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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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)°, $Z = 2$, 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-dimethylacetylacetoneamine 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 ω–2θ scan mode [scan width 0.9° (θ), scan speed 0.04° (θ) s^{-1}]. With graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), 2546 reflexions up to $2\theta = 44°$ were measured. Three reference reflexions, recorded after every 56 measured reflexions, remained constant to within ±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^3
$b = 10.622$ (5)	$D_m = 1.89$ g cm^{-3}
$c = 8.123$ (5)	$D_c = 1.90$ for $Z = 2$
$\alpha = 105.5$ (2)°	$\mu = 74.91$ cm^{-1}
$\beta = 87.6$ (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-

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

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

	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 (4)
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 Å^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 ($= \Sigma w^{1/2}||F_o| - |F_c||/\Sigma w^{1/2}|F_o|$) of 0.024 and an R of 0.023. A final difference map had no peaks > 0.54 e Å^{-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.

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* 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)	C(1)	98 (1)	−41 (1)	−415 (1)
H(013)		230 (1)	51 (1)	−446 (1)
H(031)	C(3)	81 (1)	262 (1)	−442 (1)
H(051)		53 (1)	470 (1)	−362 (1)
H(052)	C(5)	115 (1)	594 (1)	−174 (1)
H(053)		−17 (1)	488 (1)	−170 (1)
H(061)		260 (1)	796 (1)	628 (1)
H(062)	C(6)	134 (1)	718 (1)	520 (1)
H(063)		248 (1)	781 (1)	408 (1)
H(081)	C(8)	346 (1)	650 (1)	678 (1)
H(101)		464 (1)	522 (1)	730 (1)
H(102)	C(10)	453 (1)	366 (1)	576 (1)
H(103)		364 (1)	372 (1)	744 (1)
H(111)		99 (1)	−196 (1)	36 (1)
H(112)	C(11)	115 (1)	−74 (1)	−80 (1)
H(113)		65 (1)	−44 (1)	127 (1)
H(131)	C(13)	265 (1)	−207 (1)	82 (1)
H(151)		405 (1)	152 (1)	267 (1)
H(152)	C(15)	526 (1)	134 (1)	177 (1)
H(153)		497 (1)	112 (1)	383 (1)
H(161)		479 (1)	−339 (1)	95 (1)
H(162)	C(16)	384 (1)	−308 (1)	−26 (1)
H(163)		356 (1)	−324 (1)	184 (1)
H(171)		611 (1)	−180 (1)	203 (1)
H(172)	C(17)	585 (1)	−51 (1)	371 (1)
H(173)		617 (1)	−21 (1)	170 (1)
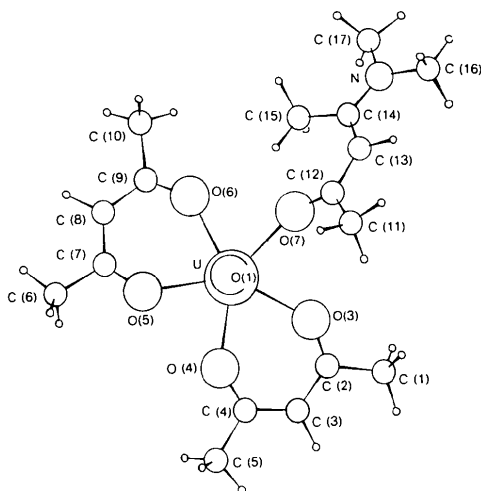
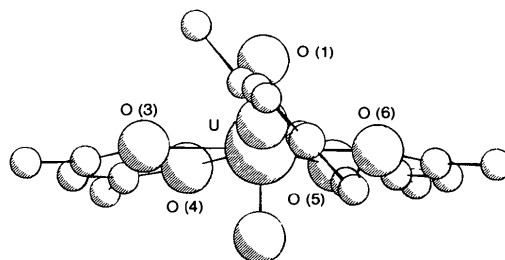Fig. 1. Perspective view of the molecule with atomic nomenclature.

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

$$10 \cdot 1466X + 3 \cdot 0414Y - 3 \cdot 4818Z = 2 \cdot 7047$$

	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

$$10 \cdot 6992X + 2 \cdot 9613Y - 2 \cdot 3820Z = 2 \cdot 7085$$

	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

$$9 \cdot 3083X + 3 \cdot 2232Y - 4 \cdot 4709Z = 2 \cdot 2396$$

	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

$$-3 \cdot 5035X - 2 \cdot 1742Y + 7 \cdot 7215Z = 0 \cdot 0223$$

	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

$$10 \cdot 2394X + 3 \cdot 1617Y - 3 \cdot 1766Z = 2 \cdot 7657$$

	d		d		d
U	0·000	O(3)	0·000	O(4)	0·000

Plane 6

$$9 \cdot 5538X + 3 \cdot 5146Y - 3 \cdot 9255Z = 2 \cdot 6274$$

	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

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)		
O(4)—U—O(5)	73·7 (1)	U—O(7)—C(12)	144·8 (4)
O(5)—U—O(6)	70·9 (1)	O(7)—C(12)—C(11)	117·3 (5)
O(6)—U—O(7)	72·1 (1)	O(7)—C(12)—C(13)	124·3 (5)
O(7)—U—O(3)	73·4 (1)	C(11)—C(12)—C(13)	118·3 (5)
U—O(3)—C(2)	137·6 (4)	C(12)—C(13)—C(14)	127·3 (5)
C(1)—C(2)—C(3)	118·6 (5)	C(13)—C(14)—C(15)	121·8 (5)
O(3)—C(2)—C(3)	124·8 (5)	C(13)—C(14)—N	121·7 (5)
C(1)—C(2)—O(3)	116·6 (5)	C(15)—C(14)—N	116·5 (5)
C(2)—C(3)—C(4)	124·3 (5)	C(14)—N—C(16)	121·8 (5)
C(3)—C(4)—C(5)	120·7 (5)	C(14)—N—C(17)	123·5 (5)
C(3)—C(4)—O(4)	123·3 (5)	C(16)—N—C(17)	114·7 (5)

The β-ketoamine coordinates through O, and the U atom exhibits pentagonal-bipyramidal coordination. In our previous determination (Haigh, Nassimbeni, Pauptit, Rodgers & Sheldrick, 1976), intramolecular hydrogen bonding between the amino H and keto O atoms causes the β-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 β-ketoamine adopts an open chain structure which is not planar (plane 4, Table 5). As expected, the intersection angle (48°) of the β-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 acetylacetone O atom holds the ligand plane at 32° 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 acetylacetone ring is slightly folded about an axis through its O atoms making angles of 6·0 and 5·0°.

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The Stereochemistry of Disulfides. The Crystal Structure of 1α,5α-Epidithioandrostane-3α,17β-diol (C₁₉O₂S₂H₃₀)

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Crystals of the title compound (I) are monoclinic, space group $P2_1$. Unit-cell constants $[\lambda(\text{Mo }K\alpha) = 0·71069$ Å, $t = -160 \pm 5\,°\text{C}]$ are $a = 12·480\,(14)$, $b = 7·210\,(9)$, $c - 20·978\,(24)$ Å; $Z = 4$ with two crystallographically independent molecules $[(\text{I}a)$ and $(\text{I}b)]$. A final set of 3495 unique intensities, of which 3459 were non-zero, was obtained by averaging redundancies in the 7011 reflections collected by diffractometry. The structure was solved by direct methods and refined by full-matrix least squares to $R(F) = 0·044$ and $R_w(F) = 0·037$. The C—S—S—C torsion angles are $-2·5$ and $-4·5°$, with S—S bond distances of $2·104\,(2)$ and $2·101\,(2)$ Å, for $(\text{I}a)$ and $(\text{I}b)$. Geometries of 18 molecules containing C—S—S—C fragments are compared and the conformations of 1,2-dithiolane rings are discussed. Large conformational differences are observed in the D rings of $(\text{I}a)$ and $(\text{I}b)$. Comparisons of the structures of (I) and 5α-androstane-3α,17β-diol (II) [Precigoux, Busetta, Courseille & Hospital, Cryst. Struct. Commun. (1972), 1, 265–268] show the distortions of the androstane skeleton necessary to accommodate the 1,5-diaxial disulfide. Short intramolecular O—H···S contact distances of 2·50 to 2·65 Å are observed. The molecules form continuous intermolecular hydrogen-bonded chains arranged in a left-handed helix parallel to the b axis.

Introduction

1α,5α-Epidithioandrostane-3α,17β-diol (I) is of current interest as a model compound for correlations of the chiroptical properties and stereochemistry of disulfides (Neubert & Carmack, 1974). The structure determination of (I) has been undertaken to (1) confirm the

proposed structure (Tweit & Dodson, 1959; Harpp & Gleason, 1970); (2) establish the disulfide dihedral angle which has been previously estimated, from model studies and from the wavelength of the lowest-energy electronic transition (Bergson, Sjoberg, Tweit & Dodson, 1960), to be close to 0°; and (3) establish the environment about the disulfide chromophore. Comparisons of the structures of (I) and 5α-androstane-3α,17β-diol (II) (Precigoux, Busetta, Courseille & Hospital, 1972) have been undertaken to show the

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