Structure of Diaqua(4-oxoheptanedioato)zinc(II), [Zn(C₇H₈O₅)(H₂O)₂]

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Abstract. $M_r = 273 \cdot 6$, monoclinic, $P2/c$, $a = 9 \cdot 307$ (3), $b = 5 \cdot 194$ (2), $c = 10 \cdot 850$ (5) Å, $\beta = 99 \cdot 74$ (1)°, $V = 516 \cdot 9$ Å^3, $Z = 2$, $D_m = 1 \cdot 74$, $D_x = 1 \cdot 76$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0 \cdot 246$ cm^{-1}, $F(000) = 280$, $T = 293$ K. Final $R = 0 \cdot 042$ for 1172 unique observed reflections. The Zn^{2+} and 4-oxoheptanedioate ions are each constrained by the space group to lie on sites of C_2 symmetry. The severely distorted 'octahedral' ZnO$_6$ polyhedron consists of two water molecules (*cis* configuration) at 2·020 (2) Å and four carboxylate O atoms from two different 4-oxoheptanedioate ions at 2·213 (3) and 2·179 (2) Å. The oxo O atom is not coordinated to the Zn^{2+} ion.

Introduction. For some time, we have been interested in the variability of metal-ion binding by carboxylate ligands (Karipides, 1979; Karipides & Reed, 1980; Karipides, Ault & Reed, 1977). As part of these studies, the crystal structure of diaqua(4-oxoheptanedioato)zinc(II) has been determined to investigate the nature of the zinc(II) coordination polyhedron as well as the role of the oxo O atom in the structure.

Experimental. Colorless prisms grown by slow evaporation of an aqueous solution prepared by dissolving zinc carbonate in a solution of 4-oxoheptanedioic acid; approximate crystal dimensions $0 \cdot 2 \times 0 \cdot 2 \times 0 \cdot 3$ mm. Picker FACS-I diffractometer, Mo $K\alpha$. 12 reflections used for measuring lattice parameters. $2\theta_{max} = 55°$. Range of hkl: -12–11, 0–6, 0–14. 1302 reflections collected, 1172 unique data with $F_o > \frac{1}{2}\sigma(F_o)$, $\sigma(F_o)$ derived from previously defined $\sigma(I)$ (Karipides, 1979). [Four strong reflections (100, 130, 002, 211) judged to be suffering from extinction removed.] No absorption corrections. No significant variation in intensities for two standard reflections. Structure solved using conventional heavy-atom methods. H-atom positions located from a difference Fourier synthesis. Full-matrix least-squares refinement (based on F); anisotropic thermal parameters for non-H atoms; H positional and thermal parameters not varied; refinement converged to $R = 0 \cdot 042$, $R_w = 0 \cdot 063$ with $w = [\sigma(F_o)]^{-2}$; $S = 2 \cdot 02$. $(\Delta/\sigma)_{max} = 0 \cdot 01$. 70 parameters refined. Final difference electron density map revealed no peaks $> 0 \cdot 38$ e Å^{-3}. Atomic scattering factors for all atoms and anomalous-dispersion correc-

tions for Zn from *International Tables for X-ray Crystallography* (1974).

Discussion. Computer programs used have been described (Karipides, 1979). Final atom coordinates and isotropic thermal parameters are given in Table 1.* A view of the structure and atom-numbering scheme is shown in Fig. 1. Bond distances and angles are given in Table 2. For two formula units in the unit cell, space group $P2/c$ requires that both the Zn^{2+} and the 4-oxoheptanedioate ions lie on different crystallographic sites each with C_2 symmetry. Thus, the asymmetric unit contains half of the anion as well as one water molecule.

The irregular ZnO$_6$ coordination polyhedron consists of two water molecules, O(W) and O(W^i), and four carboxylate O atoms, O(1), O(2), O(1^i) and O(2^i) from two different 4-oxoheptanedioate ions. Although the coordination about Zn^{2+} may be considered approximately 'octahedral', extensive deviations from the idealized angles are present. This is primarily due to the small bite angle of 58·9 (1)° from the carboxylate group. In addition, there is the somewhat large angle of 102·3 (1)° between the coordinated water molecules.

The bidentate Zn^{2+}–carboxylate coordination is symmetric with Zn–O(1) and Zn–O(2) bond distances of 2·213 (3) and 2·179 (2) Å respectively. With the exception of zinc acetate dihydrate (Zn–O, 2·17, 2·18 Å) (van Niekerk, Schoening & Talbot, 1953), this mode of binding involving four-membered chelate rings has not been observed in previously reported Zn^{2+}–carboxylate structures. It is particularly noteworthy that the Zn–O bond lengths in the two cases of symmetric bidentate coordination are appreciably longer than the average 2·02 ± 0·08 Å (range 1·914 to 2·166 Å) reported for unidentate carboxylate–Zn^{2+} interactions in anhydrous zinc acetate (Capilla & Aranda, 1979), zinc formate dihydrate (Burger & Fuess, 1977), zinc propionate (Goldschmiel, Rae & Stephenson, 1977), zinc 2-chlorobenzoate (Nakacho,

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* Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38775 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Misawa, Fujiwara, Wakahara & Tomita, 1976), zinc tetrafluorosuccinate tetrahydrate (Karipides, 1980), zinc o-ethoxybenzoate monohydrate (Natarajan, Sake Gowda & Cartz, 1974) and zinc malonate dihydrate (Ray & Hathaway, 1982). This lengthening is the result of the steric constraint imposed on a carboxylate group in binding a small ion such as Zn^{2+}. The observed $Zn^{2+}\cdots C(1)$ distance of 2·556 (3) Å probably represents an approximate limit for such an interaction (Smith, O'Reilly, Kennard, Stadnicka & Oleksyn, 1981). Carboxylate four-membered chelate-ring formation is much more common with larger cations such as Ca^{2+} (Einspahr & Bugg, 1977; Karipides et al., 1977; Karipides & Reed, 1980).

The 4-oxoheptanedioate anion, which binds two different Zn^{2+} ions in a bidentate fashion from each of its two carboxylate groups, has C_2 symmetry. A twofold axis is collinear with the C(4)—O(3) bond direction. The central portion of the ligand is approxi-
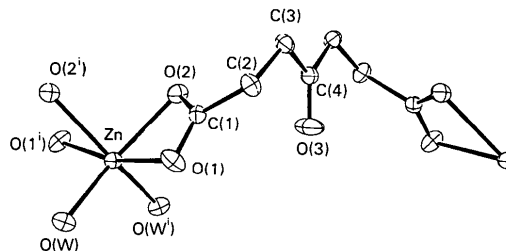

Fig. 1. A view of a portion of the structure showing the ZnO_6 coordination polyhedron, mode of ligand–Zn^{2+} binding and the atom-numbering scheme.

mately planar as indicated by the torsion angle C(2)—C(3)—C(4)—C(3^{iv}) of 171·3°. The carboxylate group is twisted by about 18° from the C(1)—C(2)—C(3) plane. An interesting feature is that the oxo O atom, O(3), does not participate in any binding to Zn^{2+} ions nor is it involved in the hydrogen-bonding scheme. The shortest intermolecular contact to O(3) is H2(C3^v) [(v) x, 1 + y, z] at 2·90 Å, which is too long for a C—H···O hydrogen bond.

The crystal structure consists of chains of ···(H₂O)₂-$ZnO_2CCH_2CH_2C(O)CH_2CH_2COOZn(H_2O)_2$··· units linked together along [100]. Besides ionic interactions, these chains are held together by hydrogen bonds involving both H atoms from the water molecules. Hydrogen-bonding parameters are given in Table 2.

Table 1. *Fractional coordinates* ($\times 10^4$ *for non-*H *atoms;* $\times 10^3$ *for* H) *and equivalent isotropic temperature factors with e.s.d.'s*

$B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$; isotropic temperature factors for H atoms were fixed at 5·0 Å².

	x	y	z	B_{eq}(Å²)
Zn	0	8226·3 (8)	2500	2·57 (2)
O(1)	−1088 (3)	7782 (6)	4150 (2)	3·8 (1)
O(2)	−1616 (3)	5218 (4)	2573 (2)	3·2 (1)
O(3)	−5000	6709 (6)	2500	6·0 (2)
O(W)	1424 (3)	10665 (5)	3515 (2)	3·3 (1)
C(1)	−1819 (3)	5930 (6)	3643 (2)	2·6 (1)
C(2)	−2890 (3)	4551 (7)	4332 (3)	3·3 (1)
C(3)	−4006 (4)	2885 (6)	3494 (4)	3·3 (1)
C(4)	−5000	4416 (9)	2500	3·2 (2)
H1(C2)	−343	582	489	
H2(C2)	−222	332	500	
H1(C3)	−473	186	400	
H2(C3)	−343	152	300	
H1(OW)	124	1123	432	
H2(OW)	178	1218	316	

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

Zn—O(1)	2·213 (3)	C(4)—O(3)	1·191 (6)
Zn—O(2)	2·179 (2)	O(W)···O(1^{ii})	2·727 (4)
Zn—O(W)	2·020 (2)	O(W)···O(2^{iii})	2·663 (4)
C(1)—O(1)	1·251 (4)	O(W)—H1(OW)	0·96
C(1)—O(2)	1·263 (4)	O(W)—H2(OW)	0·96
C(1)—C(2)	1·522 (4)	H1(OW)···O(1^{ii})	1·77
C(2)—C(3)	1·528 (5)	H2(OW)···O(2^{iii})	1·76
C(3)—C(4)	1·521 (4)		
O(W)—Zn—O(W^i)	102·3 (1)	O(1)—C(1)—O(2)	118·3 (3)
O(W)—Zn—O(1)	88·4 (1)	O(1)—C(1)—C(2)	119·9 (3)
O(W)—Zn—O(1^i)	99·1 (1)	O(2)—C(1)—C(2)	121·7 (3)
O(W)—Zn—O(2)	145·4 (1)	C(1)—C(2)—C(3)	114·2 (3)
O(W)—Zn—O(2^i)	94·4 (1)	C(2)—C(3)—C(4)	113·3 (3)
O(1)—Zn—O(1^i)	168·0 (1)	O(3)—C(4)—C(3)	121·5 (2)
O(1)—Zn—O(2)	58·9 (1)	C(3)—C(4)—C(3^{iv})	117·0 (4)
O(2)—Zn—O(2^i)	88·4 (1)	O(W)—H1(OW)···O(1^{ii})	174
O(2)—Zn—O(1^i)	111·6 (1)	O(W)—H2(OW)···O(2^{iii})	155
C(1)—O(1)—Zn	90·8 (2)		
C(1)—O(2)—Zn	92·0 (2)		

Symmetry code: (i) −x, y, $\frac{1}{2}$ − z; (ii) −x, 2 − y, 1 − z; (iii) −x, 1 + y, $\frac{1}{2}$ − z; (iv) −1 − x, y, $\frac{1}{2}$ − z.

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