

Größe nahezu identischen Kationen: Die unsymmetrische, mit dem Schwerpunkt an der Peripherie lokalisierte Ladung des {(CH<sub>3</sub>)<sub>3</sub>C}NH<sub>3</sub><sup>+</sup>-Ions erzeugt ein Dipolmoment und erzwingt eine Orientierung durch Coulomb-Wechselwirkung und H-Brücken. [(CH<sub>3</sub>)<sub>4</sub>N]I unterliegt auf Grund der kugelsymmetrisch verteilten Ladung des Kations nicht diesen Beschränkungen in Bezug auf die Anordnung der Ionen. Das wirkt sich auf die Raumerfüllung aus. Das Volumen pro Formeleinheit ist für [(CH<sub>3</sub>)<sub>3</sub>C}NH<sub>3</sub>]I mit 213,9 Å<sup>3</sup> um ca 18% größer als das von [(CH<sub>3</sub>)<sub>4</sub>N]I mit 181,9 Å<sup>3</sup> (die zugehörigen Dichten betragen 1,56 und 1,84 g cm<sup>-3</sup>). Die Gitterkonstanten der mit [(CH<sub>3</sub>)<sub>3</sub>C}NH<sub>3</sub>]I isotypen Verbindungen [(CH<sub>3</sub>)<sub>3</sub>C}NH<sub>3</sub>]Cl und [(CH<sub>3</sub>)<sub>3</sub>C}NH<sub>3</sub>]Br wurden anhand indizierter Pulverdiffraktogramme bestimmt:  $a = 17,49$  (3),  $b = 9,01$  (2),  $c = 8,66$  (3) Å,  $V = 1364,7$  Å<sup>3</sup> für das Chlorid;  $a = 18,34$  (2),  $b = 9,16$  (2),  $c = 9,02$  (2) Å,  $V = 1515,3$  Å<sup>3</sup> für das Bromid. Die zunehmende Stärke der Wasserstoffbrückenbindungen der leichteren Halogenide bewirkt hier eine deutlich stärkere Volumenabnahme als bei den entsprechenden Tetramethylammoniumhalogeniden: Die Volumenabnahme der *tert*-Butylammoniumhalogenide vom Iodid zum Bromid beträgt 11%, vom Bromid zum Chlorid 10%, während diese bei den Tetramethylammoniumhalogeniden (Chlorid: Phase II) nur Werte von 9,6 bzw. 5,3% annimmt (Dufourcq, Haget-Bouillaud, Chanh & Lemanceau, 1972).

Eine Phasenumwandlung konnte bei *tert*-Butylammoniumiodid, -bromid und -chlorid anhand von DTA-Messungen im Temperaturbereich von 143 K bis zum Schmelzpunkt nicht festgestellt werden (Schmp. 584–586 K für das Chlorid, 547–551 K für das Bromid, 491–493 K für das Iodid).

Die vorliegenden Röntgenstrukturaufklärungen zeigen, daß das *tert*-Butylammoniumion selbst zu Elementen mit relativ geringer Elektronegativität wie Iod strukturbestimmende Wasserstoffbrückenbindungen ausbilden kann. Daher bietet dieses Kation eine interessante Variante in Ionenverbindungen, in denen häufig das isomere, ebenfalls angenähert kugelförmige Tetramethylammoniumion mit einem deutlich unterschiedlichen Packungsverhalten eingesetzt wird. Eindrucksvolle Beispiele dafür sind die Iodometallate Cu<sub>2</sub>I<sub>3</sub><sup>-</sup> und Ag<sub>2</sub>I<sub>3</sub><sup>-</sup>, bei denen (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup> bzw. {(CH<sub>3</sub>)<sub>3</sub>C}NH<sub>3</sub><sup>+</sup> zu jeweils völlig unterschiedlichen polymeren Anionenstrukturen führen (Herrschaft & Hartl, 1987; Andersson & Jagner, 1985; Meyer, 1963).

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## Lithium Hydrogen Maleate Dihydrate

BY P. POPELIER, A. T. H. LENSTRA AND H. J. GEISE

*University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium*

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**Abstract.** Li(C<sub>4</sub>H<sub>3</sub>O<sub>4</sub>)·2H<sub>2</sub>O,  $M_r = 158.04$ , monoclinic,  $P2_1/n$ ,  $a = 5.858$  (1),  $b = 6.051$  (1),  $c = 18.800$  (2) Å,  $\beta = 91.47$  (2)°,  $V = 666.2$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.576$  Mg m<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.14$  mm<sup>-1</sup>,  $F(000) = 328$ , room temperature,  $wR = 0.042$  for 2443 reflections and 128 parameters. Crystals of the title compound consist of sheets of hydrogen maleate (HM) ions, linked by hydrogen

bonds from two water molecules in the same layer. The layers are interconnected through Li...O interactions. Li is coordinated in a distorted tetrahedron. Two crystallographically independent water molecules occur, which act as donors but not as acceptors of hydrogen bonds, and have markedly different environments. O(W1) is coordinated along  $sp^3$  lone-pair orbitals to two Li ions, whereas O(W2) is coordinated

to one Li ion only along the H—O—H bisectrix. Allowing for the systematic difference between X-ray and neutron OH distances, the asymmetry of the intramolecular hydrogen bond in the HM ion is estimated to be roughly equal for the Li and Ca salt, and less than for the Na salt. A rationalization is given in terms of the asymmetry in the environment of the HM ions in the three salts. Cluster analysis on the heavy-atom geometries of five hydrogen maleate salt hydrates and on the asymmetry parameters of their intramolecular hydrogen bonds shows that environmental asymmetry affects both the hydrogen-bond and the HM geometry.

**Introduction.** The crystal structure of the title compound was investigated as part of a series aimed at the determination of the effect different metal ions have on the geometry of the HM ion and on the hydrogen-bonding scheme in the crystals. The wide possibilities in hydrogen-bond schemes have already been shown from the small investigative series of monovalent metal hydrogen maleates: the potassium salt has no water of crystallization (Darlow & Cochran, 1961), the sodium salt is a trihydrate (Olovsson, Olovsson & Lehmann, 1984) and the lithium salt a dihydrate (Gupta, Prasad & Gupta, 1975). A re-investigation of the last compound was undertaken since the conclusions of Gupta *et al.* (1975) were based on photographic data only. Although we were unable to obtain single crystals large enough to perform a neutron diffraction analysis, the present X-ray investigation should be sufficiently accurate to allow the location of the H atoms.

**Experimental.** Extremely long and thin, colourless crystals of the title compound were obtained by slow evaporation of an aqueous solution, prepared by mixing maleic acid with an appropriate amount of lithium carbonate. Unit-cell dimensions deduced from 25 high-order reflections ( $15 \leq \theta \leq 18^\circ$ ). Enraf-Nonius CAD-4 diffractometer,  $\omega/2\theta$ -scan mode, Mo radiation monochromatized by pyrolytic graphite. Intensity-control reflections (three), every 2 h, showed no drift, orientation-control reflections (three), every 150 reflections, showed no angular deviations. Maximum Bragg angle  $35^\circ$ , 2743 independent measurements of which 2447 with  $I > 3\sigma(I)$  were considered observed. During the analysis four reflections omitted because of dead time errors not prevented by applied attenuator ( $10 \times$ ).  $hkl$  range:  $0 \leq h \leq 9$ ,  $0 \leq k \leq 9$ ,  $-30 \leq l \leq 30$ . Space group from systematic extinctions. No absorption correction ( $\mu = 0.14 \text{ mm}^{-1}$ , crystal size  $0.20 \times 0.15 \times 0.20 \text{ mm}$ , cut from long needle). Structure solved using *MULTAN* (Germain, Main & Woolfson, 1971). All H atoms located in difference electron density maps. Full-matrix least-squares refinements (on  $F^2$ 's) on all positional parameters. Non-H atoms refined anisotropically, H atoms isotropically except H(O2), which

Table 1. *Positional parameters in fractions of the cell edges and isotropic temperature parameters ( $\text{\AA}^2$ )*

The e.s.d.'s given in parentheses refer to the last significant digit. Isotropic temperature parameters are calculated from anisotropic temperature parameters using  $B_{\text{iso}} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ . All anisotropic temperature parameters were physically acceptable. Starred atoms were refined isotropically.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}$
C(1)	0.5605 (1)	0.2582 (1)	0.40922 (4)	1.83 (1)
C(2)	0.7824 (1)	0.2505 (1)	0.44964 (4)	2.15 (1)
C(3)	0.8264 (1)	0.2463 (1)	0.51959 (4)	2.11 (1)
C(4)	0.6687 (1)	0.2462 (1)	0.58085 (4)	1.84 (1)
O(1)	0.5629 (1)	0.2714 (1)	0.34390 (3)	2.66 (1)
O(2)	0.3691 (1)	0.2513 (1)	0.44229 (3)	2.14 (1)
O(3)	0.4519 (1)	0.2439 (1)	0.56967 (3)	2.12 (1)
O(4)	0.7559 (1)	0.2486 (1)	0.64140 (3)	2.98 (1)
O(W1)	0.6923 (1)	0.2110 (1)	0.19125 (3)	2.24 (1)
O(W2)	1.0910 (1)	0.2700 (1)	0.27959 (4)	3.95 (2)
Li	0.7863 (2)	0.3845 (3)	0.27770 (7)	2.63 (3)
H(C2)	0.914 (2)	0.249 (1)	0.4194 (6)	1.6 (2)*
H(C3)	0.982 (2)	0.241 (1)	0.5358 (6)	1.3 (2)*
H(1,W1)	0.551 (2)	0.233 (2)	0.1727 (7)	2.3 (3)*
H(2,W1)	0.783 (2)	0.227 (2)	0.1524 (7)	2.2 (3)*
H(1,W2)	1.140 (3)	0.259 (2)	0.2388 (8)	3.7 (3)*
H(2,W2)	1.210 (3)	0.270 (2)	0.3082 (8)	3.8 (3)*
H(O2)	0.399 (3)	0.246 (2)	0.4989 (8)	4.0

was given a fixed value of  $B$  equal to  $4.0 \text{ \AA}^2$ . Reflections given individual weights according to counting statistics. No extinction correction refined. Convergence reached at  $R = 0.034$  and  $wR = 0.042$ ,  $S = 5.5$ ,  $(\Delta/\sigma)_{\text{max}} = 0.01$ , 128 variables. The final difference Fourier map showed a maximum of  $0.4 \text{ e \AA}^{-3}$  coinciding with the midpoint of the C=C bond. In fact all main features in the difference density could be correlated to features typical for a deformation density, *i.e.* maxima at interatomic bonds and lone-pair positions and minima at atomic positions. Atomic scattering functions from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius SDP (Frenz, 1978) employed. Refined parameters\* are given in Table 1, atomic numbering scheme in Fig. 1.

**Discussion.** The crystal contains layers of HM ions, separated by  $b/2$ . Within the layers the HM ions are linked together by hydrogen bonds originating from two water molecules. In each of these hydrogen bonds HM is the acceptor, while the water molecules act as donors. The layers are linked to one another through  $\text{Li}^+ \cdots \text{O}$  electrostatic interactions. A short  $[\text{O} \cdots \text{O} = 2.432 (1) \text{ \AA}]$  intramolecular hydrogen bond closes the HM ion into an almost planar ring structure. The details of the bonding are described below and compared with other hydrogen maleate salts. At this

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51716 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

point we note that the structure reported by Gupta *et al.* (1975) is in qualitative agreement with our results, except for a proposed bifurcated hydrogen bond which proved absent in our findings.

**The lithium ion.** Lithium is surrounded by four O atoms: O(1), belonging to the carboxyl group of the HM ion, O(W2), O(W1) and a symmetry-related O(W1) atom. The arrangement is that of a distorted tetrahedron, the particulars of which are given in Table 2. Hydrogen-bond formation is undoubtedly the cause of the distortion.

**The water molecules.** The two crystallographically independent water molecules are involved in normal, slightly bent hydrogen bonds (see Table 2) with HM O atoms acting as acceptors in each case. A short O(W1)···O(W2) distance of 2.853 (1) Å is observed, previously interpreted by Gupta *et al.* (1975) as part of a bifurcated hydrogen-bond system in which O(3) and O(W2) share H(2,W1). Considering our experimental H positions, however, we reject this description, because H(2,W1)···O(W2) [2.970 (6) Å] is longer than O(W1)···O(W2) [2.853 (1) Å] and the angle O(W1)—H(2,W1)···O(W2) is only 74°. Thus, O(W1)—H(2,W1) does not point towards O(W2) and O(W1)···O(W2) is merely a short O···O contact.

Furthermore, the water molecules show marked differences in their environment. O(W1) is coordinated to two Li ions and inspection of Table 2 suggests that the interaction involves  $sp^3$ -type water lone pairs. According to Ferraris & Franchini-Angela (1972) and Chiari & Ferraris (1982) O(W1) should be put in class 2, type A and has a coordination situation (see Fig. 1b) most frequently observed in hydrate water molecules. In contrast, O(W2) is coordinated to one Li ion only with the Li···O interaction approximately along the

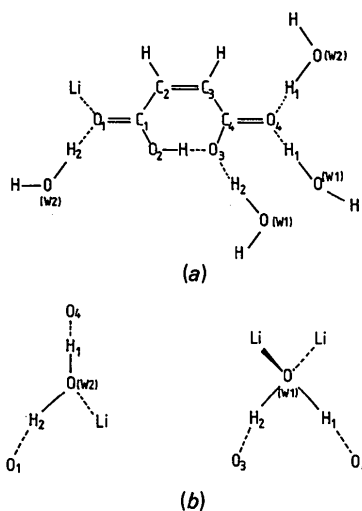


Fig. 1. Atomic numbering scheme of the title compound also showing (a) surroundings of HM ions by Li ions and H<sub>2</sub>O molecules and (b) environment of H<sub>2</sub>O molecules.

Table 2. Geometry of the title compound: distances in Å, angles in °, with e.s.d.'s in parentheses

The Li coordination					
Li—O(1)	1.952 (1)	O(1)—Li—O(W1)	99.2 (1)		
Li—O(W1)	2.000 (1)	O(1)—Li—O(W1')	101.1 (1)		
Li—O(W1')	2.063 (1)	O(1)—Li—O(W2)	120.1 (1)		
Li—O(W2)	1.914 (1)	O(W1)—Li—O(W1')	138.2 (1)		
		O(W1)—Li—O(W2)	93.6 (1)		
		O(W1')—Li—O(W2)	107.0 (1)		
Environment of H <sub>2</sub> O (W1)					
	O—H	H···O	O···O/Li	∠O—H···O	
O(W1)—H(2)···O(3 <sup>ii</sup> )	0.921 (7)	1.871 (7)	2.791 (1)	176.4 (5)	
O(W1)—H(1)···O(4 <sup>iii</sup> )	0.901 (7)	1.815 (7)	2.711 (1)	173.4 (5)	
O(W1)···Li <sup>i</sup>			2.063 (1)		
O(W1)···Li			2.000 (1)		
Li <sup>i</sup> ···O(W1)—H(1)	107.6 (6)	Li···O(W1)—H(1)		117.9 (7)	
Li <sup>i</sup> ···O(W1)—H(2)	107.2 (6)	Li···O(W1)—H(2)		115.9 (6)	
Li <sup>i</sup> ···O(W1)···Li	105.0 (1)	H(1)—O(W1)—H(2)		102.7 (9)	
Environment of H <sub>2</sub> O (W2)					
	O—H	H···O	O···O	∠O—H···O	
O(W2)—H(1)···O(4 <sup>ii</sup> )	0.829 (8)	1.970 (8)	2.797 (1)	176.8 (6)	
O(W2)—H(2)···O(1 <sup>ii</sup> )	0.870 (8)	2.157 (8)	2.989 (1)	159.9 (7)	
O(W2)···Li			1.914 (1)		
Li···O(W2)—H(1)	110.8 (6)	H(1)—O(W2)—H(2)		106.4 (9)	
Li···O(W2)—H(2)	138.2 (6)				
The HM ion					
	Li salt	Na salt <sup>a</sup>	Ca salt <sup>a</sup>	Zn salt <sup>a</sup>	Mg salt <sup>a</sup>
	This work	Reference (1)	Reference (2)	Reference (3)	Reference (4)
C(1)—C(2)	1.490 (1)	1.493 (1)	1.492 (3)	1.488 (2)	1.502 (4)
C(2)=C(3)	1.334 (1)	1.343 (1)	1.346 (3)	1.342 (2)	1.344 (4)
C(3)—C(4)	1.495 (1)	1.503 (1)	1.496 (3)	1.489 (2)	1.505 (4)
C(1)=O(1)	1.231 (1)	1.228 (1)	1.239 (3)	1.229 (2)	1.235 (4)
C(1)—O(2)	1.296 (1)	1.304 (1)	1.285 (3)	1.295 (3)	1.282 (4)
C(4)=O(4)	1.236 (1)	1.251 (1)	1.238 (3)	1.250 (2)	1.219 (4)
C(4)—O(3)	1.282 (1)	1.268 (1)	1.274 (3)	1.261 (2)	1.288 (4)
C(2)—H	0.97 (1)	1.090 (2)	1.085 (4)	1.080 (5)	1.099 (6)
C(3)—H	0.95 (1)	1.090 (2)	1.081 (4)	1.070 (5)	1.106 (6)
O(2)—H	1.074 (10)	1.079 (2)	1.121 (4)	1.097 (7)	1.186 (7)
O(3)—H	1.360 (10)	1.367 (2)	1.305 (4)	1.317 (5)	1.228 (7)
O(2)···O(3)	2.432 (1)	2.445 (1)	2.424 (3)	2.410 (4)	2.414 (5)
O(1)=C(1)—C(2)	118.6 (1)	118.6 (1)	118.3 (1)	118.3 (2)	118.6 (3)
O(1)=C(1)—O(2)	120.8 (1)	120.9 (1)	121.0 (1)	121.7 (2)	120.4 (3)
C(2)—C(1)—O(2)	120.6 (1)	120.5 (1)	120.7 (1)	120.0 (2)	121.0 (3)
C(1)—C(2)=C(3)	130.4 (1)	130.6 (1)	130.2 (1)	130.6 (2)	130.0 (3)
C(2)=C(3)—C(4)	130.7 (1)	130.4 (1)	130.2 (1)	129.5 (2)	130.4 (2)
C(3)—C(4)=O(4)	117.4 (1)	116.9 (1)	117.6 (1)	116.0 (2)	118.8 (3)
C(3)—C(4)—O(3)	120.2 (1)	120.2 (1)	120.0 (1)	121.0 (2)	118.9 (3)
O(3)—C(4)=O(4)	122.4 (1)	123.0 (1)	122.4 (1)	123.0 (2)	122.3 (3)
H—C(2)—C(1)	113.4 (6)	112.3 (2)	112.9 (2)	111.8 (2)	112.2 (4)
H—C(2)=C(3)	116.3 (6)	117.2 (2)	116.9 (2)	117.6 (2)	117.7 (4)
H—C(3)=C(2)	118.3 (6)	116.9 (2)	116.7 (2)	117.8 (2)	117.4 (4)
H—C(3)—C(4)	111.0 (6)	112.7 (2)	113.1 (2)	112.7 (2)	112.1 (4)
C(1)—O(2)—H	110.9 (6)	110.4 (2)	110.8 (2)	111.8 (3)	110.5 (4)
O(2)—H···O(3)	175.9 (9)	176.1 (3)	175.9 (3)	174.7 (4)	176.0 (10)

Note: (a) Neutron geometry is given.

References: (1) Olovsson *et al.* (1984); (2) Hsu & Schlemper (1980); (3) Sequeira, Rajagopal, Gupta, Vanhouteghem, Lenstra & Geise (1989); (4) Vanhouteghem, Lenstra & Schweiss (1987).

Symmetry code: (i)  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (ii)  $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (iii)  $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$ ; (iv)  $1+x, y, z$ .

bisectrix of the H—O—H angle (see Fig. 1b). The conclusion follows from the Li···O(W2)—H angles [Table 2; angles  $\delta_1$  and  $\delta_2$  of Ferraris & Franchini-Angela (1972)] and the 20° angle ( $\epsilon_1$  of Ferraris) between the Li···O(W2) vector and the H—O(W2)—H plane. Consequently, O(W2) is to be put in class 1, type C and constitutes a coordination rarely met in hydrate water molecules when univalent ions are involved.

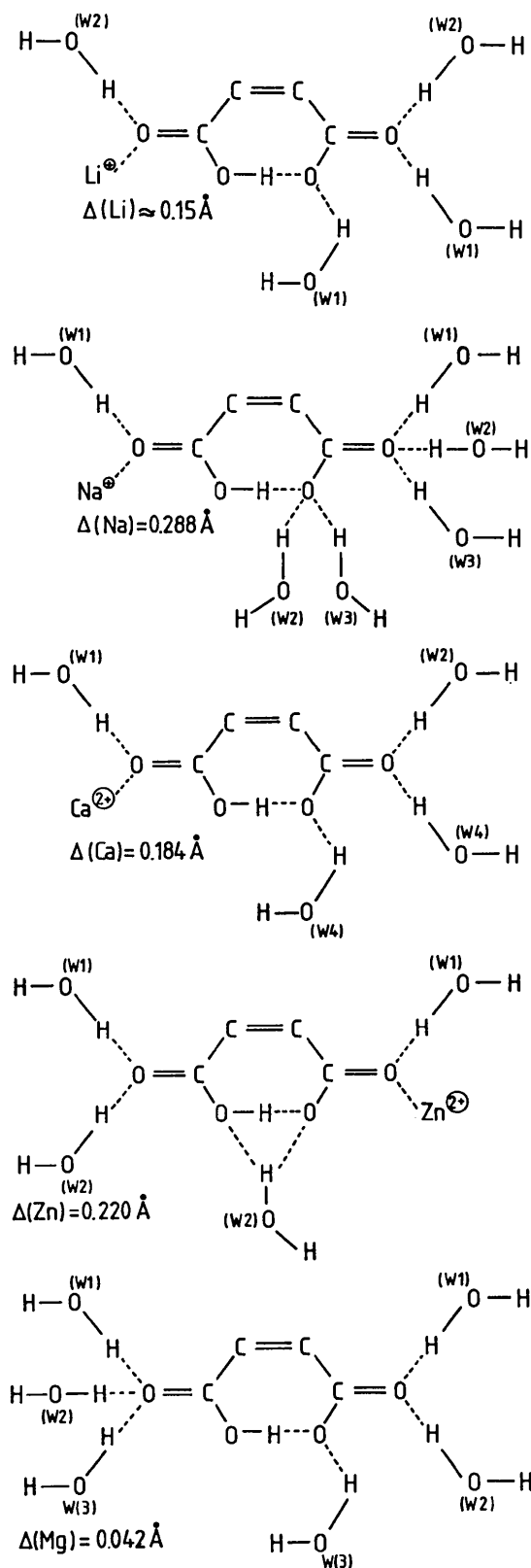


Fig. 2. Immediate environment of an HM ion in  $\text{LiHM} \cdot 2\text{H}_2\text{O}$ ,  $\text{NaHM} \cdot 3\text{H}_2\text{O}$ ,  $\text{Ca}(\text{HM})_2 \cdot 5\text{H}_2\text{O}$ ,  $\text{Zn}(\text{HM})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Mg}(\text{HM})_2 \cdot 6\text{H}_2\text{O}$ .

*The HM ion.* The intramolecular hydrogen bridge in the HM ion requires a nearly planar ring structure, which at the same time introduces strain in the molecule, as discussed by Olovsson *et al.* (1984). Two relief mechanisms are in operation. First, the angles  $\text{C}(1)\text{--}\text{C}(2)\text{--}\text{C}(3)$  and  $\text{C}(2)\text{--}\text{C}(3)\text{--}\text{C}(4)$  open up to  $130.4$  and  $130.7^\circ$ , respectively. Second, disrotatory movements of the carboxyl groups occur. The plane through  $\text{C}(1)\text{--}\text{O}(1)\text{--}\text{O}(2)$  rotates over  $3.1(2)^\circ$  and the plane through  $\text{C}(4)\text{--}\text{O}(3)\text{--}\text{O}(4)$  over  $2.4(2)^\circ$  along  $\text{C}(1)\text{--}\text{C}(2)$  and  $\text{C}(3)\text{--}\text{C}(4)$ . This leaves the outer atoms  $\text{O}(1)$  and  $\text{O}(4)$  on one side of the  $\text{C}(1)\text{--}\text{C}(2)\text{--}\text{C}(3)\text{--}\text{C}(4)$  plane at distances of  $-0.060(1)$  and  $-0.046(1) \text{ \AA}$ , and the inner atoms  $\text{O}(2)$  and  $\text{O}(3)$  on the other side of the carbon plane at distances of  $+0.057(1)$  and  $+0.049(1) \text{ \AA}$ . These features are common to all hydrogen maleate salts studied so far. Table 2 presents the other particulars of the HM geometry.

We note the following details for the short intramolecular hydrogen bridge:  $\text{O}(2)\cdots\text{O}(3) = 2.432(1)$ ,  $\text{O}(2)\text{--}\text{H} = 1.074(10)$ ,  $\text{H}\cdots\text{O}(3) = 1.360(10) \text{ \AA}$ , asymmetry  $\Delta = 1.360 - 1.074 = 0.286 \text{ \AA}$ . If we compare these values (Table 2) with those of the corresponding sodium hydrogen maleate we observe a great similarity, suggesting that the hydrogen bond in both salts is equally asymmetric. However, the sodium data represent a neutron geometry and it is well known that, compared to neutron values, the X-ray value of the  $\text{H}\text{--}\text{O}$  bond length will be about  $0.05$  to  $0.10 \text{ \AA}$  too

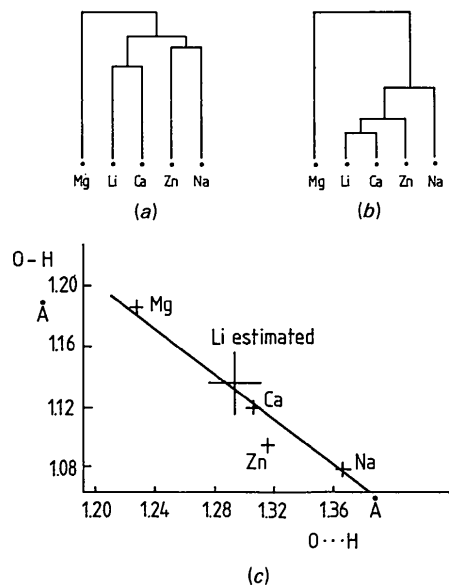


Fig. 3. Dendrograms of hydrogen maleate salt hydrates with (a) heavy-atom geometry (bond lengths and valence angles) of HM ion as attributes and (b) asymmetry parameter  $\Delta$  of intramolecular hydrogen bond as attributes. To be confronted with (c) correlation between  $\text{H}\text{--}\text{O}(2)$  and  $\text{H}\cdots\text{O}(3)$  distances for hydrogen maleate salt hydrates studied by neutron diffraction.

short. Consequently, the O...H distance will be about 0.05 to 0.10 Å too long. Taking this into account, the neutron ('true') asymmetry of the Li salt is expected to be in the order of 0.15 Å, a value close to  $\Delta = 0.184$  Å (see Table 2) observed in the neutron analysis of the Ca salt (Hsu & Schlemper, 1980). An asymmetry sequence  $\Delta(\text{Li}) \approx \Delta(\text{Ca}) < \Delta(\text{Na})$  may be rationalized in terms of the asymmetry of the surroundings of the HM ion. Fig. 2 depicts the direct environment of HM *inter alia* the three salts. One notes the large asymmetry in the Na salt and the lesser one in the Li and Ca salts, which moreover show a strong mutual resemblance. Evidence, suggesting that the surroundings not only affect the asymmetry of the intramolecular hydrogen bond but also to some extent the geometry of the HM ion itself, can be obtained by comparing the X-ray geometry of the heavy-atom skeleton with the neutron geometry of the Na, Zn, Ca and Mg salts. The comparison is meaningful, because we know from a previous observation in magnesium bis(hydrogen maleate) hexahydrate (Vanhouteghem *et al.*, 1987) and from a statistical study by Allen (1986) that only very small differences exist between neutron and X-ray values of CC and CO lengths. We performed a cluster analysis (e.g. Everitt, 1981) on the five salts using the heavy-atom geometry (bond lengths in pm and valence angles in decimal degrees) as the attributes. From the Euclidean metric distance matrix and the nearest-neighbour method the dendrogram of Fig. 3(a) is obtained. The same analysis on the asymmetry parameters gives the dendrogram of Fig. 3(b). There is a distinct similarity. The only difference is that the Zn salt is closer to the Na salt in a hierarchical associative clustering based on bond lengths and angles, whereas it is closer to the Ca salt (see also Fig. 3c) in a clustering based on  $\Delta$  values. We interpret the similarity to reveal that the asymmetry of the HM surroundings, which

correlates with  $\Delta$  values (Fig. 2), also correlates with HM geometry.

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## 2-(O-Ethyl dithiocarbonato)succinic Acid

BY M. DUARTE, C. FRAMPTON, H. E. HOWARD-LOCK,\* C. J. L. LOCK AND H. WU

Laboratories for Inorganic Medicine, Departments of Chemistry and Pathology, McMaster University, ABB-426, Hamilton, Ontario, Canada L8S 4M1

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**Abstract.** C<sub>7</sub>H<sub>10</sub>O<sub>5</sub>S<sub>2</sub>,  $M_r = 238.3$ , monoclinic,  $P2_1/c$ ,  $a = 11.906$  (3),  $b = 5.363$  (1),  $c = 19.167$  (4) Å,  $\beta = 114.71$  (2)°,  $V = 1111.8$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_m =$

1.420 (4),  $D_x = 1.424$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 4.62$  cm<sup>-1</sup>,  $F(000) = 496.9$ ,  $T = 297$  K,  $R = 0.0834$ ,  $wR = 0.0510$  for 1326 unique reflections and 127 parameters. The structure is described by the name and bond lengths and angles are normal, although the

\* To whom correspondence should be addressed.