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The Crystal Structure of Zn^{II} Propionate $(C_6H_{10}O_4Zn)_n$

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Zinc^{II} propionate, $(C_6H_{10}O_4Zn)_n$, crystallizes in space group $P2_1/c$ with a = 19·144 (4), b = 4·794 (1), c = 9·286 (2) Å, β = 91·8 (2)°, Z = 4, ρ_c = 1·65 g cm^{-3}. Refinement by full-matrix least squares gave a final $R = \Sigma|\Delta F|/\Sigma|F_o|$ = 0·076 for the 876 independent observed counter reflexions with $|h| > 3$. The C_2H_5COO groups bridge Zn atoms to form a two-dimensional polymer perpendicular to [100]. The Zn atoms have a tetrahedral coordination with a mean Zn–O distance of 1·95 Å. The crystals were tabular on (100) and were mounted within 5° of this direction. The standard reflexion reduced to 0·65 of its original value during data collection. An uncorrected systematic error in the observed data was largely eliminated by excluding data with $|h| < 4$, the excluded data corresponding to reflexions with long path lengths in the crystal. The inappropriateness of standard deviations determined by scaling weights to make $\Sigma w\Delta^2/(n-m) = 1$ is indicated.

Introduction

The structure of Zn^{II} propionate was determined to detail further the various roles of the anions of carboxylic acids acting as coordinating agents in transition-metal complexes. Two O atoms in groups such as NO_3, CO_2 and RCOO (R = alkyl) subtend an angle of only about 60° when acting as a bidentate ligand compared with 90° for undistorted square planar or octahedral coordination and 109·5° for undistorted tetrahedral coordination.

The bite of such bidentate groups is too small for satisfactory space-filling around the central metal atom and consequently these coordinating agents are often monodentate with respect to a single transition-metal atom, the coordination sphere being filled by coordinated water molecules or by the coordinating agents bridging adjacent transition-metal atoms to form dimeric or polymeric complexes.

Co^{II} and Ni^{II} acetates occur as tetrahydrates (Van Niekerk & Schoening, 1953*a*) and form monomeric octahedral complexes with *trans* unidentate acetate groups. Zn^{II} acetate occurs as a dihydrate (Van Niekerk & Schoening, 1953*b*) and forms a monomeric complex of distorted octahedral coordination with *cis* bidentate acetate groups. This coordination could alternatively be described as a tetrahedral coordination with the bidentate acetate groups occupying single tetrahedral coordination positions. Cu^{II} acetate occurs as a monohydrate but exists as a dimer (Van Niekerk & Schoening, 1953*c*) with four acetate groups bridging two Cu atoms 2·64 Å apart. The sixth octahedral coordination position about each Cu atom is occupied by a water molecule.

Anhydrous forms of these complexes and their homologues may be prepared by recrystallization from a mixture of the appropriate acid and its anhydride, thus enforcing the formation of complexes in which the bidentate ligands, because of their small bite, must act as bridging groups between adjacent transition-metal atoms. The structure of anhydrous Cu^{II} propionate has been determined (Simonov & Malinovskii, 1970) and exists as one-dimensional polymeric chains consisting of dimeric units in which the two Cu atoms are linked by four bridging propionate groups in a manner similar to the monohydrate of Cu^{II} acetate. These dimeric units are linked through the sixth coordination position (formerly occupied by the water molecule) now being occupied by an O atom in the adjacent dimeric unit.

The structures of Cu^{II} formate (Barclay & Kennard, 1961), Cu^{II} formate dihydrate (Bukowska-Strzyżewska, 1965), Cu^{II} formate tetrahydrate (Kiriyama, Ibamoto & Matsuo, 1954) and Ni^{II} formate dihydrate (Krogman & Mattes, 1963) have also been determined and in all cases the formate group acts as a bridge between different transition-metal atoms in one, two or three-dimensional polymeric networks.

Zn can exist in both octahedral [Zn^{II} dihydrazine diacetate, Ferrari, Braibanti, Bigliardi & Lanfredi (1965)] and tetrahedral coordinations [Zn^{II} di-*n*-alkyl phosphinates, Giancotti, Giordano, Randaccio & Ripamonti (1968)], sometimes occurring with both

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* Deceased 6 May 1975.

coordinations in the same structure (Ghose, 1964). The anhydrous Zn^{II} di-*n*-alkyl phosphinates occur as one-dimensional polymeric chains, adjacent Zn atoms being linked by alternately one and three phosphinate groups.

The isomorphous incorporation of a small amount of Co^{II} in anhydrous Zn^{II} acetate, propionate and butyrate gives a blue colour that suggests the Zn atoms in these compounds have a tetrahedral coordination as has been borne out by the structure of Zn^{II} propionate.

Experimental

Anhydrous Zn^{II} propionate was crystallized after $ZnCO_3$ was added to propionic acid containing 10% propionic anhydride. The colourless crystals are tabular on (100) with the faces (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, (001) and $(00\bar{1})$ all well developed. Approximate density measurement by flotation and examination of final electron density maps verified the formula imposed by the structural determination.

Intensities and cell dimensions were obtained at 20 °C on a Siemens automatic single-crystal diffractometer with Cu $K\alpha$ radiation and Ni filters and attenuators. The integrated intensities were recorded by the four-value method (Hoppe, 1965; Stephenson, Beale & Craig, 1968). The scanning procedure used the moving-crystal, moving-detector method (θ–2θ scan). Estimation of errors was from counting statistics. Data with a count above background of less than 3σ were regarded as unobserved and given a value for I of σ and were included in the refinement of $\Sigma\, w|\Delta F_o|^2$ only if $|F_c| > |F_o|$. Weights of $w = 1/\sigma^2(F_o)$ were used. Intensities were corrected for absorption with a weighted Gaussian grid (Coppens, Leiserowitz & Rabinovich, 1965). The crystal used was bounded by planes at distances 0·0187 mm for (100) and $(\bar{1}00)$, 0·125 mm for (010) and $(0\bar{1}0)$ and 0·362 mm for (001) and $(00\bar{1})$ giving a mean free path length $\bar{T}$ in the crystal ranging between 0·004 and 0·029 cm ($\mu\bar{T}$ between 0·15 and 1·10 where $\mu = 38{\cdot}5$ cm^{-1}). 1613 nonequivalent reflexions were collected. During the data collection the standard reflexion (006) dropped in intensity to 0·65 of its original value. $C_6H_{10}O_4Zn$ has $a = 19{\cdot}144\,(4)$, $b = 4{\cdot}794\,(1)$, $c = 9{\cdot}286\,(2)$ Å, $\beta = 91{\cdot}8\,(2)°$, $Z = 4$, $\rho_c = 1{\cdot}65$ g cm^{-3} and crystallizes in space group $P2_1/c$ ($h0l$, $l = 2n$ only; $0k0$, $k = 2n$ only). The crystal was mounted with (100) at 5·1° to the spindle axis, the orientation matrix being

$$UB = \begin{bmatrix} 0{\cdot}00228 & -0{\cdot}18530 & 0{\cdot}04938 \\ 0{\cdot}00448 & -0{\cdot}09440 & -0{\cdot}09529 \\ 0{\cdot}05202 & 0{\cdot}01624 & 0{\cdot}00952 \end{bmatrix}.$$

The crystal appeared to be curved and in the subsequent refinement reflexions with $|h| < 4$ were seen consistently to have a higher value of $|F_o|$ than $|F_c|$, this discrepancy being as much as 50%. Exclusion of these data left 876 non-equivalent observed reflexions ($\bar{T}$ between 0·004 and 0·015 cm, $\mu\bar{T}$ between 0·15 and 0·58), the excluded data corresponding to reflexions with long path lengths in the crystal.

Structure determination and refinement

The Zn atom was readily located at $\frac{1}{4},\frac{1}{4},\frac{1}{8}$ from the Patterson function. Equivalent positions for $P2_1/c$ are then $\frac{1}{4},\frac{1}{4},\frac{1}{8}$; $\frac{3}{4},\frac{3}{4},\frac{3}{8}$; $\frac{5}{4},\frac{5}{4},\frac{5}{8}$; $\frac{7}{4},\frac{7}{4},\frac{7}{8}$ corresponding to x,y,z; $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; $x,\frac{1}{2}-y$, $\frac{1}{2}+z$; $\bar{x},\bar{y},\bar{z}$ respectively. These atoms lie in a straight line at points $\frac{1}{2},\frac{1}{2},\frac{1}{4}$ apart and so contribute only to reflexions with $2h + 2k + l = 4n$. A Fourier map with just these reflexions gives an artificial $2/m$ site symmetry about each Zn atom site. A general discussion of pseudosymmetry has been given by Rae (1975). Since the Zn atom is actually on a general position it was necessary to select a ZnO_4 tetrahedron from the 16 $\frac{1}{4}$-weight O atoms about each Zn atom site. Since $y = \pm\frac{1}{4}$ corresponds to the height of the glide plane only two possible tetrahedra needed to be considered, both giving an R of about 0·65 for all data. The remaining C atoms could be located by inference. The correct structure was determined by least-squares refinement of each possibility, refinement of the incorrect structure terminating at $R = 0{\cdot}30$. Full-matrix least-squares refinement reduced the value of R to 0·121 for anisotropic atoms. A difference map located H atoms. These H atoms could not be refined and were included with the same thermal parameters as the atoms to which they were attached. Comparison of F_o and F_c showed $|F_o| > |F_c|$ for data with $|h| < 4$ while data with $|h| > 3$ had moderately good agreement. Further refinement with only observed data with $|h| > 3$ reduced R for these data from 0·125 to 0·079, changing the scale constant by 20% in the process. A final refinement cycle reduced R to 0·076, no positional shifts being greater than 1·0σ. Scattering factors for neutral atoms were used, the Zn atom scattering anomalously ($\Delta f' = -1{\cdot}612$, $\Delta f'' = 0{\cdot}678$) (*International Tables for X-ray Crystallography*, 1974). Extinction corrections were made with an anisotropic extinction parameter $R^* = (e^2/mc^2 V)\lambda^3 r^*$ where the modified $F_c^* = k|F_c|(1 + 2r^*|F_c|^2\delta)^{-1/4}$,

$$\delta = \left(\frac{e^2}{mc^2 V}\right)^2 \frac{\lambda^3}{\sin 2\theta}\,\frac{1+\cos^4 2\theta}{1+\cos^2 2\theta} \times \bar{T}$$

and $\bar{T}$ is the mean path length in the crystal (in cm) (Larson, 1970). A value of 0·0006 (5) for R^* was obtained.

Structural results

Structural parameters are listed in Table 1.* The quoted standard deviations are not those calculated by standard procedures. They are obtained by multiplying the inverse of the least-squares matrix by such a factor as to make the observed variances for sets of equivalent bond lengths become reasonable. The reason for doing this is given in Table 2 where results of bond-length calculations for the non-hydrogen atoms are given for (*a*) refinement giving all reflexions weights from counting statistics and (*b*) excluding all reflexions with $|h| <$

Table 1. *Structural parameters for* $(C_6H_{10}O_4Zn)_n$

Fractional coordinates of atoms

	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$
Zn	0·2507 (2)	0·2834 (7)	0·1455 (4)
O(1)	0·1663 (7)	0·148 (4)	0·235 (2)
O(2)	0·3323 (7)	1·065 (3)	0·194 (2)
O(3)	0·2259 (7)	0·233 (4)	0·437 (2)
O(4)	0·2774 (7)	0·676 (4)	0·167 (2)
C(1)	0·1750 (12)	0·128 (5)	0·374 (3)
C(2)	0·3263 (11)	0·808 (6)	0·218 (3)
C(3)	0·1225 (13)	−0·051 (8)	0·455 (3)
C(4)	0·3817 (14)	0·658 (7)	0·302 (4)
C(5)	0·0675 (14)	−0·188 (9)	0·374 (4)
C(6)	0·4323 (17)	0·837 (10)	0·383 (6)
H(C3)	0·150	−0·07	0·525
H′(C3)	0·095	0·10	0·485
H(C4)	0·394	0·48	0·260
H′(C4)	0·350	0·50	0·350
H(C5)	0·090	−0·30	0·300
H′(C5)	0·044	−0·10	0·290
H″(C5)	0·020	−0·30	0·425
H(C6)	0·465	0·88	0·275
H′(C6)	0·480	0·75	0·400
H″(C6)	0·425	1·00	0·420

Bond distances [Å(σ)]

Zn–O(1)	1·953 (13)	C(3)–H(C3)	0·8 (2)
Zn–O(2)$^{\rm i}$	1·923 (15)	C(3)–H′(C3)	0·9 (2)
Zn–O(3)$^{\rm ii}$	1·977 (16)	C(4)–H(C4)	1·0 (2)
Zn–O(4)	1·957 (18)	C(4)–H′(C4)	1·1 (2)
O(1)–C(1)	1·30 (3)	C(5)–H(C5)	1·0 (2)
O(2)–C(2)	1·26 (3)	C(5)–H′(C5)	1·0 (2)
O(3)–C(1)	1·23 (3)	C(5)–H″(C5)	1·2 (2)
O(4)–C(2)	1·21 (3)	C(6)–H(C6)	1·2 (2)
C(1)–C(3)	1·54 (3)	C(6)–H′(C6)	1·0 (2)
C(2)–C(4)	1·49 (4)	C(6)–H″(C6)	0·9 (2)
C(3)–C(5)	1·43 (4)		
C(4)–C(6)	1·48 (5)		

Bond angles [°(σ)]

O(1)–Zn–O(2)$^{\rm i}$	113·3 (7)	O(2)$^{\rm i}$–Zn–O(3)$^{\rm ii}$	112·1 (7)
O(1)–Zn–O(3)$^{\rm ii}$	103·1 (6)	O(2)$^{\rm i}$–Zn–O(4)	107·0 (7)
O(1)–Zn–O(4)	119·6 (7)	O(3)$^{\rm ii}$–Zn–O(4)	101·0 (7)
O(1)–C(1)–O(3)	121 (2)	O(2)–C(2)–O(4)	121 (3)
O(1)–C(1)–C(3)	117 (2)	O(2)–C(2)–C(4)	120 (2)
O(3)–C(1)–C(3)	121 (3)	O(4)–C(2)–C(4)	119 (3)
C(1)–C(3)–C(5)	119 (3)	C(2)–C(4)–C(6)	116 (3)
Zn–O(1)–C(1)	111 (2)	Zn–O(2)$^{\rm i}$–C(2)$^{\rm i}$	120 (2)
Zn–O(3)$^{\rm ii}$–C(1)$^{\rm ii}$	128 (2)	Zn–O(4)–C(2)	137 (2)

Symmetry code

(i) equivalent position $x, -1+y, z$

(ii) equivalent position $x, \frac{1}{2}-y, -\frac{1}{2}+z$

Table 2. *Comparison of bond lengths* (Å) *for two refinements*

(*a*) Refinement with all data, (*b*) refinement excluding data with $|h|<4$. Standard deviations calculated by the usual procedures are given for case (*a*).

	(*a*)	(*b*)
Zn–O distances		
Zn–O(1)	1·932 (9)	1·953
Zn–O(2)$^{\rm i}$	1·885 (10)	1·923
Zn–O(3)$^{\rm ii}$	1·972 (10)	1·977
Zn–O(4)	1·976 (9)	1·957
Mean	1·942	1·953
Range	0·092	0·054
O–C distances		
O(1)–C(1)	1·348 (16)	1·299
O(2)–C(2)	1·315 (16)	1·256
O(3)–C(1)	1·244 (15)	1·229
O(4)–C(2)	1·195 (14)	1·214
Mean	1·276	1·250
Range	0·153	0·085
C–C distances		
C(1)–C(3)	1·491 (19)	1·537
C(2)–C(4)	1·477 (22)	1·486
C(3)–C(5)	1·408 (21)	1·433
C(4)–C(6)	1·443 (25)	1·480
Mean	1·455	1·484
Range	0·083	0·104

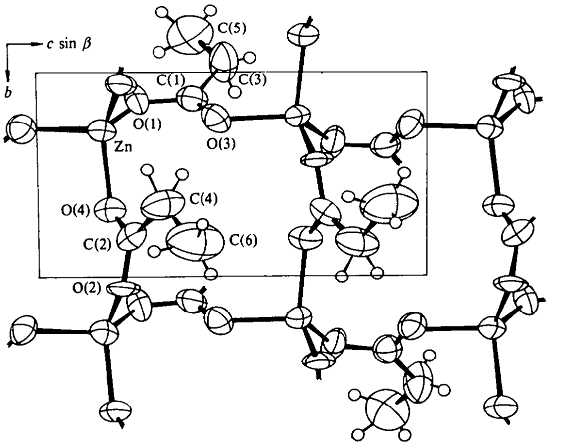

Fig. 1. The [100] projection of the two-dimensional polymer layer at $x = \frac{1}{4}$. To aid visualization C(3) and C(5) have not everywhere been included.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32417 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

4. Standard deviations calculated by standard procedures for case (*a*) are given, and demonstrate the inappropriateness of scaling weights to make $\Sigma\, w\Delta^2/(n-m) = 1$ for error estimation when systematic errors occur in the assigning of relative weights.

The improvement in the ranges of comparable bond lengths for (*b*) is obvious for the Zn–O and O–C distances, and while this is not so for the C–C distances, the mean C–C distance is much more realistic. A systematic error in the data was reduced by excluding certain reflexions. However, the error still remains and its unknown covariance with the refined parameters has caused an underestimate of standard deviations. This characteristic is discussed by Rae (1975).

The structure consists of two-dimensional polymer sheets perpendicular to (100). Zn atoms at x,y,z and x, $1+y$, z are linked by one propionate group and Zn atoms at x,y,z and x, $\frac{1}{2}-y$, $\frac{1}{2}+z$ by the other (Fig. 1).

The Zn atoms have a tetrahedral coordination and are linked in an *anti–syn* arrangement (Barclay & Kennard, 1961). Associated with this linkage is an apparent difference in Zn–O and C–O lengths: mean for Zn–O(1) and Zn–$O(2)^{i}$ of 1·938 (10) Å compared with the mean for Zn–$O(3)^{ii}$ and Zn–O(4) of 1·967 (12) Å, and mean for O(1)–C(1) and O(2)–C(2) of 1·28 (2) Å compared with the mean for O(3)–C(1) and O(4)–C(2) of 1·22 (2) Å, but a comparison with variations in C–C lengths makes it impossible to say that these differences are statistically significant.

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X-ray and Neutron Diffraction Studies of the Hydroquinone Clathrate of Hydrogen Chloride

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The crystals of $C_6H_6O_2.xHCl$, obtained from an ethereal solution of 1,4-dihydroxybenzene saturated with HCl gas, have been examined by X-ray and neutron diffraction: rhombohedral, space group $R3$, with a(hex) = 16·650 (1), c = 5·453 (1) Å. In two independent analyses the structure was refined to R(X-ray) = 0·036 and R(neutron) = 0·069. The HCl molecule is oriented within the quinol cavity because of a large number of weak

$$-\mathrm{OH}\cdots\mathrm{Cl{-}H}\cdots\overset{|}{\mathrm{O}}\mathrm{H}$$

interactions, which are responsible for lowering the symmetry.

Introduction

The X-ray photoelectron spectrum of HCl, clathrated in a β-quinol framework (Copperthwaite, 1976), differs appreciably from the gas-phase spectrum, suggesting that the structure of the clathrate is not adequately described by the model of Palin & Powell (1947) for the SO_2 clathrate. According to this model the