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Polymeric (Aqua-1κO)bis[(R,R)-tartrato-1κ²O¹,O²:2κ²O³,O⁴]dimanganese(II) Trihydrate

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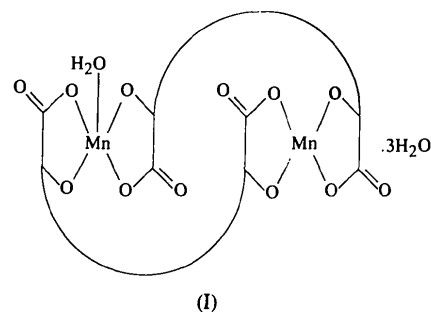
Abstract

The structure of the title compound, {[Mn$_2$(C$_4$H$_2$O$_6$)$_2$-(H$_2$O)].3H$_2$O}$_n$, is comprised of corrugated polymeric sheets of dimeric [Mn$_2${(R,R)-C$_4$H$_2$O$_6$}$_2$(H$_2$O)] units and water molecules (O2W, O3W and O4W). The manganese ions are coordinated by two (R,R)-tartrate ligands in a cis arrangement. The Mn1···Mn2 intradimeric distance is 5.527 (2) Å.

Comment

This investigation has been motivated by the increasing interest in the coordination of metal atoms with carboxylic acids. The structure of polymeric (aqua-1κO)-bis[(R,R)-tartrato-1κ²O¹,O²:2κ²O³,O⁴]dimanganese(II) trihydrate, (I), has been determined.

(I)

The smallest structural subunit in the title compound, (I), appears to be the dimeric entity [Mn$_2${(R,R)-C$_4$H$_2$O$_6$}$_2$(H$_2$O)] (Fig. 1). Each Mn^{2+} ion is coordinated by two halves of two different tartrate dianions via chelation through the alcohol and carboxylate groups. The octahedral geometry around the Mn2 ion is completed by a water molecule (O1W) and a non-chelating carboxylate O82 atom of another dimer at $(-x, y - \frac{1}{2}, -z + 1)$. The geometry around Mn1 ion is completed by two non-chelating carboxylate O42 and O52 atoms from two other dimers at $(-x + 1, y + \frac{1}{2}, -z + 1)$ and $(-x, y + \frac{1}{2}, -z)$, respectively.

Bond lengths and angles (Table 2) for each tartrate ligand are usual and do not deviate significantly from
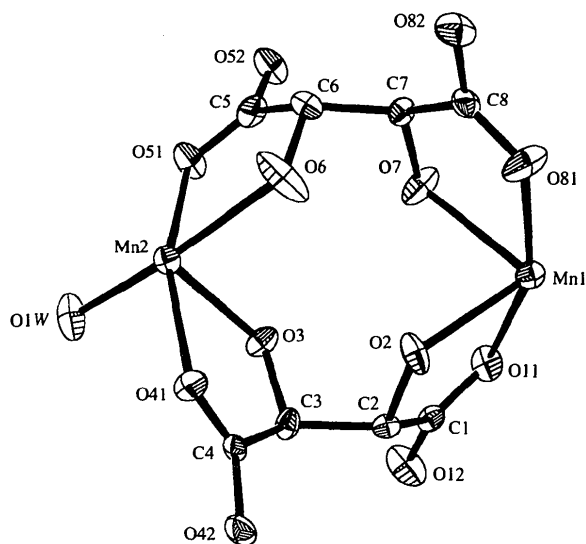

Fig. 1. Perspective drawing of the title compound showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms and water molecules (O2W, O3W and O4W) have been omitted for clarity.

other reported tartrate coordination compounds (Tapscott, 1982; Prout, Carruthers & Rossoti, 1971; Bostelaar, de Graaff, Hulsbergen, Reedijk & Schatler, 1984). The chelate rings (–Mn–OCCO–) are not planar, the maximum deviation from the least-squares plane being –0.100 Å for atom O51. The angle between the two *cis* chelate rings around the Mn1 atom is 84.80 (7)°, while around the Mn2 atom this angle is 89.60 (7)° and the geometry is found to be Δ, with a *trans* orientation of the carboxylate groups (Tapscott, 1974; Ortega, Tapscott & Campana, 1982). The Mn—O distances vary between 2.105 (4) and 2.318 (3) Å, which are significantly shorter than the sum of the ionic radii of Mn^{2+} and O^{2-} (2.4–2.6 Å). The coordination around the manganese ions is distorted octahedral. The distortion is in accordance with the valence-sum rule (Brown, 1992), where the sum around the Mn1 and Mn2 ions is 2.088 and 2.207 v.u., respectively, and is partly caused by the chelating five-membered rings and partly by the conformation of the tartrate ligands and the coordinated water molecule. The water molecules O2W, O3W and O4W are linked to the tartrate ligands by intramolecular hydrogen bonds; O2W···O41 2.853 (5), O3W···O2 2.733 (4) and O4W···O6 2.640 (6) Å.

The crystals can be regarded as a stacked pile of corrugated polymeric sheets of [Mn$_2$\{(R,R)-C$_4$H$_2$O$_6$\}$_2$-(H$_2$O)] dimeric units (described above) and water molecules (O2W, O3W and O4W). The dimers are linked together through the carboxylate O42, O52 and O82 atoms. The packing of the dimers in the polymeric sheets and the stacking of these corrugated sheets on one another are shown in Fig. 2. A comparison with the structures of nickel(II) (R,R)-tartrate (Bostelaar *et al.*, 1984) and copper(II) (R,R)-tartrate (Prout, Carruthers & Rossoti, 1971) reveals that these structures also contain distorted octahedrally-coordinated metal ions, two distinct groups of tartrate ligands, nearly planar *cis* chelate rings, dimeric entities as building blocks for the structure [with Ni···Ni and Cu···Cu distances of 5.202 and 5.43 Å, respectively, in a dimer compared with an distance of Mn···Mn of 5.527 (2) Å] and two-
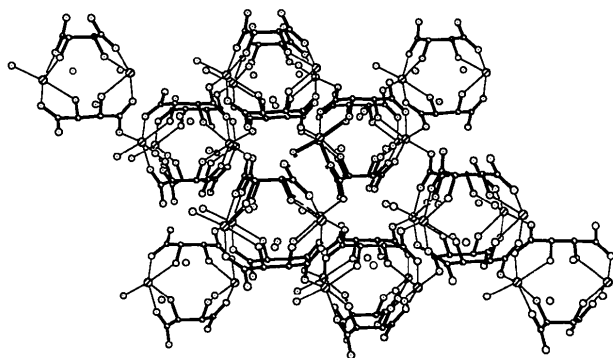

Fig. 2. A projection of the crystal structure of (I) along the *c* axis. H atoms have been omitted for clarity.
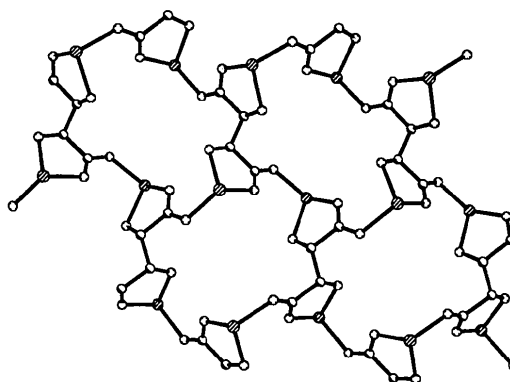

Fig. 3. The binding scheme within polymeric layers of (I). Water molecules, H atoms and tartrate groups that do not establish bonds between the dimers (other than hydrogen bridges) have been omitted.

dimensional polymeric sheets. The binding schemes of the dimeric units within the polymeric sheets is similar to that of nickel(II) (R,R)-tartrate. The binding within the sheets, established by the metal ion and the tartrate 2 groups, is schematically depicted in Fig. 3 (water molecules and tartrate 1 groups have been omitted for clarity).

Experimental

The growth experiments were carried out by single diffusion methods using sodium silicate solution (Yanes, López, Stockel, Peraza & Torres, 1995). Single crystals suitable for X-ray crystallography appeared within one week on the surface of the gel solution.

Crystal data

[Mn$_2$(C$_4$H$_2$O$_6$)$_2$(H$_2$O)].3H$_2$O	Mo $K\alpha$ radiation
M_r = 474.04	λ = 0.71073 Å
Monoclinic	Cell parameters from 25
$P2_1$	reflections
a = 9.003 (2) Å	θ = 6–18°
b = 11.142 (3) Å	μ = 1.71 mm^{-1}
c = 7.568 (2) Å	T = 293 K
β = 99.51 (2)°	Prism
V = 748.7 (3) Å^3	0.4 × 0.2 × 0.1 mm
Z = 2	Yellow
D_x = 2.102 Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	R_{int} = 0.026
diffractometer	θ_{max} = 30°
$\omega/2\theta$ scans	h = −12 → 12
Absorption correction:	k = 0 → 15
none	l = 0 → 10
2430 measured reflections	3 standard reflections
2283 independent reflections	frequency: 60 min
1886 observed reflections	intensity decay: none
[$I > 2\sigma(I)$]	

Refinement

Refinement on F^2
$R(F) = 0.068$
$wR(F^2) = 0.2053$
$S = 1.116$
1886 reflections
238 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1514P)^2 + 2.51P]$
where $[\max(F_o^2,0) + 2F_o^2]/3$
$(\Delta/\sigma)_{max} = -0.069$
$\Delta\rho_{max} = 1.22$ e Å^{-3}
$\Delta\rho_{min} = -1.68$ e Å^{-3}

Extinction correction:
SHELXL93 (Sheldrick, 1993)
Extinction coefficient:
0.0065
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)
Absolute configuration:
Flack (1983)
Flack parameter = −0.3 (10)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Mn1	0.23860 (2)	1.00000 (2)	0.23011 (3)	1.39 (3)
Mn2	0.21388 (3)	0.51228 (2)	0.35574 (2)	1.32 (3)
C1	0.4940 (2)	0.85981 (2)	0.12692 (3)	1.4 (2)
C2	0.4953 (2)	0.80372 (3)	0.31318 (3)	1.1 (2)
C3	0.4930 (2)	0.66724 (3)	0.30184 (3)	1.5 (2)
C4	0.5214 (2)	0.61348 (4)	0.48930 (4)	1.4 (2)
O11	0.3953 (2)	0.93893 (3)	0.07164 (3)	1.8 (2)
O12	0.5906 (2)	0.81980 (3)	0.04409 (4)	3.1 (2)
O2	0.3658 (2)	0.84702 (3)	0.38432 (3)	1.8 (2)
O3	0.3535 (3)	0.62489 (3)	0.21070 (3)	1.7 (2)
O41	0.4141 (3)	0.56451 (4)	0.54383 (3)	1.7 (1)
O42	0.6501 (2)	0.62865 (4)	0.58242 (3)	1.9 (2)
C5	−0.0554 (3)	0.60850 (3)	0.11174 (3)	1.8 (2)
C6	−0.0517 (2)	0.69938 (3)	0.26266 (3)	1.5 (2)
C7	−0.0453 (2)	0.82572 (3)	0.19770 (3)	1.3 (2)
C8	−0.0426 (3)	0.91576 (4)	0.35415 (3)	1.6 (2)
O51	0.0314 (6)	0.51948 (3)	0.13900 (4)	2.4 (2)
O52	−0.1501 (4)	0.62407 (3)	−0.02485 (4)	2.5 (2)
O6	0.0768 (4)	0.67638 (4)	0.39942 (4)	3.5 (2)
O7	0.0793 (3)	0.84674 (3)	0.10941 (4)	2.5 (2)
O81	0.0573 (5)	0.99098 (4)	0.38197 (5)	3.1 (2)
O82	−0.1481 (7)	0.90440 (4)	0.44235 (4)	2.2 (2)
O1W	0.3113 (6)	0.35798 (3)	0.25969 (5)	2.5 (2)
O2W	0.3005 (6)	0.61740 (5)	0.86548 (4)	6.1 (4)
O3W	0.2954 (7)	0.89692 (4)	0.71429 (4)	6.5 (5)
O4W	0.0599 (8)	0.75267 (5)	0.72571 (6)	5.4 (8)

Table 2. *Selected geometric parameters (Å, °)*

Mn1—O11	2.109 (3)	Mn2—O1W	2.113 (4)
Mn1—O52^i	2.133 (3)	Mn2—O51	2.123 (4)
Mn1—O42^{ii}	2.145 (3)	Mn2—O41	2.183 (2)
Mn1—O81	2.148 (5)	Mn2—O3	2.194 (3)
Mn1—O2	2.266 (3)	Mn2—O6	2.260 (4)
Mn1—O7	2.318 (3)	Mn1—Mn2	5.527 (2)
Mn2—O82^{iii}	2.105 (4)		
O11—Mn1—O81	158.1 (1)	O51—Mn2—O41	160.7 (1)
O52^i—Mn1—O2	163.4 (1)	O82^{iii}—Mn2—O3	160.5 (1)
O42^{ii}—Mn1—O7	160.7 (1)	O1W—Mn2—O6	167.5 (1)

Symmetry codes: (i) $-x, \frac{1}{2} + y, -z$; (ii) $1 - x, \frac{1}{2} + y, 1 - z$; (iii) $-x, y - \frac{1}{2}, 1 - z$.

Table 3. *Average geometry values (Å, °) for the tartrate ligands*

C—C	1.540 (3)	C—O(carboxyl)	1.247 (4)
C—O(hydroxyl)	1.428 (4)	C=O	1.248 (4)
C—C—C	111.4 (3)	C—C—O(carboxyl)	118.4 (3)
C—C—O(hydroxyl)	110.6 (4)	C—C=O	116.2 (4)
O—C=O	125.3 (4)		

The data were corrected for Lorentz and polarization effects. The structure was solved by initial location of the Mn atoms by Patterson methods using SHELXS86 (Sheldrick, 1990), followed by location of the light atoms from difference electron-density maps, and refined by anisotropic full-matrix least squares on F^2 for all non-H atoms. In the difference Fourier map, four peaks were found which were attributed to water O atoms. From the large value of B for the O4W atom, we concluded that the position of this O atom is only partially occupied (0.56). H atoms were treated as riding on their parent atom at a distance of 0.98 Å, which refined to 0.026 (2) Å^2, except for the water H atoms which were not located and therefore not included in the refinement. The major residual features in the ΔF synthesis lie close to the metal atoms.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: CFEO (Solans, 1978). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: PC version of ORTEP (Brueggemann & Schmid, 1990). Software used to prepare material for publication: PARST (Nardelli, 1983).

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