Amide Complexes of Uranium Tetrahalides and Uranyl Chloride

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Uranium tetrachloride and tetrabromide form 1 : 2 complexes with amides of the type $R^1{\cdot}CO{\cdot}NR^2R^3$ when R^1 or R^2 and R^3 are bulky branched chains (R^1 = CMe_3, Me_2CHCH_2, or Me_2CH with R^2 = R^3 = Me, and R^1 = Me with R^2 = R^3 = Pr^i) but form 1 : 4 complexes when R^1 = Me, R^2 = H, and R^3 = Et or Pr^i. The corresponding uranyl chloride complexes are all of composition $UO_2Cl_2,2L$ except where L is $CH_3CONHEt$, when a 1 : 3 complex is obtained. I.r. spectroscopic results are reported for these, and some analogous thorium tetrachloride complexes. Studies of the u.v.–visible spectra of the complexes $UX_4,4L$ indicate that 1 : 2 complexes are formed first in the reaction of the tetrahalide with the ligand and that the 1 : 4 complexes react with halide ion in non-aqueous solvents to form octahedral anions $[UX_5L]^-$ and $[UX_6]^{2-}$.

COMPLEXES of the actinoid tetrahalides with acetamide,[1] *NN*-dimethylformamide (dmf) (Th,[2] U[3,4]), *NN*-dimethylacetamide [1,5] (dma), and the analogous dicarboxylamides [6] have demonstrated differences in the complexing behaviour of thorium as compared with uranium and the later actinoids. Thus with dmf or dma the thorium tetrachloride complexes are of composition $ThCl_4,4L$, whereas the other actinoid tetrachlorides [1,3,5] form complexes of composition $2MCl_4,5L$. The amides $R^1{\cdot}CO{\cdot}NR^2R^3$, where R^1, R^2, or R^3 are aromatic [7] (R^1 = Ph, R^2 = R^3 = Me, dmba; R^1 = H, R^2 = R^3 = Ph, dpf; R^1 = Ph_2CH, R^2 = R^3 = Me, ddma; R^1 = R^2 = Ph, R^3 = Me, baa) yield the solid complexes $UX_4,3dmba$, $UX_4,4dpf$, $2UX_4,5ddma$ (X = Cl or Br), and $UCl_4,2(baa)$, acetone. In spite of the relatively large size of the ligand, the co-ordination number of the uranium atom in the dmba and dpf complexes is greater than six in the solid. Although the uranium atom appears to be octahedrally co-ordinated in the solid ddma and baa complexes, their stoicheiometry is not $UX_4,2L$ and in solution in methyl cyanide the central atom appears to be at least eight-co-ordinate.[7] This is in marked contrast to the behaviour of the tetra-*N*-substituted ureas, which form [8] octahedral bis-complexes, $UX_4,2L$, when the substituents are alkyl groups or equal numbers of alkyl and aryl groups.

It was therefore of interest to study the effect of ligand size in these systems using aliphatic amides, $R^1{\cdot}CO{\cdot}NR^2R^3$, in which R^1 or R^2 and R^3 were branched or straight chains, in order to ascertain whether the bulkiest of these ligands would yield octahedral complexes of stoicheiometry $UX_4,2L$, isolable as solids, and also to investigate the equilibria that might be established when the ligand was added systematically to a solution of a uranium tetrahalide in a non-aqueous medium, such as acetone. The electronic spectra of six- and eight-co-ordinate uranium(IV) differ in a sufficiently marked manner for it to be possible to identify changes in co-ordination number in solution, thus enabling the latter to be studied by a titrimetric method. The influence of excess halide ion on the uranium(IV)–amide complex species present in such solutions can also be studied in the same way, as found in recent work on other oxygen donor complexes of the uranium tetrahalides.[9] It was also of interest to prepare the analogous complexes of dioxouranium(VI) dichloride, and some of the corresponding thorium tetrachloride complexes, in order to check whether there were any significant changes in the stoicheiometry of the isolable complexes with increasing ligand size.

The ligands investigated, and the abbreviations used for them in this work, are as follows:

$R^1{\cdot}CO{\cdot}NR^2R^3$

R^1 = Me, R^2 = H, R^3 = Et	ea
R^1 = Me, R^2 = H, R^3 = Pr^i	pa
R^1 = Me, R^2 = R^3 = Pr^n	dpa
R^1 = Me, R^2 = R^3 = Pr^i	ipa
R^1 = Me_2CH, R^2 = R^3 = Me	iba
R^1 = Me_2CHCH_2, R^2 = R^3 = Me	iva
R^1 = Me_3C, R^2 = R^3 = Me	pva

Di-N-*substituted Amides*.—The solid **1 : 2** complexes, $UX_4,2L$, with the branched chain ligands, pva, ipa, and iba, separated as crystalline solids on mixing solutions of the ligand and the uranium tetrahalide in acetone (pva) or ethyl acetate (ipa, iba), whereas the complexes with the other branched chain ligand, iva, in which the branching is more remote from the donor atom, were difficult to isolate from either solvent, and were only obtained by precipitation from an acetone solution of the components with light petroleum (b.p. 30—40°) ($UCl_4,2iva$) or evaporation of an ethyl acetate solution of the components to an oily residue which could be crystallized from a 4 : 1 mixture of ethyl acetate and

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

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[5] K. W. Bagnall, D. Brown, F. Lux, and G. Wirth, *Z. Naturforsch.*, 1969, **24b**, 214.

[6] K. W. Bagnall, D. Brown, and P. J. Jones, *J. Chem. Soc.* (*A*), 1966, 741.

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

[8] K. W. Bagnall J. G. H. du Preez and M. L. Gibson *J. Chem. Soc.* (*A*), 1971, 2124.

[9] J. G. H. du Preez, R. A. Edge, M. L. Gibson, H. E. Rohwer, and C. P. J. van Vuuren, to be published.

nitromethane. The ipa and iba complexes did not crystallize from acetone, and complexes of the tetrahalides with the straight chain ligand, dpa, could not be isolated as solids from either solvent. The ease of isolation is in the order pva > ipa > iba > iva > dpa, and it is clear that this sequence is related to the proximity of the bulky, branched chain part of the ligand to the donor atom, the carbonyl oxygen. In addition, it was observed that the uranium tetrabromide complexes with the more bulky ligands were less soluble in these organic solvents than the uranium tetrachloride analogues, which is consistent with a greater lattice stabilization resulting from a more even balance in size between the larger bromide ion and the large ligand.

The molar conductivities of these complexes in nitromethane were quite low; for example, Λ_{1000} for UCl_4,2pva and UCl_4,2iba were found to be 31·4 and 29·4 Ω^{-1} cm^{-2}, comparable with the molar conductivity[10] of $2UCl_4$,5dma.

The thorium tetrachloride complexes, $ThCl_4$,2pva and $ThCl_4$,3iba, were precipitated from acetone solutions of the components on the addition of 2-methylbutane. The difference in stoicheiometry between the latter and its uranium tetrachloride analogue is not unexpected in view of the larger size of the thorium atom, and a similar difference has been observed[8] with tetramethylurea (tmu) in the complexes $ThCl_4$,3tmu and UCl_4,2tmu. All five amide ligands formed 1 : 2 complexes with dioxouranium(VI) dichloride in which the metal atom is presumably six-co-ordinate.

The electronic spectra of the solid 1 : 2 complexes closely resemble the spectra of the known octahedrally co-ordinated uranium(IV) species, UCl_4,2hmpa and $[UCl_6]^{2-}$. In addition, the magnetic susceptibility of UCl_4,2pva was found to be temperature independent [$\chi_m = 1901 \times 10^{-6}$ c.g.s. units] over the temperature range 291—103 K confirming octahedral co-ordination in this complex. The electronic spectra of the complexes in acetone also indicated that octahedrally co-ordinated uranium(IV) was present, but in all cases a small amount of an eight-co-ordinate uranium(IV) species was observed. This suggests that although the ligands are bulky enough to produce only the octahedral arrangement in the solid, they are weaker donors than, for example, hmpa, so that when the complexes are dissolved in a moderately powerful donor solvent, such as acetone, a part of the ligand is replaced by the smaller solvent molecules, and an equilibrium is established between the high symmetry six- and low symmetry eight-co-ordinate species present in the solution. The latter are present only to a small extent, but are easily detectable because of the high molar extinction coefficients of the eight-co-ordinate uranium(IV) at 675 and 1135 nm.

This assumption was investigated by studying the changes in the electronic spectrum that occurred when the ligand was added stepwise to a solution of uranium tetrachloride in acetone. After the addition of two moles of ligand, the original eight-co-ordinate uranium(IV) spectrum of uranium tetrachloride in acetone almost completely disappeared, and the octahedral species predominated. After the addition of a third mole of pva for each mole of uranium tetrachloride present, the electronic spectrum was consistent with virtually complete conversion to the octahedral species, whereas with the rather less crowded ligands iba and ipa, addition of further ligand led to the reappearance of the eight-co-ordinate uranium(IV) spectrum, shifted slightly as a result of the change in ligand from acetone to iba or ipa.

The equilibria that are involved can probably be represented by:

$$\begin{tikzcd} UCl_4,x(\text{acetone}) + 2L \arrow[r, "", shift left] & UCl_4,2L + x(\text{acetone}) \arrow[l, shift left] \arrow[d, "L", shift left] \\ & UCl_4,4L \arrow[u, shift left] \end{tikzcd}$$

The addition of an excess of the ligand decreases the concentration of the octahedral species, UCl_4,2L, present and leads to a marked increase in the solubility of the uranium(IV) species present which makes it more difficult to isolate the bis-complex. The behaviour of iva is qualitatively similar to that of iba and ipa, and the order of ease of formation of the eight-co-ordinate species in solution in the presence of an excess of ligand is iva > iba > ipa > pva, the reverse of the order of the ease of isolation of the bis-complexes. The corresponding uranium tetrabromide–ligand systems exhibited similar behaviour, but the changes in the electronic spectra were somewhat less pronounced than those of the analogous chloride systems.

Mono-N-*substituted Amides*.—The ligands ea and pa both yielded tetrakis-complexes, UCl_4,4L, when diethyl ether was added to a mixture of the ligand (50% excess) and uranium tetrachloride in acetone and, less satisfactorily, when 2-methylbutane was added to the solution obtained by treating caesium hexachlorouranate(IV) with an excess of ea in acetone. UBr_4,4pa began to crystallize from an acetone solution of the tetrabromide after the addition of 6 moles of ligand, but the corresponding ea complex was soluble in acetone and was therefore isolated in the same way as its chloride analogue. The lower solubility of UBr_4,4pa is probably attributable to better packing of the more spherical, branched chain *N*-substituted amide with the larger bromide ions in the lattice, leading to an increase in lattice stabilization as compared with the corresponding situation with the smaller chloride ions or straight chain *N*-substituted amide. The corresponding dioxouranium(VI) dichloride complexes, UO_2Cl_2,3ea and UO_2Cl_2,2pa, were obtained from a solution of the hydrated chloride and the ligand in acetone by precipitation with 2-methylbutane. Unlike the dioxouranium(VI) dichloride bis(amide)complexes, UO_2Cl_2,3ea in the solid state is rapidly reduced to a uranium(IV) species on exposure to sunlight.

[10] K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc.*, **1965**, 3594.

The electronic spectra of the complexes $UX_4,4L$ in acetone were typical of eight-co-ordinate uranium(IV) species. As with the di-*N*-substituted amides, the stepwise addition of the ligand to a solution of the uranium tetrahalide in acetone led to the disappearance of the original spectrum of eight-co-ordinate uranium(IV); after the addition of 2 moles of ligand, some turbidity developed in the UCl_4 systems (ea, pa) and, to a lesser extent, in the UBr_4–ea system. In all four cases the predominant species present in the solution at this point was six-co-ordinate uranium(IV), the largest proportion of which occurred in the UCl_4–pa system (Figure 1). It is noteworthy that pa includes a single branched chain substituent. However, the six-co-ordinate species could not be isolated and on the addition of further ligand the turbidity, if any, cleared and the eight-co-ordinate uranium(IV) spectrum reappeared, shifted, as before, as a result of the change in ligand from acetone to ea or pa.

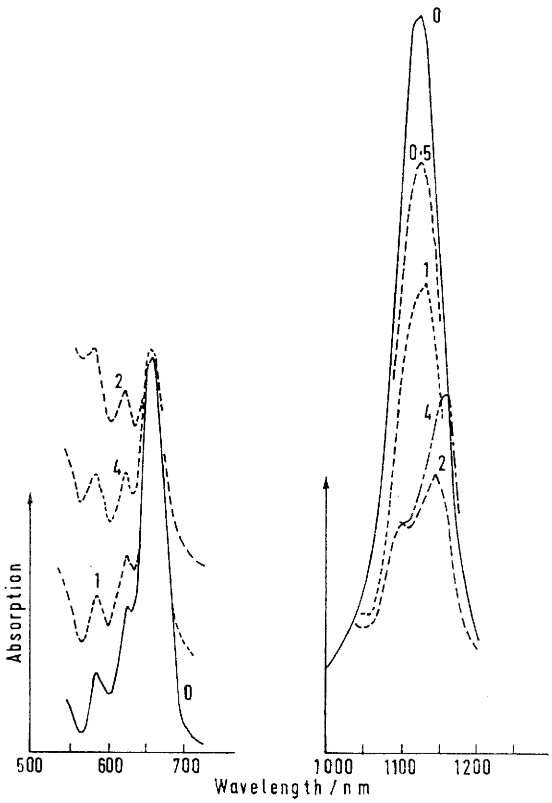

FIGURE 1 Electronic spectra of 0·012M-UCl_4 in acetone solution containing 0, 0·5, 1, 2, and 4 mole equivalents of pa respectively (Curves 0, 0·5, 1, 2, and 4)

The addition of halide ion, in the shape of a tetra-alkylammonium salt in acetone, to a solution of the tetrakis-complex, $UX_4,4L$, in the same solvent had a very marked effect on the u.v.–visible spectrum. The high co-ordination number uranium(IV) species was completely eliminated after the addition of the first equivalent of chloride ion (Figure 2) and the spectrum of the solution was consistent with the presence of six-co-ordinate uranium(IV).[9] Further addition of chloride ion markedly reduced the intensity of the bands due to this species, leaving the spectrum otherwise unaltered, which suggests that the major final product is the centrosymmetric UCl_6^{2-} anion. Thus the changes in the spectra as halide ion is added are consistent with successive displacement of the neutral ligand, L, by that ion:

$$UX_4,4L + X^- \rightleftharpoons [UX_5,L]^- + 3L$$

and
$$[UX_5,L]^- + X^- \rightleftharpoons [UX_6]^{2-} + L$$

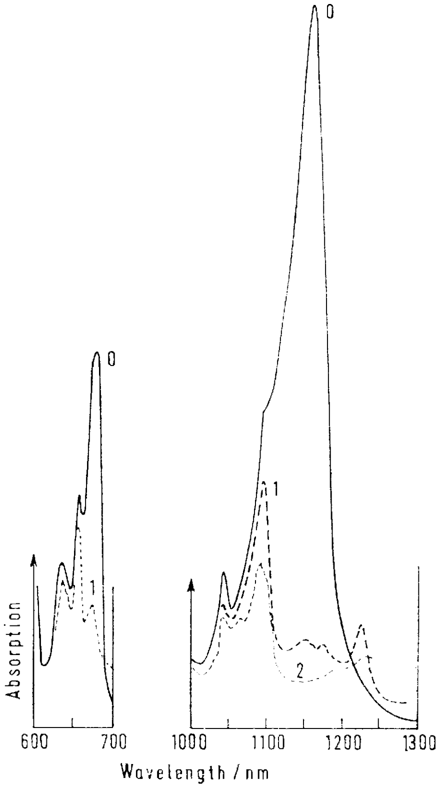

FIGURE 2 Electronic spectra of 0·0234M-UCl_4,4pa in acetone solution containing 0, 1, and 2 equivalents of tetrabutylammonium chloride respectively (curves 0, 1, and 2)

Equilibria of this nature also explain why it is possible to prepare [1] amide complexes by treating the dicaesium hexachloroactinate(IV) with a solution of the ligand in acetone, but not from the analogous tetra-alkylammonium salt, for in the case of the caesium salt the equilibria will be over to the left because of removal of halide ion as the insoluble caesium halide.

The formation of an intermediate anion of the type $[UX_5,L]^-$ has previously been postulated to explain the u.v.–visible spectra of the sulphoxide complexes,[11] $UCl_4,3R_2SO$, as well as the lactam complexes of the uranium tetrahalides.[12]

I.r. Spectra.—The shifts in the C=O stretching frequencies in the complexes (Table 1) are comparable to

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[11] P. J. Alvey, K. W. Bagnall, D. Brown, and J. Edwards, *J.C.S. Dalton*, 1973, 2308.

[12] J. G. H. du Preez, M. L. Gibson, and P. J. Steenkamp, *J. Inorg. Nuclear Chem*, in the press.

those previously observed[5] for the analogous *NN*-dimethylacetamide (dma) complexes, $2UX_4$,5dma, for which the shifts are 40 and 37 cm^{-1} for the chloride and bromide respectively, indicating that the carbonyl oxygen atom is the donor. The i.r. spectra of UX_4,4L in solution in methyl cyanide indicated the presence of free ligand as found previously for the corresponding lactam[12] and dpf[7] complexes.

TABLE 1

M.p.s and i.r. spectra

Compound	Colour	M.p. (°C)	ν(C=O) (cm^{-1})	Δν(C=O) (cm^{-1})
ea			1655	
UCl_4,4ea	Green	106	1595	60
UBr_4,4ea	Green	152	1603	52
UO_2Cl_2,3ea	Yellow	79	1600	55
pa			1655	
UCl_4,4pa	Green	148(d)	1595	60
UBr_4,4pa [a]	Green	210	1595	60
UO_2Cl_2,2pa	Yellow	129	1595	60
ipa			1630	
UCl_4,2ipa	Pale bluish green	205	1580	50
UBr_4,2ipa	Pale green	228	1576	54
UO_2Cl_2,2ipa	Yellow	186	1570	60
iba			1637	
$ThCl_4$,3iba	White	274(d)	1595	42
UCl_4,2iba	Pale bluish green	190	1612	25
UBr_4,2iba	Pale green	244(d)	1610	27
UO_2Cl_2,2iba	Yellow	160	1606	31
iva			1640	
UCl_4,2iva	Pale bluish green	130	1612	28
UBr_4,2iva	Pale green	162	1611	29
UO_2Cl_2,2iva	Yellow	157	1600	40
pva			1632	
ThCl,2pva [b]	White	*c*	1594	38
UCl_4,2pva	Pale bluish green	238(d)	1592	40
UBr_4,2pva	Pale bluish green	256(d)	1592	40
UO_2Cl_2,2pva	Yellow	209	1565	67
dpa			1642	
UO_2Cl_2,2dpa	Yellow	129	1585	57

[a] Solution in McCN; free ligand also present. [b] $ThCl_4$,-2pva,$2H_2O$ ν(C=O) 1562 cm^{-1}, Δν(C=O) 70 cm^{-1}. [c] Decomposes above 300 °C; some sublimation at 1 atmosphere.

EXPERIMENTAL

All work with the moisture sensitive tetrahalides was carried out in nitrogen-atmosphere dry boxes.

Materials.—Thorium[13] and uranium[14] tetrachlorides, UBr_4,4MeCN,[7] Cs_2UCl_6,[1] and hydrated dioxouranium(VI) dichloride[15] were prepared by published methods. The ligands were prepared by standard procedures (reaction of the acyl chloride with the appropriate amine in ether) except for ipa, which was obtained from Kodak Ltd. All ligands were redistilled before use.

Preparative Methods.—(a) *pva and iba complexes*. The pva ($ThCl_4$,2pva, UCl_4,2pva, UBr_4,2pva) and iba *complexes* ($ThCl_4$,3iba, UCl_4,2iba) were prepared by treating a solution of the tetrachloride or UBr_4,4MeCN (1·58—2·03 mmol) with a relatively small excess of the ligand (7·7—8·5 mmol) in acetone (*ca.* 20 ml). The pva complexes and $ThCl_4$,3iba crystallized on standing or on cooling in rather poor yield (45%) but the yield of the tetrachloride complexes was increased to 50% ($ThCl_4$,3iba) and 65—75% (pva complexes) by the addition of light petroleum (b.p. 30—40°), 2-methylbutane or warm diethyl ether. UCl_4,2iba was precipitated from the acetone solution of the components with diethyl ether (yield 60%). UO_2Cl_2,2iba and UO_2Cl_2,2pva (yield *ca.* 75%) crystallized from an acetone solution of the components to which 2-methylbutane was added until the solution became turbid. In all cases the products were washed with a volatile hydrocarbon solvent and then vacuum dried.

(b) *UBr_4,2iba and the ipa complexes*. These *complexes* were prepared in the same way as the pva complexes, but with the UCl_4 : ligand ratio approximately 1 : 3—4, and with ethyl acetate as the solvent. In all three cases the complexes crystallized immediately the components were mixed. UCl_4,2ipa and UBr_4,2iba were recrystallized by dissolving them in hot nitromethane to which ethyl acetate was added until a turbidity developed (yields, 40% and 45% respectively). These products and the precipitated UBr_4,2ipa, were washed with diethyl ether, or a mixture of ether and ethyl acetate, followed by light petroleum (b.p. 30—40°), and were then vacuum dried. UCl_4,2ipa was also prepared by treating Cs_2UCl_6 with an excess (6 : 1 mole ratio) of ligand in acetone; an oil was precipitated from the acetone solution by 2-methylbutane, and the complex crystallized when a solution of this oil in the minimum volume of acetone was cooled to 0 °C. UO_2Cl_2,2ipa was prepared in the same way as UO_2Cl_2,2pva (yield 77%).

(c) *iva complexes*. The addition of diethyl ether to a mixture of the ligand (3 : 1 mole ratio) with dilute (0·045M) UCl_4 in acetone precipitated a green oil which was redissolved in the minimum volume of ethyl acetate. Diethyl ether was added to this solution until a turbidity developed and on cooling blue-green crystals of the *bis complex* separated (30—40% yield). Direct precipitation from more concentrated solutions of UCl_4 by means of an added hydrocarbon yielded products in which the ratio UCl_4 : iva was 2—2·5. These are presumably mixtures of UCl_4,2iva with complexes containing more ligand, but the latter could not be isolated. The $ThCl_4$–iva system yielded oily products of uncertain stoicheiometry. UBr_4,2iva was prepared by vacuum evaporating an ethyl acetate solution of UBr_4,4MeCN and the ligand (3 : 1 mole ratio) until a viscous oil remained. The oil was washed with warm ether and dissolved in a hot 4 : 1 *v*/*v* mixture of ethyl acetate and nitromethane. Ether was added to the hot solution until a turbidity developed; on cooling the solution blue-green crystals of the complex separated (yield 50%). UO_2Cl_2,2iva was prepared in the same way as UO_2Cl_2,2pva (yield 75%). As before, the products were washed with a hydrocarbon and vacuum dried.

(d) *ea, pa, and dpa complexes*. UBr_4,4pa crystallized from an acetone solution of the ligand (6 : 1 mole ratio) and UBr_4,4MeCN (yield 80%), whereas the crystallization of UBr_4,4ea (yield 60%), UCl_4,4ea (yield 65%) and UCl_4,4pa (yield 60%) required the addition of diethyl ether. UCl_4,4ea was also prepared by treating Cs_2UCl_6 with a similar excess of the ligand in acetone, followed by the addition of 2-methylbutane to precipitate an oily product

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[13] G. W. A. Fowles and F. H. Pollard, *J. Chem. Soc.*, 1953, 4128.

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

[15] J. Aloy, *Bull. Soc. chim. France*, 1901, **25**, 153.

which crystallized when left for a prolonged period under 2-methylbutane at 0 °C. In all cases the products tended to cake and were not free flowing powders. UCl_4,4pa appeared to lose ligand on melting, but the decomposition product was not identified.

The preparation of UO_2Cl_2,3ea, UO_2Cl_2,2dpa, and UO_2Cl_2,2pa by the method used for UO_2Cl_2,2pva yielded yellow oils. After vacuum drying, these were dissolved in the minimum volume of acetone, and reprecipitated as oils with 2-methylbutane; on standing under 2-methylbutane at 0 °C the crystalline complexes were ultimately obtained (yields: 16—20%, ea and pa; 80%, dpa). In both cases the solids became green at liquid nitrogen temperature but reverted to the normal yellow colour at room temperature. All the products were washed and vacuum dried as described above.

TABLE 2

Analytical data

	Metal (%)		Halogen (%)		C (%)		H (%)		N (%)	
Compound	Required	Found	Required	Found	Required	Found	Required	Found	Required	Found
UCl_4,4ca	32·7	31·6	19·5	19·9	26·4	26·2	5·0	4·9	7·7	7·7
UBr_4,4ca	26·3	27·3								
UCl_4,4pa	30·3	29·9	18·1	18·5	30·6	29·8	5·7	5·7	7·1	7·8
UBr_4,4pa	24·7	25·8	33·2	33·7	25·0	25·3	4·6	4·7	5·8	5·8
UCl_4,2ipa	35·7	35·8	21·3	21·4	28·8	28·7	5·1	5·1	4·2	4·2
UBr_4,2ipa	28·2	28·3	37·9	37·3	22·8	22·7	4·1	4·2	3·3	3·4
$ThCl_4$,3iba	32·3	32·7	19·8	19·9	30·0	28·7	5·4	5·4	5·8	5·6
UCl_4,2iba	39·0	39·1	23·3	22·9	23·8	23·4	4·3	4·4	4·6	4·9
UBr_4,2iba	30·0	30·2	40·6	40·2	18·3	18·3	3·3	3·6	3·6	3·4
UCl_4,2iva	37·3	37·2	22·2	22·3	25·3	26·6	4·7	4·5	4·4	4·3
UBr_4,2iva	29·2	29·1	39·2	39·2	20·6	20·7	3·7	3·8	3·4	3·6
$ThCl_4$,2pva	36·3	35·8	22·6	22·3	26·7	25·8	4·8	4·7	4·4	4·5
UCl_4,2pva	37·3	37·3	22·2	22·4	25·3	26·1	4·7	4·6	4·4	4·4
UBr_4,2pva	29·2	29·3	39·2	38·8	20·6	20·5	3·7	3·7	3·4	3·9

Analyses.—Thorium,[16] uranium(IV),[1] and uranium(VI)[17] were determined by published methods, and carbon, hydrogen, and nitrogen were determined by combustion. The analytical results are summarized in Table 2.

Physical Measurements.—I.r. spectra were recorded with the Infrascan, Perkin-Elmer 421, 257, or 157 spectrometers (4000—625 cm^{-1}) with samples mounted as mulls in Nujol, hexachlorobutadiene, or Fluorolube between potassium bromide or sodium chloride plates. Visible and near-i.r. spectra (400—2000 nm) were recorded using a Beckman DK2a spectrophotometer with samples in solution in 1 cm silica cells or using a Cary 14 spectrophotometer for solid transmission spectra, in the form of mulls in Voltalef 901 grease between silica plates.[18]

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[17] C. J. van Nieuwenburg and J. W. L. van Ligten, 'Quantitative Chemical Microanalysis,' Elsevier, Amsterdam, 1963, p. 75.

[18] D. Brown and J. Edwards, unpublished method.