Preparation and Crystal Structure of Aqua[bis(2-hydroxyphenylimino)-ethanato-*OO'NN'*-]dioxouranium

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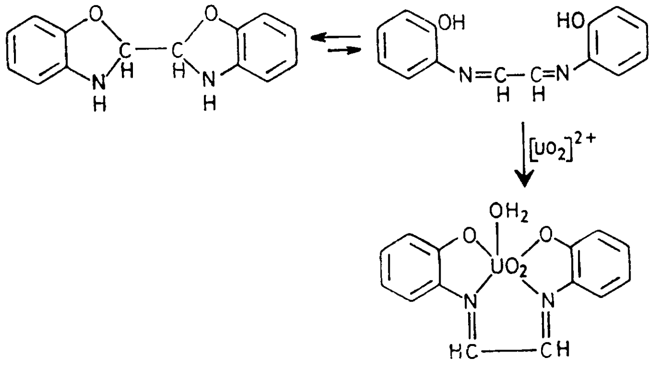
The preparation and *X*-ray crystal structure of the title complex determined by three-dimensional *X*-ray methods are reported. The blue crystals are monoclinic, space group $P2_1/c$, with cell dimensions: a = 7·834(9), b = 15·483(14), c = 11·824(13) Å, β = 92·65(7)°, and Z = 4. The structure was solved by the heavy-atom method from 2130 counter reflections, and refined by least-squares methods to R 0·067. The uranyl group is surrounded equatorially by a roughly regular pentagon formed by two oxygen and two nitrogen atoms of the Schiff base and by the oxygen atom of a water molecule. The pentagon is slightly puckered around the uranium, only the water oxygen having a significant deviation (0·12 Å). Bond lengths and angles are as expected [U–O (apical) 1·77(2) and 1·76(2), U–O(eq) 2·33(1) and 2·37(2), U–OH_2 2·41(1), U–N 2·53(2) and 2·54(2) Å].

FOLLOWING previous investigations [1] on ligands with mixed nitrogen–oxygen donors specially designed to interact with actinide ions of the type $[UO_2]^{2+}$, we have investigated complexes of uranyl salts with 2,2′-bibenzoxazoline. We wished to ascertain (i) the co-ordination number in the equatorial plane of this complex which contains three five-membered chelating rings and can be compared with analogous quadridentate Schiff-base complexes also containing six-membered rings,[1a-c] (ii) to investigate in the likely presence of small molecules of solvent or water in the equatorial plane, and/or the possible intermolecular bond involved, and (iii) whether the system of condensed rings aids the planarity of the quadridentate molecule in its arrangement in the equatorial plane (the complex has a blue colour, whereas analogous Schiff-base complexes [1a-c] are red-yellow).

Preliminary reports have been published.[2]

EXPERIMENTAL

Preparation.—The complex was obtained from uranyl salts ($[UO_2]Cl_2,3H_2O$ or $[UO_2][NO_3]_2,6H_2O$) with stoicheiometric amounts of 2,2′-bibenzoxazoline in absolute ethanol at room temperature. Such a ligand reacts with transition metals in the Schiff-base tautomeric form [3,4] and the $[UO_2]^{2+}$ ion undergoes similar reaction, according to Scheme:



SCHEME

The tautomeric Schiff-base form is confirmed by the presence in the i.r. spectrum of ν(C=N) stretch bands (1585 and 1578 cm^{-1}) and, consequently, by the relative absence of the ν(NH) stretch band present for the free ligand at 3370 cm^{-1}. The ^1H n.m.r. spectrum is also consistent with this formulation (Found: C, 32·05; H, 2·45; N, 5·45. Calc. for $C_{14}H_{12}N_2O_5U$: C, 31·95; H, 2·30; N, 5·32%). The co-ordinated water undergoes substitution in solution with unidentate ligands such as pyridine, $PhNH_2$, Me_2SO, and Ph_3PO under mild conditions.

Crystal Data.—$C_{14}H_{12}N_2O_5U$, M = 526·3, Monoclinic, a = 7·834(9), b = 15·483(14), c = 11·824(13) Å, β = 92·65(7)°, U = 1432·6 Å^3, D_m = 2·45 (by flotation), Z = 4, D_c = 2·44 g cm^{-3}, $F(000)$ = 1024. Cu-K_α radiation, λ = 1·54178 Å; μ(Cu-K_α) = 445·9 cm^{-1}. Space group $P2_1/c$. Crystal dimensions: 0·09 × 0·05 × 0·07 mm^3.

Data were collected on a Siemens AED automated four-circle diffractometer with nickel-filtered Cu-K_α radiation and a Na(Tl)I scintillation counter. Lattice and orientation parameters were derived by use of the Busing and Levy procedure [5] on 30 reflections. In the reciprocal space corresponding to 2θ = 120° there are 2130 non-equivalent lattice sites, of which 1836 were considered observed having $I > 2\sigma(I)$.[6] Also, all reflections were remeasured with the same tube-current setting; the $|F_o|$ data were the best least-squares values derived from the two sets of measurements, by the method of Hamilton, Rollett, and Sparks.[7] The scale of the $|F_o|$ data and the overall temperature factor were estimated from a Wilson plot.

Solution and Refinement of the Structure.—An unsharpened three-dimensional Patterson revealed the position of the uranium atom, refinement of which gave R 0·17. An electron-density difference synthesis, based upon the uranium signs, revealed the positions for all 21 non-hydrogen atoms;

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[1] (*a*) G. Bandoli, D. A. Clemente, U. Croatto, M. Vidali, and P. A. Vigato, *Chem. Comm.*, 1971, 1330; (*b*) *Inorg. Nuclear Chem. Letters*, 1972, **8**, 961; *J. Chem. Soc.* (*A*), 1973, 2331; (*c*) G. Bandoli, D. A. Clemente, F. Benetollo, M. Vidali, P. A. Vigato, and U. Casellato, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 433; *J. Inorg. Nuclear Chem.*, 1974, **36**, 1999; (*d*) M. Vidali, P. A. Vigato, G. Bandoli, D. A. Clemente, and U. Casellato, *Inorg. Chim. Acta*, 1972, **6**, 671.

[2] G. Bandoli, L. Cattalini, D. A. Clemente, M. Vidali, and P. A. Vigato, *J.C.S. Chem. Comm.*, 1972, 344.

[3] H. Jadamus, Q. Fernando, and H. Freser, *J. Amer. Chem. Soc.*, 1964, **86**, 3056.

[4] E. Bayer, *Chem. Ber.*, 1957, **90**, 2324.

[5] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

[6] G. Bandoli, C. Panattoni, D. A. Clemente, A. Dondoni, and A. Mangini, *J. Chem. Soc.* (*B*), 1971, 1407.

[7] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

three least-squares cycles with the neutral atom scattering factors of ref. 8, and the weighting scheme of ref. 9 and isotropic temperature factors, reduced R to 0·10. A weighting scheme based on counter statistics was unsuccessful.[10]

A weighting function $w^{-1} = A|F_o|^2 + B|F_o| + C$ with $A = 0{\cdot}0004$, $B = 1{\cdot}0$, $C = 40$ was checked by plotting $w(|F_o| - |F_c|)^2$ vs. $|F_o|$. At this stage, anisotropic temperature factors of the form, $\exp[-0{\cdot}25(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$, were assigned to the uranium atom and refinement of the structure proceeded to R 0·067 with the full-matrix least-squares method. A difference-Fourier map computed at this stage showed few peaks up to a maximum of 2·1 e$Å^{-3}$ in the vicinity of the uranium atom position, whilst elsewhere peaks were $<0{\cdot}7$ e$Å^{-3}$, occurring in some cases at positions expected for hydrogen atoms. We attempted to apply geometrical and experimental absorption corrections, but no significant improvement over refinement was observed.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21240 (11 pp., 1 microfiche).† Final atomic positional and thermal parameters are given in Table 1, bond lengths and angles, and details of selected planes within the molecule in Tables 2 and 3. Standard deviations for the atomic parameters are derived from the full-matrix least-squares program.

The solution and refinement of the structure were carried out by the use of the Crystal Structure Calculations System '*X*-Ray '70'[11] with calculations on the Consorzio Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), CDC 6600 computer.

TABLE 1

Final fractional co-ordinates ($\times 10^4$) and thermal parameters, with standard deviations in parentheses

	x/a	y/b	z/c	$B/Å^2$
U	2513(1)	777(0)	1534(1)	*
O(1)	1520(21)	1581(11)	666(13)	3·21(31)
O(2)	3522(21)	−33(11)	2370(14)	3·27(31)
O(3)	5181(18)	1272(9)	1031(12)	2·30(26)
O(4)	−183(20)	91(10)	1631(13)	2·92(29)
O(5)	2696(18)	−141(9)	−105(12)	2·45(26)
N(1)	3816(25)	1920(13)	2840(16)	2·87(35)
N(2)	842(24)	1172(13)	3255(15)	2·74(34)
C(1)	6118(29)	1875(15)	1605(19)	2·60(40)
C(2)	7719(29)	2106(15)	1272(15)	2·59(40)
C(3)	8657(33)	2740(17)	1916(21)	3·41(46)
C(4)	8017(33)	3076(17)	2869(21)	3·40(47)
C(5)	6404(37)	2851(19)	3265(24)	4·19(55)
C(6)	5454(31)	2238(16)	2586(20)	3·09(44)
C(7)	3042(31)	2159(15)	3726(19)	2·85(42)
C(8)	1471(30)	1754(15)	3981(19)	2·85(42)
C(9)	−619(36)	673(17)	3438(22)	3·52(49)
C(10)	−1490(37)	677(17)	4500(23)	3·72(52)
C(11)	−2837(33)	79(17)	4556(21)	3·52(49)
C(12)	−3192(41)	−577(20)	3776(26)	4·51(59)
C(13)	−2316(33)	−554(16)	2733(21)	3·07(43)
C(14)	−997(25)	35(13)	2609(16)	1·77(34)

* Anisotropic parameters in the form: $\exp[-0{\cdot}25(B_{11}a^{*2}h^2 + 2B_{12}a^*b^*hk + \ldots]$ with coefficients ($\times 10^3$):

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	527(27)	1627(31)	2268(31)	177(20)	−189(23)	−169(22)

DISCUSSION

The uranyl group is surrounded equatorially by four ligand atoms in three five-membered chelating rings, the fifth equatorial position being taken up by the entering water molecule; the pentagon of donor atoms is thus composed of two oxygen and two nitrogen atoms of the Schiff base and the water oxygen atom (Figure 1). This pentagon is only slightly puckered around the uranium, only the water oxygen having any significant deviation (−0·12 Å) from the least-squares plane through the U and the other four atoms [Table 3, plane (2)].

TABLE 2

Distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Bond lengths

U–O(1)	1·77(2)	C(1)–C(2)	1·38(3)
U–O(2)	1·76(2)	C(1)–C(6)	1·41(3)
U–O(3)	2·33(1)	C(2)–C(3)	1·42(4)
U–O(4)	2·37(2)	C(3)–C(4)	1·36(4)
U–O(5)	2·41(1)	C(4)–C(5)	1·41(4)
U–N(1)	2·53(2)	C(5)–C(6)	1·43(4)
U–N(2)	2·54(2)	C(9)–C(10)	1·46(4)
O(3)–C(1)	1·35(3)	C(9)–C(14)	1·41(3)
O(4)–C(14)	1·35(2)	C(10)–C(11)	1·41(4)
N(1)–C(6)	1·42(3)	C(11)–C(12)	1·39(4)
N(1)–C(7)	1·29(3)	C(12)–C(13)	1·44(4)
N(2)–C(8)	1·32(3)	C(13)–C(14)	1·39(3)
N(2)–C(9)	1·41(3)		

(*b*) Bond angles

O(1)–U–O(2)	178·7(0·6)	C(1)–C(2)–C(3)	118·6(1·1)
O(3)–U–N(1)	65·5(0·3)	C(2)–C(3)–C(4)	120·4(1·2)
N(1)–U–N(2)	63·4(0·5)	C(3)–C(4)–C(5)	123·5(1·3)
N(2)–U–O(4)	65·0(0·4)	C(4)–C(5)–C(6)	115·4(1·1)
O(4)–U–O(5)	82·0(0·3)	C(5)–C(6)–C(1)	121·6(1·1)
O(5)–U–O(3)	84·3(0·3)	C(5)–C(6)–N(1)	124·3(1·0)
U–O(3)–C(1)	124·9(1·3)	N(1)–C(6)–C(1)	114·0(0·9)
U–O(4)–C(14)	121·8(1·2)	N(2)–C(9)–C(10)	123·2(1·2)
U–N(1)–C(6)	117·1(1·2)	N(2)–C(9)–C(14)	115·0(0·9)
U–N(1)–C(7)	120·3(1·4)	C(10)–C(9)–C(14)	120·6(1·1)
C(6)–N(1)–C(7)	122·4(0·8)	C(9)–C(10)–C(11)	114·8(1·2)
U–N(2)–C(8)	119·5(0·9)	C(10)–C(11)–C(12)	125·2(1·4)
U–N(2)–C(9)	116·3(1·3)	C(11)–C(12)–C(13)	117·5(1·0)
C(8)–N(2)–C(9)	123·7(1·1)	C(12)–C(13)–C(14)	119·5(1·1)
O(3)–C(1)–C(6)	118·4(1·0)	O(4)–C(14)–C(9)	117·2(0·8)
O(3)–C(1)–C(2)	121·1(1·0)	O(4)–C(14)–C(13)	121·0(1·0)
C(6)–C(1)–C(2)	120·4(1·1)	C(13)–C(14)–C(9)	121·2(1·2)

(*c*) 'Bite' distances and contact distances within the 'inner core'

N(1) · · · N(2)	2·67	O(1) · · · N(2)	3·19
N(1) · · · O(3)	2·63	O(1) · · · N(1)	3·11
N(2) · · · O(4)	2·64	O(2) · · · O(3)	2·91
O(3) · · · O(5)	3·18	O(2) · · · O(5)	2·97
O(4) · · · O(5)	3·14	O(2) · · · O(4)	3·00
O(1) · · · O(3)	2·92	O(2) · · · N(2)	3·03
O(1) · · · O(5)	2·98	O(2) · · · N(1)	3·08
O(1) · · · O(4)	2·92		

The basic features of the structure closely resemble those of similar compounds,[1a–c] containing mixed five- and six-membered chelating rings, at least as far as the co-ordination geometry is concerned. In fact the apical U–O distances [1·77(2) and 1·76(2) Å] are as expected considerably shorter than the equatorial U–O distances [2·33(1), 2·37(2), and 2·41(1) Å]. Furthermore,

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† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974 Index Issue.

[8] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[9] D. W. J. Cruickshank and D. E. Pilling, in 'Computing methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon, Oxford, 1961, p. 32.

[10] S. Asbrink and L. J. Norbby, *Acta Cryst.*, 1970, **B26**, 8.

[11] '*X*-Ray '70,' System of Programs, University of Maryland Technical Report, TR 646.

from consideration of previous uranyl structure determinations, the U–N(sp^2) bond lengths [2·53(2) and 2·54(2) Å] are as expected and longer than the U–O equatorial distances [for a complete list see Table 7 of ref. 1(*c*)].

TABLE 3

(*a*) Least-squares planes with the deviations (Å) of relevant atoms in square brackets. The equation of a plane in direct space is given by $Px + Qy + Rz = S$

		P	*Q*	*R*	*S*
Plane (1):	All atoms except O(1), O(2)	−3·820	11·060	−5·662	−1·122
	[U 0·15, O(3) −0·03, O(4) 0·37, O(5) 0·0, N(1) 0·18, N(2) 0·25, C(1) −0·05, C(2) −0·22, C(3) −0·24, C(4) −0·16, C(5) −0·02, C(6) 0·05, C(7) 0·24, C(8) 0·25, C(9) 0·16, C(10) −0·11, C(11) −0·29, C(12) −0·43, C(13) −0·15, C(14) 0·06]				
Plane (2):	U, O(3), N(1), N(2), O(4)	−3·304	11·349	−6·073	−0·866
	[U −0·01, O(3) −0·03, N(1) 0·06, N(2) −0·06, O(4) 0·04, O(5) −0·12, C(1) 0·0, C(6) 0·03, C(7) 0·05, C(8) −0·05, C(9) −0·25, C(14) −0·35]				
Plane (3):	C(1)—(6), O(3), N(1)	−3·104	11·349	−6·314	−0·801
	[C(1) 0·02, C(2) −0·01, C(3) 0·01, C(4) −0·01, C(5) −0·01, C(6) 0·01, O(3) −0·01, N(1) 0·0, U −0·07, O(5) −0·13, C(7) −0·05]				
Plane (4):	C(9)—(14), O(4), N(2)	−4·992	10·096	−4·505	−0·617
	[C(9) 0·06, C(10) 0·02, C(11) 0·06, C(12) −0·07, C(13) −0·02, C(14) −0·02, O(4) 0·07, N(2) −0·09, U −0·54, O(5) −0·82, C(8) −0·14]				
Plane (5):	N(1), C(7), C(8), N(2)	−3·649	11·032	−5·943	−0·955
	[N(1) −0·01, C(7) 0·01, C(8) −0·01, N(2) 0·01, U −0·02, O(3) −0·14, O(4) 0·15, O(5) −0·12, C(6) −0·10, C(9) −0·12]				
Plane (6):	U, O(3), O(4), O(5), N(1), N(2), C(1)—(8)	−3·264	11·253	−6·221	−0·915
	[U 0·01, O(3) 0·01, O(4) 0·06, O(5) −0·06, N(1) 0·06, N(2) −0·07, C(1) 0·03, C(2) −0·03, C(3) −0·02, C(4) −0·03, C(5) 0·0, C(6) 0·04, C(7) 0·03, C(8) −0·07, C(9) −0·26, C(10) −0·64, C(11) −0·90, C(12) −1·04, C(13) −0·65, C(14) −0·34]				

Equations of least-squares line (*L*) defined by O(1), U, O(2) in parametric form in direct space is:

$$X = 0{\cdot}2518 - 0{\cdot}0567T,\ Y = 0{\cdot}0775 + 0{\cdot}0457T,\ Z = 0{\cdot}1523 - 0{\cdot}0482T$$

[U 0·01, O(1) 0·01, O(2) 0·01]

(*b*) Angles (°) between the mean planes and between plane (2) and the line *L* (for a plane and a line, the angle is to the normal of the plane)

(2)–(3)	1·8	(3)–(4)	16·7
(2)–(4)	15·0	(3)–(5)	4·6
(2)–(5)	2·8	(4)–(5)	12·3
(2)–(L)	2·5	(4)–(6)	15·5

However, the most interesting feature of the complex is that it is almost planar. The only significant deviations [plane (6) of Table 3] involving one benzene ring [C(9)—(14)]. This planarity is due to the fact that the planarity of the ligand is required for co-ordination; the planar tautomeric quadridentate Schiff-base form of 2,2′-bibenzoxazoline has all three ' bites ' of *ca.* 2·7 Å (estimated assuming ' normal ' bond lengths and angles), values very close to those after co-ordination [part (*c*) of Table 2]. The lack of planarity of the C(9)—(14) benzene ring is therefore due not to co-ordination, but to packing effects.

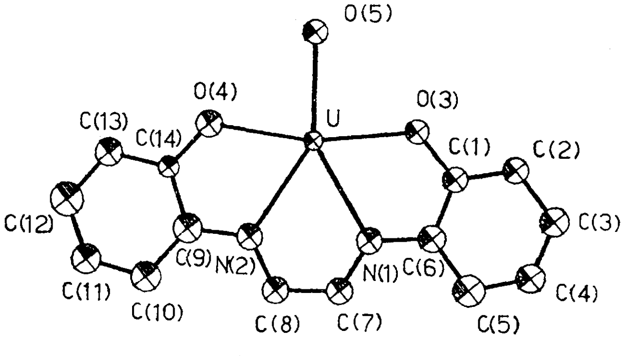

FIGURE 1 Projection of the molecule on the mean molecular plane; O(1) and O(2) omitted for clarity. The atom numbering system used in the analysis is shown

In order to clarify this feature further, it is necessary to consider the packing of the molecules (Figure 2): the co-ordinated water molecule is hydrogen-bonded to two oxygen atoms of two adjacent molecules (O · · · O 2·61 and 2·68 Å, O · · · HOH · · · O 101·5°, Table 4). Thus, in order to form the highest number of hydrogen bonds, two different molecules are constrained to approach each other as shown in Figures 3 and 4. This overlap, which

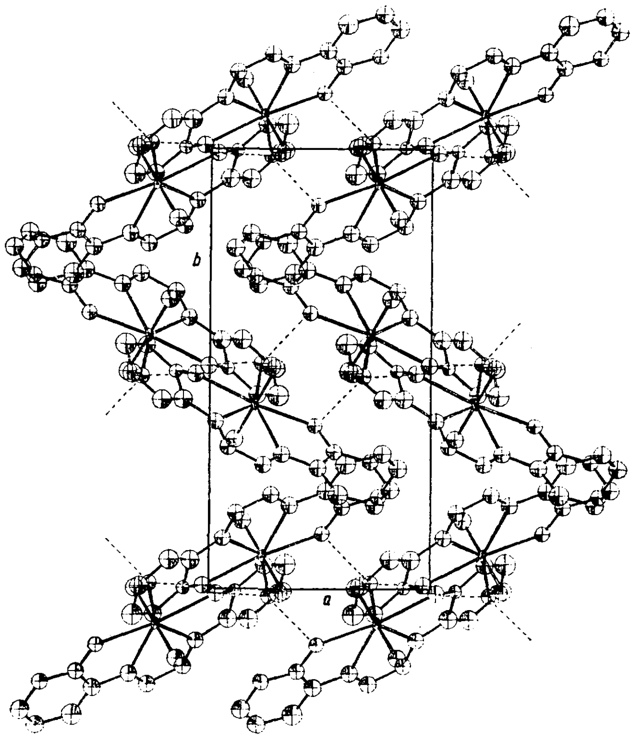

FIGURE 2 Arrangement of the molecules in the unit cell viewed along the c^* axis; dashed lines show hydrogen bonding

brings one uranyl oxygen atom in a direction perpendicular to the C(9)—(14) benzene ring, brings this ring out of the molecular plane (6). In fact, if the whole molecule were planar, so that the C(9)—(14) benzene ring were constrained in the molecular plane (6), the distance between the uranyl O(2) atom and the C(12$^{\text{III}}$) atom would become impossibly short (1·3 Å, Figure 3). The molecule is therefore not strictly planar, the angle between the normals to planes (4) and (6) being 15·5° (Table 3). The crystal energy is mainly due to the three-dimensional network of hydrogen bonds, which has grown at the expense of little distortions in the molecular geometry. This, as far as we are aware, is the first Schiff-base complex to be coloured blue, other similar complexes being yellow or red-yellow.[1] We consider the blue colour to be due to the mesomerism of the co-ordinated organic ligand, and the presence of an almost planar system of conjugated double bonds.

TABLE 4

Intermolecular distances (Å) <3·5 Å

O(5) · · · O(4$^{\text{I}}$)	2·61 *	O(5) · · · C(13$^{\text{I}}$)	3·29
O(5) · · · O(3$^{\text{II}}$)	2·68 *	C(10) · · · C(10$^{\text{V}}$)	3·31
O(2) · · · C(12$^{\text{III}}$)	3·11	C(3) · · · N(2$^{\text{III}}$)	3·33
O(2) · · · C(4$^{\text{IV}}$)	3·17	O(5) · · · C(2$^{\text{II}}$)	3·35
C(14) · · · O(5$^{\text{I}}$)	3·19	O(2) · · · C(5$^{\text{IV}}$)	3·36
C(2) · · · O(1$^{\text{III}}$)	3·20	O(5) · · · C(1$^{\text{II}}$)	3·37
C(8) · · · O(1$^{\text{IV}}$)	3·26	O(2) · · · C(13$^{\text{III}}$)	3·37
C(7) · · · O(1$^{\text{IV}}$)	3·28	C(8) · · · C(12$^{\text{V}}$)	3·44
C(3) · · · O(1$^{\text{III}}$)	3·28	C(8) · · · C(11$^{\text{V}}$)	3·47

Roman numerals as superscripts refer to atoms in the following equivalent positions, relative to the reference molecule at x, y, z:

I $\bar{x}, \bar{y}, \bar{z}$
II $1 - x, \bar{y}, \bar{z}$
III $1 + x, y, z$
IV $1 - x, -\frac{1}{2} + y, \frac{1}{2} -$
V $\bar{x}, \bar{y}, 1 - z$

* Geometry of the hydrogen-bond system

O(4$^{\text{I}}$) · · · O(5) · · · O(3$^{\text{II}}$)	101·5°
O(4$^{\text{I}}$) · · · O(5) · · · U	117·8°
O(3$^{\text{II}}$) · · · O(5) · · · U	140·6°

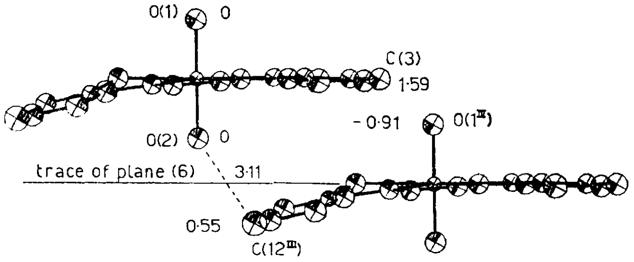

FIGURE 3 Projection of two molecules at x, y, z, and $1 + x, y, z$ (III) towards the U–O(5) bond [O(5) omitted for clarity]. Relative heights in Å are shown

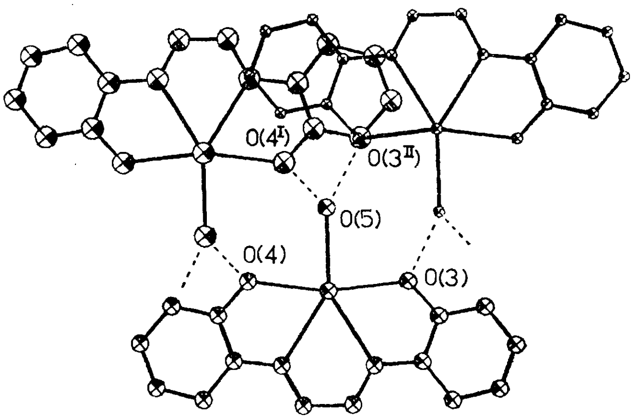

FIGURE 4 Projection of the three molecules at x, y, z, $\bar{x}, \bar{y}, \bar{z}$ (I) and $1 - x, \bar{y}, \bar{z}$ (II) on the mean molecular plane; dashed lines denote hydrogen bonding and the arbitrary thicknesses of the atoms represent their respective levels from the observer's point of view. O(4$^{\text{I}}$) · · · O(5) 2·61, O(3$^{\text{II}}$) · · · O(5) 2·68 Å

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