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Structures of Disodium Malonate Trihydrate, $Na_2C_3H_2O_4.3H_2O$, and Dilithium Malonate, $Li_2C_3H_2O_4$

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Abstract. Na_2mal, $M_r = 202{\cdot}0$, triclinic, $P\bar{1}$, $a = 7{\cdot}643\ (1)$, $b = 16{\cdot}215\ (3)$, $c = 6{\cdot}308\ (1)$ Å, $\alpha = 121{\cdot}27\ (1)$, $\beta = 78{\cdot}41\ (1)$, $\gamma = 109{\cdot}53\ (1)°$, $V = 732{\cdot}9\ (3)$ Å^3; $Z = 4$; $D_m = 1{\cdot}86$, $D_x = 1{\cdot}83$ g cm^{-3}; μ(Cu $K\alpha$) = 2·28 mm^{-1}, $F(000) = 416$, $R = 0{\cdot}07$ for 2690 reflections. Li_2mal, $M_r = 115{\cdot}9$, monoclinic, $P2_1/c$, $a = 7{\cdot}232\ (2)$, $b = 7{\cdot}041\ (1)$, $c = 9{\cdot}085\ (2)$ Å, $\beta = 114{\cdot}53\ (2)°$, $V = 420{\cdot}9\ (3)$ Å^3; $Z = 4$; $D_m = 1{\cdot}83$, $D_x = 1{\cdot}83$ g cm^{-3}; μ(Cu $K\alpha$) = 1·54 mm^{-1}, $F(000) = 232$, $R = 0{\cdot}04$ for 855 reflections; $T = 295 \pm 3$ K. Na_2mal occurs as two independent molecules, *A* and *B*, with different conformations; molecule *A* and the molecule in Li_2mal have conformations which distort the C—C—C angles. Four Na^+ ions have six O atoms as coordinators in an approximately octahedral arrangement forming infinite chains along **b** by sharing edges. Each Li ion is tetrahedrally surrounded by four O atoms. The tetrahedral coordination groups are connected in pairs by apex sharing and are linked *via* the malonate ions in layers parallel to the *ab* plane. The environment of the three water molecules is approximately tetrahedral.

Introduction. Interest in the structural chemistry of the malonate ion in the solid state stems from the fact that there is a change in conformation of the carboxylate groups due to ionization.

Experimental. Crystals of Na_2mal and Li_2mal obtained by neutralizing aqueous solutions of malonic acid with sodium and lithium hydroxide, respectively, in 1:2 stoichiometric amounts; Na_2mal crystal, 0·26 × 0·42 × 0·40 mm (Li_2mal, 0·13 × 0·17 × 0·34 mm) mounted on a glass fiber with a^* (c^*, Li_2mal) along the φ axis of a GE-XRD6 manual goniostat; unit-cell constants determined by least-squares refinement of the *d* spacings of 60 large-angle reflections; Cu $K\alpha$ radiation, $2\theta_{\max} = 160°$, stationary-crystal–stationary-counter (Furnas & Harker, 1955) method; 2750 non-equivalent reflections (918 non-equivalent reflections, Li_2mal) measured, of which 2690 (855, Li_2mal) had $I > 2\sigma(I)$ and were used in the refinement; in both crystals, the difference in absorption as a function of φ was measured for the axial reflections and used to correct approximately for the anisotropy of absorption; Lorentz and polarization corrections applied, both structures determined with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by block-diagonal least-squares procedure; H atoms located from difference electron density maps and their parameters refined isotropically; during the refinement of the Na_2mal structure 40 mainly large low-angle reflections had been omitted, where $F_c/F_o > 1{\cdot}3$; the *R* values with and without these reflections were 0·075 and 0·070; $\sum w[|F_o| - (1/k)|F_c|]^2$ was minimized with $w = 1/f_C$ where f_C is the scattering factor for C; *Rw* for Na_2mal and Li_2mal = 0·07 and 0·04 respectively; atomic scattering factors for C, O, Li^+ and Na^+ were taken from *International Tables for X-ray Crystallography* (1968) and for H from Stewart, Davidson & Simpson (1965).

Discussion. The final atomic coordinates are given in Table 1.* Covalent bond lengths and interbond angles are listed in Table 2. The C—C distances in Li_2mal are not significantly different. However, in the two independent malonate ions of Na_2mal this difference is significant and their dimensions are quite similar to those found in $Na_2C_3H_2O_4.H_2O$ (Oskarsson, 1978). It has been pointed out that the sum of the carboxylic C–O distances, whether ionized or not, is reasonably constant (2.52 Å), their difference ranging from 0·03 to 0·10 Å (Manojlović & Speakman, 1967). In Na_2mal the sums of the C—O distances in the carboxylate ions, *A* and *B*, are 2·528, 2·520, 2·513 and 2·519 Å,

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, lengths and angles involving H atoms and details of the coordination geometry of the metal ions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38368 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic fractional coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^4)

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

(i) Na_2mal	x	y	z	U_{eq}
Na(1)	891 (2)	8420 (1)	3951 (2)	221
Na(2)	383 (2)	2920 (1)	2430 (3)	262
Na(3)	1918 (2)	9616 (1)	338 (3)	329
Na(4)	1585 (2)	4621 (1)	308 (3)	273
O(*W*1)	5867 (4)	5960 (2)	2253 (5)	291
O(*W*2)	7527 (4)	2051 (2)	3823 (5)	301
O(*W*3)	1831 (4)	2312 (2)	4172 (5)	283
O(1)	7264 (4)	5404 (2)	6587 (4)	238
O(2)	9134 (4)	5427 (2)	3393 (5)	236
O(3)	9038 (4)	3179 (2)	−314 (5)	237
O(4)	6979 (4)	3546 (2)	−1488 (5)	311
O(5)	3507 (4)	9039 (2)	1890 (6)	331
O(6)	5740 (3)	8858 (2)	−1046 (5)	260
O(7)	8987 (4)	10021 (2)	2483 (5)	243
O(8)	9231 (3)	8516 (2)	1309 (5)	257
C(1)	7820 (5)	4990 (2)	4340 (6)	184
C(2)	6787 (5)	3899 (2)	2696 (6)	194
C(3)	7655 (4)	3494 (2)	111 (5)	154
C(4)	5061 (4)	8909 (2)	1017 (6)	171
C(5)	6215 (5)	8797 (3)	2531 (7)	279
C(6)	8292 (4)	9130 (2)	2069 (5)	155
(ii) Li_2mal	x	y	z	U_{eq}
Li(1)	1902 (5)	5966 (5)	6009 (4)	214
Li(2)	5748 (5)	4126 (5)	6498 (4)	181
O(1)	3881 (2)	4176 (2)	7486 (2)	238
O(2)	4793 (2)	1866 (2)	9303 (2)	199
O(3)	−369 (2)	4381 (2)	6303 (2)	213
O(4)	−1622 (2)	3305 (2)	7992 (2)	218
C(1)	3663 (2)	3242 (3)	8571 (2)	139
C(2)	1954 (2)	3807 (3)	9050 (2)	167
C(3)	−155 (2)	3821 (3)	7667 (2)	149

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(i) Na_2mal			
C(1)–O(1)	1·266 (4)	C(4)–O(5)	1·242 (4)
C(1)–O(2)	1·262 (5)	C(4)–O(6)	1·271 (5)
C(3)–O(3)	1·248 (4)	C(6)–O(7)	1·261 (5)
C(3)–O(4)	1·272 (4)	C(6)–O(8)	1·258 (4)
C(1)–C(2)	1·522 (5)	C(4)–C(5)	1·534 (5)
C(2)–C(3)	1·509 (5)	C(5)–C(6)	1·518 (5)
C(2)–C(1)–O(1)	116·9 (3)	C(5)–C(4)–O(5)	117·4 (3)
C(2)–C(1)–O(2)	118·9 (3)	C(5)–C(4)–O(6)	118·4 (3)
C(2)–C(3)–O(3)	119·1 (3)	C(5)–C(6)–O(7)	117·5 (3)
C(2)–C(3)–O(4)	117·2 (3)	C(5)–C(6)–O(8)	119·1 (3)
O(1)–C(1)–O(2)	124·2 (3)	O(5)–C(4)–O(6)	124·2 (3)
O(3)–C(3)–O(4)	123·7 (3)	O(7)–C(6)–O(8)	123·4 (3)
C(1)–C(2)–C(3)	110·9 (3)	C(4)–C(5)–C(6)	113·3 (3)
(ii) Li_2mal			
C(1)–O(1)	1·248 (2)	C(3)–O(4)	1·267 (2)
C(1)–O(2)	1·265 (2)	C(1)–C(2)	1·524 (3)
C(3)–O(3)	1·247 (2)	C(2)–C(3)	1·522 (3)
C(2)–C(1)–O(1)	118·1 (2)	O(1)–C(1)–O(2)	123·7 (2)
C(2)–C(1)–O(2)	118·3 (2)	O(3)–C(3)–O(4)	123·4 (2)
C(2)–C(3)–O(3)	119·4 (2)	C(1)–C(2)–C(3)	114·8 (2)
C(2)–C(3)–O(4)	117·1 (2)		

respectively, while those of Li_2mal are 2·512 and 2·514 Å, in good agreement with the above observation.

In the malonate dianion, due to steric hindrance between O atoms, the two carboxylate groups cannot be in the plane of the central C atoms, but must twist with respect to this plane. In Na_2mal (*A*), the planes of the carboxyl group are inclined to one another at 93·8 (3)° whereas in Na_2mal (*B*), they are inclined at 71·7 (3)° and in Li_2mal at 48·5 (3)°. In Na_2mal (*A*), the O(1)—C(1)—C(2)—C(3) and C(1)—C(2)—C(3)—O(4) torsion angles are −177·4 (3) and −93·3 (3)°, giving a shortest O···O distance of 3·2 Å within the malonate ion, so there is no internal strain caused by O···O repulsion and the C(1)–C(2)–C(3) angle is near to the tetrahedral value, whereas in (*B*) and Li_2mal the shortest non-bonded O···O distances are 3·00 and 2·81 Å, respectively. This repulsion causes some internal strain and the C–C–C angles are distorted from the tetrahedral value to 113·3 and 114·8° respectively. In almost planar malonate ions, namely $KC_3H_3O_4$ (Sime, Speakman & Parthasarathy, 1970) and $Mg(C_3H_3O_4)_2.2H_2O$ (Briggman & Oskarsson, 1978), the strain effect is highly significant and the C–C–C angles are 119·4 and 119·8°, respectively.

In Na_2mal water molecules link the malonate ions by fairly linear hydrogen bonds. *W*(1) and *W*(3) (see Table 3) are linked to one another by a linear hydrogen bond. The crystal environment of the three water molecules is approximately tetrahedral. *W*(2) and *W*(3) molecules are coordinated to Na^+ along lone-pair directions.

Table 3. *Hydrogen bonds in* Na_2mal

D is the donor and *A* is the acceptor atom.

D—H···*A*	H···*A* (Å)	*D*···*A* (Å)	∠ *D*—H···*A*
O(*W*1)—H(1)···O(1^{iii})	2·11 (9)	2·932 (4)	155 (8)
O(*W*1)—H(2)···O(4^{ii})	1·99 (8)	2·756 (4)	157 (9)
O(*W*2)—H(3)···O(6^{ii})	2·07 (9)	2·845 (4)	172 (10)
O(*W*2)—H(4)···O(4^{i})	1·96 (9)	2·746 (4)	172 (9)
O(*W*3)—H(5)···O(6^{ii})	1·92 (9)	2·817 (4)	167 (9)
O(*W*3)—H(6)···O(*W*1^{iii})	2·15 (9)	2·788 (4)	175 (11)

Symmetry code: (i) $x, y, 1 + z$; (ii) $1 - x, 1 - y, -z$; (iii) $1 - x, 1 - y, 1 - z$.

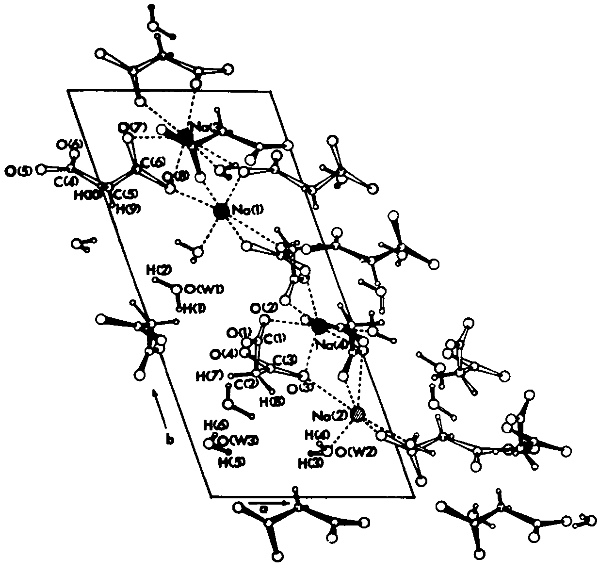

Fig. 1. The crystal structure of disodium malonate trihydrate, seen in its c axial projection.

However, in *W*(1) one of its lone pairs is directed to Na^+ and the other to a H of a different water molecule. O(1), O(4) and O(6), which are at distances of 1·266, 1·272 and 1·271 Å from their respective C atoms, accept hydrogens of water molecules and take part in hydrogen-bond formation. The other O atoms whose bonding involves more double-bond character, as judged by their shorter C–O distances, are not involved in hydrogen-bond formation. Na(1) and Na(2) are coordinated by four carboxylate O atoms and two water molecules (see Fig. 1); Na(3) and Na(4) are coordinated by five carboxylate O atoms and one water molecule. The malonate dianions form four- and six-membered chelate rings with the different Na^+ ions. Similar sixfold coordination of Na is found in salts of other carboxylic and dicarboxylic acids (Speakman & Mills, 1961; Narasinga Rao & Parthasarathy, 1974).

Fig. 2 shows the approximately tetrahedral coordination of both the crystallographically distinct Li^+ ions in Li_2mal, made up by four O atoms. The malonate dianion forms a six-membered chelate ring with Li(1). Fourfold coordination of Li had been found in salts of other carboxylic and dicarboxylic acids (Soriano-Garcia & Parthasarathy, 1978; Gonschorek & Küppers, 1975).

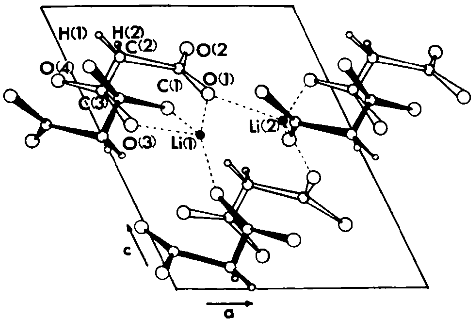

Fig. 2. The crystal structure of dilithium malonate, seen in its *b* axial projection.

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Bis{3-[2-(2-pyridyl)ethyl]imino-2-butanone oximato}cobalt(III) Perchlorate, $C_{22}H_{28}CoN_6O_2^+.ClO_4^-$

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Abstract. $M_r = 566{\cdot}89$, triclinic, $P\bar{1}$, $a = 8{\cdot}803$ (4), $b = 11{\cdot}785$ (6), $c = 13{\cdot}333$ (7) Å, $\alpha = 95{\cdot}55$ (4), $\beta = 91{\cdot}58$ (4), $\gamma = 111{\cdot}79$ (3)°, $V = 1275$ (1) Å^3, $Z = 2$, $D_m = 1{\cdot}48$ (2), $D_x = 1{\cdot}476$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}86$ mm^{-1}, $F(000) = 588$, $T = 298$K, $R = 0{\cdot}043$ for 3964 observed reflections. The structure comprises $[Co(C_{11}H_{14}N_3O)_2]^+$ cations and ClO_4^- anions. Co is coordinated to six N atoms of the two tridentate ligand molecules in the form of a slightly distorted octahedron.

Introduction. Though metal complexes of tridentate 3-[2-(2-pyridyl)ethyl]imino-2-butanone oxime have been investigated fairly thoroughly (Uhling & Schneider,

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