

**The Structure of Aliphatic Amine Adducts of Uranyl Acetylacetonate.**  
**II.\* Dioxobis(2,4-pentanedionato)mono(2-*N,N*-dimethylaminopentan-4-one)uranium(VI)**

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(Received 29 July 1976; accepted 3 September 1976)

Crystals of the title compound are triclinic with  $a = 13.068(6)$ ,  $b = 10.622(5)$ ,  $c = 8.123(5)$  Å,  $\alpha = 105.5(2)$ ,  $\beta = 87.6(2)$ ,  $\gamma = 107.0(2)^\circ$ ,  $Z = 2$ , space group  $P\bar{1}$ . The structure was determined by Patterson and Fourier methods and refined by full-matrix least squares to a final  $R$  of 0.023 for 2365 independent reflexions. The U atom has pentagonal-bipyramidal coordination and the *N*-dimethylacetylacetonamine is bonded to U *via* O.

### Introduction

In a previous analysis of a compound of this type, we have established that the adduct molecule is bonded through O and that the geometry about U is pentagonal bipyramidal (Haigh, Nassimbeni, Pauptit, Rodgers & Sheldrick, 1976). We have carried out the present analysis to study the conformational effects on the ligand brought about by substitution at N.

### Experimental

The compound was prepared as described by Haigh & Thornton (1971). The crystal used for data collection was a cube of size 0.1 mm and the cell parameters were obtained by least squares from the settings of 25 reflexions measured on a four-circle diffractometer with Mo  $K\alpha$  radiation. The crystal data are listed in Table 1. The density was measured by flotation in a mixture of methyl iodide and bromobenzene.

Intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer operating in the  $\omega$ - $2\theta$  scan mode [scan width  $0.9^\circ$  ( $\theta$ ), scan speed  $0.04^\circ$  ( $\theta$ )  $s^{-1}$ ]. With graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å), 2546 reflexions up to  $2\theta = 44^\circ$  were measured. Three reference reflexions, recorded after every 56 measured reflexions, remained constant to within  $\pm 2\%$ . With the

Table 1. *Crystal data*

Molecular formula	$C_{17}H_{27}NO_7U$
$M_r$	595
$a = 13.068(6)$ Å	$V = 1038.56$ Å <sup>3</sup>
$b = 10.622(5)$	$D_m = 1.89$ g cm <sup>-3</sup>
$c = 8.123(5)$	$D_c = 1.90$ for $Z = 2$
$\alpha = 105.5(2)^\circ$	$\mu = 74.91$ cm <sup>-1</sup>
$\beta = 87.6(2)$	$F(000) = 568$
$\gamma = 107.0(2)$	Space group $P\bar{1}$

criterion  $I_{rel} > 2\sigma I_{rel}$  for an observed reflexion, 181 reflexions were omitted as unobserved, leaving 2365 unique reflexions which were employed in the structure determination. The data were corrected for Lorentz-polarization effects but not for absorption.

### Solution and refinement of the structure

The U atom was located from a Patterson map and the ensuing difference map yielded the positions of all the non-H atoms. Refinement with only U anisotropic yielded an  $R$  of 0.034. All but three of the H atoms appeared in a subsequent difference map. Final refinement was carried out with all non-H atoms anisotropic. H atoms were constrained at 1.08 Å from their corresponding C atoms, their positions being dictated by the geometry of the molecule. The methyl H's were refined as rigid groups. The isotropic temperature factors of the H atoms were refined as two single param-

\* Part I: Haigh, Nassimbeni, Pauptit, Rodgers & Sheldrick (1976).



Table 2. Fractional atomic coordinates of all non-hydrogen atoms and their e.s.d.'s ( $\times 10^4$ ) and anisotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

$$T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)].$$

	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
U	2158 (0)	3098 (0)	1332 (0)	39 (0)	33 (0)	33 (0)	5 (0)	-2 (0)	16 (0)
O(1)	906 (4)	2348 (5)	2125 (6)	46 (3)	59 (3)	57 (3)	11 (2)	-1 (2)	17 (2)
O(2)	3420 (4)	3854 (5)	578 (6)	59 (3)	45 (3)	57 (3)	14 (2)	10 (2)	20 (2)
O(3)	1742 (4)	1626 (5)	-1471 (6)	81 (4)	44 (3)	38 (3)	-4 (2)	-18 (2)	34 (3)
O(4)	1340 (4)	4082 (5)	-325 (6)	83 (4)	58 (3)	39 (3)	1 (2)	-12 (3)	46 (3)
O(5)	2106 (4)	5234 (5)	3119 (6)	71 (3)	48 (3)	40 (3)	-1 (2)	-12 (2)	30 (3)
O(6)	3088 (4)	3514 (5)	3968 (5)	58 (3)	47 (3)	35 (3)	0 (2)	-10 (2)	21 (2)
O(7)	2681 (4)	1106 (4)	1288 (6)	51 (3)	31 (3)	51 (3)	9 (2)	-7 (2)	13 (2)
N	4637 (4)	-1396 (6)	1724 (7)	50 (3)	42 (3)	54 (3)	19 (3)	5 (3)	19 (3)
C(1)	1476 (7)	516 (9)	-4411 (11)	85 (6)	65 (5)	55 (5)	-11 (4)	-8 (4)	41 (5)
C(2)	1437 (5)	1678 (7)	-2892 (8)	43 (4)	41 (4)	35 (4)	1 (3)	-2 (3)	14 (3)
C(3)	1079 (5)	2713 (7)	-3145 (8)	56 (4)	48 (4)	34 (4)	10 (3)	5 (3)	23 (4)
C(4)	1037 (5)	3866 (7)	-1859 (8)	32 (3)	56 (4)	38 (4)	16 (3)	1 (3)	18 (3)
C(5)	607 (6)	4925 (8)	-2241 (10)	65 (5)	67 (5)	61 (5)	28 (4)	10 (4)	39 (4)
C(6)	2193 (8)	7320 (8)	5091 (11)	103 (7)	47 (5)	61 (5)	-7 (4)	-5 (5)	34 (5)
C(7)	2487 (6)	6000 (6)	4541 (8)	60 (4)	31 (4)	41 (4)	4 (3)	1 (3)	13 (3)
C(8)	3134 (6)	5719 (7)	5611 (9)	69 (5)	40 (4)	41 (4)	-1 (3)	-10 (4)	13 (3)
C(9)	3396 (5)	4479 (7)	5285 (8)	35 (4)	56 (5)	34 (4)	14 (4)	1 (3)	8 (3)
C(10)	4088 (6)	4272 (8)	6572 (9)	55 (5)	68 (5)	50 (4)	12 (4)	-8 (4)	17 (4)
C(11)	1199 (6)	-884 (8)	455 (12)	41 (4)	44 (4)	91 (6)	12 (4)	-16 (4)	0 (3)
C(12)	2357 (5)	-176 (7)	1035 (8)	48 (4)	35 (4)	37 (4)	5 (3)	0 (3)	9 (3)
C(13)	3009 (5)	-979 (6)	1195 (8)	49 (4)	28 (3)	49 (4)	11 (3)	-4 (3)	12 (3)
C(14)	4069 (5)	-529 (6)	1779 (8)	53 (4)	30 (3)	36 (3)	8 (3)	1 (3)	15 (3)
C(15)	4632 (6)	972 (7)	2571 (10)	52 (4)	38 (4)	61 (5)	8 (3)	-9 (4)	10 (3)
C(16)	4181 (7)	-2871 (7)	1012 (11)	82 (6)	38 (4)	76 (6)	17 (4)	10 (5)	29 (4)
C(17)	5762 (6)	-965 (9)	2349 (11)	61 (5)	76 (6)	76 (6)	31 (5)	12 (4)	43 (5)

eters, one for the methine and one for the methyl. These refined to  $u = 0.058$  and  $0.132 \text{ \AA}^2$  respectively.

The weighting scheme was  $w = (\sigma^2 F + gF)^{-1}$ . The final value of  $g$  (0.00061) was chosen to give the smallest systematic variation of  $w\Delta^2$  with the magnitude of  $F$ . The refinement converged to an  $R_w$  ( $= \sum w^{1/2} ||F_o| - |F_c|| / \sum w^{1/2} |F_o|$ ) of 0.024 and an  $R$  of 0.023. A final difference map had no peaks  $> 0.54 \text{ e \AA}^{-3}$ . The final atomic coordinates and temperature factors 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 the program system *SHELX* (Sheldrick, 1977).

### Description of the structure and discussion

A perspective view of the molecule with the numbering scheme is shown in Fig. 1. The principal bond lengths and angles are given in Table 4. Table 5 lists computed least-squares planes with their equations and the distances of various atoms from these planes.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32127 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

Atom bonded to	x	y	z
H(011)	122 (1)	59 (1)	-562 (1)
H(012)	98 (1)	-41 (1)	-415 (1)
H(013)	230 (1)	51 (1)	-446 (1)
H(031)	81 (1)	262 (1)	-442 (1)
H(051)	53 (1)	470 (1)	-362 (1)
H(052)	115 (1)	594 (1)	-174 (1)
H(053)	-17 (1)	488 (1)	-170 (1)
H(061)	260 (1)	796 (1)	628 (1)
H(062)	134 (1)	718 (1)	520 (1)
H(063)	248 (1)	781 (1)	408 (1)
H(081)	346 (1)	650 (1)	678 (1)
H(101)	464 (1)	522 (1)	730 (1)
H(102)	453 (1)	366 (1)	576 (1)
H(103)	364 (1)	372 (1)	744 (1)
H(111)	99 (1)	-196 (1)	36 (1)
H(112)	115 (1)	-74 (1)	-80 (1)
H(113)	65 (1)	-44 (1)	127 (1)
H(131)	265 (1)	-207 (1)	82 (1)
H(151)	405 (1)	152 (1)	267 (1)
H(152)	526 (1)	134 (1)	177 (1)
H(153)	497 (1)	112 (1)	383 (1)
H(161)	479 (1)	-339 (1)	95 (1)
H(162)	384 (1)	-308 (1)	-26 (1)
H(163)	356 (1)	-324 (1)	184 (1)
H(171)	611 (1)	-180 (1)	203 (1)
H(172)	585 (1)	-51 (1)	371 (1)
H(173)	617 (1)	-21 (1)	170 (1)



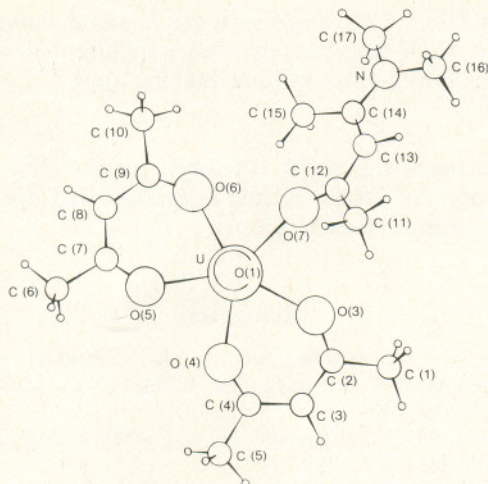


Fig. 1. Perspective view of the molecule with atomic nomenclature.

Table 4. Bond lengths (Å), bond angles (°) and their e.s.d.'s

U—O(1)	1.775 (4)	C(6)—C(7)	1.510 (8)
U—O(2)	1.774 (4)	C(7)—O(5)	1.247 (7)
U—O(3)	2.373 (4)	C(7)—C(8)	1.379 (8)
U—O(4)	2.359 (4)	C(8)—C(9)	1.412 (8)
U—O(5)	2.363 (4)	C(9)—O(6)	1.251 (7)
U—O(6)	2.378 (4)	C(9)—C(10)	1.508 (8)
U—O(7)	2.398 (4)	C(11)—C(12)	1.511 (8)
C(1)—C(2)	1.506 (8)	C(12)—O(7)	1.264 (6)
C(2)—O(3)	1.256 (7)	C(12)—C(13)	1.401 (8)
C(2)—C(3)	1.378 (8)	C(13)—C(14)	1.385 (8)
C(3)—C(4)	1.395 (8)	C(14)—C(15)	1.518 (8)
C(4)—C(5)	1.499 (8)	C(14)—N	1.333 (7)
C(4)—O(4)	1.264 (6)	N—C(16)	1.464 (8)
		N—C(17)	1.473 (8)
O(1)—U—O(2)	178.9 (2)	C(5)—C(4)—O(4)	116.1 (5)
O(1)—U—O(3)	93.9 (2)	C(4)—O(4)—U	139.0 (4)
O(1)—U—O(4)	91.4 (2)	U—O(5)—C(7)	138.0 (4)
O(1)—U—O(5)	88.3 (2)	O(5)—C(7)—C(6)	115.6 (5)
O(1)—U—O(6)	92.7 (2)	O(5)—C(7)—C(8)	125.0 (5)
O(1)—U—O(7)	89.1 (2)	C(6)—C(7)—C(8)	119.4 (5)
O(2)—U—O(3)	87.1 (2)	C(7)—C(8)—C(9)	124.2 (5)
O(2)—U—O(4)	89.4 (2)	C(8)—C(9)—C(10)	119.5 (5)
O(2)—U—O(5)	91.2 (2)	C(8)—C(9)—O(6)	123.8 (5)
O(2)—U—O(6)	86.2 (2)	C(10)—C(9)—O(6)	116.7 (5)
O(2)—U—O(7)	90.7 (2)	C(9)—O(6)—U	137.6 (4)
O(3)—U—O(4)	70.2 (1)	U—O(7)—C(12)	144.8 (4)
O(4)—U—O(5)	73.7 (1)	O(7)—C(12)—C(11)	117.3 (5)
O(5)—U—O(6)	70.9 (1)	O(7)—C(12)—C(13)	124.3 (5)
O(6)—U—O(7)	72.1 (1)	C(11)—C(12)—C(13)	118.3 (5)
O(7)—U—O(3)	73.4 (1)	C(12)—C(13)—C(14)	127.3 (5)
U—O(3)—C(2)	137.6 (4)	C(13)—C(14)—C(15)	121.8 (5)
C(1)—C(2)—C(3)	118.6 (5)	C(13)—C(14)—N	121.7 (5)
O(3)—C(2)—C(3)	124.8 (5)	C(15)—C(14)—N	116.5 (5)
C(1)—C(2)—O(3)	116.6 (5)	C(14)—N—C(16)	121.8 (5)
C(2)—C(3)—C(4)	124.3 (5)	C(14)—N—C(17)	123.5 (5)
C(3)—C(4)—C(5)	120.7 (5)	C(16)—N—C(17)	114.7 (5)
C(3)—C(4)—O(4)	123.3 (5)		

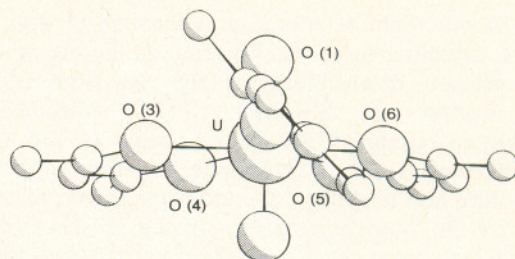


Fig. 2. Molecule viewed along the O(3)—U—O(6) bisector. H atoms have been omitted.

Table 5. Least-squares planes

The equations of the planes are expressed in orthogonalized space as  $lX + mY + nZ = P$ .  $d$  is the perpendicular distance (Å) from each atom to the plane. Atoms marked (\*) were not included in the least-squares calculations.

Plane 1					
$10.1466X + 3.0414Y - 3.4818Z = 2.7047$					
	$d$		$d$		$d$
U	-0.037	O(4)	0.009	O(6)	0.116
O(3)	0.070	O(5)	-0.062	O(7)	-0.096
Plane 2					
$10.6992X + 2.9613Y - 2.3820Z = 2.7085$					
	$d$		$d$		$d$
U*	0.200	C(1)*	0.074	C(4)	-0.012
O(3)	-0.012	C(2)	0.014	C(5)*	-0.067
O(4)	0.011	C(3)	-0.002		
Plane 3					
$9.3083X + 3.2232Y - 4.4709Z = 2.2396$					
	$d$		$d$		$d$
U*	0.172	C(6)*	-0.115	C(9)	0.002
O(5)	0.013	C(7)	-0.021	C(10)*	0.004
O(6)	-0.007	C(8)	0.012		
Plane 4					
$-3.5035X - 2.1742Y + 7.7215Z = 0.0223$					
	$d$		$d$		$d$
U*	-0.424	C(13)	0.059	C(16)	-0.082
O(7)	-0.207	C(14)	0.041	C(17)	-0.018
C(11)	0.101	C(15)	0.129	N	-0.012
C(12)	-0.011				
Plane 5					
$10.2394X + 3.1617Y - 3.1766Z = 2.7657$					
	$d$		$d$		$d$
U	0.000	O(3)	0.000	O(4)	0.000
Plane 6					
$9.5538X + 3.5146Y - 3.9255Z = 2.6274$					
	$d$		$d$		$d$
U	0.000	O(5)	0.000	O(6)	0.000
Intersection angles (°)					
	Planes 1 and 4	48.0			
	Planes 2 and 5	6.0			
	Planes 3 and 6	5.0			



The  $\beta$ -ketoamine coordinates through O, and the U atom exhibits pentagonal-bipyramidal coordination. In our previous determination (Haigh, Nassimbeni, Paup-tit, Rodgers & Sheldrick, 1976), intramolecular hydrogen bonding between the amino H and keto O atoms causes the  $\beta$ -ketoamine to adopt a ring-like structure and to display pseudo-aromaticity, as evidenced by the ligand's planarity. In the present complex, which is di-substituted at N, the  $\beta$ -ketoamine adopts an open chain structure which is not planar (plane 4, Table 5). As expected, the intersection angle ( $48^\circ$ ) of the  $\beta$ -ketoamine and the plane through the five equatorial O atoms is larger than that observed in part I, where a second hydrogen bond between the amino H and an acetylacetonate O atom holds the ligand plane at  $32^\circ$  to the equatorial plane.

Fig. 2 is a view of the complex along the bisector of

the O(3)—U—O(6) angle with the H atoms omitted for clarity. Each acetylacetonate ring is slightly folded about an axis through its O atoms making angles of  $6.0$  and  $5.0^\circ$ .

We thank the CSIR (Pretoria) for the data collection, and the CSIR and the University of Cape Town for awards of research grants.

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