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Preparation and Crystal Structure of a New β-Ketoamine Uranyl(VI) Complex

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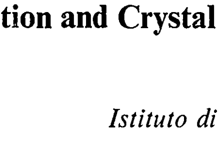
The structure of a new complex of the uranyl ion with the anionic ligand derived from the condensation of heptane-2,4,6-trione with ethylenediamine has been determined from diffractometer data and refined to an R of 4·4%. The crystals are monoclinic, $P2_1/c$, $a=20{\cdot}53$ (2), $b=7{\cdot}72$ (1), $c=27{\cdot}20$ (2) Å and $\beta=101{\cdot}49$ (5)°, with two molecules of complex per asymmetric unit. The two independent molecules have substantially similar molecular conformations but the ligands are not chemically equivalent. Each unit is involved in a network of intra- and intermolecular hydrogen bonds.

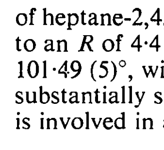
Introduction

Condensation of ethylenediamine with heptane-2,4,6 trione yields the macrocyclic hexadentate ligand (I).

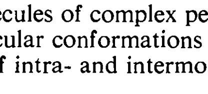


(I)

By reacting this ligand with Co^{II}, Ni^{II}, Cu^{II} and uranyl salts, different types of complexes are obtained. In particular, with copper acetate and uranyl nitrate, it partially hydrolyses giving complexes (II) and (III).

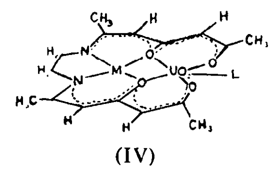


(II)



(III)

These models are supported by analytical and physico-chemical measurements and the structure of (III) is confirmed and elucidated by the present study. The results clearly show that its molecular conformation allows a second metal ion to be coordinated by the free N_2O_2 donor set. The possibility of obtaining binuclear complexes was proved by reaction of (III) with Ni^{II} and Cu^{II} acetates. On the basis of the X-ray analysis of (III) reported here a structure of the type (IV) can be attributed to these complexes.



(IV)

Experimental

To a methanol solution of (I) prepared by the method of Yano, Ushiyima, Sasaki, Kobayashi & Ueno (1972), $UO_2(NO_3)_2.6H_2O$ was added in the molar ratio 1:1 and the reaction medium neutralized with a water/methanol solution of LiOH. The resulting material was extracted with methanol and b prismatic red crystals of (III) were obtained on cooling the solution. Lattice constants were obtained from a least-squares fit of 25 2θ values determined on a diffractometer. Preliminary Weissenberg and precession photographs indicated a monoclinic lattice with systematic absences $0k0$, k odd; $h0l$, l odd, compatible with space group $P2_1/c$. Unit-cell parameters are $a=20{\cdot}53\pm0{\cdot}02$, $b=7{\cdot}72\pm0{\cdot}01$, $c=27{\cdot}20\pm0{\cdot}02$ Å, $\beta=101{\cdot}49\pm0{\cdot}05°$, $V=4224$ Å^3. $D_{\rm obs}=1{\cdot}87$, $D_{\rm calc}=1{\cdot}87$ g cm^{-3} for M.W. 591·4 and $Z=8$.

Intensity data were collected (Mo $K\alpha$, $2\theta\leq50°$) on a computer-controlled Siemens diffractometer by a coupled θ–2θ scan. Of the 3562 reflexions examined, 2928 met the peak-height criterion and were used for the X-ray work. No significant deterioration of the crystal was observed throughout the period of data collection. The data were corrected for Lorentz and polarization effects but no absorption correction was made.

Determination of the structure

Space group $P2_1/c$ has four general positions, and the presence of eight molecules per cell requires two monomers per asymmetric unit. The structure was solved by the heavy-atom method. Atomic parameters were refined by full-matrix least-squares calculations, minimizing $\sum(k|F_o|-|F_c|)^2$. Scattering factors for neutral uranium, oxygen, nitrogen and carbon were taken from Cromer & Waber (1965), and those for hydrogen from *International Tables for X-ray Crystallography* (1962). Anomalous dispersion corrections

(Cromer & Waber, 1965) were applied to the scattering factors of uranium. With individual anisotropic thermal factors for the non-hydrogen atoms, the structure was refined to an R of 4·6%. An electron-density difference synthesis showed clearly the positions of twenty hydrogen atoms. Inclusion of these in the refinement with temperature factors fixed at 5·0 Å^2 gave a final R of 4·4%.* The residual electron densities were not sufficient to resolve reasonable positions for

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31613 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic positional and thermal parameters* ($\times 10^4$ *and* $\times 10^3$ *respectively*) *with standard deviations in parentheses*

The temperature factor is in the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U(*A*)	3807 (1)	2616 (1)	1105 (1)	43 (1)	39 (1)	32 (1)	−4 (1)	13 (1)	2 (1)
O(*A*1)	3814 (6)	4909 (15)	1088 (4)	78 (9)	44 (8)	28 (8)	−11 (7)	12 (7)	2 (6)
O(*A*2)	3806 (7)	337 (17)	1147 (5)	77 (10)	53 (9)	31 (8)	−1 (8)	6 (7)	2 (7)
O(*A*3)	4459 (7)	2684 (19)	1910 (5)	75 (10)	83 (11)	32 (9)	−14 (9)	17 (7)	−25 (8)
O(*A*4)	4926 (6)	2461 (16)	1027 (4)	79 (10)	34 (8)	42 (9)	−12 (7)	16 (7)	−3 (6)
O(*A*5)	3747 (6)	2644 (18)	220 (4)	61 (9)	77 (10)	22 (8)	−13 (8)	33 (7)	−14 (7)
O(*A*6)	2677 (6)	2363 (19)	696 (5)	43 (8)	76 (11)	73 (10)	−10 (8)	13 (8)	21 (9)
O(*A*7)	3037 (6)	2898 (17)	1701 (5)	56 (9)	49 (9)	65 (10)	8 (7)	33 (8)	3 (8)
N(*A*1)	5667 (9)	2467 (22)	334 (6)	71 (13)	66 (12)	39 (12)	−15 (10)	18 (10)	2 (10)
N(*A*2)	4530 (9)	2472 (25)	−468 (6)	69 (13)	68 (13)	51 (12)	−15 (11)	14 (11)	0 (11)
C(*A*1)	5013 (10)	1883 (24)	2105 (8)	49 (14)	43 (13)	62 (18)	−12 (10)	18 (12)	−3 (11)
C(*A*2)	5107 (10)	1702 (30)	2689 (7)	53 (14)	97 (18)	30 (16)	4 (12)	11 (11)	1 (12)
C(*A*3)	5478 (9)	1327 (24)	1851 (8)	49 (13)	50 (13)	27 (15)	−19 (10)	19 (10)	−1 (10)
C(*A*4)	5458 (10)	1765 (26)	1326 (9)	58 (15)	54 (14)	56 (18)	−18 (11)	24 (12)	−15 (12)
C(*A*5)	6072 (9)	1366 (24)	1146 (8)	64 (14)	41 (12)	49 (16)	−14 (10)	50 (12)	−4 (11)
C(*A*6)	6159 (10)	1717 (26)	675 (9)	51 (15)	56 (14)	45 (16)	−27 (11)	21 (13)	−4 (11)
C(*A*7)	6830 (10)	1257 (30)	549 (9)	55 (14)	81 (17)	127 (21)	−3 (12)	66 (14)	−8 (15)
C(*A*8)	5725 (11)	2894 (31)	−197 (9)	81 (17)	88 (18)	58 (18)	−28 (14)	31 (14)	9 (14)
C(*A*9)	5181 (10)	1958 (34)	−571 (8)	49 (14)	122 (21)	59 (17)	−8 (13)	26 (12)	−13 (14)
C(*A*10)	4038 (14)	3227 (27)	−779 (8)	107 (21)	55 (14)	33 (17)	−19 (14)	45 (16)	−10 (11)
C(*A*11)	4092 (12)	3611 (32)	−1326 (7)	150 (22)	99 (19)	7 (13)	3 (16)	39 (13)	−3 (11)
C(*A*12)	3431 (12)	3630 (25)	−660 (8)	119 (20)	44 (13)	13 (15)	−27 (13)	28 (13)	−4 (10)
C(*A*13)	3282 (11)	3362 (23)	−163 (8)	70 (16)	20 (11)	74 (19)	−21 (10)	−8 (13)	2 (10)
C(*A*14)	2632 (10)	3816 (24)	−93 (7)	61 (15)	47 (13)	36 (14)	−20 (11)	19 (11)	4 (10)
C(*A*15)	2362 (10)	3327 (28)	307 (8)	46 (14)	62 (15)	70 (17)	9 (11)	3 (13)	−2 (13)
C(*A*16)	1638 (10)	3664 (32)	343 (9)	40 (14)	101 (19)	87 (18)	−2 (13)	11 (12)	−9 (15)
C(*A*17)	2854 (15)	4365 (41)	1925 (12)	134 (26)	96 (25)	172 (30)	−10 (21)	93 (23)	−48 (23)
U(*B*)	8683 (1)	4438 (1)	3495 (1)	43 (1)	50 (1)	35 (1)	−2 (1)	18 (1)	−2 (1)
O(*B*1)	8488 (7)	2199 (17)	3391 (5)	75 (10)	42 (9)	73 (11)	5 (7)	51 (8)	4 (7)
O(*B*2)	8850 (7)	6681 (18)	3620 (5)	71 (10)	62 (10)	52 (10)	−19 (8)	24 (8)	−28 (8)
O(*B*3)	9211 (8)	3659 (29)	4296 (5)	91 (13)	99 (21)	34 (10)	−5 (13)	37 (9)	24 (12)
O(*B*4)	9835 (6)	4049 (20)	3488 (4)	55 (9)	96 (12)	31 (9)	1 (8)	20 (7)	5 (8)
O(*B*5)	8755 (6)	4601 (18)	2639 (4)	42 (8)	75 (9)	23 (8)	−4 (7)	9 (6)	1 (7)
O(*B*6)	7644 (6)	5306 (18)	3016 (5)	43 (8)	75 (10)	53 (9)	7 (7)	17 (7)	−16 (8)
O(*B*7)	7856 (7)	4538 (18)	4043 (5)	76 (10)	62 (10)	64 (11)	6 (8)	60 (9)	12 (8)
N(*B*1)	10661 (10)	4484 (31)	2861 (8)	98 (15)	136 (20)	60 (15)	−37 (14)	28 (12)	18 (13)
N(*B*2)	9638 (10)	4450 (27)	2030 (7)	68 (14)	102 (15)	76 (15)	−2 (12)	21 (12)	3 (12)
C(*B*1)	9759 (9)	3070 (24)	4519 (7)	47 (13)	52 (13)	51 (15)	−5 (9)	4 (11)	16 (10)
C(*B*2)	9776 (10)	2517 (32)	5065 (8)	83 (17)	112 (20)	49 (15)	−22 (15)	12 (12)	28 (14)
C(*B*3)	10296 (10)	2893 (28)	4322 (7)	53 (14)	88 (16)	38 (15)	2 (12)	16 (11)	13 (12)
C(*B*4)	10359 (9)	3471 (23)	3808 (7)	55 (14)	44 (12)	57 (15)	−14 (10)	17 (11)	−2 (10)
C(*B*5)	11001 (9)	3395 (27)	3674 (9)	53 (14)	68 (15)	81 (19)	9 (11)	38 (13)	−1 (13)
C(*B*6)	11144 (12)	3788 (25)	3231 (9)	107 (20)	47 (12)	60 (17)	2 (12)	68 (16)	−13 (11)
C(*B*7)	11855 (10)	3608 (33)	3158 (9)	62 (14)	107 (20)	128 (22)	18 (13)	56 (14)	−25 (17)
C(*B*8)	10753 (16)	5008 (55)	2343 (10)	143 (27)	366 (49)	45 (20)	−106 (29)	34 (18)	−1 (23)
C(*B*9)	10316 (13)	4624 (42)	1960 (10)	68 (19)	203 (29)	88 (22)	23 (18)	47 (17)	44 (20)
C(*B*10)	9155 (14)	3845 (28)	1701 (8)	106 (21)	70 (15)	53 (18)	38 (14)	68 (16)	44 (12)
C(*B*11)	9250 (14)	3275 (36)	1165 (9)	166 (25)	92 (21)	80 (20)	9 (18)	66 (18)	10 (16)
C(*B*12)	8507 (12)	3600 (28)	1747 (8)	102 (20)	69 (15)	50 (17)	3 (14)	27 (15)	−16 (12)
C(*B*13)	8320 (10)	4053 (25)	2242 (8)	60 (15)	49 (13)	93 (19)	3 (11)	30 (13)	−7 (12)
C(*B*14)	7614 (10)	3844 (24)	2255 (7)	80 (16)	45 (13)	40 (14)	5 (11)	19 (12)	−4 (10)
C(*B*15)	7307 (10)	4466 (26)	2623 (8)	77 (16)	52 (13)	55 (15)	8 (12)	7 (12)	−1 (12)
C(*B*16)	6551 (9)	4371 (31)	2590 (8)	39 (13)	106 (18)	83 (17)	−4 (12)	15 (11)	−2 (14)
C(*B*17)	7647 (15)	3150 (46)	4326 (11)	122 (25)	136 (31)	122 (26)	20 (22)	79 (21)	31 (22)

the hydrogen atoms of the methyl groups, which are probably freely oscillating. The final atomic parameters are listed in Tables 1 and 2. Computer programs used in this determination were those included in the X-RAY 70 system (Stewart, Kundell & Baldwin, 1970).

Description of the structure

Molecular structure

The crystal of (III) consists of discrete $UO_2L.MeOH$ units which are involved in hydrogen bonding, as illustrated in the stereo diagram (Fig. 1) and in the packing projection (Fig. 2). Surprisingly, the chemical composition of L is not completely the same in the two molecules (*A* and *B*) of the asymmetric unit. The X-ray analysis clearly shows that whereas in *A* the ligand has the expected formula and the nitrogen atoms are bonded through a $-CH_2-CH_2-$ aliphatic chain, in *B* there is a $-CH{=}CH-$ chain with a double bond between two sp^2 hybridized carbon atoms. As a consequence two resulting complexes, similar but chemically different, are present in a cell with four equivalent positions and this explains the presence of eight molecules. Apart from this, the main structures are the same in *A* and *B* and most bond lengths and angles are fully comparable. The coordination polyhedron is a slightly distorted trigonal bipyramid. The pentagonal girdle in the molecules carries the relatively long O(4)· · ·O(5) contacts (2·93 Å in *A* and 2·90 Å in *B*) which are greater than the sum of the van der Waals radii (2·80 Å). The mean O(L)· · ·O(methanol) contacts are 2·80 Å, but the O(3)· · ·O(4) and O(5)· · ·O(6) 'bites' of the anionic ligand are slightly shorter in both units so that the presence of destabilizing energy must not be excluded. The five equatorial atoms bonded to the uranyl groups are not exactly coplanar and their deviations from the planes of best fit are characteristic of a puckered structure (Table 3), and this is probably related to the observed differences in the U–O bond lengths.

The equatorial planes of the *A* units lie parallel to the *ac* plane of the cell, whereas those of the *B* units are inclined at about 9° to this plane. Nevertheless both types of molecules extend through the structure roughly parallel to (010) accounting for the shortness of the *b* axis. Fig. 3 illustrates the molecular packing in the unit cell looking down the *a* axis. It can be seen that *A* and *B* are progressively bent, as shown by the

Table 2. *Positional parameters* ($\times 10^3$) *for the hydrogen atoms, with standard deviations in parentheses*

Hydrogen atoms are numbered according to the atom to which they are bonded.

	Molecule *A*			Molecule *B*		
	x	*y*	*z*	*x*	*y*	*z*
H(N1)	533 (8)	281 (25)	59 (7)	1025 (9)	476 (25)	306 (7)
H(N2)	424 (8)	233 (25)	12 (7)	942 (9)	503 (25)	233 (7)
H(O7)	264 (9)	231 (25)	155 (7)	776 (9)	557 (26)	420 (7)
H(C3)	596 (9)	87 (25)	206 (7)	1082 (9)	288 (26)	451 (7)
H(C5)	653 (9)	63 (25)	125 (7)	1145 (9)	282 (25)	385 (7)
H1(C8)	631 (8)	280 (25)	−21 (6)	1124 (8)	489 (25)	230 (7)
H2(C8)	573 (8)	437 (25)	−29 (7)	*	*	*
H1(C9)	543 (9)	96 (25)	−61 (7)	1024 (9)	511 (25)	164 (6)
H2(C9)	534 (8)	250 (26)	−91 (7)	*	*	*
H(C12)	307 (8)	385 (25)	−92 (6)	815 (8)	296 (26)	148 (7)
H(C14)	233 (9)	404 (25)	−39 (7)	733 (8)	288 (25)	202 (7)

* There is only one hydrogen atom bonded to C(*B*8) and to C(*B*9).

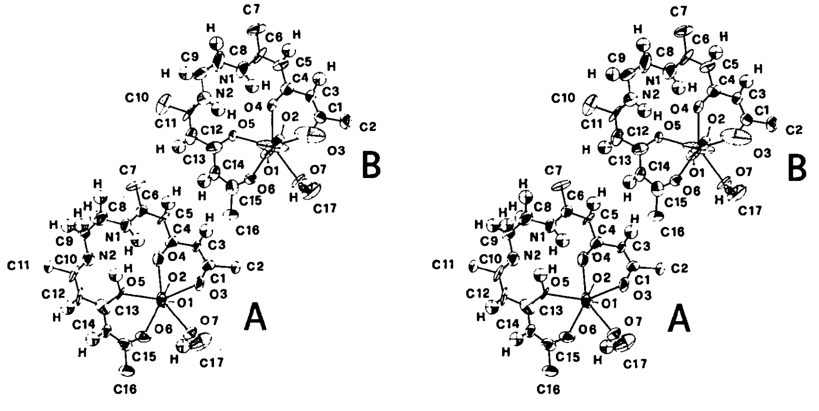

Fig. 1. Stereo diagram of the asymmetric unit viewed along the *b* axis. Ellipsoids represent the thermal motion of all atoms except the hydrogens, which are represented by spheres. For clarity, uranium atoms are not labelled.

angles between the mean planes of the ligand moieties (Table 3).

Bond lengths and bond angles

The agreement between corresponding bond lengths and angles in *A* and *B* (Tables 4 and 5) is quite good except for the C(8)–C(9) bonds which are chemically different. Bond angles differing by more than 3·0σ are U–O(3)–C(1) and U–O(4)–C(4). These differences, although significant, are not large and may reflect the effect of differing intermolecular interactions. The U–O (uranyl) bond distances (mean 1·775 Å) are normal. The four U–O(L) bond lengths are not equal, ranging between 2·31 and 2·38 Å. These differences could be attributed to small differences in the negative charges on the oxygen atoms or to some strain in the structure which is asymmetric with respect to uranium. The mean (2·35 Å) agrees well with a mean 2·36 Å in [UO$_2$(CH$_3$COO)$_2$(C$_6$H$_5$)$_3$PO]$_2$ (Panattoni, Graziani, Bandoli, Zarli & Bombieri, 1969), and with U–O(equatorial) distances in other five-coordinated uranyl complexes. The U–O(methanol) bond (mean 2·48 Å) is significantly longer and has the value expected when the neutral ligand is an alcohol. The C–O bond lengths of the ligands (mean 1·33 Å) are significantly longer than a ketonic bond (1·215 Å; Sutton, 1965) as expected for a delocalized system. The C–C bond lengths within the ligands are not equivalent. In particular the C–C bonds involving C(4) and C(13), which have comparable values in both units (mean 1·48 Å), are only slightly shorter than the accepted C–C(=C) length of 1·510 Å (Sutton, 1965), whereas a strong double bond character must be attributed to all other C(sp^2)–C(sp^2) bonds of the ligand system. The only true difference between *A* and *B* units is at the C(8)–C(9) level. Bond lengths and angles unequivocally show C(8) and C(9) to be sp^3 hybridized in *A* and sp^2 hybridized in *B*. Thus the C(*A*8)–C(*A*9) bond is a single covalent bond but C(*B*8)–C(*B*9) is a double bond. The chemical difference is also supported by the number and the positions of the bonded hydrogen

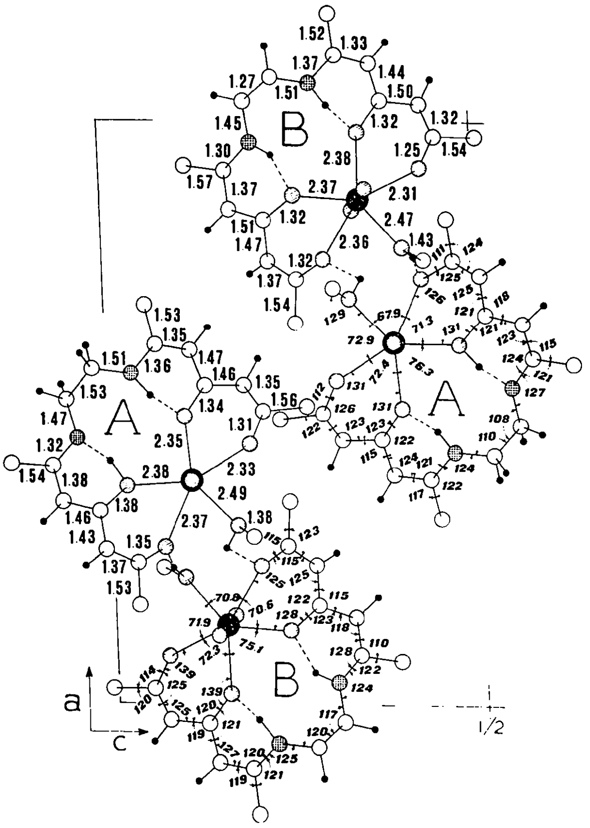

Fig. 2. Projection of the structure down the *b* axis.

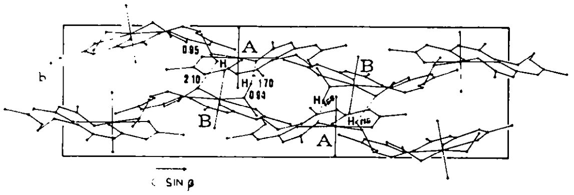

Fig. 3. Projection of the structure down the *a* axis.

Table 3. *Least-squares planes and distances* (× 10^2) *in* Å *of atoms from the planes*

The equation of a plane is $PI+QJ+RK=S$ with coordinates and distances referred to orthogonal axes *a*, *b* and *c'*.

Plane*	Atoms	*P*	*Q*	*R*	*S*
A (I)	O(3) to O(7)	0·015	0·999	0·046	1·983
A (II)	O(3), O(4), C(1) to C(4)	0·419	0·889	0·180	6·185
A (III)	O(4), N(1), C(4) to C(7)	0·296	0·907	0·296	5·374
A (IV)	O(5), N(2), C(10) to C(13)	0·309	0·908	0·282	4·347
A (V)	O(5), O(6), C(13) to C(16)	0·203	0·866	0·458	3·511
B (I)	O(3) to O(7)	0·177	0·968	0·174	7·756
B (II)	O(3), O(4), C(1) to C(4)	0·219	0·923	0·317	9·863
B (III)	O(4), N(1), C(4) to C(7)	0·145	0·927	0·345	8·764
B (IV)	N(1), N(2), C(8), C(9)	−0·184	0·979	0·090	0·394
B (V)	N(1), C(8), C(9)	0·496	−0·863	−0·084	6·460
B (VI)	N(2), C(8), C(9)	−0·093	0·971	−0·219	0·447
B (VII)	O(5), N(2), C(10) to C(13)	0·175	−0·928	0·327	1·868
B (VIII)	O(5), O(6), C(13) to C(16)	0·034	−0·885	0·463	0·617

* Planes *A* refer to molecule *A*, planes *B* to molecule *B*.

Table 3 (*cont.*)

Deviations of atoms included in the planes calculation

A (I)		*A* (II)		*A* (III)		*A* (IV)		*A* (V)	
O(3)	−2	O(3)	−2	O(4)	−1	O(5)	1	O(5)	6
O(4)	−7	O(4)	1	N(1)	1	N(2)	−1	O(6)	−4
O(5)	14	C(1)	−4	C(4)	1	C(10)	2	C(13)	−8
O(6)	−17	C(2)	6	C(5)	−1	C(11)	0	C(14)	3
O(7)	12	C(3)	−8	C(6)	0	C(12)	1	C(15)	3
		C(4)	6	C(7)	0	C(13)	0	C(16)	0

B (I)		*B* (II)		*B* (III)	
O(3)	−8	O(3)	1	O(4)	−1
O(4)	14	O(4)	−2	N(1)	0
O(5)	−15	C(1)	0	C(4)	2
O(6)	11	C(2)	1	C(5)	−2
O(7)	−1	C(3)	−3	C(6)	0
		C(4)	4	C(7)	2

B (IV)		*B* (VII)		*B* (VIII)	
N(1)	−6	O(5)	5	O(5)	6
N(2)	6	N(2)	−4	O(6)	−4
C(8)	12	C(10)	0	C(13)	−3
C(9)	−12	C(11)	3	C(14)	3
		C(12)	−2	C(15)	3
		C(13)	−2	C(16)	0

Angles between the planes

Planes	Angle (°)	Planes	Angle (°)
A (I)—*B* (I)	15·8	*B* (I)—*B* (V)	40·2
A (I)—*A* (II)	27·6	*B* (I)—*B* (VI)	27·6
A (I)—*A* (III)	26·1	*B* (I)—*B* (VII)	35·8
A (I)—*A* (IV)	26·0	*B* (II)—*B* (III)	4·6
A (I)—*A* (V)	32·1	*B* (II)—*B* (VIII)	48·4
A (II)—*A* (III)	9·8	*B* (III) –*B* (IV)	24·2
A (II)—*A* (V)	20·3	*B* (III) –*B* (V)	40·7
A (III)–*A* (IV)	1·1	*B* (III) –*B* (VII)	43·7
A (IV)–*A* (V)	12·0	*B* (IV)—*B* (V)	19·2
B (I)—*B* (II)	8·9	*B* (IV)—*B* (VI)	18·6
B (I)—*B* (III)	10·3	*B* (VI)—*B* (VII)	8·2
B (I)—*B* (IV)	21·4	*B* (VII)–*B*(VIII)	11·5

Table 4. *Interatomic distances* (Å) *and their estimated standard errors*

	Molecule *A*	Molecule *B*
U——O(1)	1·77 (1)	1·78 (1)
U——O(2)	1·76 (1)	1·78 (1)
U——O(3)	2·33 (1)	2·31 (1)
U——O(4)	2·35 (1)	2·38 (1)
U——O(5)	2·38 (1)	2·37 (1)
U——O(6)	2·37 (1)	2·36 (1)
U——O(7)	2·49 (1)	2·47 (1)
O(3)—C(1)	1·31 (2)	1·25 (2)
O(4)—C(4)	1·34 (2)	1·32 (2)
O(5)—C(13)	1·38 (2)	1·33 (2)
O(6)—C(15)	1·35 (2)	1·32 (2)
O(7)—C(17)	1·38 (4)	1·43 (4)
C(1)—C(2)	1·56 (3)	1·54 (3)
C(1)—C(3)	1·35 (3)	1·32 (3)
C(3)—C(4)	1·46 (3)	1·50 (3)
C(4)—C(5)	1·47 (3)	1·44 (3)
C(5)—C(6)	1·35 (3)	1·33 (4)
C(6)—C(7)	1·53 (3)	1·52 (3)
N(1)—C(6)	1·36 (3)	1·37 (3)
N(1)—C(8)	1·51 (3)	1·51 (4)
C(8)—C(9)	1·53 (3)	1·27 (4)
N(2)—C(9)	1·47 (3)	1·45 (3)
N(2)—C(10)	1·32 (3)	1·30 (3)
C(10)–C(11)	1·54 (3)	1·57 (4)
C(10)–C(12)	1·38 (4)	1·37 (4)
C(12)–C(13)	1·46 (3)	1·51 (3)
C(13)–C(14)	1·43 (3)	1·47 (3)
C(14)–C(15)	1·37 (3)	1·37 (3)
C(15)–C(16)	1·53 (3)	1·54 (3)

atoms which were clearly revealed by inspection of the Fourier difference map. The N(1)–C(8) and N(2)–C(9) bonds are single covalent in both units. On the other hand the N(1)–C(6) and N(2)–C(10) lengths show that these bonds participate in conjugate systems with the contiguous C(5)–C(6) and C(10)–C(12) bonds, respectively. In addition, N(2)–C(10) is 0·04 Å in *A* and 0·07 Å in *B* shorter than N(1)–C(6) whereas C(10)–C(12) is longer (0·03 Å in *A* and 0·04 Å in *B*) than C(5)–C(6). The differences are only a few standard

Table 5. *Bond angles* (Å) *and their estimated standard errors*

	Molecule *A*	Molecule *B*
O(1)—U——O(2)	177·7 (6)	177·2 (7)
O(3)—U——O(4)	72·4 (5)	72·3 (5)
O(4)—U——O(5)	76·3 (4)	75·1 (4)
O(5)—U——O(6)	71·3 (4)	70·6 (4)
O(6)—U——O(7)	67·9 (4)	70·8 (4)
O(7)—U——O(3)	72·9 (5)	71·9 (5)
U——O(3)—C(1)	131 (1)	139 (1)
U——O(4)—C(4)	131 (1)	136 (1)
U——O(5)—C(13)	131 (1)	128 (1)
U——O(6)—C(15)	126 (1)	125 (1)
U——O(7)—C(17)	129 (2)	128 (2)
O(3)—C(1)—C(2)	112 (2)	114 (2)
O(3)—C(1)—C(3)	126 (2)	125 (2)
C(2)—C(1)—C(3)	122 (2)	120 (2)
C(1)—C(3)—C(4)	123 (2)	125 (2)
O(4)—C(4)—C(3)	123 (2)	120 (2)
O(4)—C(4)—C(5)	122 (2)	121 (2)
C(3)—C(4)—C(5)	115 (2)	119 (2)
C(4)—C(5)—C(6)	124 (2)	127 (2)
C(5)—C(6)—C(7)	117 (2)	119 (2)
N(1)—C(6)—C(5)	121 (2)	120 (2)
N(1)—C(6)—C(7)	122 (2)	121 (2)
C(6)—N(1)—C(8)	124 (2)	125 (2)
N(1)—C(8)—C(9)	110 (2)	120 (2)
N(2)—C(9)—C(8)	108 (2)	117 (2)
C(9)—N(2)—C(10)	127 (2)	124 (2)
N(2)—C(10)–C(11)	121 (2)	122 (2)
N(2)—C(10)–C(12)	124 (2)	128 (2)
C(11)–C(10)–C(12)	115 (2)	110 (2)
C(10)–C(12)–C(13)	123 (2)	118 (2)
O(5)—C(13)–C(12)	121 (2)	123 (2)
O(5)—C(13)–C(14)	121 (2)	122 (2)
C(12)–C(13)–C(14)	118 (2)	115 (2)
C(13)–C(14)–C(15)	125 (2)	125 (2)
O(6)—C(15)–C(14)	125 (2)	121 (2)
O(6)—C(15)–C(16)	111 (2)	115 (2)
C(14)–C(15)–C(16)	124 (2)	123 (2)

Table 6. *Shortest contact distances* (Å)

(*a*) Intramolecular contacts

	Molecule *A*	Molecule *B*
O(3)···O(4)	2·76	2·77
O(4)···O(5)	2·93	2·90
O(5)···O(6)	2·77	2·74
O(6)···O(7)	2·72	2·80
O(7)···O(3)	2·86	2·81
N(1)···N(2)	2·86	2·76
N(1)···O(5)	3·89	3·84
N(2)···O(4)	3·98	3·92
N(1)···O(4)	2·65	2·65
N(2)···O(5)	2·70	2·69

Table 6 (*cont.*)

(*b*) Intermolecular contacts

O(*A*6)····O(*B*7$^{\mathrm{i}}$)	2·60
O(*A*7)····O(*B*6$^{\mathrm{i}}$)	2·64
O(*A*6)····C(*B*17$^{\mathrm{i}}$)	3·32
O(*A*7)····O(*B*7$^{\mathrm{i}}$)	3·56
O(*A*7)····C(*B*15$^{\mathrm{i}}$)	3·38
O(*A*7)····C(*B*16$^{\mathrm{i}}$)	3·34
O(*B*6)····C(*A*17$^{\mathrm{ii}}$)	3·31
O(*B*7)····C(*A*16$^{\mathrm{ii}}$)	3·65
O(*A*3)····C(*A*2$^{\mathrm{ii}}$)	3·35
C(*B*2)····C(*B*11$^{\mathrm{iii}}$)	3·43
C(*A*8)····O(*A*5$^{\mathrm{iv}}$)	3·62
C(*A*10)···N(*A*1$^{\mathrm{iv}}$)	3·55
C(*A*11)···O(*A*4$^{\mathrm{iv}}$)	3·64
C(*A*12)···N(*A*1$^{\mathrm{iv}}$)	3·56
N(*A*2)····C(*A*6$^{\mathrm{v}}$)	3·53
C(*A*4)····C(*A*9$^{\mathrm{v}}$)	3·62
C(*A*5)····N(*A*2$^{\mathrm{v}}$)	3·58
O(*A*4)····C(*A*9$^{\mathrm{v}}$)	3·62
C(*B*9)····O(*B*4$^{\mathrm{vi}}$)	3·62
N(*B*1)····C(*B*12$^{\mathrm{vi}}$)	3·66
N(*B*2)····C(*B*5$^{\mathrm{vi}}$)	3·66
N(*B*1)····C(*B*10$^{\mathrm{vi}}$)	3·57
C(*B*10)···C(*B*5$^{\mathrm{vi}}$)	3·65

The symmetry transformations implied by the superscript letters used in the atom designations are:

Symmetry code Superscript	Atom position x	 y	 z
None	x	y	z
(i)	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
(ii)	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(iii)	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
(iv)	$1-x$	$1-y$	$\bar{z}$
(v)	$1-x$	$\bar{y}$	$\bar{z}$
(vi)	$2-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

Table 7. *Distances* (Å) *and angles* (°) *in the* D–H···A *hydrogen-bond system*

D = donor, A = acceptor.

	D	H	A	D–H	H···A	D···A	∠D–H···A
(*a*) Intramolecular bonding							
Molecule *A*	N(1)	H(N1)	O(4)	1·10	1·60	2·65	155
	O(5)	H(O5)	N(2)	1·12	1·82	2·70	132
Molecule *B*	N(1)	H(N1)	O(4)	1·11	1·66	2·65	145
	N(2)	H(N2)	O(5)	1·10	1·76	2·69	139
(*b*) Intermolecular bonding							
	O(*A*7)	H(O*A*7)	O(*B*6$^{\mathrm{i}}$)	0·95	2·10	2·64	115
	O(*B*7)	H(O*B*7)	O(*A*6$^{\mathrm{i}}$)	0·94	1·70	2·60	158

deviations but they are systematic, which supports the conclusion that the N(2)–C(10) bonds have more double bond character than N(1)–C(6). This is also supported by the fact that the angles at C(6) can be considered equal, within experimental error, but those at C(10) are different, the C(11)–C(10)–C(12) angles being significantly smaller than 120°, according to a higher concentration of electrons along the N(2)–C(10) bonds.

Hydrogen bonding

Within the somewhat large standard deviations the positions of the hydrogen atoms appear normal with respect to both bond lengths and bond angles. Intra- and intermolecular short contacts which can reasonably be considered hydrogen bonds are schematically represented by dashed lines in Figs. 2 and 3. There are four strong intramolecular hydrogen bonds (mean 2·67 Å) between the nitrogen atoms and the near O(4) and O(5) atoms (Table 6). One highly unusual feature of the structure is the location of H(N*A*2) closer to O(*A*5) than to N(*A*2). This position was accurately derived by the presence on the Fourier difference map of a well-defined peak, and was successively refined by least squares. The relatively good O–H···N distances and angles (see Table 7) and the lack of electron density residuals around N(*A*2) strongly suggest that the position of the hydrogen atom is substantially correct. Both van der Waals forces and hydrogen bonds are determining the packing and controlling the stability. Intermolecular hydrogen bonding occurs between molecules *A* and *B* as shown in Fig. 3. Only two hydrogen bonds are formed between each pair of molecules, joining O(*A*7) to O(*B*6$^{\mathrm{i}}$) and O(*A*6) to O(*B*7$^{\mathrm{i}}$) with separations of 2·64 and 2·60 Å respectively.

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