neighbour, whereas in the *b* direction the chlorine atom of one molecule lies near to the axis of the benzene rings of both its neighbours. It seems possible that some polarization effect associated with this arrangement may be responsible for the orientation of the (010) cleavage plane which cuts across the network of hydrogen bonds.

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The Crystal Structure of Zinc Acetate Dihydrate, $Zn(CH_3COO)_2.2H_2O$

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Crystals of zinc acetate dihydrate, $Zn(CH_3COO)_2.2H_2O$, are monoclinic with space group $C2/c$. The unit cell, of dimensions $a = 14{\cdot}50$, $b = 5{\cdot}32$, $c = 11{\cdot}02$ Å, $\beta = 100°\ 0'$, contains only four formula units. The zinc atoms lie on twofold axes.

Projections of the structure on two crystallographic planes are given. The six nearest neighbours of a zinc atom are four oxygen atoms and two water molecules which form a badly distorted octahedron around the zinc atom. The acetate groups have normal bond distances and angles.

The formula units are firmly linked by strong hydrogen bonds to form 'two-dimensional' sheets. Only feeble van der Waals forces exist between such sheets. This sheet-like nature of the structure accounts for such physical properties as the mosaic character, softness and ready cleavage of the crystals.

Introduction

Direct X-ray evidence for the existence of metal-to-metal bonds in the structures of cupric and chromous acetate (van Niekerk & Schoening, 1953*a*, *b*; van Niekerk, Schoening & de Wet, 1953) has raised the question whether the acetates of the other transition elements have similar or related structures. The present investigation was therefore undertaken as part of a systematic X-ray examination of the structural features of such compounds.

Crystal data and space group

Crystals of zinc acetate dihydrate, $Zn(CH_3COO)_2.2H_2O$, are colourless and generally crystallize in the form of needles. They are extremely soft and split very readily along the needle direction (*b* axis). Good single crystals are the exception, as the crystals usually assume the form of thin, elongated plates which are stacked together to form prismatic needles. The prism faces are the (100) and (001) faces, the angle between them being 80° 0'.

The crystals are monoclinic and the unit-cell dimensions, as determined from rotation photographs and goniometer measurements, are

$$a = 14{\cdot}50,\ b = 5{\cdot}32,\ c = 11{\cdot}02\ \text{Å},\ \beta = 100°\ 0'.$$

The axial ratios

$$a{:}b{:}c = 2{\cdot}726{:}1{:}2{\cdot}071$$

agree well with the values

$$3c{:}b{:}3a = 2{\cdot}713{:}1{:}2{\cdot}069,\ \beta = 80°\ 0'$$

given by Rammelsberg (1881).

Systematic extinctions occur only for hkl with $h+k$ odd, $h0l$ with h odd and l odd and $0k0$ with k odd. The space group is therefore either Cc or $C2/c$. In order to distinguish between the two possible space groups a statistical $N(z)$ test, in which all the hkl spectra were used, was made. The result was, however, not decisive. The crystals were also tested for pyro-electricity, following methods described by Bunn (1946). The results were negative, so that these experiments, although not conclusive, at least do not contradict the $C2/c$ space group. The successful structural analysis probably gives the best evidence that the space group is $C2/c$.

Assuming four formula units in the unit cell, the calculated density is 1·76 g.cm.$^{-3}$, in good agreement with the measured density 1·77 g.cm.$^{-3}$.

Preliminary estimate of the structure

Since the general point position in the $C2/c$ space group is eightfold, and since there are only four formula units in the unit cell, it follows that the zinc atoms must occupy special positions. These positions are symmetry centres and twofold axes. Should the zinc atoms occupy symmetry centres, the *hkl* intensities should conform approximately to certain extinction conditions. As these conditions were not convincingly obeyed, it seemed reasonable to infer that the zinc atoms lie on twofold axes. This point was tested by evaluating the $P(0, v, \frac{1}{2}c)$ section. For this purpose equi-inclination Weissenberg photographs, using Cu $K\alpha$ radiation, were taken of the first four layers for a crystal rotating about the b axis, and the above Harker section was evaluated (Fig. 1). It is evident from this diagram that the zinc atom lies at a distance $\frac{1}{8}b$ from the glide plane, thus ruling out the possibility of the zinc atoms occupying symmetry centres as these lie either on or midway (at a distance $\frac{1}{4}b$) between the c-glide planes. Using as origin that given in *International Tables* for the $C2/c$ space group, the position of the zinc atom was taken at $(0, \frac{1}{8}b, \frac{1}{4}c)$.

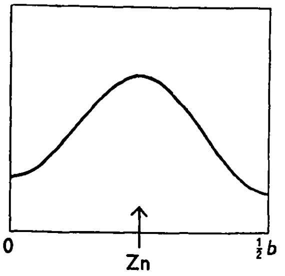

Fig. 1. Harker section $P(0, v, \frac{1}{2}c)$. The final zinc position is indicated.

Projections of the structure on two crystallographic planes

For evaluating the $\sigma(x, z)$ and $\sigma(y, z)$ projections, the intensities of the spectra recorded on multiple-film zero-layer Weissenberg photographs were estimated visually and corrected for Lorentz and polarization factors. Cu $K\alpha$ radiation was used and in view of the small size of the crystals no corrections were made for absorption and extinction effects. Using Lipson & Beevers' strips, the $\sigma(x, z)$ projection was evaluated first. The signs of the relevant $F(h0l)$ terms were calculated from the zinc co-ordinates only, terms of doubtful sign being omitted during the preliminary projections. Successive refinements, using all the recorded spectra, finally gave the projection shown in Fig. 2. In this diagram the atoms are well resolved and the crosses indicate the atomic positions finally chosen. Atoms assigned with small circle suffixes are related to correspondingly marked ones by the twofold axis.

The final $\sigma(y, z)$ projection is shown in Fig. 3. The notation is the same as for Fig. 2, crosses again indicating the positions of atoms belonging to the same formula unit. The two heavy dots on the projection indicate the positions of a carbon atom and of a water molecule which are derived by symmetry from corresponding atoms indicated by crosses.

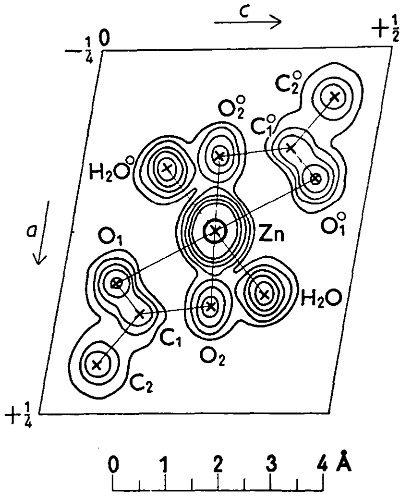

Fig. 2. Electron density projected along b on to the ac plane. Contours are drawn at 2 e.Å^{-2} intervals, the outer line is the two-electron level. The heavy contour is the 40-electron level. Crosses indicate the final atomic positions. Atoms assigned with small circle suffixes are related to correspondingly marked ones by the twofold axis on which lies the zinc atom.

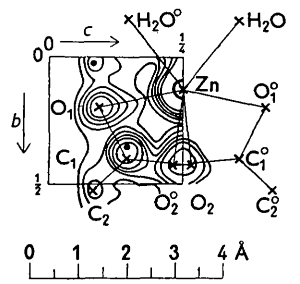

Fig. 3. Electron density projected on the bc plane. Contours and labelling of atoms are as for Fig. 2. The inner contour of the two double peaks is the fourteen-electron level. The two heavy dots represent atoms related by symmetry to corresponding ones marked by crosses. Atoms marked by crosses all belong to the same formula unit.

The co-ordinates given in Table 1 were estimated from the two projections.

With these co-ordinates, structure factors were

Table 1. *Final parameters*

Atom	x	y	z
Zn	0·000	0·125	0·250
O_1	0·071	0·200	0·095
O_2	0·103	0·423	0·267
H_2O	0·088	−0·150	0·354
C_1	0·113	0·400	0·145
C_2	0·183	0·527	0·083

Table 2. *Observed and calculated structure factors*

hkl	F_o	F_c
200	185	+174
400	31	−11
600	8	+ 6
800	46	+50
10,0,0	77	+96
12,0,0	48	+60
14,0,0	15	+15
16,0,0	15	+19
18,0,0	9	+15
020	6	+ 6
040	65	−62
060	< 7	0
002	130	−150
004	21	+33
006	92	−103
008	77	+72
0,0,10	49	−41
0,0,12	35	+31
0,0,14	< 4	0
202	152	−157
204	13	+20
206	58	−50
208	87	+67
2,0,10	24	−19
2,0,12	16	+ 7
$20\bar{2}$	89	−90
$20\bar{4}$	147	+134
$20\bar{6}$	110	−94
$20\bar{8}$	52	+46
$2,0,\overline{10}$	69	+53
$2,0,\overline{12}$	40	+33
$2,0,\overline{14}$	10	−10
402	27	−43
404	68	+70
406	58	−49
408	37	+31
4,0,10	6	−11
4,0,12	< 7	+ 4
$40\bar{2}$	93	−70
$40\bar{4}$	144	+132
$40\bar{6}$	68	−69
$40\bar{8}$	13	+20
$4,0,\overline{10}$	25	−23
$4,0,\overline{12}$	26	+28
$4,0,\overline{14}$	17	−20
602	47	−66
604	73	+73
606	57	−56
608	38	+41
6,0,10	13	−12
6,0,12	10	+10
$60\bar{2}$	43	−39
$60\bar{4}$	129	+111
$60\bar{6}$	50	−52
$60\bar{8}$	< 8	0
$6,0,\overline{10}$	12	−17
$6,0,\overline{12}$	20	+26
802	97	−102
804	78	+81
806	22	−25
808	28	+33
8,0,10	31	−33
8,0,12	< 5	+10
$80\bar{2}$	73	−80
$80\bar{4}$	79	+73
$80\bar{6}$	28	−26
$80\bar{8}$	48	+45
$8,0,\overline{10}$	37	−37
$8,0,\overline{12}$	9	+ 2
10,0,2	70	−62
10,0,4	53	+60
10,0,6	15	−23
10,0,8	< 6	+ 9
10,0,10	27	−26
$10,0,\bar{2}$	66	−86
$10,0,\bar{4}$	18	+21
$10,0,\bar{6}$	39	−55
$10,0,\bar{8}$	82	+74
$10,0,\overline{10}$	28	−29
$10,0,\overline{12}$	6	+ 5
12,0,2	24	−29
12,0,4	18	+17
12,0,6	18	−23
12,0,8	< 7	+ 9
$12,0,\bar{2}$	28	−42
$12,0,\bar{4}$	15	+30
$12,0,\bar{6}$	35	−45
$12,0,\bar{8}$	30	+36
$12,0,\overline{10}$	13	−21
$12,0,\overline{12}$	12	+17
14,0,2	10	− 5
14,0,4	9	+11
14,0,6	12	−17
$14,0,\bar{2}$	23	−32
$14,0,\bar{4}$	20	+29
$14,0,\bar{6}$	13	−16
$14,0,\bar{8}$	< 8	+ 9
$14,0,\overline{10}$	8	−11
$16,0,\bar{2}$	17	−19
$16,0,\bar{4}$	16	+16
$16,0,\bar{6}$	15	−15
021	19	−33
022	28	−20
023	47	+52
024	19	+20
025	78	−89
026	< 8	− 8
027	50	+51
028	< 8	+ 1
029	< 8	− 5
0,2,10	< 7	− 4
0,2,11	< 7	+11
0,2,12	< 6	+ 2
0,2,13	20	−20
041	33	+17
042	61	+62
043	14	+ 6
044	30	−35
045	6	+11
046	16	+16
047	11	−11
048	30	−32
049	9	+ 1
0,4,10	29	+28
061	< 7	+ 9
062	< 7	+ 7
063	27	−30
064	< 6	− 8
065	21	+18

calculated using the following temperature corrections: for the carbon atoms the *f* values obtained by Robertson (1935) were used, while for the oxygen atoms proportionately reduced *f* values were used; for the zinc ion the f_0 values given by James & Brindley (1931) for the neutral zinc atom were modified in the same way as their f_0 values for neutral copper have to be modified to give their calculated copper ion values. To these modified zinc values an isotropic temperature factor with $B = 3{\cdot}2$ was then applied.

The observed and calculated structure factors are tabulated in Table 2. The agreement is good and, neglecting absent spectra, *R* factors of 0·15 and 0·16 were obtained for the *h*0*l* and 0*kl* spectra respectively.

The interatomic distances and angles given in Table 3 were calculated from the co-ordinates tabulated in Table 1.

Considering the agreement between the observed and calculated structure factors, together with the sound interatomic distances that were obtained, there seems little reason to doubt the validity of the space group and of the structure. The correctness of the structure is further substantiated by a $P(u, 0, w)$ projection (Fig. 4), for which only observed data were utilized. On this projection the final atomic positions, as derived from the two Fourier projections, are indicated by crosses and it is clear that the Patterson

Table 3. *Interatomic distances and angles*

(All distances are in Ångström units and all angles in degrees)

$Zn–O_1$	2·18	$O_1–C_1–O_2$	111
$Zn–O_2$	2·17		
$Zn–H_2O$	2·14	$O_1–Zn–O_2$	61
$O_1–C_1$	1·30	$O_1–Zn–H_2O$	103
$O_2–C_1$	1·38	$O_1–Zn–O_1^\circ$	158
$C_1–C_2$	1·48	$O_1–Zn–O_2^\circ$	104
$O_1–O_2$	2·21	$O_2–Zn–H_2O$	96
		$O_2–Zn–O_2^\circ$	85
		$H_2O–Zn–H_2O^\circ$	94
		$H_2O–Zn–O_1^\circ$	92
		$H_2O–Zn–O_2^\circ$	152

vectors to the peak maxima coincide almost exactly with these crosses. The interpretation of the Patterson vectors is obvious when this diagram is compared with Fig. 2.

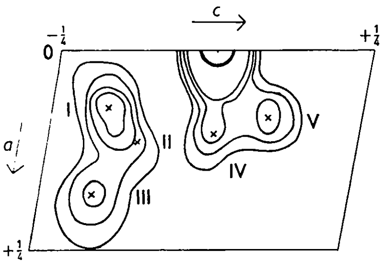

Fig. 4. Patterson projection $P(u, 0, w)$. Contours are drawn at arbitrary levels. Crosses indicate the final atomic positions obtained from the two electron density projections. The five Patterson peaks are numbered.

Description of the molecule

The structure is best described by referring to Fig. 2. The six nearest neighbours of a zinc ion are four oxygen atoms at distances 2·17 and 2·18 Å and two water molecules at distances 2·14 Å. These six bonds are probably mainly ionic in character. The six atoms form a greatly distorted octahedron around the zinc ion. The degree of distortion is probably accounted for by the O_1–O_2 distance (2·21 Å) of the acetate group which is much too short to allow for the formation of a regular octahedron. The two acetate groups are separately planar, the angle between their planes being 85°. The O_1–C_1 distance (1·30 Å) is shorter than the O_2–C_1 distance (1·38 Å). However, as C_1 is not clearly resolved in either of the two Fourier projections, this difference may not be very reliable. The C_1–C_2 distance is 1·48 Å.

Discussion of the bonding

The arrangement of formula units in the structure is such that along the *c* direction each unit lies at a height $\frac{1}{4}b$ above or below the one preceding it, while in the *a* direction adjacent units differ in height by $\frac{1}{2}b$. Along the *b* direction the units are separated by the *b* spacing (5·32 Å) and form extended columns parallel to the *b* axis. Along such columns the units comprising them are firmly linked by hydrogen bonds of length 2·49 Å. Referring to Fig. 2, such bonds exist between the two water molecules (H_2O and H_2O°) of one unit which are bonded respectively to the two oxygen atoms (O_2 and $O_2{}^\circ$) of the unit immediately above.

Adjacent columns of formula units are also linked in the *c* direction in the following manner. The two water molecules (H_2O and H_2O°) belonging to a unit in one reference column are bonded respectively to the two oxygen atoms O_1 and $O_1{}^\circ$ of two units belonging to the two columns which are adjacent to the reference column. These are again hydrogen bonds of length 2·74 Å.

From the above discussion it is clear that hydrogen bonds firmly link the units in the structure in such a manner as to form effectively 'two-dimensional' sheets parallel to the *bc* plane. Considering the bonds between such sheets, i.e. in the *a* direction, it is found that the separation between adjacent sheets is much too large to allow for any but comparatively weak van der Waals forces between them. This sheet-like nature of the zinc acetate structure accounts for its stacked plate-like crystal habit, the softness and the marked cleavage of the crystals.

In conclusion we wish to thank Mr H. Schumann of the National Chemical Research Laboratory for preparing the crystals and the Council for Scientific and Industrial Research for permission to publish this paper.

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