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The crystal structure of lithium acetate dihydrate $CH_3COOLi.2H_2O$.

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Lithium acetate dihydrate belongs to the orthorhombic class (Groth). Rotation and Weissenberg photographs taken around the three axes gave

$$a = 6{\cdot}86,\quad b = 11{\cdot}49 \quad\text{and}\quad c = 6{\cdot}59\ \text{Å}\,,$$

giving

$$a:b:c = 0{\cdot}60:1:0{\cdot}57\,.$$

Groth's value is 0·62:1:—.

The density is found to be 1·30 g.cm.$^{-3}$ (flotation method) giving four molecules per unit cell.

The extinctions lead to the space groups *C*222, *Cmm*2 and *Cmmm*, but packing considerations of the four acetate ions uniquely fix the space group as *Cmm*2. The multiple-film technique was used to obtain intensity data with Cu $K\alpha$ radiation. The intensity values were corrected for all factors and were put to absolute scale by Wilson's method.

The four acetate ions were placed on the four-fold special positions $(0, y, z)$ as the other set $(x, 0, z)$ was found to be untenable. Similarly the four lithium atoms were found to occupy the positions $(x, 0, z)$. The eight water molecules occupy the general positions, the approximate positions being fixed by Patterson's method. The final structure was obtained after a series of trial and error and Fourier refinements. The mean reliability factor for $(h0l)$, $(0kl)$ and $(hk0)$ reflections is 0·18 (hydrogen contribution neglected). The atomic coordinates, bond lengths and angles are listed in Table 1.

As reported on zinc acetate (Niekerk, Schoening & Talbot, 1953), lithium acetate also exhibits a 'two-dimensional sheet' structure. The acetate ions are separated along *a* by *a*/2 and linked by weak hydrogen bonds of the water molecules (hydrogen-bond linkage 3·08 Å and 3·14 Å) and along *c* by the *c* spacing. Along *b* the nearest distance is 3·68 Å and along *c* 3·87 Å. Such weak forces account for the low melting point of the crystal. Lithium is surrounded by six oxygens, four of which belong to the acetate ions and the two other to the water molecules.

Table 1 *Atomic coordinates, bond lengths and angles*

Atomic parameters

	x	*y*	*z*
C_1	0	0·325	−0·248
C_2	0	0·272	−0·032
O_1	0	0·334	0·118
O_2	0	0·156	0·005
H_2O	0·156	0·140	0·452
Li	0·162	0	0·147

Bond distances and angles

C_1–C_2	1·55 Å	Li–O_2	2·27 Å
C_2–O_1	1·22	Li–H_2O	2·57
C_2–O_2	1·33	∢ O_1–C_2–O_2	119° 24′

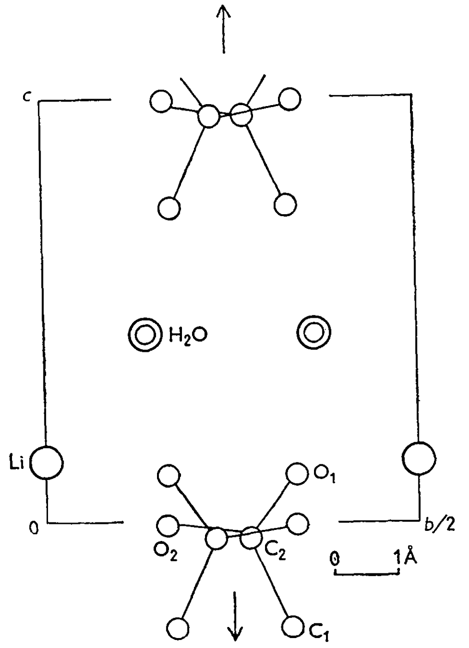

Fig. 1. The crystal structure of CH_3COOLi, 2 H_2O viewed down the *a*-axis.

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Redetermination of the oxygen parameters in zircon ($ZrSiO_4$).

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The crystal structure of zircon has been determined by Vegard (1926), Hassel (1926) and Wyckoff & Hendricks (1927), the results being in fairly good agreement. Since zircon is one of the first minerals on which the metamict state has been studied, and since the bond lengths in this structure have been used in the discussion of the nature of the metamict state, it appeared worth while to redetermine the oxygen parameters in this structure.

The crystal used for this investigation came from Ilmen Mt. Ural; it showed slight radioactivity (72 αmg.hr.$^{-1}$) and the specific gravity was 4·67 g.cm.$^{-3}$. These results showed that this specimen was 'normal' zircon, i.e. not affected by metamictization. The unit-cell dimensions were determined from a Straumanis powder photograph using Cu filtered radiation (λ = 1·54050 Å). The following results were obtained

$$a = 6{\cdot}6164 \pm 0{\cdot}0005,\quad c = 6{\cdot}0150 \pm 0{\cdot}0005 \text{ Å}\,.$$

Single-crystal photographs (taken with Cu-filtered radiation) included zero, first and second level normal Weissenberg c-axis photographs and first, second and third level a-axis photographs. Systematic absences confirmed the space group $I4_1/amd$; $Z = 4$.

To determine the oxygen parameters an electron-density projection on (100) with the origin at a symmetry centre ($2/m$) was made. The intensities of 90 $0kl$ reflexions were obtained (using Mo filtered radiation) with an integrating Weissenberg goniometer. The intensities of the spots were measured with a Kipp (Delft) photometer. After allowing for Lorentz and polarization factors and for absorption, F values were placed on an absolute scale by scaling them to the calculated structure amplitudes for various regions of $\sin\theta/\lambda$. To calculate structure amplitudes Vegard's parameters were used, the atomic scattering factors being taken from *Internationale Tabellen* (1935).

For the refinement of the oxygen parameters both F_o and $F_o - F_c$ syntheses were used. After the third $F_o - F_c$ synthesis it was concluded that the error due to series termination was largely eliminated; the final parameters for oxygen atoms were $y = 0{\cdot}067$, $z = 0{\cdot}198$. The value of the reliability index R is 0·07.

Interatomic distances in the SiO_4 tetrahedron are as follows

O–O = 2·42 Å (two), O–O = 2·73 Å (four), Si–O = 1·61 Å,

with $\sigma(x)$ estimated to be 0·02 Å (Cruickshank, 1949).

As can be seen there is a distorted tetrahedron with the length of the Si–O bond in good agreement with the values found in other silicates; each atom of zirconium is surrounded by four atoms of oxygen at 2·15 Å, and by another four at 2·29 Å. These values are nearer to the sum of the ionic radii of Zr and O than those given by the previous investigators (2·05 and 2·41 Å respectively), and the distribution of oxygen atoms around zirconium is more regular. The first set of these distances is close to the sum of the Goldschmidt ionic radii corrected for coordination (2·16 Å) while the other set is larger by 0·14 Å. This may be of some significance in connexion with the process of metamictization in zircon but it is interesting to note here that the same irregular oxygen polyhedra occur in the structure of Xenotime* (YPO_4); this is of the same structural type as zircon, but, although it is sometimes strongly radioactive, it is never found in the metamict state. Corresponding distances in Xenotime are 2·32 and 2·56 Å, while the sum of the corrected ionic radii for yttrium and oxygen is 2·35 Å. Some authors (e.g. Pellas, 1954) claim a high degree of covalent bonding as one of the causes of the metamict state but the interatomic distances zirconium–oxygen in this structure would not suggest this.

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A refinement of the crystal structure of ketene dimer.

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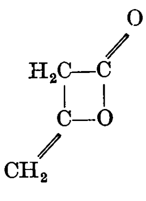
The structure of ketene dimer in the solid state was determined by Katz & Lipscomb (1952). They found the molecule to have the 3-butenoic acid β-lactone structure.



The emphasis of their study was on finding the correct molecular configuration rather than on determining 'highly accurate atomic parameters'. Thus, when the C–C single bond lengths were found to be unusually short, it was not known whether this was due simply to inaccuracy in the structure determination, or whether it would be necessary to invoke a significant amount of double bond character to explain the shrinkage. Electron-diffraction results (Bauer & Bregman, 1955) showed normal values of 1·52 Å for the ring C–C bond lengths.

A refinement of the structure determination was considered worth while when an I.B.M. 704 least-squares program and computer time became available. The data

Table 1. *New co-ordinates, temperature factors, and standard deviations for diketene*

Atom	x	y	z	B	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C_1	0·3049	0·0599	0·1652	3·324	0·007	0·0010	0·0006
O_1	0·7211	0·1033	0·5565	3·156	0·005	0·0007	0·0004
C_2	0·5032	0·1062	0·2884	2·964	0·007	0·0010	0·0004
C_3	0·8409	0·1650	0·5223	2·664	0·006	0·0010	0·0004
C_4	0·6399	0·1738	0·2412	2·356	0·006	0·0009	0·0004
O_2	0·0584	0·1920	0·6901	3·629	0·005	0·0007	0·0006

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[*] Guest Scientist on leave from Pennsylvania State University.