

1.0 Å from N(15) in the correct geometric positions. The length C(11a)—C(12) of 1.358 Å is typical for a localized double bond. In comparison with the other tetracycline structures both the C—N bonds are somewhat elongated, but the remaining C—C lengths are similar.

The conformation of the molecule is similar to that of 5-hydroxytetracycline (Cid-Dresner, 1965). Table 7 lists the torsion angles in the tetracycline ring system. The structure is extensively hydrogen-bonded. Table 8 lists both the intra- and inter-molecular hydrogen bonds. The water molecules form a network of hydrogen bonds which is concentrated in columns about alternate twofold screw axes running in the [001] direction. Figs. 3 and 4 show the [001] and [100] projections of one such column of the hydrogen-bonding network.

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

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

BY A. L. RODGERS

Department of Physiology and Medical Biochemistry, Medical School, University of Cape Town, South Africa

L. R. NASSIMBENI

Department of Physical Chemistry, University of Cape Town, South Africa

AND J. M. HAIGH

School of Pharmaceutical Sciences, Rhodes University, Grahamstown, South Africa

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Crystals of the title compound are monoclinic with $a = 8.392(5)$, $b = 18.274(7)$, $c = 16.713(6)$ Å, $\beta = 114.4(2)^\circ$, $Z = 4$, 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 0.059 for 1891 reflexions. The U atom has pentagonal-bipyramidal coordination and the *N*-isopropylacetylacetoneamine is bonded to U *via* O. There is an intramolecular N—H...O hydrogen bond which governs the geometry of the molecule.

Introduction

In two earlier structural determinations of compounds of this type we have shown that the conformation of the adduct moiety is dependent on the formation of intramolecular N—H...O hydrogen bonds (part I: Haigh, Nassimbeni, Pauptit, Rodgers & Sheldrick, 1976; part II: Nassimbeni, Orpen, Pauptit, Rodgers & Haigh, 1977). We have carried out the present analysis

to study the conformational effects on the ligand brought about by the steric influence of an isopropyl substituent at N.

Experimental

The compound was prepared as previously described (Haigh & Thornton, 1971). A single crystal was ground

to a sphere of radius 0.10 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 $K\alpha$ 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 - 2θ scan mode (scan width $1.0^\circ \theta$, scan speed $0.04^\circ \theta \text{ s}^{-1}$). With graphite-monochroma-

ted Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$), 2970 reflexions up to $2\theta = 44^\circ$ were measured. Throughout the data collection, three reference reflexions were recorded after every 68 reflexions: their intensities remained constant to within $\pm 2.5\%$. 203 reflexions were excluded as systematically absent and a further 876 were omitted as they did not satisfy the criterion $F_{\text{rel}} > 2.5\sigma F_{\text{rel}}$ for an observed reflexion. This left 1891 reflexions which were used for the analysis. Lorentz-polarization corrections were applied but absorption was ignored.

Table 1. *Crystal data*

Molecular formula	$\text{C}_{18}\text{H}_{29}\text{NO}_7\text{U}$
Molecular weight	609
$a = 8.392 (5) \text{ \AA}$	$V = 2333.41 \text{ \AA}^3$
$b = 18.274 (7)$	$D_m = 1.74 \text{ g cm}^{-3}$
$c = 16.713 (6)$	$D_c = 1.73 \text{ for } Z = 4$
$\beta = 114.4 (2)^\circ$	$\mu = 66.69 \text{ cm}^{-1}$
Space group $P2_1/c$	$F(000) = 1168$

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 21 of the 28 H atoms. All, however, were constrained to be 1.08 \AA

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	41 (0)	321 (0)	-123 (0)	*
O(1)	-28 (1)	245 (1)	-81 (1)	73 (4)
O(2)	113 (2)	380 (1)	-165 (1)	70 (4)
O(3)	-248 (2)	351 (1)	-223 (1)	81 (4)
O(4)	-89 (2)	397 (1)	-52 (1)	62 (4)
O(5)	274 (1)	342 (1)	16 (1)	61 (3)
O(6)	291 (2)	258 (1)	-118 (1)	71 (4)
O(7)	-33 (1)	249 (1)	-250 (1)	51 (3)
N	57 (2)	108 (1)	-219 (1)	63 (4)
C(1)	-262 (2)	455 (1)	10 (1)	78 (6)
C(2)	-247 (2)	415 (1)	-66 (1)	53 (5)
C(3)	-387 (3)	400 (1)	-138 (1)	70 (6)
C(4)	-390 (3)	370 (1)	-215 (1)	69 (6)
C(5)	-550 (3)	365 (1)	-299 (1)	122 (9)
C(6)	555 (2)	198 (1)	-94 (1)	68 (6)
C(7)	444 (2)	246 (1)	-62 (1)	57 (5)
C(8)	516 (2)	273 (1)	21 (1)	67 (6)
C(9)	429 (2)	321 (1)	57 (1)	56 (4)
C(10)	527 (2)	349 (1)	149 (1)	79 (6)
C(11)	-11 (2)	310 (1)	-370 (1)	69 (5)
C(12)	12 (2)	242 (1)	-315 (1)	44 (4)
C(13)	77 (2)	178 (1)	-334 (1)	58 (5)
C(14)	101 (2)	115 (1)	-285 (1)	70 (6)
C(15)	174 (3)	47 (1)	-311 (1)	99 (7)
C(16)	65 (3)	44 (1)	-163 (1)	91 (7)
C(17)	-101 (3)	38 (1)	-149 (2)	129 (9)
C(18)	221 (4)	50 (2)	-79 (2)	170 (12)

* 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: $U_{11} = 40 (0)$, $U_{22} = 48 (0)$, $U_{33} = 50 (0)$, $U_{23} = 5 (1)$, $U_{13} = 22 (0)$, $U_{12} = -6 (1)$.

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	6 (2)	156 (1)	-201 (1)
H(16)	C(16)	79 (3)	-5 (1)	-196 (1)
H(3)	C(3)	-512 (3)	412 (1)	-137 (1)
H(8)	C(8)	649 (2)	258 (1)	63 (1)
H(11)*	C(1)	-401 (2)	452 (1)	-8 (1)
H(12)*		-221 (2)	512 (1)	15 (1)
H(13)*		-193 (2)	428 (1)	72 (1)
H(51)	C(5)	-665 (3)	371 (1)	-286 (1)
H(52)		-557 (3)	314 (1)	-333 (1)
H(53)*		-543 (3)	411 (1)	-338 (1)
H(61)*	C(6)	683 (2)	183 (1)	-46 (1)
H(62)*		567 (2)	234 (1)	-142 (1)
H(63)*		482 (2)	150 (1)	-125 (1)
H(101)*	C(10)	643 (2)	317 (1)	185 (1)
H(102)*		439 (2)	345 (1)	181 (1)
H(103)*		562 (2)	405 (1)	146 (1)
H(111)*	C(11)	17 (2)	292 (1)	-425 (1)
H(112)*		69 (2)	357 (1)	-339 (1)
H(113)*		-148 (2)	325 (1)	-394 (1)
H(131)*	C(13)	110 (2)	178 (1)	-389 (1)
H(151)*		253 (3)	53 (1)	-348 (1)
H(152)		58 (3)	16 (1)	-348 (1)
H(153)*	C(15)	249 (3)	19 (1)	-250 (1)
H(171)*		-125 (3)	-14 (1)	-125 (2)
H(172)*		-217 (3)	54 (1)	-206 (2)
H(173)*	C(17)	-71 (3)	79 (1)	-99 (2)
H(181)		213 (4)	1 (2)	-44 (2)
H(182)*		229 (4)	98 (2)	-39 (2)
H(183)	C(18)	336 (4)	47 (2)	-92 (2)

* Indicates H atoms which were found in the difference synthesis.

from the atoms to which they were attached, their positions being dictated by the geometry of the molecule. The methyl H atoms were refined as rigid groups and, because the geometry of the β -ketoamine showed that N is trigonal planar, H(1) was appropriately located and constrained to ride at 1.08 Å from N. The isotropic temperature factors of the methyl and methine H atoms were refined as two single parameters with final U values of 0.14 (2) and 0.07 (6) Å² respectively; that of H(1) was refined independently and had a final value of $U = 0.04$ (4) Å².

After the final cycles of refinement, R was 0.059 and R_w was 0.044 with $w = 1/\sigma^2$. A final difference map had no peaks > 0.39 e Å⁻³, indicating satisfactory convergence. 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 the program system *SHELX* (Sheldrick, 1977).

Description of the structure and discussion

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 their equations and the distances of various atoms from these planes.

The β -ketoamine coordinates through O, and the U atom exhibits pentagonal-bipyramidal coordination. This is consistent with the structures described in parts

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32208 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Bond lengths (Å) and their *e.s.d.*'s

U—O(1)	1.76 (2)	C(7)—O(6)	1.26 (2)
U—O(2)	1.78 (2)	C(7)—C(8)	1.36 (2)
U—O(3)	2.36 (2)	C(8)—C(9)	1.42 (2)
U—O(4)	2.37 (2)	C(9)—O(5)	1.26 (2)
U—O(5)	2.36 (2)	C(9)—C(10)	1.50 (2)
U—O(6)	2.37 (2)	C(11)—C(12)	1.52 (2)
U—O(7)	2.36 (2)	C(12)—O(7)	1.29 (2)
C(1)—C(2)	1.51 (2)	C(12)—C(13)	1.37 (2)
C(2)—O(4)	1.30 (2)	C(13)—C(14)	1.37 (2)
C(2)—C(3)	1.32 (2)	C(14)—C(15)	1.53 (2)
C(3)—C(4)	1.38 (2)	C(14)—N	1.31 (2)
C(4)—C(5)	1.49 (2)	N—C(16)	1.48 (2)
C(4)—O(3)	1.31 (2)	C(16)—C(17)	1.51 (3)
C(6)—C(7)	1.51 (2)	C(16)—C(18)	1.48 (3)

I and II of this series. The interesting feature of the present structure is the strong N—H(1)···O(7) intramolecular hydrogen bond which exists despite the presence of the relatively bulky isopropyl substituent at N. The N···O(7) and H(1)···O(7) distances are 2.674 and 1.846 Å respectively, while the N—H(1)—O(7) angle is 130.2°. This interaction causes the ligand to adopt a ring-like conformation similar to that adopted by the 2-*N*-methylaminopentan-4-one ligand in part I. Pseudoaromaticity is again indicated by the planarity of the ligand (plane 4, Table 6).

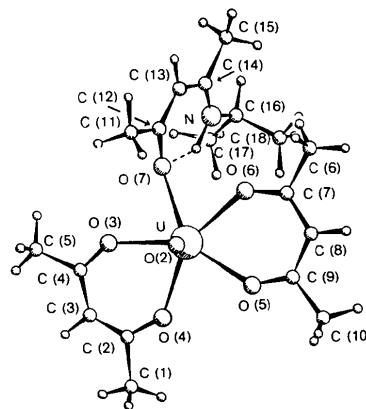


Fig. 1. Perspective view of the molecule with atomic nomenclature. The hydrogen bond is shown as a broken line.

Table 5. Bond angles (°) and their *e.s.d.*'s

O(1)—U—O(2)	180 (1)	C(5)—C(4)—O(3)	113 (2)
O(1)—U—O(3)	93 (1)	C(4)—O(3)—U	135 (2)
O(1)—U—O(4)	88 (1)	U—O(5)—C(9)	137 (2)
O(1)—U—O(5)	91 (1)	O(5)—C(9)—C(10)	117 (2)
O(1)—U—O(6)	92 (1)	O(5)—C(9)—C(8)	124 (2)
O(1)—U—O(7)	85 (1)	C(8)—C(9)—C(10)	119 (2)
O(2)—U—O(3)	87 (1)	C(7)—C(8)—C(9)	125 (2)
O(2)—U—O(4)	92 (1)	O(6)—C(7)—C(8)	125 (2)
O(2)—U—O(5)	89 (1)	O(6)—C(7)—C(6)	115 (2)
O(2)—U—O(6)	88 (1)	C(6)—C(7)—C(8)	120 (2)
O(2)—U—O(7)	95 (1)	U—O(6)—C(7)	137 (2)
O(3)—U—O(4)	70 (1)	U—O(7)—C(12)	139 (2)
O(4)—U—O(5)	77 (1)	O(7)—C(12)—C(11)	115 (1)
O(5)—U—O(6)	72 (1)	O(7)—C(12)—C(13)	124 (2)
O(6)—U—O(7)	70 (1)	C(11)—C(12)—C(13)	122 (2)
O(7)—U—O(3)	72 (1)	C(12)—C(13)—C(14)	123 (2)
U—O(4)—C(2)	136 (2)	C(13)—C(14)—C(15)	119 (2)
C(1)—C(2)—C(3)	121 (2)	C(13)—C(14)—N	125 (2)
O(4)—C(2)—C(3)	125 (2)	C(15)—C(14)—N	116 (2)
C(1)—C(2)—O(4)	114 (2)	C(14)—N—C(16)	131 (2)
C(2)—C(3)—C(4)	127 (2)	N—C(16)—C(17)	110 (2)
C(3)—C(4)—C(5)	125 (2)	N—C(16)—C(18)	110 (2)
C(3)—C(4)—O(3)	122 (2)	C(17)—C(16)—C(18)	112 (2)

Table 6. *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. Asterisks indicate atoms not included in the least-squares calculations.

Plane 1 $4.1497X + 14.2907Y - 9.1915Z = 5.8799$					
	d		d		d
U	0.010	O(4)	0.160	O(6)	0.097
O(3)	-0.100	O(5)	-0.002	O(7)	-0.165
Plane 2 $2.0717X + 16.6906Y - 6.6330Z = 6.8099$					
	d		d		d
U*	-0.549	C(1)*	0.176	C(4)	-0.014
O(3)	-0.027	C(2)	0.039	C(5)*	0.125
O(4)	0.019	C(3)	-0.017		
Plane 3 $4.2964X + 14.4788Y - 8.5893Z = 5.9952$					
	d		d		d
U*	-0.113	C(6)*	0.060	C(9)	0.004
O(5)	-0.003	C(7)	0.000	C(10)*	0.035
O(6)	0.002	C(8)	-0.003		
Plane 4 $6.1528X + 5.1641Y + 4.3421Z = 0.0447$					
	d		d		d
U*	1.425	C(13)	-0.013	C(16)	-0.035
O(7)	0.041	C(14)	0.026	C(17)*	-1.029
C(11)	-0.031	C(15)	0.013	N	0.005
C(12)	0.000				
Plane 5 $4.2852X + 14.7994Y - 7.9243Z = 5.9035$					
	d		d		d
U	0.000	O(3)	0.000	O(4)	0.000
Plane 6 $3.9075X + 14.7359Y - 8.7671Z = 5.9710$					
	d		d		d
U	0.000	O(5)	0.000	O(6)	0.000
Intersection angles (°)					
	Planes 1 and 4	69.6			
	Planes 2 and 5	16.4			
	Planes 3 and 6	3.4			

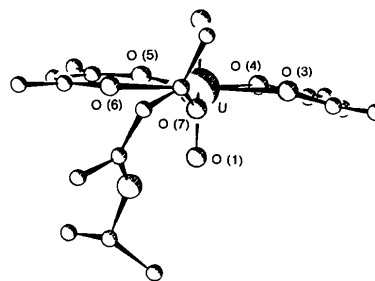


Fig. 2. Molecule viewed along the O(3)—U—O(6) bisector. H atoms have been omitted.

The large angle (69.6°) between the β -ketoamine ligand and the plane defined by the five equatorial O atoms is a result of the steric influence of the isopropyl group.

Fig. 2 views the complex along the bisector of the O(3)—U—O(6) angle, and shows that one acetylacetonone ring is folded about an axis through its O atoms (the angle between planes 2 and 5 is 16.4°). The corresponding angle in the other ring is much smaller (the angle between planes 3 and 6 is 3.4°). The same effect is observed in part I.

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