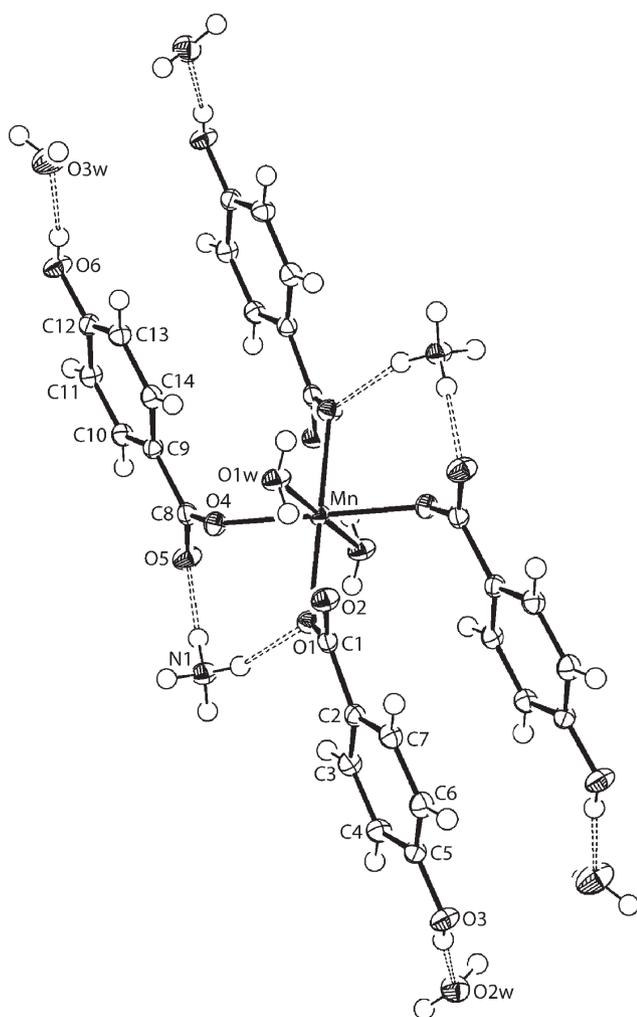


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Crystal structure of bis(ammonium) diaquatetrakis(4-hydroxybenzoato)-manganese(II) tetrahydrate, $[\text{NH}_4]_2[\text{C}_{28}\text{H}_{24}\text{MnO}_{14}] \cdot 4(\text{H}_2\text{O})$



Abstract

$\text{C}_{28}\text{H}_{40}\text{MnN}_2\text{O}_{18}$, monoclinic, $P2_1/c$ (no. 14), $a = 7.1069(1) \text{ \AA}$, $b = 20.5238(2) \text{ \AA}$, $c = 10.8978(1) \text{ \AA}$, $\beta = 96.029(1)^\circ$, $V = 1580.77(3) \text{ \AA}^3$, $Z = 2$, $R_{\text{gt}}(F) = 0.0255$, $wR_{\text{ref}}(F^2) = 0.0746$, $T = 294(2) \text{ K}$.

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The molecular structures are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

| | |
|--|--|
| Crystal: | Red block |
| Size: | $0.40 \times 0.20 \times 0.20 \text{ mm}$ |
| Wavelength: | Mo $K\alpha$ radiation (0.71073 \AA) |
| μ : | 0.51 mm^{-1} |
| Diffractometer, scan mode: | Bruker SMART APEX, ω |
| θ_{max} , completeness: | 28.4° , $>99\%$ |
| $N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} : | 15856, 3966, 0.020 |
| Criterion for I_{obs} , $N(hkl)_{\text{gt}}$: | $I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3684 |
| $N(\text{param})_{\text{refined}}$: | 259 |
| Programs: | Bruker [1], SHELX [2, 3], WinGX/ORTEP [4] |

Source of material

All chemicals and solvents were used as purchased without purification. The melting point of the complex was measured on a Mel-Temp II digital melting point apparatus and was uncorrected. The IR spectrum was measured on a Bruker Vertex 70v FTIR spectrophotometer from 4000 to 400 cm^{-1} .

Manganese chloride tetrahydrate (Merck; 0.20 g , 1 mmol) and 4-hydroxybenzoic acid (Merck; 0.55 g , 4 mmol) were dissolved in methanol (25 mL) and the mixture was refluxed for 1 h . After filtration, the filtrate was evaporated slowly until pink-red crystals were formed.

The crystals were filtered, washed with a minimum amount of methanol and air-dried. Yield: 0.30 g (40%). **M.pt:** $495\text{--}497 \text{ K}$. **IR** (cm^{-1}) 3389 (br) $\nu(\text{O-H})$, 1670 (s) $\nu(\text{C-O})$, 1594 (s) $\nu(\text{C-O})$, 1167 (m) $\nu(\text{C-O})$, 1100 (m) $\nu(\text{C-O})$.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2).

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|------------|------------|----------------------------------|
| Mn | 0.5000 | 0.5000 | 0.5000 | 0.01015(7) |
| O1 | 0.33897(10) | 0.41344(4) | 0.55311(7) | 0.01404(15) |
| O2 | 0.41845(11) | 0.41431(4) | 0.75735(7) | 0.01518(15) |
| O3 | 0.27846(11) | 0.11113(4) | 0.66820(7) | 0.01529(16) |
| H3O | 0.243(2) | 0.0963(7) | 0.6000(7) | 0.023* |
| O4 | 0.23371(10) | 0.54453(4) | 0.43953(7) | 0.01319(15) |
| O5 | 0.10129(11) | 0.54170(4) | 0.24551(7) | 0.01742(16) |
| O6 | 0.18658(11) | 0.84730(4) | 0.32227(7) | 0.01695(16) |
| H6O | 0.236(2) | 0.8658(7) | 0.3842(9) | 0.025* |
| O1W | 0.45536(11) | 0.53725(4) | 0.68341(7) | 0.01551(16) |
| H1W | 0.441(2) | 0.5019(4) | 0.7173(12) | 0.023* |
| H2W | 0.5296(17) | 0.5611(5) | 0.7256(11) | 0.023* |
| C1 | 0.36385(14) | 0.38519(5) | 0.65759(9) | 0.01196(19) |
| C2 | 0.33176(14) | 0.31313(5) | 0.66129(9) | 0.01141(19) |
| C3 | 0.24899(14) | 0.28002(5) | 0.55782(9) | 0.01264(19) |
| H3 | 0.2057 | 0.3035 | 0.4875 | 0.015* |
| C4 | 0.22990(15) | 0.21281(5) | 0.55765(9) | 0.01333(19) |
| H4 | 0.1736 | 0.1915 | 0.4879 | 0.016* |
| C5 | 0.29555(14) | 0.17742(5) | 0.66259(9) | 0.01230(19) |
| C6 | 0.37880(14) | 0.20962(5) | 0.76686(9) | 0.01306(19) |
| H6 | 0.4235 | 0.1860 | 0.8368 | 0.016* |
| C7 | 0.39493(14) | 0.27706(5) | 0.76627(9) | 0.01241(19) |
| H7 | 0.4485 | 0.2985 | 0.8367 | 0.015* |
| C8 | 0.17051(14) | 0.57273(5) | 0.33891(9) | 0.01206(19) |
| C9 | 0.17638(14) | 0.64532(5) | 0.33642(9) | 0.01138(19) |
| C10 | 0.10795(14) | 0.67931(5) | 0.22992(9) | 0.01266(19) |
| H10 | 0.0593 | 0.6564 | 0.1601 | 0.015* |
| C11 | 0.11155(14) | 0.74660(5) | 0.22697(9) | 0.01322(19) |
| H11 | 0.0643 | 0.7687 | 0.1558 | 0.016* |
| C12 | 0.18616(14) | 0.78133(5) | 0.33087(9) | 0.01242(19) |
| C13 | 0.25670(14) | 0.74827(5) | 0.43760(9) | 0.01251(19) |
| H13 | 0.3073 | 0.7713 | 0.5068 | 0.015* |
| C14 | 0.25075(14) | 0.68065(5) | 0.43973(9) | 0.01227(19) |
| H14 | 0.2970 | 0.6586 | 0.5111 | 0.015* |
| N1 | 0.00094(13) | 0.42852(4) | 0.36697(8) | 0.01452(17) |
| H1N | 0.1026(13) | 0.4157(7) | 0.4158(11) | 0.017* |
| H2N | 0.0287(19) | 0.4632(5) | 0.3232(11) | 0.017* |
| H3N | -0.0900(15) | 0.4388(7) | 0.4137(11) | 0.017* |
| H4N | -0.0472(19) | 0.3978(5) | 0.3155(11) | 0.017* |
| O2W | 0.19263(11) | 0.05218(4) | 0.44468(7) | 0.01777(16) |
| H3W | 0.2745(14) | 0.0625(8) | 0.3998(11) | 0.027* |
| H4W | 0.0887(10) | 0.0499(8) | 0.4030(11) | 0.027* |
| O3W | 0.33058(14) | 0.92190(4) | 0.50879(8) | 0.02565(19) |
| H5W | 0.364(2) | 0.9160(7) | 0.5826(6) | 0.038* |
| H6W | 0.285(2) | 0.9584(4) | 0.4956(14) | 0.038* |

Experimental details

The C-bound H atoms were geometrically placed ($\text{C-H} = 0.93 \text{ \AA}$) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The O- and N-bound H-atoms were located from difference Fourier maps and then refined with $\text{O-H} = 0.82 \pm 0.01 \text{ \AA}$ and $\text{N-H} = 0.89 \pm 0.01 \text{ \AA}$, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ or

$1.2U_{\text{eq}}(\text{N})$. Owing to poor agreement, one reflection, i.e. (-211) , was omitted from the final cycles of refinement.

Comment

Manganese carboxylates have been investigated extensively owing to their important roles in many biological systems. In particular, they are known to participate in a variety of reactions related to the metabolism and evolution of molecular oxygen. The evidence for this conclusion derives from the fact that manganese is required for activity in enzymes such as catalases or pseudocatalase and superoxide dismutase [5, 6]. The availability of a large number of manganese carboxylates in the literature [7] with different structural motifs and, crucially, variable oxidation states prompted the investigation of the synthesis and X-ray structure determination of the title manganese(II) carboxylate complex salt hydrate, $[\text{NH}_4]_2[\text{Mn}(\text{O}_2\text{CC}_6\text{H}_4\text{-4-OH})_4(\text{OH}_2)_2] \cdot 4 \text{ H}_2\text{O}$, (I), with the source of ammonium presumed to arise from a contaminant in a solvent used in the synthesis.

The molecular structures of the extended asymmetric unit of (I), comprising two NH_4^+ cations, a $[\text{Mn}(\text{O}_2\text{CC}_6\text{H}_4\text{-4-OH})_4(\text{OH}_2)_2]^{2-}$ di-anion and four water molecules of crystallisation, are shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation $(i) 1-x, 1-y, 1-z$). The manganese(II) centre is located on a crystallographic centre of inversion and is complexed by four oxygen atoms derived from four 4-hydroxybenzoate ligands and two oxygen atoms derived from two aqua ligands. The Mn—O1, O4 and O1w bonds lengths are 2.2226(7), 2.1422(7) and 2.1940(7) \AA , respectively. The evidence that the 4-hydroxybenzoate anions are coordinating in the monodentate mode is seen in the long Mn···O2 and O5 separations of 3.4111(8) and 3.8474(8) \AA , respectively. The resulting O_6 donor set defines an octahedral geometry with the three *trans* angles, from symmetry, being 180° . The maximum deviation from the ideal *cis* angle of 90° is seen in the O1—Mn—O1w angle of $85.05(3)^\circ$.

As expected from the composition of (I), there are numerous hydrogen-bonding interactions in the structure, both intra- and inter-molecular. The O1w-water molecule forms a hydrogen bond with the non-coordinating O2(carboxylate) atom [$\text{O1w-H1w} \cdots \text{O2}$: $\text{H1w} \cdots \text{O2} = 1.861(9) \text{ \AA}$, $\text{O1w} \cdots \text{O2} = 2.6700(12) \text{ \AA}$ with angle at $\text{H1w} = 166(1)^\circ$]. The second aqua-H atom forms a hydrogen bond to the hydroxy-O3 atom of a symmetry-related di-anion [$\text{O1w-H2w} \cdots \text{O3}^{\text{ii}}$: $\text{H2w} \cdots \text{O3}^{\text{ii}} = 1.981(12) \text{ \AA}$, $\text{O1w} \cdots \text{O3}^{\text{ii}} = 2.8018(11) \text{ \AA}$ with angle at $\text{H2w} = 175(1)^\circ$ for (ii) $1-x, 1/2+y, 3/2-z$]. As shown in the figure, each of the hydroxy groups forms a hydrogen bond to a water molecule of crystallization [$\text{O3-H3o} \cdots \text{O2w}$: $\text{H3o} \cdots \text{O2w} = 1.920(10) \text{ \AA}$, $\text{O3} \cdots \text{O2w} = 2.7308(11) \text{ \AA}$

with angle at $\text{H3o} = 171(1)^\circ$ and $\text{O6} - \text{H6o} \cdots \text{O3w}$: $\text{H6o} \cdots \text{O3w} = 1.852(12) \text{ \AA}$, $\text{O6} \cdots \text{O3w} = 2.6620(12) \text{ \AA}$ with angle at $\text{H6o} = 169(1)^\circ$. Also as shown in the figure, the N1-ammonium cation spans the coordinating-O1 and non-coordinating-O5 atoms to close an eight-membered $\{\cdots \text{HNH} \cdots \text{OCOMnO}\}$ synthon $[\text{N1} - \text{H1n} \cdots \text{O1} : \text{H1n} \cdots \text{O1} = 2.130(11) \text{ \AA}$, $\text{N1} \cdots \text{O1} = 2.9930(12) \text{ \AA}$ with angle at $\text{H1n} = 163(1)^\circ$ and $\text{N1} - \text{H2n} \cdots \text{O5} : \text{H2n} \cdots \text{O5} = 1.916(11) \text{ \AA}$, $\text{N1} \cdots \text{O5} = 2.8026(12) \text{ \AA}$ with angle at $\text{H2n} = 174(1)^\circ$. The third proton of the N1-ammonium cation forms an intermolecular hydrogen bond with a coordinating carboxylate-O4 atom $[\text{N1} - \text{H3n} \cdots \text{O4}^{\text{iii}} : \text{H5w} \cdots \text{O4}^{\text{iii}} = 2.015(12) \text{ \AA}$, $\text{N1} \cdots \text{O4}^{\text{iii}} = 2.8762(12) \text{ \AA}$ with angle at $\text{H3n} = 163(1)^\circ$ for (iii) $-x, 1-y, 1-z]$ and the fourth, with a hydroxyl-O6 atom $[\text{N1} - \text{H4n} \cdots \text{O6}^{\text{iv}} : \text{H4n} \cdots \text{O6}^{\text{iv}} = 1.999(12) \text{ \AA}$, $\text{N1} \cdots \text{O6}^{\text{iv}} = 2.8689(12) \text{ \AA}$ with angle at $\text{H4n} = 166(1)^\circ$ for (iv) $-x, -1/2+y, 1/2-z]$. Finally, the O2w-water molecule donates hydrogen bonds to two non-coordinating carboxylate-O atoms $[\text{O2w} - \text{H3w} \cdots \text{O2}^{\text{v}} : \text{H3w} \cdots \text{O2}^{\text{v}} = 2.004(12) \text{ \AA}$, $\text{O2w} \cdots \text{O2}^{\text{v}} = 2.8115(11) \text{ \AA}$ with angle at $\text{H3w} = 166(1)^\circ$ and $\text{O2w} - \text{H4w} \cdots \text{O5}^{\text{iv}} : \text{H4w} \cdots \text{O5}^{\text{iv}} = 2.003(11) \text{ \AA}$, $\text{O2w} \cdots \text{O5}^{\text{iv}} = 2.7921(11) \text{ \AA}$ with angle at $\text{H4w} = 159(1)^\circ$ for (v) $x, 1/2-y, -1/2+z]$ and the O3w-water molecule forms hydrogen bonds to a non-coordinating carboxylate-O atom and to a water molecule $[\text{O3w} - \text{H5w} \cdots \text{O2}^{\text{ii}} : \text{H5w} \cdots \text{O2}^{\text{ii}} = 2.206(10) \text{ \AA}$, $\text{O3w} \cdots \text{O2}^{\text{ii}} = 2.9573(12) \text{ \AA}$ with angle at $\text{H5w} = 152(1)^\circ$ and $\text{O3w} - \text{H6w} \cdots \text{O2w}^{\text{vi}} : \text{H6w} \cdots \text{O2w}^{\text{vi}} = 2.090(10) \text{ \AA}$, $\text{O3w} \cdots \text{O2w}^{\text{vi}} = 2.9077(12) \text{ \AA}$ with angle at $\text{H6w} = 173(1)^\circ$ for (vi) $x, 1+y, z]$. The result of the hydrogen bonding specified above is a three-dimensional architecture. Globally, molecules assemble into hydrophilic and hydrophobic layers along the *b*-axis direction. The phenyl rings from one layer are connected to the adjacent hydrophilic layer by the hydrogen bonds formed by their hydroxy groups.

The C—O(carboxylate) bond lengths are not greatly different from each other, i.e. $\text{C1} - \text{O1}$, $\text{O2} = 1.2734(12)$ and $1.2654(12) \text{ \AA}$, and $\text{C8} - \text{O4}$, $\text{O5} = 1.2789(12)$ and $1.2563(12) \text{ \AA}$ when they might be expected to be significantly disparate owing to the monodentate mode of coordination of the carboxylate anions. While the coordinating O1 and O4 atoms form the longer bonds, as anticipated, the bond involving the formally carbonyl-O2 and -O5 atoms are relatively long. This observation is rationalized in terms of the hydrogen bonding interactions just described. Thus, while each of the coordinating O1 and O4 atoms accepts a single hydrogen bond, the O2 atom accepts three strong hydrogen bonds and the O5

atom, two. This pattern of hydrogen bonding, explains the relatively small difference in the C—O bond lengths and the longer C1—O2 bond length compared with the C8—O5 bond.

Similar *trans*-Mn(O-benzoate) $_4(\text{OH}_2)_2$ coordination geometries as seen in the title di-anion have been reported previously, namely in the structures of $\text{Mn}(\text{O}_2\text{CC}_6\text{H}_4\text{-4-OMe})_2(\text{OH}_2)_2$ [8] and $\text{Mn}(\text{O}_2\text{CC}_6\text{H}_4\text{-4-OC}_6\text{H}_4\text{CO}_2\text{H-4})_2(\text{OH}_2)_2$ [9]. In these anhydrous manganese(II) complexes, the benzoate ligands are bidentate bridging with the result that each of the literature structures is a two-dimensional coordination polymer with a flat topology. In (I), it is likely that the intervention of the NH_4^+ cations along with the water molecules of crystallization militates the bridging propensity of the benzoate anions.

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References

1. Bruker. SADABS, APEX2 and SAINT. Bruker AXS Inc., Madison, WI, USA (2008).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
5. Wiegardt, K.; Bossek, U.; Nuber, B.; Weiss, J.; Bonvoisin, J.; Corbella, M.; Vitols, S. E.; Girerd, J. J.: Synthesis, crystal structures, reactivity, and magnetochemistry of a series of binuclear complexes of manganese(II), -(III), and -(IV) of biological relevance. the crystal structure of $[\text{L}^{\text{Mn}}\text{Mn}^{\text{IV}}(\mu\text{-O})_3\text{Mn}^{\text{IV}}\text{L}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ containing an unprecedented short Mn \cdots Mn distance of 2.296 Å. *J. Am. Chem. Soc.* **110** (1988) 7398–7411.
6. Sheats, J. E.; Czernuszewicz, R. S.; Dismukes, G. C.; Rheingold, A. L.; Petrouleas, V.; Stubbe, J.; Armstrong, W. H.; Beer, R. H.; Lippard, S. J.: Binuclear manganese(III) complexes of potential biological significance. *J. Am. Chem. Soc.* **109** (1987) 1435–1444.
7. Christou, G.: Manganese carboxylate chemistry and its biological relevance. *Acc. Chem. Res.* **22** (1989) 328–335.
8. Chiragov, F. M.; Musaev, F. N.; Gambarov, D. G.; Abbasov, R. M.; Mamedov, Kh. S.: Crystal structure and thermal conversion of bis(*p*-methoxybenzoato)manganese dihydrate. *Koord. Khim.* **13** (1987) 1412–1417.
9. Chai, Y.; Yang, X.; Sun, W.; Zhou, X.; Wu, Z.; Zhou, W.; Yang, X.: Flexible *N*-donor ligand-induced coordination polymers: syntheses, structures and magnetic properties. *Inorg. Chim. Acta* **410** (2014) 76–81.