Table 6. *Torsional angles*

Ring *A*		Ring *B*	
C(12)–C(13)–C(14)–C(15)	−53·5°	C(16)–C(17)–C(22)–C(23)	3·14°
C(13)–C(14)–C(15)–C(16)	47·7	C(17)–C(22)–C(23)–C(24)	−33·62
C(14)–C(15)–C(16)–C(17)	−46·0	C(22)–C(23)–C(24)–C(16)	53·34
C(15)–C(16)–C(17)–C(12)	55·8	C(23)–C(24)–C(16)–C(17)	−60·88
C(16)–C(17)–C(12)–C(13)	−58·2	C(24)–C(16)–C(17)–C(22)	40·57
C(17)–C(12)–C(13)–C(14)	54·8		
Ring *C*		Ring *D*	
C(23)–C(25)–C(15)–C(16)	2·68°	C(16)–C(17)–C(22)–C(23)	3·14°
C(25)–C(15)–C(16)–C(24)	−39·06	C(17)–C(22)–C(23)–C(25)	75·03
C(15)–C(16)–C(24)–C(23)	56·03	C(22)–C(23)–C(25)–C(15)	−71·10
C(16)–C(24)–C(23)–C(25)	−56·94	C(23)–C(25)–C(15)–C(16)	2·68
C(24)–C(23)–C(25)–C(18)	35·05	C(25)–C(15)–C(16)–C(17)	74·05
		C(15)–C(16)–C(17)–C(22)	−68·22

Physics Department, I.I.Sc. for many useful discussions and Mr. B. S. Reddy of the same department for assistance in computation. One of us (RR) thanks the CSIR (India) for financial assistance.

References

Altona, C. & Sundaralingam, M. (1970). *J. Amer. Chem. Soc.* **92**, 1995–1999.

Cesur, A. F. & Grant, D. F. (1965). *Acta Cryst.* **18**, 55–59.

Coetzer, J., Baxter, V. J. & Gafner, G. (1971). *Acta Cryst.* **B27**, 1434–1440.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Destro, R., Filippini, G., Gramaccioli, C. M. & Simonetta, M. (1969). *Acta Cryst.* **B25**, 2465–2472.

Dwivedi, G. L. & Srivastava, R. C. (1972). *Acta Cryst.* **B28**, 2567–2576.

Flippen, J. L. (1972). *Acta Cryst.* **B28**, 2046–2048.

Gilardi, R. D. (1972). *Acta Cryst.* **B28**, 742–746.

Hall, S. R. & Maslen, E. N. (1965). *Acta Cryst.* **18**, 265–279.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.

Kaneda, M. & Iitaka, Y. (1972). *Acta Cryst.* **B28**, 1411–1420.

Karle, I. L. (1972). *Acta Cryst.* **B28**, 2000–2007.

Kasturi, T. R., Ramachandra, R., Damodaran, K. M. & Kalyani Vijayan (1972). *Tetrahedron Lett.* pp. 5059–5062.

Kitaigorodskii, A. I. (1961). *Organic Chemical Crystallography*, English ed. New York: Consultants Bureau.

Palm, J. H. (1964). *Acta Cryst.* **17**, 1326–1327.

Shimanouchi, H. & Sasada, Y. (1970). *Acta Cryst.* **B26**, 563–577.

Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Supplement 1956–1959, M 1125. London: The Chemical Society.

Acta Cryst. (1973). B**29**, 1950

The Crystal Structure of Lithium Maleate Dihydrate

By W. G. Town* and R. W. H. Small

The Chemistry Department, The University, Lancaster, England

(*Received* 16 *April* 1973; *accepted* 17 *April* 1973)

The structure of $Li_2C_4H_2O_4.2H_2O$, with cell dimensions $a=9·6306$, $b=12·1307$, $c=12·7051$ Å, $\beta=107·96°$, has been determined with counter-measured X-ray intensites (1535 planes). The maleate ion is non-planar and unsymmetrical, the principal bond distances (Å) being C(1)–C(2) 1·495 (3), C(2)–C(3) 1·330 (3), C(3)–C(4) 1·505 (3), C(1)–O(1) 1·277 (2), C(1)–O(2) 1·252 (2), C(4)–O(3) 1·273 (2), C(4)–O(4) 1·252 (2). Each lithium ion has an approximately tetrahedral coordination of oxygen atoms.

Experimental

(*a*) *Preparation*

The compound was prepared by the neutralization of an aqueous solution of maleic acid with equivalent amounts of lithium hydroxide. Crystals obtained from the aqueous solution were monoclinic prisms, usually showing the forms {010}, {110}, {001} and occasionally elongated parallel to **a**. A melting point could not be determined as dehydration occurred at 160°C. The composition was confirmed by elemental chemical analysis (C, H, and Li).

---

* Present address: Crystallographic Data Centre, Lensfield Road, Cambridge, England.

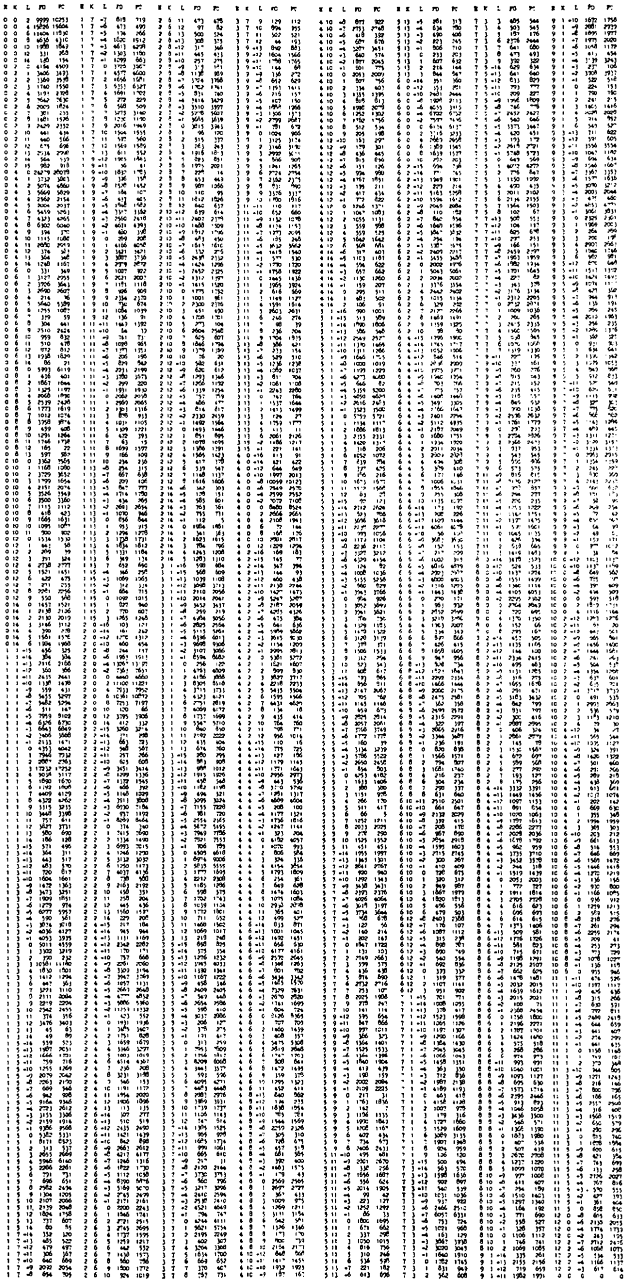
(*b*) *Crystallographic*

Weissenberg photographs, taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) were used to determine approximate cell dimensions and to show that the space group was either *Cc* or *C*2/*c*. Accurate cell dimensions were obtained from measured θ values of all observable orders of 100, 010, 001, 101, and $10\bar{1}$ by least-squares refinement. Measurements were made on the three circle diffractometer. The crystal data are given in Table 1.

Table 1. *Crystal data*

$a = 9{\cdot}6306\ (9)$ Å	$D(\text{exp}) = 1{\cdot}537\ (1)$ g cm^{-3}
$b = 12{\cdot}1307\ (13)$	$D(\text{calc}) = 1{\cdot}543$
$c = 12{\cdot}7051\ (20)$	$Z = 8$
$\beta = 107{\cdot}96\ (1)°$	Space group *Cc* or *C*2/*c*

Table 2. *Observed and calculated structure factors* ($\times 10^2$)



Intensity measurements were made on the diffractometer of Small & Travers (1961) with a proportional counter and Cu $K\alpha$ radiation. A crystal of dimensions $0{\cdot}1 \times 0{\cdot}1 \times 0{\cdot}5$ mm was used for most of the measurements. The intensities of the 118 weakest reflexions were measured with a larger crystal ($1 \times 1 \times 2$ mm). 1535 independent reflexions within the sphere $\theta \le 82{\cdot}5°$ had significantly measurable reflexions with only 7 too weak to be observed.

X-ray transmission factors for the paths within the smaller crystal were calculated by the method of de Meulenaer & Tompa (1965) with a computer program written by Tompa. The transmission factors varied between 0·656 and 0·865.

An analysis of the distribution of the intensities by the method of Howells, Phillips & Rogers (1950) showed that the crystals were centric, indicating the space group *C*2/*c* with a structural unit of formula $Li_2C_4H_2O_4.2H_2O$. The scale factor used in the conversion of the intensity data to structure factors and an overall isotropic temperature factor ($B = 3{\cdot}4$ Å^2) were obtained by the statistical method of Wilson (1942).

Determination and refinement of the structure

Initially some difficulty was encountered in finding an approximation solution to the structure. Although several non-planar models of the maleate ion were considered, none was sufficiently close to the shape eventually found to yield a solution. The problem was solved without any assumption about the nature of the anion when the symbolic addition method became available. The programs *GSR* and *LSAM* of Germain,

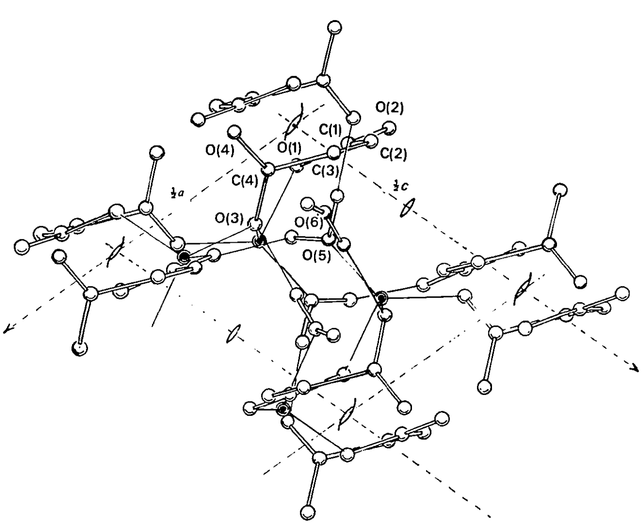


Fig. 1. Projection of the crystal structure along **b**.

Main & Woolfson were used with 250 of the largest E values. An E map, computed with one of the sets of signs, gave positions of all the atoms except those of hydrogen. Refinement of the positional parameters and anisotropic temperature factors was carried out with the program *FMLS* of Bracher & Taylor (1967). At an intermediate stage of the refinement all the hydrogen atoms were located from a three-dimensional difference synthesis.

During the refinement it became apparent that, for planes of high intensity, the observed structure factors were appreciably less than those calculated. On the assumption that the differences were due to extinction, a correction was calculated and applied to the observed structure factors. Following the method described by Larson (1970) the correction was calculated as a modification of the calculated structure factors in the form

$$F_c^* = k|F_c|\left\{1+r|F_c^2|\left[\frac{1+\cos^4 2\theta}{\sin 2\theta(1+\cos^2 2\theta)}\right]T\right\}^{-1/4}$$

where k is a scale factor, r is a constant involving the extinction parameter and T is the mean path length for a particular reflexion. The parameters k and r were refined by a separate least-squares procedure involving all values of F_o and F_c^*, the latter being derived from the F_c values output from the *FMLS* program. The correction factors derived in this way were applied inversely to the F_o values and refinement of the structural parameters by least-squares calculations (*FMLS*) resumed. As a result of this correction the conventional R fell from 0·064 to a final value of 0·041. The calculated value of F_{040}, although improved by this proce-

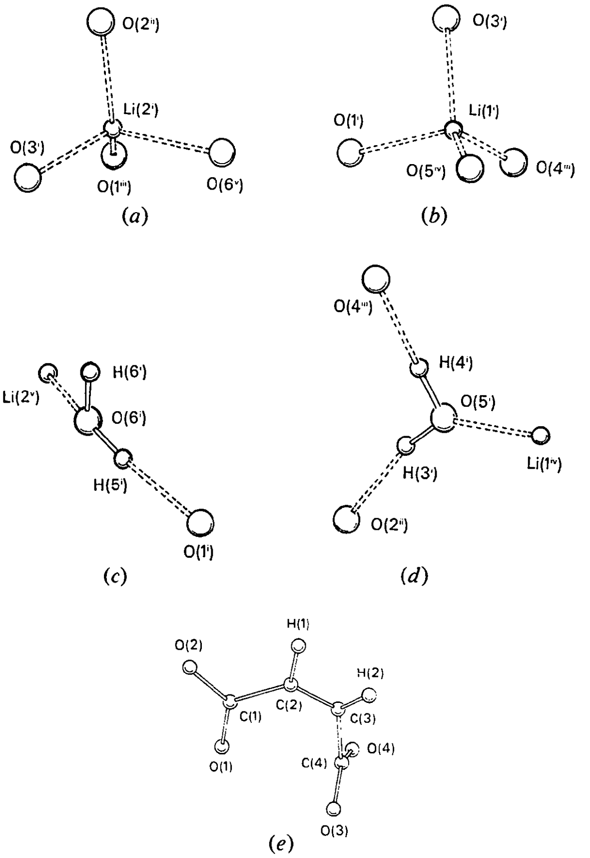


Fig. 2. (*a*), (*b*) Lithium ion environment. (*c*), (*d*) Water molecule environment. (*e*) Maleate ion configuration.

Table 3. *Fractional atomic coordinates and their standard deviations (in parentheses)* × 10^5

	x	y	z
C(1)	96198 (18)	14537 (14)	9118 (13)
C(2)	92381 (20)	26216 (15)	10562 (16)
C(3)	−581 (20)	34972 (14)	8512 (15)
C(4)	12362 (18)	35064 (13)	4275 (14)
O(1)	7830 (12)	12467 (10)	6727 (10)
O(2)	87653 (13)	8254 (10)	10364 (11)
O(3)	24992 (13)	33521 (10)	11015 (10)
O(4)	9945 (13)	37275 (11)	94290 (10)
O(5)	17537 (14)	61480 (13)	21279 (11)
O(6)	12314 (16)	89670 (12)	16615 (12)
Li(1)	27327 (33)	17219 (26)	14103 (24)
Li(2)	41703 (34)	41717 (26)	8081 (26)
H(1)	83543 (220)	27367 (173)	12738 (166)
H(2)	96325 (245)	41642 (195)	9687 (185)
H(3)	23193 (265)	60590 (203)	17716 (195)
H(4)	8533 (328)	61833 (250)	16541 (241)
H(5)	17066 (366)	86952 (298)	23519 (289)
H(6)	14254 (394)	96643 (323)	15929 (302)

Table 4. *Temperature factors*

(*a*) b_{ij} values for C, O and Li atoms, $\exp\{-10^{-5}(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)\}$ with standard deviations (in parentheses).

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	522 (18)	294 (11)	246 (10)	−12 (23)	225 (22)	2 (16)
C(2)	678 (21)	325 (11)	468 (13)	68 (25)	643 (27)	−17 (19)
C(3)	761 (22)	252 (11)	461 (13)	89 (25)	610 (27)	−5 (19)
C(4)	626 (19)	171 (9)	367 (11)	−14 (22)	362 (24)	−6 (16)
O(1)	488 (13)	326 (8)	344 (8)	−58 (17)	369 (17)	−107 (13)
O(2)	649 (15)	300 (8)	569 (10)	−131 (18)	685 (20)	−46 (15)
O(3)	583 (14)	297 (8)	339 (8)	−104 (17)	195 (17)	30 (13)
O(4)	651 (15)	464 (9)	320 (8)	127 (19)	346 (18)	150 (14)
O(5)	640 (16)	812 (13)	333 (9)	−42 (23)	323 (19)	−253 (17)
O(6)	1022 (20)	530 (11)	435 (10)	163 (24)	100 (22)	206 (17)
Li(1)	625 (34)	298 (21)	320 (19)	−33 (44)	298 (42)	28 (33)
Li(2)	726 (37)	373 (21)	388 (21)	−5 (45)	416 (45)	−41 (33)

Table 4 (*cont.*)

(*b*) Isotropic B values (Å^2) for H atoms, with standard deviations (in parentheses).

	B
H(1)	0·456 (403)
H(2)	1·220 (472)
H(3)	1·628 (509)
H(4)	3·674 (712)
H(5)	5·616 (911)
H(6)	6·494 (997)

dure, was still considerably greater than that observed and it was therefore omitted from the last refinement cycles. The atomic scattering factors used throughout were those listed in *International Tables for X-ray Crystallography* (1962). The final values of F_o and F_c (including 040) are given in Table 2. The coordinates of all atoms in the structural unit are given in Table 3 and the b_{ij} values in Table 4.

Interpretation of the thermal vibration parameters

On the assumption that the anions in this compound behave as rigid bodies, the three tensors T, ω and S described by Schomaker & Trueblood (1968) were evaluated from b_{ij} values with the program *MGTL* of Gantzel & Trueblood. These three tensors and their estimated standard deviations referred to orthogonal axes a, b, c^* are listed in Table 5. The validity of the rigid-body model of the anion may be conveniently tested by a comparison of the U_{ij} values of each atom derived from the b_{ij} values with those values calculated from the rigid-body parameters T, ω and S. The two sets are listed side by side in Table 6. The r.m.s. ΔU_{ij} between the two sets is 0·0021 Å^2 and the mean σU_{ij} of those obtained from the b_{ij} values is 0·007 Å^2. Bond distances and angles within the anion have been corrected for librational motion and are given in Table 7.

Table 5. *Rigid-body tensors*

Translational tensor, T
Elements ($T_{ij} \times 10^4$) of the mean square tensor (Å^2)

210 (14)	8 (11)	12 (14)
	201 (12)	−17 (12)
		161 (23)

Librational tensor, ω
Elements ($\omega_{ij} \times 10^4$) of the mean square tensor (rad^2)

53 (11)	25 (7)	−13 (6)
	56 (11)	−13 (6)
		9 (5)

Cross tensor, S
Elements ($S_{ij} \times 10^6$) rad. Å)

6 (8)	15 (7)	16 (5)
14 (8)	2 (10)	24 (5)
−8 (4)	−11 (4)	−

Table 7. *Bond distances and angles in the maleate ion*

(*a*) Intra-ion distances (after libration correction) and their standard deviations (Å).

C(1)–C(2)	1·495 (3)	C(1)–O(1)	1·277 (2)
C(2)–C(3)	1·330 (3)	C(1)–O(2)	1·252 (2)
C(3)–C(4)	1·505 (3)	C(4)–O(3)	1·273 (2)
C(2)–H(1)	1·09 (2)	C(4)–O(4)	1·252 (2)
C(3)–H(2)	0·88 (2)		

(*b*) Bond angles (after libration correction) and their standard deviations (°).

O(1)–C(1)–O(2)	123·5 (2)	C(1)–C(2)–H(1)	116 (1)
O(1)–C(1)–C(2)	119·2 (2)	C(3)–C(2)–H(1)	118 (1)
O(2)–C(1)–C(2)	117·3 (2)	C(2)–C(3)–H(2)	120 (2)
C(1)–C(2)–C(3)	125·1 (2)	C(4)–C(3)–H(2)	113 (2)
C(2)–C(3)–C(4)	127·4 (2)		
C(3)–C(4)–O(3)	119·1 (2)		
C(3)–C(4)–O(4)	116·8 (2)		
O(3)–C(4)–O(4)	124·1 (2)		

Description and discussion of the structure

(*a*) *General arrangement*

A projection of the structure along **b** is shown in Fig. 1. The main plane of each maleate ion is approximately parallel to (001). The water molecules are sandwiched between layers of maleate ions and the lithium ions lie between the water molecules and the anions. The structure is continuously bonded in three dimensions by either ionic or hydrogen bonds. Each lithium ion forms bonds to four oxygen atoms and each maleate ion is bonded by its four oxygen atoms to lithium ions and water molecules.

(*b*) *Lithium ion environment*

The approximately tetrahedral coordination of both the crystallographically distinct lithium ions is made up of one water oxygen and three anion oxygen atoms as depicted in Fig. 2(*a*) and (*b*). The angles and distances involved are given in Table 8. It will be noted that one of the lithium ions, Li(1), has two oxygen neighbours from the same anion.

Table 6. *Values of* $U_{ij} \times 10^4$ (Å^2) (*a*) *from* b_{ij} *values* (*b*) *from rigid-body model*

	U_{11}		U_{22}		U_{33}		U_{12}		U_{13}		U_{23}	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
C(1)	222	243	218	160	182	180	−3	−5	63	60	1	6
C(2)	288	285	240	259	346	328	19	33	181	163	−6	−8
C(3)	323	340	186	181	341	347	25	17	172	158	−2	26
C(4)	266	280	127	93	271	293	−4	−21	102	101	−2	34
O(1)	207	193	241	237	254	306	−16	−16	104	121	−40	−65
O(2)	276	283	222	205	421	403	−37	−38	193	196	−17	14
O(3)	248	229	220	240	251	257	−29	−29	55	68	11	11
O(4)	277	254	343	411	237	191	36	51	97	99	56	64

(*c*) *The water molecules*

The shape and environment of each water molecule is shown in Fig. 2(*c*), (*d*), and the distances and angles involved are given in Table 9. Each water molecule has its oxygen atom coordinated to a lithium ion and in one of the molecules both hydrogen atoms, H(3), H(4), are hydrogen bonded to anion oxygens. Only one hydrogen atom H(5) in the other molecule of water can be considered to be involved in a hydrogen bond. The other H(6) is 2·15 Å from the nearest oxygen atom O(1), a distance considerably in excess of that usually interpreted as constituting a hydrogen bond. The large thermal vibration of O(6) (Table 4) may be explained by the weaker bonding in which it is involved.

(*d*) *The maleate ion*

The ion is illustrated in Fig. 2(*e*). The distances of all atoms from the plane defined by the four carbon atoms are given in Table 10. Apart from O(3) and O(4) the anion is approximately planar; in terms of torsion angles the plane of one carboxylate group, C(2)O(1)O(2), is rotated 7·0° from the plane of the carbon atoms whilst for the opposite carboxylate group the rotation is 81·4°. This unsymmetrical configuration may be contrasted with the planar arrangement found in maleic acid (Shahat, 1952) and in the hydrogen maleate ion (Darlow & Cochran, 1961). In both these structures the planarity is due to internal hydrogen bonding; in the maleate ion, with no corresponding hydrogen bond, repulsion between oxygen atoms of the opposite carboxylate groups leads to a non-planar configuration. The nearest approach of these oxygen atoms, 2·999 Å O(1)–O(3), is quite close to the sum of the

Table 10. *Distances of atoms in the maleate ion from the 'best' plane defined by* C(1), C(2), C(3), C(4) (*referred to orthogonal axes a, b, c**) (Å)

$$0{\cdot}3385x-0{\cdot}0172y+0{\cdot}9408z=0{\cdot}7605$$

C(1)	0·001	O(1)	0·145
C(2)	−0·003	O(2)	−0·137
C(3)	0·003	O(3)	1·091
C(4)	−0·001	O(4)	−1·088
H(1)	−0·124		
H(2)	−0·001		

Table 8. *Lithium ion environment*

(*a*) Distances (Å)

Li(1$^{\text{i}}$)—O(1$^{\text{i}}$)	1·911 (4)	Li(2$^{\text{i}}$)—O(2$^{\text{ii}}$)	1·964 (3)
Li(1$^{\text{i}}$)—O(3$^{\text{i}}$)	2·015 (3)	Li(2$^{\text{i}}$)—O(1$^{\text{iii}}$)	1·963 (3)
Li(1$^{\text{i}}$)—O(4$^{\text{iii}}$)	1·935 (4)	Li(2$^{\text{i}}$)—O(6$^{\text{v}}$)	1·962 (4)
Li(1$^{\text{i}}$)—O(5$^{\text{iv}}$)	1·901 (3)	Li(2$^{\text{i}}$)—O(3$^{\text{i}}$)	2·022 (4)

(*b*) Angles (°)

O(1$^{\text{i}}$)—Li(1$^{\text{i}}$)–O(3$^{\text{i}}$)	99·6 (2)	O(2$^{\text{ii}}$)–Li(2$^{\text{i}}$)–O(1$^{\text{iii}}$)	117·0 (2)
O(1$^{\text{i}}$)—Li(1$^{\text{i}}$)–O(4$^{\text{iii}}$)	109·8 (2)	O(2$^{\text{ii}}$)–Li(2$^{\text{i}}$)–O(6$^{\text{v}}$)	104·7 (2)
O(1$^{\text{i}}$)—Li(1$^{\text{i}}$)–O(5$^{\text{iv}}$)	106·8 (2)	O(2$^{\text{ii}}$)–Li(2$^{\text{i}}$)–O(3$^{\text{i}}$)	103·8 (2)
O(3$^{\text{i}}$)—Li(1$^{\text{i}}$)–O(4$^{\text{iii}}$)	102·8 (2)	O(1$^{\text{iii}}$)–Li(2$^{\text{i}}$)–O(6$^{\text{v}}$)	100·3 (2)
O(3$^{\text{i}}$)—Li(1$^{\text{i}}$)–O(5$^{\text{iv}}$)	122·0 (2)	O(1$^{\text{iii}}$)–Li(2$^{\text{i}}$)–O(3$^{\text{i}}$)	107·7 (2)
O(4$^{\text{iii}}$)–Li(1$^{\text{i}}$)–O(5$^{\text{iv}}$)	114·7 (2)	O(6$^{\text{v}}$)—Li(2$^{\text{i}}$)–O(3$^{\text{i}}$)	124·3 (2)

The labelling code for symmetry related atoms is:

Superscript	Coordinates		
i	x	y	z
ii	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
iii	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$
iv	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
v	$\frac{1}{2}+x$	$-\frac{1}{2}+y$	z
vi	$\frac{1}{2}-x$	$\frac{3}{2}-y$	$-z$

Table 9. *Water molecule distances and angles*

(*a*) Distances (Å)

O(5$^{\text{i}}$)–H(3$^{\text{i}}$)	0·86 (3)	O(6$^{\text{i}}$)—H(5$^{\text{i}}$)	0·96 (4)
O(5$^{\text{i}}$)–H(4$^{\text{i}}$)	0·95 (3)	O(6$^{\text{i}}$)—H(6$^{\text{i}}$)	0·93 (4)
O(5$^{\text{iv}}$)–Li(1$^{\text{i}}$)	1·901 (3)	O(6$^{\text{v}}$)–Li(2$^{\text{i}}$)	1·962 (4)
O(5$^{\text{i}}$)–O(2$^{\text{ii}}$)	2·756 (2)	O(6$^{\text{vi}}$)–O(1$^{\text{iii}}$)	3·013 (2)
O(5$^{\text{v}}$)–O(4$^{\text{iii}}$)	2·777 (2)	O(6$^{\text{iv}}$)–O(3$^{\text{i}}$)	2·826 (2)
H(3$^{\text{i}}$)–O(2$^{\text{ii}}$)	1·91 (3)	H(6$^{\text{vi}}$)–O(1$^{\text{iii}}$)	2·15 (4)
H(4$^{\text{v}}$)–O(4$^{\text{iii}}$)	1·82 (3)	H(5$^{\text{iv}}$)–O(3$^{\text{i}}$)	1·87 (4)

(*b*) Angles (°)

H(3$^{\text{i}}$)–O(5$^{\text{i}}$)—H(4$^{\text{i}}$)	99 (3)	H(5$^{\text{i}}$)–O(6$^{\text{i}}$)—H(6$^{\text{i}}$)	105 (3)
Li(1$^{\text{i}}$)–O(5$^{\text{iv}}$)–H(3$^{\text{iv}}$)	120 (3)	Li(2$^{\text{i}}$)–O(6$^{\text{v}}$)—H(5$^{\text{v}}$)	131 (3)
Li(1$^{\text{i}}$)–O(5$^{\text{iv}}$)–H(4$^{\text{iv}}$)	120 (3)	Li(2$^{\text{i}}$)–O(6$^{\text{v}}$)—H(6$^{\text{v}}$)	92 (3)
O(5$^{\text{i}}$)–H(3$^{\text{i}}$)—O(2$^{\text{ii}}$)	166 (2)	O(6$^{\text{iv}}$)–H(5$^{\text{iv}}$)–O(3$^{\text{i}}$)	173 (3)
O(5$^{\text{v}}$)–H(4$^{\text{v}}$)—O(4$^{\text{iii}}$)	179 (3)	O(6$^{\text{vi}}$)–H(6$^{\text{vi}}$)–O(1$^{\text{iii}}$)	154 (3)

van der Waals 'radii' for carbonyl oxygens in directions parallel and perpendicular to the bond (1·35 and 1·63 Å respectively) (Bondi, 1964).

Bond distances and angles within the maleate ion are given in Table 7. The carbon–carbon double bond, C(2)C(3), is of the expected length and differs slightly from that found in the hydrogen maleate ion, 1·348 (4) Å. The bonds C(1)C(2) and C(3)C(4) have lengths which are not significantly different nor do they differ from the comparable bond in the hydrogen maleate ion, 1·498 (3) Å. Since C(1)C(2) and C(3)C(4) involve greatly different degrees of torsion of the carboxylate planes relative to the carbon atom plane, they can be considered to be free from double-bond character. The bond angles C(1)–C(2)–C(3) (125·1°) and C(2)–C(3)–C(4) (127·4°) are smaller than the strained value of 130·4 (2)° found in the hydrogen maleate ion but considerably greater than the value of 121·5° assumed by Darlow (1961) to represent the strain-free angle for this type of carbon framework. Further evidence of strain due to oxygen–oxygen repulsion is found in the significant non-planarity of the group C(3)C(4)O(3)O(4) (Table 11). The two carboxylate groups are closely similar in shape and dimensions and in each of them one C–O bond is significantly larger than the other. There is no obvious explanation of this difference and no similar effect has been found in comparable structures.

We are indebted to the S.R.C. for the award of a Research Studentship to one of us (W.G.T.).

Table 11. *Planarity of the carboxylate groups*

Distances of atoms from the planes (*a*) C(1), C(2), O(1), O(2), (*b*) C(3), C(4), O(3), O(4) (Å)

(*a*) $0{\cdot}2214x-0{\cdot}0532y+0{\cdot}9737z=0{\cdot}8196$

C(1)	−0·0005	O(1)	0·0002
C(2)	0·0001	O(2)	0·0002

(*b*) $0{\cdot}0477x+0{\cdot}9783y+0{\cdot}2017z=4{\cdot}3337$

C(3)	0·0055	O(3)	0·0070
C(4)	−0·0195	O(4)	0·0070

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Bracher, B. H. & Taylor, R. I. (1967). U.K.A.E.A. Research Report A.E.R.E.-5478.

Darlow, S. F. (1961). *Acta Cryst.* **14**, 1257–1259.

Darlow, S. F. & Cochran, W. (1961). *Acta Cryst.* **14**, 1250–1257.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210–214.

International Tables for X-ray Crystallography. (1962). Vol. III. Birmingham: Kynoch Press.

Larson, A. C. (1970). *Crystallographic Computing*: Edited by F. R. Ahmed. pp. 291–294. Copenhagen: Munksgaard

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Shahat, M. (1952). *Acta Cryst.* **5**, 763–768.

Small, R. W. H. & Travers, S. (1961). *J. Sci. Instrum.* **38**, 205–206.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.

Acta Cryst. (1973). B**29**, 1955

Stéréochimies du Zirconium et du Cuivre dans les Fluorozirconates de Cuivre Hydratés. I. Structure Cristalline de $CuZrF_6.4H_2O$

Par J. Fischer et R. Weiss

Institut de Chimie, Université Louis Pasteur, BP 296/R8, 67008 Strasbourg Cedex, France*

(*Reçu le* 19 *mars* 1973, *accepté le* 10 *avril* 1973)

The crystal structure of $CuZrF_6.4H_2O$ has been solved using three-dimensional X-ray diffraction data recorded on a automatic diffractometer. The crystals are monoclinic with $a=5{\cdot}691$, $b=10{\cdot}030$, $c=7{\cdot}592$ Å, $\beta=103{\cdot}53°$, $Z=2$, space group $P2_1/c$. The structure is built up from infinite$\cdots[ZrF_6]^{2-}\cdots[Cu(H_2O)_4]^{2+}\cdots[ZrF_6]^{2-}\cdots$ chains linked by hydrogen bonds.

Introduction

Dans le cadre d'une étude générale des fluorozirconates de cuivre hydratés, et dans le but de déterminer les stéréochimies du zirconium et du cuivre dans ce type de composés, les structures cristallines de $CuZrF_6.4H_2O$, $K_2Cu(ZrF_6)_2$ $6H_2O$, $Cu_3(ZrF_7)_2$ $16H_2O$ et $Cu_2ZrF_8.12H_2O$ ont été déterminées. Le présent mémoire rend compte de la structure cristalline de $CuZrF_6.4H_2O$.

Partie expérimentale

$CuZrF_6.4H_2O$ se forme comme premier composé lors de la préparation à chaud de $Cu_3(ZrF_7)_2.16H_2O$ (Marignac, 1860) en retirant les cristaux de la solution mère à une température supérieure à 50°C à mesure qu'ils se forment pour éviter leur redissolution et la forma-

---

* Laboratoire de Cristallochimie associé au CNRS (ERA no. 8).