Acta Cryst. (1979). B35, 1699–1701

Manganese(II) D-Gluconate Dihydrate

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(*Received* 9 *February* 1979; *accepted* 22 *March* 1979)

Abstract. $Mn(C_6H_{11}O_7)_2.2H_2O$, $2C_6H_{11}O_7^-.Mn^{2+}.2H_2O$, triclinic, $P1$, $a = 7{\cdot}205\ (5)$, $b = 8{\cdot}184\ (4)$, $c = 11{\cdot}157\ (6)$ Å, $\alpha = 90{\cdot}96\ (4)$, $\beta = 94{\cdot}40\ (5)$, $\gamma = 137{\cdot}34\ (4)°$, $M_r = 481{\cdot}3$, $V = 441{\cdot}9\ (5)$ Å^3, $Z = 1$, $D_m = 1{\cdot}79$, $D_x = 1{\cdot}81$ Mg m^{-3}, μ(Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å) $= 7{\cdot}24$ mm^{-1}, final $R = 0{\cdot}033$ and $R_w = 0{\cdot}045$. The Mn atom is octahedrally coordinated by one carboxylate O atom and one hydroxyl O atom from both gluconate ligands and two water O atoms in *cis* positions. Mn–O distances range between 2·091 (5) and 2·275 (5) Å. The independent gluconate ions assume different bent-chain conformations and one is bonded to two adjacent Mn atoms forming polymeric chains parallel to **b**. There is extensive intermolecular hydrogen bonding (and one intramolecular hydrogen bond) involving all the hydroxyl and water H atoms and holding the polymeric units together.

Introduction. Sawyer, Bodini, Willis, Riechel & Magers (1977) have suggested that the Mn complexes formed by the gluconate ion in basic media undergo oxidation–reduction which may parallel the behaviour of the Mn group in photosystem-II of green-plant photosynthesis. The structure of these complexes was investigated by UV–VIS spectrometry, polarography, ESR and magnetic-susceptibility measurements (Sawyer & Bodini, 1975; Bodini & Sawyer, 1976; Sawyer *et al.*, 1977). The present paper presents the crystal structure of $Mn(gluconate)_2.2H_2O$. Attempts to isolate the other gluconate complexes of higher oxidation states of Mn in crystalline form were unsuccessful.

Single crystals were grown at room temperature by slow evaporation of an aqueous solution of a commercial product obtained through ICN–K&K Labs. Weissenberg photographs showed that the crystal system is triclinic. An irregular crystal, 0·10 to 0·16 mm on edge, was selected for data collection. A Syntex $P2_1$ diffractometer and Cu $K\alpha$ radiation with a graphite monochromator were used for lattice-parameter and intensity measurements. The intensities were measured by the 2θ–ω scan technique. After each group of 30 reflexions two standards were measured; no significant change in intensity was observed. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. Of 1885 (hkl and $\bar{h}k\bar{l}$) accessible reflexions below $2\theta \simeq 114{\cdot}5°$, 1867 with $I > 1{\cdot}96\sigma(I)$ were used. All calculations were performed with the Syntex XTL structure determination system (Nova 1200 computer and additional external disc memory). Neutral-atom scattering factors were from *International Tables for X-ray Crystallography* (1974); both real and imaginary components of the anomalous dispersion were included for Mn and O.

Since the compound is optically active, the space group $P1$ was assumed, in which all atoms occupy general positions. The coordinates of Mn were held invariant to fix the origin. All non-H atoms were found from difference syntheses, which were phased by the atoms already located. The trial structure was refined by full-matrix least squares, first with isotropic then anisotropic thermal parameters, to $R = 0{\cdot}046$ and $R_w = 0{\cdot}062$. Twelve H atoms (bonded to C) were placed in geometrically calculated positions at 1·08 Å from the bonded atoms. All remaining H atoms were found from subsequent difference syntheses. Further refinement with fixed parameters for H atoms reduced R to 0·033 and R_w to 0·045. (The refinement of the inverted structure gave $R = 0{\cdot}132$ and $R_w = 0{\cdot}165$.) A final difference synthesis was essentially flat. The final atomic coordinates are listed in Table 1.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34297 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

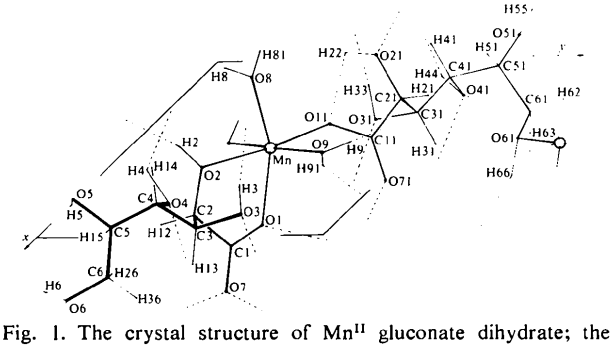

Fig. 1. The crystal structure of Mn^{II} gluconate dihydrate; the projection is on the (001) plane.

0567-7408/79/071699-03$01.00

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

	x	*y*	*z*
Mn	0·5 (fixed)	0·5 (fixed)	0·5 (fixed)
O(1)	0·9389 (8)	0·7578 (7)	0·5266 (4)
O(2)	0·6008 (9)	0·3297 (7)	0·5985 (4)
O(3)	0·8795 (8)	0·6439 (7)	0·8162 (4)
O(4)	0·8177 (9)	0·3480 (8)	0·9655 (4)
O(5)	0·7741 (9)	−0·0132 (8)	0·8569 (4)
O(6)	1·3657 (11)	0·3389 (9)	0·8720 (5)
O(7)	1·3156 (8)	0·8703 (7)	0·6063 (4)
O(8)	0·0929 (9)	0·1795 (7)	0·5230 (4)
O(9)	0·5335 (10)	0·7010 (8)	0·6446 (4)
O(11)	0·3691 (11)	0·6216 (9)	0·3914 (4)
O(21)	−0·0349 (9)	0·5293 (8)	0·2813 (4)
O(31)	0·3421 (9)	0·7704 (8)	0·1050 (4)
O(41)	0·2158 (9)	0·9857 (7)	0·0002 (4)
O(51)	−0·1377 (9)	0·9673 (9)	0·0991 (4)
O(61)	0·4722 (10)	1·3360 (8)	0·3235 (4)
O(71)	0·6930 (10)	1·0211 (9)	0·3691 (5)
C(1)	1·0594 (13)	0·7224 (10)	0·5854 (5)
C(2)	0·8872 (12)	0·4800 (10)	0·6385 (5)
C(3)	0·9531 (12)	0·5338 (10)	0·7782 (5)
C(4)	0·8096 (12)	0·3036 (10)	0·8398 (5)
C(5)	0·9490 (13)	0·2283 (11)	0·8238 (6)
C(6)	1·2323 (13)	0·4025 (12)	0·8964 (7)
C(11)	0·4501 (15)	0·8111 (13)	0·3582 (6)
C(21)	0·2301 (13)	0·7824 (11)	0·3010 (6)
C(31)	0·3103 (13)	0·8888 (11)	0·1787 (6)
C(41)	0·1088 (13)	0·8780 (11)	0·1121 (6)
C(51)	0·0576 (14)	1·0031 (12)	0·1797 (6)
C(61)	0·3135 (15)	1·2790 (12)	0·2125 (6)
H(2)	0·483	0·172	0·586
H(3)	0·704	0·527	0·831
H(4)	0·616	0·156	0·985
H(5)	0·810	0·002	0·946
H(6)	1·318	0·235	0·921
H(22)	−0·034	0·414	0·310
H(33)	0·153	0·616	0·063
H(44)	0·096	0·852	−0·074
H(55)	−0·280	0·912	0·129
H(66)	0·690	1·448	0·328
H(8)	0·040	0·045	0·555
H(81)	−0·054	0·110	0·469
H(9)	0·473	0·760	0·637
H(91)	0·608	0·751	0·722
H(12)	0·939	0·392	0·609
H(13)	1·171	0·655	0·807
H(14)	0·596	0·161	0·794
H(15)	0·975	0·230	0·730
H(26)	1·208	0·391	0·993
H(36)	1·356	0·583	0·876
H(21)	0·208	0·872	0·359
H(31)	0·502	1·078	0·200
H(41)	−0·090	0·689	0·096
H(51)	−0·012	0·920	0·263
H(62)	0·244	1·360	0·220
H(63)	0·442	1·355	0·140

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

Mn–O(1)	2·136 (6)	Mn–O(11)	2·143 (7)
Mn–O(2)	2·258 (6)	Mn–O(61)	2·275 (5)
Mn–O(8)	2·091 (5)	Mn–O(9)	2·153 (5)
C(1)–C(2)	1·535 (8)	C(11)–C(21)	1·506 (16)
C(2)–C(3)	1·550 (8)	C(21)–C(31)	1·541 (8)
C(3)–C(4)	1·542 (8)	C(31)–C(41)	1·520 (14)
C(4)–C(5)	1·535 (15)	C(41)–C(51)	1·525 (13)
C(5)–C(6)	1·511 (12)	C(51)–C(61)	1·542 (9)
C(1)–O(1)	1·247 (11)	C(11)–O(11)	1·266 (10)
C(1)–O(7)	1·251 (11)	C(11)–O(71)	1·252 (10)
C(2)–O(2)	1·441 (11)	C(21)–O(21)	1·445 (8)
C(3)–O(3)	1·413 (11)	C(31)–O(31)	1·413 (11)
C(4)–O(4)	1·428 (7)	C(41)–O(41)	1·454 (7)
C(5)–O(5)	1·436 (7)	C(51)–O(51)	1·437 (12)
C(6)–O(6)	1·428 (14)	C(61)–O(61)	1·428 (10)
O(1)–Mn–O(2)	72·1 (2)	O(1)–Mn–O(8)	155·8 (2)
O(1)–Mn–O(61)	90·7 (2)	O(1)–Mn–O(11)	112·4 (3)
O(1)–Mn–O(9)	89·4 (3)	O(2)–Mn–O(11)	173·0 (3)
O(2)–Mn–O(61)	88·0 (2)	O(2)–Mn–O(8)	84·1 (2)
O(2)–Mn–O(9)	102·8 (2)	O(11)–Mn–O(61)	86·5 (3)
O(11)–Mn–O(8)	91·8 (3)	O(11)–Mn–O(9)	83·0 (3)
O(61)–Mn–O(8)	92·4 (3)	O(61)–Mn–O(9)	168·6 (3)
O(8)–Mn–O(9)	92·2 (3)	Mn–O(11)–C(11)	142·5 (6)
Mn–O(1)–C(1)	123·1 (5)	Mn–O(61)–C(61)	125·0 (5)
Mn–O(2)–C(2)	117·9 (5)	O(11)–C(11)–O(71)	127·3 (9)
O(1)–C(1)–O(7)	125·4 (7)	O(11)–C(11)–C(21)	116·6 (8)
O(1)–C(1)–C(2)	119·2 (7)	O(71)–C(11)–C(21)	116·1 (8)
O(7)–C(1)–C(2)	115·4 (7)	C(11)–C(21)–C(31)	108·4 (7)
C(1)–C(2)–C(3)	107·8 (6)	C(11)–C(21)–O(21)	110·6 (7)
C(1)–C(2)–O(2)	107·2 (6)	C(31)–C(21)–O(21)	109·4 (7)
C(3)–C(2)–O(2)	111·5 (6)	C(21)–C(31)–C(41)	114·1 (7)
C(2)–C(3)–C(4)	111·8 (6)	C(21)–C(31)–O(31)	109·5 (7)
C(2)–C(3)–O(3)	108·2 (6)	C(41)–C(31)–O(31)	110·4 (7)
C(4)–C(3)–O(3)	112·7 (6)	C(31)–C(41)–C(51)	116·4 (7)
C(3)–C(4)–C(5)	111·2 (7)	C(31)–C(41)–O(41)	106·7 (6)
C(3)–C(4)–O(4)	109·2 (6)	C(51)–C(41)–O(41)	109·3 (7)
C(5)–C(4)–O(4)	110·0 (6)	C(41)–C(51)–C(61)	115·2 (7)
C(4)–C(5)–C(6)	112·2 (7)	C(41)–C(51)–O(51)	105·8 (7)
C(4)–C(5)–O(5)	109·3 (7)	C(61)–C(51)–O(51)	107·0 (7)
C(6)–C(5)–O(5)	110·6 (7)	C(51)–C(61)–O(61)	112·0 (7)
C(5)–C(6)–O(6)	110·9 (7)		

Table 3. *Geometry of the hydrogen bonds*

O–H···O	O···O	O–H	H···O	∠O–H···O
O(2)–H(2)···O(7)|$\bar{1}\,\bar{1}\,0$|*	2·654 (6) Å	0·88 Å	1·82 Å	160°
O(3)–H(3)···O(6)|$1\,\bar{1}\,00$|	2·672 (9)	0·89	1·79	170
O(4)–H(4)···O(41)|$0\,1\,1$|	3·022 (8)	1·15	2·11	133
O(5)–H(5)···O(51)|$1\,\bar{1}\,1$|	2·763 (6)	0·99	1·79	165
O(6)–H(6)···O(41)|$1\,1\,1$|	2·712 (7)	0·87	1·85	169
O(21)–H(22)···O(11)	2·595 (11)	1·01	2·11	108
O(31)–H(33)···O(4)|$\bar{1}\,0\,1$|	2·891 (7)	1·01	1·89	172
O(41)–H(44)···O(3)|$\bar{1}\,0\,\bar{1}$|	2·643 (5)	1·05	1·60	172
O(51)–H(55)···O(31)|$1\,\bar{1}\,00$|	2·795 (10)	0·86	2·01	150
O(61)··H(66)···O(21)|$1\,1\,0$|	2·712 (10)	1·08	1·70	154
O(8)–H(8)···O(1)|$\bar{1}\,\bar{1}\,0$|	2·744 (7)	0·95	1·89	148
O(8)–H(81)···O(7)|$1\,\bar{1}\,0$|	2·569 (9)	0·90	1·67	172
O(9)–H(9)···O(7)|$1\,\bar{1}\,00$|	2·771 (10)	0·86	1·92	175
O(9)–H(91)···O(5)|$0\,1\,0$|	2·703 (6)	0·89	1·91	147

* Lattice translation.

Discussion. The crystal structure and atom numbering are shown in Fig. 1, in which the structure is projected along **c**. Interatomic distances and angles are given in Table 2. The gluconate ion containing C(1) is referred to as ion *A* and the other as ion *B*. A carboxylate O(1) and the hydroxyl O(2) form a five-membered chelate ring, Mn–O(1)–C(1)–C(2)–O(2). Two other coordination positions are filled by terminal O(11) and O(61) from two different gluconate ions *B*. The sixfold coordination is completed by O(8) and O(9) from

water molecules in *cis* positions. The six O atoms assume a distorted octahedral arrangement, with Mn–O ranging from 2·091 (5) to 2·275 (5) Å. The Mn–gluconate interactions and the geometry of the Mn coordination polyhedron are closely related to those found in other Mn^{II} carboxylate salts (Karipides & Reed, 1976; Carrell & Glusker, 1973; Osaki, Nakai & Watanabé, 1964; Lis, 1977).

The crystal structure consists of straight polymeric units formed by the coordination of the terminal O(11) and O(61), from each gluconate ion *B*, to two different Mn atoms. In addition to the polymeric structure there is an extensive network of hydrogen bonds utilizing all the hydroxyl and water H atoms and holding the polymeric units together. The data on these hydrogen bonds are given in Table 3.

The two gluconate ions assume different bent-chain conformations about C(3)–C(4) [C(31)–C(41)] and C(4)–C(5) [C(41)–C(51)] (Table 4). The difference in the conformations of the gluconate ions is probably due to differences in the metal-binding interactions. The overall conformation of gluconate ion *B* is similar to that of the gluconate ion in crystals of the monoclinic modification of potassium D-gluconate monohydrate (Panagiotopoulos, Jeffrey, La Placa & Hamilton, 1974). A straight-chain conformation for the gluconate ion was found in anhydrous potassium D-gluconate (Littleton, 1953) and in the orthorhombic form of potassium D-gluconate monohydrate (Panagiotopoulos *et al.*, 1974).

Table 4. *Deviations from least-squares planes in manganese D-gluconate dihydrate*

Atoms marked with an asterisk were excluded from the calculation of the least-squares plane, $Ax + By + Cz = D$.

Ion *A*	*P*1	*P*2	*P*3
C(1)	0·033 (6)	1·137 (7)*	3·937 (6)*
C(2)	−0·027 (6)	1·263 (7)*	2·562 (6)*
C(3)	−0·038 (6)	0·000 (7)	1·405 (6)*
C(4)	0·034 (6)	0·000 (7)	0·000 (6)
C(5)	1·465 (6)*	0·000 (8)	0·000 (7)
C(6)	2·502 (7)*	−1·207 (8)*	0·000 (7)
O(6)	3·841 (5)*	−1·145 (7)*	0·115 (6)*
A	0·1782	−0·6006	0·2864
B	−0·9747	−0·3633	0·3732
C	−0·1350	−0·7123	−0·8824
D	3·0023	−8·2061	−6·7806

Angles between normals to planes

*P*1, *P*2	69·9°	*P*1, *P*3	101·2°	*P*2, *P*3	71·3°

Ion *B*	*P*11	*P*22	*P*33
C(11)	−0·008 (8)	−1·078 (9)*	−3·599 (7)*
C(21)	0·005 (7)	−1·230 (8)*	−2·515 (6)*
C(31)	0·006 (7)	0·000 (7)	−1·187 (6)*
C(41)	−0·006 (7)	0·000 (8)	0·000 (6)
C(51)	−0·780 (8)*	0·000 (8)	0·000 (7)
C(61)	−1·709 (8)*	1·280 (9)*	0·000 (7)
O(61)	−2·066 (6)*	1·129 (6)*	−1·300 (5)*
A	−0·5342	0·6445	−0·0851
B	−0·8057	0·5662	0·5146
C	−0·2558	−0·5139	−0·8532
D	−3·8312	2·8457	2·0259

Angles between normals to planes

*P*11, *P*22	132·0°	*P*11, *P*33	98·7°	*P*22, *P*33	47·6°

The author thanks Miss D. Długosz and Mr J. Matuszewski for technical assistance.

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