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Structure of Monoclinic Zinc *n*-Butanoate

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(*Received* 29 *August* 1991; *accepted* 30 *June* 1992)

Abstract. $Zn^{2+}.2C_4H_7O_2^-$, $M_r = 239.57$, monoclinic, $P2_1/c$, $a = 23.48\ (3)$, $b = 4.795\ (4)$, $c = 9.380\ (9)$ Å, $\beta = 90.08\ (9)°$, $V = 1056\ (2)$ Å^3, $Z = 4$, $D_x = 1.506$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.36$ mm^{-1}, $F(000) = 496$, room temperature, $R = 0.091$ for 1397 observed reflections with $I > 4\sigma(I)$. The structure consists of polymeric sheets parallel to (100) in which tetrahedrally coordinated Zn ions are connected by butanoate bridges in a *syn-anti* arrangement. There is some disorder in the stacking of the sheets.

Introduction. This structure analysis was undertaken to provide information pertinent to an investigation of the nature of the coordination of Zn in carboxylate glasses.

Experimental. The compound was prepared by reaction of ZnO with freshly distilled *n*-butanoic acid and recrystallized from methanol/water (2/1). X-ray diffraction data were obtained from a suitable crystal (*ca* 0.43 × 0.7 × 0.14 mm) on a Nicolet *P*3 four-circle diffractometer with Mo $K\alpha$ radiation and graphite monochromator. Cell dimensions were determined using 14 reflections at 17–21° in 2θ. Data were collected corresponding to a primitive monoclinic supercell with $a = 46.96$ Å, *i.e.* twice the value given above to take account of reflections observed in an oscillation photograph. The intensities of 4257 reflections with $2\theta \leq 50°$ and h 0–55, k 0–5 and l −11–11 were measured from ω scans with a fixed width of 0.6°, scan rates in the range 1.0–29.3° min^{-1} related to pre-scan intensity, and stationary crystal–stationary counter background counts taken at ± 1.0° in ω from the calculated position of the Bragg peak. An empirical absorption correction based on ψ-scan data was applied. The minimum and maximum transmission factors were 0.26 and 0.47. Two reference reflections, monitored periodically, showed no significant variation in intensity. The data were reduced to structure amplitudes in the usual way. No solution could be found for the structure on the basis of the supercell. Thus a was halved to give the value quoted above and the reflection data re-indexed by eliminating the uniformly weak reflections with h odd, including 795 F_o which would have been classed as observed according to the criterion given above, and then halving h for the remainder to yield a total of 1867 unique reflections ($R_{\rm int} = 0.033$). The coordinates of Zn(1) were obtained by Patterson (vector) map analysis with *SHELXS86* (Sheldrick, 1985). All remaining non-H atoms were located in successive

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0108-2701/93/020219-03$06.00

Table 1. *Coordinates* ($\times 10^4$), *site occupancies* ($\times 10^3$) *and isotropic or equivalent isotropic thermal vibration parameters* ($\text{Å}^2 \times 10^3$) *for non-*H *atoms with e.s.d.'s in parentheses*

All sites other than Zn are fully occupied. U_{eq} are calculated as $(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ except for Zn(2) where U_{iso} is given.

	x	y	z	Occupancy	U_{iso}/U_{eq}
Zn(1)	2519 (1)	2109 (3)	740 (2)	880 (8)	37 (1)
Zn(2)	2521 (5)	2484 (28)	6654 (21)	120 (8)	46 (5)
O(11)	2724 (4)	−3177 (19)	5927 (11)		70 (3)
O(12)	3194 (4)	750 (19)	6272 (10)		60 (3)
O(21)	2364 (5)	2668 (19)	3706 (9)		67 (3)
O(22)	1853 (4)	3441 (23)	1731 (10)		68 (3)
C(11)	3157 (5)	−1942 (28)	6359 (15)		54 (4)
C(12)	3598 (6)	−3350 (31)	7251 (16)		63 (5)
C(13)	3998 (6)	−1521 (35)	8048 (18)		73 (5)
C(14)	4462 (6)	−3254 (41)	8836 (19)		86 (7)
C(21)	1912 (6)	3588 (33)	3035 (14)		62 (5)
C(22)	1449 (6)	5300 (38)	3922 (16)		80 (6)
C(23)	977 (7)	6566 (45)	3085 (18)		90 (7)
C(24)	558 (9)	8135 (48)	3882 (24)		122 (10)

difference syntheses using *SHELX*76 (Sheldrick, 1976). H atoms were given ideal geometries with C—H = 1.08 Å and allowed to ride on their attached C atoms. The methyl groups were treated as rigid bodies.

Full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$ with anisotropic thermal parameters for non-H atoms other than Zn(2) and common U_{iso} values for all H atoms (131 parameters) converged at $R = 0.091$ and $wR = 0.098$ with $w = 1.0/[\sigma^2(F_o) + 0.00366(F_o)^2]$; maximum shift/e.s.d. = 0.43 excluding two rotational parameters for the C(14) methyl group where some disorder is probable; minimum/maximum $\Delta\rho = -0.99/1.25$ e Å^{-3}. In the course of structure solution a large feature was observed in the difference maps which was eventually identified as arising from disorder affecting principally Zn, resulting in the presence in Table 1 of Zn(1) and Zn(2) less than 1 Å apart with occupancies of 0.880 (8) and 0.120 (8), respectively. The relatively high value of R and shift/e.s.d are attributed to this disorder (see *Discussion*). Atomic parameters are given in Table 1.* Calculations were carried out on a SUN SPARC 480 system of the Computing Centre of University of Aberdeen. Scattering curves for neutral Zn atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). For C, H and O the values installed in *SHELX*76 were used. *STRUPLO*82 (Fischer, 1982) was used to prepare Figs. 1–3.

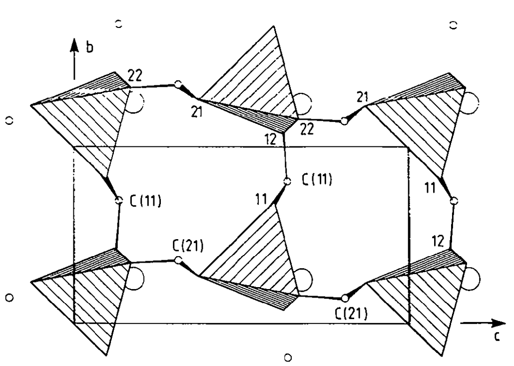

Fig. 1. A single layer of Zn–O tetrahedra in monoclinic zinc butanoate. Representative O, at the corners of the Zn(1)-centred tetrahedra, are identified by number. Large and small circles are respectively Zn(2) and C(11) and C(21). All other C atoms have been omitted for clarity. The C—O bond taper indicates the height of the C atoms shown relative to the Zn plane and thus the direction of propagation of the alkyl chains of the anions.

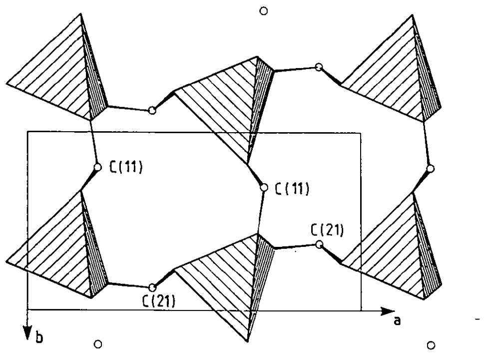

Fig. 2. A single layer in the structure of orthorhombic zinc propionate in the same representation as Fig. 1. The data of Clegg *et al.* (1987) were used but the layer has been chosen and the cell oriented so that the tetrahedra appear as they would in a layer related by a 2_1 screw axis to the lower (unmarked tetrahedra) layer of Fig. 3; the C atoms are numbered as in Fig. 1. The coincidence of Zn(2) in Fig. 1 with the centroids of the tetrahedra of Fig. 2, readily seen by superposition of copies of Figs. 1 and 2 scaled such that the cell edges are identical in length, should be noted.

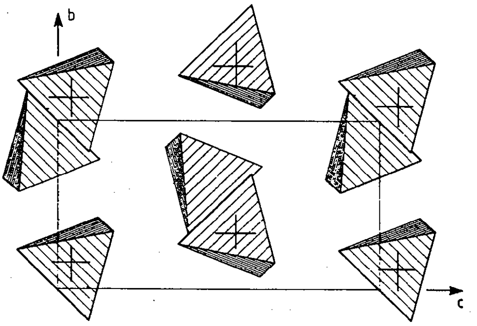

Fig. 3. Two adjacent layers of Zn–O tetrahedra in monoclinic zinc butanoate. The tetrahedra in the upper layer, corresponding to those shown in Fig. 1, are marked with crosses. Zn(2) and all C atoms have been omitted for clarity.

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* Lists of anisotropic thermal vibration parameters, H-atom coordinates, bond lengths, bond angles, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55564 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0285]

Discussion. The structure of monoclinic zinc butanoate (1) described here has several features in common with the structures of the monoclinic and orthorhombic forms of zinc propionate (2) and (3) as described, respectively, by Goldschmied, Rae & Stephenson (1977) and Clegg, Little & Straughan (1987). In all three compounds the basic structural unit is a polymeric sheet of tetrahedrally coordinated Zn ions connected by carboxylate bridges in a *syn-anti* arrangement. The crystallographic symmetry which governs the geometry of the sheets is the same in all three compounds and can be described with reference to the butanoate (Fig. 1). It is convenient for this purpose to define labels for the carboxylate anions. Thus, in what follows, *Cb*(11) represents the butanoate anion consisting of O(11–12) and C(11–14), and *Cb*(21) represents the anion comprising O(21–22) and C(21–24). The interconnection of the Zn tetrahedra parallel to the shortest unit-cell edge, *b* in this case, involves only unit-cell translation and the anion involved in *Cb*(11), which extends below the layer as it appears in Fig. 1. The interconnection parallel to the intermediate cell edge, *c* in this case, is developed under the control of a *c* glide perpendicular to *b* and involves the anion *Cb*(21), which extends up out of the layer. This description applies exactly to compounds (2) and (3) allowing for the different atom numbers and, in the case of (3), the different labelling of the unit-cell edges used in the descriptions of their structures. The shortest and intermediate unit-cell edges in all three compounds are virtually identical in length. The Zn—O distances, 1.928 (9)–1.954 (9) with mean 1.945 Å, and O—Zn—O angles, 100.8–118.4 with mean 109.41°, in (1) are very similar in range and mean value to those observed for (2) and (3). In all three compounds the carboxylate groups have bond lengths and angles as usually found. Thus the compounds can be regarded as isostructural at the level of the component sheets of interconnected Zn tetrahedra.

In all three cases the complete structure requires that the component sheets be stacked to develop the structure in the direction of the longest unit-cell edge. The stacking of the sheets is controlled solely by van der Waals interaction between the alkyl 'tails' of the anions which protrude on either side of the individual sheets. It is noticeable that in the butanoate the longest unit-cell edge is approximately 22% longer than it is in either of the propionates in order to accommodate the longer 'tail' of the butanoate.

It is apparent from the known structures of (2) and (3) that there are two possible stacking arrangements each with its own crystallographic consequences. In the monoclinic structures (1) and (2) the layers are related by centres of symmetry. Thus alkyl 'tails' of the same kind are in contact at every interlayer boundary, either *Cb*(11) with *Cb*(11′) or *Cb*(21) with *Cb*(21′). For the butanoate this results in interlayer contacts C(14)···C(14′) and C(24)···C(24′) of 3.73 (2) and 3.80 (2) Å.

The other possibility is exemplified by the structure of the orthorhombic propionate (3). Here the relationship between adjacent layers is defined by the operation of a twofold screw axis parallel to the longest unit-cell edge and therefore perpendicular to the layers. Thus the layers are all the same way up and at every interlayer boundary *Cb*(11) of one layer interacts with *Cb*(21) of its neighbour.

The possibility of Zn being disordered over two sites, Zn(1) and Zn(2) (Table 1), was introduced in the *Experimental* section. The discussion above together with consideration of Figs. 1–3 suggests that Zn(1) is associated with the majority of the layers of tetrahedra related to one another by monoclinic symmetry. Zn(2) indicates the presence of occasional layers, roughly one in every eight, related to the remainder in the manner of the orthorhombic propionate. The possibility that the butanoate is in fact orthorhombic was disproved on obtaining $R_{\rm int} = 0.33$ on attempting to merge F_o (indexed for a cell with $a = 23.48$ Å) in a manner consistent with orthorhombic symmetry. On the other hand, an indication of the presence of layers related by orthorhombic symmetry was available in the original data corresponding to the supercell where it was noticed that the *hk*0 reflections with *h* odd were generally stronger for *k* odd also. The same type of disorder, involving the presence of a higher proportion of layers related by orthorhombic symmetry, would be consistent with the difficulties described by Goldschmied *et al.* (1977) in their analysis of the structure of monoclinic zinc propionate. Further, the introduction of such layers into a monoclinic structure with β appreciably greater than 90° could well be the basis of their statement that their sample crystal 'appeared to be curved'. The present results also suggest that under suitable conditions, zinc butanoate should be obtainable in an orthorhombic form.

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