

The Structure of Diaquabis(crotonato)dioxouranium(VI)

BY N. W. ALCOCK, T. J. KEMP AND P. DE MEESTER

Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL, England

(Received 8 December 1980; accepted 2 June 1981)

Abstract

[U(C₄H₅O₂)₂(H₂O)₂O₂] is monoclinic, space group *P*2₁/*c*, with *a* = 7.994 (1), *b* = 7.658 (1), *c* = 10.585 (2) Å, β = 95.09 (1)°, *U* = 645.4 (2) Å³, *Z* = 2, *D_m* = 2.43, *D_c* = 2.45 Mg m⁻³, μ(Mo *K*α) = 11.94 mm⁻¹. 949 reflections with *I*/*σ*(*I*) ≥ 3.0 were measured by four-circle diffractometry and the structure was refined to *R* = 0.026. The linear UO₂ groups [U—O 1.759 (7) Å] are coordinated by the CO₂ groups of two crotonate anions [U—O 2.453 (7) and 2.543 (7) Å], and two water molecules [U—O 2.479 (6) Å]. Internal hydrogen bonds are formed between the coordinated water molecules and the uranyl O atoms.

The title compound was prepared in the course of studies of the photochemistry of uranium compounds containing either unsaturated or carboxylate ligands (Alcock, de Meester & Kemp, 1979). Its photochemical behaviour proved to be complex, with the formation of at least four products in solution, which could not be fully characterized, while in the solid state no appreciable reaction appeared to take place. The crystal structure provides the explanation for this, as the double bonds are a considerable distance apart, preventing cycloaddition. It also reveals unusual interactions between the H atoms of the ligands and the uranyl O atoms.

Experimental

The complex was prepared by adding 1 mmol of uranyl nitrate hexahydrate dissolved in 10 ml of water to 2 mmol of crotonic acid dissolved in 20 ml of water. Dilute aqueous NaOH was added to the mixture until a yellow precipitate appeared. The solution was warmed to ca 353 K, filtered and allowed to cool. Yellow prismatic crystals appeared in a few hours. A crystal of approximate size 0.30 × 0.17 × 0.05 mm, bounded by the faces (100), ($\bar{1}$ 00), ($\bar{2}$ 11), ($\bar{2}$ $\bar{1}$ 1), ($\bar{2}$ 1 $\bar{1}$) and ($\bar{2}$ $\bar{1}$ $\bar{1}$) was mounted on a Syntex *P*2₁ diffractometer. Graphite-monochromatized Mo *K*α radiation was used. Accu-

rate unit-cell dimensions were obtained by least-squares methods.

The data were collected to 2θ = 55°, by the θ–2θ scan technique, with a scan starting 0.9° below the *K*α₁ position and ending 0.9° above the *K*α₂ position. The scan time was twice the background time. The scan speed varied between 2.0 and 29.3° min⁻¹, depending on the intensity of a 2 s prescan. The intensities of three standard reflections, remeasured every 97 reflections, did not vary significantly during data collection. A total of 949 independent reflections had *I* ≥ 3σ(*I*), and only those were used in the subsequent solution and refinement of the structure. The data were corrected for Lorentz and polarization effects, and for absorption (Alcock, 1970). For the crystal used, the transmission coefficients (*F*) ranged from 0.431 to 0.791.

Solution and refinement of the structure

The XRAY 76 system (Stewart, 1976) was used for the calculations. Full-matrix least-squares refinement was used throughout and the function minimized was ∑ *w*(*F_o* – *F_c*)². Atomic scattering factors and the real and imaginary parts of the anomalous dispersion for U were taken from *International Tables for X-ray Crystallography* (1974). The density and the volume of the unit cell indicated that the U atom is in special position 2(*a*) (symmetry $\bar{1}$). Its location at the origin allowed all non-hydrogen atoms to be recognized in a subsequent difference Fourier map. Anisotropic refine-

Table 1. Fractional coordinates (×10⁴) and average principal *U* values for the non-hydrogen atoms with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
U	0	0	0	0.0193
O(1)	–1979 (8)	875 (10)	248 (7)	0.033
O(2)	1302 (9)	2453 (9)	1209 (6)	0.032
O(3)	1104 (8)	2851 (9)	–835 (6)	0.028
O(4)	617 (9)	–506 (9)	2307 (6)	0.033
C(1)	1696 (12)	3358 (12)	266 (8)	0.028
C(2)	2727 (11)	4903 (30)	452 (8)	0.032
C(3)	3359 (12)	5410 (12)	1601 (10)	0.036
C(4)	4455 (16)	6951 (18)	1891 (14)	0.053

ment of these atoms reduced R to 0.028. The next difference Fourier map showed the seven independent H atoms with heights ranging from 0.4 to 0.7 e. In the final cycles of refinement, a weight $w = XY$ was used, where $X = 1.0$ or $(\sin \theta/\lambda)/0.31$ if $(\sin \theta/\lambda) < 0.31$, or $0.47/(\sin \theta/\lambda)$ if $(\sin \theta/\lambda) > 0.47$, and $Y = 1.0$ or $F/47$ if $F < 47$ or $80/F$ if $F > 80$.

All non-hydrogen atoms were varied anisotropically, and the H atoms were included as fixed atoms with U^s set at 0.05 \AA^2 . The final agreement factors are $R = 0.026$ and $R_w = 0.031$. The final difference Fourier map did not show any peak higher than 0.6 e except for two of 2.1 and 1.9 e around the U atom. The fractional coordinates of the non-hydrogen atoms are given in Table 1, those of the H atoms in Table 2.* Bond lengths and angles are in Table 3.

* Anisotropic temperature factors of the non-hydrogen atoms and a list of observed and calculated structure amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36370 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates of the H atoms ($\times 10^3$)

	x	y	z
H(1)	303	542	-28
H(2)	294	484	235
H(3)	430	775	141
H(4)	426	759	265
H(5)	553	651	201
H(6)	20	17	310
H(7)	-33	3	182

Table 3. Bond lengths (\AA) and bond angles ($^\circ$)

U—O(1)	1.759 (7)	C(1)—O(3)	1.279 (11)
U—O(2)	2.453 (7)	C(1)—C(2)	1.445 (21)
U—O(3)	2.543 (7)	C(2)—C(3)	1.332 (15)
U—O(4)	2.479 (6)	C(3)—C(4)	1.486 (16)
C(1)—O(2)	1.278 (11)		
O(1)—U—O(2)	88.6 (3)	O(2)—C(1)—O(3)	116.9 (8)
O(1)—U—O(3)	94.0 (3)	O(2)—C(1)—C(2)	121.0 (8)
O(2)—U—O(4)	90.9 (3)	O(3)—C(1)—C(2)	122.2 (8)
O(2)—U—O(3)	51.7 (2)	C(1)—C(2)—C(3)	121.9 (1.2)
O(2)—U—O(4)	64.4 (2)	C(2)—C(3)—C(4)	126.1 (1.2)
O(3)—U—O(4)	64.4 (2)		
Hydrogen bonding			
O(4)···O(3 ⁱⁱ)	2.831 (9)	H(6)···O(3 ⁱⁱⁱ)	1.99
O(4)···O(1)	3.062 (9)	H(7)···O(1)	2.13
		O(4)—H(6)···O(3 ⁱⁱⁱ)	134
		O(4)—H(7)···O(1)	161
C=C···C=C interaction			
		C(2)···C(2 ⁱⁱⁱ)	3.84 (1)
		C(3)···C(3 ⁱⁱⁱ)	4.46 (1)

Roman superscripts refer to atoms in the following positions: (i) $-x, -y, -z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, 1 - y, -z$.

Results and discussion

The crystal structure reveals the expected uranyl system coordinated by two bidentate carboxylate groups and two water molecules (Fig. 1). The U—O(uranyl) distance of 1.759 (7) \AA is standard for an uncrowded hexacoordinated UO_2^{2+} group [cf. 1.759 (4) and 1.760 (4) \AA in two forms of $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$: the dihydrate (Dalley, Mueller & Simonsen, 1971), the hexahydrate (Taylor & Mueller, 1965)]. The equatorial U—O distances are also within the range observed, though the U—O(H_2O) is rather longer than in either of the two nitrates (2.446–2.457 and 2.397 \AA respectively). The bond lengths in the ligands are also normal. The nearest C=C to C=C contact is 3.84 \AA at one end of the double bond and 4.46 \AA at the other. The contrast between this and the

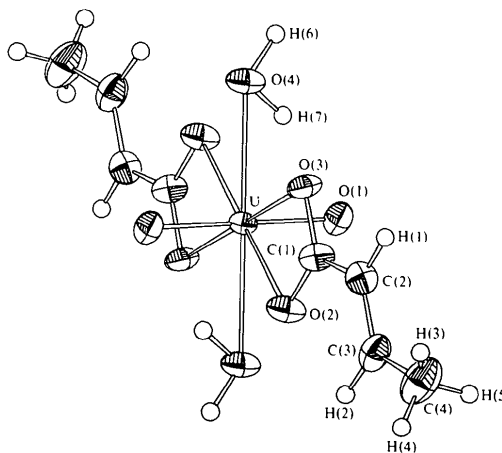


Fig. 1. View of the complex. Ellipsoids for the non-hydrogen atoms are scaled at the 50% probability level. H atoms are represented by circles of arbitrary size.

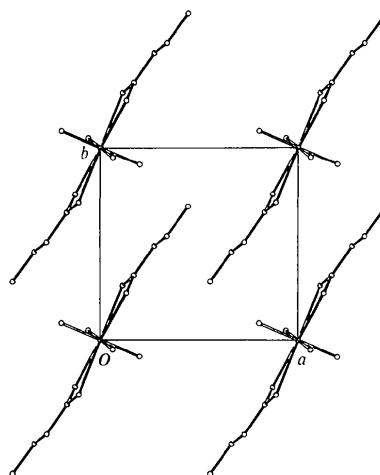


Fig. 2. Packing of the molecules in the cell viewed down c , showing the layer of molecules with $z_1 = 0.0$.

3.50 Å contacts in $\text{UO}_2\text{Cl}_2(\text{dibenzylideneacetone})_2$ (Alcock, de Meester & Kemp, 1979) immediately explains why the crotonate complex does not dimerize in the solid state.

The most striking feature of the structure is the interaction between the coordinated H_2O and the uranyl oxygen [O(1)]. The two O atoms are 3.06 Å apart, this distance being controlled by the geometry around the U atom. The protons on O(4) are not constrained by the rest of the structure, and H(7) is found to be close to the O(4)—O(1) line, with O(4)—H(7)···O(1) 161°. This is undoubtedly a hydrogen-bond interaction even though the unfavourable orientation at O(1) implies that the attraction is principally electrostatic. A normal hydrogen bond is formed by H(6), to O(3) of another molecule.

Comparisons can only usefully be made with the two uranyl nitrate complexes, as these are the only H_2O -containing uranyl complexes where the protons have been located. In the hexahydrate (Taylor & Mueller, 1965), there is a network of intermolecular hydrogen bonds, and the protons of the water molecules lie in the uranyl equatorial plane. In the dihydrate (Dalley *et al.*, 1971), one water molecule again forms intermolecular hydrogen bonds, but the other is twisted towards the orientation in the crotonate

complex; however, the bond angle O—H···O(uranyl) is 111°, indicating that the involvement with the uranyl oxygen must be weaker than in the crotonate. It seems likely that the bulk of the crotonate ligand, compared to nitrate, has the effect of holding the complex molecules too far apart for them to form a full intermolecular hydrogen-bonding network.

Fig. 2 shows the packing of the molecules.

We thank SRC for a postdoctoral fellowship (PdeM).

References

- ALCOCK, N. W. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 271–278. Copenhagen: Munksgaard.
- ALCOCK, N. W., DE MEESTER, P. & KEMP, T. J. (1979). *J. Chem. Soc. Dalton Trans.* pp. 921–926.
- DALLEY, N. K., MUELLER, M. H. & SIMONSEN, S. H. (1971). *Inorg. Chem.* **10**, 323–328.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Centre. Univ. of Maryland, College Park, Maryland.
- TAYLOR, J. C. & MUELLER, M. H. (1965). *Acta Cryst.* **19**, 536–543.

Acta Cryst. (1982). B38, 107–111

Structural Studies on Metal Complexes of Chiral Cyclen. II. Chloro[(2*R*,5*R*,8*R*,11*R*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]copper(II) Chloride, and Related Complexes

BY TOSIO SAKURAI, KIMIKO KOBAYASHI, AKIRA HASEGAWA, SEI TSUBOYAMA AND KAORU TSUBOYAMA

The Institute of Physical and Chemical Research (Rikagaku Kenkyusho), Wako-shi, Saitama 351, Japan

(Received 26 February 1981; accepted 8 June 1981)

Abstract

Three related metal complexes, $\text{C}_{16}\text{H}_{36}\text{Cl}_2\text{CuN}_4$ [tetragonal, space group $P4_12_1$, $a = b = 15.564$ (2), $c = 9.843$ (1) Å, $U = 2384.5$ (6) Å³, $Z = 4$, $D_o = 1.30$, $D_c = 1.298$ Mg m⁻³, final $R = 5.5\%$ for 1246 observed reflections], $\text{C}_{44}\text{H}_{60}\text{Cl}_2\text{CuN}_4$ [orthorhombic, space group $C222_1$, $a = 15.487$ (9), $b = 20.013$ (9), $c = 14.287$ (7) Å, $U = 4429$ (4) Å³, $Z = 4$, $D_o = 1.31$, $D_c = 1.27$ Mg m⁻³, final $R = 7.0\%$ for 1780 observed reflections], and $\text{C}_{44}\text{H}_{60}\text{Cl}_2\text{CoN}_4$ [orthorhombic, space group $C222_1$, $a = 15.31$ (1), $b = 19.84$ (1), $c = 15.02$ (1) Å, $U = 4566$ (6) Å³, $Z = 4$, $D_o = 1.26$, $D_c =$

1.24 Mg m⁻³ (first crystal); $a = 15.37$ (1), $b = 20.07$ (1), $c = 14.54$ (1) Å, $U = 4489$ (6) Å³, $Z = 4$, $D_o = 1.26$, $D_c = 1.26$ Mg m⁻³ (second crystal); final $R = 12.4\%$ for 741 observed reflections], were studied. The 12-membered ligand ring forms a square conformation. The metal atoms form a square-pyramidal structure with five coordination. The deviations of metal atoms from the plane formed by the four N atoms are 0.544 (3) and 0.73 (1) Å for Cu and Co respectively. Markedly short apical metal–chlorine distances are observed; *viz.* 2.42 (2) Å for Cu and 2.26 (1) Å for Co.

0567-7408/82/010107-05\$01.00

© 1982 International Union of Crystallography