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

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Crystals of the title compound are monoclinic with $a=8.314$ (5), $b=22.723$ (9), $c=12.589$ (6) Å, $\beta=123.0$ (2)°, $Z=4$, space group $P2_1/c$. The structure was determined by Patterson and Fourier methods and refined by full-matrix least squares to a final R of 0.030 for 2043 independent reflexions. The U atom has pentagonal bipyramidal coordination and the *N*-methylacetylacetonamine is bonded to U *via* O. There are two intramolecular N-H...O hydrogen bonds which govern the geometry of the adduct molecule.

Introduction

The reaction of uranyl nitrate with acetylacetonate (HAA) in the presence of ammonia and a variety of primary and secondary amines has recently been re-investigated (Haigh & Thornton, 1971). It was found that the product of the reaction of uranyl nitrate with acetylacetonate in the presence of methylamine could be formulated as the β -ketoamine adduct of uranylacetylacetonate, $\text{UO}_2(\text{AA})_2[\text{CH}_3\text{-CO-CH}=\text{C}(\text{CH}_3)\text{-NHCH}_3]$. The stoichiometry of the complex was deduced from IR and PMR measurements, and it was suggested that the structure was probably analogous to that established for the hydrate, $\text{UO}_2(\text{AA})_2(\text{H}_2\text{O})$, (Frasson, Bombieri & Panattoni, 1966), which is

pentagonal bipyramidal. It was suggested (Haigh & Thornton, 1971), that the adduct molecule would be bonded to U *via* the O atom, but no suggestions were made concerning the spatial arrangements of the three ring systems present in the complex. We are undertaking the structural determination of a series of compounds of this type to determine whether the adduct is bonded through O or N and to investigate the hydrogen bonding. The methylamine derivative was chosen first due to its crystalline excellence.

Experimental

The compound was prepared as previously described (Haigh & Thornton, 1971).

A single crystal was ground to a sphere of radius 0.14 mm and the lattice constants were obtained from a least-squares analysis of the settings of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$

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Table 1. *Crystal data*

Molecular formula	C ₁₆ H ₂₅ NO ₇ U
M.W.	581
Space group	P2 ₁ /c (monoclinic, 2nd setting)
a =	8.314 (5) Å
b =	22.723 (9)
c =	12.589 (6)
β =	123.0 (2)°
V =	1993.59 Å ³
	D _m = 1.84 g cm ⁻³
	D _c = 1.94 for Z = 4
	μ = 103.59 cm ⁻¹
	F(000) = 1104

radiation. The crystal data are listed in Table 1. The density was measured by flotation in a mixture of diiodomethane and *m*-xylene.

Intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer operating in the ω -scan mode (scan width 0.9° θ , scan speed 0.03° θ s⁻¹). With graphite-monochromated Mo K α radiation ($\lambda = 0.7107$ Å), 2528 reflexions up to $2\theta = 44^\circ$ were measured. Throughout the data collection, three reference reflexions were recorded after every 56 measured reflexions. They remained constant to within $\pm 4\%$. 147 reflexions were rejected as being systematically absent or space-group equivalent. With the criterion $F_{\text{rel}} < 2.5\sigma(F_{\text{rel}})$ for an observed reflexion, a further 338 reflexions were omitted as unobserved, leaving 2043 unique reflexions which were employed in the structural determination. The data were corrected for Lorentz-polarization effects. Absorption corrections were carried out with A^* for a sphere with $\mu R = 1.45$ (*International Tables for X-ray Crystallography*, 1967).

Solution and refinement of the structure

The U atom was located from a Patterson map. A difference map was calculated with the weighting scheme $w = \exp[-g \sin^2 \theta / \lambda^2 s^2]$, in which s is the value of $\sin \theta / \lambda$ for which the weight is half that at $\theta = 0$ (Sheldrick, 1976). With a value of $s = 0.5$ the difference map yielded the positions of all the non-hydrogen atoms. Full-matrix least-squares refinement (SHEL-X program system; Sheldrick, 1976) with U anisotropic and the remaining non-hydrogen atoms isotropic, yielded an R of 0.050. At this stage a difference map showed the position of some of the H atoms. The H atoms were constrained to be 1.08 Å from their corresponding C atoms, their positions being dictated by the geometry of the molecule. The methyl H were refined as rigid

groups and, because the geometry of the β -ketoamine showed that N(1) is trigonal planar, H(1) was appropriately located and constrained to ride at 1.08 Å from N(1).

The final full-matrix least-squares refinement was carried out with the U and the seven O atoms anisotropic, the remaining non-hydrogen atoms having individual isotropic temperature factors. The isotropic temperature factors of the H atoms were refined as two single parameters, one for the methine and amine hydrogens [H(1), H(131), H(031), H(081)] and the other for the methyl H atoms. These refined to $U = 0.108$ and 0.122 Å² respectively. This technique of constrained least-squares refinement, with rigid groups, bond length constraints and location and refinement of H atoms, is discussed by Sheldrick (1976). The refinement converged to $R_w = \sum w^{1/2} |F_o - F_c| / \sum w^{1/2} |F_o| = 0.028$ and $R = 0.030$ with $w = 1/\sigma^2$. Table 2 shows an analysis of variance computed after the final cycle. As a check of the correctness of the structure a difference map was computed. This had no peaks > 0.25 e Å⁻³.

Table 3. *Fractional atomic coordinates of the heavy atoms ($\times 10^4$)*

	x	y	z
U	3586 (0)	1364 (0)	1819 (0)
O(1)	5084 (9)	1981 (3)	2342 (6)
O(2)	2083 (9)	746 (3)	1277 (6)
O(3)	2704 (9)	1576 (3)	3291 (5)
O(4)	863 (9)	1975 (3)	851 (5)
O(5)	2764 (9)	1558 (3)	-260 (5)
O(6)	5752 (8)	876 (3)	1475 (5)
O(7)	5784 (8)	899 (3)	3807 (5)
C(1)	924 (18)	1578 (6)	4254 (11)
C(2)	1061 (13)	1676 (4)	3123 (8)
C(3)	-535 (13)	1882 (4)	2038 (8)
C(4)	-524 (12)	2053 (4)	987 (8)
C(5)	-2212 (13)	2381 (4)	-67 (8)
C(6)	2214 (15)	1665 (5)	-2275 (9)
C(7)	3345 (12)	1401 (4)	-952 (8)
C(8)	4800 (12)	1032 (4)	-619 (8)
C(9)	6001 (12)	787 (4)	597 (8)
C(10)	7646 (13)	409 (4)	870 (9)
C(11)	6947 (15)	-45 (5)	3753 (10)
C(12)	6686 (13)	452 (4)	4426 (8)
C(13)	7473 (13)	392 (4)	5731 (9)
C(14)	7350 (12)	818 (4)	6462 (8)
C(15)	8390 (15)	725 (5)	7897 (9)
C(16)	6187 (16)	1777 (5)	6704 (10)
N(1)	6363 (10)	1294 (3)	5994 (7)

Table 2. *Analysis of variance*

(a) As a function of $\sin \theta$	
$\sin \theta$	0.00-0.17-0.22-0.25-0.27-0.30-0.32-0.33-0.35-0.36-0.38
N	212 240 198 173 282 235 108 265 126 204
V	332 265 232 246 228 197 185 189 209 173
(b) As a function of $(F/F_{\text{max}})^{1/2}$	
$(F/F_{\text{max}})^{1/2}$	0.00-0.22-0.27-0.30-0.34-0.39-0.42-0.46-0.51-0.59-1.00
N	211 243 161 203 248 162 212 202 207 194
V	215 201 236 241 236 236 221 219 238 277

Table 4. Temperature factors of the heavy atoms ($\text{\AA}^2 \times 10^3$)

U	46 (0)	49 (0)	32 (0)	0 (0)	23 (0)	4 (0)
O(1)	81 (5)	62 (5)	51 (4)	3 (3)	24 (4)	-7 (4)
O(2)	68 (4)	70 (5)	72 (4)	0 (4)	38 (4)	-7 (4)
O(3)	78 (5)	108 (6)	45 (4)	21 (4)	38 (4)	50 (4)
O(4)	73 (4)	88 (5)	44 (4)	18 (3)	37 (3)	30 (4)
O(5)	76 (4)	116 (6)	49 (4)	19 (4)	44 (4)	38 (4)
O(6)	61 (4)	91 (5)	46 (3)	12 (3)	36 (3)	25 (4)
O(7)	71 (4)	56 (4)	43 (3)	12 (3)	29 (3)	30 (3)
	U	U	U			
C(1)	94 (4)	C(7)	52 (2)	C(13)	63 (3)	
C(2)	58 (2)	C(8)	55 (2)	C(14)	55 (2)	
C(3)	54 (2)	C(9)	52 (2)	C(15)	79 (3)	
C(4)	51 (2)	C(10)	63 (3)	C(16)	88 (3)	
C(5)	62 (3)	C(11)	79 (3)	N(1)	59 (2)	
C(6)	75 (3)	C(12)	55 (2)			

Table 5. Fractional atomic coordinates of the hydrogen atoms ($\times 10^3$)

	x	y	z
H(1)	558 (1)	134 (0)	498 (1)
H(011)	-51 (2)	150 (1)	402 (1)
H(012)	154 (2)	195 (1)	490 (1)
H(013)	179 (2)	119 (1)	470 (1)
H(031)	-186 (1)	192 (0)	200 (1)
H(051)	-348 (1)	231 (0)	-5 (1)
H(052)	-250 (1)	226 (0)	-99 (1)
H(053)	-181 (1)	284 (0)	11 (1)
H(061)	267 (2)	155 (1)	-290 (1)
H(062)	222 (2)	214 (1)	-219 (1)
H(063)	78 (2)	150 (1)	-266 (1)
H(081)	508 (1)	91 (0)	-134 (1)
H(101)	771 (1)	37 (0)	4 (1)
H(102)	744 (1)	-2 (0)	114 (1)
H(103)	897 (1)	60 (0)	164 (1)
H(111)	778 (2)	-44 (1)	419 (1)
H(112)	741 (2)	16 (1)	319 (1)
H(113)	545 (2)	-16 (1)	316 (1)
H(131)	822 (1)	-1 (0)	619 (1)
H(151)	889 (2)	28 (1)	810 (1)
H(152)	745 (2)	80 (1)	822 (1)
H(153)	960 (2)	102 (1)	838 (1)
H(161)	531 (2)	214 (1)	611 (1)
H(162)	764 (2)	193 (1)	734 (1)
H(163)	563 (2)	162 (1)	725 (1)

Tables 3, 4 and 5 show the final atomic coordinates and temperature factors.*

Description of the structure and discussion

A perspective view of the molecule with the numbering is shown in Fig. 1. The β -ketoamine coordinates through O, and the U atom exhibits pentagonal bipyramidal coordination in agreement with prediction (Haigh & Thornton, 1971). The principal bond lengths and angles are shown in Tables 6 and 7. The coordination geometry round U closely resembles that found in

other pentagonal bipyramidal uranyl compounds. The apical U—O distances (mean 1.75 \AA) are, as expected, considerably shorter than the equatorial (mean 2.37 \AA). An interesting feature of the complex is the strong hydrogen bond N(1)—H(1)···O(7), with H(1)···O(7) at 1.87 \AA . It is because of this hydrogen bond that the β -ketoamine adopts a ring-like structure and in fact displays pseudo-aromaticity as evidenced by its planarity. It is also of interest to note a second, weaker hydrogen bond N(1)—H(1)···O(3), with H(1)···O(3) at 2.23 \AA . It is probably due to the presence of this bond that the β -ketoamine is situated only at a slight angle (32.0°) to the plane defined by the five equatorial O atoms.

Table 6. Bond lengths (\AA)

U—O(1)	1.748 (6)	C(2)—C(3)	1.37 (1)
U—O(2)	1.751 (6)	C(3)—C(4)	1.38 (1)
U—O(3)	2.385 (5)	C(4)—C(5)	1.50 (1)
U—O(4)	2.351 (5)	C(6)—C(7)	1.52 (1)
U—O(5)	2.358 (5)	C(7)—C(8)	1.34 (1)
U—O(6)	2.347 (5)	C(8)—C(9)	1.41 (1)
U—O(7)	2.395 (5)	C(9)—C(10)	1.49 (1)
O(3)—C(2)	1.283 (9)	C(11)—C(12)	1.50 (1)
O(4)—C(4)	1.266 (8)	C(12)—C(13)	1.41 (1)
O(5)—C(7)	1.256 (8)	C(13)—C(14)	1.38 (1)
O(6)—C(9)	1.248 (8)	C(14)—C(15)	1.53 (1)
O(7)—C(12)	1.250 (9)	C(14)—N(1)	1.289 (9)
C(1)—C(2)	1.51 (1)	N(1)—C(16)	1.47 (1)

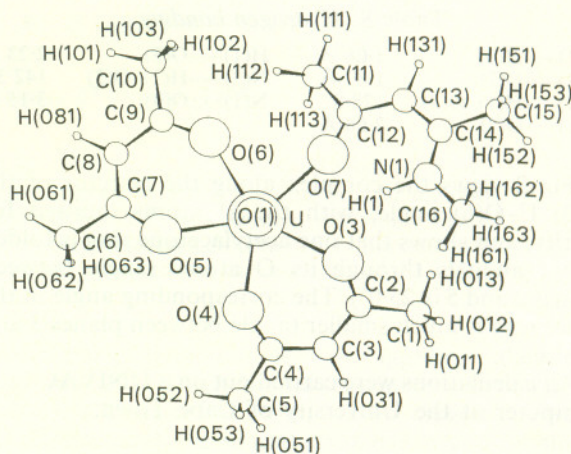


Fig. 1. Perspective view of the molecule with atomic nomenclature.

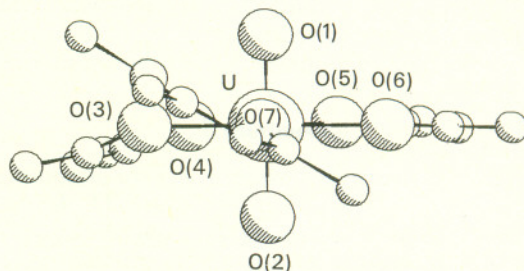


Fig. 2. Molecule viewed along O(3)—U—O(6) bisector. H atoms have been omitted.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31475 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 7. Bond angles ($^{\circ}$)

O(1)—U—O(2)	79.2 (3)	U—O(5)—C(7)	136.8 (5)
O(1)—U—O(3)	90.2 (3)	O(5)—C(7)—C(8)	125.7 (7)
O(1)—U—O(4)	90.5 (2)	O(5)—C(7)—C(6)	113.9 (7)
O(1)—U—O(5)	89.1 (2)	C(8)—C(7)—C(6)	120.3 (7)
O(1)—U—O(6)	89.3 (2)	C(7)—C(8)—C(9)	124.9 (8)
O(1)—U—O(7)	88.8 (2)	C(8)—C(9)—O(6)	122.5 (7)
O(2)—U—O(3)	90.5 (2)	C(8)—C(9)—C(10)	119.8 (7)
O(2)—U—O(4)	89.4 (2)	O(6)—C(9)—C(10)	117.7 (7)
O(2)—U—O(5)	90.2 (2)	C(9)—O(6)—U	139.0 (5)
O(2)—U—O(6)	90.3 (2)		
O(2)—U—O(7)	91.7 (2)	U—O(7)—C(12)	150.1 (5)
O(3)—U—O(4)	70.5 (2)	O(7)—C(12)—C(11)	118.8 (7)
O(4)—U—O(5)	72.6 (2)	O(7)—C(12)—C(13)	123.1 (8)
O(5)—U—O(6)	70.8 (2)	C(13)—C(12)—C(11)	118.1 (8)
O(6)—U—O(7)	76.0 (2)	C(12)—C(13)—C(14)	123.8 (8)
O(7)—U—O(3)	70.1 (2)	C(13)—C(14)—N(1)	123.0 (8)
		C(13)—C(14)—C(15)	119.3 (8)
U—O(3)—C(2)	131.2 (5)	N(1)—C(14)—C(15)	117.7 (7)
O(3)—C(2)—C(3)	126.3 (8)	C(14)—N(1)—C(16)	126.6 (7)
O(3)—C(2)—C(1)	116.1 (8)		
C(3)—C(2)—C(1)	117.6 (8)		
C(2)—C(3)—C(4)	122.8 (8)		
C(3)—C(4)—O(4)	124.8 (7)		
C(3)—C(4)—C(5)	119.6 (7)		
O(4)—C(4)—C(5)	115.5 (7)		
C(4)—O(4)—U	134.7 (5)		

The hydrogen bond data are listed in Table 8. Table 9 gives the equations of selected least-squares planes and interplanar angles.

Table 8. Hydrogen bonding

N(1)—H(1)	1.08 Å	H(1)—O(3)	2.23 Å
H(1)—O(7)	1.87 Å	N(1)—H(1)—O(3)	142.3 $^{\circ}$
N(1)—H(1)—O(7)	128.8 $^{\circ}$	N(1)···O(3)	3.15 Å
N(1)···O(7)	2.68 Å		

Fig 2 views the complex along the bisector of the O(3)—U—O(6) angle, with the H atoms omitted for clarity, and shows that one acetylacetonate ring is folded about an axis through its O atoms (angle between planes 2 and 5 is 23.0 $^{\circ}$). The corresponding angle in the other ring is much smaller (angle between planes 3 and 6 is 3.4 $^{\circ}$).

All calculations were carried out on a UNIVAC 1106 computer at the University of Cape Town.

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Table 9. 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 calculation.

$$\text{Plane 1 } (4.123)X + (18.397)Y + (-0.090)Z = 3.987$$

d		d		d	
U(1)	-0.015	O(4)	-0.006	O(6)	-0.017
O(3)	-0.002	O(5)	0.021	O(7)	0.018

$$\text{Plane 2 } (1.021)X + (21.134)Y + (2.811)Z = 4.524$$

d		d		d	
U(1)*	-0.764	C(1)*	0.101	C(4)	0.039
O(3)	0.008	C(2)	0.004	C(5)*	0.264
O(4)	-0.023	C(3)	-0.028		

$$\text{Plane 3 } (4.484)X + (17.953)Y + (-0.626)Z = 4.059$$

d		d		d	
U(1)*	-0.117	C(6)*	0.065	C(9)	0.008
O(5)	-0.007	C(7)	0.016	C(10)*	0.048
O(6)	-0.001	C(8)	-0.016		

$$\text{Plane 4 } (7.323)X + (10.046)Y + (-4.258)Z = 3.460$$

d		d		d	
U(1)*	-0.239	C(13)	-0.036	C(16)	0.001
O(7)	0.057	C(14)	-0.008	N(1)	-0.053
C(11)	-0.016	C(15)	0.049	H(1)*	-0.143
C(12)	0.005				

$$\text{Plane 5 } (4.166)X + (18.343)Y + (-0.147)Z = 3.969$$

d		d		d	
U(1)	0.000	O(3)	0.000	O(4)	0.000

$$\text{Plane 6 } (4.126)X + (18.253)Y + (0.068)Z = 3.982$$

d		d		d	
U(1)	0.000	O(5)	0.000	O(6)	0.000

Angles between normals to planes ($^{\circ}$)

Plane 1 to plane 4	32.0
Plane 2 to plane 5	23.0
Plane 3 to plane 6	3.4

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