

6. Vergleich der Kristallstrukturen von $\text{Eu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ und $\text{Eu}(\text{OH})_3$

Wie in der *Einleitung* bereits erwähnt wurde, wandelt sich die zu $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$ isotype Verbindung $\text{Eu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ schon bei Zimmertemperatur unter Wasserstoffentwicklung allmählich in $\text{Eu}(\text{OH})_3$ um. Man kann vermuten, dass strukturelle Beziehungen, die offenbar zwischen diesen Kristallarten existieren und an Hand von Fig. 6 und 7 verdeutlicht werden sollen, den Ablauf der Reaktion begünstigen. In beiden Verbindungen sind die Atome auf zwei Spiegelebenen parallel zu (001) im Abstand $\frac{1}{2}c$ angeordnet. Die Gitterkonstanten c unterscheiden sich nur geringfügig voneinander ($\text{Eu}(\text{OH})_2 \cdot \text{H}_2\text{O}$: $c = 3,652 \text{ \AA}$; $\text{Eu}(\text{OH})_3$ nach Rau & Glover (1964): $c = 3,645 \text{ \AA}$), so dass bei Fig. 6 und 7 der räumliche Aufbau in Blickrichtung übereinstimmt. Allerdings stellt Fig. 6 insofern schon eine Abwandlung der eigentlichen $\text{Eu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ -Struktur dar (vgl. Fig. 5), als die Atome Eu und O(2) unter Beibehaltung der x - und y -Koordinaten um $\frac{1}{2}c$ verschoben sind, während sich alle Atome des Eu'-Polyeders noch in ihren ursprünglichen Lagen befinden. Die gewählte Form der Abbildungen lässt leicht erkennen, dass $\text{Eu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ durch eine horizontale Scherung in $\text{Eu}(\text{OH})_3$ übergehen kann. Die hierzu erforderliche Energie dürfte nicht besonders gross sein, da zwischen den gegeneinander zu verschiebenden Schichten keine elektrostatischen Bindungen, sondern nur Wasserstoffbrücken, z.B. zwischen O(1) und O(2''), gelöst werden müssen. Die Gesamtenergiebilanz ist sicherlich auch deshalb nicht ungünstig, weil bei der Umwandlung durch die Erhöhung der Koordinationszahl des Europiums von 8 auf 9 (vgl. Fig. 4) ein Gewinn an Gitterenergie auftritt.

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The Crystal Structure of the Chloroform Solvate of Dioxodi-8-quinolinolato-8-quinolinoluranium(VI)

BY D. HALL, A. D. RAE AND T. N. WATERS
Chemistry Department, University of Auckland, New Zealand

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The crystal structure of the compound formed when uranium(VI) is precipitated with 8-quinolinol has been determined by three-dimensional X-ray methods, and the molecule formed shown to be dioxodi-8-quinolinolato-8-quinolinoluranium(VI). Two 8-quinolinol molecules are coordinated as bidentate ligands and a third as a monodentate ligand, all three lying approximately in the plane normal to a near-linear uranyl group. Chloroform molecules which co-crystallize exist as solvent of crystallization only, and are slightly disordered.

The compound produced by the precipitation of the uranyl ion with oxine (8-quinolinol) has the formula $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_7\text{NO}$ and contains what appears to

be an extra molecule of oxine. This molecule is lost at 210°C , though at lower temperatures the compound is sufficiently stable for the precipitation of the complex

to be a standard procedure for the gravimetric analysis of uranium(VI). Similar compounds containing excess oxine may be formed with scandium(III), thorium(IV), uranium(IV) and plutonium(VI) (Wendlandt & Horton, 1961), and with various substituted oxines (Horton & Wendlandt, 1963).

It has been shown calorimetrically (von Tassel & Wendlandt, 1959) that there is little energy difference between the systems $[\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2\text{C}_9\text{H}_7\text{NO}(\text{solid})]$ and $[\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2(\text{solid}) \text{ and } \text{C}_9\text{H}_7\text{NO}(\text{solid})]$, and this was taken to indicate that only weak lattice forces bind the extra molecule. The absence of an absorption band characteristic of free oxine has been noted (Charles, Freiser, Friedel, Hilliard & Johnston, 1956) and the formation of salts such as $\text{NaUO}_2(\text{C}_9\text{H}_6\text{NO})_3$ (Bullwinkels & Nobel, 1958) has led to the proposal of an acidic structure $\text{HUO}_2(\text{C}_9\text{H}_6\text{NO})_3$ in which the three oxines are equivalent and the uranium 8-coordinate as in sodium uranyl acetate (Zachariasen, 1959).

It appeared that knowledge of the coordination chemistry of uranium is so fragmentary that the unequivocal solution of this problem could be achieved only by crystal-structure analysis. Crystals of appreciable size were extremely difficult to grow, and the only ones at all suitable for X-ray photography were obtained from chloroform solution. These crystals contained one molecule of chloroform per molecule of uranium complex, but it was thought probable that the chloroform existed only as solvent of crystallization, and that its presence was unlikely to affect any conclusions concerning the nature of the uranium complex. The structure analysis has justified this assumption.

Experimental

Orange-red monoclinic crystals, elongated along [010] and bounded by faces of the forms {100} and $\{\bar{1}01\}$, were grown from chloroform solution. The cell

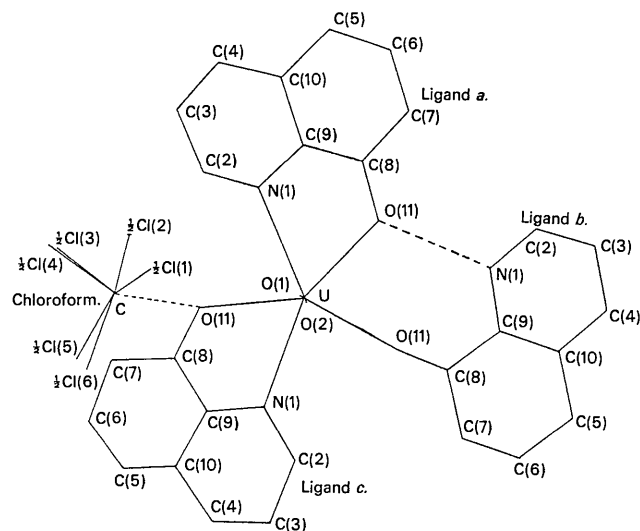


Fig. 1. Numbering of the atoms.

parameters a , c and β were obtained from the $h0l$ Weissenberg photograph by the method of Main & Woolfson (1963), and b from a sodium-chloride-calibrated rotation photograph, as $a=20.76 \pm 0.015$, $b=8.75 \pm 0.02$, $c=15.625 \pm 0.01 \text{ \AA}$, $\beta=97^\circ 30' \pm 5'$. The density was measured by flotation in aqueous zinc bromide solution as 1.94 g.cm^{-3} , whereas the calculated density for 4 molecules per unit cell is 1.95 g.cm^{-3} . The space group is $P2_1/n$, with reflexions systematically absent for $h0l$ with $h+l$ odd, and $0k0$ with k odd.

Weissenberg photographs were taken of the layers ($h0l$) to ($h3l$). All the crystals were slightly deformed and the spot shape on layers for $k > 3$ was too variable to permit satisfactory intensity measurement. Intensities were measured visually, and corrected for absorption by a method based on that of Busing & Levy (1957). Photographs were also taken about the c axis, but the small needle-like crystals gave most unsuitable spots which rapidly fell off in intensity for high values of k . The $hk0$ intensities were measured and were corrected for absorption, but as these corrections were large, the resultant values may not be reliable.

Structure determination

The uranium atom position was readily obtained from projections of the Patterson function, and the R index based on this atom alone was 0.24. All the light atoms other than hydrogen were then located by a three-dimensional electron-density difference synthesis. It was noted that the uranium atom showed a strong apparent preferred vibration along the [010] direction, although it was not known to what extent this was a genuine thermal motion, and to what extent it represented erroneous interlayer scaling due to imperfectly corrected absorption in the $hk0$ data. An electron density difference synthesis projected on (001) gave a satisfactory (but considerably overlapped) representation of the structure and again indicated a marked preferred vibration along [010] for the uranium atom. It appeared that any residual of the absorption effect, if present, was effectively concentrated on the dominant uranium, and it was then practical to correct the uranium as for thermal anisotropy, irrespective of the meaning of the parameters obtained. The values of the relevant uranium temperature parameters were then derived from electron density difference projections on (001), using a two-dimensional modification of the method of Leung, Marsh & Schomaker (1957); see Hall, Rae & Waters (1966).

Refinement then proceeded by three-dimensional electron density difference syntheses, using the $h0l$ to $h3l$ data only. All the atoms except uranium were assumed to be thermally isotropic.

Because of the large covariance between the individual scale constants and the B_{22} parameter of the dominant uranium atom, the value of B_{22} , previously derived, was held constant and the layers of data

individually scaled. Subsequently a least-squares program became available, and refinement was continued in a similar manner.

It was noted that the chlorine temperature parameters were high, and after several cycles anisotropic parameters were introduced. These assumed such extreme values (the effective B along the major axes of the vibration ellipsoid being 22.9, 14.0 and 10.7 Å² for the three atoms respectively) that it was assumed that positional disorder must occur. Each atom was then represented by two half-weight atoms, separated by $2u$ (where $B_{\max} = 8\pi^2 u^2$) along the major axis, and assumed to vibrate isotropically with $B = 7.0$ Å². The half-atoms were then refined independently.

No data appeared to suffer from extinction, but it was that noted the intensities of all high angle data, for

which the Cu $K\alpha_1 - \alpha_2$ splitting was greater than 0.6 mm, had been underestimated. These reflexions were omitted from the final refinement.

Table 2. Values of the uranium temperature parameters in the directions of the principle axes of the vibrational ellipsoid

Axis	$B(\text{Å}^2)$	Direction cosines relative to the a^*bc axes		
1	3.971	0.0084	0.9925	-0.0080
2	3.028	0.7126	-0.0032	0.7016
3	1.375	-0.6962	0.1127	0.7090

β_{ij} values ($\times 10^5$):

β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
132	57	174	1285	-67	254

Table 1. The final values for the fractional coordinates and temperature parameters (Å²)

	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$	$B(\sigma_B)$
U	0.3233 (0)	0.1139 (2)	0.5133 (1)	—
O(1)	0.2991 (12)	0.2401 (46)	0.4526 (16)	4.990 (370)
O(2)	0.3418 (13)	-0.0216 (49)	0.5746 (17)	5.400 (440)
Ligand a				
N(1)	0.3129 (12)	-0.0399 (50)	0.3711 (16)	3.350 (300)
C(2)	0.2617 (18)	-0.1159 (70)	0.3348 (24)	4.950 (712)
C(3)	0.2564 (17)	-0.2089 (85)	0.2582 (22)	4.480 (830)
C(4)	0.3121 (20)	-0.2004 (77)	0.2130 (26)	5.800 (990)
C(5)	0.4273 (19)	-0.1403 (76)	0.2144 (24)	5.280 (800)
C(6)	0.4798 (20)	-0.0558 (73)	0.2568 (26)	5.080 (920)
C(7)	0.4799 (14)	0.0157 (59)	0.3349 (18)	2.810 (350)
C(8)	0.4203 (14)	0.0296 (62)	0.3742 (19)	3.090 (400)
C(9)	0.3666 (15)	-0.0367 (64)	0.3327 (20)	3.620 (480)
C(10)	0.3667 (18)	-0.1372 (71)	0.2538 (23)	4.780 (681)
O(11)	0.4180 (9)	0.0863 (39)	0.4503 (12)	2.950 (160)
Ligand b				
N(1)	0.5076 (13)	0.2815 (53)	0.5311 (18)	4.030 (380)
C(2)	0.5663 (13)	0.2958 (58)	0.5974 (17)	2.570 (310)
C(3)	0.6147 (19)	0.3826 (74)	0.5293 (26)	5.900 (900)
C(4)	0.6030 (20)	0.4707 (80)	0.6038 (27)	6.320 (1.040)
C(5)	0.5403 (20)	0.5424 (77)	0.7159 (27)	7.060 (1.010)
C(6)	0.4764 (20)	0.5375 (76)	0.7443 (26)	6.810 (1.030)
C(7)	0.4270 (20)	0.4465 (77)	0.7052 (26)	6.260 (1.000)
C(8)	0.4386 (15)	0.3297 (66)	0.6363 (20)	3.620 (450)
C(9)	0.4988 (15)	0.3625 (65)	0.6019 (20)	3.630 (440)
C(10)	0.5470 (18)	0.4592 (70)	0.6384 (23)	4.590 (710)
O(11)	0.3964 (10)	0.2486 (42)	0.6014 (14)	3.720 (250)
Ligand c				
N(1)	0.2508 (14)	0.1960 (54)	0.6233 (18)	4.200 (420)
C(2)	0.2682 (20)	0.2483 (76)	0.7009 (27)	5.480 (1.010)
C(3)	0.2216 (20)	0.3346 (76)	0.7535 (26)	7.250 (930)
C(4)	0.1573 (20)	0.3243 (77)	0.7141 (26)	6.420 (960)
C(5)	0.0761 (19)	0.2730 (76)	0.5907 (26)	5.500 (930)
C(6)	0.0563 (20)	0.2057 (77)	0.5220 (26)	5.750 (1.000)
C(7)	0.1015 (18)	0.1097 (70)	0.4771 (23)	4.840 (690)
C(8)	0.1706 (15)	0.1210 (64)	0.5165 (20)	3.590 (410)
C(9)	0.1867 (16)	0.1953 (66)	0.5930 (20)	3.910 (510)
C(10)	0.1360 (15)	0.2600 (64)	0.6303 (20)	3.640 (490)
O(11)	0.2161 (10)	0.0386 (40)	0.4825 (13)	3.240 (200)
Chloroform				
C	0.1140 (20)	-0.2714 (77)	0.5118 (26)	5.820 (1.028)
$\frac{1}{2}$ Cl(1)	0.2279 (14)	-0.4327 (51)	0.5545 (17)	7.520 (350)
$\frac{1}{2}$ Cl(2)	0.2128 (13)	-0.4624 (50)	0.4987 (17)	6.160 (330)
$\frac{1}{2}$ Cl(3)	0.1171 (13)	-0.3421 (50)	0.4304 (17)	8.100 (430)
$\frac{1}{2}$ Cl(4)	0.1043 (13)	-0.2969 (51)	0.4015 (17)	6.920 (410)
$\frac{1}{2}$ Cl(5)	0.1132 (12)	-0.2916 (47)	0.5944 (16)	7.130 (440)
$\frac{1}{2}$ Cl(6)	0.1191 (12)	-0.2599 (48)	0.6041 (16)	7.130 (420)

Table 3. *Bond lengths and bond angles*

(a) The coordination about the uranium atom

Bond lengths			
U—O(1)	1.50 Å	U—O(11) <i>c</i>	2.31 Å
U—O(2)	1.54	U—N(1) <i>a</i>	2.58
U—O(11) <i>a</i>	2.33	U—N(1) <i>c</i>	2.54
U—O(11) <i>b</i>	2.24	(U—N(1) <i>b</i>)	(4.07)

Angles			
O(11) <i>a</i> —U—N(1) <i>a</i>	63.7°	O(11) <i>b</i> —U—O(11) <i>a</i>	77.0°
O(11) <i>c</i> —U—N(1) <i>c</i>	65.0	O(11) <i>b</i> —U—N(1) <i>c</i>	81.4
O(11) <i>c</i> —U—N(1) <i>a</i>	73.1	O(1)—U—O(2)	174.8
O(1)—U—O(11) <i>a</i>	92.2°	O(2)—U—O(11) <i>a</i>	91.8°
O(1)—U—N(1) <i>a</i>	81.9	O(2)—U—N(1) <i>a</i>	96.8
O(1)—U—O(11) <i>b</i>	98.1	O(2)—U—O(11) <i>b</i>	86.2
O(1)—U—N(1) <i>c</i>	92.4	O(2)—U—N(1) <i>c</i>	85.2
O(1)—U—O(11) <i>c</i>	81.3	O(2)—U—O(11) <i>c</i>	93.4

(b) The ligands *a*, *b*, *c*

Bond lengths			
N(1)—C(2)	1.31 Å	Ligand <i>b</i>	1.40 Å
N(1)—C(9)	1.34	Ligand <i>c</i>	1.30 Å
C(2)—C(3)	1.44		1.35
C(3)—C(4)	1.44		1.30
C(4)—C(10)	1.34		1.55
C(5)—C(10)	1.48		1.39
C(5)—C(6)	1.40		1.44
C(6)—C(7)	1.37		1.31
C(7)—C(8)	1.46		1.24
C(8)—C(9)	1.34		1.50
C(8)—O(11)	1.30		1.48
C(9)—C(10)	1.51		1.36

Angles			
C(9)—N(1)—C(2)	119.5°	Ligand <i>b</i>	119.1°
N(1)—C(2)—C(3)	127.4	Ligand <i>c</i>	117.5°
C(2)—C(3)—C(4)	113.9		123.6
C(3)—C(4)—C(10)	118.2		111.4
C(10)—C(5)—C(6)	116.4		125.6
C(5)—C(6)—C(7)	124.4		122.9
C(6)—C(7)—C(8)	121.0		121.0
C(7)—C(8)—C(9)	117.2		113.5
C(7)—C(8)—O(11)	124.0		120.1
C(9)—C(8)—O(11)	118.4		122.7
C(8)—C(9)—N(1)	118.7		119.2
N(1)—C(9)—C(10)	116.6		120.0
C(8)—C(9)—C(10)	123.3		114.8
C(4)—C(10)—C(5)	120.5		118.8
C(4)—C(10)—C(9)	122.0		119.4
C(5)—C(10)—C(9)	116.6		128.1
			117.0
C(8)—O(11)—U	124.6		123.1
C(9)—N(1)—U	113.6		123.1
C(2)—N(1)—U	127.0		112.7
			124.0
			118.1
			114.2
			128.1

(c) The chloroform molecule

Bond lengths					
C— $\frac{1}{2}$ Cl(1)	1.99 Å	C— $\frac{1}{2}$ Cl(3)	1.62 Å	C— $\frac{1}{2}$ Cl(5)	1.78 Å
C— $\frac{1}{2}$ Cl(2)	1.98	C— $\frac{1}{2}$ Cl(4)	1.99	C— $\frac{1}{2}$ Cl(6)	1.82

Half-atom separation					
$\frac{1}{2}$ Cl(1)— $\frac{1}{2}$ Cl(2)	0.92 Å	$\frac{1}{2}$ Cl(3)— $\frac{1}{2}$ Cl(4)	0.63 Å	$\frac{1}{2}$ Cl(5)— $\frac{1}{2}$ Cl(6)	0.33 Å

(d) The N(1)—O(11) hydrogen bond between ligands *a* and *b*

Bond lengths			
N(1) <i>b</i> —O(11) <i>a</i>	2.71 Å		

Bond angles			
U—O(11) <i>a</i> —C(8) <i>a</i>	124.6°	C(2) <i>b</i> —N(1) <i>b</i> —O(11) <i>a</i>	117.4°
U—O(11) <i>a</i> —N(1) <i>b</i>	107.7	C(9) <i>b</i> —N(1) <i>b</i> —O(11) <i>a</i>	123.5
C(8) <i>a</i> —O(11) <i>a</i> —N(1) <i>b</i>	124.0	C(9) <i>b</i> —N(1) <i>b</i> —C(2) <i>b</i>	119.1

Table 3 (*cont.*)(e) The C—O(11) hydrogen bond between chloroform and ligand *c*.

Bond length			
C — O(11)	2.98 Å		
Bond angles			
U — O(11) — C	126.1°	U — O(11) — C(8)	118.1°
C(8) — O(11) — C	97.9	$\frac{1}{2}$ Cl — C — O(11)	117.3, 114.9, 117.7 123.4, 99.5, 107.9

(f) Other intramolecular approaches

O(11) <i>b</i> —N(1) <i>c</i>	3.12 Å	O(11) <i>b</i> —C(2) <i>c</i>	3.26 Å
O(11) <i>c</i> —N(1) <i>a</i>	2.91	O(11) <i>c</i> —C(2) <i>a</i>	2.94
O(11) <i>a</i> —O(11) <i>b</i>	2.84		

Table 4. *Intermolecular approaches*

The equivalent position of the first atom is *x, y, z*.
The equivalent position of the second atom is as shown.

(a) Approaches to the chloroform molecule

<i>x, y - 1, z</i>			
$\frac{1}{2}$ Cl(1) — O(1)	3.68 Å	$\frac{1}{2}$ Cl(2) — O(1)	3.30 Å
$\frac{1}{2}$ Cl(1) — N(1) <i>c</i>	3.43	$\frac{1}{2}$ Cl(2) — N(1) <i>c</i>	3.60
$\frac{1}{2}$ Cl(1) — C(9) <i>c</i>	3.44	$\frac{1}{2}$ Cl(2) — C(9) <i>c</i>	3.41
$\frac{1}{2}$ Cl(1) — C(10) <i>c</i>	3.59	$\frac{1}{2}$ Cl(2) — C(10) <i>c</i>	3.68
$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$			
$\frac{1}{2}$ Cl(3) — C(6) <i>a</i>	3.62	$\frac{1}{2}$ Cl(4) — C(6) <i>a</i>	3.81
$\frac{1}{2}$ Cl(3) — C(5) <i>a</i>	3.49	$\frac{1}{2}$ Cl(4) — C(5) <i>a</i>	3.52
$1 - x, -y, 1 - z$			
$\frac{1}{2}$ Cl(1) — C(3) <i>b</i>	3.71	$\frac{1}{2}$ Cl(2) — C(3) <i>b</i>	3.73
$\frac{1}{2} - x, -\frac{1}{2}y, 1\frac{1}{2} - z$			
$\frac{1}{2}$ Cl(5) — C(2) <i>c</i>	3.78	$\frac{1}{2}$ Cl(6) — C(2) <i>c</i>	3.58

(b) Approaches between centrosymmetrically related molecules

$1 - x, -y, 1 - z$			
O(2) — C(2) <i>b</i>	3.35 Å	C(7) <i>a</i> — C(8) <i>b</i>	3.46 Å
O(11) <i>a</i> — C(2) <i>b</i>	3.45	C(7) <i>a</i> — C(9) <i>b</i>	3.46
C(8) <i>a</i> — C(2) <i>b</i>	3.47	C(7) <i>a</i> — O(11) <i>b</i>	3.50
C(8) <i>a</i> — N(1) <i>b</i>	3.35	C(6) <i>a</i> — C(8) <i>b</i>	3.26
C(7) <i>a</i> — N(1) <i>b</i>	3.33	C(6) <i>a</i> — C(9) <i>b</i>	3.46
C(5) <i>a</i> — C(10) <i>b</i>	3.61	C(10) <i>a</i> — C(4) <i>b</i>	3.67
C(10) <i>a</i> — C(10) <i>b</i>	3.63	C(9) <i>a</i> — C(3) <i>b</i>	3.70
C(9) <i>a</i> — C(2) <i>b</i>	3.62		
$1 - x, 1 - y, 1 - z$			
N(1) <i>b</i> — C(10) <i>b</i>	3.55	C(2) <i>b</i> — C(9) <i>b</i>	3.55
N(1) <i>b</i> — C(4) <i>b</i>	3.62	C(2) <i>b</i> — C(10) <i>b</i>	3.64
C(3) <i>b</i> — C(9) <i>b</i>	3.66	O(1) — C(4) <i>b</i>	3.44
N(1) <i>b</i> — C(9) <i>b</i>	3.74	C(3) <i>b</i> — O(11) <i>b</i>	3.81
C(3) <i>b</i> — C(8) <i>b</i>	3.67	C(2) <i>b</i> — C(8) <i>b</i>	3.88

(c) Approaches to uranyl oxygen atoms

$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$			
O(1) — C(4) <i>a</i>	3.27 Å	O(1) — C(3) <i>a</i>	3.37 Å
$\frac{1}{2} - x, -\frac{1}{2} + y, 1\frac{1}{2} - z$			
O(2) — C(3) <i>c</i>	3.39	O(2) — C(4) <i>c</i>	3.56
<i>x, 1 + y, z</i>			
O(1) — $\frac{1}{2}$ Cl(1)	3.68	O(1) — $\frac{1}{2}$ Cl(2)	3.30
$1 - x, -y, -z$			
O(2) — C(2) <i>b</i>	3.35	O(2) — C(3) <i>b</i>	3.72
$1 - x, 1 - y, 1 - z$			
O(1) — C(4) <i>b</i>	3.44	O(1) — C(3) <i>b</i>	3.75

(d) Some other approaches

$\frac{1}{2} - x, -\frac{1}{2} + y, 1\frac{1}{2} - z$			
C(2) <i>c</i> — C(3) <i>c</i>	3.69 Å	C(3) <i>a</i> — C(2) <i>a</i>	3.85 Å
$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$			
C(5) <i>a</i> — C(7) <i>c</i>	3.69	C(3) <i>a</i> — C(2) <i>a</i>	3.85

van der Waals radii: O = 1.4 Å, N = 1.5 Å, Cl = 1.8 Å, half thickness of aromatic molecule, 1.7 Å.

The scattering factors used were those of Thomas, Umeda & King (1958) for uranium [using a real dispersion correction of $-6.8e$ (Roof, 1961)], of Viervoll & Øgrim (1949) for chlorine and of Freeman (1959) for the light atoms. The final R index for the 2090 observed reflexions was 0.104. Individual values for the layers of data were $h0l$, 0.086; $h1l$, 0.085; $h2l$, 0.112; $h3l$, 0.132; $hk0$, 0.123.

The atom coordinates, with standard deviations in parenthesis, are listed in Table 1, together with the isotropic temperature parameters. The apparent temperature parameters of the uranium atom are listed in Table 2, bond lengths, bond angles and other intramolecular approaches in Table 3, and intermolecular approaches of note in Table 4. The scheme for the labelling of atoms is shown in Fig. 1.

The average standard deviation for bonds involving the uranium atom is 0.03 Å, and for bonds between

light atoms, 0.06 Å. A block-diagonalization approximation was used in the least-squares refinement, making no allowance for covariance between the parameters of different atoms, and it is likely that the standard deviations relevant to the uranyl oxygen atoms [O(1) and O(2)] are greater than indicated, as these atoms proved to be particularly sensitive to changes in the uranium or scale parameters.

Discussion

The three oxine molecules are all coordinated to the uranium, two as bidentate ligands through the nitrogen and the phenolic oxygen atoms, and the third as a monodentate ligand through the oxygen only (Fig. 1). All three oxines lie approximately (but only approximately – see Fig. 2) in a plane perpendicular to the linear uranyl group [$O(1)-U-O(2)=174.8^\circ$]. The $U-O(11)$

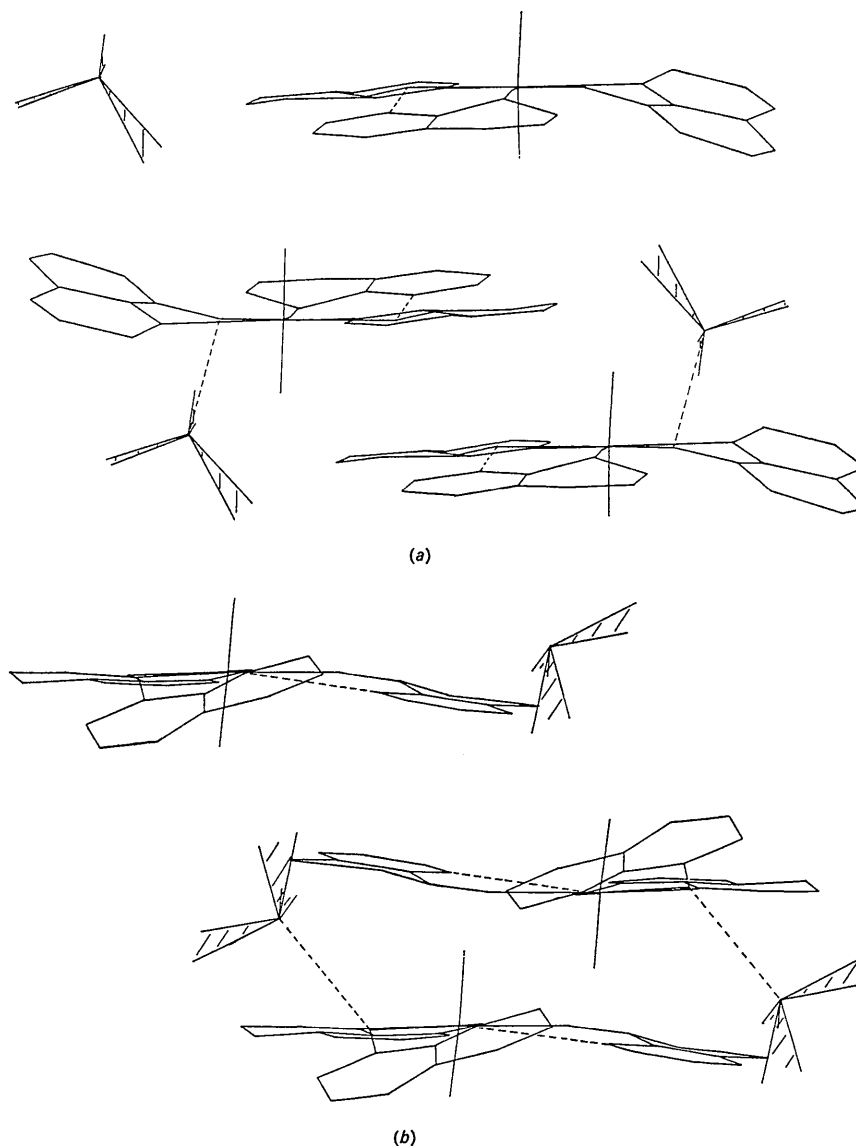


Fig. 2. Projections of the structure along axes parallel to the mean molecular plane. (a) along X , (b) along Y .

Table 5 (cont.)

Table with multiple columns of numerical data, organized in groups of 5 columns each. Each group has a header row with labels H, K, L, FO, FC. The data consists of rows of numbers, some with asterisks, representing various measurements or observations.

* = UNOBSERVED (FO = FMIN)

DIOXDI-8-QUINOLINOLATO-8-QUINOLINOLURANIUM(VI)

Table 5 (cont.)

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
1	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
2	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
3	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
4	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
5	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
6	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
7	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
8	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
9	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
10	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
11	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
12	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
13	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
14	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
15	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
16	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
17	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
18	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
19	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
20	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
21	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
22	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
23	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
24	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6
25	2	2	27.8	21.1	5	2	3	21.0	24.7-	19	2	5	12.2	4.1-	0	2	8	11.0	0.1-	4	2	11	24.0	21.6

* = UNOBSERVED (FO = FMIN)

Table 5 (cont.)

Table with multiple columns of numerical data, organized in groups of 4 columns each. Each group has a header row with labels H, K, L, FO, FC. The data consists of rows of numbers, some with asterisks, representing various measurements or values.

* = UNOBSERVED (FO = FMIN)

bonds are similar in length, 2.33, 2.24 and 2.31 Å, while the coordinated U–N(1) bond lengths are 2.58 and 2.54 Å. The ligand *b* is twisted away from the uranium atom so that the angle U–O(11)*b*–C(8)*b* is 169.3°, as compared with 124.6° and 118.1° for ligands *a* and *c*. The N(1)*b*–U distance is 4.07 Å, *i.e.* the atom is not coordinated, but instead makes an approach of 2.71 Å ($\sigma=0.04$ Å) to atom O(11) of ligand *a*. It is reasonable to suppose that the proton associated with the additional ligand is involved in a hydrogen bond between O(11)*a* and N(1)*b*, and the angles about this approach support this postulate. The singly coordinated ligand *b* must then exist as a zwitterion, which fact would account for the acid properties of the complex (Bullwinkel & Nobel, 1958).

The mean plane through the uranium and five coordinated ligand atoms was calculated as $-0.1571x + 0.8354y - 0.5267z = -4.222$ and the individual displacements from this plane are:

U	O(11) <i>a</i>	O(11) <i>b</i>
-0.013 Å	-0.031 Å	+0.044 Å
O(11) <i>c</i>	N(1) <i>a</i>	N(1) <i>c</i>
+0.027 Å	+0.009 Å	-0.036 Å

The atomic coordinates may be referred to orthogonal axes, the *Z* direction being normal to this plane, by the transformation

$$\begin{aligned} X &= 11.707x + 4.495y + 8.810z, \\ Y &= 16.839x - 1.709y - 10.271z, \\ Z &= -3.262x + 7.310y - 7.819z. \end{aligned}$$

Projections of the structure down *X* and *Y* are shown in Fig. 2, whence it may be seen that although the ligand molecules are approximately planar individually, they (particularly ligand *c*) are twisted out of the coordination plane to facilitate packing. The mean planes through ligands *a*, *b* and *c* are (with respect to the crystal axes)

$$\begin{aligned} -0.2179x + 0.8331y - 0.5084z &= -4.500 \\ -0.3169x + 0.7333y - 0.6015z &= -6.150 \\ 0.2403x + 0.8433y - 0.4808z &= -2.394 \end{aligned}$$

and these make angles of 3.7, 11.7 and 23.1° with the coordination plane.

It is notable that atom O(11) of ligand *c*, which is the ligand most severely twisted from coplanarity, makes an approach of 2.98 Å ($\sigma=0.07$ Å) to the carbon atom of the chloroform molecule. The angles $\frac{1}{2}\text{Cl}-\text{C}-\text{O}(11)c$ vary from 99.5 to 123.4°, and the angles about the oxygen from 97.9 to 126.1°. This geometry would be appropriate for a C–H···O hydrogen bond, which is thought to occur when the C···O approach is less than 3.3 Å (Sutor, 1963). The distortion of ligand *c* has the effect of permitting this without causing any unduly close approach of the chloroform to the uranyl oxygen atoms.

The chloroform molecule occupies a hole between complex molecules separated by a distance *b*. It may be seen from Table 4 that none of the approaches involving the half-weight chlorine atoms is particularly short, and the absence of any strong intermolecular force apparently permits the small degree of disorder observed.

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