Pentahalogeno-oxouranates(VI)

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Pentafluoro- and tetrabromochloro-oxouranate(VI) salts, $[Ph_4P][UOF_5]$ and $[Ph_4P][UOClBr_4]$, have been prepared by reaction of $[Ph_4P][UOCl_5]$ with hydrogen fluoride and bromide respectively. Hydrolysis of $[Ph_4P][UOCl_5]$ leads to a uranium(VI) anion which may contain a *cis*-dioxouranium(VI) group. The electron-transfer and vibrational spectra of these salts are discussed and compared with those of the corresponding tungsten(VI) species. A simple method for the preparation of $[Ph_4P][WOF_5]$ is also reported.

HALOGENO-OXO-IONS of the types $[MOX_5]^-$, $[MOX_5]^{2-}$, and $[MOX_4]^-$ are well known for the *d*-transition metals,[1] whereas the only *f*-transition-metal analogues so far recorded are the actinoid(V) ions $[MOX_5]^{2-}$ (M = Pa,[2] X = Cl or Br; M = U,[3] X = F, Cl, or Br); the corresponding neptunium(V) ion,[4] $[NpOCl_5]^{2-}$, has been shown [5] to be an equimolar mixture of $[NpO_2Cl_4]^{2-}$ and $[NpCl_6]^{2-}$.

The only recorded oxouranium(VI) chloride is UO_2Cl_2, from which the anion $[UO_2Cl_4]^{2-}$ is derived, and a trioxospecies, $M^I_2[UO_3Cl_2]$, is also known.[6] More recently, the oxotetrafluoride UOF_4 has been reported,[7,8] but the analogous chloride, $UOCl_4$, has not been isolated, although it has been postulated [9] to be an intermediate in the chlorination of uranium trioxide. It therefore appeared worthwhile to study the chlorination of dioxouranium(VI) dichloride and its derivatives with the aim of isolating intermediate chloromono-oxouranium(VI) species; this led to the isolation [10] of $[Ph_4P][UOCl_5]$, the first example of this type of actinoid(VI) anion.

In this paper we report an improved method of preparing this complex together with an investigation of its chemistry, leading to formation of the analogous $[UOF_5]^-$ and $[UOClBr_4]^-$ salts, and a comparison with the corresponding fluoro-oxo- [11] and other halogeno-oxotungstates(VI),[12] $[WOX_5]^-$.

RESULTS

The Pentachloro-oxouranate(VI) *Ion*.—Chlorination of hydrated dioxouranium(VI) dichloride with thionyl chloride on the 10 g scale under reflux was extremely slow, requiring a number of weeks for completion as in the reaction of uranium trioxide with $SOCl_2$.[13] Reaction in the presence of dissolved chloride ion, on the other hand, was almost instantaneous under similar conditions. The size of the counter cation associated with the chloride ion is critical for the isolation of the intermediate $[UOCl_5]^-$ ion in this reaction. With the large tetraphenylphosphonium cation, red crystals of $[Ph_4P][UOCl_5]$ separated readily from the dark red reaction mixture on cooling, whereas with smaller cations ($[Et_4N]^+$ or Cs^+) no solid products could be isolated and reductive chlorination to the uranium(V) chloro-anion, $[UCl_6]^-$, occurred more readily.

The salt $[Ph_4P][UOCl_5]$, prepared from dioxouranium(VI) chloride trihydrate and $[Ph_4P]Cl$ in $SOCl_2$, was invariably contaminated with unchanged UO_2Cl_2, but chlorination of the much more soluble $[Ph_4P]_2[UO_2Cl_4]$ yielded the pure mono-oxo-complex. The red mother liquor from this reaction became orange-yellow on standing. The electronic spectrum of this solution shows that the concentration of U^V increases with time and that U^{IV} is absent, indicating that chlorination and reduction of the $[UOCl_5]^-$ ion take place in $SOCl_2$ solution in the cold.

The salt $[Ph_4P][UOCl_5]$ is slightly soluble in rigorously dried organic solvents such as dichloromethane or methyl cyanide and is stable indefinitely in the former, being recoverable unchanged from the orange-red solution. However, even trace amounts of water in these solvents lead to hydrolysis. For example, when dichloromethane dried over calcium hydride was used, hydrogen chloride was evolved and a yellow solution of a dioxouranium(VI) species formed. Crystals of $[Ph_4P][UOCl_5]$ placed in contact with such inadequately dried dichloromethane were gradually converted into thin orange needles, which we tentatively formulate as $[Ph_4P][UO_2Cl_3]\cdot HCl$ on the basis of the analytical results. This salt decomposes at room temperature in a nitrogen atmosphere in 2—3 d, and rapidly at 80 °C *in vacuo*, to give a pale yellow solid of composition $[Ph_4P][UO_2Cl_3]$. Both products are very sensitive to moisture.

A tetradecylammonium salt, $[(H_{21}C_{10})_4N][UO_2Cl_3]$, a yellow viscous oil, is known [14] and is obtained by saturating a benzene solution of the ammonium chloride with $UO_2Cl_2\cdot OH_2$ and removing the solvent. In the i.r. spectrum [14] of this salt ν_{asym} ($U{=}O_2$) appears at 943, ν(U–Cl) at 243 and 216, and $\delta(UO_2)$ at 270 cm^{-1}, in good agreement with the i.r. spectrum of $[Ph_4P][UO_2Cl_3]$ (Table 1; 948; 245 and 220; and 270 cm^{-1} respectively); the feature at 220 cm^{-1} is presumably associated with a bridging chlorine atom. In contrast, the i.r. spectrum of $[Ph_4P][UO_2Cl_3]\cdot HCl$ exhibited

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strong features at 943 and 854 cm^{-1} and a very strong feature at 287 cm^{-1}, with a shoulder at 295 cm^{-1}. It seems probable that in this instance the U–Cl stretching and U–O deformation modes are coincident at *ca.* 290 cm^{-1} and it is clear from i.r. (Table 1) and electronic spectra of this product that it is not a mixture of $[Ph_4P][UOCl_5]$ and $[Ph_4P][UO_2Cl_3]$. Now for a dioxo-ion $[MO_2X_4]^{n-}$ two stretching (ν_{sym} and ν_{asym}) and one deformation metal–oxygen modes are expected.[15] For the *trans* isomer (D_{4h}), $\nu_{sym}(MO_2)$ is an a_{1g} mode, Raman active but i.r. inactive, while $\nu_{asym}(MO_2)$, a_{2u}, and $\delta(MO_2)$, e_u, are i.r. active only. For the *cis* isomer (C_{2v}), however, $\nu_{sym}(MO_2)$ and $\delta(MO_2)$ are a_1 modes and $\nu_{asym}(MO_2)$ is a b_2 mode, all three being Raman and i.r. active, as observed for $[Ph_4P][UO_2Cl_3]\cdot HCl$. We suggest, therefore, that the *cis*-UO_2 group is present in this salt, probably as a $[UO_2Cl_4]$ entity, resulting from hydrolytic attack on the weaker equatorial U–Cl bonds in the $[UOCl_5]^-$ anion (see *Metal–Halogen Vibrations*). Rearrangement then occurs, even at room temperature and in the solid state, to the thermodynamically more stable *trans*-UO_2 group in $[Ph_4P][UO_2Cl_3]$. The tungsten analogue, $[Ph_4P][WOCl_5]$, is hygroscopic, but is far less reactive towards traces of water in dichloromethane.

TABLE 1

I.r. and Raman spectra (cm^{-1}) of the complexes

Salt	ν(M=O)		δ(M=O)		ν(M–X)		Ref.
	I.r.	Raman	I.r.	Raman	I.r.	Raman	
$[Ph_4P][UOF_5]$	815vs	817w	238m		595vs, 505vs, 490vs (sh)		*
$[Ph_4P][UOCl_5]$	834vs	836s	231m	229w	345m, 341m (sh), 302vs, 298vs, 291vs	347vs, 341vs, 293s	*
$[Ph_4P][UOClBr_4]$	838vs		222m		331m, 215vs, 208m		*
$[Et_4N]_2[UOF_5]$	(835)						3
	760s						
$[Et_4N]_2[UOCl_5]$	(917)						
	813s		?		296m, 253vs, 197m		3
$[Et_4N]_2[UOBr_5]$	(919)						
	817s		?		250m (?), 190s		3
$[Et_4N]_2[PaOCl_5]$	830s		?		289w, 251s		2
$[Et_4N]_2[PaOBr_5]$	840s						2
$[Ph_4P]_2[UO_2Cl_4]$	913s	832s	253s		238, 230s	264s	*
$[Ph_4P]_2[UO_2Br_4]$	919s	837s	260s		164s	188s	*
$[Ph_4P]_2[UO_2Cl_3]\cdot HCl$	943s	948w					
	854s	857s			295vs (sh), 287vs		*
$[Ph_4P][UO_2Cl_3]$	948s		270s		245m, 220w		*
$[Ph_4P][WOF_5]$	970vs	976w	248s		670vs, 610vs, 510vs, 333m, 280m		*
$[Ph_4P][WOCl_5]$	955vs	957s	242s		382w, 330vs	387s	*
$[Ph_4P][WOBr_5]$	960vs		238m		202vs		*
$Cs_2[WOCl_5]$	957vs		230s		333w, 309s		22
$Cs_2[WO_2Cl_4]$	937s, 891s	935s, 886s	370s	370s	315s, 244vs		15

* This work.

The interaction of $[Ph_4P][UOCl_5]$ with various ligands was followed in solution by i.r. spectroscopy. When 1 mol equivalent of triphenylphosphine oxide was added to the chloro-complex in dichloromethane, features were observed in the i.r. spectrum at 847 ($[UOCl_5]^-$), 922 ($[UO_2]^{2+}$), 1 145 (bound P=O), and 1 192 cm^{-1} (free Ph_3PO). Addition of 2-methylbutane to this solution precipitated an orange-yellow solid, the i.r. spectrum of which exhibited features attributable to $[UOCl_5]^-$ (834 cm^{-1}) and $[UO_2]^{2+}$ (920 cm^{-1}), but none due to bound or free Ph_3PO. When a large excess (*ca.* 5 mol equivalents) of Ph_3PO was used the feature at 847 cm^{-1} disappeared, and for a solution of $[Ph_4P]_2[UO_2Cl_4]$ in dichloromethane containing 1 mol equivalent of Ph_3PO the i.r. spectrum exhibited features at 922 ($[UO_2]^{2+}$), 1 145 (bound P=O), and 1 192 cm^{-1} (free Ph_3PO).

These observations suggest that the equilibria in (1) are established in solution. It is possible that the final stage

$$[Ph_4P][UOCl_5] + Ph_3PO \rightleftharpoons [Ph_4P][Ph_3ClP][UO_2Cl_4] \rightleftharpoons [Ph_4P][Ph_3ClP][UO_2Cl_4\cdot OPPh_3] \quad (1)$$

may involve chloride ion elimination [equation (2)]. Oxygen abstraction from Ph_3PO has also been reported for other

$$[UO_2Cl_4\cdot OPPh_3]^{2-} \rightleftharpoons [UO_2Cl_3(OPPh_3)]^- + Cl^- \quad (2)$$

transition-metal halides in high oxidation states, such as niobium pentachloride.[16,17]

Similar experiments with pyridine and with *NN*-dimethylpivalamide (dmp) indicated that no reaction occurred with $[Ph_4P][UOCl_5]$. The corresponding tungsten salt, $[Ph_4P][WOCl_5]$, did not chlorinate Ph_3PO nor did it form complexes with Ph_3PO, dmp, or pyridine.

The Pentafluoro-oxouranate(VI) *Ion.*—Dioxouranium(VI) dichloride is known [18] to react at room temperature with anhydrous hydrogen fluoride to form the corresponding difluoride. When anhydrous HF was condensed on to $[Ph_4P][UOCl_5]$ at −196 °C and the mixture allowed to warm up to room temperature a vigorous reaction took place, with evolution of hydrogen chloride and formation of a pale yellow dioxouranium(VI) fluoride species. The Raman spectrum of the HF phase showed [19] that uranium hexafluoride was present. However, when the temperature of the reaction mixture was maintained at *ca.* −30 °C an orange solution resulted which yielded a peach-coloured solid on removal of HF. This was shown to be $[Ph_4][UOF_5]$, contaminated with only small amounts (*ca.* 2%) of dioxouranium(VI) impurity. It therefore appears that disproportionation occurs when the reaction is carried out at too

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[16] D. B. Copley, F. Fairbrother, and A. Thompson, *J. Less-Common Metals*, 1965, **8**, 256.

[17] D. Brown, J. F. Easey, and J. G. H. de Preez, *J. Chem. Soc.* (*A*), 1966, 258.

[18] C. A. Kraus, U.S. Report CC-1717, 1944 (according to J. J. Katz and E. Rabinowitch, 'The Chemistry of Uranium,' Nat. Nuclear Energy Series, McGraw-Hill, New York, 1951, vol. VIII-5, p. 566).

[19] B. Frlec and H. H. Hyman, *Inorg. Chem.*, 1967, **6**, 1596.

high a temperature (*i.e.* room temperature) probably according to equation (3).

$$2[UOF_5]^- \longrightarrow [UO_2F_4]^{2-} + UF_6 \qquad (3)$$

The tungsten analogue, $[Ph_4P][WOCl_5]$, reacted with anhydrous HF at −78 °C, with evolution of HCl; $[Ph_4P][WOF_5]$ remained as a pale yellow solid after removal of the excess of reactant and there are no complicating side reactions. Both the pentafluoro-oxometallates(VI) are stable in air and are insoluble in dichloromethane or MeCN.

The Tetrabromochloro-oxouranate(VI) *Ion*.—Attempted preparation of $[Ph_4P][UOBr_5]$ by reaction of $[Ph_4P]_2[UO_2Br_4]$ with $SOBr_2$ at room temperature was unsuccessful; reduction to the uranium(V) salt $[Ph_4P][UBr_6]$ occurred immediately. Bromo-complexes can often be prepared [20] by halogen exchange using anhydrous hydrogen bromide, but repeated condensation of this reagent on to $[Ph_4P][UOCl_5]$ led only to partial replacement of chloride with much of the starting material being recovered unchanged. However, when HBr was passed into a dichloromethane solution of $[Ph_4P][UOCl_5]$ the colour changed almost instantaneously from orange-red to dark brown. Immediate evaporation of the solvent yielded dark brown $[Ph_4P][UOClBr_4]$, free from U^V or lower oxidation states. This salt was shown by *X*-ray powder photography to be isostructural with $[Ph_4P][UOCl_5]$. When a solution of $[Ph_4P][UOClBr_4]$ was saturated with HBr the colour changed to red-brown over a period of hours and the product was mainly U^V, probably as $[UBr_6]^-$. In contrast, $[Ph_4P][WOCl_5]$ reacted smoothly with anhydrous HBr in dichloromethane to form the isostructural, dark brown pentabromo-complex, $[Ph_4P][WOBr_5]$. Both this and $[Ph_4P][UOClBr_4]$ are hygroscopic and soluble in dichloromethane and MeCN.

The stability of the U–O bond in $[UOCl_5]^-$ towards reaction with HBr is in marked contrast to that in the corresponding uranium(V) complex, $[UOCl_5]^{2-}$, which is converted [3] into the anion $[UCl_6]^-$ by even small amounts of anhydrous HCl. Both $[UO_2Cl_4]^{2-}$ and $[UOCl_5]^-$ are unaffected by HCl in anhydrous solvents, and $[UO_2Cl_4]^{2-}$ is converted into $[UO_2Br_4]^{2-}$ by HBr, observations which seem to indicate that the oxygen atom in $[UOCl_5]^{2-}$ is much less strongly bonded to the uranium atom than are those in $[UOCl_5]^-$ and $[UO_2Cl_4]^{2-}$.

Metal–Oxygen Vibrations.—Vibrational spectra of the mono-oxo-uranium(VI) and -tungsten(VI) complexes $[Ph_4P][MOX_5]$ are summarised in Table 1 together with those for other related metal halogeno-oxo-species. Features due to the cation were identified by comparison [21] with the i.r. and Raman spectra of $[Ph_4P]X$ (X = Cl, Br, or I). At lower frequencies (<220 cm^{-1}) it was not possible to distinguish between features due to the cation and the anions. All attempts to surmount this problem by preparing the uranium(VI) species with simple cations, such as Cs^+, were unsuccessful, so that a complete normal-co-ordinate analysis of the uranium(VI) anions, $[UOX_5]^-$, was not possible.

For an ion of the type $[MOX_5]^{n-}$, assuming C_{4v} symmetry, group theory predicts 15 normal modes of vibration which span the representations (4). All these are Raman active, while a_1 and e are also i.r. active. The modes of interest are [22] ν(M=O) (a_1), ν(M–X)(axial) (a_1), ν(M–X)(equatorial) ($a_1 + b_1 + e$), and δ (M=O) (e). The Raman (*a*) and i.r. (*b*) spectra of $[Ph_4P][UOCl_5]$ are shown in Figure 1. The strong features at 834 (i.r.) and 836 (Raman) cm^{-1} are assigned to the U=O stretching mode and the weaker features at 231 (i.r.) and 229 cm^{-1} (Raman) to the U=O wagging mode. The corresponding features in the spectra of $[Ph_4P][UOClBr_4]$ and $[Ph_4P][UOF_5]$ appear at 838 and 222 cm^{-1} (i.r.) and at 815 (i.r.) (817 Raman) and 238 cm^{-1} respectively. The rather low frequency of the U=O stretching mode in $[Ph_4P][UOCl_5]$ is certainly not associated with bridging oxygen according to the preliminary *X*-ray work,[23] and this view is supported by the 1 : 1 electrolyte behaviour of the salt in MeCN (Table 3) and by the appearance of ν(U=O) at 847 cm^{-1} in the i.r. spectrum in dichloromethane.

$$\Gamma_{vib} = 4a_1 + 2b_1 + b_2 + 4e \qquad (4)$$

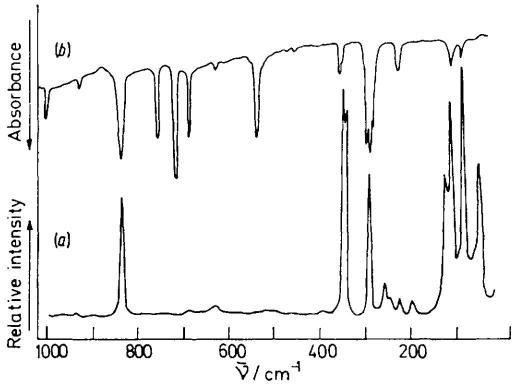

FIGURE 1 Raman (*a*) and i.r. (*b*) spectra of $[Ph_4P][UOCl_5]$

TABLE 2

Force constants (N cm^{-1}) * for ν(M=O) of the halogeno-oxo-species

	ν(M=O)	f_r		ν(M=O)	f_r
$[Ph_4P][UOF_5]$	815	5.87	$[Et_4N]_2[UOF_5]$	760	5.10
$[Ph_4P][UOCl_5]$	834	6.14	$[Et_4N]_2[UOCl_5]$	813	5.84
$[Ph_4P][UOClBr_4]$	838	6.20	$[Et_4N]_2[UOBr_5]$	817	5.90
$[Ph_4P][WOF_5]$	970	8.16	$[Et_4N]_2[PaOCl_5]$	830	6.07
$[Ph_4P][WOCl_5]$	955	7.91	$[Et_4N]_2[PaOBr_5]$	840	6.22
$[Ph_4P][WOBr_5]$	960	7.99			

	ν_{sym}	ν_{asym}	f_r	f_{rr}	
$K_2[OsO_2Cl_4]$	904	837	6.68	1.03	*trans*
$Cs_2[UO_2Cl_4]$	832	919	6.77	−0.25	*trans*
$Cs_2[WO_2Cl_4]$	935	886	7.19	0.39	*cis*

* Simplified force field–valence force constants, f_r, for bond stretching and the interaction constant between adjacent bonds, f_{rr}. $\lambda_i = 0.5892\,(\nu_i/cm^{-1})^2\,10^{-3}$, $\mu_x = 1/m_x$.

	M=O	$C_{\infty v}$	a_1	I.r., Raman	$\lambda = (\mu_0 + \mu_m)f_r$
cis	O=M=O	C_{2v}	a_1	I.r., Raman	$\lambda = (\mu_0 + \mu_m)(1 + \cos\phi)(f_r + f_{rr})$
			b_2	I.r., Raman	$\lambda = (\mu_0 + \mu_m)(1 - \cos\phi)(f_r - f_{rr})$
trans	O=M=O	D_{4h}	a_{1g}	Raman	$\lambda = \mu_0(f_r + f_{rr})$
			a_{2u}	I.r.	$\lambda = (\mu_0 + 2\mu_m)(f_r - f_{rr})$

Two features attributable to the U=O stretching vibration have been reported [3] for $[Et_4N]_2[UOX_5]$ (X = F, Cl, or Br); the lower of the two frequencies agrees with those observed

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[20] See, for example, J. L. Ryan, *Inorg. Chem.*, 1969, **8**, 2053, 2058.

[21] J. Goubeau and G. Wenzel, *Z. phys. Chem.* (*Frankfurt*), 1965, **45**, 31.

[22] A. Sabatini and I. Bertini, *Inorg. Chem.*, 1966, **5**, 204.

[23] J. F. de Wet, personal communication.

for $[UOX_5]^-$ and for[24] $[PaOX_5]^{2-}$, whereas Selbin *et al.*[25] assign the higher of the two frequencies to the U=O stretching mode on the basis of the high frequency of the M=O stretching mode in analogous *d*-transition-metal halogeno-oxo-anions. Such a comparison may be misleading, for in the vibrational spectra of the $[UOX_5]^-$ ions the U=O stretching mode appears at significantly lower wavenumber (815 to 838 cm^{-1}) than the W=O stretching mode in the analogous $[WOX_5]^-$ ions (955 to 970 cm^{-1}) and, more important, in the tungsten species the frequency of the W=O stretching mode increases with change of halogen in the order F > Cl ∼ Br, which is in the opposite direction to the change observed for the $[UOX_5]^-$ ions. The force constants (Table 2) for the mono-oxo-uranium(VI), -uranium(V), and -tungsten(VI) species show the opposing trends very clearly.

TABLE 3

Optical electronegativities

Compound	Colour	10^{-3} $\sigma_{obs.}/cm^{-1}$	$\chi_{uncorr.}$ (U) [a]	10^{-3} $\sigma_{obs.}/cm^{-1}$	$\chi_{uncorr.}$ (U) [b]
UCl_6	Black-green	17	2.4 [c]		
$[UCl_6]^-$	Orange	25.3	2.2 [d]	22.8	2.2
$[UBr_6]^-$	Dark brown	17.4	2.2 [d]		
$[UI_6]^{2-}$	Orange-red	20.9	1.8 [e]		
$[UO_2Cl_4]^{2-}$	Yellow			33.4	1.9
$[UO_2Br_4]^{2-}$	Dark yellow	29.8	1.8 [e]	26.0	1.9
$[UO_2I_4]^{2-}$	Red-brown	19.2	1.8		
$[UOCl_5]^-$	Red			24.0	2.2
$[UOClBr_4]^-$	Dark brown			17.2	2.2
$[UOCl_5]^{2-}$	Blue			32.6	1.9 [f]
$[UOBr_5]^{2-}$	Green	26.7	1.9 [d]		
$[UO_2Cl_3]^-\cdot HCl$	Orange			27.0	2.1

[a] From the literature. [b] This work, cation $[Ph_4P]^+$. [c] H. C. Urey, U.S. report A-750, 1943; A. B. F. Duncan, U.S. report A-584, 1943 (according to J. J. Katz and E. Rabinowitch, 'The Chemistry of Uranium,' Nat. Nuclear Energy Ser., McGraw-Hill, New York, 1951, div. VIII, vol. 5, p. 504). [d] Ref. 3, $[Et_4N]^+$ salts. [e] J. L. Ryan and C. K. Jørgensen, *Mol. Phys.*, 1963, **7**, 17. [f] $[Et_4N]^+$ Salt.

This difference between the spectra of the tungsten(VI) and uranium(VI) complexes is probably due to a markedly diminished degree of p_π interaction between the oxygen and the metal atoms in the *f*-transition-element case, resulting from less favourable *f*-orbital symmetry considerations and the relatively high energies of the 5*f* and 6*d* orbitals of uranium, particularly in high oxidation states, as compared with the 5*d* orbitals of tungsten. Thus the increasing electronegativity of the halogen serves only to withdraw electron density from the U=O bond in the uranium case, so weakening that bond, whereas in *d*-transition-metal complexes the high electronegativity of fluorine increases the extent of p_π interaction, strengthening the M=O bond, because of the more favourable conditions for p_π–d_π as compared with p_π–f_π interactions in the uranium case. This view is consistent with the observed reactions of UO_3 and WO_3 with $SOCl_2$, the former ultimately yielding the uranium(V) complex, $[UCl_6]^-$, whereas the latter yields $WOCl_4$.

The frequencies of the M=O stretching modes are expected to decrease in the order $[MO]^{4+} > [MO]^{3+} > [MO_2]^{2+}$ in a series of salts or ions of the same geometry derived from these species. Taking the root mean square of ν_{sym} and ν_{asym} for the MO_2 group to represent the frequency of an isolated M=O bond having the same force constant,[26] this appears to hold for the tungsten chloro-complexes for which differences in the cations are probably responsible for the near equality of the values for the first two species, $[Ph_4P][WOCl_5]$ (955 cm^{-1}) ∼ $Cs_2[WOCl_5]$ (957 cm^{-1}) > $Cs_2[WO_2Cl_4]$ (914 cm^{-1}), whereas the reverse holds for the uranium analogues, $[Ph_4P]_2[UO_2Cl_4]$ (873 cm^{-1}) > $[Ph_4P][UOCl_5]$ (834 cm^{-1}) > $[Et_4N]_2[UOCl_5]$ (813 cm^{-1}). It should be noted, however, that the MO_2 group is *trans* in $[UO_2Cl_4]^{2-}$ and *cis* in $[WO_2Cl_4]^{2-}$. These observations could be taken to indicate that the U=O bond in the $[UOCl_5]^-$ ion is somewhat weaker than those in the uranyl, $[UO_2]^{2+}$, group, whereas the U=O bond length in the latter (1.81 Å)[27] is longer than that in the $[UOCl_5]^-$ ion (1.7 Å).[23]

The relatively strong bonding in the $[UO_2]^{2+}$ group has been ascribed[28] to the p_π interaction with vacant *f* orbitals of the uranium atom; certainly (f_{xz^2}, f_{yz^2}) and $(f_{y(3x^2-y^2)}, f_{x(x^2-3y^2)})$ are of suitable symmetry (E_u in D_{4h}) for such interactions with non-bonding electrons of identical atoms X in a linear UX_2 group of a species $[UX_2Y_4]^{2-}$, but *f* or *d* covalent contributions probably play only a minor role in the bonding in uranium-(V) or -(VI) complexes.

Metal-Halogen Vibrations.—The frequencies and intensities of the very strong Raman features at 347 and 341 cm^{-1} in the spectrum of $[Ph_4P][UOCl_5]$, which correspond to the weak i.r. features at 345 and 341 cm^{-1}, suggest that they are associated with totally symmetric (U–Cl) stretching modes. We assign these features to an in-phase symmetrical breathing mode, strong in the Raman and weak in the i.r. spectrum, and to the corresponding out-of-phase breathing mode at lower energy in both the Raman and i.r. spectra. The broad feature at 300 cm^{-1} in the i.r. spectrum can be resolved into a triplet at 302, 298, and 291 cm^{-1}, the corresponding feature in the Raman spectrum appearing at 293 cm^{-1}. These are assigned to the equatorial U–Cl modes, an assignment which is supported by the disappearance of these features in the i.r. spectrum of $[Ph_4P][UOClBr_4]$ in which the medium-intensity feature at 331 cm^{-1} was assigned to the axial (U–Cl) stretching mode and the feature at 215 cm^{-1} to the (U–Br) stretching mode. The (U–Cl) assignments are supported by *X*-ray structural work[23] on $[Ph_4P][UOCl_5]$ which indicates that the U–Cl bond *trans* to the U=O bond is shorter than the equatorial U–Cl bonds, an effect which has also been reported[24] for the $[PaOCl_5]^{2-}$ ion. The same pattern of metal–chlorine features was observed in the i.r. spectra of $[Et_4N]_2[PaOCl_5]$,[2] $[Et_4N]_2[UOCl_5]$,[3] and $[Ph_4P][WOCl_5]$. It is possible that the equatorial W–Cl bonds in the tungsten salt are shorter than the axial one, in which case the higher-energy W–Cl feature is due to the symmetric stretching mode of the equatorial W–Cl bonds.

The U–F stretching modes observed at 595, 505, and 490 cm^{-1} in the i.r. spectrum of $[Ph_4P][UOF_5]$ correspond to those observed[7] for UOF_4 (667, 558, and 478 cm^{-1}) and β-UF_5 (605, 557, and 512 cm^{-1}), but features attributable to fluorine bridging [as observed for UOF_4 (375 cm^{-1}) and β-UF_5 (388 cm^{-1})] were absent. The salt $[Et_4N]_2[UOF_5]$ has been shown[3] to be isostructural with $[Et_4N]_2[UF_6]$, in

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which the anion is octahedral,[29] and it is therefore reasonable to suppose that the $[UOF_5]^-$ ion is also monomeric and octahedral.

Electron-transfer Spectra.—The electronic spectra of some related uranium chloro-complexes are shown in Figure 2. The optical electronegativities of uranium in these and several other uranium compounds were calculated from relation (5),[30] where $\sigma_{obs.}$ is the wavenumber of the first

$$\sigma_{obs.} = 30\,000[\chi_{opt.}(X) - \chi_{uncorr.}(M)]\ cm^{-1} \qquad (5)$$

electron-transfer band. The calculated, and some other reported, values are given in Table 3. The extent of stabilisation resulting from replacement of chloride by oxide ion is illustrated by the optical electronegativity values for uranium in UCl_6 (2.4), $[UOCl_5]^-$ (2.2), and $[UO_2Cl_4]^{2-}$ (1.9) and in $[UCl_6]^-$ (2.2) and $[UOCl_5]^{2-}$ (1.9). This corresponds to a decrease in U–Cl interaction which is also reflected in the decrease in frequency of the U–Cl stretching mode. The value of 2.2 obtained for both $[UOCl_5]^-$ and $[UCl_6]^-$ indicates that the U–Cl interaction can, however, be kept constant by replacing one chloride by an oxide ligand, so increasing the oxidation state of uranium by one unit.

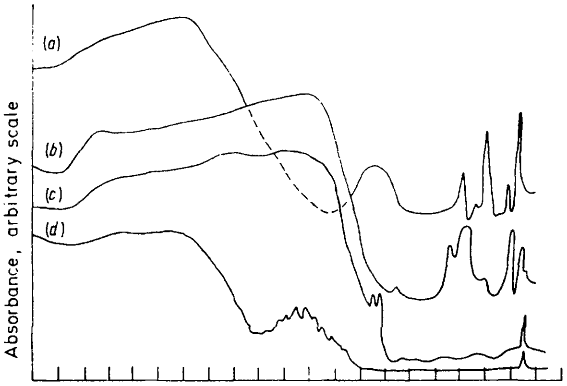

FIGURE 2 Diffuse-reflectance spectra of $[Et_4N]_2[UOCl_5]$ (*a*), $[Ph_4P][UCl_6]$ (*b*), $[Ph_4P][UOCl_5]$ (*c*), and $[Ph_4P]_2[UO_2Cl_4]$ (*d*)

DISCUSSION

The ease of replacement of oxygen by chlorine in the uranium chloro-oxo-species examined in this work is $[UOCl_5]^- < [UO_2Cl_4]^{2-} \ll [UOCl_5]^{2-}$. This follows the order of U–O bond lengths in the first two species mentioned above, although from the vibrational spectra it seems that the U–O bonds in $[UO_2Cl_4]^{2-}$ are stronger than that in $[UOCl_5]^-$. However, in the latter case the products of oxygen replacement would be either UCl_6 or the rather unlikely anion $[UCl_7]^{2-}$, neither of which would be stable with respect to reduction to U^V, so that the lability of the U=O bond in the $[UOCl_5]^{2-}$ ion, in which the frequency of the U=O stretching mode is very close to that in $[UOCl_5]^-$, probably depends on the thermodynamic stability of the chlorination product $[UCl_6]^-$.

The reaction of $[Ph_4P][UOCl_5]$ with HBr to form $[Ph_4P][UOClBr_4]$ depends on the stronger U–Cl bond *trans* to the U=O bond. When the *trans*-chlorine atom is ultimately replaced by bromine the U^{VI} is so strongly electron accepting that electron transfer takes place, resulting in reduction to U^V. The reaction of $[UO_2Br_4]^{2-}$ with $SOBr_2$ presumably goes through this intermediate $[UOBr_5]^-$ stage, but reduction to U^V is too rapid to allow isolation of $[Ph_4P][UOBr_5]$.

EXPERIMENTAL

All compounds were prepared and handled using vacuum-line and dry-nitrogen-atmosphere glove-box techniques to afford protection against atmospheric moisture and oxygen.

Reagents.—Hydrated uranyl chloride (B.D.H.) and $[Ph_4P]Br$ and $[Ph_4P]Cl$ (Fluorochem, Ltd.) were used as supplied; Ph_3PO (B.D.H.) was vacuum sublimed before use. Tungsten(VI) tetrachloride oxide,[31] *NN*-dimethylpivalamide (dmp),[32] thionyl bromide,[33] and $[Et_4N]_2[UOCl_5]$ [3] were prepared by published methods. The last was shown to contain less than 2% U^{IV}. Attempted preparation of $[Ph_4P]_2[UOCl_5]$ yielded products contaminated with >5% U^{IV} and U^{VI}. The salts $[Ph_4P]_2[UO_2X_4]$ (X = Cl or Br),[34] $[Ph_4P][UCl_6]$,[35] and $[Ph_4P]_2[UCl_6]$[36] were prepared following established procedures.

Solvents were rigorously dried over phosphorus pentaoxide, distilled, freed from dissolved air by purging with nitrogen, and stored over molecular sieves (type 4A). Drying over powdered calcium hydride was less efficient for dichloromethane. Pyridine was dried over potassium hydroxide and dmp was distilled before use. Hydrogen fluoride was dried by treatment with fluorine followed by fractional distillation (3 times) in an all-nickel vacuum line. All reactions with anhydrous HF were carried out in all-Kel-F reactor tubes which were attached to this vacuum line. The tubes were treated with fluorine and then evacuated to 10^{-6} Torr before use.* Hydrogen chloride and bromide were dried over P_4O_{10}.

Preparations.—(a) *Tetraphenylphosphonium pentachloro-oxouranate*(VI). The salt $[Ph_4P]_2[UO_2Cl_4]$ (5 g) was dissolved in $SOCl_2$ (15 cm^3) and heated under reflux (5 min). The deep red solution was cooled, whereupon the red solid *product* crystallised. This was washed with thionyl chloride–2-methylbutane (1 : 1, 10 cm^3), then 2-methylbutane (15 cm^3), and vacuum dried (10^{-5} Torr, 2 h), yield 74%.

(b) *Tetraphenylphosphonium trichlorodioxouranate*(VI)–*hydrogen chloride* (1/1). Slightly moist dichloromethane (30 cm^3), which had been dried over calcium hydride, was added to $[Ph_4P][UOCl_5]$ (1 g); the red crystals gradually changed to thin orange *needles*, with the evolution of HCl. The product was washed with 2-methylbutane (10 cm^3) and vacuum dried (10^{-2} Torr, 30 min), yield 55%.

(c) *Tetraphenylphosphonium trichlorodioxouranate*(VI).

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* Torr = (101 325/760) Pa.

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The salt $[Ph_4P][UO_2Cl_3]{\cdot}HCl$ was heated to 80 °C at 10^{-6} Torr for 1 h. The yield was quantitative.

(d) *Tetraphenylphosphonium pentachloro-oxotungstate*(VI). The salts $WOCl_4$ (2.0 g) and $[Ph_4P]Cl$ (2.2 g) were mixed in $SOCl_2$ (20 cm^3) and 2-methylbutane (20 cm^3) was added to induce crystallisation. The red *product* was then treated as in (a), yield 76%. It is hygroscopic and more soluble in $SOCl_2$ and dichloromethane than the uranium(VI) salt.

(e) *Tetraphenylphosphonium pentafluoro-oxouranate*(VI). Hydrogen fluoride (10 cm^3) was condensed onto $[Ph_4P][UOCl_5]$ (1.0 g) at −196 °C. The mixture was allowed to warm up to *ca.* −30 °C with constant agitation and was maintained at this temperature for 6 h. Hydrogen chloride was evolved and an orange solution resulted from which the peach coloured *product* was isolated in near quantitative yield on careful vacuum evaporation of the solvent at 25 °C followed by vacuum drying at 10^{-6} Torr (1 h). The pale yellow tungsten *salt* was prepared similarly in near quantitative yield with the reaction mixture being allowed to warm up to −78 °C only.

TABLE 4

Analytical results [a]

Compound	Colour	M	Halogen	C	H	P	M.p. (θ_c/°C)	Λ [b]
$[Ph_4P][UOF_5]$	Peach	35.4 (34.55)	13.5 (13.8)	42.3 (41.85)	3.2 (2.95)	4.3 (4.50)	110 (decomp.)	
$[Ph_4P][UOCl_5]$	Red	31.1 (30.9)	23.3 (23.0)	37.9 (37.4)	2.5 (2.60)	4.3 (4.00)	224	124
$[Ph_4P][UOClBr_4]$	Dark brown	24.6 (25.1)	32.3 [c] (33.7 [c]) 3.5 [d] (3.74 [d])	30.0 (30.4)	2.2 (2.15)	3.5 (3.25)	196 (decomp.)	131
$[Ph_4P][UO_2Cl_3]{\cdot}HCl$	Orange	31.7 (31.65)	18.5 (18.75)	39.6 (38.3)	3.1 (2.80)	4.4 (4.10)	80 (decomp.)	
$[Ph_4P][UO_2Cl_3]$	Yellow	33.3 (33.25)	15.0 (14.85)	40.0 (40.25)	2.8 (2.85)	4.3 (4.35)		
$[Ph_4P]_2[UO_2Cl_4]$	Yellow	21.7 (21.85)	12.8 (13.0)	53.1 (52.85)	3.8 (3.70)	5.5 (5.70)	298	258
$[Ph_4P]_2[UO_2Br_4]$	Dark yellow	18.7 (18.75)	24.8 (25.2)	45.8 (45.45)	3.2 (3.20)	4.9 (4.90)	296	266
$[Ph_4P][WOF_5]$	Pale yellow	29.5 (29.0)	12.9 (14.95)	44.7 (45.45)	3.1 (3.20)	4.7 (4.90)	130 (decomp.)	
$[Ph_4P][WOCl_5]$	Red	26.4 (26.25)	25.3 (25.3)	40.6 (41.15)	2.8 (2.90)	4.3 (4.45)	258	127
$[Ph_4P][WOBr_5]$	Brown	19.8 (19.6)	42.7 (42.55)	30.7 (30.7)	2.1 (2.15)	3.5 (3.30)	204 (decomp.)	140
$[Ph_4P]Cl$								169

[a] Calculated values are given in parentheses. [b] In S cm^2 mol^{-1} (in MeCN at 25 °C). [c] Br. [d] Cl.

(f) *Tetraphenylphosphonium tetrabromochloro-oxouranate*-(VI). Hydrogen bromide was passed slowly into a solution of $[Ph_4P][UOCl_5]$ (0.5 g) in rigorously dried dichloromethane (100 cm^3) at 0 °C for 2—3 min; the resulting dark solution was vacuum evaporated, leaving the dark brown *product*, which was dried at 10^{-2} Torr (1 h). The analogous reaction with $[Ph_4P][WOCl_5]$ (1.6 g) in dichloromethane (50 cm^3) yielded $[Ph_4P][WOBr_5]$.

Analyses and Physical Measurements.—The oxidation state of uranium was checked by dichromate titration; [37] chloride and bromide were determined by potentiometric titration against silver(I) nitrate. Uranium,[38] tungsten,[39] phosphorus,[40] and fluoride [41] were determined by published methods, carbon and hydrogen by combustion. The results are in Table 4.

Electronic spectra were recorded using a Unicam SP 700 spectrophotometer (diffuse reflectance); special sample holders were constructed to allow all spectral measurements to be made in a dry nitrogen atmosphere. I.r. spectra were recorded using Perkin-Elmer 225 (4 000—300 cm^{-1}, CsI plates) and Research and Industrial Instruments, Ltd. FS-720 Fourier spectrometers (300—30 cm^{-1}, Polythene plates); the Fourier transforms were made on a CDC-7600 computer using associated programs.[42] Raman spectra of solids were recorded using a Cary 82 laser-Raman spectrometer with He–Ne excitation (6 328 Å); the fluoro-complexes gave poor Raman spectra and the bromo-complexes were too dark for spectra to be obtained. Conductivities were measured using a Mullard conductivity cell (type E751/B) with a Wayne Kerr universal bridge (B221). The measurements were carried out in a dry-box. *X*-Ray-diffraction powder photographs were obtained as described previously.[43]

We thank Mr. M. A. Hart for microanalyses (C, H, P, Cl, Br, F, W, and U), Dr. J. I. Bullock for far-i.r. and diffuse-reflectance measurements, and the S.R.C., the South African Atomic Energy Board, C.S.I.R. (to J. G. H. du P.), and the University of Port Elizabeth for support.

[5/096 *Received*, 16*th January*, 1975]

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