(1·986–1·993 Å), and in the bis(diethyldithiophosphinato)nickel(II) complex (2·00–2·01 Å) (McConnell & Kastalsky, 1967; Shetty & Fernando, 1969). The bonding of the P atom to a C atom of an ethyl group and to an O atom with a partial negative charge is reflected in the longer P—S bond in this unsymmetrically substituted complex. The P—C and C—C distances are close to the normal values. As expected, the P—O distance of 1·521 (5) Å is significantly shorter than the corresponding P—O distances in complexes of the type $Ni[S_2P(OR)_2]_2$ (Wasson, Woltermann & Stoklosa, 1973). The C—N distance in the ethylammonium ion is close to the normal value, but the C—C distance is about 0·06 Å shorter than the corresponding distance in ethylammonium tetrachloromanganate(II) (Depmeier, 1975).

References

CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.
DEPMEIER, V. W. (1975). *Acta Cryst.* B**32**, 303–305.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B**26**, 274–285.
HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
MCCONNELL, J. F. & KASTALSKY, V. (1967). *Acta Cryst.* **22**, 853–859.
SHETTY, P. S. & FERNANDO, Q. (1969). *Acta Cryst.* B**25**, 1294–1298.
SHETTY, P. S., JOSE, P. & FERNANDO, Q. (1968). *Chem. Commun.* pp. 788–790.
WASSON, J. R., WOLTERMANN, G. M. & STOKLOSA, H. J. (1973). *Fortschr. Chem. Forsch.* **35**, 65–129.

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Magnesium Bis(hydrogen malonate) Dihydrate

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Abstract. $Mg(C_3H_3O_4)_2.2H_2O$, $M_r = 266·5$, monoclinic, $P2_1/c$, $a = 4·9391$ (5), $b = 11·3100$ (13), $c = 9·6497$ (9) Å and $\beta = 90·312$ (7)°, $V = 539·0$ Å^3, $Z = 2$, $R = 0·038$. The compound consists of hydrogen malonate chains crosslinked by the Mg^{2+} ion. The Mg ion is surrounded by two water molecules and four carboxylate O atoms forming a slightly distorted octahedron. The short (2·589 Å) hydrogen bond in the hydrogen malonate chain is probably asymmetric.

Introduction. Crystals of $Mg(C_3H_3O_4)_2.2H_2O$ were obtained by evaporation of an aqueous solution of magnesium hydrogen malonate. Weissenberg photographs showed that the compound is monoclinic; systematic absences $0k0$ with $k \neq 2n$ and $h0l$ with $l \neq 2n$ uniquely define the space group as $P2_1/c$. Accurate cell dimensions were obtained by a least-squares treatment of powder spectra recorded with a Guinier–Hägg focusing camera (Cu $K\alpha_1$ radiation, $\lambda = 1·54056$ Å, 22°C). Aluminium (cubic, $a = 4·04934$ Å) was used as internal standard. A four-circle single-crystal diffractometer (CAD-4) was used in the intensity data collection. Experimental conditions and data reduction are described by Oskarsson (1978). Some specific experimental parameters and information concerning the least-squares refinement are given in Table 1. The positions of the non-H atoms were determined by symbolic addition (Karle & Karle, 1963, 1966). Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ was performed with weights $w^{-1} = \sigma_c^2(|F_o|^2)/4|F_o|^2 + C|F_o|^2$. $\sigma_c(|F_o|^2)$ is estimated from counting statistics. 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 H atoms were located in a difference synthesis using data corrected for isotropic extinction (Zachariasen, 1967) and obeying $\sin\theta/\lambda < 0·5$ Å^{-1}. In the last cycle of refinement, the shifts in the parameters were less than 10% of the e.s.d.'s. Atomic

Table 1. *Summary of data collection and least-squares refinement*

Crystal size: 0·282 × 0·150 × 0·140 mm
$\bar{\lambda} = 0·7107$ Å (graphite-monochromated Mo $K\alpha$)
$\mu = 2·4$ cm^{-1}
Range of transmission factor: 0·95–0·97
θ interval: 3–30°
ω–2θ 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: 1612
Number of reflections with zero weight ($I \leq 0$): 74
Number of parameters refined: 100
$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0·038$
$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0·40$
$S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2} = 1·6$
C (weighting function): 0·015
$g \times 10^4 = 0·11$ (5) (extinction)

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

	x	*y*	*z*
Mg	10000	0000	5000
C(1)	11659 (2)	2543 (1)	4810 (1)
C(2)	9852 (3)	2960 (1)	5959 (1)
C(3)	7852 (2)	2105 (1)	6615 (1)
O(1)	11830 (2)	1531 (0)	4378 (1)
O(2)	13109 (2)	3399 (1)	4297 (1)
O(3)	7690 (3)	1054 (1)	6248 (1)
O(4)	6390 (2)	2554 (1)	7538 (1)
O(5)	7177 (4)	162 (1)	3428 (1)
H(1)	10844 (4)	3342 (1)	6718 (1)
H(2)	8746 (2)	3652 (1)	5671 (1)
H(3)	14133 (3)	3094 (1)	3658 (1)
H(4)	5773 (2)	−209 (1)	3504 (1)
H(5)	6868 (4)	810 (1)	3156 (1)

scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The atomic coordinates are given in Table 2.*

Discussion. The crystal structure of $Mg(C_3H_3O_4)_2.2H_2O$ has been determined as part of a systematic study of the geometry of different species of malonic acid in the solid state. The packing coefficient calculated as described previously (Briggman & Oskarsson, 1977) is 0·78. The ionic radius for Mg^{2+} was assumed to be 0·65 Å. The value of the packing coefficient is within the interval 0·74–0·81 found in the malonates previously investigated (Briggman & Oskarsson, 1977; Oskarsson, 1978; Albertsson, Oskarsson & Svensson, 1978).

The structure is shown in Fig. 1. The hydrogen malonate ions are linked end-to-end through hydrogen bonds, forming infinite chains running in the [102] direction. The chains are cross-linked by Mg^{2+} ions and hydrogen bonds donated by the water molecule. The Mg^{2+} ion, which is situated at a center of symmetry, is coordinated by four carboxylate O atoms and two water O atoms forming an almost perfect octahedron (Fig. 2). It is slightly elongated along the $O(5)–O(5^{i})$ axis. Table 3 gives selected distances within the coordination polyhedron.

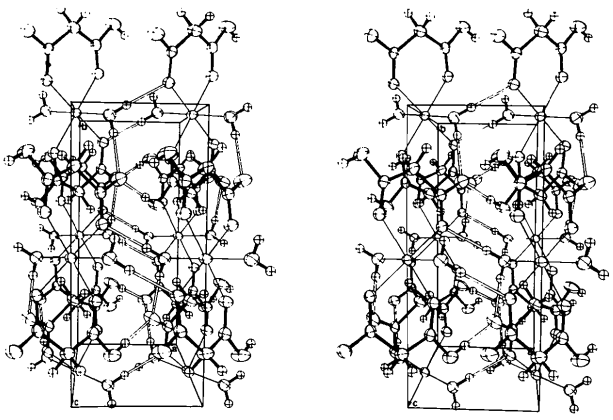

Fig. 1. The structure of magnesium bis(hydrogen malonate) dihydrate.

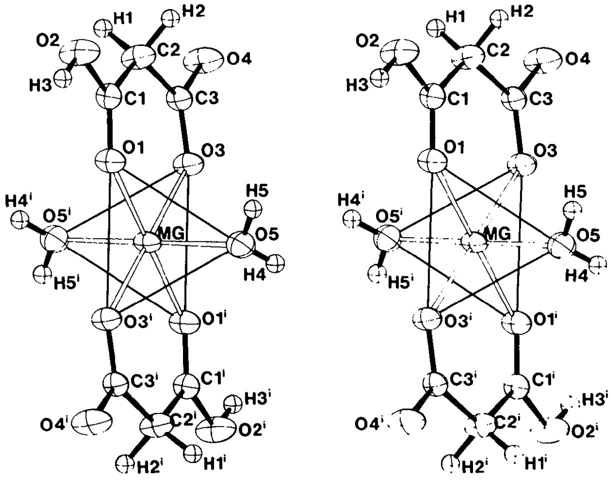

Fig. 2. The coordination polyhedron.

Table 3. *Selected distances* (Å) *within the* Mg^{2+} *coordination polyhedron*

Atoms with superscript (i) are at 2 − *x*, −*y*, 1 − *z*, with respect to *x*,*y*,*z* in Table 2.

Mg–O(1)	2·045 (1)	$Mg–O(3^{i})$	2·046 (1)
$O(1^{i})$	2·045 (1)	O(5)	2·063 (1)
O(3)	2·046 (1)	$O(5^{i})$	2·063 (1)

The hydrogen malonate ion forms a six-membered chelate ring with the Mg^{2+} ion. The O–C–C–C torsion angles are −5 and 1° giving an almost planar chelate ring with Mg^{2+}. The intramolecular O(1)···O(3) distance is very short, 2·787 Å. The O···O repulsion distorts the C(1)–C(2)–C(3) angle from the expected tetrahedral value to 119·8°. A similar conformation of the hydrogen malonate ion is found in potassium hydrogen malonate (Sime, Speakman & Parthasarathy, 1970). The hydrogen malonate ion is depicted in Fig. 2, and Table 4 gives the bond distances and angles.

The position of H(3) indicates that the hydrogen malonate ion has one carboxylic and one carboxylate group. This is further supported by the bonding geometry of these groups. Using the bond length–bond number curve reported for iminodiacetates (Oskarsson, 1976) the bond numbers for the C–O bonds are esti-

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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 33722 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Selected interatomic distances* (Å) *and angles* (°) *in the hydrogen malonate ion*

Distances		Bond angles	
C(1)–C(2)	1·503 (1)	C(1)–C(2)–C(3)	119·8 (1)
C(2)–C(3)	1·523 (1)	O(1)–C(1)–C(2)	126·1 (1)
C(1)–O(1)	1·220 (1)	O(2)–C(1)–C(2)	112·1 (1)
C(1)–O(2)	1·303 (1)	O(1)–C(1)–O(2)	121·9 (1)
C(3)–O(3)	1·242 (1)	O(3)–C(3)–C(2)	122·0 (1)
C(3)–O(4)	1·257 (1)	O(4)–C(3)–C(2)	114·5 (1)
C(2)–H(1)	0·980 (i)	O(3)–C(3)–O(4)	123·6 (1)
C(2)–H(2)	0·992 (1)	C(1)–C(2)–H(1)	113·2 (2)
O(2)–H(3)	0·870 (1)	C(3)–C(2)–H(2)	105·1 (1)
		H(1)–C(2)–H(2)	97·7 (1)
		C(3)–C(2)–H(1)	107·0 (1)
		C(1)–C(2)–H(2)	111·7 (1)
		C(1)–O(2)–H(3)	107·3 (1)

Torsion angles	
O(1)–C(1)–C(2)–C(3)	−4·9 (1)
O(2)–C(1)–C(2)–C(3)	175·5 (1)
O(3)–C(3)–C(2)–C(1)	1·3 (2)
O(4)–C(3)–C(2)–C(1)	−178·1 (1)

mated to be 1·25 and 1·70 in the carboxylic group and 1·40 and 1·60 in the carboxylate. This is in contrast to the situation found in potassium hydrogen malonate, where the two halves of the hydrogen malonate ion are related to each other through a twofold axis (Sime, Speakman & Parthasarathy, 1970).

Table 5. *The geometry of the water molecule and the hydrogen bonds.*

Distances are in Å and angles in degrees. The superscripts indicate atoms related to *x,y,z* in Table 2: (ii) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iii) $1 - x, -y, 1 - z$; (iv) $1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

O(5)–H(4)	0·814 (2)	$O(4^{ii})\cdots O(5)$	2·749 (1)
O(5)–H(5)	0·792 (1)	$O(4^{ii})\cdots H(5)$	1·958 (1)
H(4)–O(5)–H(5)	110·1 (3)	$O(4^{ii})\cdots H(5)–O(5)$	175·5 (2)
$O(3^{iii})\cdots O(5)$	2·789 (2)	$O(4^{iv})\cdots O(2)$	2·589 (1)
$O(3^{iii})\cdots H(4)$	1·975 (2)	$O(4^{iv})\cdots H(3)$	1·721 (2)
$O(3^{iii})\cdots H(4)–O(5)$	177·3 (1)	$O(4^{iv})\cdots H(3)–O(2)$	173·8 (1)

The two water H atoms and the carboxylic H atom are within hydrogen-bonding distance of the O atoms ($H\cdots O$ 2·2 Å). The geometry of the hydrogen bonds and the water molecule are given in Table 5. The short hydrogen bond $O(4^{iv})\cdots O(2)$ linking the hydrogen malonate ions end-to-end is most probably asymmetric.

References

ALBERTSSON, J., OSKARSSON, Å. & SVENSSON, C. (1978). *Acta Cryst.* B**34**, 2737–2743.

BRIGGMAN, B. & OSKARSSON, Å. (1977). *Acta Cryst.* B**33**, 1900–1906.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KARLE, J. & KARLE, I. L. (1963). *Acta Cryst.* **16**, 969–975.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

OSKARSSON, Å. (1976). *Acta Chem. Scand. Ser. B*, **30**, 125–132.

OSKARSSON, Å. (1978). *Acta Cryst.* B**34**, 1350–1352.

SIME, J. G., SPEAKMAN, J. C. & PARTHASARATHY, R. (1970). *J. Chem. Soc. A*, pp. 1919–1923.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

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New Form of *trans*-Chlorobis(2,4-pentanedionato)(triphenylphosphine)technetium(III)

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Abstract. $C_{28}H_{29}ClO_4PTc$, $M_r = 595$, triclinic, $P\bar{1}$, $a = 15·330$ (8), $b = 10·369$ (5), $c = 9·309$ (6) Å, $\alpha = 106·82$ (11), $\beta = 104·58$ (8), $\gamma = 92·13$ (7)°, $U = 1361$ Å^3, $D_c = 1·45$ g cm^{-3}, $Z = 2$, $\mu = 7·1$ cm^{-1}. The title complex was synthesized by treating *trans*-[Tc(PPh$_3$)$_2$Cl$_4$] with anhydrous 2,4-pentanedione. The X-ray diffraction study of this new crystalline form, designated β, confirms the molecular structural details for the α modification [Bandoli, Clemente & Mazzi (1977). *J. Chem. Soc. A*, pp. 1837–1844].

Introduction. *trans*-Tetrachlorobis(triphenylphosphine)technetium(IV) (1 g) was heated under reflux in anhydrous 2,4-pentanedione (30 ml) for 12 h, under nitrogen. The orange-red solution was evaporated to dryness *in vacuo* and the residue was treated with acetone (0·5 ml) and filtered. The yellow powder was washed with ethanol (1 ml) and then with diethyl ether (2 ml). Yellow-orange crystals were obtained from an acetone/diethyl ether mixture (yield *ca* 50%), where this second crystalline phase seems to be the most stable, for all efforts to grow crystals of the original modification (Bandoli, Clemente & Mazzi, 1977), designated α, were unsuccessful. A poorly formed crystal (0·07 × 0·13 × 0·33 mm) was used for data collection on an automatic Philips four-circle