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Magnesium Bis(hydrogen maleate) Hexahydrate, $Mg[C_4H_3O_4]_2.6H_2O$

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Abstract. $M_r = 308{\cdot}5$, monoclinic, $P2_1/a$, $a = 6{\cdot}742\,(2)$, $b = 10{\cdot}201\,(1)$, $c = 11{\cdot}816\,(2)$ Å, $\gamma = 104{\cdot}06\,(2)°$, $V = 788{\cdot}3\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}167$ mm^{-1}, $F(000) = 320$, room temperature. Final $R_w = 0{\cdot}038$ for 1365 observed reflections. The Mg cation, at a centre of inversion, is coordinated by a slightly distorted octahedron of O atoms, all of which belong to water molecules of crystallization. Linkage of the Mg^{2+} ion with the hydrogen maleate ion is brought about by extra-strong hydrogen bonds. The extra strength is due to an enhanced charge on the H atoms of the water molecules caused by a polarization in the $[Mg(H_2O)_6]^{2+}$ unit. The non-H atoms of the hydrogen maleate moiety show nearly C_s symmetry, but this symmetry is broken when the intermolecular hydrogen bond is taken into account, thus rendering the complete hydrogen maleate ion unsymmetrical. Carboxyl groups are rotated over 3 and 4° with respect to the plane through the carbon skeleton. There is strong evidence that this rotation of the opposite carboxyl groups follows a concerted pattern as a compromise between steric hindrance and electronic effects.

Introduction. In an *ab initio* study of the hydrogen maleate moiety (henceforth abbreviated as HM) George, Bock & Trachtman (1983) investigated an unsymmetrical form of the ion (Fig. 1*b*) and a form with C_{2v} symmetry (Fig. 1*a*). Evidently one can discriminate only in the unsymmetrical form between donor and acceptor oxygen in the short intramolecular hydrogen bond. In fact when one shifts the hydrogen from the original donor to the original acceptor one passes the symmetrical form. X-ray and neutron-diffraction determinations of potassium hydrogen maleate and maleic acid show the heavy-atom backbone to be symmetrical (Darlow & Cochran, 1961; James & Williams, 1974), consistent with symmetrical hydrogen bonding. NMR measurements (Gunnarsson, Wennerström, Egan & Forsén, 1976; Altman, Laungani, Gunnarsson, Wennerström & Forsén, 1978) also favour symmetrical bonding. The *ab initio* calculations using the 4-31G basis set and full geometry optimization, however, found the unsymmetrical form 5·74 kJ mol^{-1} more stable than the C_{2v} form.

An obvious explanation for the discrepancy is the difference between an isolated ion and one in a crystalline environment. We will show that the X-ray study of the title compound will provide experimental information related to the *isolated* HM ion. Also we will deal with the following questions:

(i) Is the HM moiety planar as was assumed by George *et al.* (1983)?

(ii) Can donor and acceptor O atoms be discriminated? If the C_{2v} form is present it would indicate that the shift barrier (Fig. 1*c*) is lower than 5·74 kJ mol^{-1} calculated by George *et al.* (1983).

(iii) Is there experimental evidence for a disordered hydrogen bond in HM? If so the double potential-energy well, typical for an isolated HM ion, is detectable in the solid phase. If the equivalence of these two energy minima is broken then crystal-packing forces must have a decisive influence upon the HM moiety.

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Such an influence was detected in the structure of tetraaquabis(hydrogen maleato)nickel(II) (Gupta, Geise & Lenstra, 1984), in which the ionized carboxyl group of the HM ion is directly linked to the Ni^{2+} ion. Therefore the energy minima along the internal HM hydrogen bond become inequivalent as a result of Coulomb forces, which can be quite high over a small (here a van der Waals) distance. However, structural results of a nickel salt can not be simply extrapolated to a magnesium salt.

Surprising effects are sometimes observed in structures of salts of organic acids with a series of cations having the same charge and similar ionic radii (*e.g.* Zn^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}). For example the malate ion in cobalt(II) malate trihydrate (Kryger & Rasmussen, 1972) behaves as a tridentate ligand, whereas in magnesium malate pentahydrate (Van Havere & Lenstra, 1980) it behaves as a bidentate ligand with one COO^- group coordinated only by water molecules and not by an Mg^{2+} ion. With this in mind we decided to analyse magnesium bis(hydrogen maleate) hexahydrate. Also, as the title salt is a light-atom compound, an accurate determination of H-atom positions should be possible.

Experimental. Crystals grown from a hot solution of the compound in water, prepared by addition of maleic acid to magnesium carbonate, crystal dimensions $0{\cdot}1 \times 0{\cdot}1 \times 0{\cdot}15$ mm, Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation monochromatized by pyrolitic graphite, lattice parameters from angle settings of 25 high-order reflections, in view of small size of crystal and low value of μ no absorption correction considered necessary, intensity data collected up to $\theta = 27°$ using an ω/θ scan, $-8 \le h \le 8$, $0 \le k \le 12$, $0 \le l \le 14$, three intensity- and orientation-control reflections measured every 2 h, no significant drift noted, 1798 independent measurements, 1365 observed reflections with $I > 2\sigma(I)$. Structure solved by *MULTAN* (Germain, Main & Woolfson, 1971) in space group $P2_1/a$ (*c*-axis unique). The most likely *E* map based on 200 terms showed all non-H atoms. After a few cycles of least-squares refinement on *F* the difference electron density map revealed the positions of all H atoms. The peak height of the H in the internal hydrogen bond of the HM entity was comparable to those maxima, which were identified as the H atoms of the three crystallographically independent water molecules. In the subsequent refinement employing the Gauss–Seidel block method (Sparks, 1974) and giving each reflection a weight based on counting statistics the R_w value dropped to 0·038. The Debye–Waller temperature factor of the H atoms was kept fixed at 3 Å^2 (B_{overall} from the Wilson plot ~2·7 Å^2). $(\Delta/\sigma)_{\max} = 0{\cdot}2$, max. noise level in final difference Fourier map $0{\cdot}13$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. *Positional parameters in fractions of the cell edges, with e.s.d.'s in parentheses, and isotropic thermal parameters*

Isotropic temperature parameters (Å^2) of non-H atoms were calculated from anisotropic temperature parameters according to Lipson & Cochran (1968) [$B_{\text{iso}} = 8\pi^2(U_{11}{}^{o}U_{22}{}^{o}U_{33}{}^{o})^{1/3}$], assuming equal volume of the 50% probability region. All anisotropic thermal parameters were physically acceptable. H(*j*,*x*) with $j = 1,2$ is attached to atom *x*.

	x	*y*	*z*	B_{iso}
Mg	0·0000	0·0000	0·0000	1·99
O(*W*1)	0·1763 (3)	−0·1388 (2)	0·0057 (1)	3·27
O(*W*2)	−0·0228 (3)	−0·0075 (2)	0·1718 (1)	2·78
O(*W*3)	0·2556 (3)	0·1569 (2)	0·0112 (2)	3·20
O(1)	0·2244 (3)	0·6369 (2)	0·3606 (1)	3·04
O(2)	0·2800 (3)	0·7630 (2)	0·2079 (1)	3·09
O(3)	0·1374 (3)	0·4005 (2)	0·4094 (1)	2·85
O(4)	0·0847 (3)	0·2071 (2)	0·3224 (1)	3·14
C(1)	0·2317 (4)	0·6522 (2)	0·2532 (2)	2·52
C(2)	0·1818 (4)	0·5300 (2)	0·1793 (2)	2·56
C(3)	0·1354 (4)	0·3989 (2)	0·2058 (2)	2·46
C(4)	0·1189 (4)	0·3317 (2)	0·3186 (2)	2·37
H(C2)	0·173 (3)	0·553 (2)	0·102 (2)	3·00
H(C3)	0·095 (3)	0·336 (2)	0·140 (2)	3·00
H(O3)	0·169 (3)	0·489 (2)	0·402 (2)	3·00
H(1,O*W*1)	0·251 (3)	−0·149 (2)	−0·051 (2)	3·00
H(2,O*W*1)	0·200 (3)	−0·176 (2)	0·061 (2)	3·00
H(1,O*W*2)	−0·079 (3)	−0·078 (2)	0·212 (2)	3·00
H(2,O*W*2)	0·008 (3)	0·056 (2)	0·213 (2)	3·00
H(1,O*W*3)	0·362 (3)	0·160 (2)	0·054 (2)	3·00
H(2,O*W*3)	0·278 (3)	0·225 (2)	−0·035 (2)	3·00

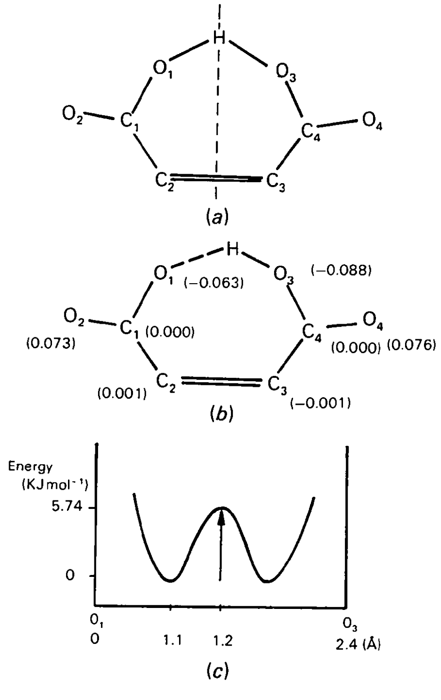

Fig. 1. (*a*) Form of the HM ion having C_{2v} symmetry, with the numbering of the atoms used in the analysis of the title compound. (*b*) Unsymmetrical form of the HM ion found. In parentheses are the distances (Å, e.s.d.'s about 0·003 Å) of the atoms with reference to a plane through C(1), C(2), C(3), C(4). (*c*) Energy profile calculated by George *et al.* (1983) in an HM ion with C_{2v} symmetry when shifting an H atom from O(3) to O(1).

Discussion. Refined parameters are listed in Table 1 and the numbering of the atoms is given in Fig. 1(*a*).*

The Mg cation is coordinated by six O atoms forming a slightly distorted octahedron (Table 2). It should be noted that all coordinating O atoms belong to the water molecules of crystallization and thus none of the O atoms of the HM ion is a nearest neighbour of the Mg cation. This can be understood if the central Mg cation polarizes the ligand water molecules leading to H atoms which are substantially more positively charged than in free water molecules. In a series of semi-empirical molecular-orbital calculations we used the program of Rinaldi (1975) and assumed the $[Mg(H_2O)_6]^{2+}$ complex to be a perfect octahedron (O_h symmetry). These calculations confirmed our hypothesis of polarization and charge transfer. Next we used the experimental X-ray coordinates as input into the *ab initio* program *TEXAS* (Pulay, 1969, 1979) using a 4-21G basis set (Pulay, Fogarasi, Pang & Boggs, 1979), but without geometry relaxation. The results of all calculations are summarized in Table 3. We give here the maximum and minimum value of the *ab initio* calculated charges on O and H, because the input geometry has not exactly O_h symmetry. Our results show that the effective charge on the central Mg cation is about 1 e less than its formal charge, while on the 12 H atoms we find an increase in charge of about 0·08 e per H atom compared to a free water molecule.

Although the absence of carboxyl O atoms in the Mg coordination is remarkable it did not come as a complete surprise. A similar result was reported (Van Havere & Lenstra, 1980) in the crystal structure of magnesium malate pentahydrate. In the latter compound, however, one COO^- group of the two deprotonated carboxyl functions of the malate ions participates in the Mg coordination. In the title compound none of the carboxyl groups is in the Mg coordination and thus the environment of the HM ion resembles that of an isolated ion. This has a marked influence on the dimensions of the two carboxyl groups of one single HM ion in the crystal. As can be seen from the list of bond lengths and valence angles given in Table 2, the internal coordinates of the ionized and the un-ionized group at opposite ends of the HM ion are very similar. This is in contrast to observations in tetraaquabis(hydrogen maleato)nickel(II) (Gupta *et al.*, 1984), where the geometry of the ionized carboxyl group, linked to Ni^{II}, is different from the dimensions of the un-ionized carboxyl group. The different behaviour is undoubtedly due to the different type of linkage of the HM ion to the divalent metal ions, *i.e.* a direct linkage as in $[Ni(C_4H_3O_4)_2(H_2O)_4]$ and a linkage *via* water molecules as in the title compound.

Table 2. *Distances* (Å) *and angles* (°) *in the title compound with e.s.d.'s in parentheses*

In the HM-anion details column *A* gives the present experimental results, column *B* the *ab initio* results of George *et al.* (1983).

Mg coordination

Mg—O(*W*1)	2·059 (1)	O(*W*1)—Mg—O(*W*2)*	89·6 (1)
Mg—O(*W*2)	2·036 (1)	O(*W*1)—Mg—O(*W*3)*	91·1 (1)
Mg—O(*W*3)	2·052 (1)	O(*W*2)—Mg—O(*W*3)*	90·4 (1)

Hydrogen maleate anion

	A	*B*		*A*	*B*
O(1)—C(1)	1·279 (1)	1·272	O(1)—C(1)—O(2)	122·8 (1)	127·2
O(2)—C(1)	1·221 (1)	1·237	O(1)—C(1)—C(2)	119·0 (1)	117·9
C(1)—C(2)	1·491 (2)	1·515	O(2)—C(1)—C(2)	118·2 (1)	
C(2)—C(3)	1·335 (2)	1·325	C(1)—C(2)=C(3)	130·6 (1)	131·5
C(3)—C(4)	1·491 (2)	1·489	C(2)=C(3)—C(4)	130·1 (1)	131·7
O(3)—C(4)	1·272 (1)	1·314	O(3)—C(4)—O(4)	120·4 (1)	121·9
O(4)—C(4)	1·236 (1)	1·221	O(3)—C(4)—C(3)	121·0 (1)	119·8
C(2)—H(C2)	0·953 (10)	1·073	O(4)—C(4)—C(3)	118·7 (1)	
C(3)—H(C3)	1·000 (15)	1·072	C(1)—C(2)—H(C2)	112·1 (7)	
O(3)—H(O3)	0·876 (12)	1·016	C(3)—C(2)—H(C2)	117·1 (7)	117·2
			C(2)—C(3)—H(C3)	114·9 (7)	118·1
O(3)···O(1)	2·410 (1)	2·463	C(4)—C(3)—H(C3)	114·9 (7)	
			C(4)—O(3)—H(O3)	116·9 (8)	115·8
			O(3)—H(O3)···O(1)	166·9 (1·3)	166·1

* Other angles in the Mg coordination are either 180° or supplementary to those given.

Table 3. *Charges on atoms* (e) *in* $[Mg(OH_2)_6]^{2+}$ *and in free* H_2O *calculated by MO methods*

		CNDO/2	MINDO/3	*Ab initio* (4-21G)
$[Mg(OH_2)_6]^{2+}$	Mg	+1·20	+1·09	+0·96
	O	−0·31	−0·33	−0·68 to −0·71
	H	+0·22	+0·24	+0·41 to +0·45
H_2O	O	−0·27	−0·32	−0·70
	H	+0·14	+0·16	+0·35

The HM skeleton is not exactly planar. Atoms C(1), C(2), C(3) and C(4) are in one plane, the largest deviation being 0·001 (3) Å. The four O atoms lie outside the plane, the deviations of these atoms from the least-squares plane through the carbon skeleton being shown in Fig. 1(*b*). Fragments C(2), C(1), O(1), O(2) and C(3), C(4), O(3), O(4) are individually nearly planar [largest deviations 0·004 (3) Å]. The dihedral angle between these planes is 6·0 (1)°, while the planes are at angles of 3·6 (1) and 4·3 (1)° respectively with the mean plane through the carbon backbone. Rotation of the carboxyl group, either in a conrotatory or in a disrotatory fashion, reduces the steric hindrance a planar HM ion would have. After a conrotatory motion O(1) and O(3) end up at different sides of the plane through the carbon skeleton, whereas a disrotatory motion leaves O(1) and O(3) at the same side of this plane. Both types of rotation equally allow the formation of the short hydrogen bond O(3)—H···O(1) that is observed (see below). The conrotatory movement, however, is the more efficient mechanism to

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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 39437 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

reduce steric crowding, but the disrotatory fashion is actually observed (Fig. 1*b*). We take this as an indication that the geometry of the HM ion is determined by electronic bonding effects between *p*-type lone pairs on O(1) and O(3) in combination with hydrogen-bonding and steric effects.

The group C(4)O(3)O(4) must be regarded as the un-ionized carboxyl function because H(O3) – experimentally found and with least-squares-optimized positional coordinates – is bonded to O(3). Consequently, the HM ion, non-planar in the present compound, favours an unsymmetrical hydrogen bonding in accordance with the *ab initio* calculations. Internal coordinates of the experimental HM ion and of a planar HM ion with an unsymmetrical hydrogen bond calculated by George *et al.* (1983) are given in Table 2, columns *A* and *B* respectively. The correspondence is not unsatisfactory, although far from perfect. Discrepancies may be due to three reasons. First, an X-ray study yields distances between the centres of gravity of the electron clouds, whereas an *ab initio* study gives distances between nuclear positions of non-vibrating atoms. This difference in operational definitions of internal coordinates in combination with the experimental uncertainties sufficiently explain the poor agreement in bond lengths in which H atoms participate, but not the discrepancies in CO and CC distances.

The final difference Fourier map with a highest maximum of 0·13 e Å^{-3} does not give any indication of a possible proton connected to O(1) or O(2). In other words there is no indication of proton disorder and thus the symmetrical double-well energy profile (Fig. 1*c*), characteristic of the HM ion in a truly free form, has undergone a substantial change by incorporating the ion in a crystalline environment. The second reason for the discrepancies in Table 2 therefore may be the force field in the crystal. The third reason is sought in the influence of intermolecular hydrogen bonds not taken into account in the *ab initio* calculations.

The packing in the crystal is controlled by metal—oxygen linkages, hydrogen bonds and van der Waals interactions. The inter- and intramolecular hydrogen bonds are given in Table 4. All six crystallographically independent H atoms belonging to the water molecules of crystallization participate in this bonding scheme. Apparently these water molecules play only the role of proton donor, whereas the O(1), O(2) and O(4) of the HM ion are acceptor atoms. Remarkably enough O(3), acting as a donor in the intramolecular hydrogen bond, does not occur as an acceptor atom in the intermolecular hydrogen bridges. Due to a charge transfer from the Mg cation the water H atoms in the title compound are more positively charged than in a free water molecule, and thus the intermolecular hydrogen bonds are stronger than a geometrical distance criterion suggests.

Table 4. *Hydrogen-bonding scheme in the title compound*

E.s.d.'s are in parentheses. *D*: donor, *A*: acceptor.

D–H···*A*	*D*–H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A* (°)	H–*D*–H (°)
Intermolecular					
O(*W*2)–H(1)···O(2^{i})	0·87 (1)	1·92 (1)	2·785 (1)	175 (1)	108 (1)
O(*W*2)–H(2)···O(4^{ii})	0·79 (1)	1·99 (1)	2·776 (1)	177 (1)	
O(*W*1)–H(1)···O(4^{iii})	0·86 (1)	2·03 (1)	2·746 (1)	170 (1)	114 (1)
O(*W*1)–H(2)···O(2^{iv})	0·79 (1)	1·96 (1)	2·885 (1)	171 (1)	
O(*W*3)–H(1)···O(4^{v})	0·87 (1)	2·07 (1)	2·900 (1)	164 (1)	111 (1)
O(*W*3)–H(2)···O(1^{vi})	0·88 (1)	1·87 (1)	2·732 (1)	169 (1)	
Intramolecular					
O(3)–H···O(1^{ii})	0·88 (1)	1·55 (1)	2·410 (1)	167 (1)	

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

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