Preparation and Properties of Halogeno-, Oxyhalogeno-, and Ethoxyhalogeno-complexes of Uranium(v)

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Hexahalogenouranates(v), [M][UX$_6$] [M = N(C$_2$H$_5$)$_4$ or As(C$_6$H$_5$)$_4$; X = Cl or Br], and pentahalide–tppo complexes, UX$_5$·tppo (X = Cl or Br; tppo = triphenylphosphine oxide), react with anhydrous oxygen-free ethanol at room temperature to yield new complexes of the types [M][U(OC$_2$H$_5$)$_2$X$_4$] and U(OC$_2$H$_5$)$_2$X$_3$.tppo, respectively. Controlled hydrolysis of [N(C$_2$H$_5$)$_4$][U(OC$_2$H$_5$)$_2$Cl$_4$] and interaction of [N(C$_2$H$_5$)$_4$][UCl$_6$] and As$_2$O$_3$ in non-aqueous solvents containing [N(C$_2$H$_5$)$_4$]Cl provide new routes to [N(C$_2$H$_5$)$_4$]$_2$[UOCl$_5$], which crystallises in the monoclinic space group *Cc* with *a* = 14.20(1), *b* = 14.36(1), *c* = 13.29(1) Å, and β = 90.25(3)°. Oxygen-18 substitution studies have been undertaken in order to facilitate assignment of the vibrational spectrum of this compound. Infrared and electronic spectral data are also reported for the ethoxyhalogeno-complexes and for the previously uncharacterised fluoro-complexes [N(C$_2$H$_5$)$_4$][UF$_6$] and [N(C$_2$H$_5$)$_4$]$_2$[UF$_7$]. Attempts to obtain oxychloro-complexes of the type UOX$_3$·2tppo by controlled hydrolysis of the appropriate ethoxy-complex or by reactions involving UX$_5$·tppo and As$_2$O$_3$ have resulted in disproportionation of U^{V} to U^{IV} and U^{VI}.

RYAN[1] prepared quinquevalent uranium oxychloro-complexes of the type M$_2$UOX$_5$ [M = N(C$_2$H$_5$)$_4$ with X = F or Cl; M = As(C$_6$H$_5$)$_4$ with X = Cl or Br], [N(C$_2$H$_5$)$_4$]$_2$[UOBr$_5$]·2.5[N(C$_2$H$_5$)$_4$]Br, and [C$_5$H$_5$NH]$_2$[UOCl$_5$]·2.5[C$_5$H$_5$NH]Cl by reactions involving hexahalogeno-complexes, [M][UX$_6$], and undried MX in solvents such as acetone and nitromethane–acetone mixtures at −78 °C. Selbin and co-workers[2,3] employed a similar method with UCl$_5$·Cl$_2$C=CClCOCl as starting material to obtain [N(C$_2$H$_5$)$_4$]$_2$[UOX$_5$] (X = F or Cl), whilst the pyridinium salt [C$_5$H$_5$NH]$_2$[UOCl$_5$] is reported[4,5] to form on addition of pyridine to ethanolic solutions of UCl$_5$·SOCl$_2$ saturated with hydrogen chloride. It has also been obtained recently[6] by the interaction of UOCl$_3$ and [C$_5$H$_5$NH]Cl in non-aqueous media, and by photolysis of UO$_2$Cl$_2$·2C$_5$H$_5$N in ethanol.[7] Analogous protactinium(v) complexes, [N(C$_2$H$_5$)$_4$]$_2$[PaOX$_5$] (X = Cl or Br), and oxytrihalide complexes of the type PaOX$_3$·2tppo (tppo = triphenylphosphine oxide) have been prepared[8] by controlled hydrolysis of ethoxyhalogeno-complexes, [N(C$_2$H$_5$)$_4$][Pa(OC$_2$H$_5$)$_2$X$_4$] and Pa(OC$_2$H$_5$)$_2$X$_3$·tppo, respectively, in commercial methyl cyanide containing an excess of ligand. Apart from UOCl$_3$·C$_2$H$_5$OH,[4] complexes of uranium(v) oxytrihalides appear to be unknown.

Two i.r. vibrations have been reported[1-3,5-7] for the [UOX$_5$]$^{2-}$ species in the region expected to contain ν(U=O) bands; for example,[1] 853 and 760 cm^{-1} for X = F, 913 and 813 cm^{-1} for X = Cl, and 919 and 817 cm^{-1} for X = Br. In contrast to this, a single band (830 cm^{-1} for X = Cl and 840 cm^{-1} for X = Br) occurs in each of the spectra of the protactinium(v) analogues,[8] of which [PaOCl$_5$]$^{2-}$ has been shown to possess distorted octahedral stereochemistry.[9] Similarly, only one band is observed in the spectra of PaOCl$_3$·2tppo and PaOBr$_3$·2tppo.[8]

Thus, it appeared worthwhile to investigate new preparative methods for the uranium(v) oxypentahalogeno-complexes which would permit ^{18}O substitution and also possibly result in crystals suitable for *X*-ray structure analysis. Additional information has also been obtained on the UCl$_5$·SOCl$_2$–C$_2$H$_5$OH reaction and attempts have been made to characterise further uranium(v) oxytrihalide complexes with donor ligands. During the course of these investigations the new fluoro-complexes [N(C$_2$H$_5$)$_4$][UF$_6$] and [N(C$_2$H$_5$)$_4$]$_2$[UF$_7$] have been prepared and certain of their chemical and physical properties studied.

RESULTS AND DISCUSSION

Preparation of Complexes.—The hexahalogenouranates(v), [M][UX$_6$] [M = N(C$_2$H$_5$)$_4$ or As(C$_6$H$_5$)$_4$; X = Cl or Br], reacted at room temperature with anhydrous ethanol to yield the new complexes [M][U(OC$_2$H$_5$)$_2$X$_4$] analogous to those reported previously[8] for protactinium(v). Attempts to obtain [N(C$_2$H$_5$)$_4$][U(OC$_2$H$_5$)$_2$F$_4$] from the hexafluoro-complex were unsuccessful, presumably as a consequence of the greater strength of the U–F bond relative to those with the other halides.

Addition of commercial methyl cyanide containing MCl to the ethoxytetrachloro-complexes resulted in the rapid formation of blue oxypentachloro-complexes, [M]$_2$[UOCl$_5$]. The use of anhydrous methyl cyanide to which 0.5% by volume H$_2$^{18}O had been added gave a high yield of [N(C$_2$H$_5$)$_4$]$_2$[U^{18}OCl$_5$]. Alternatively, the reaction between [N(C$_2$H$_5$)$_4$][UCl$_6$] and the stoicheiometric amount of As$_2$O$_3$ (3 : 1 mol ratio) suspended in anhydrous methylene dichloride containing [N(C$_2$H$_5$)$_4$]Cl gave a quantitative yield of the oxypentachlorouranate(v). Neither method yielded crystals, and to-date all attempts to obtain single crystals suitable for *X*-ray work have been unsuccessful. Attempts to prepare the bromo-analogue by both methods at room temperature resulted in disproportionation, yielding [N(C$_2$H$_5$)$_4$]$_2$[UBr$_6$] and [N(C$_2$H$_5$)$_4$]$_2$[UO$_2$Br$_4$]; this is in agreement with the earlier observations[1,3] on the instability of [UOBr$_5$]$^{2-}$ and the need for low temperatures for its successful formation. In addition, neither [N(C$_2$H$_5$)$_4$][UF$_6$] nor [N(C$_2$H$_5$)$_4$]$_2$[UF$_7$] reacted with As$_2$O$_3$ in methylene dichloride during a period of several days.

Addition of anhydrous ethanol to quinquevalent complexes of the type UX$_5$·tppo (X = Cl or Br) produced the previously unknown ethoxyhalogeno-complexes U(OC$_2$H$_5$)$_2$X$_3$·tppo. Unlike their protactinium(v) analogues,[8] these were not converted into oxytrihalide complexes of the type $UOX_3{\cdot}2tppo$ on addition of commercial methyl cyanide containing tppo. Similarly, reactions between $UCl_5{\cdot}tppo$ and As_2O_3 (3 : 1 mol ratio) in anhydrous CH_2Cl_2 or CS_2 containing tppo failed to yield the oxytrichloride complex. In both types of reaction disproportionation occurred with the formation of insoluble tetrahalide complexes, $UX_4{\cdot}2tppo$, and more soluble uranyl(VI) species. Neither $UOCl_3$ nor $[N(C_2H_5)_4]_2[UOCl_5]$ reacted with tppo in CH_2Cl_2.

In view of these observations the earlier work [4] on the formation of $UOCl_3{\cdot}C_2H_5OH$ was repeated. Room-temperature vacuum evaporation of the green solution obtained by dissolving $UCl_5{\cdot}SOCl_2$ in anhydrous ethanol gave a brown oil which was not completely converted into a solid after several hours at 70 °C *in vacuo*, and which at slightly higher temperature decomposed to a black carbonaceous material. Analysis of the oily product obtained after pumping for several hours at room temperature (Cl : U ratio of ~1.6 : 1) indicated appreciable decomposition even at this temperature. The presence of an ethoxychloride, presumably $U(OC_2H_5)_2Cl_3$, in the freshly prepared, green, ethanol solution was demonstrated by precipitation of $[N(C_2H_5)_4][U(OC_2H_5)_2Cl_4]$ and $U(OC_2H_5)_2Cl_3{\cdot}tppo$ by addition of $[N(C_2H_5)_4]Cl$ and tppo, respectively. These new observations are more in agreement with those of Jones *et al.*[10] who prepared $U(OC_2H_5)_2Cl_3$ by interaction of $U(OC_2H_5)_5$ and gaseous hydrogen chloride in diethyl ether and observed that the green liquid obtained by removal of the solvent turned brown when heated, and decomposed on attempted vacuum distillation.

Since uranium(V) fluoro-complexes were required for the attempted preparation of ethoxyfluoro-complexes, and of oxypentafluoro-complexes by the As_2O_3 route, the formation of the previously uncharacterised compounds $[N(C_2H_5)_4][UF_6]$ and $[N(C_2H_5)_4]_2[UF_7]$ was studied by a slightly different method from those previously employed for fluorouranates(V). Thus, condensation of anhydrous hydrogen fluoride onto $[N(C_2H_5)_4][UCl_6]$ yielded a pale blue solution when the mixture was allowed to warm to room temperature. Removal of hydrogen chloride and excess of hydrogen fluoride *in vacuo* gave $[N(C_2H_5)_4][UF_6]$, a blue solid which was recrystallised from methylene dichloride. The heptafluoro-complex was obtained in a similar manner from $[N(C_2H_5)_4]_2[UOCl_5]$.

Crystallographic Properties.—*X*-Ray powder data indicate that $[N(C_2H_5)_4]_2[UOCl_5]$ is isostructural with the protactinium(V) analogue, possessing monoclinic symmetry, space group *Cc*, with $a = 14.20(1)$, $b = 14.36(1)$, $c = 13.28(1)$ Å, and $\beta = 90.25(3)°$. The observed and calculated $\sin^2\theta$ values are listed in Table 1 with estimated intensities. Full structural data, to permit a detailed comparison with those available [9] for $[N(C_2H_5)_4]_2[PaOCl_5]$, have not yet been obtained because all attempts to grow single crystals have met with no success.

TABLE 1

X-Ray powder diffraction results for $[N(C_2H_5)_4]_2[U^{18}OCl_5]$

$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	*h*	*k*	*l*	$I_{est.}$ *
0.0094	0.0092	1	1	−1	s+
	0.0093	1	1	1	
0.0118	0.0119	2	0	0	m
0.0140	0.0135	0	0	2	m−
0.0235	0.0234	2	2	0	m+
0.0255	0.0255	2	0	2	s
0.0263	0.0267	2	2	−1	w
0.0328	0.0328	3	1	−1	s
0.0335	0.0329	3	1	1	w−
0.0371	0.0370	2	2	2	s−
0.0429	0.0428	3	1	−2	w− −
0.0467	0.0462	0	4	0	w
0.0477	0.0473	4	0	0	w
0.0557	0.0559	3	3	−1	w+
0.0586	0.0588	4	2	0	w+
0.0607	0.0610	4	0	2	m
0.0623	0.0623	4	2	1	w
0.0723	0.0721	4	2	−2	m−
	0.0725	4	2	2	
0.0795	0.0799	5	1	−1	m+
0.0930	0.0934	4	4	0	w+
0.1031	0.1030	5	3	−1	w+
	0.1032	5	3	1	
0.1071	0.1071	4	4	2	m−
0.1132	0.1133	3	1	−5	w− −
	0.1133	1	3	5	
0.1188	0.1190	2	6	−1	w+
0.1247	0.1240	4	4	3	w−
0.1303	0.1304	0	4	5	m
0.1337	0.1335	2	0	6	w− −
0.1358	0.1364	3	3	−5	w− −
0.1415	0.1420	2	4	−5	w−
0.1489	0.1491	5	5	−1	w
0.1512	0.1513	3	1	6	w
0.1613	0.1613	7	1	2	w+
0.1658	0.1655	6	4	−2	w+
	0.1661	6	4	2	
0.1722	0.1723	6	2	4	w+
0.1766	0.1766	5	5	3	m−
0.1814	0.1812	3	7	−2	w−
	0.1815	3	7	2	
0.1847	0.1846	5	3	5	w−
	0.1846	0	8	0	
0.1973	0.1971	5	1	−6	w−
0.2017	0.2018	8	0	−2	w−
0.2048	0.2045	4	6	−4	w−
0.2115	0.2113	0	4	7	w−
0.2203	0.2201	7	5	1	w− −
	0.2202	5	3	−6	
	0.2204	3	5	6	
0.2313	0.2312	8	2	3	w− −

* s = Strong, m = medium, w = weak.

Partial *X*-ray powder data for $[N(C_2H_5)_4][U(OC_2H_5)_2Cl_4]$ and $U(OC_2H_5)_2Cl_3{\cdot}tppo$ are available as Supplementary Publication No. SUP 22606 (2 pp.); * these complexes, which are also isostructural with their protactinium(V) analogues,[8] obviously possess low symmetry and unit-cell data have not been deduced. As indicated the bromo-complexes are isostructural with the chloro-complexes.

Infrared Spectra.—Of the two i.r. features which could be attributed to the U=O stretching vibration in the spectra of M_2UOX_5 complexes, the lower of the two frequencies agrees with those observed [8] for $[PaOX_5]^{2-}$ (and for [11] $[UOX_5]^-$), whereas Selbin *et al.*[2] assign the higher of the two frequencies to the U=O stretching mode on the basis of the positions of the M=O stretching modes in analogous *d* transition-metal oxyhalogeno-complexes. However, it is the lower frequencies which occur as

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 2

Infrared data (cm^{-1}) for $[N(C_2H_5)_4]_2[UOCl_5]$

$[N(C_2H_5)_4]_2[U^{16}OCl_5]$		$[N(C_2H_5)_4]_2[U^{18}OCl_5]$	
This work	Ref. 1	This work	Assignment
913m	913	899m	?
813s	813	771s	ν(U=O)str.
294m	296	292m	ν(U–Cl)ax.
255vs	253	252vs	ν(U–Cl)eq.
195m	197	186m	δ(U=O)rock
118m	120	120m	ν(U–Cl)rock

s = Strong, m = medium.

vibronic bands in the electronic spectra of the uranium(v) complexes.[2,3]

In an attempt to clarify this problem and to try to understand why two bands occur for the uranium(v) compounds but not for other oxypentahalogeno-complexes [8,12,13] the i.r. spectrum of ^{18}O-substituted $[N(C_2H_5)_4]_2[UOCl_5]$ has been studied; despite numerous attempts using different equipment no satisfactory Raman spectra could be obtained. As indicated in Table 2, the i.r. data for the ^{16}O complex are in good agreement with those recorded by Ryan.[1] On the basis of reduced masses, ^{18}O substitution would be expected to shift the bands at 813 and 195 cm^{-1} by 43 and 10 cm^{-1}, respectively. These values are in excellent agreement with those observed (Table 2) and the bands are assigned to the U=O stretching and rocking modes, respectively. It is interesting to note that similar shifts occur on ^{18}O substitution in $Cs_2UO_2Cl_4$.[14] The smaller shift, 14 cm^{-1}, for the band at 913 cm^{-1} indicates some contribution from a U=O mode but on the i.r. evidence available, and in the absence of Raman data, it is not possible to make a reliable assignment, particularly since the band is very much stronger than would be expected for a combination or overtone mode. However, the suggestion * that the two bands may arise from site-symmetry splitting of a single U=O mode can be rejected in view of the different shifts observed on ^{18}O substitution. The U–Cl axial and equatorial assignments shown in Table 2 are based on the structural data for $[N(C_2H_5)_4]_2[PaOCl_5]$ in which the axial Pa–Cl bond is shorter than the equatorial bonds, for which the i.r. vibrations occur at 289 and 251 cm^{-1}, respectively.[9] The U–Cl bending mode (118 cm^{-1}) is assigned by analogy with $Cs_2UO_2Cl_4$.[14]

TABLE 3

Infrared data (cm^{-1}) for ethoxyhalogeno-complexes of uranium(v) [a]

Compound	ν(U–X)	δ(U–X)	ν(U–O) [b]	ν(P=O)	$\Delta\nu$(P=O)	Additional vibrations
$[N(C_2H_5)_4][U(OC_2H_5)_2Cl_4]$	271s, br	118m	537m, br			320w (sh), 183w
$[As(C_6H_5)_4][U(OC_2H_5)_2Cl_4]$	262s, br		525m, br			314vw
$U(OC_2H_5)_2Cl_3$ [c]	265vs, 285 (sh)	115m	522m, br			311w (sh), 187w
$U(OC_2H_5)_2Cl_3$·tppo	270vs, 278 (sh)		*d*	1 062m	130	210w
$[N(C_2H_5)_4][U(OC_2H_5)_2Br_4]$	195vs, br	77m	538m, br			268w, 125m
$U(OC_2H_5)_2Br_3$·tppo	188vs, br		*d*	1 060m	132	206 (sh), 160 (sh)

[a] Ligand (tppo and ethoxy) and cation vibrations are not included. [b] Tentative assignment as discussed in the text. [c] In solution in ethanol. [d] Masked by strong tppo vibration.

Comparison of the i.r. spectra of the ethoxyhalogeno-complexes with each other and with ligand and cation spectra permits the assignments listed in Table 3. The shifts observed on co-ordination of tppo, $\Delta\nu$(P=O), are 3—6 cm^{-1} larger than those recorded for the protactinium(v) analogues.[8] Whilst the uranium–halogen assignments are probably reliable, those for ν(U–O) must be considered *tentative*; they are based on the absence of a band in this region of the spectrum of ethanol, the presence of a similar band (at 554 cm^{-1}) in the spectrum of $[N(C_2H_5)_4][Ta(OC_2H_5)_2Cl_4]$, and the assignments previously reported [15,16] for $Ta(OC_2H_5)_5$, $Nb(OC_2H_5)_5$, and $U(OC_2H_5)_5$ (*ca.* 556, *ca.* 571, and 502 cm^{-1}). As previously observed [8] for a variety of complexes containing tppo, an additional band occurs in the 400—450 cm^{-1} region of the spectra of the uranium(v) ethoxyhalogeno-complexes relative to that of the free ligand. It is tempting to assign this, at 421 cm^{-1} in each case, to ν[U–O(tppo)] as done by Day and Venanzi [17] for the band of UCl_4·2tppo at 417 cm^{-1}. However, since, as discussed previously,[18] an extra band is present in the 410—425 cm^{-1} region of spectra of tppo complexes of various pentahalides,[19] tin tetrahalides,[20] actinide tetrahalides,[18] indium trihalides,[21] and uranyl chloride,[22] and additional changes, although somewhat minor, occur in other regions of the spectra below 400 cm^{-1} on co-ordination of tppo, and because in view of the differences in molecular weights and valence states of the binary halides involved one would anticipate a large variation in the positions of ν[M–O(tppo)], any assignment must be deferred until a full co-ordinate analysis is available. Of the additional bands listed in Table 3, those at 210 and 206 cm^{-1} may be ligand modes which have shifted slightly (from 190 cm^{-1}) on co-ordination; similarly, the shoulder at 160 cm^{-1} could originate from the ligand mode at 170 cm^{-1}.

Electronic Spectra.—The solid-state electronic spectrum of $[N(C_2H_5)_4]_2[UOCl_5]$ was virtually identical with that reported and interpreted by Selbin *et al.*[2] The spectra of $[N(C_2H_5)_4][U(OC_2H_5)_2X_4]$, $U(OC_2H_5)_2X_3$·tppo (X = Cl or Br), and that of $U(OC_2H_5)_2Cl_3$ in ethanol are very similar to that of the oxypentachloro-complex. In view of the complicated vibronic structure, energy-level assignments have not been attempted. The spectra are illustrated in ref. 23.

The spectra recorded for $[N(C_2H_5)_4][UF_6]$ indicate the presence of octahedral or close to octahedral UF_6^- groups both in non-aqueous solution and in the solid. The energy-level assignments shown in Table 4 are based on previous interpretations [1,24] of spectra of hexahalogeno-complexes of uranium(v) and protactinium(IV). The vibronic side-bands observed around 500—516 and

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* This suggestion was made by a referee for the paper in ref. 2 and is cited in that paper as ref. 11.

TABLE 4

Electronic spectral data (cm^{-1}) for solid $[N(C_2H_5)_4][UF_6]$ [a]

Assignment	Room temperature		80 K	
	Band position	Vibrational frequency	Band position	Vibrational frequency
Γ_7–Γ_6 [b]			16 500	+450
	16 150	+200	16 230	+180
	(15 950)	0	(16 050)	0
	15 750	−200	15 870	−180
Γ_7–$\Gamma_{8'}$	14 245	+552	14 124w	+500
	(13 693)	0	(13 624)	0
			13 459m	−165
	13 141	−552	13 123m	−501
Γ_7–$\Gamma_{7'}$			8 032w	+636
	7 930m	+512	7 912m	+516
			7 708w	+312
	7 576m	+158	7 559m	+163
	7 515m	+123	7 525m	+129
			7 440w	+44
	7 418s	0	7 396s	0
			7 348w (sh)	−48
			7 257m	−139
	7 241m	−177	7 231m	−165
	6 897w,br	−521	6 881w	−514
Γ_7–Γ_8 [c]	5 186	0	5 182m	0

[a] Transitions in parentheses not observed; they are estimated as discussed previously in refs. 1 and 24. [b] There was a relatively high background in this region of the spectrum, possibly arising from a decomposition product formed on contact of $[N(C_2H_5)_4][UF_6]$ with the mulling agent, and the band positions are therefore not as accurate as those recorded for other regions of the spectrum. [c] A single broad band occurs in this region.

163—165 cm^{-1} in the spectrum at 80 K are close to the positions of the bands recorded directly in the i.r. spectrum at 532 cm^{-1} (ν_3) and 161 cm^{-1} (ν_4), respectively. On the basis of the electronic spectral results the position of ν_6 (i.r. and Raman inactive) is deduced as *ca.* 135 cm^{-1}, close to that obtained by Ryan[1] (≈124 cm^{-1}) for $[As(C_6H_5)_4][UF_6]$. In addition, the electronic transitions are very close to those for this compound.

EXPERIMENTAL

Materials.—Solutions of uranium(V) in thionyl chloride,[14] $[N(C_2H_5)_4][UCl_6]$,[25] $[N(C_2H_5)_4][UBr_6]$,[26] $[As(C_6H_5)_4][UCl_6]$,[25] UCl_5·tppo,[27] and UBr_5·tppo [26] were prepared by methods in the references cited. Solvents were dried, distilled, and stored over molecular sieves in an inert-atmosphere box. Commercially available $[N(C_2H_5)_4]Cl$, $[As(C_4H_5)_4]Cl$, and tppo were dried before use. Anhydrous hydrofluoric acid was provided by Dr. J. Holloway (University of Leicester). The compound $H_2{}^{18}O$ (>95%) was stored and handled in a dry inert atmosphere; As_2O_3 was vacuum sublimed prior to use.

On account of the instability of uranium(V) complexes in the atmosphere, all preparations were performed in a nitrogen-filled glove-box (H_2O and O_2 ⩽ 20 p.p.m.) in which samples were dispensed for analysis, *X*-ray, and spectral studies.

Preparations.—Ethoxyhalogeno-complexes. The appropriate hexahalogenouranate(V), $[M][UX_6]$ [$M = N(C_2H_5)_4$ or $As(C_6H_5)_4$; X = Cl or Br] (0.1—0.5 g), or pentahalide–tppo complex, UX_5·tppo (X = Cl or Br) (0.1—0.5 g), was stirred with anhydrous ethanol (1—3 cm^3) at room temperature. The slightly soluble products (Table 5) were isolated by centrifugation, washed with ethanol, and dried under vacuum. Yields were all >90%. Alternatively, UCl_5·$SOCl_2$ was dissolved in ethanol to which $[N(C_2H_5)_4]Cl$ or tppo was added; the resulting solids were isolated as before.

Oxypentachlorouranates(V). The ethoxyhalogeno-complex, $[N(C_2H_5)_4][U(OC_2H_5)_2Cl_4]$ (0.1—0.3 g), was treated with commercial methyl cyanide containing MCl (2—3 cm^3) at room temperature. The resulting precipitate was washed with cold methyl cyanide and dried under vacuum. The salt $[N(C_2H_5)_4]_2[U^{18}OCl_5]$ was prepared in a similar fashion using anhydrous methyl cyanide to which 0.5% by volume $H_2{}^{18}O$ had been added; the yield was 90%. An alternative route to $[N(C_2H_5)_4]_2[UOCl_5]$ involved stirring stoicheiometric amounts of $[N(C_2H_5)_4][UCl_6]$ and As_2O_3 (3 : 1 mol ratio) together in anhydrous methylene dichloride containing $[N(C_2H_5)_4]Cl$ for several hours. The insoluble blue product was washed with anhydrous methylene dichloride and dried under vacuum.

Hexa- and hepta-fluorouranates(V). The salt $[N(C_2H_5)_4][UCl_6]$, or $[N(C_2H_5)_4]_2[UOCl_5]$, (0.5 g) was dissolved in anhydrous hydrofluoric acid to yield a blue solution. Removal of excess of HF and the by-product HCl by vacuum evaporation at room temperature yielded pale blue solids which were recrystallised from anhydrous, oxygen-free, methylene dichloride. Yields were >90%.

Analyses.—Uranium was weighed as U_3O_8 following ignition of the hydrated oxide obtained by treatment of the compounds with carbonate-free aqueous ammonia. Chloride and bromide were precipitated and weighed as the silver salts. The results are shown in Table 5.

TABLE 5

Analytical results

Compound	Colour	Analysis (%) *	
		U	X
$[N(C_2H_5)_4][U(OC_2H_5)_2Cl_4]$	Pale green	39.65 (39.65)	23.65 (23.65)
$[As(C_6H_5)_4][U(OC_2H_5)_2Cl_4]$	Pale green	27.85 (27.9)	16.7 (16.65)
$[N(C_2H_5)_4][U(OC_2H_5)_2Br_4]$	Orange-yellow	30.7 (30.6)	41.15 (41.1)
$U(OC_2H_5)_2Cl_3$·tppo	Pale green	33.6 (33.4)	15.2 (14.9)
$U(OC_2H_5)_2Br_3$·tppo	Greenish yellow	27.95 (28.15)	28.4 (28.35)
$[N(C_2H_5)_4]_2[UOCl_5]$	Blue	34.35 (34.4)	25.8 (25.6)
$[N(C_2H_5)_4][UF_6]$	Pale blue	49.3 (49.35)	23.85 (23.65)
$[N(C_2H_5)_4]_2[UF_7]$	Blue-white	37.6 (37.7)	20.6 (21.05)

* Calculated values are given in parentheses.

Physical Investigations.—*X*-Ray powder data were collected and processed as described previously.[28] The techniques used for recording i.r. and electronic spectra are described in refs. 29 and 30, respectively.

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