Crystal structure of hexaaquamanganese(II) succinate hexamethylene-tetramine disolvate tetrahydrate, $[\text{Mn}(\text{H}_2\text{O})_6](\text{C}_4\text{H}_4\text{O}_4) \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot 4\text{H}_2\text{O}$

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Abstract

$\text{C}_{16}\text{H}_{48}\text{MnN}_8\text{O}_{14}$, triclinic, $P\bar{1}$ (no. 2), $a = 9.388(2)$ Å, $b = 9.421(2)$ Å, $c = 9.449(2)$ Å, $\alpha = 80.88(3)^\circ$, $\beta = 78.48(3)^\circ$, $\gamma = 61.50(3)^\circ$, $V = 717.7$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.028$, $wR_{\text{ref}}(F^2) = 0.076$, $T = 293$ K.

Source of material

Addition of 4.0 ml (1M) Na_2CO_3 to a stirred aqueous solution of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.423 g, 2.5 mmol) in 5.0 ml H_2O yielded white precipitate, which was centrifugalized and washed with double-distilled water for several times until no SO_4^{2-} anions detectable in supernatant. Then, the fresh precipitate, 3.505 g (25 mmol) hexamethylenetetramine and 0.295 g (2.5 mmol) succinic acid were successively added to 30 ml H_2O and the mixture was further stirred for 30 minutes. After filtration, the filtrate was maintained at room temperature. Slow evaporation for 30 days afforded hexagonal plate-like colorless crystals (yield 0.866 g).

Experimental details

The hydrogen atoms bound to oxygen atoms were refined freely. Those hydrogen atoms fixed by geometrical constraints were refined using riding models and with an overall U_{iso} value.

Discussion

The crystal structure consists of the complex $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ cations, succinate $(\text{C}_4\text{H}_4\text{O}_4)^{2-}$ anions, hexamethylenetetramine (hmt) molecules and lattice H_2O molecules. The complex $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ cations are centered at the crystallographic $1a$ positions and the Mn atoms are each octahedrally coordinated by six H_2O molecules with $d(\text{Mn}-\text{O}) = 2.149(1)$ Å – $2.220(1)$ Å. The *transoid* bond angles about the central Mn atom are equal to 180° due to the local crystallographic imposition whereas the *cisoid* bond angles fall in region 83.1° – 96.9° . The complex cations are each hydrogen bonded to six hmt molecules to form two-dimensional cationic layers parallel to (001) with $d(\text{O} \cdots \text{N}) = 2.837$ Å – 2.889 Å and $\angle \text{O}-\text{H} \cdots \text{N} = 168^\circ$ – 171° . Out of the two crystallographically distinct lattice H_2O molecules (O6 and O7), the latter ones are each hydrogen bonded to two carboxylate oxygen atoms of different succinate anions centered at the $1b$ sites to generate 1D anionic chains extending in the $[1\bar{1}0]$ direction. The anionic chains are sandwiched between cationic layers. Being involved in a hydrogen bond from the O1 aqua ligand, the O6 water molecule forms hydrogen bonds to one hmt nitrogen atom and to one lattice water O7 atom. The structure was further stabilized by hydrogen bonds from the remaining aqua ligands to carboxylate oxygen atoms between the cationic layers and the anionic chains. The bond distances and angles in the succinate $\text{C}_4\text{H}_4\text{O}_4^{2-}$ anion and hexamethylenetetramine molecule are within normal ranges [1–4].

Table 1. Data collection and handling.

Crystal:	colorless block, size $0.24 \times 0.47 \times 0.53$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	5.36 cm^{-1}
Diffractionmeter, scan mode:	Bruker P4, θ - 2θ
$2\theta_{\text{max}}$:	54.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3882, 3275
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3066
$N(\text{param})_{\text{refined}}$:	220
Programs:	SHELXS-97 [5], SHELXL-97 [6]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1A)	2i	0.1556	0.1712	0.3371	0.044(1)
H(1B)	2i	0.0363	0.3575	0.3374	0.044
H(2A)	2i	0.5071	0.1934	0.3644	0.044
H(2B)	2i	0.4405	0.0716	0.3542	0.044
H(3A)	2i	0.3721	0.1802	−0.0046	0.044
H(3B)	2i	0.3583	0.0635	0.1296	0.044
H(4A)	2i	0.5283	0.3717	0.1570	0.044
H(4B)	2i	0.4747	0.3663	0.0118	0.044
H(5A)	2i	0.1383	0.5450	0.3543	0.044
H(5B)	2i	0.3241	0.4801	0.3650	0.044
H(6A)	2i	0.1910	0.4652	−0.0048	0.044
H(6B)	2i	0.0573	0.5366	0.1292	0.044

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(8A)	2i	−0.0008	−0.0394	0.6507	0.044
H(8B)	2i	0.0808	0.0644	0.5607	0.044
H(9A)	2i	0.293(3)	−0.031(2)	0.870(2)	0.048(5)
H(9B)	2i	0.190(3)	0.114(3)	0.811(2)	0.059(6)
H(10A)	2i	0.219(3)	−0.275(3)	1.130(2)	0.055(5)
H(10B)	2i	0.208(2)	−0.167(2)	1.214(2)	0.045(5)
H(11A)	2i	0.133(3)	−0.237(2)	0.808(2)	0.056(5)
H(11B)	2i	−0.005(3)	−0.239(2)	0.889(2)	0.056(5)
H(12A)	2i	0.220(4)	0.284(3)	0.597(3)	0.094(9)
H(12B)	2i	0.264(3)	0.315(3)	0.705(3)	0.066(7)
H(13A)	2i	0.492(3)	0.344(3)	0.677(2)	0.062(6)
H(13B)	2i	0.374(3)	0.490(3)	0.680(2)	0.064(6)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Mn	1a	0	0	0	0.0268(2)	0.0259(2)	0.0254(2)	−0.0135(1)	−0.00457(9)	−0.00111(9)
O(1)	2i	0.1953(1)	0.0391(1)	0.8694(1)	0.0282(5)	0.0357(5)	0.0481(6)	−0.0139(4)	−0.0008(4)	0.0089(4)
O(2)	2i	0.1869(1)	−0.1755(1)	1.1362(1)	0.0446(5)	0.0286(4)	0.0328(5)	−0.0115(4)	−0.0166(4)	−0.0014(3)
O(3)	2i	0.0683(1)	−0.2131(1)	0.8897(1)	0.0359(5)	0.0328(4)	0.0290(4)	−0.0194(4)	−0.0042(4)	−0.0043(3)
N(1)	2i	0.2621(2)	0.3009(2)	0.3731(1)	0.0440(6)	0.0493(7)	0.0302(5)	−0.0290(5)	−0.0076(4)	0.0043(5)
N(2)	2i	0.1792(1)	0.2927(1)	0.1463(1)	0.0322(5)	0.0353(5)	0.0374(5)	−0.0195(4)	−0.0063(4)	−0.0036(4)
N(3)	2i	0.4686(1)	0.1911(1)	0.1631(1)	0.0284(5)	0.0322(5)	0.0463(6)	−0.0126(4)	−0.0056(4)	0.0024(4)
N(4)	2i	0.2836(1)	0.4818(1)	0.1631(1)	0.0378(6)	0.0296(5)	0.0342(5)	−0.0188(4)	−0.0067(4)	0.0005(4)
C(1)	2i	0.1473(2)	0.2777(2)	0.3053(2)	0.0386(7)	0.0502(8)	0.0384(7)	−0.0305(6)	−0.0019(5)	0.0004(6)
C(2)	2i	0.4294(2)	0.1790(2)	0.3219(2)	0.0406(7)	0.0439(7)	0.0452(7)	−0.0215(6)	−0.0176(6)	0.0144(6)
C(3)	2i	0.3483(2)	0.1710(2)	0.1002(2)	0.0382(7)	0.0306(6)	0.0465(7)	−0.0165(5)	−0.0039(5)	−0.0064(5)
C(4)	2i	0.4502(2)	0.3559(2)	0.1165(2)	0.0315(6)	0.0390(7)	0.0400(6)	−0.0215(5)	−0.0037(5)	0.0031(5)
C(5)	2i	0.2482(2)	0.4632(2)	0.3223(1)	0.0474(8)	0.0424(7)	0.0336(6)	−0.0260(6)	−0.0055(5)	−0.0064(5)
C(6)	2i	0.1680(2)	0.4545(2)	0.1000(1)	0.0320(6)	0.0312(6)	0.0346(6)	−0.0127(5)	−0.0094(5)	0.0000(5)
O(4)	2i	0.2882(1)	−0.1911(2)	0.3981(1)	0.0327(5)	0.0649(7)	0.0311(5)	−0.0008(5)	−0.0028(4)	−0.0093(4)
O(5)	2i	0.2664(1)	−0.2780(1)	0.6308(1)	0.0378(5)	0.0324(5)	0.0383(5)	−0.0029(4)	−0.0079(4)	0.0018(4)
C(7)	2i	0.2154(1)	−0.1771(2)	0.5258(1)	0.0247(5)	0.0322(6)	0.0296(5)	−0.0096(5)	−0.0066(4)	−0.0049(4)
C(8)	2i	0.0561(1)	−0.0237(1)	0.5566(1)	0.0283(5)	0.0267(5)	0.0246(5)	−0.0088(4)	−0.0061(4)	−0.0009(4)
O(6)	2i	0.1987(2)	0.2863(2)	0.6831(1)	0.0594(7)	0.0586(7)	0.0398(6)	−0.0363(6)	−0.0003(5)	0.0069(5)
O(7)	2i	0.4071(2)	0.3986(2)	0.7227(1)	0.0409(6)	0.0361(5)	0.0558(6)	−0.0113(5)	0.0019(5)	−0.0033(5)

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