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The Chemistry of Uranium.
Part 34. Structural and Thermal Properties of UX_4L_2 Complexes (X = Cl and Br; L = *N,N,N',N'*-Tetramethylurea)

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Abstract

The crystal structure of the isomorphous pair UX_4L_2 has been determined by X-ray crystallography. The compounds crystallize in the triclinic system, space group $P\bar{1}$. Cell constants are: UCl_4L_2, a = 15.061(5), b = 9.255(4), c = 8.515(4) Å, α = 62.57(3), β = 106.50(3), γ = 98.86(3)°; UBr_4L_2, a = 15.413(5), b = 9.443(3), c = 8.710(4) Å, α = 62.58(3), β = 106.40(3), γ = 99.76(3)°. Density values are 2.01 g cm^{-3} for UCl_4L_2 and 2.43 g cm^{-3} for UBr_4L_2. There are two independent molecules of the compound in the unit cell, with the uranium atoms on the inversion centres at the origin and at the centre of the cell. Structural details in the isomorphous compounds are fully comparable. Selected bond lengths are: U–Cl(mean) 2.62 Å, U–Br(mean) 2.78 Å, U–O(mean) 2.22 Å (chloride) and 2.21 Å (bromide). The uranium atom is six-coordinated octahedral. IR spectra data are reported. It is indicated that the C=O vibration of the ligand is greatly lowered upon complexation and the antisymmetric N–C–N stretching vibration highered to the extent that these interchange in terms of their relative positions in the free ligand. The C=O peaks are fairly broad in the complexes which is in agreement with the two independent molecules in the unit cell. Thermal degradation studies in a nitrogen atmosphere were done and oxygen abstraction of the ligand by uranium(IV) occurred, resulting in the formation of UO_2. Two stable intermediates could be isolated from the UCl_4tmu_2, *viz.* $UOCl_2tmu$ and UO_2Cl. This method thus produced a convenient method of preparation of the latter compound.

Introduction

The preparation and some physical properties of *N,N,N',N'*-tetramethylurea (tmu) complexes of the type UX_4tmu_2 (X = Cl and Br) have been reported earlier by us [1]. In recent years it became of interest to correlate structural features of complexes of this type [2] with their donor strength as determined by various solution studies [3, 4]. Particularly large shifts in the carbonyl stretch frequencies upon complexation were reported [1] namely 100 cm^{-1} and 113 cm^{-1} for UCl_4tmu_2 and UBr_4tmu_2, respectively. It was, however, indicated [5, 6] by studies of infrared spectra of tmu and tmu complexes that caution must be exercised in interpreting the spectra in the 1500–1700 cm^{-1} region since there are a variety of vibrations in this region which are influenced differently by complexation. It was, therefore, of interest to obtain the crystal structures of these complexes and reinvestigate their infrared spectra in order to interpret these in terms of the structures. Thermal degradation studies of these complexes in a nitrogen atmosphere were also undertaken.

Experimental

Materials

N,N,N',N'-tetramethylurea (tmu) (Merck) was dried over activated molecular sieves (4 Å) before use. All solvents were dried over activated molecular sieves (3 Å) and distilled in a N_2 atmosphere before use. UCl_4tmu_2 and UBr_4tmu_2 were prepared as described previously [1].

IR Studies

IR spectra, of the solids, were recorded on a Beckman 4250 (4000–200 cm^{-1}) instrument, as nujol

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mulls mounted between CsI cells. Solution spectra were recorded in CH_2Cl_2 using KBr liquid cells.

Thermogravimetric Analysis

A Perkin Elmer TGS-2 thermobalance was used as described previously [7]. Nitrogen was used as carrier gas. Note that all samples were first grinded to a fine powder in a N_2 atmosphere dry-box and sealed in an aluminium pan to exclude all moisture and oxygen. The lid of the container was subsequently pierced under N_2 before inserting into the oven. This was done to allow the escape of gaseous decomposition products. A constant heating rate of 2.5 °C per minute (unless otherwise stated) was used.

Analytical

Uranium was precipitated as the hydrous oxide and weighed as U_3O_8 after ignition and halide was determined as reported earlier [1].

X-ray Data

The crystal and experimental data and structure refinement parameters for UCl_4L_2 and UBr_4L_2 are given in Table I. Because the compounds are isomorphous (and isostructural) only the structure of UCl_4L_2 was solved independently and was successively used as a starting point for the refinement of UBr_4L_2. Two independent UCl_4L_2 molecules are present in the centrosymmetric triclinic cell, with the U atoms lying at 0,0,0 and 1/2,1/2,1/2, respectively, that is, on the two independent sets of inversion centres of the cell. Thus, the centrosymmetric unit of the structure is formed by half molecule A (at the corners) and half molecule B (at the centre of the cell). Atomic parameters for non-hydrogen atoms were refined anisotropically. At convergence the shift on the refined parameters was less than 0.1σ for UCl_4L_2 and less than 0.2σ for UBr_4L_2. At this point, different Fourier syntheses were calculated to check the correctness of the overall structures. The maps showed maximum residuals of only 1.2 and 0.9 e/Å^3, respectively. Final atomic coordinates and thermal parameters for UCl_4L_2 and UBr_4L_2 are listed in Tables II and III, respectively. Bond distances and angles are given in Tables IV and V.

TABLE I. Crystal and Intensity Data for UX_4L_2 Compounds

Compound	UCl_4L_2	UBr_4L_2
Formula	$C_{10}H_{24}Cl_4N_4O_2U$	$C_{10}H_{24}Br_4N_4O_2U$
Formula weight	612	790
System	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	15.061(5)	15.413(5)
b (Å)	9.255(4)	9.443(4)
c (Å)	8.514(4)	8.710(4)
α (°)	62.57(3)	62.58(3)
β (°)	106.50(3)	106.40(3)
γ (°)	98.86(3)	99.76(3)
V (Å^3)	1009.6	1078.3
D_x (g cm^{-3})	2.01	2.43
Z	2	2
Max. crystal size (mm)	0.2	0.2
Radiation	Mo Kα	Mo Kα
μ(Mo Kα) (cm^{-1})	105.9	176.3
Technique and geometry	Four-circle diffractometer (Philips PW 1100); $\theta/2\theta$ scan mode; scan rate 2° min^{-1}.	
θ max (°)	25	25
Stability	No significant variation	
No. of recorded reflections	5754	4921
No. of observed reflections	3526	3285
Criterion for obs. reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Corrections applied	Lp, absorption [8]	
Atomic scattering factors	U:[9]; C,N,O,Cl,Br:[10]	
Programs used	SHELX [10], PARST [11], PLUTO [12]	
Correction for anomalous dispersion	U:$\Delta F' = -10.673$, $\Delta F'' = 9.654$; Cl, Br:[8]	
Solution	Patterson and Fourier methods	
Refinement	Full-matrix least-squares	
No. of refl. per parameter	36.4	33.9
R (obs.)	0.034	0.044
Weighing scheme	$w = 1$	$w = 1$

TABLE IIa. Atomic Coordinates for UCl_4L_2

Atom	*x*/*a*	*y*/*b*	*z*/*c*
U(1)	0.00000	0.00000	0.00000
Cl(1)	0.07157(22)	0.78495(37)	0.33202(40)
Cl(2)	0.05660(25)	0.83842(40)	−0.13704(48)
N(1)	−0.20284(78)	0.60673(112)	0.09943(140)
N(2)	−0.28813(69)	0.84416(130)	−0.05466(134)
O(1)	−0.13114(48)	0.85513(87)	0.00699(111)
C(1)	−0.20505(69)	0.77064(125)	0.01709(138)
C(2)	−0.11218(110)	0.53162(153)	0.14146(209)
C(3)	−0.27554(118)	0.49755(176)	0.19560(204)
C(4)	−0.28538(99)	1.02305(174)	−0.10142(203)
C(5)	−0.37494(94)	0.77855(224)	−0.14174(222)
U(2)	0.50000	0.50000	0.50000
Cl(3)	0.44338(25)	0.66156(40)	0.14481(38)
Cl(4)	0.42824(22)	0.71486(36)	0.54534(44)
N(3)	0.21241(60)	0.34616(124)	0.42102(138)
N(4)	0.29815(70)	0.10376(112)	0.59337(134)
O(2)	0.36765(53)	0.35311(87)	0.50718(109)
C(6)	0.29080(75)	0.26684(127)	0.50614(141)
C(7)	0.38727(107)	1.02849(151)	−0.28685(187)
C(8)	0.22486(115)	−0.00122(173)	0.53213(221)
C(9)	0.12566(92)	0.27962(213)	0.48889(220)
C(10)	0.21401(100)	0.52322(162)	0.29244(189)

TABLE IIb. Thermal Parameters for UCl_4L_2 ($\times 10^4$). Thermal Parameters are in the Form $T = \exp[-2\pi^2(\Sigma U_{ij}h_ih_ja_i{}^*a_j{}^*)]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	279(3)	273(2)	404(3)	−167(2)	104(2)	−48(2)
Cl(1)	562(17)	507(16)	454(15)	−149(12)	69(13)	45(13)
Cl(2)	753(22)	547(17)	703(20)	−379(16)	259(17)	45(15)
N(1)	708(73)	336(47)	607(64)	−219(46)	151(54)	−83(46)
N(2)	437(54)	627(64)	506(56)	−251(50)	94(44)	−5(46)
O(1)	272(34)	395(38)	676(50)	−231(36)	145(33)	−99(28)
C(1)	341(48)	437(53)	427(54)	−265(45)	112(41)	−79(40)
C(2)	804(102)	392(65)	815(100)	−261(67)	132(79)	49(64)
C(3)	963(119)	605(84)	699(92)	−215(72)	414(86)	−427(81)
C(4)	584(83)	604(82)	764(94)	−257(72)	72(69)	195(66)
C(5)	392(69)	1212(138)	862(106)	−627(104)	73(68)	−229(78)
U(2)	324(3)	293(3)	317(3)	−109(2)	70(2)	−11(2)
Cl(3)	749(21)	570(17)	347(13)	−122(12)	82(13)	18(15)
Cl(4)	566(17)	491(15)	649(18)	−288(14)	182(14)	42(13)
N(3)	291(43)	608(60)	642(61)	−331(51)	114(41)	−58(40)
N(4)	558(60)	425(51)	585(59)	−223(45)	281(49)	−200(44)
O(2)	415(41)	346(37)	599(47)	−153(34)	101(35)	−73(31)
C(6)	425(56)	417(54)	422(54)	−218(45)	161(44)	−167(44)
C(7)	797(99)	401(64)	616(81)	15(57)	164(71)	136(63)
C(8)	934(115)	596(83)	952(112)	−503(83)	387(92)	−416(79)
C(9)	395(68)	1138(128)	904(106)	−575(99)	286(69)	−209(74)
C(10)	658(87)	512(72)	649(83)	−141(62)	−30(66)	233(64)

TABLE IIIa. Atomic Coordinates for UBr_4L_2

Atom	*x/a*	*y/b*	*z/c*
U(1)	0.00000	0.00000	0.00000
Br(1)	0.07122(12)	0.77539(20)	0.34397(22)
Br(2)	0.05521(13)	0.83263(22)	−0.14533(26)
N(1)	−0.20307(96)	0.61687(149)	0.09319(188)
N(2)	−0.28337(86)	0.85231(187)	−0.05536(186)
O(1)	−0.12931(58)	0.85984(112)	0.00650(146)
C(1)	−0.20353(89)	0.77850(166)	0.01375(186)
C(2)	−0.11953(152)	0.53882(197)	0.13402(295)
C(3)	−0.27416(150)	0.51446(244)	0.18675(264)
C(4)	−0.28056(120)	1.02413(220)	−0.09752(268)
C(5)	−0.36634(116)	0.78627(306)	−0.14319(272)
U(2)	0.50000	0.50000	0.50000
Br(3)	0.44496(13)	0.66723(22)	0.13233(21)
Br(4)	0.42868(12)	0.72438(20)	0.54800(24)
N(3)	0.21704(84)	0.35302(167)	0.42207(185)
N(4)	0.29639(101)	0.11550(153)	0.58480(179)
O(2)	0.36865(71)	0.35806(118)	0.50577(139)
C(6)	0.29150(95)	0.27480(184)	0.50433(198)
C(7)	0.38081(136)	0.03966(199)	0.70676(253)
C(8)	0.22558(150)	0.01281(240)	0.52563(282)
C(9)	0.13428(117)	0.29485(276)	0.48709(289)
C(10)	0.21911(122)	0.52235(230)	0.29758(264)

TABLE IIIb. Thermal Parameters for UBr_4L_2 ($\times 10^4$). Thermal Parameters are in the Form $T = \exp[-2\pi^2(\Sigma U_{ij}h_ih_ja_i^*a_j^*)]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U(1)	235(3)	283(3)	406(4)	−155(3)	56(3)	−14(3)
Br(1)	514(9)	486(9)	464(9)	−106(7)	35(7)	69(7)
Br(2)	646(11)	581(10)	697(11)	−389(9)	183(9)	53(8)
N(1)	546(83)	346(63)	672(91)	−230(64)	166(71)	−168(58)
N(2)	300(65)	787(103)	577(88)	−285(79)	46(61)	−52(66)
O(1)	189(41)	395(51)	752(72)	−270(52)	161(45)	−234(37)
C(1)	303(63)	407(72)	409(78)	−221(65)	55(57)	−59(53)
C(2)	844(148)	322(80)	986(158)	−268(95)	155(120)	−5(86)
C(3)	813(143)	713(127)	650(122)	−216(103)	333(108)	−453(109)
C(4)	492(94)	564(104)	869(137)	−262(99)	58(90)	196(81)
C(5)	290(83)	1363(200)	736(131)	−542(136)	24(84)	−278(104)
U(2)	271(3)	280(3)	326(4)	−84(3)	37(3)	−2(3)
Br(3)	521(9)	481(9)	632(10)	−266(8)	110(8)	66(7)
Br(4)	646(11)	566(10)	357(8)	−82(7)	29(8)	63(8)
N(3)	328(65)	602(84)	650(90)	−352(74)	51(62)	−21(59)
N(4)	674(94)	390(67)	539(82)	−187(63)	253(72)	−186(63)
O(2)	428(58)	376(53)	513(63)	−82(47)	43(48)	97(44)
C(6)	289(68)	497(84)	453(86)	−189(72)	174(63)	−202(61)
C(7)	674(122)	386(85)	657(120)	29(82)	92(96)	−8(80)
C(8)	849(147)	707(124)	866(143)	−529(117)	290(117)	−464(111)
C(9)	365(89)	1094(165)	948(149)	−609(134)	297(96)	−274(97)
C(10)	439(95)	612(112)	762(129)	−140(98)	−12(88)	95(83)

TABLE IV. Bond Lengths (Å) with Estimated Standard Deviations for UX_4L_2

Molecule A	UCl_4L_2	UBr_4L_2
U(1)–X(1)	2.619(2)	2.786(1)
U(1)–X(2)	2.625(5)	2.781(3)
U(1)–O(1)	2.209(7)	2.197(9)
C(1)–O(1)	1.26(1)	1.26(2)
C(1)–N(1)	1.35(1)	1.36(2)
C(1)–N(2)	1.36(1)	1.36(2)
N(1)–C(2)	1.50(2)	1.47(3)
N(1)–C(3)	1.51(2)	1.49(3)
N(2)–C(4)	1.51(2)	1.48(3)
N(2)–C(5)	1.50(2)	1.49(3)
Molecule B	UCl_4L_2	UBr_4L_2
U(2)–X(3)	2.622(4)	2.781(2)
U(2)–X(4)	2.621(3)	2.782(2)
U(2)–O(2)	2.232(7)	2.230(10)
C(6)–O(2)	1.30(1)	1.31(2)
C(6)–N(3)	1.32(1)	1.31(2)
C(6)–N(4)	1.35(1)	1.34(2)
N(4)–C(7)	1.51(2)	1.47(2)
N(4)–C(8)	1.50(2)	1.48(3)
N(3)–C(9)	1.50(2)	1.46(2)
N(3)–C(10)	1.48(2)	1.46(2)

TABLE V. Bond Angles (°) with Estimated Standard Deviations for UX_4L_2

Molecule A	UCl_4L_2	UBr_4L_2
X(1)–U(1)–X(2)	90.8(1)	91.3(1)
X(1)–U(1)–O(1)	89.1(2)	89.0(2)
X(2)–U(1)–O(1)	90.2(3)	90.1(4)
U(1)–O(1)–C(1)	178(1)	179(1)
O(1)–C(1)–N(1)	121(1)	120(1)
O(1)–C(1)–N(2)	120(1)	120(1)
N(1)–C(1)–N(2)	119(1)	120(1)
C(1)–N(1)–C(2)	117(1)	120(1)
C(1)–N(1)–C(3)	124(1)	122(2)
C(2)–N(1)–C(3)	117(1)	116(1)
C(1)–N(2)–C(4)	116(1)	118(1)
C(1)–N(2)–C(5)	124(1)	122(2)
C(4)–N(2)–C(5)	117(1)	117(1)
Molecule B	UCl_4L_2	UBr_4L_2
X(3)–U(2)–X(4)	90.8(1)	91.3(1)
X(3)–U(2)–O(2)	90.0(2)	90.7(4)
X(4)–U(2)–O(2)	90.9(3)	90.1(4)
U(2)–O(2)–C(6)	178(1)	178(1)
O(2)–C(6)–N(3)	118(1)	118(1)
O(2)–C(6)–N(4)	117(1)	116(1)
N(3)–C(6)–N(4)	126(1)	126(1)
C(6)–N(3)–C(9)	121(1)	122(1)
C(6)–N(3)–C(10)	120(1)	121(2)
C(9)–N(3)–C(10)	116(1)	115(2)
C(6)–N(4)–C(7)	121(1)	121(1)
C(6)–N(4)–C(8)	120(1)	121(2)
C(7)–N(4)–C(8)	118(1)	117(1)

Results and Discussion

X-ray Structure

The structural arrangement of molecules A and B of UCl_4tmu_2 is given in Fig. 1. Both of these are *trans*-octahedral molecules. Because the uranium atoms lie on the crystallographic inversion centres, the molecules have point group symmetry *Ci*; molecules A, with the U atom at the corners of the cell, are independent from molecules B, with the U atom at the centre. This feature, of two independent molecules in the unit cell, is the first reported for *trans*-octahedral molecules of the type UX_4l_2 [13] (X = Cl and Br and l = monodentate neutral oxygen donor ligand). The linearity of the U–O–C sequences for both the chloro and bromo complexes is similarly uncommon. Only one known structure, that of UBr_4ddu_2 (ddu = *N,N′*-dimethyl-*N,N′*-diphenylurea) of a total of thirteen structures known have the U–O–Y (Y = As, P, S or C) angles close to 180°. All those of the others vary from 152 to 171° [13]. The important bond distances and angles of the UX_4tmu_2 complexes are compared with those of the similar UX_4ddu_2 complexes [13] in Table VI. The characteristics correspond well except for an unexpectedly short U–O bond distance in the UCl_4tmu_2 complex, since the U–O bonds for the weaker ligands like sulphoxides and amides are normally in the region of 2.25 Å, e.g. that of $UCl_4\{(iso\text{-}but)_2SO\}_2$ (2.248 Å) [13] and $UCl_4\{(Cme_3)(Nme_2)CO\}_2$ (2.246 Å) [14].

The replacement of two methyl groups by phenyl groups in going from tmu to ddu will, however, result in the latter being a weaker donor ligand than tmu. More stereochemical crowding will occur in UCl_4ddu_2 than in the UCl_4tmu_2 complex. These factors could account for the shorter U–O distance in the latter compound. The above arguments are in agreement with enthalpimetric results obtained by the titration of UCl_4 in acetophenone solution by 2 mol of each of tmu and teu (*N,N,N′,N′*-tetraethylurea) [15]. The enthalpy of formation for

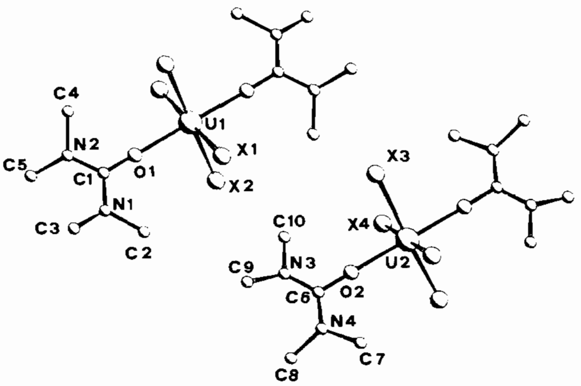

Fig. 1. Structural arrangement of molecules A and B of UCl_4tmu_2.

TABLE VI. A Comparison of some Crystallographic Data of UX_4L_2 (X = Cl and Br; L = tmu and ddu)

		UCl_4tmu_2	UCl_4ddu_2[a]	UBr_4tmu_2	UBr_4ddu_2[a]
C–O	(Å)	1.28	1.27	1.29	1.26
N–C(CO)	(Å)	1.35	1.35	1.34	1.34
N–C(me)	(Å)	1.50	1.47	1.46	1.47
U–O	(Å)	2.22	2.27	2.21	2.22
U–X	(Å)	2.62	2.61	2.78	2.77
U–O–C	(°)	178	157	178	180

[a] Data for UX_4ddu_2 complexes taken from ref. 13.

UCl_4tmu_2 was found to be 32.3 kJ/mol as compared to 24.7 kJ/mol for that of the more bulky ligand teu, *i.e.* UCl_4teu_2.

Infrared Studies

The infrared spectra of tetramethyl urea and its metal halide complexes [6] have been discussed in some detail. Infrared band assignments have been made for tetramethylurea [5]. Although most of the bands, observed in the infrared spectrum of liquid tmu arise from mixed vibrations [5], the infrared spectra of metal complexes of tmu have previously been used to discern the type of bonding involved [6]. Schafer and Curran have shown that the absorption at *ca.* 1650 cm^{-1} (taken to be mainly due to the C=O stretching frequency) shifts downwards upon coordination of tmu via the oxygen atom, whereas the absorption at *ca.* 1500 cm^{-1} (taken to be mainly the antisymmetric N–C–N stretching vibration) shifts upwards. In complexes where the metal oxygen interaction is relatively weak, e.g. in $SnCl_4tmu_2$, two separate absorptions can be observed in the 1600–1500 cm^{-1} region. In cases where the metal oxygen interaction becomes stronger, for example in $ZnBr_2$-tmu_2, only a single, broad absorption appears in the 1600–1500 cm^{-1} region (1555–1535 cm^{-1}) [6]. A similar merging of the 'C=O' and 'anti-symmetric N–C–N' stretching frequencies was also observed for the $[UO_2tmu_4](ClO_4)_2$ and $[UO_2tmu_5](ClO_4)_2$ complexes [16].

Although the infrared spectra of UCl_4tmu_2 and UBr_4tmu_2 were previously recorded and a position for the 'C=O' stretching frequency quoted [1], the present work indicated that a closer investigation of these spectra is required. The infrared spectra of tmu and UX_4L_2 are given in Figure 2. From this figure it is clear that two relatively broad absorptions occur in the region 1600–1500 cm^{-1}. The absorption occurring in the range 1540 → 1520 cm^{-1} was previously taken to be the C=O stretching frequency, but the absorption occurring at *ca.* 1590 cm^{-1} was not mentioned [1].

Considering the data given for the 3d transition metal complexes of Zn(II) and Co(II) and that of uranyl, together with the fact that uranium(IV) is a much stronger Lewis acid than the 3d transition

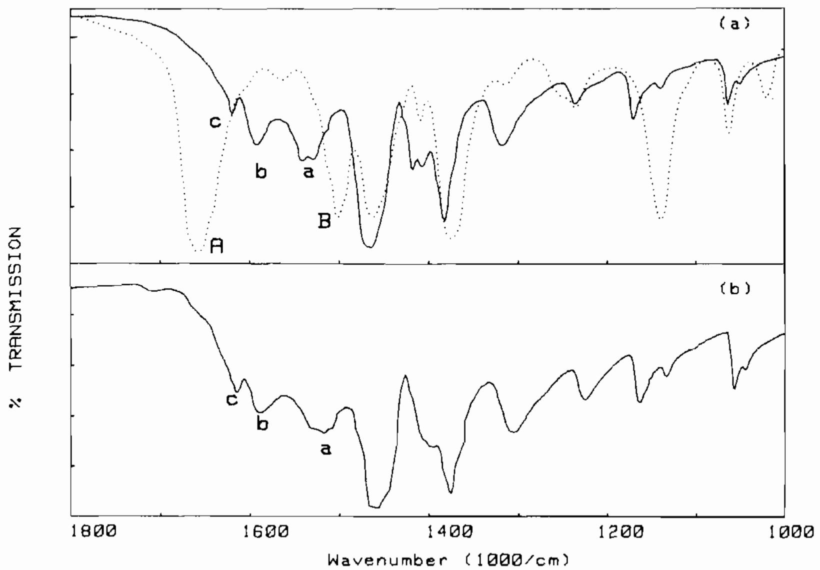

Fig. 2. Infrared spectra of UCl_4tmu_2 (a) and UBr_4tmu_2 (b). The dotted curve in (a) is the spectrum of a smear of the free ligand.

metals, it is highly unlikely that the absorption at *ca.* 1590 cm^{-1} would represent the C=O stretching frequency. It would thus appear that the essentially C=O vibration at 1656 cm^{-1} as found in the smear of the free tmu (peak A in Figure 2a) and the essentially antisymmetric N–C–N stretching vibration at 1501 cm^{-1} (peak B in Figure 2a) have passed each other in the UX_4 complexes. The latter now being at the higher wavenumber region. In terms of the above arguments the essentially C=O stretch frequencies are now assigned to the doublet at 1542 and 1530 cm^{-1} (indicated by 'a' in Figure 2a) for UCl_4tmu_2 and the broad peak ranging from ~1510–1535 cm^{-1} (indicated by 'a' in Figure 2b) for UBr_4tmu_2. The somewhat bigger shift of the bromide is to be expected even though the U–O band is only marginally shorter in the case of the bromide, *i.e.* 2.214 Å as compared to 2.22 Å for the chloride. The broad nature of the C=O peaks and even clear splitting of it in the case of the chloride can be interpreted in terms of the two different molecules (and uranium surroundings) found in the unit cells. The essentially antisymmetric N–C–N stretching vibrations are greatly highered in the complexes and found at 1590 and 1593 cm^{-1}, respectively, for the chloro and bromo complex (these are indicated by 'b' in Figure 2). The small peaks (indicated by 'c' in Figure 2) are found in all tmu complexes at the same position and cannot be related to the latter peak. There are small shifts of the other free ligand peaks in the 1400 to 1000 cm^{-1} region upon complexation as indicated by the spectra in Figure 2a.

It is of interest to note that both the C=O and N–C–N peaks of these complexes in CH_2Cl_2 solution are sharp, well-defined peaks at 1533 cm^{-1} (C=O) and 1589 cm^{-1} (N–C–N) for UCl_4tmu_2 and 1527 cm^{-1} and 1593 cm^{-1} for the corresponding UBr_4-tmu_2 complexes.

From the above spectral data it is clear that there is very strong U–O interaction thus leading to a large $^{+}N=C-O^{-}$ character in these tmu complexes.

Thermogravimetric Studies

UCl_4tmu_2 system

The thermal decomposition curve of UCl_4tmu_2 (Figure 3a) can be divided into three parts, *viz.*:

$A \longrightarrow B$ change occurs from ~ 140 ⟶ ~235 °C

$B \longrightarrow C$ change occurs from ~ 235 ⟶ ~300 °C

$C \longrightarrow D$ change occurs from ~300 ⟶ ~350 °C.

The 27.5% mass loss obtained during the $A \rightarrow B$ step corresponds to the loss of two chloride atoms together with the major part of a tmu molecule. In subsequent experiments the heating was stopped at 235 °C and the olive green product obtained proved to be $UOCl_2tmu$ by uranium and chloride analysis. The 22.0% mass loss obtained during the $B \rightarrow C$ step corresponds to the loss of one chloride atom together with the major part of the remaining tmu molecule. The yellow moisture sensitive product obtained at 300 °C proved to be UO_2Cl by uranium and chloride analyses. Although dioxouranium(V) chloride has been previously described [17] this is a new and convenient method of its preparation.

In the final step $(C \rightarrow D)$ the mass loss of 5.84% corresponds to the loss of one chloride atom to yield the stable UO_2 species. The complete thermal degradation of UCl_4tmu_2 under these conditions can be summarized as follows:

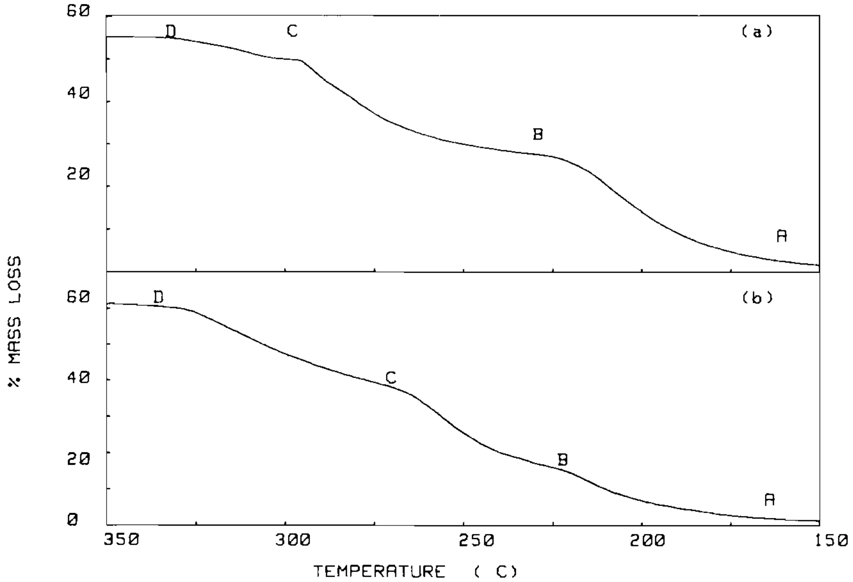

Fig. 3. Thermogravimetric curves for UCl_4tmu_2 (a) and UBr_4tmu_2 (b).

$$UCl_4tmu_2 \xrightarrow{235\ ^\circ C} UOCl_2tmu \xrightarrow{300\ ^\circ C} UO_2Cl \xrightarrow{350\ ^\circ C} UO_2$$

The overall reaction can thus be regarded as the carbonyl oxygen atom abstraction of the uranium(IV) and resulting degradation of the tmu.

UBr_4tmu_2 system

The thermal decomposition curve of UBr_4tmu_2 (Figure 3b) can similarly be divided into three sections as for UCl_4tmu_2. Although the final product obtained at D(~350 °C) was again UO_2 the intermediate products at B and C could not be unambiguously assigned. Isothermal studies at both B-(~220 °C) and C(~260 °C) resulted in continuous loss of mass and no stable intermediates could be isolated.

Conclusion

The particularly strong uranium(IV)–oxygen atom interaction is clearly illustrated by the structural, infrared spectral and thermogravimetric data. A new convenient preparative method of the uncommon dioxouranium(V) chloride is illustrated in this work.

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