

where the  $(\text{CH}_3)_2\text{Tl}$  group has an asymmetric distribution of equatorial charges. This departure from linearity of the  $(\text{CH}_3)_2\text{Tl}$  group is approximately independent of the size of the chelate ring, as evident from the angles found for the following derivatives: tropolonate  $166.9 (9)^\circ$ , acetylacetonate  $170.0 (20)^\circ$ , and acetate  $171.8 (16)^\circ$  (Chow & Britton, 1975), 1,10-phenanthroline  $168.3 (15)^\circ$  (Blundell & Powell, 1972), and for several phenoxide and thiophenoxide dimeric species,  $173 (3)$ ,  $166.2 (10)$  and  $163.5 (9)^\circ$  (Burke, Gray, Hayward, Matthews, McPartlin & Gillies, 1977).

The  $^1\text{H}$  NMR spectrum of  $(\text{CH}_3)_2\text{Tl}(\text{L-PHE})$  in aqueous solution (pH 7) shows a value of  $413 \pm 2$  Hz for  $^2J(^{205}\text{Tl}-^1\text{H})$ , similar to the  $\sim 420$  Hz found for  $(\text{CH}_3)_2\text{TlY}$  ( $Y =$  anionic species) in aqueous solutions (Burke, Matthews & Gillies, 1976; Gillies, Hoad, Matthews & Thakur, 1977).

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## Structure of Disodium Malonate Monohydrate

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**Abstract.**  $\text{Na}_2\text{C}_3\text{H}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $M_r = 167.0$ , is orthorhombic, space group  $Pbc2_1$ , with  $a = 7.7486 (8)$ ,  $b = 12.6419 (17)$ ,  $c = 5.7866 (6)$  Å,  $V = 566.84$  Å<sup>3</sup>,  $Z = 4$ . Each  $\text{Na}^+$  ion is surrounded by six O atoms forming distorted octahedra. The polyhedra form a two-dimensional network perpendicular to  $\mathbf{a}$ , by sharing faces, edges and corners. These networks are linked along  $\mathbf{a}$  through carboxylate bridges. The malonate ion has a conformation which imposes a distortion of the C–C–C angle to  $114.9 (2)^\circ$ .

**Introduction.** Weissenberg photographs revealed the Laue class  $mmm$ . The systematic absences  $0kl$ ,  $k \neq 2n$  and  $h0l$ ,  $l \neq 2n$  gave  $Pbc2_1$  and  $Pbcm$  as possible space groups. The non-centrosymmetric  $Pbc2_1$  was chosen (indicated by  $E$  statistics). Cell dimensions were obtained by least squares from powder spectra obtained with a Guinier–Hägg focusing camera (Cu  $K\alpha_1$  radiation,  $\lambda = 1.54056$  Å,  $22^\circ\text{C}$ ). Al (cubic,  $a = 4.04934$  Å) was used as internal standard. A four-circle

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diffractometer (CAD-4) was used in the data collection. Table 1 gives details of the collection and reduction of the intensities and the refinement. During data collection three standard reflexions were checked after every 50 measurements. No systematic variations in their intensities were observed. The values of  $I$  and  $\sigma_c(I)$  were corrected for Lorentz, polarization and absorption effects [ $\sigma_c(I)$  is based on counting statistics]. The expression  $p = (\cos^2 2\theta + \cos^2 2\theta_M)/(1 + \cos^2 2\theta_M)$  was used in the correction of the polarization effects.  $\theta_M$  is the Bragg angle for the monochromator.

The positions of the non-hydrogen atoms were determined with *MULTAN* (Germain, Main & Woolfson, 1971). The parameters were refined by full-matrix least squares, minimizing  $\sum w(|F_o| - |F_c|)^2$ , with weights  $w^{-1} = \sigma^2/4|F_o|^2 + C|F_o|^2$ .  $C$  was adjusted so that constant values of  $\langle w(|F_o| - |F_c|)^2 \rangle$  were obtained in different  $|F_o|$  and  $\sin \theta$  intervals. The origin was kept fixed along  $\mathbf{c}$  by not refining the  $z$  parameter of Na(1). The positions of the H atoms were obtained from a

Table 1. Collection and reduction of the intensities, and the least-squares refinement

Crystal size: 0.040 × 0.163 × 0.157 mm  
 $\lambda = 1.5418 \text{ \AA}$  (graphite-monochromated Cu K $\alpha$ )  
 $\mu = 28.3 \text{ cm}^{-1}$   
 Range of transmission factor: 0.681–0.890  
 $\theta$  interval: 5–70°  
 $\omega$ –2 $\theta$  scan width  $\Delta\omega$  (°) = 0.7 + 0.5 tan  $\theta$   
 Minimum number of counts in a scan: 3000  
 Maximum recording time: 3 min  
 Number of measured reflexions: 593  
 Number of reflexions with zero weight ( $I \leq 0$ ): 6  
 Number of parameters refined: 127  
 $R = \sum(|F_o| - |F_c|) / \sum |F_o| = 0.0298$   
 $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.0347$   
 $S = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2} = 1.8$   
 $C$  (weighting function) = 0.015  
 $g \times 10^{-4} = 1.8$  (1) (extinction)

Table 2. Atomic coordinates ( $\times 10^4$ ) with estimated standard deviations

	x	y	z
Na(1)	9901 (1)	8549 (1)	4600
Na(2)	2181 (1)	9314 (1)	–169 (3)
C(1)	8654 (3)	8909 (2)	–566 (5)
C(2)	6712 (3)	8743 (2)	–402 (6)
C(3)	5972 (3)	8833 (2)	2015 (5)
O(1)	9207 (2)	9661 (1)	–1789 (4)
O(2)	9629 (2)	8273 (1)	492 (4)
O(3)	4354 (2)	8674 (2)	2171 (4)
O(4)	6915 (3)	9046 (1)	3692 (4)
O(5)	2797 (2)	6616 (2)	1303 (5)
H(1)	6082 (44)	9344 (27)	–1442 (76)
H(2)	6351 (43)	8002 (26)	–997 (68)
H(3)	3218 (43)	7159 (27)	1467 (82)
H(4)	3330 (45)	6362 (27)	219 (88)

difference synthesis with data corrected for isotropic extinction (Zachariasen, 1967) and with  $\sin \theta / \lambda \leq 0.5 \text{ \AA}^{-1}$ . In the last cycle the shifts in the parameters were less than 10% of the e.s.d.'s. A final difference synthesis was featureless. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The atomic parameters are given in Table 2.\*

**Discussion.** The structure of  $\text{Na}_2\text{C}_3\text{H}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (NaMAL) has been determined as part of a systematic study of the geometry of the malonate ion in the solid state. The packing coefficient (Briggman & Oskarsson, 1977) is 0.77. The ionic radius for  $\text{Na}^+$  was assumed to be 1.05 Å. The packing in NaMAL is somewhat less dense than in  $\text{CaC}_3\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (0.81) but about the same as in  $\text{SrC}_3\text{H}_2\text{O}_4$  (0.78) (Briggman & Oskarsson, 1977). The structure of NaMAL is shown in Fig. 1. The malonate ion is coordinated to eight different  $\text{Na}^+$  ions. It connects two-dimensional nets of linked coordination polyhedra, through a carboxylate bridge. Each  $\text{Na}^+$  ion

is coordinated by five carboxylate O atoms and one water molecule forming distorted octahedra. Table 3 gives selected distances within the coordination poly-

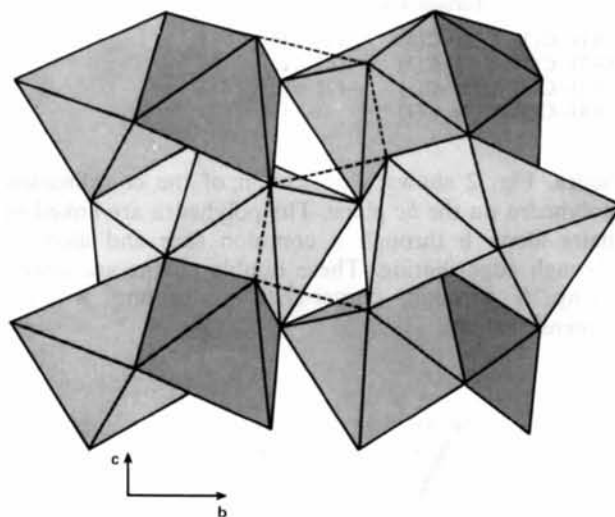


Fig. 2. A projection of the coordination polyhedra on the  $bc$  plane. The dotted line indicates hydrogen bonds.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33269 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

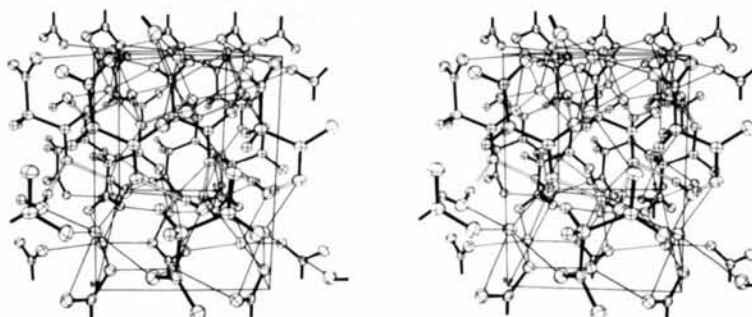


Fig. 1. The structure of NaMAL.

Table 3. Selected distances (Å) and angles (°)

(a) The coordination polyhedra. The superscripts denote the following transformations applied to the  $x, y, z$  values given in Table 2:

(i) $x, y, 1 + z$	(v) $-1 + x, y, 1 + z$		
(ii) $2 - x, 2 - y, \frac{1}{2} + z$	(vi) $1 - x, 1 - y, \frac{1}{2} + z$		
(iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$	(vii) $1 - x, 2 - y, \frac{1}{2} + z$		
(iv) $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$			

Na(1)—O(1 <sup>i</sup> )	2.576 (2)	Na(2)—O(1 <sup>v</sup> )	2.526 (2)
—O(1 <sup>ii</sup> )	2.498 (2)	—O(1 <sup>vi</sup> )	2.581 (3)
—O(2)	2.412 (2)	—O(2 <sup>v</sup> )	2.406 (2)
—O(2 <sup>iii</sup> )	2.370 (2)	—O(3 <sup>i</sup> )	2.308 (2)
—O(4)	2.454 (2)	—O(4 <sup>vii</sup> )	2.285 (2)
—O(5 <sup>iv</sup> )	2.460 (2)	—O(5 <sup>iii</sup> )	2.404 (3)

(b) The malonate ion

Distances		Bond angles	
C(1)—C(2)	1.522 (3)	C(1)—C(2)—C(3)	114.9 (2)
C(2)—C(3)	1.516 (4)	O(1)—C(1)—C(2)	118.3 (2)
C(1)—O(1)	1.262 (3)	O(2)—C(1)—C(2)	118.4 (2)
C(1)—O(2)	1.262 (3)	O(1)—C(1)—O(2)	123.3 (2)
C(3)—O(3)	1.273 (3)	C(2)—C(3)—O(3)	115.2 (2)
C(3)—O(4)	1.244 (4)	C(2)—C(3)—O(4)	120.9 (2)
C(2)—H(1)	1.09 (4)	O(3)—C(3)—O(4)	123.9 (3)
C(2)—H(2)	1.04 (3)	H(1)—C(2)—H(2)	109 (3)
C(2)···O(4)	2.967 (3)		

Torsion angles	
O(1)—C(1)—C(2)—C(3)	-119.3 (2)
O(2)—C(1)—C(2)—C(3)	62.2 (3)
O(3)—C(3)—C(2)—C(1)	-178.6 (2)
O(4)—C(3)—C(2)—C(1)	1.3 (3)

hedra. Fig. 2 shows a projection of the coordination polyhedra on the  $bc$  plane. The polyhedra are linked in pairs along  $b$  through a common face and along  $c$  through edge-sharing. These double chains are linked along  $b$  through corner-sharing forming a two-dimensional net.

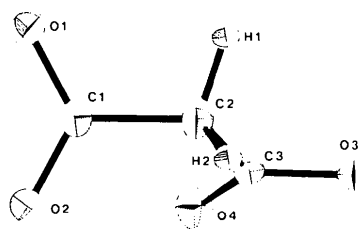


Fig. 3. The malonate ion.

Table 4. The geometry of the water molecule and the hydrogen bonds

Distances are in Å, angles in degrees.

O(5)—H(3)	0.77 (3)	O(3)···O(5)	2.911 (3)
O(5)—H(4)	0.82 (4)	O(3)···H(3)	2.15 (4)
H(3)—O(5)—H(4)	103 (4)	O(3)···H(3)—O(5)	170 (4)
		O(3)···O(5 <sup>iii</sup> )	2.703 (3)
		O(3)···H(4 <sup>iii</sup> )	1.93 (5)
		O(3)···H(4 <sup>iii</sup> )—O(5 <sup>iii</sup> )	156 (4)

The malonate ion depicted in Fig. 3 forms a six-membered chelate ring with one of the Na<sup>+</sup> ions and a four-membered ring with the other. The O—C—C—C torsion angles are 1 and 61°, giving a twist conformation in the chelate ring with Na<sup>+</sup>. The O(2)···O(4) distance is 2.967 Å. The O···O repulsion causes the C(1)—C(2)—C(3) angle to be distorted from the expected tetrahedral value to 114.9°. Similar conformations of the malonate ion are found in rare-earth malonates with six-membered chelate rings (Hansson, 1973) and in SrC<sub>3</sub>H<sub>2</sub>O<sub>4</sub> (Briggman & Oskarsson, 1977).

The C—C distances are not significantly different (Table 3) and they agree well with those found in CaC<sub>3</sub>H<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O and SrC<sub>3</sub>H<sub>2</sub>O<sub>4</sub>. The C—O distances are more dependent on the environment and, since O(3) accepts two hydrogen bonds, C(3)—O(3) is longer and C(3)—O(4) shorter than the distances observed in the other carboxylate group.

The geometry of the water molecule and the hydrogen bonds is given in Table 4. O(3) accepts two hydrogen bonds [from O(5) and O(5<sup>iii</sup>)] and forms a zigzag-shaped hydrogen-bond chain running along  $c$  (Fig. 2).

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