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The Chemistry of Uranium.
Part 35. Synthesis and Characterization of UI_4L_2 Complexes (L = Bulky Amide Ligands) and the Crystal Structure of UI_4tmu_2 (tmu = tetramethylurea)

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Abstract

A number of *trans*-octahedral complexes of uranium tetraiodide have been isolated for the first time using bulky C=O amide ligands. The solid reflectance electronic spectra of these complexes indicated a shift in the major peaks of their spectra to higher energies with reference to that of UI_6^{2-}. The infrared spectra of the substituted complexes showed a reverse of the position of the C=O stretching frequencies and the N–C–N stretching frequencies upon complexation, indicating the high Lewis acidity of UI_4. The structure of UI_4tmu_2 has been determined by X-ray crystallography. The compound crystallized in the orthorhombic system, space group *Pbcn*. Cell constants are: $a = 11.480(5)$, $b = 14.657(5)$, $c = 13.453(5)$ Å; $D_c = 2.87$ g cm^{-3}.

There are four independent molecules of the compound in the unit cell with uranium, oxygens and their attached carbon atoms lying on the twofold symmetry axis. The uranium atom is *trans*-octahedrally surrounded by meridional iodide ions and apical oxygen atoms of tmu groups. The O–U–O sequency is linear. Selected mean bond lengths are: U–I 3.01 Å, U–O 2.185 Å, C–O 1.29 Å.

A comparison was made between the UX_4tmu_2 structures (X = Cl, Br and I). UI_4tmu_2 proved to be much more thermally unstable than its chloro and bromo analogues.

Introduction

The chemistry of uranium tetraiodide and its complexes have not been well studied. Apart from the hexaiodouranate(IV) species [1] only UI_4-dma_4 [2], UI_4dma_5 [2] and UI_4dmf_4 [3] (dma = *N,N*-dimethylacetamide and dmf = *N,N*-dimethylformamide) have been isolated, except for a small number of species in which there are apparently no direct uranium iodide interactions like UI_4Cl_8 [4] and UI_4urea_8 [5] (Cl = ε-caprolactam).

Whereas six-coordinated complexes of the type UX_4L_2, for X = Cl and Br and L = a bulky neutral monodentate oxygen donor ligand, have been extensively researched, none of this type has, however, been reported for uranium tetraiodide.

Previous work [6] on the stability of UX_6^{2-} species in non-aqueous solution indicated the stability order to be chloro ≧ bromo ≫ iodo. Results of recent structural determinations [7, 8] for UX_4L_2 complexes showed somewhat greater tetragonal distortions (U–X bond lengthening and U–O bond shortening) for bromo than for chloro complexes. It will, therefore, be of interest to prepare and study the iodo analogues of these to determine whether this distortion is even more prominent in the case of the much weaker coordinating iodide ion, and also to access the role of the donor strength of the neutral ligand in comparison with that of iodide. The relatively low coordination number in these six-coordinated uranium(IV) species should also result in a relatively higher covalent character in the bonding, the extent of which will be interesting, especially for the more polarizable iodide ions.

Six-coordinated iodo complexes of the type UI_4L_2, where L = tmu, N,N′-diphenyl-*N,N′*-dimethyl urea (ddu), *N,N′*-dimethylethylene urea (dmeu), *N,N′*-dimethylpropylene urea (dmpu), bis(pentamethylene) urea (bpmu), antipyrine (apn) and *N,N*-dimethylpivaloyl amide (pva), have been synthesized and studied by spectral, thermal and conductometric

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methods. A structural determination of UI_4tmu_2, the first to be performed on this type of UI_4 complex, was done and the results compared with those of UCl_4tmu_2 and UBr_4tmu_2.

Experimental

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

Materials

Uranium tetrachloride and tetrabromide [9] and an uranium tetraiodide stock solution [10] were prepared as previously described. The ligands were obtained as follows: tmu from E. Merck; dmeu, dmpu and apn from Fluka; ddu from K. and K. Laboratories; and bpmu from Ega-Chemie. pva was prepared by standard methods [11].

Preparative

The complexes UCl_4tmu_2, UBr_4tmu_2, UCl_4ddu_2, and UBr_4ddu_2 were prepared as described previously [12].

UI_4L_2

These were all prepared as follows. An appropriate amount of the UI_4 stock solutions (usually containing 1–1.5 mmol of uranium) in a Schlenck vessel was diluted to *ca.* 40 cm^3 with dry oxygen-free methyl cyanide (mecn) and two equivalents of ligand dissolved in ~15 cm^3 of the same solvent were added. The Schlenck tube was sealed off from the atmosphere and the mixtures cooled to –18 °C. The yellow green UI_4L_2 compounds were washed with ethyl acetate (2 × 5 cm^3), followed by isopentane (2 × 5 cm^3) and dried *in vacuo.*

UCl_4dmeu_2, UCl_4pva_2 *and* UBr_4pva_2

Two equivalents of ligand were added to UX_4 (2.5–3 mmol) dissolved in acetone (20 cm^3). Ether was added until a turbidity just persisted in the solutions. The mixtures were then cooled to –18 °C upon which the pale green solids precipitated. The solids were washed twice with ethyl acetate followed by petroleum ether and dried *in vacuo.*

$UBr_4dmeu_2(Ph)$

UBr_4mecn_4 (1.0 g) was suspended in mecn (~20 cm^3) and two equivalents of dmeu were added. Addition of benzene and cooling to 4 °C resulted in the formation of large green crystals of the compound.

UCl_4bpmu_2, UBr_4bpmu_2, UCl_4dmpu_2, *and* UBr_4dmpu_2

These complexes were prepared similarly to UCl_4dmeu_2 (above), but precipitation of the solids was almost immediate.

Analysis

Uranium was determined as described previously [13]. Halides were determined by potentiometric titration after removal of the uranium(IV) by precipitation. The analytical results are summarised in Table I.

Physical Measurements

Electronic spectra of solids were recorded on a Beckman DK2A instrument with samples mounted as mulls in fluorocarbon grease. Electronic spectra of solutions were recorded in CH_2Cl_2 in 2 cm cells on a Perkin-Elmer 330 UV–Vis instrument. IR spectra of solids were recorded on a Beckman 4250 (4000–200 cm^{-1}) instrument with samples mounted as mulls, nujol or fluorocarbon grease, between CsI cells. Spectra of solutions were recorded in CH_2Cl_2 in KBr liquid cells.

Conductometric measurements were made on a Philips PW9509 conductivity meter using a Philips PW9510 immersion type conductivity cell.

Thermal decomposition studies were performed as described previously [13].

X-ray Data for UI_4tmu_2

A well-formed fragment of the compound with maximum dimension 0.2 mm was used for X-ray

TABLE I. Analytical Data of Uranium(IV) Complexes (%)

Compound	U	X	C	H	N
UCl_4tmu_2	38.7(38.88)	23.1(23.17)	19.4(19.62)	3.8(3.95)	9.2(9.15)
UBr_4tmu_2	30.0(30.13)	40.1(40.46)	15.0(15.20)	2.9(3.06)	7.1(7.09)
$UBr_4dmeu_2Ph^a$	27.3(27.55)	37.1(36.99)	22.3(22.24)	3.1(3.03)	6.5(6.48)
UI_4tmu_2	24.2(24.34)	51.7(51.91)	12.1(12.28)	2.35(2.47)	5.5(5.73)
UI_4bpmu_2	20.4(20.91)	44.4(44.60)	23.5(23.22)	3.4(3.54)	4.6(4.92)
UI_4ddu_2	19.2(19.41)	41.3(41.40)	29.1(29.38)	2.5(2.63)	4.3(4.57)
UI_4dmpu_2	23.5(23.76)	50.2(50.66)	14.5(14.38)	2.3(2.41)	5.4(5.59)
UI_4pva_2	23.4(23.71)	50.4(50.56)	16.5(16.75)	3.0(3.01)	2.8(2.79)
UI_4dmeu_2	24.4(24.44)	51.9(52.12)	12.2(12.33)	2.2(2.07)	5.6(5.75)

[a] Ph = benzene.

TABLE II. Electronic Spectral Data of Uranium(IV) Complexes (Wavelengths are given in mμ)

Compound		X = Cl⁻		X = Br⁻		X = I⁻	
UX_6^{2-}	(a)	1075	1980	1100	2050	1140	2165
UX_4tmu_2	(a)	1030	1898	1050	1932	1073	1950
	(b)		1940(36)		1973(39)		1985(86)
UX_4ddu_2	(a)	1040	1955	1050	1970	1060	2005
	(b)		1935(57)		1960(61)		2020(87)
UX_4dmeu_2	(a)	1035	1920	1050[c]	1945[c]	1085	1970
UX_4bpmu_2	(a)	1035	1915	1043	1945	1050	1955
UX_4pva_2	(a)	1035	1930	1060	1970	1070	2000
	(b)		1945(42)		1987(61)		2045(90)
UX_4apn_2	(a)	1035	1910	1030	1880	1040	1850

[a] Solid state spectra. [b] Spectra in CH_2Cl_2 solutions. Molar extinction values are given in brackets. [c] Spectrum of UBr_4dmeu_2·Ph.

work. Crystal data are: $C_{10}H_{24}I_4N_4O_2U$, Formula weight = 978, a = 11.480(5), b = 14.657(5), c = 13.453(5) Å, V = 2264 Å^3, D_c = 2.87 g cm^{-3} for Z = 4, μ(Mo Kα) = 355 cm^{-1}, orthorhombic space group *Pbcn*, general positions $\pm(x,y,z;\ \frac{1}{2}-x,\ \frac{1}{2}-y,\ \frac{1}{2}+z;\ \frac{1}{2}+x,\ \frac{1}{2}-y,\ -z;\ -x,\ y,\ \frac{1}{2}-z)$. The intensities of 2287 reflections were measured up to θ = 25° on a Philips four-circle diffractometer with the $\theta/2\theta$ technique using graphite monochromatized Mo Kα radiation (λ = 0.71069 Å). The compound slowly decomposes under irradiation. The measured intensities were corrected for the Lorentz polarization and for absorption [14] and 1215 independent reflections with $I > 3\sigma(I)$ were considered as 'observed' and used in subsequent calculations. The structure was solved by standard methods and refined to the conventional R factor of 0.093 when the maximum shift on the refined parameters was 0.01σ on the coordinates and 0.3σ on thermal parameters. The quantity minimized in the refinement was $\Sigma w\Delta F^2$ with w = 1. Scattering factors for U and I were those of Cromer and Liberman [15], corrected for the anomalous dispersion, those for C, N and O were supplied internally by SHELX [16].

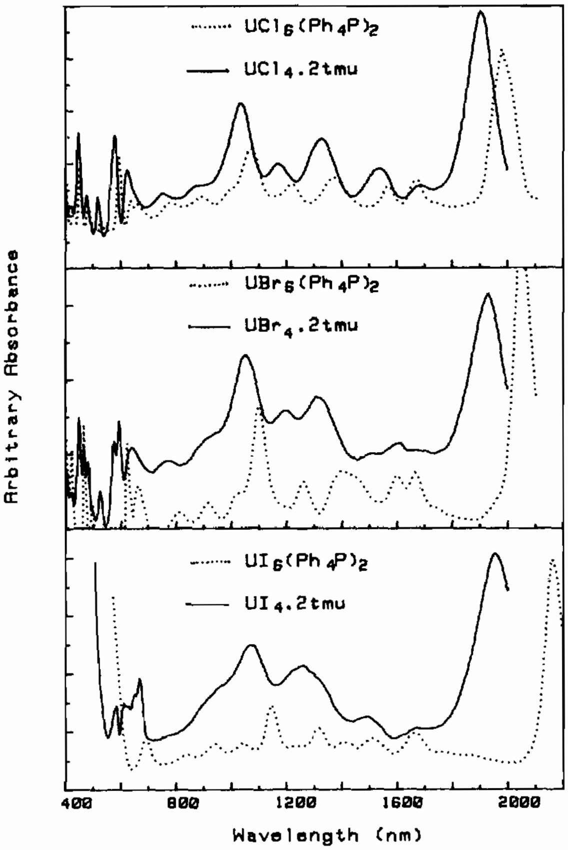

Fig. 1. Electronic spectra of UX_4tmu_2 complexes.

Results and Discussion

Electronic Spectral Data

The solid reflectance electronic spectra of all the UX_4L_2 complexes (X = Cl, Br, I) as well as their methylene dichloride solution spectra for those soluble in the solvent, *i.e.* L = tmu, ddu and pva, were obtained from 350–2200 mμ. All these spectra are typical of six-coordinated uranium(IV). The wavelengths of the most prominent peaks are recorded in Table II. The spectra of the UX_4tmu_2 species are represented in Fig. 1 and compared with the corresponding UX_6^{2-} species. Replacement of two *trans*-X⁻ ions with two neutral oxygen donor atoms shifted the main low energy peak (~1800–2000 mμ region) to higher energies. This relative effect becomes greater in the direction Cl⁻, Br⁻, and I⁻ which is illustrated by the curves in Fig. 1. This phenomenon suggests that the role of the halide ion in comparison with the neutral oxygen donor ligand decreases in going from chloride to iodide.

The spectra of UBr_4apn_2 and UI_4apn_2 are difficult to interpret in terms of the behaviour of the others.

The wavelengths of their major peaks decrease rather than increase in going from the chloro, to the iodo complex. This could possibly be interpreted in terms of greatly increasing U(IV) amide oxygen atom interaction in the same direction. This is in agreement with the infrared data (see later). In such cases, however, it is difficult to see why the U–I charge transfer band appears at such a high wavelength especially since auto ionized species containing UI_6^{2-} must be excluded. (There is no UI_6^{2-} band present in the spectrum at ~2150 $m\mu$.)

The solid reflectance spectra do not differ greatly from the analogous solution spectra in CH_2Cl_2 solution. The electronic spectra of the tmu complexes of UCl_4 and UBr_4 are very similar with respect to spread of peaks and their relative positions whereas that of UI_4tmu_2 differ slightly from these, particularly in the 1200–1400 $m\mu$ region. This fact corresponds with the slightly bigger structural differences of the iodo complex when compared to the other two (see later discussion under structural aspects).

Infrared Spectra

The infrared spectral data of the complexes are given in Table III. There exists a systematic lowering in the C=O stretching frequency of the bound ligands from the chloro to the iodo complexes for all the ligands except pva. In the substituted urea complexes, there is associated with this effect an increase in the essentially N–C–N frequency. This effect occurs to such an extent that the latter vibrations appear at higher wavelengths than their C=O analogues in the complexes. This behaviour is in contrast to results obtained from 3d transition metal complexes where overlapping, rather than complete interchange, of these bands occurs [17]. In the case of the pva complexes the C=O stretching frequencies are almost constant for the chloro-, bromo- and iodo complexes. The very small shifts appear to be in the opposite direction (Table III). This cannot readily be explained unless stereochemical factors in this very crowded C=O amide ligand play a major role. In the apn complexes the C=O bands shift very significantly from chloride to iodide. The infrared data of the tmu complexes will be discussed with the structural data.

TABLE III. Infrared Spectral Data of Complexes

Complex	ν(C=O) (cm^{-1})		$\Delta\nu$(C=O) (cm^{-1})	ν(N–C–N) (cm^{-1})	
	Solid	CH_2Cl_2 solution		Solid	CH_2Cl_2 solution
tmu	1640			1501	
UCl_4tmu_2	1542 1530	1533	107	1590	1589
UBr_4tmu_2	1535 1510	1527	113	1593	1593
UI_4tmu_2	1524	1523	117	1594	1593
ddu	1657			1498	
UCl_4ddu_2	1521	1515	142	1521	[a]
UBr_4ddu_2	1517	1540	147	1535	[a]
UI_4ddu_2	1501	1499	158	1544	1535
dmeu	1695			1508	
UCl_4dmeu_2	1603	1614	81	1578	1576
UBr_4dmeu_2(Ph)	[a]	1608	87	[a]	1580
UI_4dmeu_2	[a]	1563	132	[a]	1605
bpmu	1648			1425	
UCl_4bpmu_2	1495	i	153	1545	i
UBr_4bpmu_2	1490	i	158	1558	i
UI_4bpmu_2	1490	i	158	1570	i
dmpu	1635			1523	
UCl_4dmpu_2	1523	i	100	1590	i
UBr_4dmpu_2	1537 1526	i	105(av)	1600	i
UI_4dmpu_2	1522	i	113	1598	i
pva	1620				
UCl_4pva_2	1586	1574	46		
UBr_4pva_2	1588	1576	44		
UI_4pva_2	1582	1578	42		
apn	1660				
UCl_4apn_2	1558	1558	102		
UBr_4apn_2	1549	1549	112		
UI_4apn_2	1535		125		

[a] Overlap of ν(C=O) and ν(N–C–N) makes assignment of these absorptions impossible. i = insoluble.

X-ray Structure

Final atomic parameters for UI_4tmu_2 are listed in Table IV, bond lengths and angles are reported in Table V, and selected mean planes are given in Table VI. As shown in Fig. 2 the molecule consists of a *trans*-octahedral arrangement with meridional iodine atoms and apical oxygen atoms of the neutral ligands. The space group symmetry requires two-fold symmetry for the molecule, therefore the uranium atom, the oxygen atoms and the attached carbon atoms C(1) and C(4), which lie on the crystallographic two-fold axis, are perfectly co-linear.

The structure of UI_4tmu_2 resembles that of the isomorphous pair UX_4tmu_2 (X = Cl, Br) [13]. It is also noteworthy that in the chloro and bromo derivatives, where the only imposed molecular symmetry is the crystallographic inversion centre, the U–O–C sequencies are perfectly linear, suggesting the sp hybridization state for the coordinated oxygen atom.

The relatively low quality of experimental data, due in part to the exceptionally high absorption coefficient of UI_4tmu_2 and in part to its deterioration

TABLE IV(a). Atomic Coordinates for UI_4tmu_2

Atom	*x/a*	*y/b*	*z/c*
U1	0.0(0)	0.12000(0)	0.75000(0)
O1	0.0(0)	0.27067(195)	0.75000(0)
O2	0.0(0)	−0.02751(223)	0.75000(0)
C4	0.0(0)	−0.11605(393)	0.75000(0)
C1	0.0(0)	0.35906(284)	0.75000(0)
I1	0.13143(30)	0.12578(22)	0.55766(21)
I2	−0.22673(27)	0.11997(24)	0.63514(20)
N1	0.01135(339)	0.40164(156)	0.83764(202)
N2	−0.08387(322)	−0.16019(194)	0.78749(283)
C2	−0.04484(392)	0.49441(232)	0.85492(260)
C3	0.05569(520)	0.35021(352)	0.92153(275)
C6	−0.07019(633)	−0.25149(271)	0.83376(456)
C5	−0.19633(478)	−0.11586(420)	0.80995(314)

TABLE IV(b). Thermal Parameters for UCl_4L_2 ($\times 10^4$)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U1	543(12)	83(7)	132(9)	0(0)	45(9)	0(0)
O1	1609(476)	1(144)	1(166)	0(0)	95(264)	0(0)
O2	770(308)	157(172)	423(255)	0(0)	29(269)	0(0)
C4	686(374)	357(272)	1(204)	0(0)	67(255)	0(0)
C1	1100(536)	1(211)	209(299)	0(0)	122(363)	0(0)
I1	802(22)	509(17)	264(14)	0(16)	176(15)	23(18)
I2	635(19)	478(16)	294(14)	−13(18)	−44(13)	−48(18)
N1	790(242)	63(123)	87(147)	5(98)	−84(166)	−37(155)
N2	522(221)	150(145)	525(233)	41(149)	−93(189)	−82(150)
C2	841(318)	166(167)	27(173)	−109(136)	−1(175)	113(190)
C3	1128(445)	757(357)	1(187)	102(191)	−179(224)	−104(315)
C6	1534(586)	91(189)	838(431)	298(234)	−207(434)	14(275)
C5	873(371)	952(405)	224(261)	383(302)	101(235)	229(364)

[a] Thermal parameters are in the form $T = \exp[-2\pi^2(\Sigma U_{ij}h_ih_ja_i^*a_j^*)]$.

TABLE V. Bond Distances (Å) and Angles (°) for UI_4tmu_2[a]

U–I(1)	2.996(3)	C(1)–N(1)	1.34(3)
U–I(2)	3.027(3)	N(1)–C(2)	1.52(4)
U–O(1)	2.20(3)	N(1)–C(3)	1.45(5)
U–O(2)	2.17(3)	C(4)–N(2)	1.27(4)
C(1)–O(1)	1.29(5)	N(2)–C(5)	1.48(6)
C(4)–O(2)	1.29(6)	N(2)–C(6)	1.48(5)
I(1)–U–I(2)	89.6(1)	C(1)–N(1)–C(2)	121(3)
I(1)–U–O(1)	88.4(1)	C(1)–N(1)–C(3)	118(3)
I(2)–U–O(1)	90.1(1)	C(2)–N(1)–C(3)	120(3)
O(1)–C(1)–N(1)	118(2)	C(4)–N(2)–C(5)	121(4)
O(2)–C(4)–N(2)	121(3)	C(4)–N(2)–C(6)	123(4)
		C(5)–N(2)–C(6)	114(4)

[a] E.s.d.s reported in parentheses refer to the last significant digit.

TABLE VI. Selected Mean Planes for UI_4tmu_2[a]

Plane 1: O(1), C(1), N(1)
$0.944x + 0.0y - 0.110z = -1.108$

Plane 2: O(2), C(4), N(2)
$-0.464x + 0.0y - 0.886z = -8.938$

Plane 3: U, I(1), O(1)
$0.864x + 0.0y + 0.504z = 5.082$

Angles (deg) between the planes

Planes	Angle
1–2	68.7
1–3	36.5
2–3	32.2

[a] The equation of a plane is in the form $ax + by + cz = d$, where x, y and z are orthogonal coordinates.

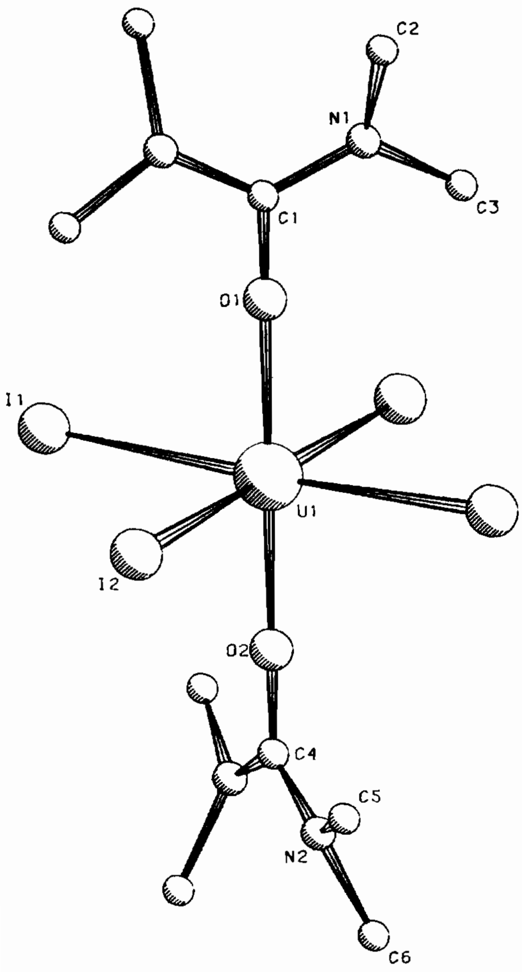

Fig. 2. Crystal structure of UI_4tmu_2.

irradiation, makes this structural determination less accurate if compared to those of the two mentioned compounds. Despite this and the related high standard deviations, bond distances and angles in the iodo compound generally agree with the values found in UCl_4tmu_2 and UBr_4tmu_2.

A comparison of the structural data of the UX_4-tmu_2 complexes (X = Cl, Br, and I) is represented in Table VII. The average U–X bond lengths correspond very closely to those in the UX_6^{2-} species, *viz.* 2.62 Å for U–Cl in $(P\phi_3et)_2UCl_6$ and 2.77 Å for U–Br in the similar bromo complex [18]. The U–I bond distance in UI_6^{2-} is not yet known, but it is 3.01 Å in UI_4 [19]. If the ionic radii of Cl, Br and I are taken to be 1.81 Å, 1.96 Å and 2.20 Å [20], respectively, and these values subtracted from the relevant U–X distances, then the U(IV) radii obtained are 0.81 Å, 0.82 Å, and 0.81 Å, respectively, in these cases. Values of 0.93 Å and 0.97 Å [20] have been suggested for the octahedral ionic radius of uranium(IV). The significantly shorter U–X bonds found here suggest some covalent character in the bonding. It should, however, be borne in mind that the U–X interaction cannot be interpreted in isolation since the average U–O bond distances are marginally shorter in the direction chloride-to-iodide, indicating stronger U–O interaction in the same direction. This fact is supported by the somewhat longer average C–O bond lengths and shorter average N–C(CO) bond lengths in the same direction (Table VII). The infrared spectral data are in agreement with the above since greater lowering of the C–O stretching frequencies upon complexation are found in the same direction as well as greater corresponding increase of the essentially N–C–N vibrations in the substituted urea complexes.

TABLE VII. Comparison of Structural Data for UX_4tmu_2

Avarage bond distances	UCl_4tmu_2	UBr_4tmu_2	UI_4tmu_2
(a)			
U–O	2.22	2.21	2.185
U–X	2.62	2.78	3.01
C–O	1.28	1.285	1.29
N–C(CO)	1.35	1.34	1.31
(b) (I) Molecule A			
U–O	2.209	2.197	
U–X	2.622	2.784	
C–O	1.26	1.26	
N–C(CO)	1.355	1.36	
(c) (II) Molecule B			
U–O	2.232	2.230	
C–O	1.30	1.31	
N–C(CO)	1.335	1.325	

There are two slightly differing coordination surroundings of the uranium atoms in each of UCl_4tmu_2 and UBr_4tmu_2 crystals labelled I (molecule A) and II (molecule B) [13]. The different important bond lengths for these are given in Table VII (b) and (c), respectively. The C–O bond lengths in these two molecules for UCl_4tmu_2 differ by 0.04 Å and for the bromo complex by 0.05 Å. In the case of the iodo complex a single C–O bond length has been obtained (Table V). The infrared spectra of these complexes indicate relatively broad C=O peaks (Fig. 4) with some indication of a split for the chloro and bromo complexes (see peak B in curves (a) and (b) whereas the corresponding peak of the iodo complex is a relatively sharp one (curve c).

The N–C(CO) bond lengths, on the other hand, have smaller mutual differences in the chloro and bromo complexes than those in the iodo complex. The infrared peaks which are essentially related to these N–C modes, *i.e.* peaks A, C and D, are very similar for the chloro and bromo complexes, but have clearly bigger splittings in the case of the iodo complex. This is again in agreement with the structural data.

A major difference between UI_4tmu_2 and the other two complexes is observed when the relative positions of the *trans*-tmu molecules are compared. The planar OCN_2 moieties of these groups are transplanar (through the U atom) in the chloro and bromo complexes because of the presence of the inversion centre, so that their atoms (excepting the methyl groups) are co-planar. On the contrary, the same groups are rotated by 68.7° in UI_4tmu_2 (see Fig. 3) so that the opposite pairs of nitrogen atoms form a pseudo-tetragonal bisphenoid. As expected they also settle in such a way as to minimize hindrance or repulsive forces from the cumbersome iodine atoms.

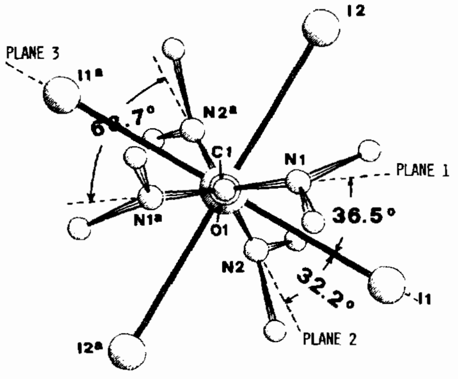

Fig. 3. Projection along the two-fold axis of selected planes in UI_4tmu_2. With reference to Table VI, planes are: Plane 1: O(1), C(1), N(1); Plane 2: O(2), C(4), N(2); Plane 3: U, I(1), O(1). Atoms with *a* subscript are related by two-fold symmetry to the corresponding non-subscripted atoms.

The thermal behaviour of the UI_4L_2 complexes differ significantly from their chloro and bromo analogues, as illustrated by the thermal degradation cuves of UX_4tmu_2 (X = Cl, Br, I) in Fig. 5. We have previously indicated [13] that UCl_4tmu_2 decomposes in a dry pure nitrogen atmosphere according to the scheme below.

$$UCl_4tmu_2 \rightarrow UOCl_2tmu \rightarrow UO_2Cl \rightarrow UO_2$$

Each of the intermediates could be isolated. The bromo complex has a similar decomposition pattern although stable intermediates could not be isolated. In the case of the iodo complex, the successive intermediate reactions follow each other so rapidly that the curve resembles that of a single reaction. It is of interest to note that the temperature at which decomposition starts is almost constant for all three. It is likely that they all start by a similar reaction to that of the chloro complex (see above). The final product in all these cases is UO_2.

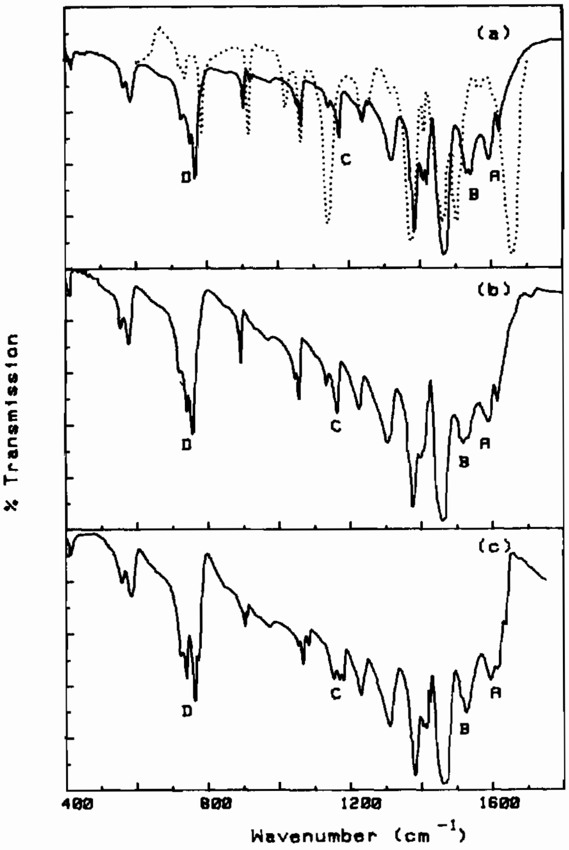

Fig. 4. Infrared spectra for UX_4tmu_2: ......, curve for tmu (free ligand); ——, curves for complex: (a) UCl_4tmu_2; (b) UBr_4tmu_2; (c) UI_4tmu_2.

The Λ_{1000} values of the iodo complexes which are soluble in acetone, *viz.* the tmu, ddu and pva complexes, were in the vicinity of 110 S cm^2 mol^{-1} (*e.g.* 109 for UI_4tmu_2) which is somewhat less than expected for a 1:1 electrolyte [21]. The Λ_{500} values of the chloro and bromo analogues are essentially those of non-electrolytes, *i.e.* 10 and 15 S cm^2 mol^{-1}, respectively.

In conclusion, the synthesis and characterization of the first UI_4-complexes of the type UI_4L_2 and their comparison with their chloro and bromo analogues with reference to solution and solid state behaviour, including structural aspects, clearly illustrates the differences between the iodo complexes and their chloro and bromo analogues.

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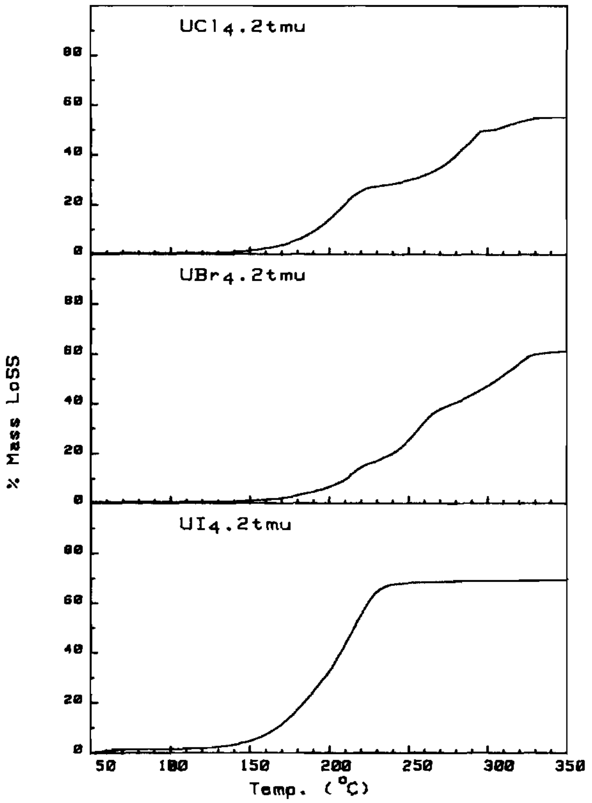

Fig. 5. Thermal behaviour of UX_4tmu_2 complexes (X = Cl, Br, I).

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