*Acta Cryst.* (1980). B**36**, 1483–1486

# The Structure of Lithium Hydrogen (+)-1-Malate and Comparison with Other Hydrogen Malates

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(*Received* 30 *October* 1979; *accepted* 14 *February* 1980)

**Abstract.** $LiH[C_4H_4O_5]$, $P4_12_12$, $a = 4{\cdot}933$ (2), $c = 44{\cdot}584$ (8) Å, $Z = 8$, $d_{calc} = 1{\cdot}714$ Mg m$^{-3}$. A tetrahedral coordination is observed for the $Li^+$ ion. The conformation of the $^-$OOC′—C—C—COOH chain in the hydrogen malate moiety is *gauche* and differs from other hydrogen malates, which have an *anti* conformation. A comparison with other hydrogen malates indicates that some geometrical and most conformational features in the anion are determined by lattice interactions.

**Introduction.** Crystals of lithium hydrogen (+)-1-malate were grown at room temperature by the slow evaporation of an aqueous solution. Integrated intensities were collected on an Enraf–Nonius CAD-4 diffractometer up to a glancing angle of 30°, using Zr-filtered Mo radiation. An $\omega/\theta$ scan with speed ratio 6:1 was used. The scan angle was set at $(0{\cdot}70 + 0{\cdot}35\ \mathrm{tg}\ \theta)°$, while the aperture of the detection unit was $(1{\cdot}0 + 1{\cdot}0\ \mathrm{tg}\ \theta)$ mm.

From the systematic extinctions the tetragonal space group $P4_12_12$ was inferred.

In view of the crystal size (0·3 × 0·3 × 0·1 mm) and the linear absorption coefficient ($\mu = 0{\cdot}1697$ mm$^{-1}$) no absorption correction was applied.

The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971); the most likely $E$ map with 200 terms showed all non-hydrogen atoms. A subsequent difference electron density map revealed the positions of the H atoms.

From a total of 1104 reflections, 732 with $I > 2\sigma(I)$ were used in the refinement employing the Gauss–Seidel block method (Sparks, 1974), in which each reflection was given a weight based on the counting statistics. During the refinement the Debye–Waller temperature factor of the H atoms was kept fixed at 2·0 Å$^2$ ($B_{\rm Wilson} = 2{\cdot}1$ Å$^2$). The isotropic extinction parameter (Zachariasen, 1963) was refined to give $r = 0{\cdot}56 \times 10^{-5}$ mm. The final $R$ value was 0·031, defined as $R = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ for observed reflections only. The maximum noise level in the last difference Fourier map was 0·23 e Å$^{-3}$.

Table 1. *Final parameter values in* $LiH[C_4H_4O_5]$ *with e.s.d.'s in parentheses*

Isotropic temperature factors are calculated from the anisotropic temperature parameters, an equal volume of the 50% probability region being assumed. All anisotropic thermal ellipsoids were physically acceptable.

| | $x$ | $y$ | $z$ | $B_{\rm iso}$ (Å$^2$) |
|---|---|---|---|---|
| Li | 0·275 (1) | 0·072 (1) | 0·14635 (9) | 2·09 |
| O(1) | 0·4249 (4) | 0·2423 (3) | 0·10928 (3) | 1·75 |
| O(2) | 0·4943 (4) | −0·1658 (4) | 0·08914 (4) | 2·07 |
| O(3) | 0·4788 (4) | 0·3784 (4) | 0·03605 (4) | 2·81 |
| O(4) | 0·7142 (5) | 0·2012 (5) | −0·00155 (4) | 3·57 |
| O(5) | 0·8910 (3) | 0·4386 (4) | 0·08437 (4) | 1·89 |
| C(1) | 0·5537 (5) | 0·0756 (5) | 0·09355 (5) | 1·53 |
| C(2) | 0·8246 (5) | 0·1599 (5) | 0·07989 (5) | 1·62 |
| C(3) | 0·8514 (6) | 0·0851 (6) | 0·04682 (5) | 2·11 |
| C(4) | 0·6615 (6) | 0·2362 (6) | 0·02705 (5) | 2·32 |
| H(O5) | 0·738 (4) | 0·519 (4) | 0·0874 (4) | 2·00 |
| H(O4) | 0·580 (5) | 0·298 (4) | −0·0113 (4) | 2·00 |
| H(C2) | 0·971 (5) | 0·056 (5) | 0·0920 (4) | 2·00 |
| H1(C3) | 1·036 (5) | 0·137 (4) | 0·0391 (4) | 2·00 |
| H2(C3) | 0·815 (4) | −0·103 (5) | 0·0440 (4) | 2·00 |

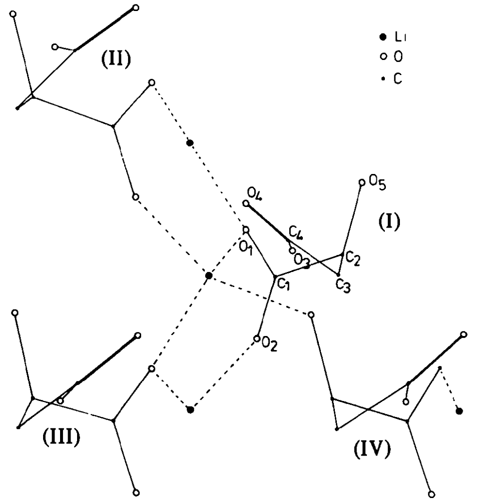

Fig. 1. The numbering of the atoms in lithium hydrogen 1-malate and the coordination of the $Li^+$ ion. Molecule (I) is at $x,y,z$; molecule (II) is at $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{4} - z$; molecule (III) is at $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{4} - z$; molecule (IV) is at $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{4} - z$.

0567-7408/80/061483-04$01.00

Refined parameters are listed in Table 1, and the numbering of the atoms is illustrated in Fig. 1.*

**Discussion.** Groth (1910) reported the existence of a monoclinic hexahydrate ($Li[C_4H_5O_5].6H_2O$) and of a tetragonal monohydrate. Since we found no water of crystallization the latter is probably incorrect.

The $Li^+$ ion is coordinated by a tetrahedron of O atoms (see Table 2). Four symmetry-related hydrogen malate moieties donate the four O atoms, three of which are from $COO^-$ groups, while the fourth is from the OH group (Fig. 1).

A survey of the crystal structure is given in Fig. 2. The packing of the title compound is largely dominated by Coulomb interactions. In the *xy* plane the $Li^+$ ions form ionic blocks with the anions and in the *z* direction the blocks are held together by two hydrogen bridges (Table 3). In contrast to this, we observed that in the corresponding ammonium hydrogen 1-malate (Versichel, Van de Mieroop & Lenstra, 1978), crystallizing in $P2_12_12_1$, and in calcium di(hydrogen 1-malate) hexahydrate (Lenstra & Van Havere, 1980), crystallizing in $P2_12_12_1$, the packing is dominated by hydrogen bridges. In yet another salt, copper di(hydrogen 1-malate) dihydrate (Van Havere & Lenstra, 1978), crystallizing in $P2_1$, the packing is determined by a combination of hydrogen bridges and complex formation. The wide variety of observed types of crystal packing enables us to test a statement of Kanters, Kroon, Peerdeman & Schoone (1967). They state that the conformation of (di)carboxylic acids, α-hydroxycarboxylic acids and their salts is independent of the space group, of the ionic or molecular character, and of the hydrogen-bond scheme of the structure. Salts of hydrogen malic acid are excellent test cases because they combine within the molecule the functional groups on which Kanters *et al.* performed their statistical survey.

Table 2. *The coordination of* $Li^+$ (*estimated standard deviations are* 0·003 Å *in the distances and* 0·2° *in the angles*)

| | O in molecule at | |
|---|---|---|
| Li–O(1) | *x,y,z* | 1·997 Å |
| Li–O(1) | $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$ | 1·917 |
| Li–O(2) | $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$ | 1·930 |
| Li–O(5) | $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$ | 1·973 |

| $O_A$ at | $O_B$ at | $O_A$–Li–$O_B$ | |
|---|---|---|---|
| *x,y,z* | $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$ | O(1)–Li–O(1) | 116·1° |
| *x,y,z* | $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$ | O(1)–Li–O(2) | 103·9 |
| *x,y,z* | $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$ | O(1)–Li–O(5) | 101·0 |
| $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$ | $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$ | O(1)–Li–O(2) | 105·9 |
| $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$ | $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$ | O(1)–Li–O(5) | 101·8 |
| $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$ | $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{4}-z$ | O(2)–Li–O(5) | 129·1 |

Table 3. *Short* O–H···O *interactions in* $LiH[C_4H_4O_5]$

| Donor *D* | Acceptor *A* | *A* at | *D*–H (Å) | H···*A* (Å) | *D*···*A* (Å) | *D*–H···*A* (°) |
|---|---|---|---|---|---|---|
| O(5)–H | O(2) | *x*, 1 + *y*, *z* | 0·86 | 2·00 | 2·81 | 156 |
| O(3)–H | O(4) | *x*, *y*, –*z* | 0·92 | 1·73 | 2·64 | 167 |
| E.s.d. | | | 0·04 | 0·04 | 0·01 | 3 |

We have collected in Tables 4, 5 and 6, respectively, the bond distances, valence angles and torsion angles of lithium hydrogen 1-malate together with the corresponding values for ammonium hydrogen 1-malate, calcium di(hydrogen 1-malate) hexahydrate (two crystallographically independent anions) and of copper(II) di(hydrogen 1-malate) dihydrate (two crystallographically independent anions). From the statistical analysis (the tests were performed at the significance level α = 0·05) we conclude:

(1) All bond distances and most valence angles do not show significant deviations from the mean values. However, the valence angles involving O(5) (α-hydroxy group) are lattice dependent.

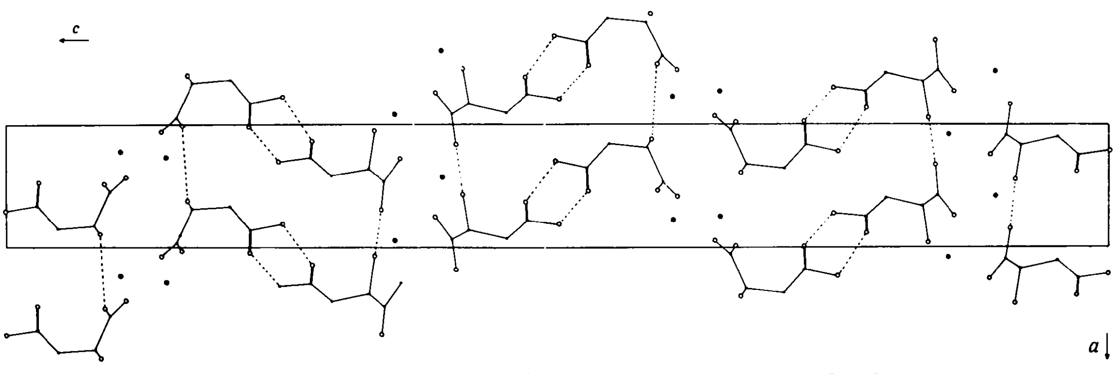

Fig. 2. The crystal structure projected on to the *xz* plane, ● Li, ○ O, • C.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35122 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

The $Li^+$ salt is compared with some other hydrogen malates.

| | Lithium hydrogen 1-malate[a] | Ammonium hydrogen 1-malate[b] | Calcium di(hydrogen 1-malate) hexahydrate[c] | | Copper(II) di(hydrogen 1-malate) dihydrate[d] | | Mean value | Standard deviation of mean |
|---|---|---|---|---|---|---|---|---|
| C(1)–C(2) | 1·526 (2) | 1·537 (3) | 1·533 (3) | 1·534 (3) | 1·512 (5) | 1·541 (5) | 1·531 | 0·010 |
| C(2)–C(3) | 1·526 (2) | 1·518 (3) | 1·520 (3) | 1·512 (3) | 1·526 (5) | 1·496 (5) | 1·516 | 0·011 |
| C(3)–C(4) | 1·486 (3) | 1·503 (3) | 1·502 (3) | 1·511 (3) | 1·524 (5) | 1·512 (5) | 1·506 | 0·012 |
| O(1)–C(1) | 1·254 (2) | 1·236 (2) | 1·254 (3) | 1·265 (3) | 1·275 (5) | 1·281 (5) | 1·261 | 0·016 |
| O(2)–C(1) | 1·255 (2) | 1·258 (2) | 1·250 (3) | 1·233 (3) | 1·261 (5) | 1·237 (5) | 1·249 | 0·012 |
| O(3)–C(4) | 1·313 (2) | 1·310 (2) | 1·296 (3) | 1·317 (3) | 1·324 (5) | 1·314 (5) | 1·312 | 0·009 |
| O(4)–C(4) | 1·211 (2) | 1·204 (2) | 1·220 (3) | 1·207 (3) | 1·178 (5) | 1·203 (5) | 1·204 | 0·014 |
| O(5)–C(2) | 1·427 (2) | 1·413 (2) | 1·420 (3) | 1·430 (3) | 1·443 (5) | 1·436 (5) | 1·428 | 0·010 |
| ⟨C–H⟩ | 0·99 (4) | 0·94 (3) | 0·98 (5) | | 1·00 (20) | | | |
| O–H | 0·89 (4) | 0·87 (3) | 0·78 (8) | | | | | |

References: (*a*) This work; (*b*) Versichel *et al.* (1978); (*c*) Lenstra & Van Havere (1980); (*d*) Van Havere & Lenstra (1978).

Table 5. *Valence angles* (°) *with e.s.d.'s in parentheses for* $Li^+$ *and other hydrogen malates*

| | Lithium hydrogen 1-malate[a] | Ammonium hydrogen 1-malate[b] | Calcium di(hydrogen 1-malate)[c] | | Copper(II) di(hydrogen 1-malate)[d] | | Mean value | Standard deviation of mean |
|---|---|---|---|---|---|---|---|---|
| C(1)–C(2)–C(3) | 113·3 (2) | 110·5 (2) | 108·5 (3) | 112·6 (3) | 112·0 (3) | 112·8 (3) | 111·6 | 1·8 |
| C(2)–C(3)–C(4) | 113·4 (2) | 110·1 (2) | 112·1 (3) | 112·9 (3) | 110·7 (3) | 112·2 (3) | 111·9 | 1·3 |
| O(1)–C(1)–O(2) | 124·9 (2) | 125·3 (2) | 124·9 (3) | 125·1 (3) | 121·6 (3) | 123·7 (3) | 124·3 | 1·4 |
| O(1)–C(1)–C(2) | 119·2 (2) | 118·6 (2) | 118·1 (3) | 115·9 (3) | 119·5 (3) | 116·7 (3) | 118·0 | 1·4 |
| O(2)–C(1)–C(2) | 115·8 (2) | 116·1 (2) | 117·0 (3) | 118·9 (3) | 118·8 (3) | 119·5 (3) | 117·7 | 1·6 |
| C(1)–C(2)–O(5) | 114·1 (2) | 111·8 (2) | 110·3 (3) | 107·0 (3) | 106·4 (3) | 104·3 (3) | 109·0 | 3·7 |
| O(5)–C(2)–C(3) | 110·4 (2) | 107·4 (2) | 110·2 (3) | 111·5 (3) | 109·4 (3) | 113·4 (3) | 110·4 | 2·0 |
| C(3)–C(4)–O(3) | 112·6 (2) | 113·0 (2) | 114·0 (3) | 111·6 (3) | 111·0 (3) | 112·3 (3) | 112·4 | 1·1 |
| C(3)–C(4)–O(4) | 124·3 (2) | 123·7 (2) | 122·1 (3) | 124·8 (3) | 124·3 (3) | 122·9 (3) | 123·7 | 1·0 |
| O(3)–C(4)–O(4) | 123·1 (2) | 123·2 (2) | 123·9 (3) | 123·6 (3) | 124·7 (3) | 124·8 (3) | 123·9 | 0·6 |
| ⟨C–C–H⟩ | 107 (3) | 110 (2) | 109 (3) | | 110 (10) | | | |
| ⟨C–O–H⟩ | 105 (2) | 110 (2) | 103 (3) | | 109 (10) | | | |
| ⟨H–C–H⟩ | 112 (4) | 107 (3) | 110 (4) | | 109 (12) | | | |

References: (*a*) This work; (*b*) Versichel *et al.* (1978); (*c*) Lenstra & Van Havere (1980); (*d*) Van Havere & Lenstra (1978).

Table 6. *Torsion angles* (°) *in lithium hydrogen* 1-*malate compared to corresponding values in other hydrogen malates*

The e.s.d. for these values is 0·3°.

| | O(1)–C(1)–C(2)–C(3) | O(1)–C(1)–C(2)–O(5) | C(1)–C(2)–C(3)–C(4) | O(5)–C(2)–C(3)–C(4) | O(4)–C(4)–C(3)–C(2) | Reference |
|---|---|---|---|---|---|---|
| Lithium hydrogen (+)-(2*R*)-1-malate | −133·4 | −5·9 | +66·6 | −62·8 | −9·2 | (*a*) |
| Lithium hydrogen (−)-(2*S*)-1-malate* | +133·4 | +5·9 | −66·6 | +62·8 | −9·2 | |
| Ammonium hydrogen (−)-(2*S*)-1-malate | +112·3 | −7·3 | +168·7 | −69·0 | −69·1 | (*b*) |
| Calcium di[hydrogen (−)-(2*S*)-1-malate] | +112·3 | −8·4 | +174·6 | −64·6 | −44·6 | (*c*) |
| | +136·7 | +14·5 | +179·4 | −60·4 | −23·9 | |
| Copper(II) di[hydrogen (−)-(2*S*)-1-malate] | +131·5 | +11·9 | +163·7 | −78·5 | −58·5 | (*d*) |
| | +148·6 | +25·2 | +172·9 | −68·8 | −23·3 | |

References: (*a*) This work; (*b*) Versichel *et al.* (1978); (*c*) Lenstra & Van Havere (1980); (*d*) Van Havere & Lenstra (1978).

* The experimental values obtained for the optically active hydrogen (+)-1-malate (2*R* form) have been transformed to a hypothetical (2*S*) form.

(2) The hydrogen malate moiety does not show conformational stability under various packing conditions. In the lithium salt we find a synclinal conformation for the $^{-}$OOC—C—C—COOH chain, in contrast to the expected antiperiplanar form which is found in the other salts.

(3) Kanters *et al.* had claimed that in the COO$^{-}$ group of $\alpha$-hydroxy acids the C—O bonded to the cation is shorter than the other C—O bonds. Our data show that a firm, statistically significant, statement about the (in)equivalence of $O_1$ and $O_2$ is as yet premature.

(4) In the hydrogen malates the bond C(1)—C(2) next to the COO$^{-}$ seems elongated with respect to C(3)—C(4) next to the COOH group.

One could speculate that the unusual conformation is coupled to the hydrogen bridge O(3)—H···O(4). Furthermore, the torsion angle O(4)—C(4)—C(3)—C(2) varies between −9 and −69°, the variations probably being dictated by the way COOH is stacked in the lattice. The only conformational feature common to all compounds is that O(5) is more or less in the plane of the COO$^{-}$ group. But, notwithstanding this, the spread in the values of torsion angle O(1)—C(1)—C(2)—O(5) and consequently also in those of O(1)—C(1)—C(2)—C(3) is rather large.

One of the authors (WVH) thanks the Belgian Organisation IWONL for a predoctoral grant.

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*Acta Cryst.* (1980). B**36**, 1486–1488

# $\mu$-Chloro-bis(triphenylphosphine)digold(I) Perchlorate Dichloromethane Solvate

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(*Received* 29 *January* 1980; *accepted* 25 *February* 1980)

**Abstract.** $C_{36}H_{30}Au_2ClP_2^+.ClO_4^-.CH_2Cl_2$, $[Au_2(C_{18}H_{15}P)_2Cl]ClO_4.CH_2Cl_2$, $M_r$ = 1138·36, triclinic, $P\bar{1}$, $a$ = 11·214 (3), $b$ = 14·675 (4), $c$ = 25·505 (6) Å, $\alpha$ = 85·62 (2), $\beta$ = 85·16 (2), $\gamma$ = 68·25 (2)°, $U$ = 3880 Å$^3$, $Z$ = 4, $D_x$ = 1·949 Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 7·9 mm$^{-1}$; final $R$ = 0·072 for 8642 reflexions. There are two formula units in the asymmetric unit. The Au—Cl—Au angles are 80·7, 82·7° with correspondingly short Au···Au contacts (3·035, 3·085 Å). Au—Cl lengths range from 2·328 to 2·345 Å.

**Introduction.** We have recently discovered a general method of preparing single-bridged binuclear Au$^{\mathrm{I}}$ complexes with anionic bridging groups (Uson, Laguna & Castrillo, 1979); only one such complex, $(Me_3PAu)_2S$, has hitherto been reported (Schmidbaur, Franke & Eberlein, 1975). A crystal structure determination of $(Ph_3PAu)_2Cl^+.ClO_4^-$ was attempted to confirm the assumed bridged structure.

Crystals were obtained as colourless flat blocks from dichloromethane/hexane. 10 712 intensities in the range 7 < 2$\theta$ < 45° were measured on a Stoe four-circle diffractometer with monochromated Mo $K\alpha$ radiation and a crystal 0·4 × 0·3 × 0·1 mm. After application of Lp and empirical absorption corrections, averaging equivalent reflexions gave 10 098 unique reflexions, 8642 with $F > 4\sigma(F)$. Cell dimensions were obtained from accurate centring of 28 strong reflexions.

0567-7408/80/061486-03$01.00