

Os(2)—Os(3) is slightly longer. The Os—P length is longer than the 2.285 (5) Å in Os<sub>3</sub>(CO)<sub>11</sub>P(OCH<sub>3</sub>)<sub>3</sub> (Benfield, Johnson, Raithby & Sheldrick, 1978). In the latter complex the introduction of the phosphite ligand also has little effect on individual Os—Os distances but causes an expansion of the twinned cuboctahedral ligand polyhedron and consequently the Os<sub>3</sub> triangle. In H<sub>2</sub>Os<sub>3</sub>(CO)<sub>9</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> little expansion of the icosahedral ligand polyhedron is observed. In this case a small increase in size of the ligand polyhedron might cause the molecule to adopt the twinned-cuboctahedral geometry which would require energetically unfavourable ligand rearrangement.

The distribution of ligands is similar to that in H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub> (Orpen *et al.*, 1978) where both hydrides bridge the short Os—Os edge. The phosphine ligand appears to have little increase in steric influence over the carbonyl in this case, the Os(1)—Os(2)—C(21) and Os(2)—Os(1)—P(1) angles being equal. The fact that hydride ligands exert a steric influence has been illustrated by Orpen (1978). The Os—Os—C(carbonyl) angles (mean 130.8°) involving Os(1), Os(2), C(11), C(12), C(22) and C(23) show that the carbonyls bend away from the short Os(1)—Os(2) edge. This indicates that in this molecule both hydrides also bridge the short edge and lie above and below the Os<sub>3</sub> plane.

Although the light atoms were not located as accurately as in the neutron study (Orpen *et al.*, 1978) the trends in Os—C distances are the same. The Os—C *trans* to the proposed hydride positions (mean 1.890 Å) are shorter than the equatorial Os—C bonds (mean 1.923 Å) which are in turn shorter than the axial bonds associated with Os(3) (mean 1.934 Å). This may be explained in terms of competition for back donation of electron density from the Os atoms. The hydrides have

no empty orbitals of suitable energy to compete for back donation with the carbonyls *trans* to them so the Os—C bonds are short. When two carbonyls are *trans* to each other there is considerable competition so the Os—C bonds are individually longer. The two Os(1)—C distances (mean 1.864 Å) are shorter than the two equivalent Os(2)—C distances (mean 1.917 Å). This may be caused by the phosphine pushing electron density on to Os(1) which is taken up by stronger back-bonding to the carbonyls. The phosphine is a better  $\sigma$  donor but a poorer  $\pi$  acceptor than the carbonyl ligand.

The carbonyls are all approximately linear with a mean Os—C—O angle of 177.8°; the average C—O distance is 1.135 Å.

We thank the Science Research Council for financial support. Calculations were performed with the University of Cambridge IBM 370/165 computer and programs written by Dr G. M. Sheldrick; the figure was drawn with *PLUTO* written by Dr W. D. S. Motherwell.

#### References

- BENFIELD, R. E., JOHNSON, B. F. G., RAITHY, P. R. & SHELDRIK, G. M. (1978). *Acta Cryst.* **B34**, 666–667.  
 BRYAN, E. G., JOHNSON, B. F. G. & LEWIS, J. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1328–1330.  
 CHURCHILL, M. R., HOLLANDER, F. J. & HUTCHINSON, J. P. (1977). *Inorg. Chem.* **16**, 2697–2700.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 ORPEN, A. G. (1978). *J. Organomet. Chem.* **159**, C1–C4.  
 ORPEN, A. G., RIVERA, A. V., BRYAN, E. G., PIPPARD, D., SHELDRIK, G. M. & ROUSE, K. D. (1978). *J. Chem. Soc. Chem. Commun.* pp. 723–724.  
 ZUCCARO, C. (1979). In preparation.

*Acta Cryst.* (1979). **B35**, 2212–2214

## Manganese(II) Malonate Dihydrate: a Reinvestigation

BY T. LIS AND J. MATUSZEWSKI

*Institute of Chemistry, The University, 50-383 Wrocław, Poland*

(Received 28 April 1979; accepted 21 May 1979)

**Abstract.** C<sub>3</sub>H<sub>2</sub>O<sub>4</sub><sup>2-</sup> · Mn<sup>2+</sup> · 2H<sub>2</sub>O, Mn(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>) · 2H<sub>2</sub>O, orthorhombic, *Pca*2<sub>1</sub>, *a* = 9.62 (1), *b* = 7.36 (1), *c* = 8.33 (1) Å, *M<sub>r</sub>* = 193.0, *V* = 589.8 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 2.17 Mg m<sup>-3</sup>,  $\mu$ (Mo *K* $\alpha$ ,  $\lambda$  = 0.71069 Å) = 2.32 mm<sup>-1</sup>. Each Mn<sup>2+</sup> ion is octahedrally coordinated by four carboxylate O atoms and two *trans* water O atoms. Mn—O distances lie between 2.127 (3) and

2.232 (5) Å. Four O atoms in the malonate ligand are involved in coordination to three different Mn<sup>2+</sup> ions forming an extensive polymeric network parallel to (001). Each H atom from water molecules is involved in a hydrogen bond linking the layers along *c*. The structure was refined to an *R* of 0.032 for 760 diffractometer data.

0567-7408/79/092212-03\$01.00

© 1979 International Union of Crystallography

**Introduction.** As part of our study on the stereochemistry of Mn malonate complexes (Lis, Matuszewski & Jezowska-Trzebiatowska, 1977*a,b*; Lis & Matuszewski, 1979) the present work was undertaken to establish the variability of the mode of Mn<sup>2+</sup> coordination by malonate ligands in the crystalline state. Preliminary data for these crystals have been given by Gupta & Chand (1977) who solved the structure by photographic methods to  $R = 0.18$  for 460 reflexions but have not reported the positional parameters.

An irregularly shaped crystal  $0.15 \times 0.15 \times 0.15$  mm was used for data collection on a Syntex  $P2_1$  automated diffractometer with monochromated Mo  $K\alpha$  radiation and the  $\theta$ - $2\theta$  scan technique. The lattice parameters were similar to those previously reported (Gupta & Chand, 1977; Walter-Lévy, Perrotey & Visser, 1973). The intensity of one periodically monitored reflexion displayed no observable trend. The data were corrected for Lorentz and polarization effects. Of 1055 accessible reflexions in the range  $10 \leq 2\theta \leq 70^\circ$ , 760 with  $I > 2\sigma(I)$  were used for the structure determination. All calculations were performed with the Syntex XTL/XTLE Structure Determination System (1976). Neutral-atom scattering factors were those listed in *International Tables for X-ray Crystallography* (1974); both real and imaginary components of the anomalous dispersion were included for all non-H atoms.

The Mn-Mn vectors were identified in a Patterson function. The noncentrosymmetric space group  $Pca2_1$  was assumed (Gupta & Chand, 1977). The  $z$  coordinate of Mn was held invariant to fix the origin. All non-H atoms were found from difference syntheses. The trial structure was refined by full-matrix least squares first with isotropic ( $R = 0.065$ ) then anisotropic thermal parameters to  $R = 0.038$  and  $R_w = 0.043$ . At this stage a difference synthesis revealed the positions of the H

atoms. They were included with isotropic temperature factors, and further refinement yielded a final  $R = 0.032$  and  $R_w = 0.032$ .<sup>\*</sup> Atomic coordinates are listed in Table 1. The final difference synthesis was featureless.

The crystal structure is depicted in Fig. 1, which also gives the numbering scheme. Bond lengths and angles are presented in Table 2.

<sup>\*</sup> Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34486 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Mn-O(1)	2.158 (3)	Mn-O(2)	2.127 (3)
Mn-O(3)	2.210 (3)	Mn-O(4)	2.147 (4)
Mn-O(5)	2.161 (6)	Mn-O(6)	2.232 (5)
C(1)-O(1)	1.267 (6)	C(2)-O(3)	1.255 (6)
C(1)-O(2)	1.244 (6)	C(2)-O(4)	1.262 (6)
C(3)-C(1)	1.507 (8)	C(3)-C(2)	1.518 (7)
C(3)-H(5)	1.02 (8)	C(3)-H(6)	0.90 (9)
O(1)-Mn-O(2)	93.3 (2)	O(1)-Mn-O(3)	81.7 (2)
O(1)-Mn-O(4)	165.5 (2)	O(1)-Mn-O(5)	93.3 (2)
O(1)-Mn-O(6)	91.8 (2)	O(2)-Mn-O(3)	173.2 (2)
O(2)-Mn-O(4)	99.3 (2)	O(2)-Mn-O(5)	89.0 (2)
O(2)-Mn-O(6)	91.3 (2)	O(3)-Mn-O(4)	86.3 (2)
O(3)-Mn-O(5)	86.7 (2)	O(3)-Mn-O(6)	93.5 (2)
O(4)-Mn-O(5)	94.1 (2)	O(4)-Mn-O(6)	80.7 (2)
O(5)-Mn-O(6)	174.8 (3)	C(1)-C(3)-C(2)	118.7 (5)
Mn-O(1)-C(1)	126.7 (4)	Mn-O(2)-C(1)	149.2 (5)
Mn-O(3)-C(2)	123.7 (4)	Mn-O(4)-C(2)	140.5 (4)
O(1)-C(1)-O(2)	121.4 (5)	O(3)-C(2)-O(4)	124.1 (5)
O(1)-C(1)-C(3)	119.9 (5)	O(3)-C(2)-C(3)	120.8 (5)
O(2)-C(1)-C(3)	118.8 (5)	O(4)-C(2)-C(3)	115.2 (5)

Table 1. The final positional parameters with e.s.d.'s in parentheses

	$x$	$y$	$z$
Mn	0.0573 (1)	0.2200 (1)	0.25 (fixed)
O(1)	-0.0686 (4)	0.4605 (4)	0.2784 (5)
O(2)	0.2466 (4)	0.3695 (4)	0.2470 (9)
O(3)	-0.1469 (4)	0.0860 (5)	0.2770 (5)
O(4)	0.1367 (4)	-0.0443 (5)	0.1909 (5)
O(5)	0.0823 (6)	0.1828 (9)	0.5057 (7)
O(6)	0.0412 (6)	0.2342 (7)	-0.0170 (7)
C(1)	-0.1919 (6)	0.4832 (7)	0.2288 (8)
C(2)	-0.2559 (6)	0.1404 (6)	0.2096 (7)
C(3)	-0.2653 (7)	0.3315 (8)	0.1418 (9)
H(1)	0.150 (9)	0.245 (8)	0.557 (8)
H(2)	0.023 (8)	0.134 (10)	0.564 (9)
H(3)	0.049 (6)	0.336 (7)	-0.088 (7)
H(4)	0.083 (13)	0.154 (19)	-0.083 (17)
H(5)	-0.207 (8)	0.299 (9)	0.043 (9)
H(6)	-0.347 (9)	0.338 (10)	0.088 (11)

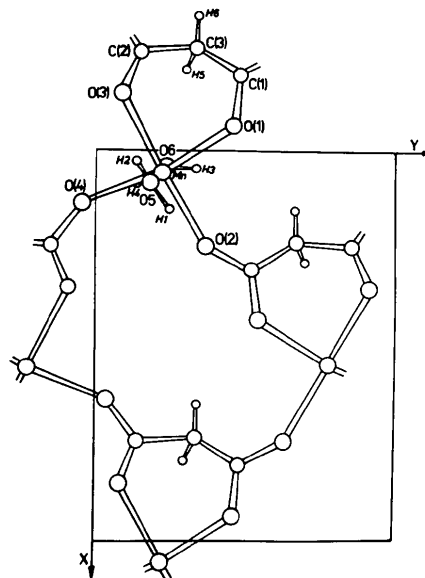


Fig. 1. The crystal structure of manganese(II) malonate dihydrate: projection on (001).

Table 3. *Geometry of the hydrogen bonds*

O—H...O	O...O	O—H	H...O	∠O—H...O
O(5)—H(1)—O(2) [ $\frac{1}{2} - x, y, \frac{1}{2} + z$ ]	2.939 (8) Å	0.90 (7) Å	2.08 (7) Å	158 (6)°
O(5)—H(2)—O(4) [ $-x, -y, \frac{1}{2} + z$ ]	2.803 (7)	0.83 (8)	1.98 (8)	172 (8)
O(6)—H(3)—O(1) [ $-x, 1 - y, z - \frac{1}{2}$ ]	2.833 (6)	0.96 (6)	1.88 (6)	178 (5)
O(6)—H(4)—O(3) [ $-x, -y, z - \frac{1}{2}$ ]	3.088 (6)	0.90 (15)	2.20 (15)	166 (12)

**Discussion.** The Mn atoms are octahedrally coordinated by four carboxylate O atoms from three different malonate ions and two *trans* water O atoms. All four O atoms of a malonate ligand participate in binding Mn<sup>2+</sup> ions. Thus, each malonate ligand is coordinated to three different Mn atoms (Fig. 1) forming an extensive two-dimensional net parallel to (001). In addition there is a network of hydrogen bonds holding the polymeric layers together. All four H atoms from the two water molecules are involved in hydrogen bonding: their parameters are summarized in Table 3.

All known carboxylates of Mn<sup>II</sup> crystallize as polymeric structures. However, the polymeric network of the Mn(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O crystals is quite different from that in Mn<sup>II</sup> formate (Osaki, Nakai & Watanabé, 1964), acetate (Tranqui, Burlet, Filhol & Thomas, 1977), propionate (Lis, 1977), citrate (Carrell & Glusker, 1973), ethylenediaminetetraacetate (Richards, Pedersen, Silverton & Hoard, 1964), malate (Karipides & Reed, 1976) and gluconate (Lis, 1979).

All bond lengths and angles in the C<sub>3</sub>H<sub>2</sub>O<sub>4</sub><sup>2-</sup> groups are unexceptional. The C—O lengths are practically equal [mean 1.257 (6) Å]. The malonate ligands are of the envelope type, which is rather common in such compounds (Butler & Snow, 1976). The C(1)—C(3)—C(2) angle of 118.7 (5)° is considerably distorted from tetrahedral. This confirms the suggestion (Karipides, Ault & Reed, 1977) that in malonate compounds in which there is a six-membered chelate ring the planes of the two carboxylate groups are twisted closer to the plane through the C-atom chain as a result of which the C—C—C angle is greater than 110°.

Reports of crystal structures of manganese malonate compounds are restricted to K<sub>3</sub>[Mn(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·2H<sub>2</sub>O and two modifications of K[Mn(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (Lis, Matuszewski & Jeżowska-Trzebiatowska, 1977a; Lis & Matuszewski, 1979). Comparison of the bond distances in Mn(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O and the [Mn(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup> ions is informative. The Mn<sup>III</sup>—H<sub>2</sub>O distances of 2.30 (2) Å are longer than those of Mn<sup>II</sup>—H<sub>2</sub>O [2.20 (3) Å] by

about 0.1 Å. This argues in favour of our earlier supposition that the bonds between Mn<sup>III</sup> ions and water molecules for the compounds investigated by us are extremely weak and may be easily disrupted in solution. The weakening of this bond in Mn<sup>III</sup> complexes explains the role of Mn ions in photosystem II, as water oxidants in the model given by Lawrence & Sawyer (1978).

### References

- BUTLER, K. R. & SNOW, M. R. (1976). *J. Chem. Soc. Dalton Trans.* pp. 251–258.
- CARRELL, H. L. & GLUSKER, J. P. (1973). *Acta Cryst.* B29, 638–640.
- GUPTA, M. P. & CHAND, P. (1977). *Curr. Sci.* 46, 557.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KARIPIDES, A., AULT, J. & REED, A. T. (1977). *Inorg. Chem.* 16, 3299–3302.
- KARIPIDES, A. & REED, A. T. (1976). *Inorg. Chem.* 15, 44–47.
- LAWRENCE, G. D. & SAWYER, D. T. (1978). *Coord. Chem. Rev.* 27, 173–193.
- LIS, T. (1977). *Acta Cryst.* B33, 2964–2966.
- LIS, T. (1979). *Acta Cryst.* B35, 1699–1701.
- LIS, T. & MATUSZEWSKI, J. (1979). *Pol. J. Chem.* To be published.
- LIS, T., MATUSZEWSKI, J. & JEŻOWSKA-TRZEBIATOWSKA, B. (1977a). *Acta Cryst.* B33, 1943–1946.
- LIS, T., MATUSZEWSKI, J. & JEŻOWSKA-TRZEBIATOWSKA, B. (1977b). *Proc. 3rd Int. Semin. Cryst. Chem. Coord. Organomet. Compd.*, Trzebieszowice, Poland, pp. 216–218.
- OSAKI, K., NAKAI, Y. & WATANABÉ, T. (1964). *J. Phys. Soc. Jpn.* 19, 717–723.
- RICHARDS, S., PEDERSEN, B., SILVERTON, J. V. & HOARD, J. L. (1964). *Inorg. Chem.* 3, 27–33.
- Syntex XTL/XTLE Structure Determination System* (1976). Cupertino: Syntex Analytical Instruments.
- TRANQUI, D., BURLET, P., FILHOL, A. & THOMAS, M. (1977). *Acta Cryst.* B33, 1357–1361.
- WALTER-LÉVY, L., PERROTEY, J. & VISSER, J. W. (1973). *Bull. Soc. Chim. Fr.* pp. 2596–2602.