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The Structure of Anhydrous Bis(hydroxyacetato)dioxouranium(VI): $UO_2(CH_2OHCOO)_2$

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Abstract

The crystal structure of anhydrous bis(hydroxyacetato)dioxouranium(VI), $U(C_2H_3O_3)_2O_2$, $C_4H_6O_8U$, has been established by X-ray diffraction on a single crystal at 291 K. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 7·964 (2), b = 7·583 (3), c = 16·807 (4) Å, β = 123·80 (2)°, Z = 4, V = 843·4 Å^3, M_r = 420·11, d_m = 3·248, d_x = 3·308 Mg m^{-3}, $F(000)$ = 744, μ(Mo $K\bar{\alpha}$) = 18·217 mm^{-1}, T = 291 K. The structure has been determined by the heavy-atom method from 1956 Mo $K\bar{\alpha}$ intensities measured on a four-circle diffractometer and refined by full-matrix least-squares computations. The final weighted residual is 0·0521 (conventional R = 0·0561). The uranium atom is surrounded by a pentagonal bipyramid of oxygen atoms. The apical oxygen atoms are those of the uranyl group which is almost linear [OUO angle = 177·8 (3)°]. There are two kinds of glycolato groups: tridentate, which are both chelating a single U atom and bridging two different U atoms, and bidentate, which only bridge two U atoms. The structure is made up of infinite chains which are linked to each other by hydrogen bonds.

Introduction

During our investigations on photochemical and structural properties of uranyl carboxylates (Mentzen, Puaux & Loiseleur, 1977; Mentzen, 1977; Mentzen, Puaux & Sautereau, 1978*a*,*b*) bis(hydroxyacetato)-dioxouranium(VI) (uranyl bisglycolate) has been prepared. A preliminary infrared and X-ray study has already been published (Mentzen & Sautereau, 1979) and we have undertaken the determination of the crystal structure in order to determine the environment of the uranium atom and its coordination in relation to our interpretation of previous data, which conflicts with the recently published assumptions of Sbrignadello, Tomat, Battiston, Vigato & Traverso (1978).

Experimental results

Uranyl bisglycolate was prepared by the method previously described by Courtois (1914). A small prismatic crystal (0·2 × 0·15 × 0·15 mm) was mounted on a four-circle Enraf–Nonius CAD-4 automatic diffractometer. 4171 independent intensities corresponding to the $hk\bar{l}$ and $h\bar{k}\bar{l}$ triplets (quarter reflexion sphere) were collected with an ω–2θ scan for $1 < \theta < 36°$. Intensity control was performed every hour on the $1\bar{3}1$ reflexion. After data reduction 1956 unique reflexions with $I > 2\sigma(I)$ were retained and their intensities corrected for Lorentz and polarization factors and absorption (μR = 1·37 was calculated assuming a cylindrical specimen). The conditions limiting possible reflexions are in agreement with the space group $P2_1/c$ (C^5_{2h} No. 14), *i.e.* $0k0$, $k = 2n$ and $h0l$, $l = 2n$.

Structure determination

The interpretation of the Patterson function gave the atomic positions of the uranium atom. A Fourier synthesis with the structure factors and the phases corresponding to the heavy atom revealed the positions of the seven oxygen atoms around uranium. A subsequent difference-Fourier synthesis revealed the remaining oxygen atom and the four carbon atoms. The atomic coordinates and the isotropic thermal parameters of the thirteen atoms of the asymmetric unit were refined by minimizing $\sum w(|F_o| - |F_c|)^2$, the weighting function being $w = (2|F_o|_{\min} + |F_o| + 2F_o^2/|F_o|_{\max})^{-1}$. After four iterations, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ = 0·0732, with conventional $R = (\sum ||F_o| - |F_c||)/(\sum |F_o|)$ = 0·0804. At this stage of the refinement the anisotropic thermal parameters and the weighting function $w = (a + b|F_o|)^2$ (Stout & Jensen, 1968) were introduced for all the atoms and $R_w(R)$ became 0·0559 (0·0549), but the Hamilton test (Hamilton, 1965) showed that the model was not significantly improved. Accordingly, the anisotropic thermal parameters were only applied to the uranium atom, the final value of $R_w(R)$ being 0·0521 (0·0561). Correction for anomalous dispersion did not improve

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Table 1. *Relative atomic coordinates with standard deviations, equivalent isotropic thermal parameter for the uranium atom and isotropic thermal parameters for the other atoms*

	x	y	z	B (Å^2)
U	0·04038 (4)	0·20391 (3)	0·13628 (2)	1·4
OU(1)	−0·1563 (8)	0·2879 (8)	0·0271 (4)	2·9
OU(2)	0·2427 (7)	0·1159 (8)	0·2440 (4)	2·5
O(1)	−0·2005 (7)	0·1842 (6)	0·1816 (4)	2·2
O(2)	0·0432 (8)	0·4596 (8)	0·2175 (4)	2·9
O(3)	0·2646 (8)	0·4530 (8)	0·1552 (4)	3·0
O(4)	0·2126 (7)	0·1361 (7)	0·0654 (4)	2·5
O(5)	−0·0942 (8)	−0·0813 (8)	0·0867 (4)	3·1
O(6)	0·4624 (7)	0·3917 (7)	0·0763 (4)	2·4
C(1)	0·349 (1)	0·296 (1)	−0·0101 (5)	2·4
C(2)	0·210 (1)	0·156 (1)	−0·0087 (5)	2·2
C(3)	0·308(1)	0·595 (1)	0·2171 (5)	2·7
C(4)	0·177 (1)	0·577 (1)	0·2543 (5)	2·3

Anisotropic thermal parameters for the uranium atom (Å^2):
U_{11} = 0·02345, U_{22} = 0·02085, U_{33} = 0·02061, U_{12} = −0·00279, U_{13} = 0·01499, U_{23} = −0·00165.

Table 2. *Interatomic distances* (Å) *and angles* (°)

U–OU(1)*	1·740 (5)	OU(1)–U–OU(2)	177·8 (3)
U–OU(2)	1·754 (4)	O(1)–U–O(2)	68·0 (2)
U–O(1)	2·431 (7)	O(2)–U–O(3)	62·0 (2)
U–O(2)	2·365 (6)	O(3)–U–O(4)	69·3 (2)
U–O(3)	2·495 (7)	O(4)–U–O(5)	84·1 (2)
U–O(4)	2·321 (7)	O(5)–U–O(1)	76·7 (2)
U–O(5)	2·351 (6)	OU(1)–U–O(1)	87·0 (2)
O(1)···O(2)	2·682 (8)	OU(1)–U–O(2)	91·3 (3)
O(2)···O(3)	2·50 (1)	OU(1)–U–O(3)	91·0 (3)
O(3)···O(4)	2·743 (8)	OU(1)–U–O(4)	89·0 (3)
O(4)···O(5)	2·217 (9)	OU(1)–U–O(5)	89·9 (3)
O(5)···O(1)	2·97 (1)	OU(2)–U–O(1)	94·9 (3)
		OU(2)–U–O(2)	90·5 (2)
O(4)–C(2)	1·25 (1)	OU(2)–U–O(3)	88·6 (3)
O(5^{iii})–C(2)	1·256 (8)	OU(2)–U–O(4)	88·8 (3)
C(2)–C(1)	1·53 (1)	OU(2)–U–O(5)	89·5 (3)
C(1)–O(6)	1·410 (8)		
O(4)···O(6)	2·709 (8)	O(4)–C(2)–C(1)	120·3 (7)
		O(5^{iii})–C(2)–C(1)	115·1 (7)
O(2)–C(4)	1·256 (9)	O(4)–C(2)–O(5^{iii})	124·6 (7)
O(1^{iv})–C(4)	1·278 (9)	C(2)–C(1)–O(6)	112·7 (6)
C(4)–C(3)	1·49 (1)		
C(3)–O(3)	1·40 (1)	O(2)–C(4)–C(3)	117·3 (7)
O(2)···O(3)	2·50 (1)	O(2)–C(4)–O(1^{iv})	123·4 (7)
		O(1^{iv})–C(4)–C(3)	119·2 (7)
O(3)···O(4)	2·743 (9)	C(4)–C(3)–O(3)	107·5 (7)
O(3)···O(6)	2·60 (1)		
O(6)···O(1^{iv})	2·743 (7)		

Symmetry code

(i) x,y,z	(v) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$	(vi) $1+x, y, z$
(iii) $-x, -y, -z$	(vii) $1-x, -y, 1-z$
(iv) $-x, \frac{1}{2}+y, \frac{1}{2}-z$	

* For the sake of clarity the (i) symmetry-code superscripts are omitted.

the model and was therefore rejected. The refined parameters are listed in Table 1: the atomic scattering factors used are those given in *International Tables for X-ray Crystallography* (1974).*

Description of the structure

The main interatomic distances and angles are given in Table 2. It appears clearly that the coordination polyhedron of the uranium atom is a pentagonal bipyramid of oxygen atoms. The apical oxygens OU(1) and OU(2) are those of the uranyl group and the five oxygen atoms O(1) through O(5) belong to the glycolato groups and constitute with the uranium atom the equatorial plane of the bipyramid. Fig. 1 depicts the projection of the structure down the *b* axis: all the uranium atoms are nearly located on the (0*yz*) plane [x_U = ±0·04038 (4)] and the pentagonal bipyramids are linked through the glycolato groups thus forming infinite chains. Furthermore, it can be clearly seen in Fig. 1 that the two glycolato groups, labelled *G*(I) and *G*(II), are respectively bidentate and tridentate.

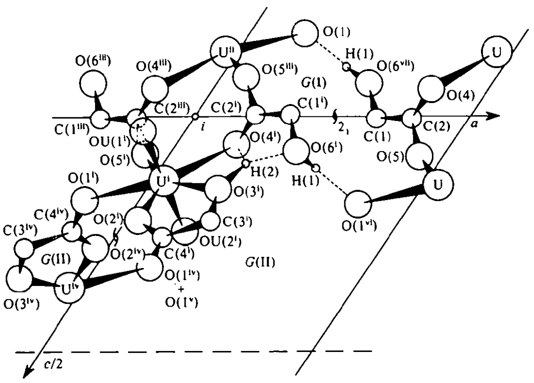

Fig. 1. Projection along [010] of $UO_2(CH_2OHCOO)_2$, showing the asymmetric unit and its immediate environment.

Discussion

The present structure provides one more example of the heptacoordination of uranium in the series of uranyl salts that we have studied (Mentzen, 1977; Mentzen, Puaux & Sautereau, 1978*a*,*b*). This result is in opposition to the hypothetical configuration based on infrared data only, recently proposed by Sbrignadello *et al.* (1978). The oxygen atoms O(1) through O(5) present a maximum deviation from the least-squares mean plane of approximately 0·07 Å (Table 3). This

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35285 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Equations of least-squares planes and deviations of atoms from the planes* (Å)

Planes are defined as $AX + BY + CZ + D = 0$, X, Y and Z being orthogonalized coordinates.

Plane 1: U, O(1), O(2), O(3), O(4), O(5)
$-0{\cdot}2977X + 0{\cdot}3836Y - 0{\cdot}8742Z - 0{\cdot}7717 = 0$

U	−0·0154 (3)	O(1)	0·071 (5)
O(2)	−0·044 (6)	O(3)	−0·005 (6)
O(4)	0·047 (5)	O(5)	−0·058 (6)

Plane 2: C(1), C(2), O(5^{iii}), O(4) [plane G(I)]
$-0{\cdot}6475X + 0{\cdot}7071Y - 0{\cdot}2843Z - 0{\cdot}2351 = 0$

C(1)	0·003 (8)	C(2)	−0·012 (8)
O(4)	0·005 (6)	O(5^{iii})	0·004 (7)
O(6)*	0·110 (6)		

Plane 3: C(3), C(4), O(1^{iv}), O(2) [plane G(II)]
$-0{\cdot}3126X + 0{\cdot}6385Y - 0{\cdot}7033Z + 0{\cdot}6119 = 0$

C(3)	0·004 (8)	C(4)	−0·013 (7)
O(1^{iv})	0·005 (8)	O(2)	0·005 (6)
O(3)*	−0·148 (6)		

* Atoms not included in the calculation of the plane.

plane, which corresponds to the highest atomic density, forms with the ($x0z$) plane a dihedral angle of 67·4°. The pentagonal base is rather irregular, and the smallest O(2)—U—O(3) angle of 63° corresponds to the chelating G(II) group. The uranyl group which is nearly linear may be considered as being normal to the pentagonal mean plane (deviation 2°). The U—OU(1) and U—OU(2) distances which are nearly equal (Table 2) are in fair agreement with the mean distance previously calculated by infrared spectroscopy (Mentzen & Sautereau, 1979). The coordination mode of the tridentate G(II) hydroxyacetato group has already been observed by Grenthe (1971*a*,*b*) and described by Nakamoto, McCarthy & Miniatas (1965). Fig. 1 shows that G(II) chelates the uranium atom through one carboxylic oxygen O(2) and the hydroxylic oxygen O(3), while the second carboxylic oxygen O(1) belongs to a neighbouring bipyramid. On the other hand, in the bidentate G(I) group the carboxylic group O(5)—C(2)—O(4) bridges two uranium atoms, and the hydroxylic oxygen O(6) does not belong to the coordination sphere of the heavy atom.

A remarkable feature of this structure is that the glycolato groups G(I) and G(II) have different roles: in Fig. 1 one may see that the $\mathrm{U^{i}}$ and $\mathrm{U^{ii}}$ atoms are linked by two G(I) groups, while two G(II) groups coordinate $\mathrm{U^{i}}$ and $\mathrm{U^{iv}}$. Furthermore, the O(2)—O(3) distance in the chelating G(II) group is significantly shorter than the O(4)—O(6) distance in G(I). The least-squares mean planes calculated for G(I) and G(II) show that both hydroxyacetato groups may be considered as being planar, the hydroxylic oxygen atoms O(6) and O(3) presenting the largest deviations from the corresponding mean planes; the C(1)—O(6) and C(3)—O(3) vectors form angles of 4·3 and 6·2° respectively with the mean planes of G(I) and G(II), and this has already been observed in the case of anhydrous europium(III) glycolate (Grenthe, 1971*a*,*b*).

We have previously reported the presence of possible hydrogen bonds in the solid under investigation (Mentzen & Sautereau, 1979). This structure reveals several oxygen–oxygen distances which may correspond to hydrogen bonding, *i.e.* the O(3^{i})—O(4^{i}), O(3^{i})—O(6^{i}) and O(6^{i})—O(1^{vi}) distances (Table 2). Accordingly, the hydrogen atom labelled H(2) which is bonded to O(3^{i}) is also hydrogen bonded to both O(4^{i}) and O(6^{i}) while the H(1) atom which is bonded to O(6^{i}) is only hydrogen bonded to O(1^{vi}). The result is that the O(6^{i})—H(1) bond should be shorter than the O(3^{i})—H(2) bond. This would be in agreement with infrared spectroscopy: the two distinct absorption bands observed at 3330 and 3020 $\mathrm{cm^{-1}}$ correspond respectively to the shorter and the longer ν(OH) stretching modes of the two hydroxylic groups of G(I) and G(II), and the two lower frequencies at 2505 and 2450 $\mathrm{cm^{-1}}$ correspond to the associated ν(OH) stretching modes of the hydrogen bonds. It thus appears that the cohesion between the uranium chains running in the ($0yz$) planes is ensured by the O(6)—H(1)···O(1) hydrogen bonds.

All computations have been performed on an IBM 370/168 computer at Orsay (CIRCE) through the terminal of the Institut de Recherches sur la Catalyse.

References

Courtois, G. (1914). *C. R. Acad. Sci.* **158**, 1688–1691.

Grenthe, I. (1971*a*). *Acta Chem. Scand.* **25**, 3347–3359.

Grenthe, I. (1971*b*). *Acta Chem. Scand.* **25**, 3721–3736.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Mentzen, B. F. (1977). *Acta Cryst.* B**33**, 2546–2549.

Mentzen, B. F., Puaux, J. P. & Loiseleur, H. (1977). *Acta Cryst.* B**33**, 1848–1851.

Mentzen, B. F., Puaux, P. J. & Sautereau, H. (1978*a*). *Acta Cryst.* B**34**, 1846–1849.

Mentzen, B. F., Puaux, J. P. & Sautereau, H. (1978*b*). *Acta Cryst.* B**34**, 2707–2711.

Mentzen, B. F. & Sautereau, H. (1979). *Inorg. Chim. Acta*, **35**(2), L347–L348.

Nakamoto, K., McCarthy, P. J. & Miniatas, B. (1965). *Spectrochim. Acta*, **21**, 379–388.

Sbrignadello, G., Tomat, G., Battiston, G., Vigato, P. A. & Traverso, O. (1978). *J. Inorg. Nucl. Chem.* **40**, 1647–1652.

Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination, a Practical Guide*, pp. 454–458. New York: Macmillan.