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The Structure of Diaquamalonatozinc(II)

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Abstract

$C_3H_6O_6Zn$ is monoclinic, space group $C2/m$, with $a = 12.58$ (5), $b = 7.41$ (5), $c = 7.23$ (5) Å, $\beta = 119.0$ (5)°, $U = 589$ Å³, $Z = 4$, $d_m = 2.31$ (2), $d_c = 2.29$ Mg m⁻³, $F(000) = 408$, $\mu(Cu K\alpha) = 5.295$ mm⁻¹. The structure was solved by the heavy-atom technique, with visually estimated integrated Weissenberg data. The final $R = 0.0849$ for 474 reflections. The structure comprises non-equivalent zinc ions at (0,0,0) and (0, $\frac{1}{2}$, $\frac{1}{2}$), site symmetry $2/m$, bridged by a carboxylate group. A water molecule is coordinated to each metal ion, and the central C of the malonate ion lies on the mirror plane. The structure develops as a sheet-type polymer parallel to (100) generating near-axial, but different, octahedral zinc environments (approximately D_{4h}), with a water molecule symmetrically H-bonded to two mirror-related carboxylate O atoms on adjacent sheets. A second symmetrical bifurcated H-bond occurs within the polymer sheets.

Introduction

The physical properties of certain dental cements can be significantly altered by the addition of suitable polydentate ligands. Examples include the improvement of the manipulative and erosion characteristics of

the glass ionomers through the addition of tartaric acid (Wilson, Crisp & Ferner, 1976), and the fortification of the ZnO/eugenol materials with 2-ethoxybenzoic acid (*o*-eba) (Brauer, 1965, 1967, 1972). The structures $[M(o\text{-eba})_2H_2O]$ ($M = Zn, Ca$) have been determined (Natarajan, Sake Gowda & Cartz, 1974); Ray & Hathaway, 1981) and are found to be seriously deficient in cohesion through the formation of limited polymeric networks.

This suggests that other ligands might be more effective in binding the metal centres, and particularly attractive in this respect are polyfunctional carboxylate systems less sterically constrained in their bridging potential than *o*-eba. The structure of diaquamalonatocalcium(II) (Karipides, Ault & Reed, 1977) involves a three-dimensional network of primary bonds linking the metal ions. A similar observation is reported for diaquasuccinatocalcium(II) monohydrate (Karipides & Reed, 1980). The present structure determination was undertaken to evaluate the binding of Zn^{2+} by the malonate ion as a potentially more attractive fortifying agent for the ZnO/eugenol cements.

Experimental

$[Zn(C_3H_2O_4)(H_2O)_2]$ was prepared as follows: malonic acid ($C_3H_2O_4$) (4.57 g, 4.4×10^{-2} mol) was dissolved

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in 50 ml hot aqueous MeOH (1:1) and added to a suspension of $\text{ZnCO}_3 \cdot 2\text{ZnO} \cdot 3\text{H}_2\text{O}$ (14.3 g, 4.2×10^{-3} mol) in 30 ml H_2O . The reaction mixture was stirred for 15 min, filtered, evaporated to 30 ml and allowed to stand at room temperature. Crystals were obtained after 6 days. Composition: found: C = 18.39, H = 2.97%; $\text{C}_3\text{H}_6\text{ZnO}_6$ requires: C = 17.71, H = 2.95%.

Unit-cell parameters were obtained from precession photographs about each axis and the space group was determined as $C2$, Cm or $C2/m$ from absences hkl for $h + k$ odd. Intensities were collected photographically using multi-film equi-inclination Weissenberg techniques with two-dimensional spot-shape integration. Intensities were estimated by visual comparison with a calibrated scale. 816 measurable intensities for levels $h0l-h6l$ and 237 intensities for $0kl-2kl$ were obtained. All reflections were retained for data reduction in which Lorentz and polarization corrections were applied, but none for absorption. Merging of equivalent reflections yielded 475 unique intensities.

The structure was solved using three-dimensional Patterson and Fourier techniques with *SHELX76* (Sheldrick, 1976). As no evidence could be found for Cm in the Patterson synthesis this was excluded from immediate investigation. Structure determination was initially attempted in $C2$, but was unsuccessful. For $Z = 4$ in $C2/m$, the metal is constrained to special positions, and a number of site symmetries are available. Of these, the highest ($2/m$) was chosen for initial investigation and two non-equivalent zinc ions were assigned to $(0,0,0)$ and $(0, \frac{1}{2}, \frac{1}{2})$ to conform with the Patterson synthesis. This approach proved successful and successive Fourier syntheses yielded the positions of all the non-hydrogen atoms. Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were used, and anisotropic thermal parameters introduced. The structure was refined by full-matrix least squares (minimizing $\sum |F_o - F_c|^2$) until the shift in any parameter was $<0.005\sigma$. As H atoms could not be satisfactorily located from the Fourier maps, these were geometrically calculated for

Table 1. Fractional coordinates ($\times 10^4$) for non-hydrogen atoms and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Zn(1)	0	0	0	21 (2)
Zn(2)	0	5000	5000	28 (2)
O(1)	1281 (8)	2090 (13)	1654 (14)	30 (5)
O(2)	591 (8)	3059 (13)	3745 (14)	30 (5)
O(3)	-664 (11)	0	2105 (19)	25 (7)
O(4)	-1684 (12)	5000	2067 (21)	35 (10)
C(1)	1224 (10)	3267 (19)	2822 (17)	20 (6)
C(2)	1918 (17)	5000	3167 (31)	28 (12)

Table 2. Interatomic distances (\AA) and bond angles ($^\circ$)

Zn(1)-O(1)	2.13 (1)	O(1)-Zn(1)-O(3)	93.0 (3)
Zn(1)-O(3)	2.06 (1)	O(1)-Zn(1)-O(1 ^{iv})	93.0 (5)
Zn(2)-O(2)	2.02 (1)	O(1)-Zn(1)-O(1 ⁱⁱⁱ)	87.0 (5)
Zn(2)-O(4)	2.15 (1)	O(2)-Zn(2)-O(2 ^v)	90.5 (5)
C(1)-O(1)	1.24 (2)	O(2)-Zn(2)-O(2 ^{vi})	89.4 (5)
C(1)-O(2)	1.27 (2)	O(2)-Zn(2)-O(4)	87.6 (4)
C(1)-C(2)	1.50 (2)		
Zn(1)-Zn(2)	5.18 (3)		
O(1)-C(1)-O(2)	122.0 (15)		
O(1)-C(1)-C(2)	119.5 (11)	O(3)-O(2)	} 2.69 (3)
O(2)-C(1)-C(2)	118.5 (11)	O(3)-O(2 ⁱⁱ)	
C(1)-C(2)-C(1 ^v)	117.2 (14)		
C(1)-O(2)-Zn(2)	127.5 (15)	O(4)-O(1 ^{vii})	} 2.89 (3)
O(2)-Zn(2)-O(2 ^v)	90.5 (5)	O(4)-O(1 ^{viii})	

Symmetry code

- | | |
|-----------------------------|-------------------------------|
| (i) $-x, -y, -z$ | (vi) $-x, y, 1.0 - z$ |
| (ii) $x, -y, z$ | (vii) $-0.5 + x, 0.5 + y, z$ |
| (iii) $-x, y, -z$ | (viii) $-0.5 + x, 0.5 - y, z$ |
| (iv) $-x, 1.0 - y, 1.0 - z$ | (ix) $0.5 + x, 0.5 + y, z$ |
| (v) $x, 1.0 - y, z$ | |

the malonate ion ($\text{C}-\text{H} = 1.08 \text{\AA}$, riding on C), but omitted from the water molecules in view of the probable steric constraints of the H-bonds. One reflection, for which $|F_o - F_c| > 5\sigma$, was omitted from the final refinement cycles. The final difference map indicated some positive and negative electron density in the vicinity of the metal ions (max. $+3.0 \text{ e \AA}^{-3}$), which is considered to arise from series-termination effects. The remaining positive peaks were $<1.5 \text{ e \AA}^{-3}$ and did not correspond to any structural entity. Attempts at refining the weighting scheme from unity were not successful. The final $R = 0.0849$. Atomic coordinates are listed in Table 1,* and interatomic distances and bond angles in Table 2.

Description of structure and discussion

The structure consists of a two-dimensional (sheet-type) polymer in which the non-equivalent zinc ions are present in near-axial, but different, octahedral oxygen environments ($2/m$ site symmetry but approximating to D_{4h}), and the methylene C of the malonate lies on the crystallographic mirror plane (Fig. 1). The coordination sphere about Zn(1) is compressed, with four longer in-plane bond lengths (R_L) and shorter apical values (R_S). The equatorial plane is established by the monodentate carboxylate group of four symmetry-

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36418 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

related bridging malonate ions [O(1), O(1ⁱ⁻ⁱⁱⁱ), Fig. 1] [$R_L = 2.13(1) \text{ \AA}$], with the apices occupied by equivalent water molecules O(3), O(3ⁱ) [$R_S = 2.06(1) \text{ \AA}$]. The coordination sphere about Zn(2) is elongated with two equivalent malonate systems defining the main plane [O(2), O(2^{iv-vi})] [$R_S = 2.02(1) \text{ \AA}$], through the formation of six-membered chelate rings, with the apices again occupied by a water molecule [O(4), O(4^{vi})] [$R_L = 2.15(1) \text{ \AA}$]. Bond angles are all near 90° (Table 2). The polymeric structure is developed (Fig. 1) parallel to (100) through the bridging of Zn(1) and Zn(2) *via* carboxylate chains [O(1), C(1), O(2)], while equivalent Zn(1) ions are linked parallel to **b** *via* the terminal carboxylates of the malonate ions [O(1), O(1^v)]. The network is only extended parallel to (001) by symmetrical bifurcated inter-sheet H-bonds between O(4) and pairs of equivalent carboxylate oxygens O(1) on adjacent sheets [O(4)—O(1^{viii}), O(4)—O(1^{viii}), 2.89(3) Å] (Fig. 2a,b). A further, but intramolecular, symmetrical interaction occurs between O(3) and the carboxylate O(2) and O(2ⁱⁱ) [O(3)—O(2), O(3)—O(2ⁱⁱ), 2.69(3) Å] (Fig. 2b). These H-bonds involve O—O separations comparable to those previously reported for metal—malonate complexes (Hansson, 1973a,b), and no unusual bond lengths or bond angles occur in the malonate ion (Hansson, 1973a,b; Butler & Snow, 1976).

In the present complex the preference for six-membered chelate-ring conformation by the malonate ligand (Karipides *et al.*, 1977) is again retained in the environment about Zn(2), with the conformation conforming to the crystallographic mirror symmetry. The geometry is intermediate between the envelope and boat conformations (Butler & Snow, 1976), with the methylene C significantly further removed from the main plane [atoms O(2), C(1), O(2^v), C(1^v)] than Zn(2) (0.54, 0.16 Å).

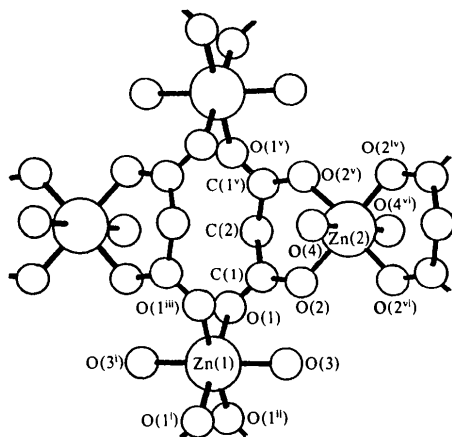


Fig. 1. Portion of the polymeric bridged structure projected approximately along **a** to indicate the atom labelling and coordination to the metals. For key to symmetry operations see Table 2.

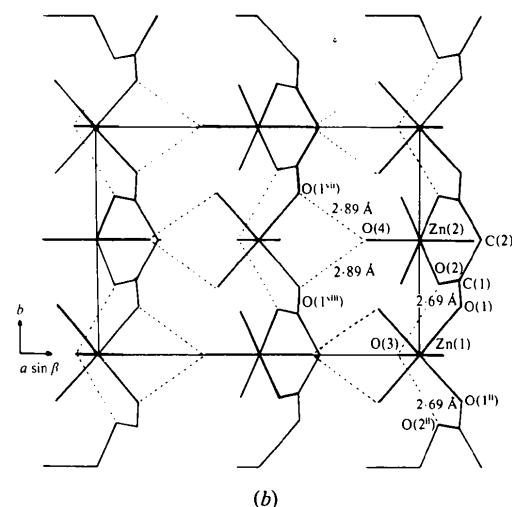
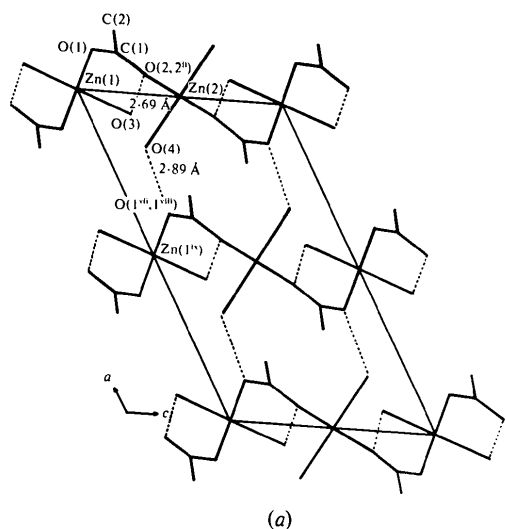


Fig. 2. Projections of chain packing in the unit cell with H-bond interactions. Axes: (a) **b** out of page, (b) **c** out of page; other axes as indicated.

The present structure does not retain the three-dimensional primary bonding network observed in $[\text{Ca}(\text{C}_3\text{H}_2\text{O}_4)(\text{H}_2\text{O})_2]$ (Karipides *et al.*, 1977). A comparison with other metal—carbonylato complexes strongly suggests that this restriction is imposed by the reduced size of the Zn^{2+} coordination sphere. Metal ions with larger coordination polyhedra appear to allow more extensive metal bridging, facilitated by the greater number of donor sites, and frequently accompanied by combined chelate and bridging functions *via* each carboxylate group, to yield tight metal—oxygen four-membered rings, *e.g.* $[\text{Ca}(\text{C}_3\text{H}_2\text{O}_4)(\text{H}_2\text{O})_2]$ Ca—Ca 3.985 Å (Karipides *et al.*, 1977), $[\text{Ca}(\text{C}_4\text{H}_4\text{O}_4)(\text{H}_2\text{O})_2](\text{H}_2\text{O})$ Ca—Ca 3.977, 4.008 Å (Karipides & Reed, 1980) and $[\text{Nd}_2(\text{C}_3\text{H}_2\text{O}_4)_3(\text{H}_2\text{O})_x]$ ($x = 6, 8$) Nd—Nd 4.33, 4.42 Å, respectively. (Hansson, 1973a,b), all of the above involving full three-dimensional linkage of the metals. The absence of a chelate function in the

bridging carboxylate of the present system results in the less effective packing of the metals [Zn(1)–Zn(2) 5.18 Å], *via* Zn–O–C–O–Zn chains, which is comparable to the metal bridging in [Zn(*o*-eba)₂(H₂O)] Zn–Zn 4.861 Å (Natarajan *et al.*, 1974). Nevertheless, the development of a sheet-type polymeric structure in the present system, together with the presence of H-bonds between adjacent sheets, would appear to favour the use of malonic acid over *o*-eba as a fortifying agent in the ZnO/eugenol cements. In addition, the structure of [Ca(C₃H₂O₄)(H₂O)₂] (Karipides *et al.*, 1977) suggests that the adhesive interaction of malonic acid with tooth material (hydroxyapatite) yields a compound of high structural integrity which would be expected to reduce marginal leakage at the cement lute. On the other hand, the polymeric structures of [M(*o*-eba)₂(H₂O)] (M = Zn, Ca) (Natarajan *et al.*, 1974; Ray & Hathaway, 1981) are both confined to chain functions, without inter-chain H-bonds, so that cohesion is due to weak lattice-packing effects.

Subject to suitable mechanical and toxicological evaluation, the addition of malonic acid to the ZnO/eugenol cement formulations as a fortifying agent would appear to offer certain advantages over *o*-eba from a structural viewpoint; these advantages might be further enhanced through the incorporation of larger cations [*e.g.* Ca(OH)₂] in the cement powder.

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Multicomponent Polyanions.

31. The Structure of Tetraguanidinium Dodecamolybdo germanate,



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Abstract

[C(NH₂)₃]₄Mo₁₂GeO₄₀, *M_r* = 2104.3, crystallizes in the triclinic system, space group *P* $\bar{1}$, with *a* = 12.123 (2), *b* = 12.159 (2), *c* = 16.655 (3) Å, α = 76.35 (1), β = 78.46 (1), γ = 66.99 (1)°, *V* = 2180 Å³ and *Z* = 2 [this is the reduced cell; Donnay's conventional reduced cell may be obtained by applying the transformation (0 $\bar{1}$ 0/001/100)]; *D_x* = 3.21 Mg

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m⁻³, $\mu(\text{Mo } K\alpha) = 4.10 \text{ mm}^{-1}$. The final *R* = 0.050, based on 5471 independent reflexions. The structure contains Mo₁₂GeO₄₀⁴⁻ anions joined in a three-dimensional framework by hydrogen and ionic bonds from the [C(NH₂)₃]⁺ cations. The heteropolyanion has the well-known Keggin structure (*α* isomer). Mean Mo–Mo distances are 3.35 Å for edge-sharing MoO₆ octahedra and 3.73 Å when a corner is shared. The Mo–O distances are distributed in three different

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