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Key indicators

Single-crystal X-ray study

$T = 295$ K

Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å

R factor = 0.052

wR factor = 0.136

Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

catena-Poly[tetraaquamanganese(II)- μ -4,4'-bipyridine] *catena*-poly[[diaquamanganate(II)-di- μ -4-carboxy- phenoxyacetato] dihydrate]

The crystal structure of the title compound, $[\text{Mn}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4]_n[\text{Mn}(\text{C}_9\text{H}_6\text{O}_5)_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$, is an unusual example of a compound displaying separated chain motifs for both the cationic and anionic portions. The cations are bridged into chains by the *N*-heterocycle, while the anions are bridged by pairs of dicarboxylate groups. In the cationic chain, the Mn atom and the *N*-heterocycle lie on centers of inversion. The cationic and anionic chains interact via a three-dimensional network of $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, which involve the uncoordinated water molecules.

Comment

The 4,4'-bipyridine heterocyclic ring system is often used for bridging metal atoms in complexes, which may demonstrate interesting structural motifs in the cases when the anionic entity is a dicarboxylate unit. Among the examples of manganese dicarboxylate complexes of 4,4'-bipyridine is the diaquaphthalatomanganese dihydrate adduct (Ma *et al.*, 2003). The dicarboxylate unit links the metals into a chain; the ligand also connects the chains in a perpendicular direction, giving rise to a layer structure. The aquasuccinatomanganese adduct co-crystallizes with 4,4'-bipyridine (Ma *et al.*, 2004): the layered structure is based on two succinate anions bridging two manganese atoms. A similar motif is adopted by the fumarate co-crystal (Shi *et al.*, 2000). These studies prompted an attempt to synthesize the 4,4'-bipyridine adduct of manganese 4-carboxyphenoxyacetate, which has been structurally characterized as a linear carboxylate-bridged polymer with the metal atom coordinated by four water molecules (Gu *et al.*, 2004). A chain motif is also noted for the water-containing 2,5-thiophene adduct (Sun & Ye, 2004). A recent study describes the layer structure of the anhydrous adduct of manganese 4-phenylenedioxyacetate (Gao *et al.*, 2004).

The reaction of freshly prepared manganese hydroxide (mixed with manganese carbonate) with succinic (as well as with fumaric) acid yields a compound formulated as $[\text{Mn}(\text{C}_4\text{H}_4\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$. Its crystal structure consists of linear polycationic $[\text{Mn}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4]^{2+}$ chains, which are hydrogen bonded to polyanionic $[\text{Mn}(\text{C}_4\text{H}_4\text{O}_4)_2]^{2-}$ ribbons (Ying *et al.*, 2004). Slightly different reaction conditions afforded a similar compound with a three-dimensional framework motif (Zheng *et al.*, 2004).

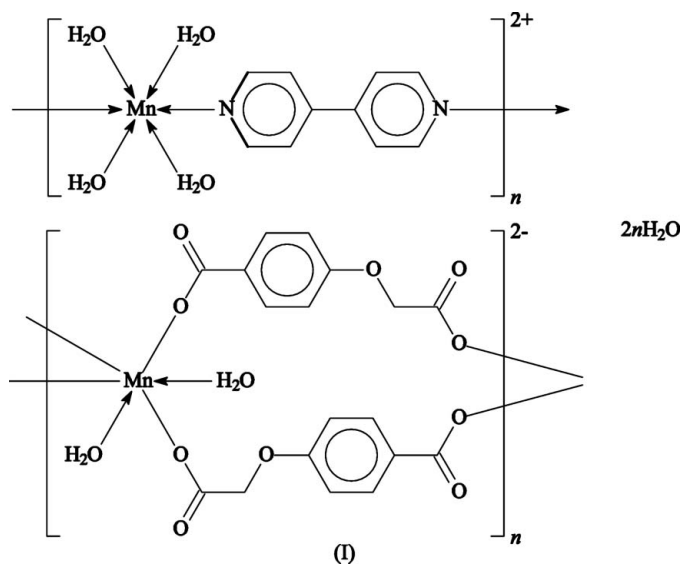
Hydrothermal synthesis of the adduct yielded the title compound, (I), an ion-pair dihydrate with separated cationic and anionic chains (Fig. 1). In the cationic $\{[\text{Mn}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4\text{Mn}]^{2+}\}_n$ chain, the Mn atom and the *N*-heterocycle lie on centers of inversion. The anionic $\{[\text{Mn}(\text{C}_9\text{H}_6\text{O}_5)_2(\text{H}_2\text{O})_2]^{2-}\}_n$ chain has a pair of dicarboxylate dianions linking

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adjacent pairs of metal atoms. In both chains, the coordination geometry of the Mn atoms (Table 1) can be described as distorted octahedral. The cationic and anionic chains interact via a three-dimensional network of O—H...O hydrogen bonds (Table 2), which involve the uncoordinated water molecules.



Experimental

Manganese dichloride hexahydrate (1.17 g, 5 mmol), 4,4'-bipyridine (0.78 g, 5 mmol) and 4-carboxyphenoxyacetic acid (0.98 g, 5 mmol) were dissolved in water (35 ml). The pH of the solution was adjusted to 7 with 0.1 M sodium hydroxide. The mixture was sealed in a 50 ml Teflon-lined stainless steel bomb. The bomb was heated at 393 K for 5 d. The bomb was cooled slowly to room temperature; colorless prismatic crystals separated from the solution after several days. Analysis calculated for $C_{28}H_{36}Mn_2N_2O_{18}$: C 42.12, H 4.54, N 3.51%; found: C 42.01, H 4.49, N 3.55%.

Crystal data

$[Mn(C_{10}H_8N_2)(H_2O)_4] \cdot [Mn(C_9H_6O_5)_2(H_2O)_2] \cdot 2H_2O$
 $M_r = 798.47$
 Triclinic, $P\bar{1}$
 $a = 7.688$ (2) Å
 $b = 10.163$ (2) Å
 $c = 10.797$ (2) Å
 $\alpha = 94.08$ (3)°
 $\beta = 101.01$ (3)°
 $\gamma = 100.46$ (3)°
 $V = 809.4$ (3) Å³

$Z = 1$
 $D_x = 1.638$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 6308 reflections
 $\theta = 3.1$ – 27.5 °
 $\mu = 0.87$ mm⁻¹
 $T = 295$ (2) K
 Prism, colorless
 $0.34 \times 0.26 \times 0.18$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{min} = 0.757$, $T_{max} = 0.860$
 6804 measured reflections

3581 independent reflections
 2567 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.044$
 $\theta_{max} = 27.5$ °
 $h = -9 \rightarrow 9$
 $k = -13 \rightarrow 13$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.136$
 $S = 1.05$
 3581 reflections
 261 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.8256P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.49$ e Å⁻³
 $\Delta\rho_{min} = -0.67$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Mn1—O1w	2.221 (3)	Mn2—O1	2.226 (2)
Mn1—O2w	2.155 (3)	Mn2—O5 ⁱ	2.144 (2)
Mn1—N1	2.262 (3)	Mn2—O3w	2.188 (3)
O1w—Mn1—O2w	85.0 (1)	O1—Mn2—O5 ⁱ	88.2 (1)
O1w—Mn1—O2w ⁱⁱ	95.0 (1)	O1—Mn2—O5 ⁱⁱⁱ	91.79 (9)
O1w—Mn1—N1	87.9 (1)	O1—Mn2—O3w	90.7 (1)
O1w—Mn1—N1 ⁱⁱ	92.1 (1)	O1—Mn2—O3w ^{iv}	89.3 (1)
O2w—Mn1—N1	87.8 (1)	O5 ⁱ —Mn2—O3w	91.4 (1)
O2w—Mn1—N1 ⁱⁱ	92.2 (1)	O5 ⁱ —Mn2—O3w ^{iv}	88.6 (1)

Symmetry codes: (i) $x - 1, y - 1, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 2$; (iv) $-x, -y + 1, -z + 2$.

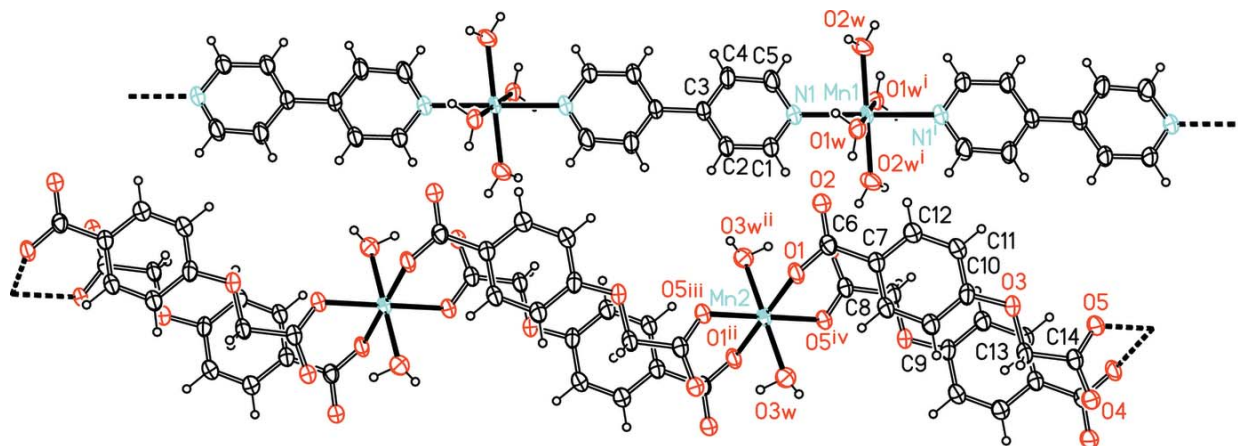


Figure 1

ORTEP (Johnson, 1976) plot of the title compound, showing a fragment of the cationic and anionic chains, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. The uncoordinated water molecules are not shown. Symmetry codes (i)–(iv) are as given in Table 1.

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1w-H1w1\cdots O2$	0.85 (3)	1.93 (4)	2.711 (4)	153 (5)
$O1w-H1w2\cdots O2^v$	0.85 (3)	1.82 (4)	2.670 (4)	172 (4)
$O2w-H2w1\cdots O1^v$	0.85 (5)	1.92 (4)	2.767 (4)	172 (5)
$O2w-H2w2\cdots O4^{vi}$	0.85 (5)	1.79 (5)	2.641 (4)	177 (6)
$O3w-H3w1\cdots O4^i$	0.85 (5)	1.96 (4)	2.743 (4)	152 (5)
$O3w-H3w2\cdots O4^{vii}$	0.85 (5)	1.96 (4)	2.770 (4)	159 (5)
$O4w-H4w1\cdots O5^{viii}$	0.85 (5)	2.17 (5)	2.929 (4)	149 (6)
$O4w-H4w2\cdots O1w$	0.85 (5)	2.17 (5)	2.991 (4)	163 (7)

Symmetry codes: (i) $x-1, y-1, z$; (v) $-x, -y+1, -z+1$; (vi) $x, y-1, z-1$; (vii) $x, y, z+1$; (viii) $-x+1, -y+2, -z+1$.

C-bound H atoms were placed in calculated positions and refined as riding, with $C-H = 0.93$ (aromatic) or 0.97Å (aliphatic) and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of water molecules were located in difference Fourier maps and were refined with an O—H distance restraint of $0.85(1)\text{Å}$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSO, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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