

Structure and Bonding in Octahedral Uranium(IV) Complexes of the Type $UX_4 \cdot 2L$ ($X = \text{Halogen}$, $L = \text{Unidentate, Neutral Oxygen Donor}$). Part 1. The Crystal Structures of Tetrabromobis(NN' -dimethyl- NN' -diphenylurea)-uranium(IV) and α - and β -Tetrachlorobis(NN' -dimethyl- NN' -diphenylurea)-uranium(IV)†

J. Ferdinand de Wet* and Mino R. Caira

Crystallography Group, Chemistry Department, University of Port Elizabeth, Port Elizabeth 6000, South Africa

The crystal structures of three complexes of uranium(IV) halides with the carbonyl donor ligand NN' -dimethyl- NN' -diphenylurea (ddu) have been determined from three-dimensional X -ray data, and refined by full-matrix least-squares methods: $U\text{Br}_4 \cdot 2\text{ddu}$ (1) and two polymorphic forms of $U\text{Cl}_4 \cdot 2\text{ddu}$, labelled α (2) and β (3). For (1) the crystals are orthorhombic, space group $Fddd$ (final $R = 0.052$), for (2) monoclinic, space group $P2_1/n$ (final $R = 0.073$), and for (3) orthorhombic, space group $Pna2_1$ (final $R = 0.052$). In each complex the co-ordination geometry of uranium is distorted octahedral, with the halogen atoms at the corners of a puckered square. The high molecular symmetry (222) of $U\text{Br}_4 \cdot 2\text{ddu}$ is shown to arise from the crowded ddu ligand (which can assume two-fold symmetry), coupled with the short U–O bonding distance and large atomic diameter of bromine. The molecules in α - and β - $U\text{Cl}_4 \cdot 2\text{ddu}$ are devoid of symmetry and their conformations are completely dissimilar. The U–Br distance is 2.771(2) Å, and the U–Cl distances are 2.604(8) Å in (2) and 2.606(9) Å in (3); U–O is 2.217(10) Å in (1), 2.252(14) Å in (2), and 2.268(18) Å in (3).

The relationships between the structure and bonding of complexes of uranium in oxidation states IV–VI which contain the UO_2X_4 ($X = \text{Cl or Br}$) chromophore have been analysed by de Wet and du Preez,¹ who showed that these confirm the essentially ionic nature of the bonding in uranium and other actinoids. Specifically, the inverse relationship between the bond-length changes $\delta(\text{U–X})$ and $\delta(\text{U–O})$ in these complexes was interpreted in terms of electrostatic repulsion between the coplanar equatorial halogen ligands and the axially co-ordinated oxygen ligands; as the bonding between uranium and oxygen becomes stronger, thereby shortening this bond, repulsion of the halogen ligands causes an increase in the U–X bond lengths. Complexes of the type $UX_4 \cdot 2L$ ($L = \text{neutral, unidentate oxygen-donor ligand}$) constitute an important class of those containing the UO_2X_4 chromophore and, in view of the limited information available in the literature, it was therefore considered worthwhile to investigate these trends more fully in such complexes. Furthermore, du Preez and co-workers have employed various techniques such as spectrophotometry,² and enthalpimetric,³ conductometric,⁴ and potentiometric⁵ titration, to establish the donor-strength sequence for a wide variety of these ligands (L). The sequence, according to the oxygen-bonded partner, is: $\text{As=O} > \text{P=O} > \text{S=O} > \text{C=O}$. Our study was therefore also directed towards finding structural confirmation for this sequence: that is, the uranium bond lengths to oxygen and the halogen should decrease and decrease, respectively, in the same sequence with respect to the oxygen-bonded partner. Since these effects are very small (the total change in bond length is *ca.* 0.05 Å) the structural analyses had to be as precise as possible; special attention was therefore given to the problem of systematic errors in the data due to X -ray absorption by the uranium.

In this paper we report on the analysis of three crystal structures of the chloro and bromo complexes involving the donor ligand NN' -dimethyl- NN' -diphenylurea (ddu). In the following paper (Part 2), we report on the chloro complexes with tris(pyrrolidinyl)phosphine oxide and di-isobutyl sulphoxide, the bromo complex with triphenylarsine oxide, and interpret the results in terms of the objectives stated above.

Experimental

Samples of monoclinic α - $U\text{Cl}_4 \cdot 2\text{ddu}$ and orthorhombic $U\text{Br}_4 \cdot 2\text{ddu}$ were kindly provided by Professor Jan du Preez of the Uranium Chemistry Research Institute at this University; their preparation has been described elsewhere.⁶ The correct stoichiometry was confirmed in each case by chemical analysis. The first two data collections resulted in the structures of the bromo complex and the α form of $U\text{Cl}_4 \cdot 2\text{ddu}$. Later we requested a further sample of crystals of the latter, and since the original preparation was no longer available the complex was resynthesised. However, despite confirmatory chemical analysis, the crystals were orthorhombic. Exhaustive efforts to reproduce crystals of the chloro complex with the original monoclinic symmetry, involving variations in preparative and recrystallisation techniques, have since met with no success, and the exact conditions under which this phase crystallises are therefore unknown. The orthorhombic phase, which is now persistently obtained, was labelled β .

Crystallography.—Weissenberg and precession photographs were taken to determine the preliminary unit-cell dimensions and the possible space groups. In order to minimise absorption during data collection (the linear absorption coefficient μ varied between 50 and 120 cm^{-1}), crystals were ground to spheres with radii of $(0.07\text{--}0.10) \pm 0.01$ mm. The crystals were hygroscopic, and were therefore ground, glued onto glass fibres, and sealed in Lindemann capillaries in a special dry-box, using micro-manipulator techniques. Intensity data were collected on a

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo- K_α radiation ($\lambda = 0.7107 \text{ \AA}$). Usually, intensities were measured in the range $3 < \theta < 20^\circ$ (ω — 2θ mode, scan width 1.2° , and scan rate 0.025 — $0.04^\circ \text{ s}^{-1}$); background was measured by static counts on both sides of the peak. During data collection the intensities of three reference reflections were monitored periodically. N Independent intensities were measured, and corrected for Lorentz and polarisation effects. The structures were solved by the usual heavy-atom methods; final refinement was conducted with a subset N_r of structure amplitudes with $|F_o| > 2\sigma(F_o)$. Because of the uniform crystal shape and small size ($\mu \text{ ca. } 0.5$), absorption corrections were not applied.

Full-matrix least-squares refinements were used throughout. Non-hydrogen atoms were usually refined with anisotropic thermal parameters, but exceptions were made if temperature matrices became non-positive-definite, or if the number of least-squares parameters was not justified by the number of observations. Phenyl groups were initially refined with idealised geometry; usually these constraints were relaxed on adding artificial hydrogen scattering contributions. Methyl groups were first refined as rigid groups and then (as for other artificially added hydrogen atoms) according to a riding model⁷ in which the C—H vector was held constant in magnitude and direction but not position. The isotropic hydrogen thermal parameters were refined groupwise as free variables, and those which refined to unacceptably high values were fixed. Structure factors were computed analytically (for U according to Cromer and Liberman,⁸ and for the remaining atoms according to Cromer and Mann;⁹ those for U and the halogen atoms were corrected for anomalous dispersion⁸). At convergence of refinement, all positional, and most thermal, parameter shifts were $< 0.01\sigma$, none of the latter exceeding 0.1σ . The function minimised was $\Sigma w\Delta^2$ with $\Delta = |F_o| - |F_c|$ and weights w either $\propto 1/\sigma^2(F_o)$ or $\propto [\sigma^2(F_o) + gF_o^2]^{-1}$, g being a refinable parameter. Residuals quoted are $R = \Sigma|\Delta|/\Sigma|F_o|$, and $R' = \Sigma(w^{1/2}|\Delta|)/\Sigma(w^{1/2}|F_o|)$; where relevant, Hamilton's¹⁰ $R_g = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$ and the number of parameters in the refinement, N_p , are given. Unless indicated otherwise, under the special features for each structure, final difference syntheses revealed no peaks $> 1e \text{ \AA}^{-3}$, and one-way sampling distributions of $\langle w\Delta^2 \rangle$ with respect to variables such as $(|F_o|/|F_o(\text{max.})|)^{1/2}$ and $(\sin\theta)/\lambda$ revealed no appreciable systematic error. The programs used were: SHELX 76⁷ for structure solution and refinement, and XANADU¹¹ and PARST¹² for processing the results; molecular drawings were executed with programs developed in this laboratory (CRISTEP¹³ and CRISTEP-F¹⁴).

Crystal data. $\text{C}_{30}\text{H}_{32}\text{Br}_4\text{N}_4\text{O}_2\text{U}$, $M = 1038.2$, orthorhombic, space group $Fddd$ (C_{2h}^{24} , no. 70), $a = 14.387(7)$, $b = 19.845(10)$, $c = 24.712(12) \text{ \AA}$, $U = 7055(10) \text{ \AA}^3$, $D_m = 1.97$, $Z = 8$, $D_c = 1.95 \text{ g cm}^{-3}$, $F(000) = 3903.8$, $\mu = 88.6 \text{ cm}^{-1}$, crystal radius = $0.075(8) \text{ mm}$, $\mu_r = 0.66$.

(α) $\text{C}_{30}\text{H}_{32}\text{Cl}_4\text{N}_4\text{O}_2\text{U}$, $M = 860.4$, monoclinic, space group $P2_1/n$ (variant of $P2_1/c$, C_{2h}^5 , no. 14), $a = 14.009(7)$, $b = 19.331(10)$, $c = 14.438(7) \text{ \AA}$, $\beta = 119.29(2)^\circ$, $U = 3410(5) \text{ \AA}^3$, $Z = 4$, $D_c = 1.68 \text{ g cm}^{-3}$, $F(000) = 1663.9$, $\mu = 48.61 \text{ cm}^{-1}$, crystal radius = $0.10(1) \text{ mm}$, $\mu_r = 0.49$.

(β) $\text{C}_{30}\text{H}_{32}\text{Cl}_4\text{N}_4\text{O}_2\text{U}$, $M = 860.4$, orthorhombic, space group $Pna2_1$ (C_{2v}^9 , no. 33), $a = 15.865(7)$, $b = 13.212(6)$, $c = 15.756(8) \text{ \AA}$, $U = 3305 \text{ \AA}^3$, $Z = 4$, $D_c = 1.73 \text{ g cm}^{-3}$, $F(000) = 1663.9$, $\mu = 50.19 \text{ cm}^{-1}$, crystal radius = $0.10(1) \text{ mm}$, $\mu_r = 0.50$.

Special features. $\text{UBr}_4 \cdot 2\text{ddu}$. The phenyl-carbon atoms were assigned isotropic thermal parameters because of the rather wide scatter in ring bond lengths and angles. The hydrogen thermal parameters were all fixed during the final refinement. Final residuals: $R = 0.052$, $R' = 0.049$ (with $10^4g = 5.25$), for $N_r = 904$ ($N = 1209$).

α - $\text{UCl}_4 \cdot 2\text{ddu}$. All non-hydrogen atoms except the phenyl-carbon and the nitrogen atoms were assigned anisotropic thermal parameters, and the hydrogen thermal parameters were fixed in the final refinement. Three structure factors (hkl : 200, 002, and 113), suspected of extinction error, were excluded. Final residuals: $R = 0.073$ and $R' = 0.069$ (with $10^4g = 18.33$) for $N_r = 2624$ ($N = 4580$).

β - $\text{UCl}_4 \cdot 2\text{ddu}$. Because of the smaller data set, only atoms in the uranium co-ordination environment were refined with anisotropic thermal parameters; carbonyl atom C(4) gave a non-positive-definite matrix and was also refined isotropically. Three structure factors (hkl : 400, 202, and 211) were omitted because of probable extinction errors. Final residuals: $R = 0.052$, $R' = 0.044$ (with $10^4g = 4.41$) and $R_g = 0.049$ ($N_r = 1552$, $N = 2339$, $N_p = 220$). As the absolute polarity had not yet been determined, a refinement was undertaken with reversed signs for the z co-ordinates (which correspond to the polar axis, c). A value of $R_g = 0.056$ was obtained; thus Hamilton's R gave preference, at an α level of 0.05, to the originally assigned polarity.

Results and Discussion

Tetrabromobis(NN'-dimethyl-NN'-diphenylurea)-uranium(IV).—The co-ordinates of the non-hydrogen and methyl-hydrogen atoms in the asymmetric unit are listed in Table 1, and selected bond lengths and angles in Tables 2 and 6. The molecular structure and atom numbering are illustrated in Figure 1. Data on least-squares planes appear in Table 3.

It is rather remarkable for a 73-atom molecule to crystallise with such high space-group symmetry. This is due to the high molecular symmetry: three mutually perpendicular two-fold axes intersect at the uranium positions (at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$, etc.). Two of these are shown in Figure 1, the third being perpendicular to the plane of projection. The 222 symmetry is evidently enforced by three special circumstances: (i) the rather rigid, crowded ddu ligands which possess two-fold symmetry around the carbonyl bond (illustrated in Figure 2); (ii) an (initially) square-planar UBr_4 moiety with $\text{Br} \cdots \text{Br}$ contact distances approximately equal to the sum of their van der Waals radii (i.e. in-plane distortions of the 90° Br-U-Br angles are not possible); (iii) unusually strong bonding between the uranium and donor-oxygen atoms, which results in strain between the methyl groups and the bromine atoms. This is accommodated by opening out the U-O-C bond angle to 180° (which is invariably smaller in all other $\text{UX}_4 \cdot 2\text{L}$ complexes) and rotating the ddu ligands so that a pair of interfering methyl-hydrogen atoms from each ligand are in contact with oppositely situated bromine atoms [dashed lines from atoms H(82), Figure 1]. This causes alternate 0.30-\AA displacements of the bromine atoms from the mean UBr_4 plane, and this square, puckered configuration, together with the associated ligand-methyl contacts, results in the further two-fold symmetry. This rigid conformation [confirmed by the large number of short, non-bonded contacts (Table 9)] is probably maintained in the free state (e.g. in solution). The molecules in the crystal are all aligned with their long axes parallel to the b axis, each being in contact with 12 neighbours at various levels in y . Efficient space filling is achieved, the packing coefficient (calculated by Kitaigorodskii's¹⁵ method) being 0.66.

α - and β -*Tetrachlorobis(NN'-dimethyl-NN'-diphenylurea)-uranium(IV)*.—The co-ordinates of the non-hydrogen and methyl-hydrogen atoms of both conformers are listed in Table 4. Labelled molecular drawings for the α and β forms appear in Figure 3 and 4 respectively, and numerical data on the geometries of the uranium environments in Tables 5 and 6.

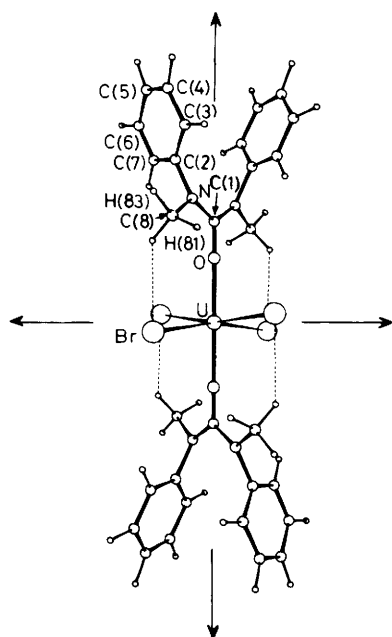


Figure 1. The $\text{UBr}_4 \cdot 2\text{ddu}$ molecule, showing the atomic numbering scheme of the asymmetric unit

Table 1. Atomic co-ordinates ($\times 10^4$) of non-hydrogen and methyl-hydrogen atoms in $\text{UBr}_4 \cdot 2\text{ddu}$

Atom	x	y	z
U	1 250(-)	1 250(-)	1 250(-)
Br	2 587(1)	1 098(1)	2 047(1)
C(1)	1 250(-)	2 999(9)	1 250(-)
O	1 250(-)	2 366(4)	1 250(-)
N	746(6)	3 343(4)	887(3)
C(8)	328(11)	2 978(5)	433(5)
C(2)	346(10)	4 020(6)	990(5)
C(3)	-202(11)	4 090(8)	1 429(6)
C(4)	-581(14)	4 736(10)	1 515(9)
C(5)	-361(15)	5 218(11)	1 157(9)
C(6)	184(16)	5 181(11)	734(9)
C(7)	597(12)	4 526(9)	620(6)
H(81)	-5(1)	332(1)	18(1)
H(82)	-14(1)	260(1)	58(1)
H(83)	87(1)	274(1)	19(1)

Both molecules have their uranium atoms at general positions in the unit cells, and are thus devoid of symmetry. Their conformations are conveniently described in terms of deviations from that of the bromo analogue, $\text{UBr}_4 \cdot 2\text{ddu}$, which possesses the maximum possible symmetry. The major deviations can be resolved into two components: (i) ligand tilt, which decreases the $\text{U}-\text{O}-\text{C}$ bond angle to less than 180° , and (ii) ligand rotation around the $\text{U}-\text{O}$ bond axis. The departure in orientation of a particular ddu ligand from that in $\text{UBr}_4 \cdot 2\text{ddu}$ may then be expressed in terms of two (polar) restoring angles required to reverse these rotational displacements. For each ddu ligand the reference frame for θ and ϕ is oriented as follows with respect to the UCl_4 groups: positive Z points along the $\text{U}-\text{O}$ bond vector with the chlorine atoms projecting onto the X and Y axes so that the two in the XZ plane have more positive Z co-ordinates than uranium. If the origin is now fixed at the carbonyl-oxygen atom, then the restoring angle θ renders the $\text{U}-\text{O}$ and $\text{O}-\text{C}$ bonds collinear, while ϕ is the smallest angle through which the ligand

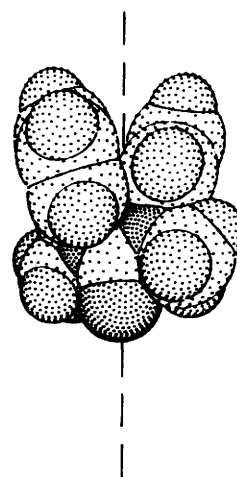


Figure 2. Space-filling perspective view of the ddu ligand, illustrating the crowded conformation with two-fold symmetry adopted in $\text{UBr}_4 \cdot 2\text{ddu}$ (two-fold axis shown as dashed line)

Table 2. Distances (\AA) and angles ($^\circ$) with estimated standard deviations in parentheses, for the uranium environment in $\text{UBr}_4 \cdot 2\text{ddu}$

U-Br	2.771(2)	Br ^{II} -U-O ^I	83.7(1)
U-O	2.217(10)	Br ^I -U-Br ^{II}	89.4(1)
O ^I -U-O ^{II}	180(-)	Br ^I -U-Br ^{III}	167.6(1)
Br ^I -U-O ^I	96.3(1)		

Symmetry equivalents: I x, y, z ; II $x, \frac{1}{2} - y, \frac{1}{2} - z$; III $\frac{1}{2} - x, y, \frac{1}{2} - z$.

Table 3. Planarity of phenyl and amide groups in $\text{UBr}_4 \cdot 2\text{ddu}$. Mean-plane deviations are in \AA ; $\langle \sigma \rangle$ is the mean estimated standard deviation (e.s.d.) for each set of deviations

(a) Phenyl ring

N* -0.022, C(2) -0.011, C(3) 0.007, C(4) 0.004, C(5) -0.012, C(6) 0.008, C(7) 0.004, $\langle \sigma \rangle$ 0.021

(b) Amide group

C(1) -0.036, N 0.097, C(2) -0.031, C(8) -0.030, $\langle \sigma \rangle$ 0.023

* Not included in mean-plane calculations.

must then be rotated to restore its orientation in $\text{UBr}_4 \cdot 2\text{ddu}$. The observed angles (Table 7) show that, apart from θ which is determined by the $\text{U}-\text{O}-\text{C}$ bond angle, the conformation of $\alpha\text{-UCl}_4 \cdot 2\text{ddu}$ is rather similar to that of $\text{UBr}_4 \cdot 2\text{ddu}$, whereas that of the β form is completely different. This is also apparent from the stereodrawings (Figures 5 and 6).

These large differences in conformation in the α and β phases of $\text{UCl}_4 \cdot 2\text{ddu}$, as well as the 10° range in $\text{U}-\text{O}-\text{C}$ bond angles (Table 5), suggest a greater degree of molecular flexibility in the free state. Notwithstanding some very short intramolecular $\text{H} \cdots \text{Cl}$ contacts (Table 9), there seems to be on the whole less severe crowding between the ddu ligands and the halogen atoms than in $\text{UBr}_4 \cdot \text{ddu}$. Thus, not only are the mean out-of-plane displacements of the halogen smaller, 0.24 and 0.15 \AA for α and β , respectively, but they are least in the β conformer, even though here one of the ligands is tilted so severely that the $\text{U}-\text{O}-\text{C}$ angle (152°) has the smallest value for $\text{U}-\text{O}-\text{Y}$ ($\text{Y} = \text{As, P, S, or C}$) hitherto observed in $\text{UX}_4 \cdot 2\text{L}$ complexes.

A somewhat more detailed discussion of the ligand geometries is justified, first, because these are the only known

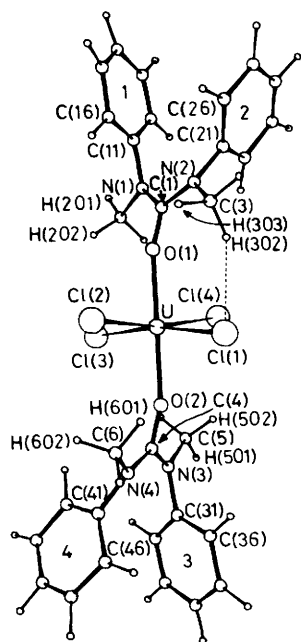


Figure 3. Perspective view of the α - $\text{UCl}_4 \cdot 2\text{ddu}$ molecule, showing the atomic numbering scheme

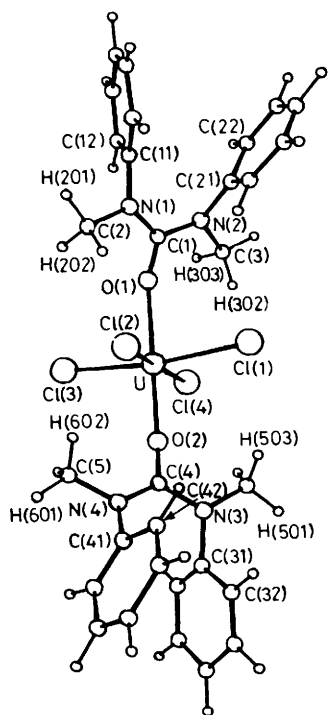


Figure 4. Perspective view of the β - $\text{UCl}_4 \cdot 2\text{ddu}$ molecule, showing the atomic numbering scheme

examples of the co-ordination of this ligand to actinoids and, secondly, because two examples of derivatives of ddu have been reported¹⁶ with two-fold symmetry, namely those with *p*-nitrophenyl and 2,4-dinitrophenyl *NN'* substituents. The configuration of the former is similar to that observed for the ddu ligands in this work, *i.e.* with the phenyl rings *anti* to the oxygen atom, while the latter adopts the *syn* configuration. Two-fold

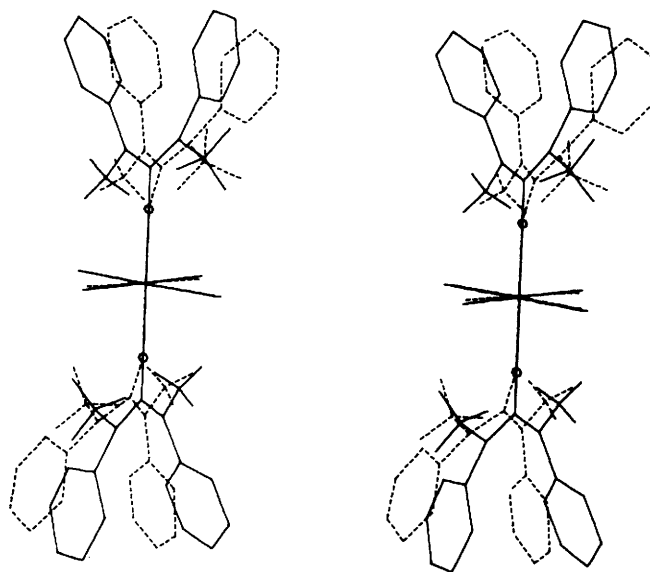


Figure 5. Schematic stereoview comparing the conformations of $\text{UBr}_4 \cdot 2\text{ddu}$ (solid lines) and α - $\text{UCl}_4 \cdot 2\text{ddu}$ (dashed lines) (oxygen atoms depicted as circles)

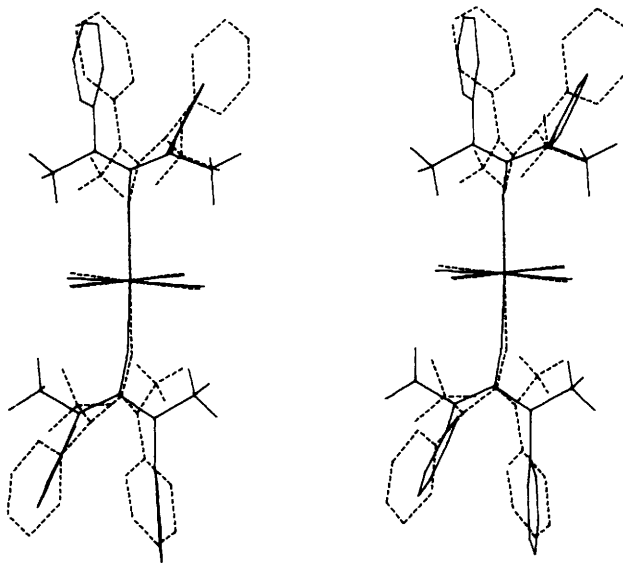


Figure 6. Schematic stereoview comparing the conformations of α - $\text{UCl}_4 \cdot 2\text{ddu}$ (dashed lines) and β - $\text{UCl}_4 \cdot 2\text{ddu}$ (solid lines)

symmetry is normally preferred when there is symmetric substitution, which causes steric hindrance and consequently parallel displacement of the substituents on both sides of the plane which bisects the N-C-N bond angle. The main sources of hindrance in the ddu ligands of the present complexes are phenyl contacts (especially between the pivot carbon atoms) and contacts between the methyl and carbonyl groups (Figure 2 and Table 9). Analysis of the contact distances on rotating the methyl groups shows that the least hindrance is achieved if one of the hydrogen atoms adopts a staggered configuration with respect to the C(carbonyl) atom, so that the other two straddle the carbonyl group symmetrically. This conformation occurs in

Table 4. Atomic co-ordinates for non-hydrogen ($\times 10^4$) and methyl hydrogen ($\times 10^3$) atoms in α - and β -UCl₄·2ddu

Atom	α phase			β phase		
	x	y	z	x	y	z
U	2 348(1)	1 304(0)	4 970(1)	74(0)	3 312(1)	0()
Cl(1)	789(5)	1 366(3)	3 012(5)	277(5)	1 479(5)	-598(5)
Cl(2)	834(5)	1 281(3)	5 510(8)	1 456(4)	3 122(11)	868(8)
Cl(3)	3 894(5)	1 487(3)	6 925(5)	-120(5)	5 217(4)	431(4)
Cl(4)	3 776(5)	1 079(3)	4 332(5)	-1 391(4)	3 308(9)	-715(8)
O(1)	2 392(13)	148(6)	5 153(12)	770(10)	3 871(14)	-1 180(11)
O(2)	2 366(12)	2 464(6)	4 819(13)	-558(11)	2 824(15)	1 212(11)
C(1)	2 474(20)	-497(9)	5 058(22)	1 316(17)	3 776(21)	-1 751(19)
C(4)	2 523(19)	3 127(10)	5 021(20)	-696(17)	2 473(27)	1 929(17)
N(1)	3 297(14)	-847(9)	5 842(15)	2 068(15)	4 182(19)	-1 681(17)
N(2)	1 792(13)	-834(9)	4 149(14)	1 109(12)	3 220(16)	-2 461(14)
C(2)	4 215(18)	-445(11)	6 698(18)	2 330(20)	4 622(24)	-872(21)
C(3)	786(17)	-472(13)	3 405(21)	192(17)	3 012(21)	-2 598(21)
C(11)	3 233(15)	-1 578(10)	6 044(16)	2 594(15)	4 439(19)	-2 399(18)
C(12)	4 028(17)	-2 034(11)	6 083(18)	2 271(18)	5 102(21)	-3 012(17)
C(13)	3 992(21)	-2 721(15)	6 296(21)	2 809(21)	5 410(26)	-3 686(24)
C(14)	3 184(22)	-2 958(17)	6 463(24)	3 627(20)	5 089(25)	-3 699(21)
C(15)	2 302(22)	-2 515(16)	6 308(21)	3 974(20)	4 462(21)	-3 066(18)
C(16)	2 366(19)	-1 790(13)	6 165(19)	3 416(17)	4 114(21)	-2 438(21)
C(21)	2 130(17)	-1 417(13)	3 763(18)	1 738(17)	2 629(22)	-2 888(19)
C(22)	1 501(21)	-2 023(15)	3 541(21)	1 795(20)	2 720(24)	-2 812(20)
C(23)	1 818(24)	-2 608(16)	3 143(22)	2 364(18)	2 104(21)	-4 217(21)
C(24)	2 703(24)	-2 525(18)	3 014(25)	2 845(20)	1 453(26)	-3 786(22)
C(25)	3 321(24)	-2 000(16)	3 256(22)	2 786(17)	1 309(22)	-2 904(20)
C(26)	3 068(20)	-1 383(15)	3 683(20)	2 215(16)	1 959(21)	-2 518(20)
N(3)	3 349(15)	3 444(10)	5 027(15)	-1 164(13)	1 586(18)	1 996(14)
N(4)	1 686(14)	3 446(9)	5 081(15)	-436(14)	2 906(17)	2 641(16)
C(5)	4 257(20)	3 042(12)	5 080(24)	-1 311(20)	1 026(24)	1 229(21)
C(6)	673(18)	3 104(14)	4 860(27)	-43(20)	3 898(20)	2 580(21)
C(31)	3 238(16)	4 176(11)	4 748(17)	-1 682(15)	1 375(19)	2 744(16)
C(32)	3 983(17)	4 632(11)	5 492(18)	-1 500(17)	491(19)	3 218(17)
C(33)	3 948(21)	5 314(14)	5 230(21)	-2 040(16)	290(21)	3 858(19)
C(34)	3 261(21)	5 540(15)	4 290(21)	-2 724(17)	888(20)	4 094(18)
C(35)	2 520(26)	5 122(17)	3 516(27)	-2 872(19)	1 758(28)	3 598(21)
C(36)	2 518(21)	4 390(15)	3 768(22)	-2 348(16)	1 998(22)	2 896(20)
C(41)	1 937(16)	4 069(11)	5 735(18)	-228(15)	2 343(20)	3 418(16)
C(42)	2 778(21)	4 040(15)	6 781(21)	353(14)	1 535(20)	3 351(16)
C(43)	3 089(24)	4 639(15)	7 502(25)	547(20)	1 046(25)	4 128(21)
C(44)	2 418(25)	5 176(18)	6 987(27)	156(16)	1 342(19)	4 872(22)
C(45)	1 656(24)	5 251(16)	6 031(24)	-407(17)	2 119(21)	4 894(28)
C(46)	1 337(21)	4 693(14)	5 266(22)	-585(15)	2 652(20)	4 155(16)
H(201)	481(1)	-80(1)	726(1)	296(2)	491(2)	-92(2)
H(202)	389(1)	-11(1)	709(1)	231(2)	404(2)	-38(2)
H(203)	459(1)	-13(1)	635(1)	190(2)	522(2)	-70(2)
H(301)	31(1)	-79(1)	271(2)	11(1)	257(2)	-316(2)
H(302)	99(1)	0(1)	316(2)	-13(1)	372(2)	-266(2)
H(303)	30(1)	-36(1)	379(2)	-5(1)	259(2)	-206(2)
H(501)	486(2)	338(1)	507(2)	-168(2)	36(2)	137(2)
H(502)	395(2)	270(1)	440(2)	-71(2)	80(2)	95(2)
H(503)	462(2)	273(1)	580(2)	-164(2)	149(2)	78(2)
H(601)	55(1)	265(1)	437(2)	13(2)	415(2)	320(2)
H(602)	0(1)	345(1)	444(2)	-48(2)	442(2)	230(2)
H(603)	71(1)	295(1)	559(2)	51(2)	384(2)	218(2)

UBr₄·2ddu, for all methyl groups in the β conformer, and for three of the four in the α conformer [methyl group C(6) being the exception]; this is also apparent in Figures 5 and 6. (While the positions to which artificially added hydrogen atoms refine should be treated with caution, we have supportive evidence, from Fourier difference sections in the planes of these hydrogen positions, that their co-ordinates are reasonably correct.) Although similar crowding occurs in all the ddu ligands (Table 9), two-fold ligand symmetry was observed only in UBr₄·2ddu, with minor deviations in the chloro complexes. In Table 8 some selected torsion and dihedral angles are listed, together with a 'misfit' parameter, which is the mean distance between pairs of

like atoms when a two-fold symmetry operation is carried out on one half of the non-hydrogen atoms (some data for *NN'*-dimethyl-*NN'*-di-*p*-nitrophenylurea are included for comparison). Only in the case of ligand 1 of the α form does the conformation closely resemble that in UBr₄·2ddu. The deviations, notably the twist of a phenyl ring about its attaching bond (torsion angle bde, Table 8), are probably due to intermolecular forces resulting from optimisation of molecular packing.

In Table 6 the ddu ligand bond lengths and angles for all three complexes are compared with values observed in *NN'*-dimethyl-*NN'*-di-*p*-nitrophenylurea. Agreement for the five ligands in the

Table 5. Uranium environment in both $UCl_4 \cdot 2ddu$ phases; distances in Å, angles in °, with e.s.d.s in parentheses

	α Conformer	β Conformer		α Conformer	β Conformer
U-Cl(1)	2.596(7)	2.617(8)	Cl(2)-U-Cl(3)	92.6(3)	93.2(4)
U-Cl(2)	2.593(9)	2.599(9)	Cl(2)-U-Cl(4)	169.1(3)	171.7(4)
U-Cl(3)	2.609(7)	2.625(7)	Cl(2)-U-O(1)	85.9(5)	93.0(5)
U-Cl(4)	2.617(8)	2.585(9)	Cl(2)-U-O(2)	95.5(5)	84.4(5)
U-O(1)	2.248(14)	2.285(18)	Cl(3)-U-Cl(4)	91.7(3)	90.5(3)
U-O(2)	2.256(14)	2.251(18)	Cl(3)-U-O(1)	92.7(4)	87.6(5)
Cl(1)-U-Cl(2)	87.2(3)	89.8(3)	Cl(3)-U-O(2)	85.8(4)	90.2(5)
Cl(1)-U-Cl(3)	169.6(3)	173.9(3)	Cl(4)-U-O(1)	83.9(4)	94.7(5)
Cl(1)-U-Cl(4)	90.3(3)	87.3(3)	Cl(4)-U-O(2)	94.8(5)	88.1(5)
Cl(1)-U-O(1)	97.7(4)	86.9(5)	O(1)-U-O(2)	178.0(7)	176.5(7)
Cl(1)-U-O(2)	83.8(4)	95.4(5)	U-O(1)-C(1)	164.9(1.8)	152.3(1.8)
			U-O(2)-C(4)	163.9(1.6)	163.1(1.8)

Table 6. Ligand geometries in the α and β conformers of $UCl_4 \cdot 2ddu$ and of $UBr_4 \cdot 2ddu$ compared to that in NN' -dimethyl- NN' -di-*p*-nitrophenylurea (ddnu).¹⁶ Bond lengths (Å) and angles (°) with more than one estimate denoted as $m \pm d(\sigma)$, where d is the mean deviation from the mean, m . Ligands 1 and 2 contain O(1) and O(2), respectively

Ligand	α Conformer		β Conformer		Overall mean	$UBr_4 \cdot 2ddu$	ddnu
	1	2	1	2			
C-O	1.26(2)	1.31(2)	1.25(3)	1.24(3)	1.27	1.26(2)	1.21
N-C(CO)	1.35 \pm 0.01(3)	1.34 \pm 0.03(4)	1.35 \pm 0.03(4)	1.36 \pm 0.03(4)	1.35	1.34(2)	1.36
N-C(Ph)	1.45 \pm 0.01(3)	1.46 \pm 0.00(3)	1.44 \pm 0.01(4)	1.46 \pm 0.00(4)	1.46	1.48(2)	1.42
N-C(Me)	1.48 \pm 0.01(3)	1.46 \pm 0.00(4)	1.48 \pm 0.02(4)	1.45 \pm 0.00(4)	1.47	1.46(2)	1.47
O-C-N	120 \pm 1(2)	117 \pm 4(2)	120 \pm 2(2)	121 \pm 3(2)	120	121(1)	122
N-C-N	119(2)	125(2)	120(2)	118(3)	120	119(1)	115
C(CO)-N-C(Ph)	123 \pm 0(2)	118 \pm 0(2)	122 \pm 1(2)	122 \pm 1(2)	122	124(1)	123
C(CO)-N-C(Me)	117 \pm 1(2)	122 \pm 2(2)	118 \pm 2(2)	117 \pm 0(2)	118	119(1)	118
C(Ph)-N-C(Me)	118 \pm 1(2)	117 \pm 3(2)	122 \pm 2(3)	117 \pm 2(2)	118	115(1)	116

Table 7. Restoring angles for ddu ligand in α - and β - $UCl_4 \cdot 2ddu$; θ and ϕ are polar angles (°), for a frame with origin at the oxygen atom, through which the ligand must be rotated to restore the conformation of $UBr_4 \cdot 2ddu$ (see text)

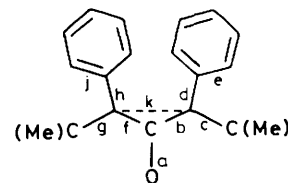
Ligand	α Conformer		β Conformer	
	1	2	1	2
θ	-15.1	-16.1	-27.7	-16.3
ϕ	-0.4	4.7	-45.0	-42.0

complexes is reasonable if the relatively low precision is taken into account. Generally the overall means agree well with the corresponding values for the nitro-derivative; notable exceptions are the carbonyl and N-C(phenyl) bond lengths, and the N-C-N bond angle.

In Table 10 data on the least-squares planes fitted through the phenyl rings and the urea (OCN₂) and amido (NC₂) moieties are given. The atomic displacements are in most cases probably not statistically significant, although some pyramidal distortion of the last two groups is suggested by the fact that, without exception, the displacement of the central atom is in a direction opposite to those of its bonded partners. This is also the case in $UBr_4 \cdot 2ddu$ (Table 3).

The agreement between the U-Cl and U-O bond lengths in the α and β forms is excellent. Comparison of these bond lengths and the corresponding distances in $UBr_4 \cdot 2ddu$ with values found in other complexes of this type will be deferred to Part 2 of this series.

The question arises why $UCl_4 \cdot 2ddu$ crystallises in the two widely different, crowded conformations observed in the α and β phases, while many other internally less strained conformations are possible. Kitaigorodskii¹⁵ has shown that for molecules

Table 8. Extent of two-fold symmetry of ddu ligands in α - and β - $UCl_4 \cdot 2ddu$; torsion and dihedral angles, γ °, and misfit parameter, Δ /Å, are compared with those for $UBr_4 \cdot 2ddu$ and NN' -dimethyl- NN' -di-*p*-nitrophenylurea (ddnu)¹⁶

Ligand	α Conformer		β Conformer		$UBr_4 \cdot 2ddu$	ddnu
	1	2	1	2		
Δ	0.30(4)	0.44(4)	0.35(4)	0.29(4)	*	*
γ (Ph-Ph)	29(1)	28(1)	37(1)	29(1)	28(1)	—
bde	53(3)	65(3)	57(3)	65(3)	56(2)	48
fhj	50(3)	53(3)	53(3)	53(3)	56(2)	48
abc	12(3)	16(3)	10(3)	12(3)	11(2)	15
afg	16(3)	5(3)	16(3)	16(3)	11(2)	15
dkh	51(3)	49(3)	49(3)	49(3)	49(2)	51

* Two-fold symmetry.

without symmetry there are relatively few space groups which offer optimum molecular packing density; of these, $P2_1/c$ (or its equivalent, $P2_1/n$) is a familiar example; $Pna2_1$, the space group of the β conformer, is also favourable. Apparently the conformations observed in these structures are such as to achieve the closest possible packing in the above space groups, and the extra strain energy of the particular crowded conformations which are adopted is offset by gains in lattice energy. Calculation of the molecular volumes (using Kitaigorodskii's¹⁵

Table 9. Short intramolecular non-bonded contacts (Å) in α - and β -UCl₄·2ddu and UBr₄·2ddu; $\sigma = 0.01$ – 0.03 Å

α Conformer		β Conformer		UBr ₄ ·2ddu	
Cl(2)···H(303)	2.88	Cl(2)···H(202)	2.69	Br···H(82)	2.90
Cl(1)···H(302)	2.64	Cl(1)···H(303)	2.79		
O(1)···H(202)	2.60	Cl(3)···H(603)	2.73		
O(1)···H(302)	2.58	O(1)···H(303)	2.54	O···H(82)	2.64
O(2)···H(601)	2.32	O(2)···H(503)	2.56		
O(2)···H(502)	2.62				
C(1)···H(302)	2.68	C(1)···H(202)	2.70	C(1)···H(83)	2.72
C(1)···H(303)	2.68	C(1)···H(203)	2.70	C(1)···H(82)	2.72
C(1)···H(202)	2.72	C(1)···H(302)	2.72		
C(1)···H(203)	2.72	C(1)···H(303)	2.72		
C(4)···H(502)	2.69	C(4)···H(502)	2.69		
C(4)···H(503)	2.69	C(4)···H(503)	2.69		
C(4)···H(601)	2.61	C(4)···H(602)	2.67		
C(11)···C(21)	2.89	C(4)···H(603)	2.69	C(2)···C(2 ^{III})*	2.90
C(31)···C(41)	2.82	C(11)···C(21)	2.86		
C(11)···H(201)	2.54	C(31)···C(41)	2.84	C(7)···H(81)	2.77
C(21)···H(301)	2.54	C(11)···H(201)	2.47	C(2)···H(81)	2.54
C(31)···H(501)	2.58	C(21)···H(301)	2.62		
C(41)···H(602)	2.71	C(31)···H(501)	2.54		
		C(41)···H(601)	2.48		

* Symmetry equivalent as in Table 2.

Table 10. Planarity of phenyl, urea, and amide groups in α - and β -UCl₄·2ddu (entries defined in Table 3). The phenyl rings of the α form are numbered as in Figure 1, those of β similarly. Urea and amide groups are numbered according to their O and N atoms, respectively. Deviations (Å) are listed in the following atom sequences: phenyl, C(1) to C(6) and the bonded N (marked * and not included in the mean-plane calculation); urea, O, C, N(*m*), N(*m* + 1); amide, C(carbonyl), N, C(Me), C(Ph)

(a) Phenyl rings	$\langle\sigma\rangle$
1(α) 0.018, -0.027, -0.007, 0.049, -0.056, 0.023, 0.028*	0.027
2(α) -0.030, 0.011, 0.016, -0.024, 0.004, -0.023, -0.051*	0.027
3(α) 0.009, -0.012, 0.008, -0.001, -0.001, -0.003, -0.109*	0.032
4(α) -0.023, 0.000, 0.022, -0.021, -0.005, 0.027, -0.051*	0.034
1(β) -0.001, 0.020, -0.014, -0.012, 0.031, -0.025, 0.131*	0.031
2(β) 0.010, -0.009, -0.006, 0.019, -0.017, 0.003, -0.080*	0.029
3(β) 0.009, 0.007, -0.015, 0.006, 0.009, -0.016, -0.087*	0.029
4(β) -0.008, -0.011, 0.017, -0.004, -0.016, 0.022, 0.009*	0.027
(b) Urea groups	$\langle\sigma\rangle$
1(α) 0.008, -0.023, 0.007, 0.007	0.023
2(α) -0.013, 0.042, -0.015, -0.013	0.020
1(β) -0.001, 0.003, -0.001, -0.001	0.023
2(β) -0.003, 0.007, -0.002, -0.003	0.023
(c) Amide groups	$\langle\sigma\rangle$
1(α) 0.029, -0.078, 0.024, 0.026	0.023
2(α) 0.032, -0.091, 0.028, 0.031	0.023
3(α) -0.026, 0.072, -0.023, -0.023	0.022
4(α) 0.041, -0.113, 0.037, 0.035	0.024
1(β) 0.028, -0.076, 0.023, 0.025	0.022
2(β) -0.034, 0.100, -0.032, -0.034	0.021
3(β) -0.031, 0.091, -0.030, -0.030	0.024
4(β) 0.045, -0.121, 0.037, 0.039	0.023

method and van der Waals radii according to Bondi¹⁷) gives packing coefficients of 0.64 and 0.66 for the α and β polymorphs, respectively. The higher value for the β form (about 3%) is reflected by a similar increase in the observed density for this phase. The correspondingly higher lattice energy provides a reason why the β phase crystallises preferentially from solution.

Finally, the close similarity in crystal structure between the α phase of UCl₄·2ddu and UBr₄·2ddu, despite the great disparity in molecular and space-group symmetries, is remarkable. The crystal lattice of the chloro complex only deviates slightly (less than 1.5% in cell dimensions) from a $P2_1/n$ lattice which can be generated by simple transformation from the $Fddd$ lattice of the bromo complex. The loss in molecular symmetry in α -UCl₄·2ddu, whilst identical packing geometry and near-isomorphous atomic positions are maintained in the two structures, can be explained in terms of the subgroup relationship between the two space groups.

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