

molécule individuelle de sulfate de cuivre car les ions sulfate forment ponts entre les atomes de cuivre.

Les calculs ont été effectués sur ordinateur IBM 370-168 à Orsay (CIRCE) par l'intermédiaire du terminal de l'Institut de Recherches sur la Catalyse et à l'aide d'une bibliothèque de programmes organisée au laboratoire de Chimie Analytique II.

#### Références

- BACON, G. E. & CURRY, N. A. (1962). *Proc. Roy. Soc. A* **226**, 95–108.  
 CHARBONNIER, F., FAURE, R. & LOISELEUR, H. (1975). *Acta Cryst.* **B31**, 2693–2694.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.

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## The Crystal Structure of Uranyl Diformate Monohydrate, $\text{UO}_2(\text{HCOO})_2 \cdot \text{H}_2\text{O}$

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The crystal structure of uranyl diformate monohydrate,  $\text{UO}_2(\text{HCOO})_2 \cdot \text{H}_2\text{O}$ , has been established by X-ray diffraction of a single crystal at room temperature. This compound crystallizes in the orthorhombic space group *Fdd2*, with  $a = 5.994$  (1),  $b = 19.331$  (3),  $c = 11.550$  (2) Å,  $Z = 8$ . The structure has been determined by Fourier synthesis and refined by full-matrix least-squares computations. The final weighted  $R_w$  was 0.056 (conventional  $R = 0.055$ ) for 568 unique reflexions. The U atom is surrounded by seven O atoms forming a pentagonal bipyramid. The apical O atoms are those of the uranyl group, which is nearly linear [ $\text{U}-\text{O} = 1.76$  (1) Å,  $\text{O}-\text{U}-\text{O} = 177$  (1)°]. The mean equatorial U–O bond distance is 2.41 (1) Å; the water molecule is coordinated to the U atom. The bipyramids are linked by the bridging of formate groups forming infinite –formate–U–formate– chains, and by hydrogen bonds involving the water molecule.

### Introduction

Infrared spectroscopic studies show that all the formate groups in  $\text{UO}_2(\text{HCOO})_2 \cdot \text{H}_2\text{O}$  are equivalent [ $\nu_s(\text{CO}) = 1360$ ,  $\nu_{as}(\text{CO}) = 1560$ ,  $\rho(\text{COO}) = 1396$ ,  $\delta(\text{OCO}) = 782 \text{ cm}^{-1}$ ] and that the uranyl group appears to be nearly linear [ $\nu_{as}(\text{UO}_2) = 930$ ,  $\nu_s(\text{UO}_2) = 864$  and  $\nu_{as} + \nu_s(\text{UO}_2) = 1796 \text{ cm}^{-1}$ ]. The relations of Jones (1959) enable us to calculate the U–O distance in the  $\text{UO}_2$  group [1.74 (2) Å (Sautereau, 1976)]. Furthermore, the  $\rho(\text{H}_2\text{O})$  band at  $640 \text{ cm}^{-1}$ , assigned to the hindered rotation of the water molecule, shows that  $\text{H}_2\text{O}$  is directly coordinated to the U atom, and the  $\nu(\text{O}_1\text{H})$  bands at 2415 and  $2355 \text{ cm}^{-1}$  indicate the presence of hydrogen bonds in the solid.

$\text{UO}_2(\text{HCOO})_2 \cdot \text{H}_2\text{O}$  is sensitive to visible, ultraviolet and X radiation, and its photolytic behaviour is presently under investigation in the Laboratoire de Cinétique et Génie Chimiques. The determination of the crystal structure of  $\text{UO}_2(\text{HCOO})_2 \cdot \text{H}_2\text{O}$  has been undertaken

in order to elucidate the mechanism of its thermal (Bideau, 1976) and photolytic decompositions (Claudé, Fève, Puaux & Sautereau, 1975; Claudé, Puaux & Renouprez, 1976).

### Experimental results

Uranyl diformate monohydrate has been prepared according to a method described elsewhere (Sahoo, Panda & Patnaik, 1960). We selected a yellow, transparent crystal which was shaped into a sphere of 0.17 mm diameter ( $\mu R = 1.96$ ) and mounted on the four-circle Enraf–Nonius CAD-4 automatic diffractometer of the Centre de Diffractométrie Automatique, Lyon. The intensities were collected with the  $\omega$ - $2\theta$  scan for  $1 < \theta < 45^\circ$ , with  $I > 2\sigma(I)$ . After data reduction, 568 unique reflexions were obtained and their intensities corrected for Lorentz and polarization factors, as well as for absorption. Furthermore, the intensities

were also corrected for the weakening of the intensity-control reflexion resulting from the photolytic effect of the X-rays on the crystal. Among these 568 reflexions, the presence of 240 with weak intensity excludes the space group *Fddd* formerly determined (Claudel, Mentzen, Navarro & Puaux, 1972). The space group has been redefined as *Fdd2*, the conditions limiting possible reflexions being:

$$\begin{aligned} hkl: & h+k, k+l, (h+l) = 2n \\ Okl: & k+l = 4n \quad (k, l = 2n) \\ hOl: & h+l = 4n \quad (h, l = 2n) \\ hk0: & (h+k = 2n) \quad (h, k = 2n) \\ h00: & (h = 4n) \\ Ok0: & (k = 4n) \\ 00l: & (l = 4n). \end{aligned}$$

The U atoms being on special positions, the  $h+k+l = 2n+1$  or  $4n$  special condition is strongly marked for all reflexions. The unit-cell parameters are:  $a = 5.944$  (1),  $b = 19.331$  (3),  $c = 11.550$  (2) Å;  $U = 1327$  Å<sup>3</sup>;  $Z = 8$ ;  $M_r = 378.12$ ;  $D_m = 3.65$ ,  $D_x = 3.77$  g cm<sup>-3</sup>,  $F(000) = 1312$ ;  $\mu(\text{Mo } K\alpha) = 230.7$  cm<sup>-1</sup>.

### Determination of the structure

The U atoms and the O atoms of the water molecules are on special positions (*a*), all the other atoms being on the general positions (*b*). A Fourier synthesis calculated with the structure factors and the phases corresponding to the heavy-atom reveals the positions of all but the H atoms. The refinement of the atomic coordinates and of the isotropic thermal parameters of the six atoms constituting the asymmetric unit, by minimizing  $\sum w(|F_o| - |F_c|)^2$ , leads after four cycles to a conventional  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.078$ . The weighting function was  $w = [2|F_o|_{\min} + |F_o| + 2F_o^2/|F_o|_{\max}]^{-1}$ .

Thereafter, anisotropic thermal parameters and anomalous dispersion factors were introduced for all the atoms. According to Stout & Jensen (1968) the weighting function  $w = (a + b|F_o|)^{-2}$  was introduced at this stage, and after five refinement cycles the final

weighted  $R_w = [\sum(w|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  was 0.056, the conventional  $R$  being 0.055.\* 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

Fig. 1 represents the coordination polyhedron of the U atom, which is the structural unit forming a slightly distorted pentagonal bipyramid. The apices of this bipyramid are occupied by the O(1) and O(1') atoms of the uranyl group. The equatorial plane, which is slightly distorted (Fig. 2), contains O(4) from the water molecule and O(2), O(2'), O(3<sup>ii</sup>) and O(3<sup>iii</sup>) from the formate groups. The U and O(4) atoms are located on the same binary axis parallel to [001], and O(4) participates in two hydrogen bonds with O(2<sup>iv</sup>) and O(2<sup>v</sup>) of two distinct neighbouring polyhedra, with O(4)-O(2<sup>iv</sup>) = O(4)-O(2<sup>v</sup>) = 2.70 (1) Å. The different polyhedra are linked together, firstly by the formate groups forming infinite -formate-U-formate- chains, and secondly by the hydrogen bonds between O(4) and O(2) (Fig. 3). The formate groups appear to be symmetrical with a C-O distance of 1.24 (1) Å and an O-C-O angle of 125.4 (9)°, corresponding to the total resonance of the formate group.

### Discussion

According to the above-mentioned results, the previous observations based on infrared investigations are confirmed. The geometrical parameters (Table 2) describing the crystal structure of uranyl diformate monohydrate are very similar to those encountered in the

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32349 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Relative atomic coordinates, anisotropic thermal parameters, equivalent isotropic thermal parameters and standard deviations for the uranium, oxygen and carbon atoms*

The z coordinate of the U atom has been arbitrarily fixed at 0.03431. The thermal factor was:  $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$ , and the equivalent isotropic factor was calculated according to:  $B_{\text{eq.}} = \frac{1}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 - 2\beta_{12}ab - 2\beta_{13}ac - 2\beta_{23}bc)$ .

	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$B_{\text{eq.}}$
U	0	0	0.03431	0.0149 (1)	0.00122 (1)	0.00238 (2)	-0.0011 (1)	0	0	2.1
O(1)	0.2604 (16)	0.0434 (5)	0.0301 (7)	0.018 (2)	0.0021 (2)	0.0047 (4)	-0.0004 (5)	0.003 (2)	-0.0002 (2)	2.5
C	-0.0773 (23)	0.1059 (5)	0.2616 (7)	0.024 (3)	0.0015 (2)	0.0030 (4)	0.001 (1)	0.003 (1)	-0.0004 (2)	1.9
O(2)	-0.1488 (16)	0.0542 (4)	0.2089 (6)	0.024 (2)	0.0016 (3)	0.0031 (6)	-0.0004 (4)	0.002 (1)	-0.0004 (2)	2.4
O(3)	0.0798 (22)	0.1436 (5)	0.2291 (8)	0.031 (3)	0.0022 (2)	0.0050 (2)	-0.002 (1)	0.002 (1)	-0.0008 (3)	4.2
O(4)	0	0	-0.1732 (8)	0.025 (3)	0.0027 (4)	0.0024 (3)	-0.002 (1)	0	0	3.4

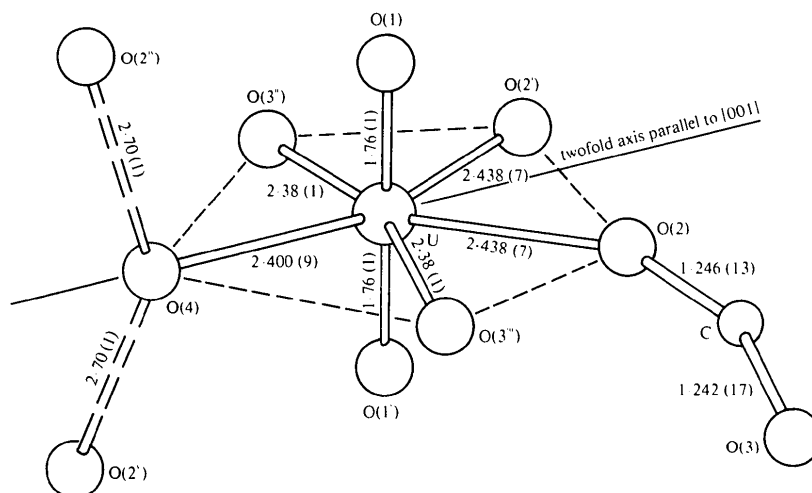


Fig. 1. Coordination polyhedron about the U atom.

literature for related compounds (Howatson, Grev & Morosin, 1975; Legros & Jeannin, 1976). The relatively high mean standard deviations for the U–O and C–O distances are also of the same order of magnitude as those given for other crystals containing very heavy atoms, and we believe that, in the present case, all the  $\sigma$  are overestimated. The pentagonal-bipyramidal environment of the atom (seven coordination) is also present in other uranyl compounds – especially uranyl diacetate dihydrate, the structure of which has recently been published (Howatson, Grev & Morosin, 1975), and which is not sensitive to visible, ultraviolet or X radiation. Hence, the fact that, in the present case, the

formate complex is photosensitive, does not result *a priori* from the pentagonal environment of the U atom alone, but is probably a result of other features, such as, perhaps, the nature of the formate ligand which is a stronger reducing agent than the acetate group. For the time being, it is not possible to give any satisfactory interpretation of the photosensitive character of uranyl diformate monohydrate. Sodium uranyl triformate monohydrate,  $\text{NaUO}_2(\text{HCOO})_3 \cdot \text{H}_2\text{O}$ , which is even more photosensitive than  $\text{UO}_2(\text{HCOO})_2 \cdot \text{H}_2\text{O}$ , has recently been investigated (Claudel, Mentzen, Navarro & Sautereau, 1976), and its crystal structure will soon be published (Mentzen, 1977). The com-

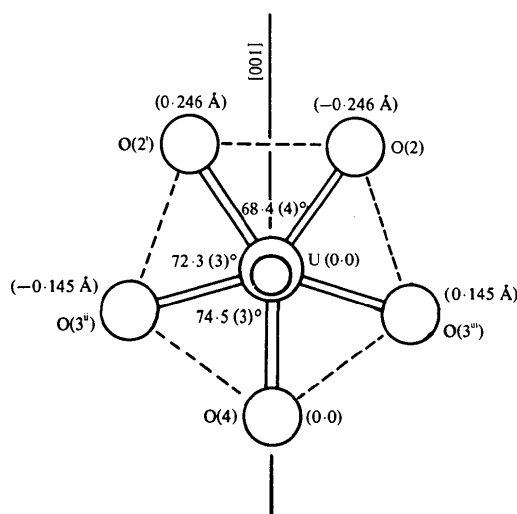


Fig. 2. The mean equatorial plane of the pentagonal bipyramid about the U atom. Numbers in parentheses indicate the distances of the atoms to the mean plane.

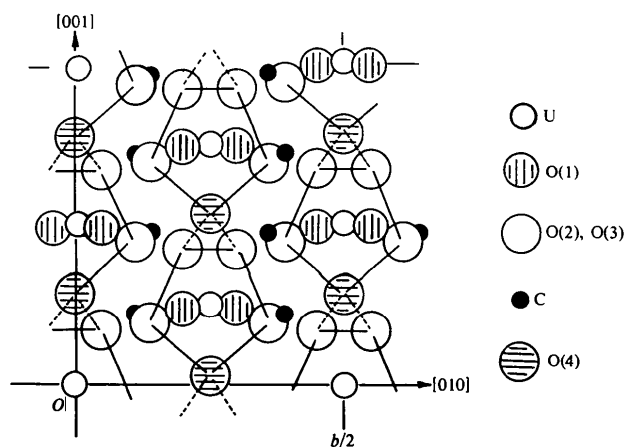


Fig. 3. Projection along the [100] axis showing the links between the coordination polyhedra of U. The dashed lines represent the hydrogen bonds between O(4) and the two O(2) atoms of two different neighbouring polyhedra which are superimposed on the figure.

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

U—O(1)	1.761 (9)	O(1)—U—O(1 <sup>i</sup> )	177.0 (5)
U—O(1 <sup>i</sup> )	1.761 (9)	O(4)—U—O(3 <sup>iii</sup> )	74.4 (3)
U—O(2)	2.438 (7)	O(3 <sup>iii</sup> )—U—O(2)	72.3 (3)
U—O(2 <sup>i</sup> )	2.438 (7)	O(2)—U—O(2 <sup>i</sup> )	68.4 (4)
U—O(3 <sup>ii</sup> )	2.38 (1)	O(2 <sup>i</sup> )—U—O(3 <sup>ii</sup> )	72.3 (3)
U—O(3 <sup>iii</sup> )	2.38 (1)	O(3 <sup>ii</sup> )—U—O(4)	74.4 (3)
U—O(4)	2.400 (9)	O(4)—U—O(1)	88.4 (3)
		O(4)—U—O(1 <sup>i</sup> )	88.4 (3)
Hydrogen bonds		O(3 <sup>iii</sup> )—U—O(1)	87.4 (5)
O(4)—O(2 <sup>iv</sup> )	2.70 (1)	O(3 <sup>iii</sup> )—U—O(1 <sup>i</sup> )	91.8 (5)
O(4)—O(2 <sup>v</sup> )	2.70 (1)	O(3 <sup>ii</sup> )—U—O(1)	91.8 (5)
		O(3 <sup>ii</sup> )—U—O(1 <sup>i</sup> )	87.4 (5)
Formato group		O(2)—U—O(1)	97.9 (4)
C—O(2)	1.246 (13)	O(2)—U—O(1 <sup>i</sup> )	84.8 (4)
C—O(3)	1.242 (17)	O(2 <sup>i</sup> )—U—O(1)	84.8 (4)
		O(2 <sup>i</sup> )—U—O(1 <sup>i</sup> )	97.9 (4)
		O(2)—C—O(3)	125.4 (9)
		O(2 <sup>v</sup> )—O(4)—O(2 <sup>iv</sup> )	119.5 (5)

## Symmetry code

(i)	$-x,$	$-y,$	$z$	(iv)	$\frac{1}{2} + x,$	$y,$	$-\frac{1}{2} + z$
(ii)	$\frac{1}{4} - x,$	$-\frac{1}{4} + y,$	$-\frac{1}{4} + z$	(v)	$-\frac{1}{2} - x,$	$-y,$	$-\frac{1}{2} + z$
(iii)	$-\frac{1}{4} + x,$	$\frac{1}{4} - y,$	$-\frac{1}{4} + z$				

parison of the structures of these two compounds with those of other uranyl compounds, photosensitive or not, should enable us to find a clue to the phenomenon of photosensitivity in the solid state.

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

Catalyse, Lyon, and with a program library at the Laboratoire de Chimie Analytique II.

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## References

- BIDEAU, M. (1976). PhD Dissertation, Lyon.
- CLAUDEL, B., FÈVE, M., PUAUX, J. P. & SAUTEREAU, H. (1975). *C. R. Acad. Sci. Paris, Sér. C*, **280**, 169–172.
- CLAUDEL, B., MENTZEN, B., NAVARRO, A. & PUAUX, J. P. (1972). *C. R. Acad. Sci. Paris, Sér. C*, **274**, 1417–1419.
- CLAUDEL, B., MENTZEN, B., NAVARRO, A. & SAUTEREAU, H. (1976). *J. Inorg. Nucl. Chem.* **38**, 759–762.
- CLAUDEL, B., PUAUX, J. P. & RENOUPEZ, A. (1976). *C. R. Acad. Sci. Paris, Sér. C*, **282**, 571–574.
- HOWATSON, J., GREV, D. M. & MOROSIN, B. (1975). *J. Inorg. Nucl. Chem.* **37**, 1933–1935.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JONES, L. H. (1959). *Spectrochim. Acta*, **15**, 409.
- LEGROS, J. P. & JEANNIN, Y. (1976). *Acta Cryst.* **B32**, 2497–2503.
- MENTZEN, B. F. (1977). *Acta Cryst.* In the press.
- SAHOO, B., PANDA, S. & PATNAIK, D. (1960). *J. Indian Chem. Soc.* **37**, 594.
- SAUTEREAU, H. (1976). PhD Dissertation, Lyon.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination, a Practical Guide*, pp. 454–458. New York: Macmillan.

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## The Crystal and Molecular Structure of DL-Lactoylcholine Iodide

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Crystals of DL-lactoylcholine iodide,  $C_8H_{18}NO_3I$ , are monoclinic, space group  $P2_1/c$  ( $C_{2h}^2$ ),  $a = 9.891$  (6),  $b = 12.286$  (8),  $c = 10.150$  (5) Å,  $\beta = 90.65$  (3)°,  $Z = 4$ . The values of the torsion angles  $-N^+-C-C-O$  (85°) and  $-C-C-O-C-$  (157°) are similar to those observed in other cholinergic agonists. The acidic end of the ester group, however, has an unusual conformation which is probably a result of the molecular packing involving hydrogen bonds to the terminal hydroxyl group.

### Introduction

Rama Sastry, Lasslo & Pfeiffer (1958, 1960) synthesized the enantiomers of lactoylcholine and

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measured their activities at cholinergic synapses. The nicotinic activities are similar to those of acetylcholine [reciprocal relative activities of  $D(-):L(+):ACh$  are 0.69:3.45:1.00] but the muscarinic activities are slight [reciprocal relative activities of  $D(-):L(+):ACh$  are 850:4700:1]. Here we describe the single-crystal