

# The Structure of Aliphatic Amine Adducts of Uranyl Acetylacetonate.

## IV. Dioxobis(2,4-pentanedionato)mono(2-aminopentan-4-one)uranium(VI)

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The title compound is orthorhombic with  $a = 18.129(5)$ ,  $b = 7.925(5)$ ,  $c = 13.556(5)$  Å,  $Z = 4$ , space group  $Pna2_1$ . The structure was refined to a final  $R$  of 0.055 for 1162 independent reflexions. The U atom has pentagonal bipyramidal coordination and the acetylacetonamine is bonded to U *via* O. There are bifurcated inter- and intramolecular N—H...O hydrogen bonds.

### Introduction

We have shown in three earlier determinations of aliphatic amine adducts of  $UO_2(AA)_2$  (part I: Haigh, Nassimbeni, Pauptit, Rodgers & Sheldrick, 1976; part II: Nassimbeni, Orpen, Pauptit, Rodgers & Haigh, 1977; part III: Rodgers, Nassimbeni & Haigh, 1977) that the conformation of the adduct is dependent on its ability to form hydrogen bonds. The present compound has two H atoms available for hydrogen bonding and may be regarded as the parent of the series.

### Experimental

The compound was prepared as previously described (Haigh & Thornton, 1971). A single crystal was ground to a sphere of radius 0.17 mm and the lattice constants were obtained by least squares from the settings of 25 reflexions measured on a four-circle diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å). The crystal data are listed in Table 1. The density was measured by flotation in a mixture of methyl iodide and bromobenzene.

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Table 1. Crystal data

$C_{15}H_{23}NO_7U$ , $M_r = 567$	$V = 1947.62 \text{ \AA}^3$
Space group: $Pna2_1$	$D_m = 1.96 \text{ g cm}^{-3}$
$a = 18.129(5) \text{ \AA}$	$D_c = 1.93$ for $Z = 4$
$b = 7.925(5)$	$\mu = 79.86 \text{ cm}^{-1}$
$c = 13.556(5)$	$F(000) = 1072$

Intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer operating in the  $\omega-2\theta$  scan mode (scan width  $1.10^\circ \theta$ , scan speed  $0.04^\circ \theta \text{ s}^{-1}$ ). With graphite-monochromated Mo  $K\alpha$  radiation, 1588 reflexions up to  $2\theta = 46^\circ$  were measured. Three reference reflexions were recorded after every 60 reflexions: their intensities remained constant to within  $\pm 4\%$ . 197 reflexions were excluded as systematically absent and a further 229 were omitted as they did not satisfy the criterion  $I_{rel} > 2\sigma I_{rel}$ . This left 1162 reflexions which were used for the analysis. Lorentz-polarization corrections were applied but absorption was ignored.

### Solution and refinement of the structure

The U atom was located from a Patterson map and all the non-H atoms were found in a subsequent difference map. Refinement, in which only U was treated anisotropically, yielded an  $R$  of 0.063. At this stage a difference map revealed the positions of 15 of the H atoms including H(1) and H(2) which are involved in hydrogen bonding. Accordingly, the positional parameters of H(1) and H(2) were refined independently, while the other H atoms were constrained to be 1.08 Å from their parent C atoms, their positions being dictated by the geometry of the molecule. The methyl H atoms were refined as rigid groups. The isotropic temperature factors of the methyl and methine H atoms were refined as two single parameters with final  $U$  values of 0.12 and 0.11 Å<sup>2</sup>

Table 2. Fractional atomic coordinates of all non-hydrogen atoms and their *e.s.d.*'s ( $\times 10^3$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ )

	x	y	z	U
U	839 (0)	954 (0)	750 (0)*	†
O(1)	766 (1)	862 (3)	696 (2)	53 (6)
O(2)	913 (1)	1051 (3)	806 (2)	59 (6)
O(3)	789 (1)	1212 (3)	692 (2)	46 (5)
O(4)	752 (1)	1061 (3)	862 (2)	55 (6)
O(5)	831 (1)	750 (3)	880 (2)	65 (7)
O(6)	912 (2)	724 (3)	709 (2)	78 (8)
O(7)	899 (1)	1038 (3)	601 (2)	53 (6)
C(1)	723 (2)	1452 (3)	642 (3)	64 (9)
C(2)	737 (2)	1308 (4)	709 (2)	48 (9)
C(3)	694 (2)	1296 (5)	794 (3)	62 (11)
C(4)	703 (2)	1166 (5)	866 (3)	62 (10)
C(5)	653 (2)	1180 (5)	953 (3)	73 (12)
C(6)	835 (2)	526 (5)	996 (3)	76 (11)
C(7)	860 (2)	608 (5)	896 (3)	64 (10)
C(8)	901 (2)	512 (5)	828 (3)	64 (11)
C(9)	923 (2)	576 (4)	742 (5)	57 (8)
C(10)	966 (2)	446 (5)	674 (3)	68 (10)
C(11)	1022 (2)	952 (6)	578 (3)	74 (11)
C(12)	955 (2)	1039 (5)	548 (3)	51 (8)
C(13)	953 (2)	1123 (4)	454 (3)	46 (8)
C(14)	893 (2)	1204 (4)	415 (2)	41 (8)
C(15)	898 (2)	1288 (5)	312 (3)	64 (10)
N	829 (2)	1224 (4)	462 (2)	52 (7)

\* This parameter was held invariant owing to space-group requirements.

† This was of the form  $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^{*}c^{*}kl + 2U_{13}a^{*}c^{*}hl + 2U_{12}a^{*}b^{*}hk)]$ . The values were  $U_{11} = 58$  (1),  $U_{22} = 39$  (1),  $U_{33} = 30$  (1),  $U_{23} = 11$  (1),  $U_{13} = 5$  (2),  $U_{12} = 8$  (1).

Table 3. Fractional atomic coordinates of the hydrogen atoms and their *e.s.d.*'s ( $\times 10^3$ )

	Bonded to	x	y	z
H(1)	N	783 (9)	1283 (26)	424 (15)
H(2)	N	816 (18)	1190 (37)	538 (10)
H(3)	C(3)	652 (2)	1390 (5)	806 (3)
H(8)	C(8)	915 (2)	383 (5)	846 (3)
H(11)		676 (2)	1523 (5)	668 (3)
H(12)	C(1)	712 (2)	1406 (5)	569 (3)
H(13)		771 (2)	1533 (5)	641 (3)
H(51)		614 (2)	1280 (5)	941 (3)
H(52)	C(5)	685 (2)	1206 (5)	1018 (3)
H(53)		624 (2)	1062 (5)	963 (3)
H(61)		862 (2)	405 (5)	1004 (3)
H(62)	C(6)	776 (2)	508 (5)	995 (3)
H(63)		851 (2)	607 (5)	1056 (3)
H(101)		982 (2)	507 (5)	606 (3)
H(102)	C(10)	931 (2)	339 (5)	658 (3)
H(103)		1015 (2)	404 (5)	712 (3)
H(111)		1064 (2)	967 (6)	522 (3)
H(112)	C(11)	1010 (2)	820 (6)	589 (3)
H(113)		1041 (2)	1006 (6)	647 (3)
H(131)	C(13)	1003 (2)	1122 (4)	411 (3)
H(151)		952 (2)	1265 (5)	281 (3)
H(152)	C(15)	889 (2)	1423 (5)	320 (3)
H(153)		856 (2)	1236 (5)	265 (3)

respectively while the final  $U$  values for H(1) and H(2) were 0.03 and 0.08  $\text{\AA}^2$  respectively.

After the final cycle  $R$  was 0.055 and  $R_w$  0.054 with  $w = 1/\sigma^2$ . A final difference map had no peaks  $> 0.86$  e  $\text{\AA}^{-3}$ . The final atomic parameters are listed in Tables 2 and 3.\*

All computations were performed at the computer centre of the University of Cape Town on a Univac 1106 computer with *SHELX* (Sheldrick, 1977).

### Description of the structure

The molecular structure and atomic nomenclature are shown in Fig. 1. The principal bond lengths and angles are given in Tables 4 and 5 respectively. Table 6 lists computed least-squares planes with the distances of various atoms from these planes.

The  $\beta$ -ketoamine coordinates through O, and the U atom exhibits pentagonal bipyramidal coordination. H(2) is involved in two intramolecular hydrogen bonds. The N—H(2)···O(7) interaction causes the ligand to adopt a ring-like structure and to exhibit pseudo-

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32636 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Bond lengths ( $\text{\AA}$ )

U—O(1)	1.68 (2)	C(2)—C(3)	1.39 (4)
U—O(2)	1.72 (2)	C(3)—C(4)	1.43 (5)
U—O(3)	2.37 (2)	C(4)—C(5)	1.49 (5)
U—O(4)	2.34 (2)	C(6)—C(7)	1.57 (5)
U—O(5)	2.40 (3)	C(7)—C(8)	1.41 (5)
U—O(6)	2.31 (3)	C(8)—C(9)	1.33 (8)
U—O(7)	2.39 (2)	C(9)—C(10)	1.59 (6)
O(3)—C(2)	1.24 (4)	C(11)—C(12)	1.45 (5)
O(4)—C(4)	1.23 (4)	C(12)—C(13)	1.43 (5)
O(5)—C(7)	1.26 (4)	C(13)—C(14)	1.36 (4)
O(6)—C(9)	1.28 (4)	C(14)—C(15)	1.55 (4)
O(7)—C(12)	1.25 (4)	C(14)—N	1.34 (4)
C(1)—C(2)	1.48 (5)		

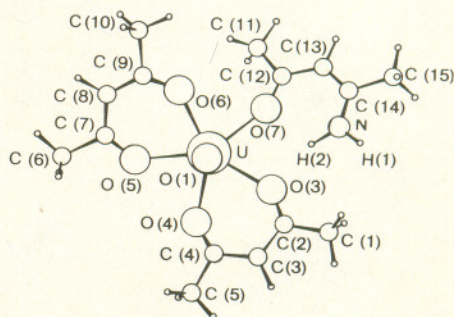


Fig. 1. Perspective view of the molecule with atomic nomenclature.

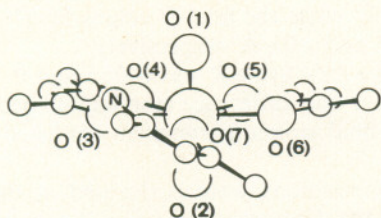


Fig. 2. Molecule viewed along O(3)—U—O(6) bisector. H atoms have been omitted.

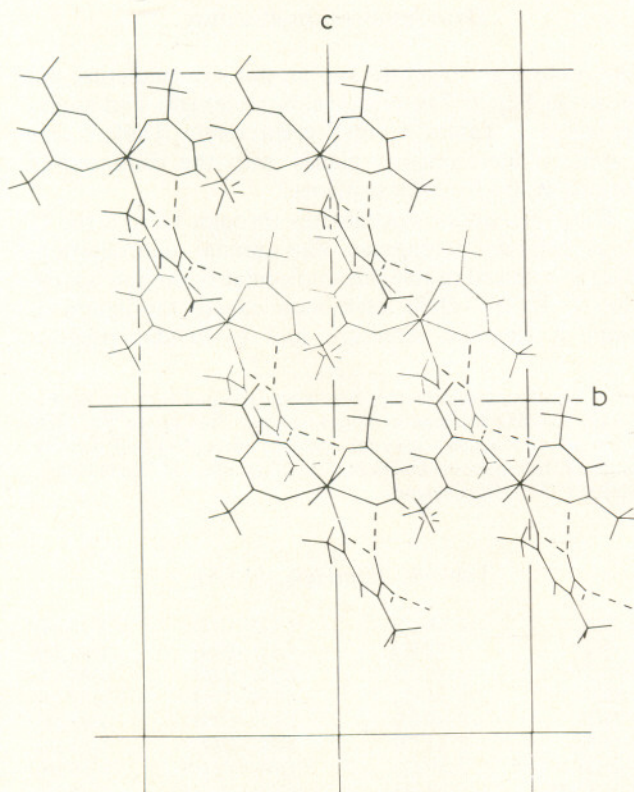


Fig. 3. Intermolecular hydrogen bonding.

aromaticity as evidenced by its planarity (plane 4, Table 6). The N—H(2)···O(3) bond orients the plane of the ligand at the relatively small angle of  $33.1^\circ$  to the plane defined by the five equatorial O atoms (intersection of planes 1 and 4, Table 6). In part I the same effect is observed with the intersection angle  $32.0^\circ$ . The intersection of these planes is illustrated in Fig. 2 which views the complex along the bisector of the O(3)—U—O(6) angle. Each acetylacetonate ring is slightly folded about an axis through its O atoms making angles of  $8.3$  and  $4.2^\circ$ .

Intermolecular hydrogen bonding is also present. The interactions between H(1) and O(4<sup>i</sup>) and H(1) and O(5<sup>i</sup>) link symmetry-related molecules in corrugated chains along the *n* glide in directions parallel to the diagonals of the *bc* face of the cell. The intermolecular hydrogen bonding is shown in Fig. 3, and the relevant bond lengths and angles are in Table 7.

Table 5. Bond angles ( $^\circ$ )

O(1)—U—O(2)	179 (1)	C(3)—C(4)—O(4)	123 (4)
O(1)—U—O(3)	86 (1)	C(3)—C(4)—C(5)	115 (4)
O(1)—U—O(4)	85 (1)	O(4)—C(4)—C(5)	122 (4)
O(1)—U—O(5)	89 (1)	C(4)—O(4)—U	140 (2)
O(1)—U—O(6)	90 (1)	U—O(5)—C(7)	135 (3)
O(1)—U—O(7)	97 (1)	O(5)—C(7)—C(8)	127 (4)
O(2)—U—O(3)	93 (1)	O(5)—C(7)—C(6)	114 (3)
O(2)—U—O(4)	94 (1)	C(8)—C(7)—C(6)	119 (3)
O(2)—U—O(5)	91 (1)	C(7)—C(8)—C(9)	121 (4)
O(2)—U—O(6)	91 (1)	C(8)—C(9)—O(6)	128 (5)
O(2)—U—O(7)	84 (1)	C(8)—C(9)—C(10)	114 (3)
O(3)—U—O(4)	69 (1)	O(6)—C(9)—C(10)	118 (5)
O(4)—U—O(5)	74 (1)	C(9)—O(6)—U	137 (3)
O(5)—U—O(6)	71 (1)	U—O(7)—C(12)	150 (2)
O(6)—U—O(7)	76 (1)	O(7)—C(12)—C(11)	121 (3)
O(7)—U—O(3)	70 (1)	O(7)—C(12)—C(13)	119 (3)
U—O(3)—C(2)	139 (2)	C(13)—C(12)—C(11)	120 (3)
O(3)—C(2)—C(3)	123 (3)	C(12)—C(13)—C(14)	126 (3)
O(3)—C(2)—C(1)	119 (3)	C(3)—C(14)—N	124 (3)
C(3)—C(2)—C(1)	118 (3)	C(13)—C(14)—C(15)	121 (3)
C(2)—C(3)—C(4)	124 (4)	N—C(14)—C(15)	115 (3)

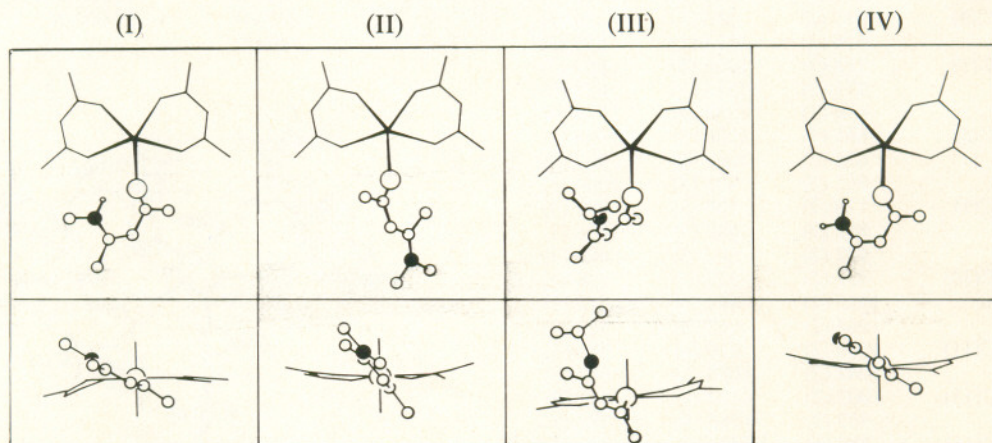


Fig. 4. Molecular structure and O(7)—U view of each complex.

Table 6. *Least-squares planes and perpendicular distances (Å) of atoms from them*

The equations of the planes are expressed in orthogonalized space as  $lX + mY + nZ = P$ . Atoms marked with an asterisk were not included in the least-squares calculation.

Plane 1	$13.3169X + 3.6444Y + 6.7638Z = 4.0257$				
U	-0.022	O(4)	-0.017	O(6)	0.123
O(3)	0.111	O(5)	-0.059	O(7)	-0.126
Plane 2	$11.3224X + 4.7828Y + 6.7198Z = 3.4501$				
U*	0.274	C(1)*	-0.073	C(4)	0.019
O(3)	0.001	C(2)	0.008	C(5)*	-0.061
O(4)	-0.010	C(3)	-0.018		
Plane 3	$14.8201X + 2.8970Y + 6.0335Z = 3.8987$				
U*	0.130	C(6)*	-0.158	C(9)	0.032
O(5)	0.047	C(7)	-0.063	C(10)*	0.171
O(6)	-0.036	C(8)	0.020		
Plane 4	$5.8676X + 6.6998Y + 5.7601Z = 2.6170$				
U*	0.078	C(12)	-0.006	C(15)	0.011
(7)	0.014	C(13)	-0.020	N	-0.014
C(11)	0.004	C(14)	0.011		
Plane 5	$13.1533X + 3.9945Y + 6.3517Z = 3.8905$				
U	0.000	O(3)	0.000	O(4)	0.000
Plane 6	$14.1727X + 3.3952Y + 6.1421Z = 3.9745$				
U	0.000	O(5)	0.000	O(6)	0.000

Intersection angles (°)

Planes 1 and 4	33.12
Planes 2 and 5	8.28
Planes 3 and 6	4.17

Table 7. *Hydrogen bonding*

N—H(1)	1.09 Å	N—H(2)	1.09 Å
N...O(4 <sup>i</sup> )	3.33	N...O(3)	3.20
N...O(5 <sup>i</sup> )	3.12	N...O(7)	2.71
H(1)...O(4 <sup>i</sup> )	2.45	H(2)...O(3)	2.15
H(1)...O(5 <sup>i</sup> )	2.17	H(2)...O(7)	2.12
N—H(1)...O(4 <sup>i</sup> )	138.4°	N—H(2)...O(3)	161.4°
N—H(1)...O(5 <sup>i</sup> )		N—H(2)...O(7)	111.3

Symmetry operator: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ .

## Discussion

Fig. 4 compares the molecular structures of the four complexes of the series, viewed perpendicular to the equatorial O atoms and along the ligand O—U bond. In all four complexes the adduct coordinates through its O rather than its N atom while the U atom displays pentagonal bipyramidal coordination. The conformation of the  $\beta$ -ketoamine ligand is seen to be dependent on its ability to form hydrogen bonds. In those cases where at least one amino H atom is present an intramolecular hydrogen bond with the amino O atom causes the ligand to adopt a ring-like pseudoaromatic structure. Only in part II, where N is disubstituted, is an open-chain structure observed.

The orientation of the ligand plane relative to the plane defined by the five equatorial O atoms is also dependent on hydrogen bonding. In parts I and IV the H atom bonded to the amine O atom is involved in a second hydrogen bond interaction with the vicinal O atom. This causes intersection angles of 32 and 33° respectively. In part III, where the bulky isopropyl substituent probably prevents the formation of the second interaction, the intersection angle is 70°. In the open-chain structure the angle is 48°.

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