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# *catena*-Poly[[[(1,10-phenanthroline-$\kappa^2N,N'$)manganese(II)]-$\mu$-L-tartrato-$\kappa^4O^1,O^2:O^3,O^4$] hexahydrate]

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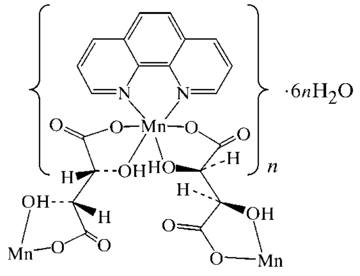
The title compound, $\{[Mn(C_4H_4O_6)(C_{12}H_8N_2)]\cdot 6H_2O\}_n$, has a linear chain structure containing monomeric $[Mn(C_4H_4O_6)(C_{12}H_8N_2)]$ repeat units. Each manganese ion is six-coordinate, with the two phenanthroline N atoms [Mn—N = 2.229 (2) and 2.235 (2) Å] and four O atoms from two tartrate anions [$Mn—O_{COO}$ = 2.1252 (19) and 2.1310 (19) Å, and $Mn—O_{OH}$ = 2.2404 (19) and 2.2424 (19) Å] forming a seriously distorted octahedral coordination environment. Six water molecules exist outside every repeat unit as solvate molecules. Extensive hydrogen-bonding interactions and $\pi$–$\pi$ stacking of the phenanthroline moieties exist between the chains.

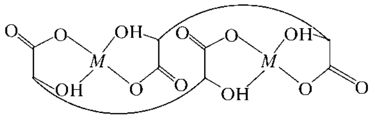
## Comment

The structures and properties of polymanganese complexes are currently of great interest on account of their promising applications in diverse areas of technology (Aubin *et al.*, 1997; Manson *et al.*, 1998) and as model complexes for the study of the photosynthetic oxygen-evolving complexes (OEC) of photosystem II in green plants (Wieghardt, 1989). L-Tartaric acid, in its role as a polydentate ligand, has been extensively studied in transition metal compounds. The coordination modes of L-tartrate are shown as (*a*) and (*b*) in the *Scheme* below, though mode (*a*) is seldom found. However, only two manganese–L-tartrate compounds have been reported (Ruiz-Pérez *et al.*, 1996; Soylu, 1983) up to now. We report here the synthesis and crystal structure of the first mixed-ligand manganese–L-tartrate complex, *viz.* $\{[Mn(C_4H_4O_6)(C_{12}H_8N_2)]\cdot 6H_2O\}_n$ [$C_4H_4O_6$ is the dianion of L(+)-tartaric acid and $C_{12}H_8N_2$ is 1,10-phenanthroline], (I), which has a polymeric linear chain structure. A similar copper complex has been reported (McCann *et al.*, 1997).

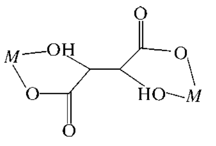
The crystal structure of (I) consists of an infinite $\{[Mn(C_4H_4O_6)(C_{12}H_8N_2)].6H_2O\}_n$ chain and the asymmetric unit is shown in Fig. 1. The Mn ion is located in a seriously distorted octahedral environment, with the three *trans* angles ranging from 155.82 (7) to 157.17 (9)°. The Mn ion is coordinated by two phenanthroline N atoms [Mn—N = 2.229 (2) and 2.235 (2) Å] and four O atoms [Mn—O = 2.1252 (19)–2.2424 (19) Å] from opposite ends of two tartrate ligands, which are symmetry related to form three chelating rings (symmetry code: $x - 1$, $y$, $z$). A tartrate anion links two neighboring Mn ions by a single ligand bridge, forming two chelating rings [form (*b*) in the *Scheme*]. Thus, Mn ions are bridged by tetradentate L-tartrate, forming a linear chain along the *a* axis of the cell. Six water molecules exist outside every repeat unit as solvate molecules.



(I)



(*a*)



(*b*)

The distortion of the coordination geometry is caused mainly by the three chelate five-membered rings. Bond lengths and angles for the L-tartrate ligand are usual and do not

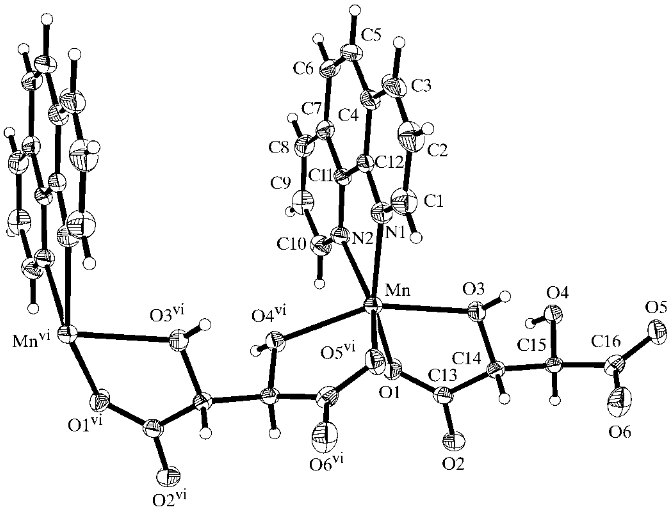


**Figure 1**
Part of the structure of (I), showing the bridging mode of the L-tartrate anion and one of the independent structural units with the atom-numbering scheme [symmetry code: (vi) $x - 1$, $y$, $z$].

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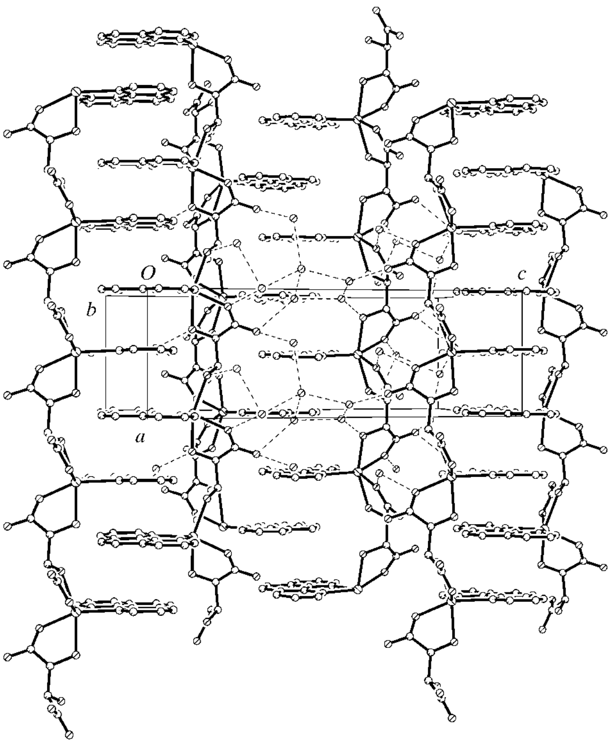

**Figure 2**
Packing diagram of the title compound.

deviate significantly from those in other reported L-tartrate coordination compounds (Ortega *et al.*, 1982; Ruiz-Pérez *et al.*, 1996). The average Mn—$O_{OH}$ distance [2.2414 (19) Å] is longer than that of Mn—$O_{COO}$ [2.1281 (19) Å], which indicates that the hydroxyl groups of the L-tartrate ligand are not deprotonated, analogous to the reaction of L-tartrate with other metal ions, such as $Cu^{II}$, $Ni^{II}$, $Zn^{II}$, $Co^{II}$ and $Cd^{II}$. According to charge-balance requirements, the oxidation state of Mn is +2. In addition, the room-temperature magnetic moments of a powdered sample of (I) (5.89 BM) were in the range expected for a manganese(II) complex where there is no significant exchange interaction between metal centres.

Extensive hydrogen-bonding interactions are observed between the chains. The packing diagram of the complex along the *a* axis is presented in Fig. 2, showing three types of hydrogen-bonding interactions as follows: (i) $O_{coord}$ to water [2.854 (3) and 2.889 (3) Å], (ii) $O_{uncoord}$ to water [2.709 (3)–2.904 (3) Å] and (iii) water to water [2.775 (4)–2.832 (4) Å] (hydrogen-bond data are listed in Table 2). In addition, the phenanthroline groups of each polymeric chain are interwoven between the chains and form a $\pi$–$\pi$ stacking along the *a* axis, with interplanar distances ranging from 3.22 to 3.35 Å.

## Experimental

A mixture of $Mn(CH_3COO)_2{\cdot}4H_2O$ (0.25 g, 1.02 mmol), phen (2.0 g, 1 mmol), $NaOCH_3$ (0.11 g, 2 mmol) and L(+)-tartaric acid (0.15 g, 1 mmol) in MeOH/$H_2O$ (16 ml, *v*/*v*, 1:1) was sealed in a 25 ml stainless-steel Teflon-lined reactor. The reaction system was heated at 453 K for 72 h. Slow cooling to room temperature yielded deep-red crystals, which were collected by filtration (yield: 34%). Analysis calculated (%): C 39.12, H 4.92, N 5.70%; found (%): C 39.24, H 4.96, N 5.72.

### Crystal data

$[Mn(C_4H_4O_6)(C_{12}H_8N_2)]{\cdot}6H_2O$
$M_r = 491.31$
Orthorhombic, $P2_12_12_1$
$a = 6.7093$ (9) Å
$b = 15.336$ (3) Å
$c = 20.210$ (3) Å
$V = 2079.4$ (6) $Å^3$
$Z = 4$
$D_x = 1.569$ Mg $m^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 146 reflections
$\theta = 1.7$–25.1°
$\mu = 0.70$ $mm^{-1}$
$T = 293$ (2) K
Block, deep red
0.36 × 0.24 × 0.20 mm

### Data collection

Siemens SMART CCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.777$, $T_{max} = 0.869$
6282 measured reflections

3372 independent reflections
3183 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.1°$
$h = -7 \rightarrow 7$
$k = -16 \rightarrow 18$
$l = -24 \rightarrow 10$

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.074$
$S = 1.02$
3372 reflections
337 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 1.1316P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e $Å^{-3}$
$\Delta\rho_{min} = -0.33$ e $Å^{-3}$
Extinction correction: *SHELXTL* (Bruker, 1997)
Extinction coefficient: 0.0119 (8)
Absolute structure: Flack (1983), 1242 Friedel pairs
Flack parameter = 0.01 (2)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Mn—$O5^{vi}$ | 2.1252 (19) | Mn—N2 | 2.235 (2) |
| Mn—O1 | 2.1310 (19) | Mn—O3 | 2.2404 (19) |
| Mn—N1 | 2.229 (2) | Mn—$O4^{vi}$ | 2.2424 (19) |
| | | | |
| $O5^{vi}$—Mn—O1 | 103.65 (8) | N1—Mn—O3 | 90.36 (8) |
| $O5^{vi}$—Mn—N1 | 93.33 (8) | N2—Mn—O3 | 108.58 (8) |
| O1—Mn—N1 | 155.84 (9) | $O5^{vi}$—Mn—$O4^{vi}$ | 73.36 (7) |
| $O5^{vi}$—Mn—N2 | 157.17 (9) | O1—Mn—$O4^{vi}$ | 93.42 (7) |
| O1—Mn—N2 | 94.25 (8) | N1—Mn—$O4^{vi}$ | 108.02 (8) |
| N1—Mn—N2 | 74.56 (8) | N2—Mn—$O4^{vi}$ | 91.76 (8) |
| $O5^{vi}$—Mn—O3 | 90.44 (8) | O3—Mn—$O4^{vi}$ | 155.82 (7) |
| O1—Mn—O3 | 72.69 (7) | | |
| | | | |
| $O5^{vi}$—Mn—N1—C1 | 19.4 (3) | $O5^{vi}$—Mn—N2—C11 | 61.1 (3) |
| $O4^{vi}$—Mn—N1—C1 | 93.0 (3) | N1—Mn—N2—C11 | 1.1 (2) |
| O1—Mn—N1—C12 | 62.3 (3) | $O5^{vi}$—Mn—O3—C14 | 77.46 (18) |
| O3—Mn—N1—C12 | 106.9 (2) | $O4^{vi}$—Mn—O3—C14 | 30.5 (3) |

Symmetry code: (vi) $x - 1, y, z$.

H atoms bonded to C atoms were placed at calculated idealized positions using a riding model (C—H = 0.93 Å for 1,10-phenanthroline and 0.98 Å for L-tartrate). H atoms bonded to O atoms were located in a difference Fourier synthesis and were subsequently refined with restrained O—H distances approximately equal to 0.85 Å.

**Table 2**
Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O8—H8*B*···O11$^{i}$ | 0.85 (3) | 1.92 (6) | 2.775 (4) | 168 (6) |
| O9—H9*B*···O6$^{ii}$ | 0.834 (19) | 1.88 (2) | 2.709 (3) | 173 (4) |
| O10—H10*B*···O8$^{iii}$ | 0.85 (2) | 2.07 (3) | 2.820 (4) | 147 (4) |
| O9—H9*C*···O7$^{iv}$ | 0.85 (2) | 1.95 (2) | 2.782 (4) | 168 (5) |
| O10—H10*C*···O12$^{v}$ | 0.837 (19) | 2.03 (2) | 2.832 (4) | 160 (4) |
| O11—H11*C*···O8$^{vi}$ | 0.86 (3) | 1.92 (3) | 2.775 (5) | 169 (6) |
| O7—H7*C*···O5$^{ii}$ | 0.840 (19) | 2.02 (2) | 2.854 (3) | 170 (5) |
| O11—H11*B*···O7 | 0.86 (4) | 1.96 (5) | 2.790 (4) | 159 (4) |
| O7—H7*B*···O1 | 0.845 (19) | 2.07 (2) | 2.889 (3) | 163 (4) |
| O12—H12*B*···O11 | 0.88 (5) | 1.94 (5) | 2.817 (4) | 174 (5) |
| O8—H8*C*···O2 | 0.86 (6) | 1.94 (6) | 2.794 (4) | 173 (6) |
| O12—H12*C*···O2 | 0.85 (4) | 2.06 (2) | 2.904 (3) | 173 (4) |

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL* (Bruker, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1417). Services for accessing these data are described at the back of the journal.

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