

## Structure of Manganese(II) Glycolate Dihydrate

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**Abstract.**  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ , monoclinic,  $P2_1/c$ ,  $a = 11.637$  (13),  $b = 5.923$  (4),  $c = 12.570$  (13) Å,  $\beta = 92.30$  (9)°,  $M_r = 241.1$ ,  $V = 866$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.85$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ Å}) = 1.62$  mm<sup>-1</sup>, final  $R = 0.029$  and  $R_w = 0.033$  for 1138 reflexions. The Mn atom is octahedrally coordinated by one carboxylate O atom and one hydroxyl O atom from each glycolate ligand and two water O atoms in *cis* positions. In this way neutral molecules  $[\text{Mn}(\text{HOCH}_2\text{COO})_2(\text{H}_2\text{O})_2]$  are formed which are held together through hydrogen bonds. Mn–O distances range between 2.124 (3) and 2.225 (3) Å.

**Introduction.** This investigation was undertaken as part of a study on the stereochemistry of Mn<sup>II</sup> carboxylate salts. Single crystals of the compound were prepared by dissolving manganese(II) carbonate in an aqueous solution of glycolic acid, in the form of the 70% solution commercially available, and allowing the solution to stand, or to evaporate. Small crystals appear nearly colorless although clumps of larger crystals have a decided pink cast.

Examination of Weissenberg photographs showed that the crystals are monoclinic; systematic extinctions  $h0l$  with  $l$  odd and  $0k0$  with  $k$  odd uniquely determined the space group to be  $P2_1/c$ . An irregular crystal  $0.2 \times 0.3 \times 0.1$  mm was selected for the data collection. A Syntex  $P2_1$  diffractometer and Mo  $K\alpha$  radiation with a graphite monochromator were used for lattice-parameter and intensity measurements. The intensities were measured by the  $\theta$ – $2\theta$  scan technique. After each group of 20 reflexions two standards were measured; no significant change in intensity was observed. The data were corrected for Lorentz and polarization effects. Of 1399 accessible reflexions in the range  $8.0 \leq 2\theta \leq 50^\circ$ , 1138 with  $I > 3\sigma(I)$  were used for the structure determination. All calculations were performed on a Nova 1200 computer with programs supplied by Syntex. Neutral-atom scattering factors were those listed in *International Tables for X-ray Crystallography* (1974).

The Mn–Mn vectors were identified in a Patterson function. All non-H atoms were found from difference syntheses. Full-matrix least-squares refinement first

Table 1. Final positional parameters

	<i>x</i>	<i>y</i>	<i>z</i>
Mn	0.25848 (5)	0.1385 (1)	0.15454 (4)
O(1)	0.3113 (3)	0.1223 (5)	–0.0097 (2)
O(2)	0.4110 (3)	–0.0692 (5)	–0.1258 (2)
O(3)	0.3120 (3)	–0.2071 (5)	0.1301 (3)
O(4)	0.1604 (3)	0.4438 (4)	0.1351 (3)
O(5)	–0.0085 (2)	0.6134 (4)	0.1207 (2)
O(6)	0.0753 (3)	0.0391 (5)	0.1272 (3)
O(7)	0.4135 (3)	0.3108 (5)	0.1978 (3)
O(8)	0.2309 (3)	0.1048 (6)	0.3238 (3)
C(1)	0.3626 (3)	–0.0525 (7)	–0.0397 (3)
C(2)	0.3661 (4)	–0.2546 (7)	0.0326 (4)
C(3)	0.0524 (3)	0.4417 (6)	0.1260 (3)
C(4)	–0.0082 (4)	0.2158 (6)	0.1228 (4)
H(21)	0.444 (4)	–0.311 (7)	0.043 (4)
H(22)	0.328 (4)	–0.371 (7)	–0.006 (3)
H(41)	–0.051 (3)	0.210 (6)	0.053 (3)
H(42)	–0.052 (4)	0.212 (7)	0.178 (3)
H(71)	0.426 (4)	0.383 (7)	0.259 (4)
H(72)	0.482 (5)	0.269 (9)	0.181 (4)
H(81)	0.156 (7)	0.110 (10)	0.343 (5)
H(82)	0.256 (9)	0.195 (16)	0.358 (8)
H(3)	0.269 (7)	–0.291 (13)	0.151 (6)
H(6)	0.024 (5)	–0.099 (10)	0.119 (5)

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

Mn–O(1)	2.180 (2)	Mn–O(4)	2.147 (2)
Mn–O(3)	2.165 (3)	Mn–O(6)	2.225 (3)
Mn–O(7)	2.124 (3)	Mn–O(8)	2.173 (3)
O(1)–C(1)	1.260 (4)	O(4)–C(3)	1.257 (4)
O(2)–C(1)	1.243 (4)	O(5)–C(3)	1.240 (4)
O(3)–C(2)	1.428 (5)	O(6)–C(4)	1.427 (4)
C(1)–C(2)	1.503 (5)	C(3)–C(4)	1.512 (5)
C(2)–H(21)	0.97 (5)	C(4)–H(41)	0.99 (4)
C(2)–H(22)	0.95 (4)	C(4)–H(42)	0.88 (4)
O(1)–Mn–O(3)	74.4 (2)	O(1)–Mn–O(4)	95.6 (2)
O(1)–Mn–O(6)	98.4 (2)	O(1)–Mn–O(7)	89.7 (2)
O(1)–Mn–O(8)	168.9 (2)	O(3)–Mn–O(4)	159.2 (2)
O(3)–Mn–O(6)	90.4 (2)	O(3)–Mn–O(7)	104.1 (2)
O(3)–Mn–O(8)	96.1 (2)	O(4)–Mn–O(6)	72.8 (2)
O(4)–Mn–O(7)	93.8 (2)	O(4)–Mn–O(8)	95.2 (2)
O(6)–Mn–O(7)	164.8 (2)	O(6)–Mn–O(8)	87.1 (2)
O(7)–Mn–O(8)	87.2 (2)		
Mn–O(1)–C(1)	118.3 (3)	Mn–O(3)–C(2)	116.6 (3)
Mn–O(4)–C(3)	121.8 (3)	Mn–O(6)–C(4)	117.3 (3)
O(1)–C(1)–O(2)	124.2 (4)	O(4)–C(3)–O(5)	124.3 (4)
O(1)–C(1)–C(2)	118.4 (4)	O(4)–C(3)–C(4)	118.3 (4)
O(2)–C(1)–C(2)	117.4 (4)	O(5)–C(3)–C(4)	117.4 (4)
O(3)–C(2)–C(1)	111.1 (4)	O(6)–C(4)–C(3)	109.4 (4)

Table 3. *Geometry of the hydrogen bonds (Å and degrees)*

O—H...O	O...O	O—H	H...O	∠O—H...O
O(7)—H(71)...O(2) ( $x, \frac{1}{2} - y, \frac{1}{2} + z$ )	2.696 (4)	0.89 (5)	1.83 (4)	163 (4)
O(7)—H(72)...O(2) ( $1 - x, -y, -z$ )	2.681 (4)	0.87 (5)	1.87 (5)	154 (5)
O(8)—H(81)...O(5) ( $-x, y - \frac{1}{2}, \frac{1}{2} - z$ )	2.708 (4)	0.91 (8)	1.80 (8)	179 (7)
O(8)—H(82)...O(1) ( $x, \frac{1}{2} - y, \frac{1}{2} + z$ )	2.777 (4)	0.74 (10)	2.06 (10)	162 (10)
O(3)—H(3)...O(4) ( $x, y - 1, z$ )	2.721 (4)	0.76 (8)	2.02 (8)	153 (8)
O(6)—H(6)...O(5) ( $x, y - 1, z$ )	2.704 (3)	1.01 (6)	1.75 (6)	156 (5)

with isotropic, then anisotropic, thermal parameters gave  $R = 0.067$  and  $0.043$  respectively. A difference synthesis at this stage showed all H atoms. They were included with isotropic temperature factors, and further refinement yielded a final  $R = 0.029$  and  $R_w = 0.033$ . 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.

**Discussion.** The Mn atom is octahedrally coordinated by one carboxylate O atom and one hydroxyl O atom from each glycolate ligand and two water O atoms in *cis* positions. The structure is built up from discrete molecules  $[\text{Mn}(\text{HOCH}_2\text{COO})_2(\text{H}_2\text{O})_2]$  held together through hydrogen bonds. The data on these hydrogen bonds are given in Table 3.

The overall structure of the title compound is similar to that of zinc glycolate dihydrate (Fischinger & Webb, 1969) but different from that of copper(II) glycolate dihydrate (Prout, Armstrong, Carruthers,

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34903 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

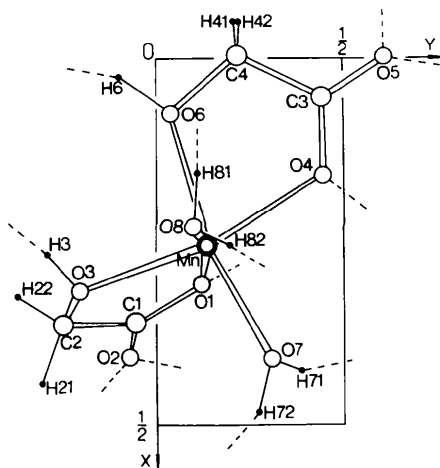


Fig. 1. The crystal structure of  $\text{Mn}^{\text{II}}$  glycolate dihydrate projected on the (001) plane.

Table 4. *Analysis of the configuration of the glycolate anions*

(a) Distances (Å) from planes through glycolate anions (atoms used to define the planes are indicated by an asterisk)

O(1)*	0.000 (3)	O(4)*	-0.001 (3)
O(2)*	0.000 (3)	O(5)*	-0.001 (3)
C(1)*	0.000 (4)	C(3)*	0.004 (4)
C(2)*	0.000 (5)	C(4)*	-0.001 (4)
O(3)	-0.063 (3)	O(6)	0.039 (3)
H(3)	0.42 (7)	H(6)	0.10 (6)

(b) Conformational angles ( $^\circ$ )

H(3)—O(3)—C(2)—C(1)	132 (7)
H(6)—O(6)—C(4)—C(3)	-176 (3)
O(3)—C(2)—C(1)—O(1)	-2.7 (7)
O(6)—C(4)—C(3)—O(4)	-2.2 (5)
O(3)—C(2)—C(1)—O(2)	177.3 (6)
O(6)—C(4)—C(3)—O(5)	178.6 (4)

Forrest, Murray-Rust & Rossotti, 1968), where the water molecules are in *trans* positions. (The crystallographic system and cell parameters suggest isomorphism of Mn and Zn crystals.)

The configuration of the C—C—O group of each molecule is planar (Table 4). There is also a tendency for the O(3) or O(6) hydroxy atoms to lie in this plane. Similar trends have been noted in other structures containing the glycolate moiety (Golič & Speakman, 1965; Colton & Henn, 1965; Johnson, Gabe, Taylor & Rose, 1965; Fischinger & Webb, 1969; Prout *et al.*, 1968; Ellison, Johnson & Levy, 1971; Pijper, 1971) as well as in other hydroxycarboxylate salts of  $\text{Mn}^{\text{II}}$ , such as citrate (Carrell & Glusker, 1973), malate (Karipides & Reed, 1976) and gluconate (Lis, 1979). The conformational phenomena of  $\alpha$ -hydroxycarbonyl systems have been investigated by Newton & Jeffrey (1977) using *ab initio* molecular-orbital theory.

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## 1,1,1,2,2,2,3,3,3-Nonacarbonyl-2-ethylene-1,3- $\mu$ -hydrido-1,3- $\mu$ -(methylthiolato)-triangulo-triosmium

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**Abstract.**  $[\text{Os}_3(\text{C}_2\text{H}_4)(\text{CH}_3\text{S})(\text{CO})_9\text{H}]$ ,  $\text{C}_{12}\text{H}_8\text{O}_9\text{Os}_3\text{S}$ , monoclinic,  $P2_1/n$ ,  $a = 10.333$  (4),  $b = 15.735$  (5),  $c = 11.792$  (4) Å,  $\beta = 98.07$  (2)°,  $U = 1898.3$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 3.144$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 20.17$  mm<sup>-1</sup>. Final  $R = 0.055$  for 2014 unique observed diffractometer data. The Os atoms lie at the vertices of an approximately equilateral triangle. The ethylene ligand  $\pi$ -bonds to an equatorial site on one Os atom and is coplanar with the Os<sub>3</sub> plane. The thiol group and the hydride bridge the other two Os atoms. The hydride position is inferred from the arrangement of the carbonyl ligands, three of which are terminally bound to each metal.

**Introduction.**  $[\text{Os}_3(\text{CH}_3\text{S})(\text{CO})_9\text{H}]$  has a high chemical reactivity and forms a wide range of adducts with small molecules. The reactivity is associated with the variable coordination of the S ligand which may change from face-capping to edge-bridging. An X-ray analysis of the title compound was undertaken to establish the coordination modes of the ethylene and thiol ligands in the solid state. A preliminary report has appeared (Johnson, Lewis, Pippard & Raithby, 1978).

Reaction of  $[\text{Os}_3(\text{CH}_3\text{S})(\text{CO})_9\text{H}]$  with ethylene at room temperature yielded a yellow solid. Upon recrystallization from pentane, yellow crystals, in the form of approximately equidimensional blocks, were deposited. Intensities were measured on a Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation and a crystal  $0.200 \times 0.125 \times 0.075$  mm.  $L_p$  and semi-empirical absorption corrections (based on a pseudo-ellipsoid model and 241 azimuthal scan data from nine independent reflections)

were applied; transmission factors ranged from 0.416 to 0.994 for the full data set. The 3795 reflections recorded in the range  $1.5 < \theta < 25.0^\circ$  were averaged to give 2014 unique observed [ $F > 5\sigma(F)$ ] intensities. Cell

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

	x	y	z
Os(1)	5429 (1)	4154 (1)	2681 (1)
Os(2)	3330 (1)	3123 (1)	1622 (1)
Os(3)	5960 (1)	2556 (1)	1722 (1)
S(1)	6235 (6)	3927 (4)	892 (6)
C(1)	8030 (32)	4169 (20)	1065 (30)
C(11)	6993 (25)	4710 (17)	3307 (23)
O(11)	7862 (21)	5046 (15)	3808 (20)
C(12)	4478 (27)	5149 (19)	2247 (25)
O(12)	3934 (20)	5784 (13)	2013 (19)
C(13)	4731 (33)	4095 (22)	4079 (31)
O(13)	4285 (22)	4066 (14)	4889 (21)
C(21)	3468 (25)	3603 (18)	167 (25)
O(21)	3456 (20)	3855 (15)	-783 (20)
C(22)	3271 (25)	2640 (16)	3077 (25)
O(22)	3273 (23)	2273 (16)	3955 (22)
C(31)	7719 (29)	2306 (19)	1927 (26)
O(31)	8813 (22)	2119 (15)	2040 (21)
C(32)	5556 (27)	2004 (19)	325 (27)
O(32)	5373 (26)	1655 (18)	-586 (24)
C(33)	5502 (25)	1625 (17)	2576 (24)
O(33)	5261 (22)	1074 (15)	3130 (22)
C(2a)	2673 (29)	1910 (29)	753 (62)
C(2b)	2644 (109)	2101 (42)	935 (124)
C(3)	1556 (34)	2414 (32)	861 (49)
O(2)	2462 (71)	1368 (40)	713 (65)
C(2'a)	1878 (63)	4066 (47)	2068 (100)
C(2'b)	2132 (69)	3960 (48)	1832 (76)
C(3')	1195 (35)	3383 (50)	1464 (77)
O(2')	1434 (36)	4502 (22)	2105 (42)