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The Chemistry of Uranium.
Part 23. Isomorphous Tetrachlorobis(hexamethylphosphoramide)uranium(IV) and Tetrabromobis(hexamethylphosphoramide)uranium(IV)

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The structures of $UCl_4 \cdot 2hmpa$ and $UBr_4 \cdot 2hmpa$ have been determined by Fourier methods from single-crystal X-ray diffraction data. Full-matrix least-squares refinement yielded final conventional R factors of 0.062 and 0.059 respectively. The complexes are isomorphous and crystallise in the space group $P2_1/n$ with a = 14.141(5), b = 10.530(5), c = 9.076(5) Å, β = 93.33° and a = 14.348(5), b = 10.698 (5), c = 9.304(5), β = 91.95 respectively. The hmpa moieties are in trans-octahedral arrangement about the uranium atom. The principal bond lengths are U–X (X = Cl, Br) = 2.615, 2.78; U–O = 2.23, 2.18; O–P = 1.50, 1.53 Å respectively.

Introduction

A recent determination [1] of the structure of $UCl_4 \cdot 2teao^{\dagger}$ has shown that the uranium–oxygen bond length is shorter and the uranium–chloride bond length larger than in similar phosphine oxide complexes [2, 3]. Infrared data for complexes of the type $UX_4 \cdot 2L$ (X = Cl, Br; L = P=O and As=O ligand) have been interpreted [4, 5] in terms of stronger uranium–oxygen interaction in the case of the bromo complexes, with weaker uranium–bromide than uranium–chloride bonding. Further, the same assumption (*i.e.* a larger tetragonal distortion) was made in explaining the magnetic behaviour of a number of such complexes [5]. In addition, solution studies [6] have shown that bromide is replaced more readily than chloride for the respective uranium(IV) halides in acetone solution. It was therefore of interest to compare the structures of a phosphine oxide complex of both uranium tetrachloride and tetrabromide. Although the molecular structure of $UCl_4 \cdot 2hmpa$ has previously been published [7], a full structural determination was not achieved. This work was therefore repeated to provide an accurate comparison with the uranium tetrabromide complex.

Experimental

Preparation of the Complexes

The complexes were prepared as previously described [4] and were crystallized from a mixture of dichloromethane and diethyl ether.

Crystal Data

The respective densities were determined by flotation in mixtures of carbon tetrachloride and methyl iodide. Preliminary rotation and Weissenberg photographs showed the compounds to be isomorphous, space group $P2_1/n$. Single crystals of each complex were ground into spheres of radii 0.165 ($UCl_4 \cdot 2hmpa$) and 0.175 ($UBr_4 \cdot 2hmpa$) mm and were used for the data collection. The lattice constants were obtained from a least squares analysis of the settings of 25 reflections measured on a four-circle diffractometer with MoKα radiation (λ = 0.71069 Å).

	$UCl_4 \cdot 2hmpa$	$UBr_4 \cdot 2hmpa$
Molecular Formula	$C_{12}H_{36}Cl_4N_6O_2P_2U$	$C_{12}H_{36}Br_4N_6O_2P_2U$
Molecular Weight	738.2	916.1
a	14.141(5) Å	14.348(5) Å
b	10.530(5)	10.698(5)
c	9.076(5)	9.304(5)
α	90.0°	90.0°
β	93.33(5)	91.95(5)
δ	90.0	90.0
D_m	1.81 gcm^{-3}	2.23 gcm^{-3}
D_c (for Z=2)	1.82	2.25

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[†] teao = triethylarsine oxide.

μ (MoKα)	62.5 cm^{-1}	116.9 cm^{-1}
μR	1.03	2.04
F(000)	712	856

Figures in parentheses are the e.s.d.'s calculated from several measured values of the parameters.

Intensity Data

The intensity data were collected on a Philips PW 1100 computer-controlled four-circle diffractometer operating in the W–2θ scan mode (scan width = 1.20° θ and scan speed 0.04° θ S^{-1}). The background and scan times were both 30 seconds. Using graphite-monochromated MoKα radiation, 1764 reflections (UCl_4·2hmpa) and 2112 reflections (UBr_4·2hmpa) were collected. Of these, 183 (UCl_4·2hmpa) and 619 (UBr_4·2hmpa) were omitted as they did not satisfy the condition $I_{rel} > 2.0\ \sigma(I_{rel})$ for an observed reflection. Throughout the course of the data collections three standard reflections were measured after every 68 reflections to ensure stability of operation and to monitor any crystal decomposition. These remained constant to within ± 2%. Lorentz-polarization corrections were applied to the data. Absorption corrections were carried out with A* for spheres with μR = 1.03 and 2.04 respectively.

Structure Determination and Refinement

With the number of molecules per unit cell having been determined as 2, space group conditions fixed the uranium atom at the origin. A difference map was calculated with weighting scheme W = exp $(-g\sin^2\theta/\lambda^2S^2)$ in which S is the value of $\sin\theta/\lambda$ for which the weight is half that at $\theta = 0$. With a value of S = 0.5 the difference map for each structure, phased on uranium alone revealed the positions of all the non hydrogen atoms and gave R factors of 0.34 (UCl_4·2hmpa) and 0.39 (UBr_4·2hmpa) where $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$). Full-matrix least-squares refinement (SHEL-X program system [8]) with the uranium and halogen atoms anisotropic and the remaining non hydrogen atoms isotropic yielded R values of 0.062 and 0.068. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$ where w is the weight of a reflection. At this stage a difference map showed the positions of some of the hydrogen atoms in both structures. All the methyl hydrogens were refined as rigid groups and were constrained to be 1.08 Å from their corresponding parent atoms, their positions being dictated by the geometry of the molecule. Their isotropic temperature factors were refined as one common parameter which had final values of 0.08(1) Å^2 (UCl_4·2hmpa) and 0.13(2) Å^2 (UBr_4·2hmpa). This technique of constrained least squares refinement using bond length constraints and location and refinement of hydrogen atoms is discussed by Sheldrick [8].

The final R values were 0.062 and 0.059 respectively, while $R_w = \Sigma w^{1/2}||F_0| - |F_c||/\Sigma w^{1/2}|F_0|$ was 0.089 and 0.059 with $w = 1/\sigma^2$. This weighting scheme was shown to be satisfactory from an analysis of variance.[†]

In the final cycle of refinement the average shift-to-error ratios were 0.15 (UCl_4·2hmpa) and 0.12 (UBr_4·2hmpa) while final difference electron density

TABLE I. Fractional Atomic Coordinates and Their Esd's (× 10^4).

UCl_4·2hmpa				UBr_4·2hmpa			
Atom	X	Y	Z	Atom	X	Y	Z
U	0(0)	0(0)	0(0)	U	0(0)	0(0)	0(0)
Cl(1)	1635(4)	95(4)	–1201(8)	Br(1)	1689(1)	57(3)	–1384(3)
Cl(2)	629(4)	–1860(4)	1693(5)	Br(2)	660(2)	–1949(3)	1725(3)
O	494(7)	1400(9)	1720(10)	O	494(9)	1384(12)	1575(14)
P	561(2)	2535(3)	2725(4)	P	601(4)	2486(6)	2616(6)
N(1)	965(7)	2047(11)	4328(11)	N(1)	1016(15)	1967(21)	4149(23)
N(2)	1241(8)	3556(11)	1963(12)	N(2)	1274(13)	3507(17)	1919(20)
N(3)	–404(8)	3234(11)	2997(13)	N(3)	–359(14)	3245(19)	2938(21)
C(1)	1055(20)	2990(27)	5544(30)	C(1)	1304(36)	2720(50)	5283(56)
C(2)	1253(28)	831(42)	4579(40)	C(2)	866(41)	681(46)	4557(64)
C(3)	1454(19)	4825(16)	2572(31)	C(3)	1452(24)	4768(31)	2485(35)
C(4)	1953(13)	3215(20)	927(22)	C(4)	1940(23)	3173(34)	779(34)
C(5)	–1082(15)	2798(22)	3992(26)	C(5)	–957(21)	2848(29)	4090(31)
C(6)	–882(12)	4046(18)	1804(19)	C(6)	–781(28)	3921(36)	1767(44)

[†] A list of hydrogen atom parameters and observed and calculated structure factors is available from A. Rodgers on request.

TABLE II (a). Anisotropic Thermal Parameters and Their Esd's ($\times 10^3$). Anisotropic Temperature Factors are of the form: $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}C^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$UCl_4 \cdot 2$(hmpa)						
U	45(1)	36(1)	38(1)	−1(0)	0(0)	−2(0)
Cl(1)	58(3)	90(4)	71(4)	−17(2)	16(3)	−6(2)
Cl(2)	126(4)	53(3)	65(3)	13(2)	−5(3)	24(3)
$UBr_4 \cdot 2$(hmpa)						
U	34(1)	38(1)	43(1)	9(1)	3(0)	−4(1)
Br(1)	46(1)	95(2)	73(2)	−4(2)	19(1)	−8(2)
Br(2)	120(3)	64(2)	74(2)	28(2)	−5(2)	25(2)

TABLE II (b). Isotropic Thermal Parameters and Their Esd's ($\times 10^3$).

Atom	$UCl_4 \cdot 2$(hmpa) U	$UBr_4 \cdot 2$(hmpa) U
O	46(3)	46(4)
P	46(1)	48(1)
N(1)	47(3)	75(6)
N(2)	53(3)	58(5)
N(3)	56(3)	67(6)
C(1)	118(9)	207(22)
C(2)	188(14)	265(26)
C(3)	79(7)	112(11)
C(4)	91(6)	104(10)
C(5)	83(6)	91(9)
C(6)	79(5)	139(14)

maps had no peaks greater than 0.52 eÅ^{-3} and 0.84 eÅ^{-3} respectively.

Atomic scattering factors for the heavy atoms were those from Cromer and Mann [9] and those for hydrogen from Stewart *et al.* [10]. The scattering curves for uranium and the halogen atoms were corrected for anomalous dispersion.

The final atomic positional and thermal parameters for the non hydrogen atoms are given in Tables I and II respectively.

All computations were performed at the Computer Centre of the University of Cape Town on a Univac 1106 computer with the program SHEL-X written by G. M. Sheldrick [8].

Discussion

The molecular structure and atomic nomenclature are illustrated in Figure 1 (Program PLUTO) [11]. The intramolecular bond lengths and angles and their associated e.s.d.'s are given in Tables III and IV respectively (Program SHEL-X) [8].

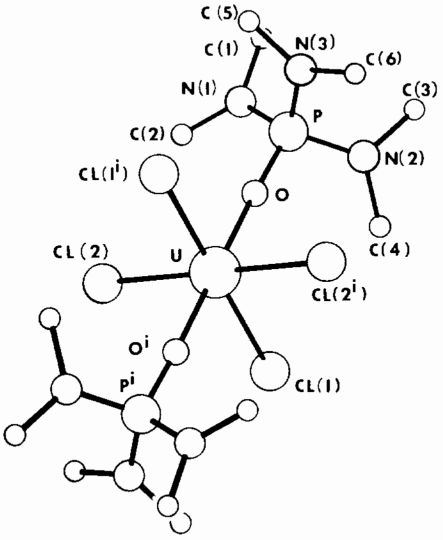

Fig. 1. Molecular structure showing atomic nomenclature for the chloro-isomer.

TABLE III. Bond Lengths and Their Esd's (Å).

	$UCl_4 \cdot 2$(hmpa)	$UBr_4 \cdot 2$(hmpa)
U–X(1)	2.615(6)	2.784(2)
U–X(2)	2.614(4)	2.778(3)
U–O	2.23(1)	2.18(1)
O–P	1.50(1)	1.53(1)
P–N(1)	1.62(1)	1.62(2)
P–N(2)	1.62(1)	1.61(2)
P–N(3)	1.58(1)	1.64(2)
N(1)–C(1)	1.49(3)	1.38(5)
N(2)–C(3)	1.47(2)	1.47(3)
N(1)–C(2)	1.36(4)	1.45(5)
N(2)–C(4)	1.46(2)	1.49(3)
N(3)–C(5)	1.43(2)	1.46(3)
N(3)–C(6)	1.51(2)	1.43(4)

$UCl_4 \cdot 2$hmpa and $UBr_4 \cdot 2$hmpa are isomorphous. The $UX_4 \cdot 2$hmpa molecule is centrosymmetric, the uranium being six-coordinate, with the neutral ligands in a *trans*-arrangement.

When the U–Cl and U–O bond lengths of a number of $UCl_4 \cdot 2$l species (l = phosphine or arsine oxide) are compared (Table V) it becomes clear that a U–Cl bond lengthening is accompanied by a U–O bond shortening. Although this is not very clear between adjacent members in the series the difference between the first and the last ones is very significant. The U–O bond shortening is also proportional to the donor strength of the neutral ligand towards U^{+4} as recently obtained [13] *i.e.* teaso > hmpa > tppa > tppo. Not only is a very significant U–O bond shortening of 0.05 Å obtained when the chloride ion is replaced by bromide (weaker anion donor) in the present study of $UX_4 \cdot 2$hmpa (Table V),

TABLE IV. Bond Angles and Their Esd's (°).

	$UCl_4 \cdot 2(hmpa)$	$UBr_4 \cdot 2(hmpa)$
X(1)–U–X(2)	89.7(2)	89.9(1)
X(1)–U–O	91.0(3)	91.6(4)
X(2)–U–O	90.1(3)	91.4(3)
U–O–P	163.1(6)	166(1)
O–P–N(1)	107.4(8)	109(1)
O–P–N(2)	106.6(6)	109(1)
O–P–N(3)	116.1(6)	116(1)
N(1)–P–N(2)	114.0(6)	112(1)
N(1)–P–N(3)	105.7(6)	107(1)
N(2)–P–N(3)	107.2(6)	105(1)
P–N(1)–C(1)	118(1)	124(3)
P–N(1)–C(2)	123(2)	120(3)
C(1)–N(1)–C(2)	120(2)	114(4)
P–N(2)–C(3)	124(1)	125(2)
P–N(2)–C(4)	124(1)	122(2)
C(3)–N(2)–C(4)	109(2)	112(3)
P–N(3)–C(5)	124(1)	121(2)
P–N(3)–C(6)	120(1)	117(2)
C(5)–N(3)–C(6)	110(1)	118(3)

but a relative U–Br bond lengthening occurs if the greater difference between U–Cl and U–Br bond lengths (0.166 Å) in the $UX_4 \cdot 2hmpa$ complexes as compared to the difference in the UX_6^{-2} complexes (0.146 Å) is considered (Table V).

The shorter U–O bond length and correspondingly stronger interaction between the U^{+4} ion and the phosphoryl oxygen atom in the bromo complex is also in agreement with the greater lowering in P=O stretching frequency upon complexation, *i.e.* 181 cm^{-1} as compared to 163 cm^{-1} in the chloro analogue [14].

If it is borne in mind, firstly, that the neutral oxygen donor ligands mentioned here are all hard ligands, secondly, that this ligand/donor strength order could recently be rationalized [13] in terms of a simplified treatment assuming only electrostatic interactions and thirdly, that the experimental method of obtaining this order involved the measurement of the concentration of the anions replaced by the neutral ligands, the uranium(IV) ligand bonding in these complexes must be regarded as highly ionic. This solid state tetragonal distortion of UX_4O_2 chromophore complexes in which relative bond shortening occurs with increasingly stronger ligands can be regarded as a kind of solid state "ionization" which, in the case of smaller and stronger neutral ligands, lead to the formation of cationic species, *e.g.* $[UCl \cdot 6tmpo]^{+3}3Cl^{-}$.

TABLE V. Comparison of Molecular Parameters of Various Uranium Complexes (Å).

	U–X	$U{-}X_{av}$	U–O	Ref.
$UCl_4 \cdot 2tppo$	2.609(4) 2.626(3)	2.618	2.242(7)	3
$UBr_4 \cdot 2tppa^a$	2.613(4) 2.628(4)	2.621	2.226(6)	2
$UCl_4 \cdot 2hmpa$	2.615(6) 2.614(4)	2.615	2.23(1)	
$UCl_4 \cdot 2teao$	2.67 2.66	2.665	2.16(1)	1
$UBr_4 \cdot 2hmpa$	2.784(2) 2.778(3)	2.781	2.18(1)	
$(PPh_3Et)_2UCl_6$	2.624(2)	2.624		12
$(PPh_3Et)_2UBr_6$	2.770	2.770		12

[a] tppa = N,N,N',N'-tetramethylphenylphosphoramide.

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