

## ADDENDUM

The referee raised some doubt about the validity of the structure proposed by us because of the angle  $\text{Si}(3)\text{--O}(4)\text{--Si}(3') = \omega$  of  $180^\circ$ : the correct space group could also have been  $P321$  or  $P3m1$ , allowing  $O(4)$  to shift and the  $\omega$ -angle to approach  $140^\circ$ . Although the intensity statistics had a slightly hypercentric distribution and the  $O(4)$  atom did not show any splitting in the Fourier map, we tried to refine the structure in the space groups  $P321$  and  $P3m1$  ( $\omega = 140^\circ$ ) to obtain ad-

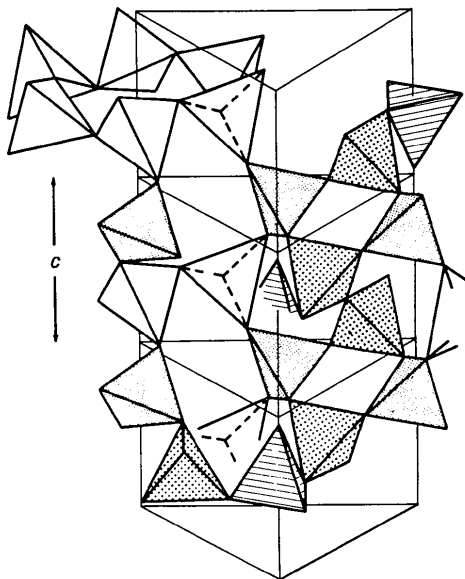


Fig. 2. Picture of the chains running along  $[001]$ . Unstippled tetrahedra refer to  $\text{Si}(1)$ , thickly stippled to  $\text{Si}(2)$ , thinly stippled to  $\text{Si}(3)$  and ruled tetrahedra to  $\text{Be}$ .

ditional evidence for the centrosymmetric model. At the end of the refinements the standard deviations had increased tenfold on average, and the  $\omega$  angle again became nearly  $180^\circ$ . The form of the  $O(4)$  thermal ellipsoid is exactly that expected with an angle  $\omega = 180^\circ$ , and confirms that the general picture of the thermal situation has physical meaning. Moreover, we used the 'DLS' program written by Meier & Villiger (1969) to find the framework with the best bond lengths and angles in space groups  $P321$  and  $P3m1$ , starting from  $\omega = 170^\circ$ , and after several least-squares cycles the symmetry again became  $P3m1$ , with  $\omega$  nearly equal to  $180^\circ$ .  $\text{Si--O--Si}$  angles of  $180^\circ$  have been detected in at least four well refined structures, such as thortveitite and coesite (Baur, 1971).

## References

- BAUR, W. H. (1971). *Amer. Min.* **56**, 1573–1599.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
 BØGGILD, O. B. (1915). *Medd. Grønland*, **51**, 427–433.  
 CODA, A. (1969). *Rend. Soc. Mineral. Ital.* **25**, 195–226.  
 CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.  
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.  
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.  
*International Tables for X-ray Crystallography* (1962). Vol. III, p. 202. Birmingham: Kynoch Press.  
 LIEBAU, F. (1961). *Acta Cryst.* **14**, 1103–1109.  
 MEIER, W. M. & VILLIGER, H. (1969). *Z. Kristallogr.* **129**, 411–423.  
 MICHEELSEN, H. & PETERSEN, O. V. (1970). *Bull. Geol. Soc. Denmark*, **20**, 134–151.  
 STRUNZ, H. (1970). *Mineralogische Tabellen*, 5th ed., p. 483. Leipzig: Akademische Verlagsges.  
 ZOLTAI, T. (1960). *Amer. Min.* **45**, 960–973.

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Crystal Structure of Zinc *o*-Ethoxybenzoate Monohydrate

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Zinc *o*-ethoxybenzoate monohydrate,  $\text{ZnC}_{18}\text{H}_{18}\text{O}_6 \cdot \text{H}_2\text{O}$ , is monoclinic with  $a = 9.535(8)$ ,  $b = 11.610(10)$ ,  $c = 8.384(9)$  Å,  $\beta = 92.9(1)^\circ$ ,  $Z = 2$ . The space group is determined as  $Pc$  after solving the structure from 1761 observed X-ray intensities collected on a diffractometer with  $\text{Cu K}\alpha$  radiation and balanced filters. The final  $R$  is 7.1% for the observed reflections. Zn is tetrahedrally coordinated by four oxygen atoms at 1.988(2), 2.076(9), 2.037(7) and 2.054(9) Å.

## Introduction

Zinc *o*-ethoxybenzoate monohydrate ( $\text{ZnC}_{18}\text{H}_{18}\text{O}_6 \cdot \text{H}_2\text{O}$ ) is the reaction product formed in ethoxybenzoic

acid (EBA) dental cement (Brauer, 1965, 1967, 1972). The same compound can be synthesized from 12.3 g of ethoxybenzoic acid dissolved in 20 ml of methanol and 8.8 g of zinc oxide by heating for 6 h in a steam

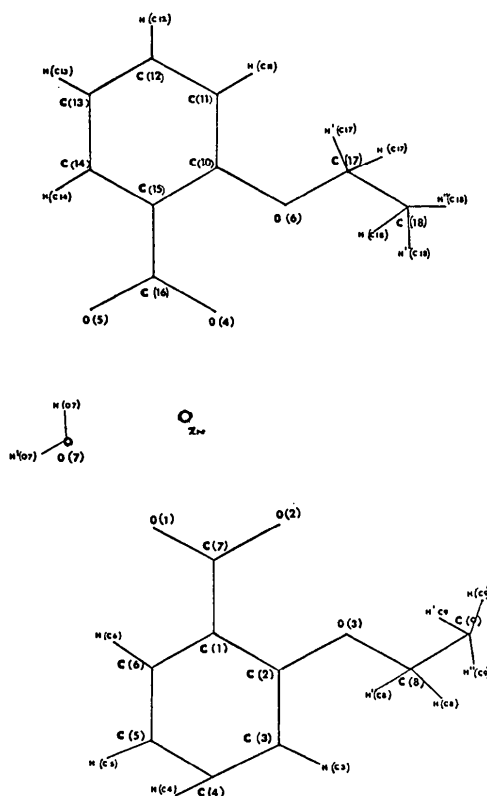


Fig. 1. Zinc *o*-ethoxybenzoate monohydrate numbering system.

bath and filtering the residue in hot chloroform. The crystals obtained from a methanol solution are orthorhombic, whilst those from aqueous methanol are monoclinic. The unit cell of the monoclinic crystals has a volume almost half that of the orthorhombic crystals and contains half the number of molecules, so that the volume per molecule is about the same in both cases. The structure of the monoclinic crystals is reported here. The orthorhombic form appears to contain a molecule of crystallization of methanol and the structure will be reported elsewhere.

The stereochemistry and numbering system is given in Fig. 1. The molecular geometry of *o*-ethoxybenzoic acid determined by Gopalakrishna & Cartz (1972) is not altered in the present structure.

### Experimental

Zinc *o*-ethoxybenzoate monohydrate crystals as transparent thick plates are obtained from an aqueous solution of methanol by slow evaporation. Preliminary X-ray data were collected on a Weissenberg camera

Table 1. Crystal data

$a$	=	9.535 (8) Å
$b$	=	11.610 (10)
$c$	=	8.384 (9)
$\beta$	=	92.9 (1)°
$V$	=	926.96 Å <sup>3</sup> , $Z=2$
$D_m$	=	1.50, $D_x=1.484$ g cm <sup>-3</sup>

with Cu  $K\alpha$  radiation. Refined cell parameters were obtained from 65 reflections in a least-squares program. The cell data are given in Table 1.

The extinction condition limiting possible reflections is  $h0l$ ,  $l=2n$ , so that the possible space groups are  $Pc$ ,  $P2/c$ . A statistical  $N(z)$  test was carried out to determine the correct space group but the result was not conclusive. The correct space group was determined to be  $Pc$  after solving the structure.

The intensities were collected on a General Electric XRD-6 manually operated diffractometer with Cu  $K\alpha$  radiation and balanced filters. The stationary-crystal stationary-counter method was used. Six standard reflections were measured twice a day to check the stability of the system. The intensities of all 1880 possible reflections ( $2\theta < 140^\circ$ ) were measured; 1761 had observable intensities. The unique axis  $b$  of the crystal was mounted parallel to the  $\phi$  axis of the goniometer. The measured intensities were corrected for Lorentz and polarization factors. No absorption correction was made, since the linear absorption coefficient is  $6.2 \text{ cm}^{-1}$ . The crystal used was approximately  $0.1 \times 0.2 \times 0.2 \text{ mm}$ .

### Structure determination and refinement

A Patterson synthesis gave the  $y$  coordinate of the zinc atom as 0.11. Since the origin can lie anywhere in the

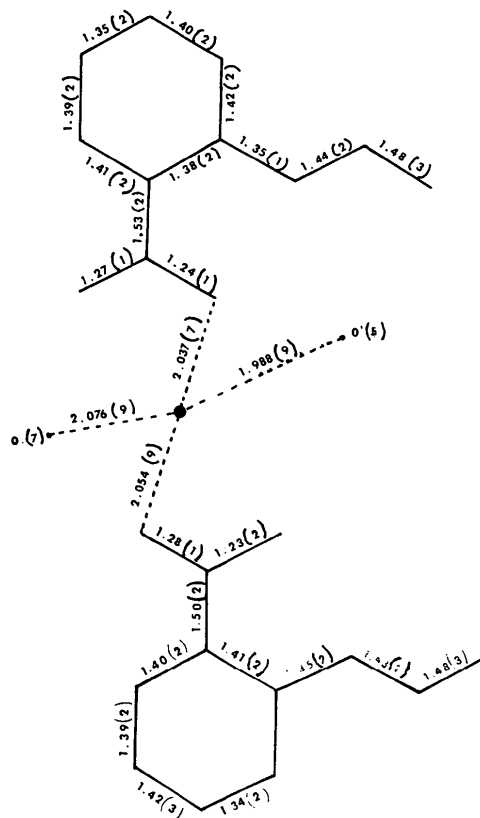


Fig. 2. Zinc *o*-ethoxybenzoate monohydrate bond distances in Å.

glide plane for the space group  $Pc$ ,  $x$  and  $y$  for the Zn atom can be fixed arbitrarily. Structure factors calculated with the Zn coordinates gave an  $R$  of 32.6%. The Zn-phased Fourier map was computed in order to locate the remaining atoms in the structure. Due to the additional center of symmetry introduced at the Zn position, it was not possible to deduce the structure. 45 Zn phases were used as the starting set for tangent refinement in the *FASTAN* (Main, 1971) program, which gave 262 phases for the normalized structure factors. An  $E$  map was computed with these 262 reflections. This map also had the additional symmetry but with fewer spurious peaks, and 23 non-hydrogen atoms were located.  $R$  after two cycles of block-diagonal least-squares fell to 22.6%. An electron density map computed at this stage gave the positions of the rest of the non-hydrogen atoms. With isotropic temperature factors for all the atoms, 3 cycles of refinement reduced  $R$  to 9.3%. 1880 reflections, including all the unobserved reflections, were used in this refinement with unit weight. Unobservable reflections were given half the threshold value of the intensities measured. A difference map computed from the final coordinates gave all the hydrogen positions. Bond distances and angles computed at this stage showed some peculiar values. An agreement analysis was carried out to check the data. Very bad agreement was noticed for reflections with  $F_o < 50$ , mostly unobserved reflections. Further refinement was carried out removing these re-

flections. During this refinement all the hydrogen atoms were given isotropic temperature factors  $B=3.0 \text{ \AA}^2$  and their parameters were not refined. Atomic scattering factors for zinc, carbon and oxygen were taken from *International Tables for X-ray Crystallography* (1962) and for hydrogen from Stewart, Davidson & Simpson (1965). The anomalous scattering-factor correction was used for the zinc atom with  $Af' = 1.7$  (Buerger, 1960). After two cycles of least-squares refinement with anisotropic thermal parameters for all the non-hydrogen atoms,  $R$  was 7.1%. The final  $R$  including all possible reflections was 9.3%. Final coordinates and thermal parameters are given in Tables 2 and 3. Ob-

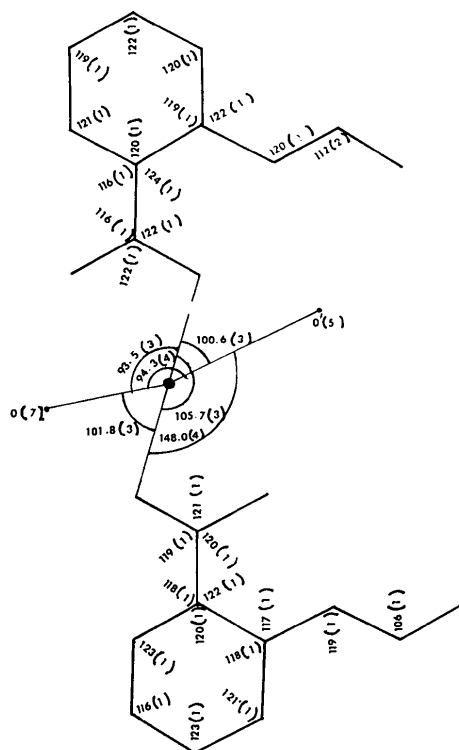
Table 2. Atomic coordinates

(a) Fractional coordinates of non-hydrogen atoms ( $\times 10^5$ )

	$x$	$y$	$z$
Zn	15000 (0)	10597 (11)	12600 (0)
O(1)	28207 (96)	24507 (79)	15341 (108)
O(2)	24296 (115)	15627 (85)	37669 (116)
O(3)	28129 (103)	47333 (73)	30786 (119)
C(1)	40820 (115)	30856 (99)	39184 (131)
C(2)	39331 (148)	42938 (112)	39220 (150)
C(3)	49468 (184)	49410 (141)	48285 (188)
C(4)	59822 (166)	44229 (153)	56940 (194)
C(5)	61568 (148)	32090 (157)	57585 (168)
C(6)	51904 (140)	25713 (123)	48253 (159)
C(7)	30388 (132)	23181 (100)	30390 (144)
C(8)	26019 (166)	59481 (134)	30970 (193)
C(9)	13048 (243)	61711 (182)	20995 (281)
O(4)	11248 (86)	87240 (67)	-11392 (87)
O(5)	-860 (84)	-1592 (88)	-29270 (110)
O(6)	-3710 (87)	23587 (74)	5555 (122)
C(10)	-15439 (110)	18568 (97)	-1020 (150)
C(11)	-29080 (122)	21845 (119)	3238 (180)
C(12)	-40853 (135)	16144 (145)	-3666 (210)
C(13)	-39600 (134)	7610 (100)	-14340 (190)
C(14)	-26260 (127)	4312 (130)	-18512 (176)
C(15)	-14120 (120)	9830 (99)	-11990 (140)
C(16)	-131 (120)	5480 (86)	-17664 (130)
C(17)	-4760 (183)	33898 (150)	14960 (213)
C(18)	-7687 (229)	31364 (187)	31789 (277)
O(7)	29035 (87)	3070 (81)	64168 (105)

(b) Fractional coordinates of hydrogen atoms ( $\times 10^3$ )

	$x$	$y$	$z$
H(C3)	38	51	53
H(C4)	63	51	62
H(C5)	66	30	50
H(C6)	51	18	50
H(C8)	23	61	41
H'(C8)	32	63	26
H(C9)	14	56	32
H'(C9)	5	63	15
H''(C9)	18	65	10
H(C11)	-35	25	14
H(C12)	-48	18	2
H(C13)	-35	8	-26
H(C14)	-25	2	-30
H(C17)	2	38	12
H'(C17)	-10	40	5
H(C18)	-1	35	29
H'(C18)	-10	37	42
H''(C18)	-15	38	26
H(O7)	30	1	51
H'(O7)	26	3	78

Fig. 3. Zinc *o*-ethoxybenzoate monohydrate bond angles in degrees.

served and calculated structure amplitudes are given in Table 4. The modified *ORFLS* program was used for the refinement.

### Discussion

The coordination around zinc is distorted tetrahedral (Figs. 2 and 3). Zn–O distances are close to the expected value  $2.02 \pm 0.05$  Å (*International Tables for X-ray Crystallography*, 1962). However, of the four ligands, three oxygens are from the COOH group of the *o*-ethoxybenzoic acid and the other from the H<sub>2</sub>O molecule. The coordination polyhedra form a chain along *c* (Fig. 4). O(4) and O(5) of molecule *EBA-A2* are coordinated to the neighboring Zn atoms in the chain. Next nearest neighbors in the coordination sphere of Zn are O(2) and O(6) at distances 2.32 and 2.39 Å, respectively.

The average carbon–carbon bond distances in rings *A1* and *A2* are 1.397 and 1.391 Å, respectively. This value is close to the expected C–C bond in aromatic

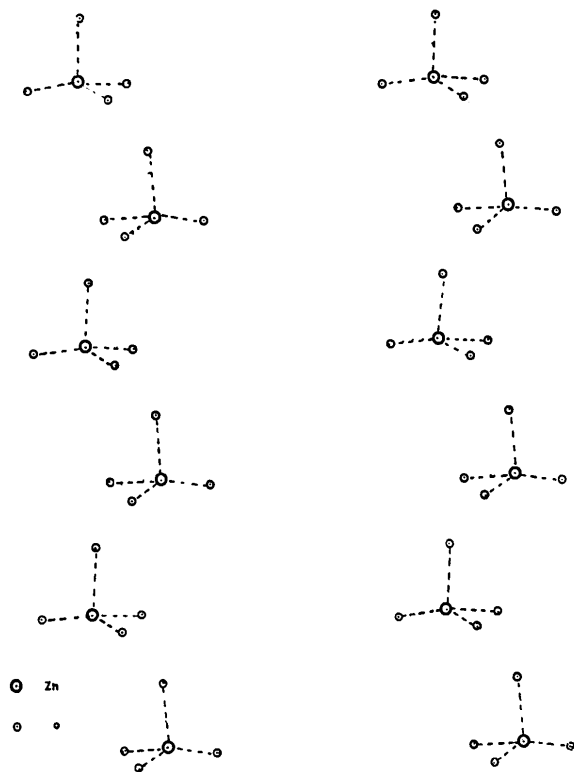


Fig. 4. The coordination along the *c* axis of zinc *o*-ethoxybenzoate monohydrate.

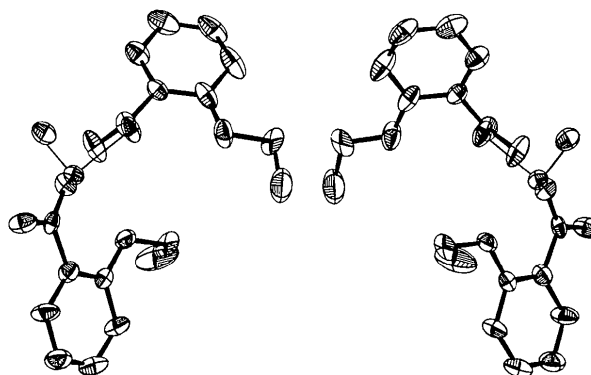


Fig. 5. Two perspective views of zinc *o*-ethoxybenzoate monohydrate with 50% probability thermal ellipsoids.

Table 3. Thermal parameters  $U_{ij}$  ( $10^{-4}$  Å<sup>2</sup>)

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Zn	286 (6)	343 (7)	277 (7)	– 18 (4)	– 10 (2)	– 16 (2)
O(1)	496 (45)	347 (55)	382 (47)	– 84 (19)	– 87 (20)	20 (2)
O(2)	741 (68)	490 (56)	409 (52)	– 156 (26)	45 (2)	34 (2)
O(3)	637 (58)	315 (46)	539 (56)	– 41 (19)	– 82 (20)	– 26 (2)
C(1)	347 (57)	515 (58)	194 (55)	– 51 (25)	– 23 (22)	– 17 (2)
C(2)	555 (78)	429 (66)	374 (64)	– 115 (29)	14 (2)	– 37 (3)
C(3)	838 (105)	587 (86)	505 (87)	– 197 (44)	– 18 (3)	– 30 (3)
C(4)	588 (93)	755 (104)	556 (88)	– 169 (41)	– 84 (37)	10 (4)
C(5)	489 (79)	879 (111)	377 (70)	– 103 (37)	– 26 (3)	39 (4)
C(6)	461 (73)	531 (77)	427 (76)	– 68 (31)	– 29 (2)	– 21 (3)
C(7)	470 (64)	343 (64)	254 (57)	– 25 (2)	25 (2)	– 80 (3)
C(8)	709 (83)	239 (82)	581 (123)	– 37 (4)	33 (5)	– 48 (4)
C(9)	909 (180)	416 (109)	1103 (217)	19 (6)	– 121 (8)	– 32 (6)
O(4)	383 (44)	399 (44)	204 (36)	– 24 (2)	– 22 (2)	– 29 (10)
O(5)	327 (41)	664 (61)	382 (49)	33 (2)	– 37 (4)	– 94 (23)
O(6)	275 (42)	352 (44)	573 (46)	32 (2)	– 43 (2)	– 67 (22)
C(10)	315 (56)	273 (55)	489 (68)	25 (2)	10 (2)	– 16 (3)
C(11)	294 (60)	524 (77)	602 (82)	69 (26)	32 (3)	– 5 (3)
C(12)	278 (63)	724 (98)	699 (93)	63 (31)	– 10 (2)	11 (4)
C(13)	314 (62)	615 (86)	654 (92)	20 (2)	– 50 (3)	– 38 (4)
C(14)	251 (57)	727 (92)	574 (82)	25 (2)	– 61 (3)	– 44 (4)
C(15)	347 (57)	350 (57)	346 (59)	27 (2)	– 10 (2)	– 24 (2)
C(16)	413 (58)	215 (48)	245 (51)	33 (2)	– 15 (2)	– 35 (2)
C(17)	541 (118)	448 (131)	1214 (216)	69 (5)	– 18 (6)	– 33 (4)
C(18)	596 (139)	1572 (289)	670 (162)	164 (82)	61 (6)	– 239 (91)
O(7)	379 (45)	516 (55)	351 (47)	– 49 (2)	– 25 (2)	– 3 (2)

rings,  $1.395 \pm 0.003 \text{ \AA}$  (*International Tables for X-ray Crystallography*, 1962). However, C(3)-C(4) and C(12)-C(13) are relatively much shorter (Fig. 2). This type

of deviation is reported in the structure of potassium *O,O*-dibenzyl phosphorodithioate (Hazel & Collin, 1972) and by Llabres, Dideberg & Dupont (1972) in

Table 4. Observed and calculated structure amplitudes

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
11	6	0	190	187	-7	0	18	18	18	11	6	0	190	187	-11	6	0	190	187
10	0	0	190	187	10	0	0	190	187	10	0	0	190	187	10	0	0	190	187
9	0	0	190	187	9	0	0	190	187	9	0	0	190	187	9	0	0	190	187
8	0	0	190	187	8	0	0	190	187	8	0	0	190	187	8	0	0	190	187
7	0	0	190	187	7	0	0	190	187	7	0	0	190	187	7	0	0	190	187
6	0	0	190	187	6	0	0	190	187	6	0	0	190	187	6	0	0	190	187
5	0	0	190	187	5	0	0	190	187	5	0	0	190	187	5	0	0	190	187
4	0	0	190	187	4	0	0	190	187	4	0	0	190	187	4	0	0	190	187
3	0	0	190	187	3	0	0	190	187	3	0	0	190	187	3	0	0	190	187
2	0	0	190	187	2	0	0	190	187	2	0	0	190	187	2	0	0	190	187
1	0	0	190	187	1	0	0	190	187	1	0	0	190	187	1	0	0	190	187
0	0	0	190	187	0	0	0	190	187	0	0	0	190	187	0	0	0	190	187
-1	0	0	190	187	-1	0	0	190	187	-1	0	0	190	187	-1	0	0	190	187
-2	0	0	190	187	-2	0	0	190	187	-2	0	0	190	187	-2	0	0	190	187
-3	0	0	190	187	-3	0	0	190	187	-3	0	0	190	187	-3	0	0	190	187
-4	0	0	190	187	-4	0	0	190	187	-4	0	0	190	187	-4	0	0	190	187
-5	0	0	190	187	-5	0	0	190	187	-5	0	0	190	187	-5	0	0	190	187
-6	0	0	190	187	-6	0	0	190	187	-6	0	0	190	187	-6	0	0	190	187
-7	0	0	190	187	-7	0	0	190	187	-7	0	0	190	187	-7	0	0	190	187
-8	0	0	190	187	-8	0	0	190	187	-8	0	0	190	187	-8	0	0	190	187
-9	0	0	190	187	-9	0	0	190	187	-9	0	0	190	187	-9	0	0	190	187
-10	0	0	190	187	-10	0	0	190	187	-10	0	0	190	187	-10	0	0	190	187
-11	0	0	190	187	-11	0	0	190	187	-11	0	0	190	187	-11	0	0	190	187
-12	0	0	190	187	-12	0	0	190	187	-12	0	0	190	187	-12	0	0	190	187
-13	0	0	190	187	-13	0	0	190	187	-13	0	0	190	187	-13	0	0	190	187
-14	0	0	190	187	-14	0	0	190	187	-14	0	0	190	187	-14	0	0	190	187
-15	0	0	190	187	-15	0	0	190	187	-15	0	0	190	187	-15	0	0	190	187
-16	0	0	190	187	-16	0	0	190	187	-16	0	0	190	187	-16	0	0	190	187
-17	0	0	190	187	-17	0	0	190	187	-17	0	0	190	187	-17	0	0	190	187
-18	0	0	190	187	-18	0	0	190	187	-18	0	0	190	187	-18	0	0	190	187
-19	0	0	190	187	-19	0	0	190	187	-19	0	0	190	187	-19	0	0	190	187
-20	0	0	190	187	-20	0	0	190	187	-20	0	0	190	187	-20	0	0	190	187

Table 5. Least-squares planes

The equation of the planes is of the form  $lx + my + nz = P$  where  $x, y, z$  and  $P$  are in  $\text{\AA}$ .

Plane	Atoms included	<i>l</i>	<i>m</i>	<i>n</i>	<i>P</i>
A1	C(1), C(2), C(3), C(4), C(5) and C(6)	-0.6215	-0.0537	+0.7816	+0.0590
B1	C(7), O(1) and O(2)	+0.7518	-0.6386	-0.1642	-12.1382
C1	O(3), C(8) and C(9)	-0.5841	-0.0923	+0.8065	+7.4147
A2	C(10), C(11), C(12), C(13), C(14), C(15)	+0.0100	-0.6669	+0.7451	-1.4396
B2	C(16), O(4) and O(5)	+0.0489	+0.7626	-0.6450	12.1964
C2	O(6), C(17) and C(18)	+0.9717	-0.0389	+0.2330	1.4084

the structure of diphenyl ditelluride. The rings *A1* and *A2* are planar, and the equations of the mean planes and deviations of the atoms from the plane are given in Tables 5 and 6, respectively. The deviation of atom C(5) in ring *A1* is large, 0.013 Å, whilst in ring *A2* the largest deviation is 0.005 Å for atom C(14). The angle between the mean planes of *A1* and *A2* is 52.3°. For both EBA molecules, the carbon atoms from the COOH groups lie close to the plane of the aromatic ring, whereas the oxygens lie one above and one below the plane. The dihedral angles are given in Table 7. The planes passing through the COOH groups make angles of 55.9 and 8.6° with their corresponding rings. In the structure of EBA this dihedral angle is not large and the deviation here may be due to the common ligand formation of the COOH group along the coordination chain.

Table 6. Deviations from the mean plane (Å)

Plane <i>A1</i>		Plane <i>A2</i>	
C(1)	-3* × 10 <sup>-3</sup>	C(10)	17* × 10 <sup>-4</sup>
C(2)	13*	C(11)	3*
C(3)	-10*	C(12)	3*
C(4)	-3*	C(13)	-30*
C(5)	13*	C(14)	50*
C(6)	-10*	C(15)	-43*
C(7)	65	C(16)	-77
C(8)	137	C(17)	-1786
C(9)	597	C(18)	4924
O(1)	-839	O(4)	1433
O(2)	968	O(5)	-1848
O(3)	75	O(6)	345

\* Atoms included for least-squares plane calculation.

Table 7. Dihedral angles

Plane 1	Plane 2	Angles
<i>A1</i>	<i>A2</i>	52.3°
<i>A1</i>	<i>B1</i>	55.9
<i>A2</i>	<i>B2</i>	8.6
<i>A1</i>	<i>C1</i>	3.4
<i>A2</i>	<i>C2</i>	77.9

Table 8. Hydrogen–non-hydrogen bond distances, in Å

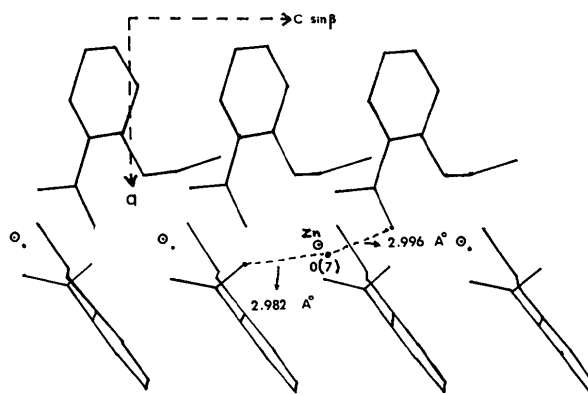
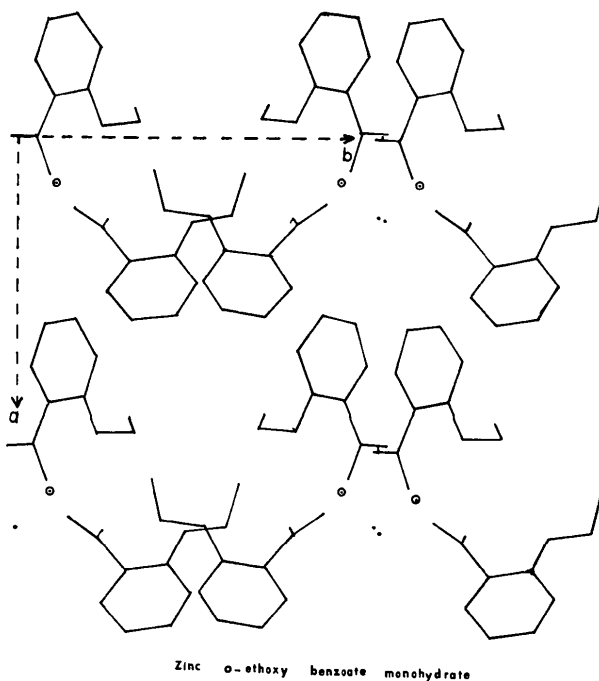
Atom 1	Atom 2	Distance
C(3)	H(C3)	1.19 (2)
C(4)	H(C4)	0.94 (2)
C(5)	H(C5)	0.82 (1)
C(6)	H(C6)	0.91 (1)
C(8)	H(C8)	0.92 (2)
C(8)	H'(C8)	0.83 (2)
C(9)	H(C9)	1.14 (2)
C(9)	H'(C9)	0.91 (2)
C(9)	H''(C9)	1.12 (2)
C(11)	H(C11)	1.15 (1)
C(12)	H(C12)	0.88 (1)
C(13)	H(C13)	1.10 (2)
C(14)	H(C14)	1.01 (2)
C(17)	H(C17)	0.85 (2)
C(17)	H'(C17)	1.18 (2)
C(18)	H(C18)	0.81 (2)
C(18)	H'(C18)	1.11 (2)
C(18)	H''(C18)	1.13 (2)
O(7)	H(O7)	1.073 (9)
O(7)	H'(O7)	1.169 (9)

Hydrogen–non-hydrogen bond distances are given in Table 8. Two perspective views of the molecule with 50% probability thermal ellipsoids of the non-hydrogen atoms are given in Fig. 5. The hydrogens from the

Table 9. Intermolecular contacts, in Å

Atom 1	Atom 2	Eqv/Cell*	Distance
O(2)	O(4)	2/000	3.092
O(2)	O(5)	2/000	3.176
O(4)	O(5)	2/00-1	3.096
O(5)	O(6)	2/00-1	2.861
O(5)	C(10)	2/00-1	2.982
O(5)	C(15)	2/00-1	3.113

\* Eqv: the equivalent positions are 1=(*x*, *y*, *z*), 2=(*x*, -*y*, ½ + *z*). Cell: 2/00 1 means the atom 2 is translated ½ along *c*.

Fig. 6. The intermolecular hydrogen bonds in zinc *o*-ethoxybenzoate monohydrate.Fig. 7. The packing arrangement of the molecules of zinc *o*-ethoxybenzoate monohydrate along the *c* axis.

water molecules form intermolecular hydrogen bonds with the COOH oxygens, and the distances O—H—O are 2.982 and 2.996 Å (Fig. 6). Other molecular contacts less than 3.2 Å are listed in Table 9. The packing of the molecules is shown in Figs. 6 and 7 along **b** and **c** respectively.

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#### References

BRAUER, G. M. (1965). *Rev. Belge Méd. Dent.* **20**, 323–364.  
BRAUER, G. M. (1967). *Ann. Dent.* **26**, 44–50.

BRAUER, G. M. (1972). *Natl. Bur. Stand. Misc. Pub.* **354**, 101–111.  
BUERGER, M. J. (1960). *Crystal Structure Analysis*, p. 546. New York: John Wiley.  
GOPALAKRISHNA, E. M. & CARTZ, L. (1972). *Acta Cryst.* **B28**, 2917–2924.  
HAZEL, J. P. & COLLIN, R. L. (1972). *Acta Cryst.* **B28**, 2279–2287.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
LLABRES, P. G., DIDEBERG, O. & DUPONT, L. (1972). *Acta Cryst.* **B28**, 2438–2444.  
MAIN, P. (1971). Univ. of York, England, private communication.  
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.

*Acta Cryst.* (1974). **B30**, 407

## Structural Studies on the Actinide Carboxylates. I. The Crystal and Molecular Structure of Oxydiacetatodioxouranium(VI)

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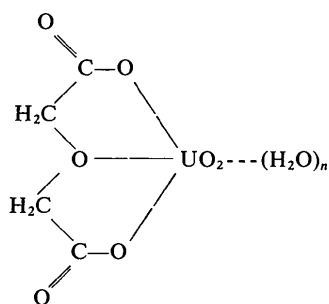
(Received 25 June 1973; accepted 28 August 1973)

The crystal structure of oxydiacetatodioxouranium(VI),  $\text{UO}_2$  (oxydiacetato), has been determined from three-dimensional X-ray diffractometer data. The complex crystallizes in the tetragonal space group  $P4_12_12$ ,  $Z=4$ ,  $a=8.148$  (3),  $c=11.051$  (3) Å. The structure was determined by the heavy-atom method and refined by full-matrix least-squares to  $R=0.038$ . The uranyl ions are equatorially surrounded by four carboxylate oxygen atoms and one ether oxygen atom, forming an irregular pentagonal bipyramid. Each ligand is shared between three uranyl units so that the structure can be described in terms of a three-dimensional network of cross-linked uranium-ligand chains.

#### Introduction

The possibility of obtaining stable complexes by reaction between the actinyl ions  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ , and  $\text{PuO}_2^{2+}$  and such ligands as oxydiacetate, iminodiacetate, thiodiacetate and glutarate has been discussed together with their probable structures in solution (Casal Di Bernardo, Portanova & Magon, 1973).

In particular the presence of monomeric species of the type:



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was proposed for the 1:1 chelate complex formed when the concentration of the oxydiacetate ligand corresponds to  $\bar{n}$  values in the range  $0 < \bar{n} < 1$  ( $\bar{n}$  = average number of ligands bound to each uranyl group). Similar structures in which the ligand behaves as tridentate through the two carboxylic groups and the central donor atom could, in principle, be postulated in the solid state also. In this case, if the water molecules are lost, the formation of polymeric species is expected.

With the aim of correlating the behaviour in solution with the coordination mode in the solid state the structure of the solid  $\text{UO}_2$ (oxydiacetate) complex has been determined by X-ray analysis.†

#### Experimental

The compound was prepared from uranyl nitrate and oxydiacetic acid as described before (Bombieri *et al.*, 1972).

*Crystal data:* —  $\text{C}_4\text{H}_4\text{O}_7\text{U}$ , F.W. 402, tetragonal,

† A preliminary account of this structure is given by Bombieri, Forsellini, Graziani, Tomat & Magon (1972).