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## Structure of Manganese Dihydrogen Diphthalate Dihydrate

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**Abstract.** Mn(C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, monoclinic, *P*2<sub>1</sub>/*c*, *Z* = 2, *a* = 13·018 (6), *b* = 5·158 (1), *c* = 12·940 (6) Å, β = 113·90 (3)°, *V* = 794·4 (6) Å<sup>3</sup> at 293 K, *D*<sub>c</sub> = 1·761 g cm<sup>-3</sup>; single-crystal diffractometer data up to sin θ/λ = 0·65 Å<sup>-1</sup>. The two carboxyl groups of the phthalate group are mutually orthogonal. Their relative orientation is determined by packing effects rather than by conjugation.

**Introduction.** Colourless, plate-shaped crystals were obtained from an aqueous solution of manganese carbonate and an excess of phthalic acid. A crystal 0·25 × 0·12 × 0·09 mm cut from a larger specimen was selected.

Data were collected in two quadrants of reciprocal space, up to sin θ/λ = 0·65 and 0·36 Å<sup>-1</sup>, respectively, on a Syntex *P*2<sub>1</sub> diffractometer with Nb-filtered Mo *K*α radiation and a step-scanning mode. 2215 reflections were obtained of which 1837 were unique. The step-scan data were analysed by profile analysis (Blessing, Coppens & Becker, 1974). Three standard reflections observed after every 50 reflections showed no significant fluctuations. The data were corrected for absorption (μ = 9·26 cm<sup>-1</sup>); the transmission factor ranged from 0·892 to 0·930. A weight was assigned to each observation according to  $w(I) = [\sigma^2(I)_{\text{counting}} + (0\cdot02I)^2]^{-1}$ . After equivalent reflections had been averaged, 1541 reflections had  $F_o^2 > 0$  and were used for the structure refinement. The structure was determined by direct methods with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Initial attempts failed because the Mn atom occupies a special position, resulting in a non-uniform distribution of *E* values over the parity groups. However, after the *E* values had been rescaled to approach the values proposed by Main (1976), a solution was obtained. Scattering factors were from *International Tables for X-ray Crystallography* (1974), except those for H which were from Stewart, Davidson & Simpson (1965). For the Mn atom the anomalous-dispersion factors of Cromer & Liberman (1970) were applied. Extinction was found to be negligible. The final *R*(*F*) = 10·7%.

Table 1. *Positional parameters*

	<i>x</i>	<i>y</i>	<i>z</i>
Mn	0·5	0·0	0·0
C(1)	0·2206 (3)	0·3372 (7)	0·8396 (3)
C(2)	0·1412 (3)	0·1396 (8)	0·8062 (4)
C(3)	0·0730 (3)	0·1044 (9)	0·6930 (4)
C(4)	0·0848 (3)	0·2601 (9)	0·6129 (4)
C(5)	0·1658 (3)	0·4528 (9)	0·6453 (3)
C(6)	0·2342 (3)	0·4929 (8)	0·7582 (3)
C(7)	0·2850 (3)	0·3769 (8)	0·9641 (3)
C(8)	0·3214 (3)	0·7068 (7)	0·7934 (3)
O(1)	0·3695 (2)	0·2599 (5)	0·0237 (2)
O(2)	0·2317 (2)	0·5392 (6)	0·0040 (2)
O(3)	0·3720 (2)	0·7451 (5)	0·8972 (2)
O(4)	0·3385 (2)	0·8329 (5)	0·7178 (2)
O(5)	0·4830 (3)	0·2027 (6)	0·8469 (2)
H(1)	0·132 (2)	0·051 (7)	0·863 (2)
H(2)	0·018 (3)	−0·026 (7)	0·672 (2)
H(3)	0·038 (2)	0·235 (6)	0·534 (2)
H(4)	0·178 (3)	0·546 (7)	0·589 (3)
H(5)	0·265 (3)	0·568 (8)	0·078 (3)
H(6)	0·433 (3)	0·121 (8)	0·787 (3)
H(7)	0·537 (3)	0·207 (9)	0·830 (3)

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Table 2. Bond distances (Å) and angles (°)

C(1)–C(2)	1.390 (6)	C(3)–H(2)	0.94 (3)
C(2)–C(3)	1.384 (6)	C(4)–H(3)	0.96 (3)
C(3)–C(4)	1.368 (7)	C(5)–H(4)	0.94 (4)
C(4)–C(5)	1.384 (6)	O(2)–H(5)	0.89 (4)
C(5)–C(6)	1.384 (5)	O(5)–H(6)	0.89 (3)
C(6)–C(1)	1.391 (6)	O(5)–H(7)	0.81 (5)
C(1)–C(7)	1.499 (5)	Mn–O(3)	2.116 (2)
C(6)–C(8)	1.515 (5)	Mn–O(3')	2.116 (2)
C(7)–O(1)	1.217 (4)	Mn–O(5)	2.170 (3)
C(7)–O(2)	1.318 (6)	Mn–O(5')	2.170 (3)
C(8)–O(3)	1.249 (4)	Mn–O(1)	2.280 (3)
C(8)–O(4)	1.267 (5)	Mn–O(1')	2.280 (3)
C(2)–H(1)	0.92 (4)		
C(6)–C(1)–C(2)	119.7 (3)	C(4)–C(5)–H(4)	119 (2)
C(6)–C(1)–C(7)	123.2 (3)	C(6)–C(5)–H(4)	120 (2)
C(2)–C(1)–C(7)	117.1 (4)	C(5)–C(6)–C(1)	119.2 (4)
C(1)–C(2)–C(3)	120.1 (4)	C(5)–C(6)–C(8)	120.6 (4)
C(1)–C(2)–H(1)	116 (2)	C(1)–C(6)–C(8)	120.2 (3)
C(3)–C(2)–H(1)	123 (2)	C(1)–C(7)–O(1)	125.6 (4)
C(2)–C(3)–C(4)	120.3 (4)	C(1)–C(7)–O(2)	110.7 (3)
C(2)–C(3)–H(2)	119 (2)	O(1)–C(7)–O(2)	123.4 (3)
C(4)–C(3)–H(2)	121 (2)	C(6)–C(8)–O(3)	116.3 (4)
C(3)–C(4)–C(5)	119.8 (4)	C(6)–C(8)–O(4)	119.1 (3)
C(3)–C(4)–H(3)	120 (2)	O(3)–C(8)–O(4)	124.6 (3)
C(5)–C(4)–H(3)	120 (2)	C(7)–O(2)–H(5)	115 (3)
C(4)–C(5)–C(6)	120.8 (4)	H(6)–O(5)–H(7)	101 (4)

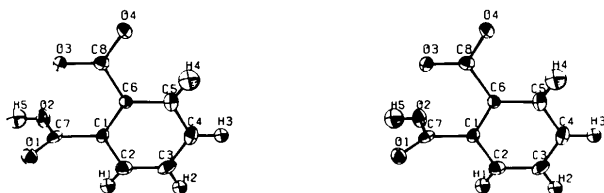


Fig. 1. Stereoscopic view of the hydrogen phthalate group. The thermal ellipsoids are the 50% probability surfaces.

Table 3. Hydrogen bonds

O–H...O	O...O	H...O	O–H–O
O(2)–H(5)...O(4)	2.628 (4) Å	1.74 (3) Å	171 (4)°
O(5)–H(6)...O(4)	2.724 (4)	1.91 (4)	152 (4)
O(5)–H(7)...O(4)	2.851 (5)	2.06 (5)	163 (4)

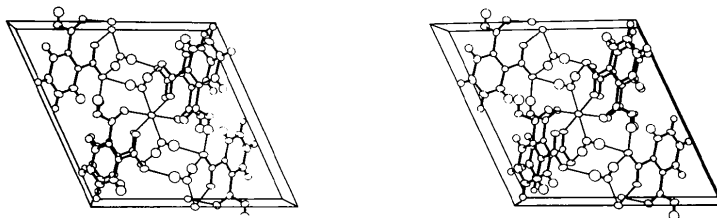


Fig. 2. Stereoscopic view of the molecular packing.

$R_w(F) = 3.9\%$  and a goodness of fit  $S = 3.03$ .\* The relatively high value of  $R(F)$  can be attributed to the large number of weak reflections, due to the small size of the crystal. The positional parameters are reported in Table 1, the observed bond lengths and angles in Table 2. A stereoscopic view of the phthalate group is shown in Fig. 1 and of the molecular packing in Fig. 2.†

**Discussion.** This determination has been undertaken in the framework of a study of hydrogen bonding in acid phthalates.  $\text{Mn}(\text{C}_8\text{H}_5\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  shows three hydrogen bonds, reported in Table 3. One, involving the phthalate proton, is relatively strong; the other two, involving the water molecule, are of moderate strength. All three hydrogen bonds have the same acceptor atom. The title compound has no short intramolecular hydrogen bond as in  $\text{LiC}_8\text{H}_5\text{O}_4 \cdot 2\text{H}_2\text{O}$  (Gonschorek & Küppers, 1975) and  $\text{Cu}(\text{C}_8\text{H}_5\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  (Cingi, Guastini, Musatti & Nardelli, 1969; Bartl & Küppers, 1978).

The Mn atom shows a distorted octahedral coordination of six O atoms, two from the hydrate and four from the phthalate groups. The O–Mn–O angles range from 87.8 to 92.2°. Least-squares planes through C(1), C(7), O(1), O(2) and C(6), C(8), O(3), O(4) make angles of 88 and 5° respectively with the plane of the benzene ring, resulting in a mutual orthogonality of the carboxyl groups. In several other acid phthalates, the un-ionized and ionized carboxyl groups make angles of approximately 30 and 70° respectively with the plane of the benzene ring (Smith, 1975). Comparison with the present study shows that the relative orientation of the carboxyl groups is determined by packing effects rather than by conjugation with the benzene ring.

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\*  $S = [\sum w(F_o - F_c)^2 / (\text{NO} - \text{NV})]^{1/2}$ .

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33346 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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## Di- $\mu$ -chloro-bis(tetracarbonylmanganese)

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**Abstract.**  $\{\text{Mn}(\text{CO})_4\}_2\text{Cl}_2$ , monoclinic,  $P2_1/c$ ,  $a = 9.421$  (2),  $b = 11.589$  (2),  $c = 12.767$  (1) Å,  $\beta = 109.68$  (2)°,  $Z = 4$ ,  $D_o = 2.02$ ,  $D_c = 2.05$  g cm<sup>-3</sup>. The complex has long Mn–C bonds [average: 1.888 (2) Å, axial; 1.816 (2) Å, equatorial] and shows a pronounced *trans* influence.

**Introduction.** Initial cell dimensions were determined by precession photography (Mo  $K\alpha$  radiation). Systematic absences ( $h0l$  for  $l$  odd,  $0k0$  for  $k$  odd) indicated space group  $P2_1/c$ .

A thin plate (*ca* 0.01 mm thick, dominant faces  $\{100\}$ ) was sealed in a Lindemann-glass tube and mounted on a Hilger & Watts Y290 four-circle diffractometer, with **b** several degrees from the  $\phi$  axis. Cell parameters and the orientation matrix were refined by least squares (12 reflexions,  $34 < 2\theta < 48^\circ$ ). Intensities were collected for all unique reflexions with  $2\theta \leq 55^\circ$  (Mo  $K\alpha$  radiation, Zr filter,  $\lambda = 0.71069$  Å,  $\theta$ – $2\theta$  scan mode). No reflexions were intense enough to require attenuation. Three standard reflexions showed a steady decay of about 10% during data collection; linear decay functions were calculated and applied to the data together with absorption corrections (Sheldrick & Sheldrick, 1970), adapted for four-circle geometry [ $\mu = 24.53$  cm<sup>-1</sup>; a minimum in the value of  $R_w = (\sum \Delta^2 / \sum wF_o^2)^{1/2}$  was obtained for  $\mu t = 0.0235$ , corresponding to a thickness of 0.0095 mm]. Of the

2057 measured reflexions with net positive recorded intensity, 57 were rejected because of plate edge effects on absorption.

Atoms were located by automatic direct methods and Fourier techniques and refined by full-matrix least squares to a minimum value of  $\sum w\Delta^2$  [ $\Delta = |F_o| - |F_c|$ ,  $w = 1/\sigma^2(F_o)$ ]. Scattering factors were those of Cromer

Table 1. *Atomic coordinates* ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
Mn(1)	5932 (1)	3791 (1)	3245 (1)
Mn(2)	1910 (1)	3734 (1)	2234 (1)
Cl(1)	3887 (2)	4895 (1)	3445 (1)
Cl(2)	3952 (2)	2619 (1)	2048 (1)
C(11)	5867 (7)	4697 (5)	1999 (4)
O(11)	5854 (6)	5211 (4)	1253 (3)
C(12)	7338 (7)	4749 (5)	4161 (4)
O(12)	8236 (5)	5333 (4)	4728 (3)
C(13)	7396 (7)	2910 (5)	3038 (4)
O(13)	8325 (5)	2378 (4)	2913 (4)
C(14)	5945 (6)	2884 (5)	4478 (4)
O(14)	6001 (6)	2340 (4)	5220 (3)
C(21)	1932 (7)	4676 (5)	1037 (5)
O(21)	1931 (6)	5244 (4)	328 (3)
C(22)	435 (8)	4628 (5)	2439 (4)
O(22)	–477 (6)	5168 (4)	2575 (4)
C(23)	495 (7)	2814 (5)	1282 (5)
O(23)	–400 (6)	2262 (4)	686 (4)
C(24)	1947 (7)	2789 (5)	3448 (4)
O(24)	1962 (6)	2224 (4)	4166 (4)