The Crystal Structure of S-Malatodiaquozinc(II) Hydrate

By A. Thomas Reed and Anastas Karipides

Department of Chemistry, Miami University, Oxford, Ohio 45056, U.S.A.

The crystal structure of S-malatodiaquozinc(II) hydrate, $[Zn(C_4H_4O_5) (H_2O)_2].H_2O$, has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter methods on a computer-automated diffractometer. The compound crystallizes in the monoclinic space group $P2_1$ (C_2^2) with two formula units in a cell of dimensions $a = 8.901$ (7), $b = 9.087$ (6), $c = 5.803$ (3) Å and $\beta = 113.20$ (3)°. The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares procedure to a conventional R index of 0.047 for 1031 independent reflections. An α-carboxyl oxygen atom and the hydroxyl oxygen form a five-membered chelate ring with the Zn^{II} ion while coordination of the β-carboxylate group creates in addition a six-membered chelate ring. The distorted octahedral coordination about the Zn^{II} ion is completed by two water molecules and a bridging β-carboxylate oxygen from a neighboring malate group. The structure consists of polymeric chains linked together along [010] by the β-carboxylate group. A network of hydrogen bonds utilizing the single water of hydration holds the chains together. The malate conformation is synclinal, which is consistent with that observed in aqueous solutions of the Zn^{II}–malate complex. The range in Zn–O bond lengths is 2.050 (5) to 2.153 (5) Å.

Introduction

As part of a general program to investigate the nature of metal ion binding of multidentate carboxylate ligands, we have determined the crystal structure of S-malatodiaquozinc(II) hydrate to establish further the ambidentate nature of the malate ligand with metal ions of similar size and charge (Karipides & Reed, 1976) as well as to determine the structural characteristics of malate–Zn^{II} binding in the crystal for comparison with that occurring in solution (Mariano & Gill, 1969).

Experimental

Colorless prismatic crystals of the title compound were grown by slow evaporation of an aqueous solution prepared by dissolving zinc carbonate in S-malic acid in a 1:2 molar ratio. These crystals may be easily selected from the mass of the 1:2 zinc:malate, $Zn(C_4H_4O_5)_2.4H_2O$, tetragonal crystals which co-crystallize.

A single crystal of approximate dimensions $0.20 \times 0.28 \times 0.31$ mm mounted along the longest dimension (b axis) was used. Indexed Weissenberg photographs revealed monoclinic crystal symmetry and systematic absences $0k0$, for k odd. The non-centrosymmetric space group $P2_1$ could be uniquely assigned since the crystals are optically active. Accurate values of the cell dimensions were obtained by the least-squares refinement of the angular settings of twelve reflections carefully measured on a Picker FACS-1 automated diffractometer. The experimental density was determined by flotation in a mixture of iodomethane and iodoethane. The pertinent crystal data are presented in Table 1.

Three-dimensional X-ray intensity data were col-

Table 1. *Crystal data for S-malatodiaquozinc*(II) *hydrate*

$[ZnC_4H_4O_5(H_2O)_2].H_2O$	Space group $P2_1$ (C_2^2)
$a = 8.901$ (7) Å	F.W. 251.5 g mol^{-1}
$b = 9.087$ (6)	$F(000) = 256$
$c = 5.803$ (3)	μ(Mo $K\alpha$) = 29.5 cm^{-1}
$\beta = 113.20$ (3)°	$D_o = 1.94$ (1) g cm^{-3}
$Z = 2$	$D_c = 1.936$
$V = 431.4$ Å^3	

lected on the diffractometer already mentioned using zirconium-filtered Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation. The crystal was mounted along the $\mathbf{b}^*$ direction which was made coincident with the instrumental φ axis. A total of 1117 reflections out to 55° in 2θ were recorded using the θ–2θ scan mode. A scan range from 1° below the Mo $K\alpha_1$ peak to 1° above the Mo $K\alpha_2$ peak was used; the scan rate was 1° min^{-1}. A background count for 20 s at the start and end of each scan was taken. During the data collection the intensities of two standard reflections were monitored after each 50 measurements and none showed any significant variation during the three days of data collection.

Each net intensity, I, was corrected for Lorentz and polarization factors (Lp) to give the observed structure factor amplitude, F_o, using $I = C - (t_c/2t_B) (B_1 + B_2)$ and $F_o = (I/\text{Lp})^{1/2}$. The estimated standard deviation in I, $\sigma(I)$, and in F_o, $\sigma(F_o)$, was computed from $\sigma(I) = [C + (t_c/2t_B)^2(B_1 + B_2) + (pI)^2]^{1/2}$ and $\sigma(F_o) = (2F_o)^{-1} \times (\text{Lp})^{-1}\sigma(I)$. In these expressions C is the total count accumulated during the scan in time t_c, B_1 and B_2 are the background counts observed at each extreme in the scan each in a time t_B, and p was taken to be 0.04. No absorption corrections were applied. As a check on possible variation in transmission factors, the intensity of the 040 reflection was measured at $\chi = 90°$ over a wide range of φ angles; no significant difference

in intensity (<6%) was noted, suggesting that absorption effects could be ignored. A total of 1031 reflections had $I > \sigma(I)$ and these were used in subsequent calculations.

Structure determination and refinement

The zinc ion was easily found from a three-dimensional Patterson synthesis. The y coordinate of the

Table 2. *Final parameters and their standard deviations* ($\times 10^4$)

The anisotropic coefficients for the heavier atoms are of the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
Hydrogen atoms were assigned a fixed isotropic temperature factor of 5·0 Å^2.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	1646·6 (8)	2500	1370 (1)	70 (1)	48·2 (8)	139 (2)	0 (1)	43 (11)	2 (2)
O(1)	2728 (7)	1968 (7)	−1053 (10)	119 (8)	99 (7)	140 (16)	49 (6)	79 (10)	48 (9)
O(2)	4501 (7)	440 (8)	−1608 (10)	111 (8)	123 (9)	190 (17)	42 (7)	85 (10)	19 (10)
O(3)	3949 (6)	1570 (6)	3811 (9)	87 (7)	63 (6)	134 (16)	−7 (6)	42 (8)	−15 (8)
O(4)	794 (6)	352 (7)	1221 (12)	66 (7)	54 (6)	354 (24)	1 (5)	39 (11)	17 (10)
O(5)	721 (6)	−2086 (6)	1084 (10)	77 (7)	52 (7)	233 (18)	−6 (5)	22 (9)	11 (8)
O(6)	1137 (7)	3127 (7)	4427 (10)	142 (9)	68 (6)	163 (16)	15 (7)	83 (10)	24 (9)
O(7)	2487 (6)	4716 (7)	1390 (10)	84 (7)	63 (6)	257 (19)	−5 (6)	60 (10)	26 (10)
O(8)	1455 (10)	−3932 (8)	−4471 (14)	212 (3)	97 (9)	332 (24)	61 (9)	158 (15)	41 (13)
C(1)	3823 (8)	988 (9)	−308 (12)	77 (9)	62 (8)	132 (20)	−5 (7)	40 (11)	−1 (12)
C(2)	4291 (8)	405 (8)	2383 (12)	57 (8)	67 (8)	124 (19)	−1 (7)	26 (10)	8 (11)
C(3)	3343 (9)	−1002 (9)	2363 (13)	84 (10)	49 (8)	183 (23)	8 (8)	26 (13)	18 (12)
C(4)	1478 (8)	−876 (8)	1488 (12)	82 (10)	49 (8)	122 (21)	11 (7)	22 (12)	19 (10)

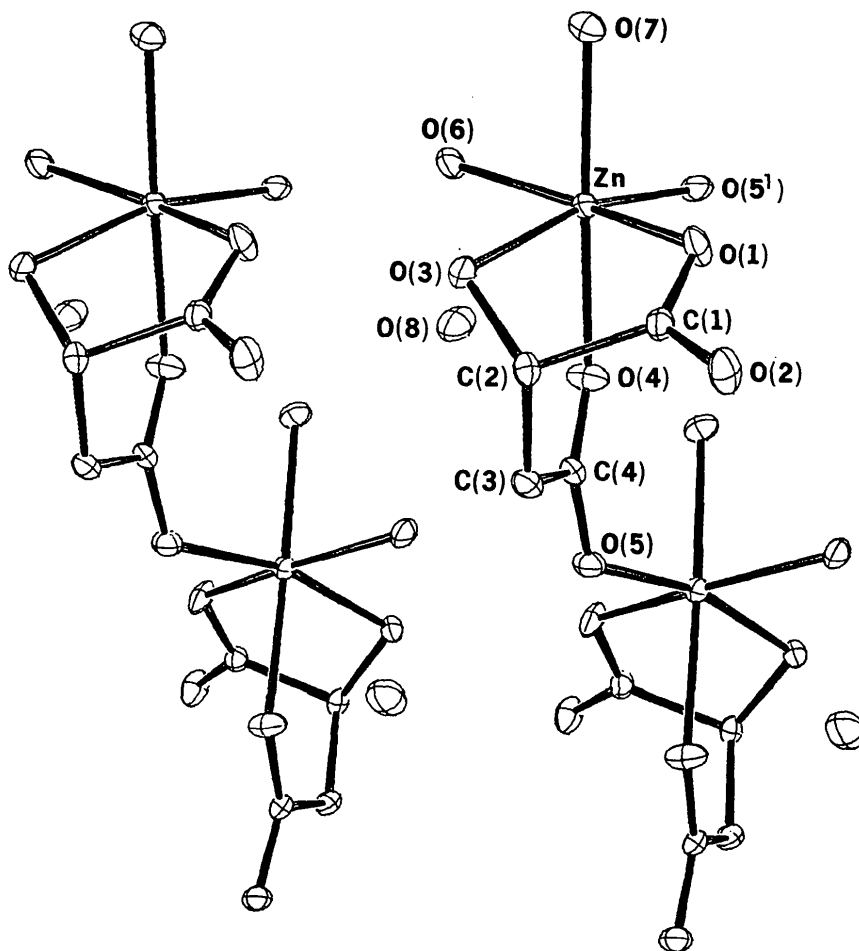|	x	y	z			x	y	z
H(O3)	4536	2159	4015		H2(C3)	3630	−1782	1290
H(C2)	5451	78	3007		H1(O8)	664	−3618	−4368
H1(C3)	3663	−1579	3974		H2(O8)	1250	−4995	−4996

Fig. 1. A perspective drawing of the crystal structure viewed along the a axis showing the coordination polyhedron, portions of the polymeric units and the atom-numbering scheme.

heavy ion was chosen as $\frac{1}{4}$ to fix the origin in space group $P2_1$. The remaining non-hydrogen atoms were located from a series of difference Fourier syntheses which were based on phases obtained from the refined parameters of the atoms previously located. The configuration of the malato ligand was fixed to be (S), consistent with the absolute configuration determined in cobalt(II) L-malate trihydrate (Kryger & Rasmussen, 1972). The trial structure was refined by a full-matrix procedure assuming at first isotropic then anisotropic motion for the zinc, carbon and oxygen atoms. A difference Fourier synthesis at this point revealed the hydrogen atoms on the malato moiety as well as the water hydrogen atoms on O(8). Despite numerous efforts, the regions around the water oxygen atoms O(6) and O(7) remained featureless and their corresponding hydrogen atoms were not located. Each hydrogen atom found was assigned an isotropic temperature factor of $5 \cdot 0$ Å^2. The entire structure was further refined by full-matrix least squares although the hydrogen atom parameters were not varied. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight, w, applied to each observation was taken to be $1/\sigma^2(F_o)$. The structure refinement converged to a conventional R_1 index, $\sum ||F_o| - |F_c||/\sum |F_o|$, of 0·047 and a weighted R_2 index, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0·057. In the last cycle of least-squares refinement the largest shift in any positional or thermal parameter was 0·02 times its own standard deviation. The standard deviation in an observation of unit weight, defined by $[\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$ was 2·32, where the number of observations (m) was 1031 and the number of variable parameters (n) was 117. An analysis of $w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ or $\sin \theta/\lambda$ revealed no dependence on these quantities.

The neutral atomic scattering factors for zinc (corrected for $\Delta f'$ and $\Delta f''$), carbon and oxygen were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). The hydrogen atom scattering factors were those of Stewart, Davidson & Simpson (1965). In addition to local programs for the IBM 370/168 computer, the following programs or modifications were used: FORDAP (Zalkin, unpublished), ORFLS and ORFFE (Busing, Martin & Levy, 1962, 1964), ORTEP-II (Johnson, 1970) and PLANET (Smith, 1962). The final atomic positional and thermal parameters and their standard deviations are given in Table 2.*

Description of the structure and discussion

Views of the coordination polyhedron about the Zn^{II} ion, ligand stereochemistry, a portion of the polymeric units occurring in the unit cell and the atom-numbering scheme are presented in Figs. 1 and 2. Intramolecular bond distances and angles are given in Table 3.

There are no symmetry conditions imposed on the structure by the space group $P2_1$. The coordination environment of the Zn^{II} ion is that of an irregular octahedron from six oxygen atoms. The range in Zn–O bond distances of 2·050 (5) to 2·153 (5) Å (average $2 \cdot 09 \pm 0 \cdot 04$ Å) is similar to the range 2·040 to 2·194 Å found in zinc lactate trihydrate (Singh, Jain, Sakore & Biswas, 1975), 1·96 to 2·19 Å in bis(L-serinato)zinc (van der Helm, Nicholas & Fisher, 1970) and 2·03 to 2·11 Å in zinc glutamate trihydrate (Gramaccioli, 1966). Four of the five oxygen atoms in the malate ligand are involved in coordination to Zn^{II} ions. The carboxylate oxygen, O(1), and the

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31681 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
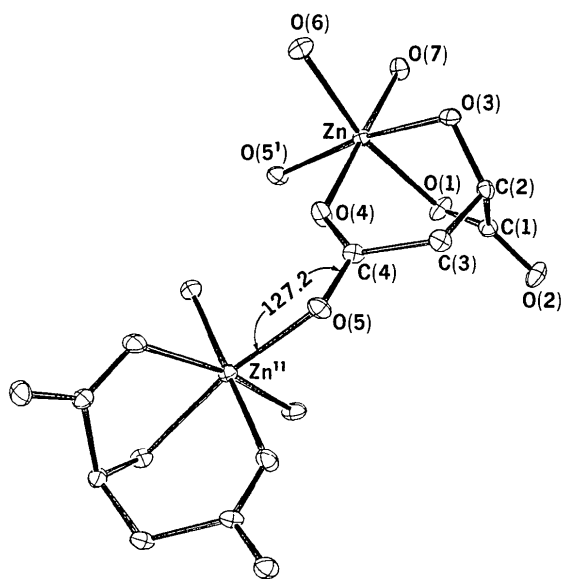

Fig. 2. A projection of the structure viewed along the c axis. The primed atoms are related to the corresponding atom positions given in Table 2 by the following symmetry transformations: O(5′) $(\bar{x},\frac{1}{2}+y,\bar{z})$; Zn″ $(\bar{x},y-\frac{1}{2},\bar{z})$.

Table 3. *Bond distances* (Å) *and angles* (°)

Zn——O(1)	2·050 (5)	C(1)–O(2)	1·241 (9)
Zn——O(3)	2·153 (5)	C(1)–C(2)	1·542 (9)
Zn——O(4)	2·084 (6)	C(2)–C(3)	1·530 (10)
Zn——O(5′)	2·060 (5)	C(2)–O(3)	1·499 (9)
Zn——O(6)	2·076 (5)	C(3)–C(4)	1·538 (10)
Zn——O(7)	2·146 (6)	C(4)–O(4)	1·251 (10)
C(1)–O(1)	1·264 (9)	C(4)–O(5)	1·262 (10)
O(1)–Zn–O(3)	77·1 (2)	Zn——O(1)–C(1)	116·0 (4)
O(1)–Zn–O(4)	90·7 (2)	Zn——O(3)–C(2)	105·7 (4)
O(1)–Zn–O(5′)	101·4 (2)	Zn——O(4)–C(4)	132·7 (4)
O(1)–Zn–O(6)	166·0 (3)	Zn——O(5′)–C(4′)	127·2 (4)
O(1)–Zn–O(7)	88·2 (2)	O(1)–C(1) –O(2)	124·7 (6)
O(3)–Zn–O(4)	84·0 (2)	O(1)–C(1) –C(2)	116·9 (6)
O(3)–Zn–O(5′)	167·4 (2)	O(2)–C(1) –C(2)	118·4 (7)
O(3)–Zn–O(6)	91·0 (2)	O(3)–C(2) –C(1)	107·1 (6)
O(3)–Zn–O(7)	97·2 (2)	C(1)–C(2) –C(3)	110·6 (5)
O(4)–Zn–O(5′)	83·4 (2)	O(3)–C(2) –C(3)	112·1 (5)
O(4)–Zn–O(6)	95·4 (2)	C(2)–C(3) –C(4)	117·4 (6)
O(4)–Zn–O(7)	178·1 (3)	O(4)–C(4) –C(3)	121·1 (7)
O(5′)–Zn–O(6)	91·8 (2)	O(5)–C(4) –C(3)	115·1 (6)
O(5′)–Zn–O(7)	95·3 (2)	O(4)–C(4) –O(5)	123·7 (6)
O(6)–Zn–O(7)	86·0 (2)		

hydroxyl oxygen, O(3), form a five-membered chelate ring Zn–O(1)–C(1)–C(2)–O(3) while simultaneous coordination of the β-carboxylate oxygen atom, O(4), creates in addition the six-membered chelate ring Zn–O(3)–C(2)–C(3)–C(4)–O(4). The other β-carboxylate oxygen, O(5), is bridged to a different Zn^{II} ion in another asymmetric unit. The two Zn^{II} ions, Zn and Zn″ (see Fig. 2), coordinated by the β-carboxylate group, lie 0·19 and 0·77 Å, respectively, from the O(4)–C(4)–O(5) plane. Two water molecules, O(6) and O(7), complete the Zn^{II} sixfold coordination polyhedron. The carboxylate oxygen, O(2), and lattice water, O(8), are not coordinated by the Zn^{II} ion. Thus, the malate ion acts as a tridentate ligand towards one Zn^{II} ion and monodentate towards another. It follows that each Zn^{II} ion is attached to two different malate ligands.

The binding of malate to Zn^{II} ion is similar to that found in the corresponding Co^{II} complex (Kryger & Rasmussen, 1972), but differs substantially from the malate–Mn^{II} binding observed in S-malatodiaquomanganese(II) hydrate (Karipides & Reed, 1976). In the Mn^{II} compound the malate ligand is bidentate towards one Mn^{II} ion utilizing an α-carboxyl oxygen atom and the hydroxyl oxygen to form only a five-membered chelate ring. The β-carboxylate group does not bend back and chelate the Mn^{II} but instead forms monodentate bridge bonds to two other Mn^{II} ions. The malate–Ca^{II} binding in the crystalline calcium malate complex resembles that found in the Zn^{II} compound; but, in addition, the malate β-carboxylate group is involved in a four-membered chelate ring with a different calcium ion. These examples establish the ambidentate nature of malate–metal ion interactions (Karipides & Reed, 1976).

The crystal structure consists of infinite chains linked together along [010] by the β-carboxylate group. These polymeric chains are held together by a network of hydrogen bonds utilizing the lattice water, O(8). Both hydrogen atoms of the lattice water are involved in hydrogen bonds. These are O(8)–H1(O8)···O(6) ($\bar{x}, y-\frac{1}{2}, \bar{z}$) and O(8)–H2(O8)···O(6) ($x, y-1, z-1$). The structural parameters for the D···A and H···A distances and the D–H···A angle respectively are: 2·979 (9), 2·25 Å, 156° and 2·736 (10), 1·73 Å, 172°, respectively. Although hydrogen atom positions could not be located for the water molecules O(6) and O(7) there are possibly, in addition, the following hydrogen bonding interactions: O(7)···O(8) ($x, 1+y, 1+z$) 3·140 (9) Å, O(7)···O(2) ($1-x, \frac{1}{2}+y, \bar{z}$) 2·715 (7) Å, O(7)···O(4) ($\bar{x}, \frac{1}{2}+y, \bar{z}$) 2·770 (8) Å, and O(6)···O(1) ($x, y, 1+z$) 2·658 (8) Å. The hydroxyl group is not involved in hydrogen-bond formation.

The five-membered chelate ring, Zn–O(1)–C(1)–C(2)–O(3), is severely buckled and exists in an asymmetric envelope conformation while the conformation of the six-membered chelate ring, Zn–O(3)–C(2)–C(3)–C(4)–O(4), is best described as an asymmetric boat (Hawkins, 1971). Pertinent dihedral angles involved in the chelate rings and ligand are summarized in

Table 4. *Dihedral angles*

A positive angle represents a clockwise rotation of the bond kl with respect to the bond ij, when viewed along the bond jk.

i	j	k	l	
Zn—	O(1)–	C(1)–	C(2)	−4·3°
O(1)–	C(1)–	C(2)–	O(3)	−27·0
C(1)–	C(2)–	O(3)–	Zn	41·6
C(2)–	O(3)–	Zn—	O(1)	−35·4
O(3)–	Zn—	O(1)–	C(1)	22·4
Zn—	O(3)–	C(2)–	C(3)	−79·8
O(3)–	C(2)–	C(3)–	C(4)	54·2
C(2)–	C(3)–	C(4)–	O(4)	−12·1
C(3)–	C(4)–	O(4)–	Zn	7·7
C(4)–	O(4)–	Zn—	O(3)	−26·8
O(4)–	Zn—	O(3)–	C(2)	56·8
C(1)–	C(2)–	C(3)–	C(4)	−65·3
O(3)–	C(2)–	C(3)–	C(4)	54·2

Table 4. The atoms C(1) and C(2) lie 0·43 and 0·81 Å, respectively, from the Zn–O(1)–O(3) plane while C(2), C(3), C(4) are 1·17, 0·92 and 0·41 Å, respectively, from the Zn–O(3)–O(4) plane.

The malate conformation is specified by the dihedral angles C(1)–C(2)–C(3)–C(4) of −65·3 and O(3)–C(2)–C(3)–C(4) of 54·2° (see Table 4). The conformation is thus synclinal with respect to the carboxylate groups and is consistent with the conformation observed in aqueous solution in a ^{1}H-NMR study of the 1:1 Zn^{II}–malate complex (Mariano & Gill, 1969). Although the indicated NMR study was inconclusive regarding the precise nature of chelation, the fact that the malate conformation is similar both in the crystal and in solution suggests that malate retains its tridentate nature with Zn^{II} ion in solution.

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