recently been solved[23] and shown to consist of cationic units $[UCl(tmpo)_6]^{3+}$ and three chloride ions. It seems reasonable to propose that, on progressing along this series of compounds, the co-ordination number of the uranium changes from seven to six (the seventh ligands, Cl^- or Br^-, being progressively pushed out of the first co-ordination sphere). Thus we propose that these solids contain partly or fully ionised species: *e.g.* $UCl_4{\cdot}6tmpo$, $[UCl(tmpo)_6]^{3+} + 3Cl^-$; $UCl_4{\cdot}6tmao$, $[UCl(tmao)_6]^{3+} + 3Cl^-$; and $UBr_4{\cdot}6tmao$, $[U(tmao)_6]^{4+} + 4Br^-$. This high degree of ionisation in the solid state is ascribed to lattice stabilisation since a much smaller degree of ionisation can exist in acetone solution. The other complexes $UCl_4{\cdot}4teao$, $UBr_4{\cdot}6teao$, and $UI_4{\cdot}6teao$ have typical spectra of six-co-ordinate species and the latter two may contain the $[UL_6]^{4+}$ ion. The reason for obtaining the complex $UCl_4{\cdot}4teao$ is probably stereochemical, six teao molecules being too crowded to be accommodated at reasonable bonding distances from the U^{4+} ion. It is interesting to note that the $ThCl_4{\cdot}6teao$ complex can be isolated, possibly due to the slightly larger size of Th^{4+}.

It has been proposed by Lane and Venanzi[5] that the ligand strength can be measured using the average-environment rule and that the spectra of $UX_4{\cdot}2L$ species can be extrapolated to a hypothetical $[UL_6]^{4+}$ species. We measured the spectra of $UX_4{\cdot}2L$, $UX_4{\cdot}4L$, and $UX_4{\cdot}6L$ and the position of band maxima do not correspond to this proposal (assuming that these contain $UX_4{\cdot}2L$, $[UX_2L_4]^{2+}$, and $[UL_6]^{4+}$ respectively). Thus the average-environment rule, which has been used to assess ligand strength in the 3*d* transition metals, does not seem to hold for U^{4+}. This may be due to large changes in spin–orbit interactions and interelectronic interactions on interchanging ligands, especially if there is a wide difference in ligand-field strength.

The shifts in E=O (E = P or As) bond-stretching frequencies of the ligands in the new complexes correspond well with those in existing complexes (Table). The similarity of the P=O stretching frequencies in $UX_4{\cdot}6tmpo$ (X = Cl and Br), As=O frequencies in $UX_4{\cdot}6tmao$ (X = Cl, Br, and I) and $UX_4{\cdot}6teao$ (X = Br and I), as well as the absence of U–X stretching frequencies in the expected regions, are in agreement with the proposed cationic uranium(IV) structures. In each of the $UCl_4{\cdot}2L$ and $UBr_4{\cdot}2L$ species the U–X stretching frequencies decrease in the direction tppo, tdpo, tepo (tmpo), tpao, teao, and tmao. The above ligand order exactly corresponds with the donor-strength order obtained experimentally.[13] This systematic lowering of the stretching frequency could therefore be interpreted in terms of weaker U–Cl and U–Br interactions in each of the two series. This is in agreement with some recently obtained structural data[25] which showed that U–Cl bond lengthening occurs in going from phosphine oxide to arsine oxide complexes of UCl_4. (U–Cl bond lengths in $UCl_4{\cdot}2tdpo$ and $UCl_4{\cdot}2teao$ are 2.62 and 2.67 Å respectively.)

Conclusions.—The results of this work suggest that arsine oxide ligands are considerably stronger ligands for U^{IV} than phosphine oxides. (Both large and small arsine

---

* Solids of approximate composition $UCl_4{\cdot}4tpao$ and $UBr_4{\cdot}$tpao can be obtained.

[24] J. W. Gonsalves, P. J. Steenkamp, J. G. H. du Preez, B. J. Gellatly, and M. L. Gibson, *J. S. African Chem. Inst.*, 1977, **30**, in the press.

[25] J. G. H. du Preez, B. J. Gellatly, and M. Laing, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1872.

oxide ligands have great ionising power on UCl_4, whereas only the smallest phosphine oxides have some ionising power.) This must be ascribed to their greater dipole moment [14] as well as their greater induced dipole moment. The latter becomes very important when the Lewis acid becomes very strong and the differences between the two types of ligands become greater. Although the ionising power of a larger arsine oxide (tpao) is much greater than its phosphine oxide analogue (tppo), as indicated by potentiometric titration, the stoicheiometry of the solid compounds isolated is similar, $UCl_4 \cdot 2L$. This apparent similarity in the solid state can be explained in terms of the relatively low lattice energy of an extremely large cationic species, *i.e.* one containing more than two tpao molecules with the relatively small chloride counter ions. Comparative structural studies thus far undertaken, although limited in number, indicate that U–Cl and U–O bonds differ between analogous phosphine and arsine oxide complexes of UCl_4. Such differences must be borne in mind when interpreting spectral and magnetic data.[26]

We thank the South African Council for Scientific and Industrial Research, the South African Atomic Energy Board, and the University of Port Elizabeth for financial assistance.

[6/903 *Received*, 11*th May*, 1976]

---

[26] J. G. H. du Preez, J. W. Gonsalves, and P. J. Steenkamp, *Inorg. Chim. Acta*, 1977, **21**, 167.