

## The Crystal and Molecular Structure of Zinc Lactate Trihydrate

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$\text{Zn}(\text{CH}_3\text{CHOHCOO})_2 \cdot 3\text{H}_2\text{O}$  is monoclinic, space group  $P2_1/c$ , with  $a=9.38$ ,  $b=5.83$ ,  $c=22.00$  Å;  $\beta=90.9^\circ$ ,  $Z=4$ . The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to a final  $R$  of 0.105 for 1434 visual reflexions. The molecular dimensions are normal. The corresponding bond lengths in the bidentate lactate groups agree well with each other. Six oxygen atoms, four from lactate groups and two from water molecules, form a distorted octahedron round the zinc atom. The average Zn–O distance is 2.11 Å. All three water molecules take part in hydrogen-bond formation.

### Introduction

A study of metal complexes of lactic acid ( $\text{CH}_3\text{CHOHCOOH}$ ) has been undertaken to understand the influence of metal ions on the conformation of lactic acid and to provide structural data for the elucidation of its function in biological systems. This paper describes the structure of zinc lactate trihydrate. Manganese lactate trihydrate is isomorphous with zinc lactate trihydrate, and the structure analysis of copper lactate dihydrate is in progress.

### Experimental

Colourless crystals grow from aqueous solution as thin plates parallel to (010). A crystal of cross-section  $0.25 \times 0.30$  mm<sup>2</sup> was used for the collection of intensities by the multiple-film equi-inclination Weissenberg technique. 1434 independent reflexions were recorded with Cu  $K\alpha$  radiation. The systematic absences ( $h0l$  for  $l=2n+1$ ,  $0k0$  for  $k=2n+1$ ) uniquely determined the space group as  $P2_1/c$ . The crystal data are  $a=9.38$  (1),  $b=5.83$  (1),  $c=22.00$  (2) Å,  $\beta=90.9$  (1)<sup>o</sup>,  $D_m=1.63$ ,  $D_x=1.64$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha)=33.00$  cm<sup>-1</sup>,  $Z=4$ . Intensities of all reflexions were estimated visually, from extended spots in higher-level photographs. They were corrected for the Lorentz–polarization factor and the effect of spot extension (Phillips, 1954); absorption was neglected. The corrected intensities were brought to absolute scale by Wilson's (1942) method.

### Determination and refinement of the structure

The position of the zinc atom was determined ( $x=0.031$ ,  $y=0.195$ ,  $z=0.142$ ) from a Patterson synthesis.

All non-hydrogen atoms were identified from the Fourier synthesis phased on Zn. Atomic coordinates, individual layer scale factors, and isotropic temperature factors were refined by a block-diagonal least-squares program which reduced  $R$  from 0.26 to 0.145. At this stage an attempt was made to locate the positions of the hydrogen atoms from a difference map. Positions of 10 of the 16 hydrogen atoms were found. Inclusion of these with an isotropic temperature factor of 4.0 Å<sup>2</sup> reduced  $R$  to 0.132. With these hydrogen atoms fixed, four cycles of full-matrix least-squares refinement with anisotropic temperature parameters for all the non-hydrogen atoms were performed. The changes in atomic coordinates after the final cycle

Table 1. Final atomic parameters (fractional) with their estimated standard deviations in parentheses ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
No e.s.d.'s are given for hydrogen atoms			
Zn	0.0317 (2)	0.1890 (3)	0.1421 (1)
O(1)	−0.1057 (9)	0.3307 (20)	0.2052 (4)
O(2)	−0.3269 (11)	0.4285 (20)	0.2269 (5)
O(3)	−0.1759 (10)	0.1694 (18)	0.0951 (4)
O(4)	0.0753 (10)	0.5067 (16)	0.0960 (4)
O(5)	0.1748 (11)	0.6702 (17)	0.0182 (4)
O(6)	0.1209 (12)	0.0882 (18)	0.0597 (5)
O(7) <sub>w</sub>	0.4077 (11)	0.5749 (20)	0.1812 (6)
O(8) <sub>w</sub>	0.2120 (11)	0.2437 (18)	0.1960 (5)
O(9) <sub>w</sub>	0.0083 (12)	−0.1389 (19)	0.1727 (5)
C(1)	−0.3804 (18)	0.0193 (29)	0.1469 (8)
C(2)	−0.2889 (14)	0.2288 (28)	0.1327 (5)
C(3)	−0.2343 (14)	0.3440 (25)	0.1941 (6)
C(4)	0.3478 (18)	0.2409 (28)	0.0196 (8)
C(5)	0.1859 (18)	0.2546 (23)	0.0228 (6)
C(6)	0.1381 (15)	0.4976 (20)	0.0477 (7)
HC(1)	0.433	0.575	0.317
HC(1)	0.328	0.389	0.334
HC(1)	0.408	0.486	0.400
HC(4)	0.389	0.217	0.058
HC(4)	0.317	0.075	0.033
HC(4)	0.375	0.181	−0.021
HC(2)	0.342	0.833	0.383
HC(5)	0.175	0.245	−0.024
HO(7)	0.328	0.625	0.201
HO(9)	0.006	0.328	0.278

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were less than 0.003 Å; the final value of  $R$  was 0.105. The final positional and temperature parameters are listed in Tables 1 and 2.\*

### Description of the structure and discussion

The dimensions of the two lactate groups are presented in Fig. 1. The corresponding bond distances agree well. C(1)–C(2) and C(4)–C(5) ( $1.528 \pm 0.02$  and  $1.524 \pm 0.02$  Å respectively) agree well with those found in the bis-(L-serinato)zinc complex [ $1.521$ ,  $1.521$  Å; Van der Helm, Nicholas & Fisher (1970)] and in zinc glutamate dihydrate [ $1.523$ ,  $1.537$  Å; Gramaccioli (1966)]. C(2)–C(3) and C(5)–C(6), ( $1.585 \pm 0.02$ ,  $1.586 \pm 0.02$  Å respectively) are expected to be longer than C(1)–C(2) and C(4)–C(5) as C(3) and C(6) are connected to more electronegative (carboxyl) groups than are C(2) and C(5) (hydroxyl). Such long bonds have been found in the (amidoxalato-*O,O*)-zinc dihydrate

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30767 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

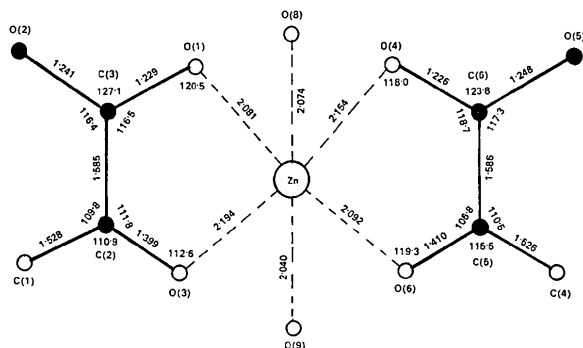


Fig. 1. Bond distances (Å) and bond angles (°) in zinc lactate trihydrate.

complex [C–C = 1.546 Å; Braibanti, Pellinghelli, Tiripicchio & Camellini (1971)], and potassium oxalate monohydrate [C–C = 1.5698 Å; Sequeira, Srikanta & Chidambaram (1970)]. C(3)–O(1), C(3)–O(2), C(6)–O(4) and C(6)–O(5) ( $1.229$ ,  $1.241$ ,  $1.226$  and  $1.248 \pm 0.018$  Å, respectively) in the two carboxylate groups suggest their ionic character. The planarity of the two carboxyl groups O(1), O(2), C(2), C(3) and O(4), O(5), C(5), C(6) is indicated by the equations of the mean planes through these atoms (Table 3).

Table 3. The equations of the least-squares planes

Plane 1	O(1), O(2), C(2), C(3)	$0.1323X + 0.8741Y - 0.4673Z + 0.5585 = 0$
Plane 2	O(4), O(5), C(5), C(6)	$0.8564X + 0.0584Y + 0.5129Z - 1.8243 = 0$
Plane 3	O(1), O(3), O(6), O(8) <sub>w</sub>	$0.1011X + 0.9345Y - 0.3413Z - 0.0970 = 0$
Deviations from the planes		

	(1)	(2)	(3)
O(1)	−0.006 Å	O(4)	0.008 Å
O(2)	−0.006	O(5)	0.008
C(2)	0.004	C(5)	0.006
C(3)	0.017	C(6)	−0.022
O(3)	0.222	O(6)	−0.167
C(1)	−1.332	C(4)	1.267
		O(1) <sub>w</sub>	0.05 Å
		O(3) <sub>w</sub>	−0.058
		O(6) <sub>w</sub>	0.048
		O(8) <sub>w</sub>	−0.047
		O(4) <sub>w</sub>	2.011
		O(9) <sub>w</sub>	2.148
		Zn	−0.109

Four oxygen atoms O(1), O(3), O(4) and O(6) from the two lactate groups and two O(8)<sub>w</sub> and O(9)<sub>w</sub> from water molecules are the six nearest neighbours of Zn. They form a distorted octahedron (Fig. 2) similar to those observed in zinc acetate dihydrate (Van Niekerk, Schoening & Talbot, 1953) and bis(amidoxalato-*O,O*)-zinc dihydrate (Braibanti *et al.*, 1971). Zn–O distances vary from 2.040 to 2.194 Å, and the average, 2.106 Å, is quite close to the 2.094 Å in bis(amidoxalato-*O,O*)-zinc dihydrate and 2.061 Å in zinc glutamate dihydrate (Gramaccioli, 1966). However Zn–O distances have been found to vary considerably, from as small as 1.954 Å in bis(thiourea)zinc acetate (Cavalca,

Table 2. Final anisotropic thermal parameters ( $\times 10^4$ ) with their estimated standard deviations in parentheses ( $\times 10^4$ )

$$\text{Temperature factor} = \exp [-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + hk B_{12} + hl B_{13} + kl B_{23})].$$

	$\beta_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Zn	90 (2)	189 (5)	15 (0)	−2 (7)	1 (1)	3 (3)
O(1)	52 (10)	287 (36)	10 (2)	−5 (35)	−11 (7)	14 (15)
O(2)	105 (14)	267 (39)	20 (3)	64 (42)	12 (10)	37 (17)
O(3)	96 (12)	182 (32)	13 (2)	33 (37)	−3 (8)	18 (14)
O(4)	118 (14)	186 (34)	6 (2)	16 (33)	20 (8)	0 (11)
O(5)	129 (15)	104 (30)	16 (2)	−4 (38)	2 (9)	0 (14)
O(6)	144 (17)	182 (36)	18 (2)	4 (40)	35 (10)	44 (15)
O(7) <sub>w</sub>	91 (14)	290 (42)	33 (4)	−83 (41)	−1 (11)	−33 (20)
O(8) <sub>w</sub>	88 (13)	249 (43)	31 (3)	−110 (36)	−52 (11)	82 (18)
O(9) <sub>w</sub>	152 (17)	203 (39)	20 (2)	−6 (41)	−6 (11)	7 (16)
C(1)	114 (22)	266 (63)	21 (4)	91 (61)	7 (15)	22 (25)
C(2)	63 (15)	320 (63)	10 (2)	39 (50)	−17 (10)	4 (19)
C(3)	75 (17)	150 (47)	18 (3)	90 (48)	0 (12)	−8 (20)
C(4)	126 (24)	243 (65)	33 (5)	82 (58)	−10 (18)	−32 (27)
C(5)	138 (23)	155 (55)	13 (3)	6 (50)	38 (13)	−15 (18)
C(6)	77 (17)	67 (40)	15 (3)	12 (39)	−13 (12)	16 (16)

Gasparri, Andreotti & Domiano, 1967) and as long as 2.27 Å in the zinc 8-hydroxyquinolate complex (Palenik, 1964). Table 4 lists Zn-O distances observed in some zinc complexes.

Table 4. Range of Zn-O distances in various zinc complexes

Zinc glutamate dihydrate (Gramaccioli, 1966)	2.03-2.11 Å
Bis-(L-serinato)zinc (Van der Helm, Nicholas & Fisher, 1970)	1.96-2.19
Trimeric bis(acetylacetonato)zinc (Bennett, Cotton & Eiss, 1968)	1.97-2.17
Zinc 8-hydroxyquinolate dihydrate (Palenik, 1964)	2.07-2.26
Bis(thiourea)zinc acetate (Cavalca <i>et al.</i> , 1967)	1.95-1.97
Bis(amidoxalato-O, O)-zinc dihydrate (Braibanti, Pellinghelli, Tiripicchio & Camellini, 1971)	2.04-2.15
Zinc lactate trihydrate	2.04-2.19

In the coordination polyhedron O(1), O(3), O(6) and O(8)<sub>w</sub> are approximately coplanar (Table 3). The zinc atom lies only 0.109 Å away from this plane and is displaced towards the next nearest neighbour O(9)<sub>w</sub>.

The crystal structure viewed down *b* is shown in Fig. 3. All three water molecules enter into hydrogen-bond formation. The various hydrogen-bond distances are presented in Table 5. O(8)<sub>w</sub> of the water molecule is coordinated to Zn and also forms two fairly strong hydrogen bonds with O(7)<sub>w</sub> (2.688 Å) belonging to the same asymmetric unit and with O(2) (2.713 Å) of the symmetry-related molecule at  $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ . O(9)<sub>w</sub> of the second water molecule is also coordinated to Zn and enters into hydrogen-bond formation with O(4) (2.746 Å) and O(1) (2.830 Å) of the symmetry-

related molecule at  $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ . The uncoordinated O(7)<sub>w</sub> of the third water molecule act as a bridging atom between two different asymmetric units (Fig. 3).

The hydroxyl groups in the molecule are also involved in hydrogen-bond formation. O(3) of the lactate group is linked strongly (2.662 Å) to O(5) of the carboxyl group from the next unit cell. O(6) in the other lactate group is also strongly hydrogen-bonded (2.655 Å) to O(5) at  $(x, -1 + y, z)$ . Thus the structure contains a network of hydrogen bonds which plays an important part in stabilization. There are several non-bonded contacts less than 3.50 Å (Table 5).

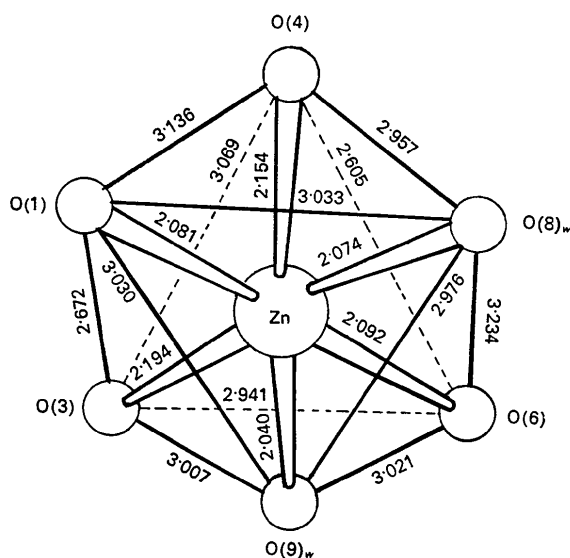


Fig. 3. Coordination polyhedron around zinc.

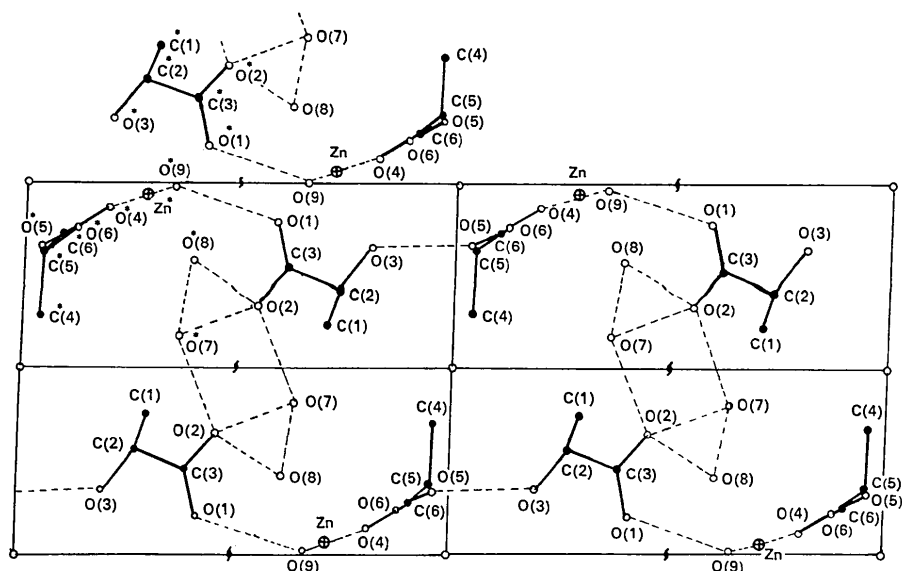


Fig. 2. Crystal structure of zinc lactate trihydrate viewed down the *b* axis. Hydrogen bonds are shown by broken lines. Atoms with asterisks correspond to one complete asymmetric molecule.

Table 5. Intermolecular distances

(i) Hydrogen-bond distances			
O(7) <sub>w</sub> ···O(2)	(-x, ½+y, ½-z)		2.995 Å
O(7) <sub>w</sub> ···O(2)	(1+x, y, z)		2.803
O(7) <sub>w</sub> ···O(8) <sub>w</sub>	(x, y, z)		2.688
O(8) <sub>w</sub> ···O(2)	(-x, -½+y, ½-z)		2.713
O(9) <sub>w</sub> ···O(1)	(-x, ½+y, ½-z)		2.830
O(9) <sub>w</sub> ···O(4)	(x, -1+y, z)		2.746
O(3)···O(5)	(-x, 1-y, -z)		2.662
O(6)···O(5)	(x, -1+y, z)		2.665
(ii) Other important non-bonded distances			
O(1)···O(8) <sub>w</sub>	(-x, ½+y, ½-z)		3.404 Å
O(1)···O(9) <sub>w</sub>	(x, 1+y, z)		3.353
O(4)···O(5)	(x, 1+y, z)		3.505
O(5)···C(5)	(x, 1+y, z)		3.410
O(5)···C(6)	(-x, 1-y, -z)		3.396
O(6)···C(6)	(x, -1+y, z)		3.457
O(7) <sub>w</sub> ···C(2)	(1+x, 1+y, ½-z)		3.358
O(8) <sub>w</sub> ···C(3)	(-x, ½+y, ½-z)		3.364
C(6)···C(6)	(-x, 1-y, -z)		3.308

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## Crystal and Molecular Structure of L-Cystine Dimethyl Ester Dihydrochloride Monohydrate\*

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$C_8H_{16}N_2O_4S_2 \cdot 2HCl \cdot H_2O$  is monoclinic, space group  $P2_1$ , with  $a=14.80$ ,  $b=9.34$ ,  $c=5.85$  Å,  $\beta=91.47^\circ$ ,  $Z=2$ . The structure was solved by the heavy-atom method and refined by block-diagonal least-squares calculations to a final  $R$  of 0.103 for 1620 observed reflexions. The structure is stabilized by an extensive network of hydrogen bonds. The disulphide dihedral angle is  $84.4^\circ$ . The helical sense of the cystinyl group in the molecule is 'left'.

### Introduction

Cystine and its derivatives form an interesting series of compounds in relation to protein structures. The disulphide bridge constitutes one of the important means by which the polypeptide chains of proteins are held together, and plays an important role in deciding their configuration. Hence a study of the conformation of the cystinyl group under a wide variety of conditions is helpful in the study of protein structures. The ester derivatives of amino acids are also of biochemical importance and undergo enzymatic hydrolysis, one of the most fundamental metabolic transformations.

### Experimental

The compound was crystallized by slow evaporation of its solution in water-ethanol mixture. Only one suitable crystal was obtained and this was cut to obtain

two very small single crystals. Preliminary photographs showed that the crystal is monoclinic. The only systematic absences were  $0k0$ ,  $k$  odd. The space group was uniquely determined to be  $P2_1$ , since it is an L compound. The cell dimensions were measured from precession photographs.

### Crystal data

$C_8H_{16}O_4N_2S_2 \cdot 2HCl \cdot H_2O$ , monoclinic,  $a=14.80$  (1),  $b=9.34$  (1),  $c=5.85$  (1) Å,  $\beta=91.47$  (0.2)°; space group  $P2_1$ ;  $0k0$ ,  $k=2n+1$  absent.  $Z=2$ ,  $M=359.3$ ,  $D_o=1.46$ ,  $D_c=1.475$  g cm<sup>-3</sup>,  $\mu=59.9$  cm<sup>-1</sup>,  $\lambda$  (for Cu  $K\alpha$  radiation)=1.5418 Å.

Intensities were collected photographically by the multiple-film equi-inclination Weissenberg technique with Ni-filtered Cu  $K\alpha$  radiation. Intensities of 1620 independent reflexions ( $hkl$ ,  $l=0-4$  and  $hkl$ ,  $k=0-2$ ) were estimated visually and corrected for Lorentz, polarization and spot-shape factors (Phillips, 1954). The data about the two axes were brought to a single scale (Rollett & Sparks, 1960). An overall temperature factor of 2.8 Å was obtained from a Wilson plot.

\* Contribution No. 387 from the Centre of Advanced Study in Physics, University of Madras, Guindy Campus, Madras-600025, India.