

Tetraaquabis(5-carboxy-2-nitrobenzoato- κ O)manganese(II) dihydrate: a metal–water chain complex containing cyclic water tetramers

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Received 4 November 2006

Accepted 22 December 2006

Online 17 February 2007

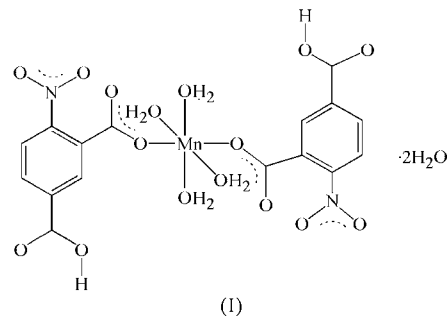
In the title complex, $[\text{Mn}(\text{C}_8\text{H}_4\text{NO}_6)_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$, cyclic water tetramers forming one-dimensional metal–water chains have been observed. The water clusters are trapped by the co-operative association of coordination interactions and hydrogen bonds. The Mn^{II} ion resides on a center of symmetry and is in an octahedral coordination environment comprising two O atoms from two 5-carboxy-2-nitrobenzoate ligands and four O atoms from water molecules.

Comment

Water clusters are bridges between a single water molecule and liquid water or ice. Recent years have witnessed numerous studies of small water clusters (Mascal *et al.*, 2006) from both theoretical (Xantheas, 1994, 1995; Kim *et al.*, 1994, 1999) and experimental aspects (Buck & Huisken, 2000; Barbour *et al.*, 1998; Raghuraman *et al.*, 2003; Janiak & Scharamann, 2002). Among them, the cyclic water tetramer is of great interest since it is a simple two-structure model for liquid water (Benson & Siebert, 1992; Ludwig, 2001). The configurations of such tetramers have been predicted by *ab initio* electronic structure calculations (Gregory & Clary, 1996; Udalde *et al.*, 2000; Radhakrishnan & Herndon, 1991), and some of them have been characterized by far-IR vibration–rotation tunneling spectroscopy (Cruzan *et al.*, 1996) or found in different crystal hosts (Mascal *et al.*, 2006; Xu *et al.*, 2000; Supriya & Das, 2003; Long *et al.*, 2004; Zuhayra *et al.*, 2006). We report here the title metal–water chain complex, $[\text{Mn}(\text{NO}_2\text{-HBDC})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ ($\text{NO}_2\text{-H}_2\text{BDC}$ is 4-nitrobenzene-1,3-dicarboxylic acid), (I), which contains the cyclic water tetramer.

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The asymmetric unit of complex (I) consists of one Mn atom, two $\text{NO}_2\text{-HBDC}$ ligands, four coordinated water molecules and two solvent water molecules (Fig. 1). The Mn^{II} ion is located on a symmetry center and is coordinated by two O atoms of two monodentate carboxylate groups from two



$\text{NO}_2\text{-HBDC}$ ligands [$\text{Mn}-\text{O1}^i = 2.1493(17) \text{ \AA}$; symmetry code: (i) $-x, -y + 2, -z + 1$] and two O atoms from two water molecules [$\text{Mn}-\text{O7} = 2.1815(19) \text{ \AA}$], which form the equatorial plane, and by two O atoms from the other two water molecules [$\text{Mn}-\text{O8} = 2.2060(18) \text{ \AA}$] at the axial positions (Table 1). The coordination geometry around the Mn^{II} ion can be described as a slightly distorted octahedron. The distortion arises from the $\text{O8}-\text{Mn1}-\text{O8}^i$ axis which is not actually perpendicular to the coordination plane ($\text{O1}/\text{O7}/\text{O1}^i/\text{O7}^i/\text{Mn1}$); in fact, the $\text{O1}-\text{Mn1}-\text{O8}$ angle is $89.26(6)^\circ$. In the $\text{NO}_2\text{-HBDC}$ ligand, the dihedral angles between the benzene ring (atoms C2–C7; plane 1) and the planes formed by the carboxylate groups are $68.8(3)$ and $27.9(2)^\circ$ for the $\text{O1}/\text{C1}/\text{O2}$ and $\text{O3}/\text{C8}/\text{O4}$ planes, respectively; the angle between plane 1 and the $\text{O5}/\text{N1}/\text{O6}$ plane is $26.1(2)^\circ$.

There are $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between the coordination water molecules and carboxylate O atoms [$\text{O8}\cdots\text{O4}^{\text{iii}} = 2.725(2) \text{ \AA}$; see Table 2 for symmetry code], which bridge molecules, forming an infinite one-dimensional chain along the *c* axis. The $\text{NO}_2\text{-HBDC}$ ligands are parallel to each other in the chain; the distance between the benzene rings of the $\text{NO}_2\text{-HBDC}$ ligands is $3.588(2) \text{ \AA}$. These chains are further

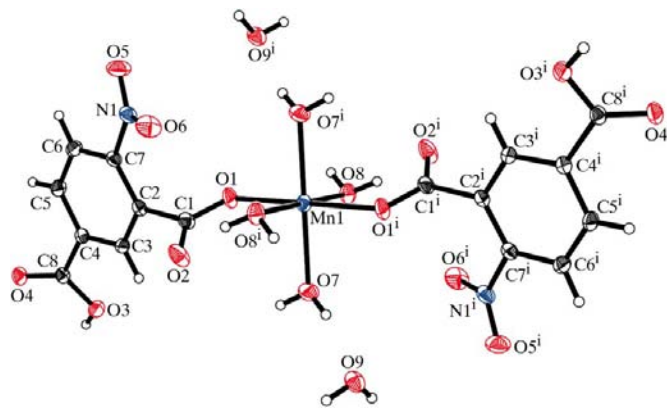


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. [Symmetry code: (i) $-x, 2 - y, 1 - z$.]

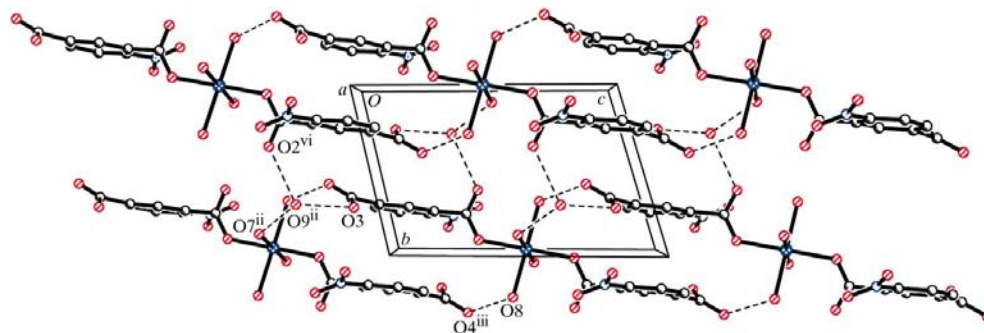


Figure 2
A view of the two-dimensional hydrogen-bonded net projected on to the *bc* plane in (I). Dashed lines indicate hydrogen bonds. [Symmetry codes: (ii) $x, y, -1 + z$; (iii) $-x, 2 - y, -z$; (vi) $1 - x, 1 - y, -z$.]

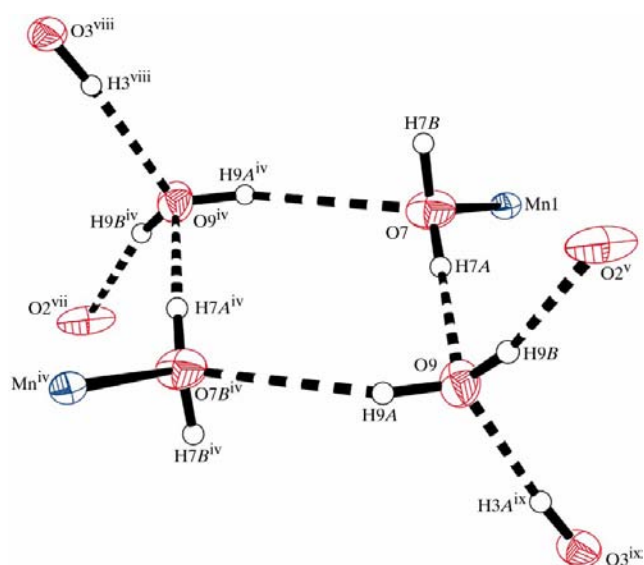


Figure 3
A view of the cyclic water tetramer and its coordination environment in (I). Dashed lines indicate hydrogen bonds. [Symmetry codes: (iv) $1 - x, 2 - y, 1 - z$; (v) $1 - x, 1 - y, 1 - z$; (vii) $x, 1 + y, z$; (viii) $1 - x, 2 - y, -z$; (ix) $x, y, 1 + z$.]

interconnected by solvent water molecules *via* hydrogen bonds [$O9 \cdots O2^v = 2.665(3) \text{ \AA}$, $O3 \cdots O9^{ii} = 2.608(2) \text{ \AA}$ and $O7 \cdots O9^{iv} = 2.829(2) \text{ \AA}$; see Table 2 for symmetry codes], giving rise to a two-dimensional structure in the *bc* plane, as shown in Fig. 2.

Interestingly, a cyclic water tetramer is observed in the solid state (Fig. 3). The solvent water molecule in the cluster is in a tetrahedral environment with two water–water hydrogen bonds and two water–carboxylate hydrogen bonds. Meanwhile, the coordinated water molecule are involved in two water–water hydrogen bonds and one water–metal coordination bond. Within the cluster, the four water molecules are completely coplanar without regard to connectivity of the H atoms. Though the $O9 \cdots O7$ distance (3.155 \AA) is longer than the sum of van der Waals radii (3.04 \AA), we think there still exist weak hydrogen-bonding interactions, as found in many of the compounds reported previously (Liu & Xu, 2005; Fabelo *et al.*, 2006). The average $O \cdots O$ distance is 2.99 \AA . This distance is significantly longer than the distance of 2.78 \AA estimated in

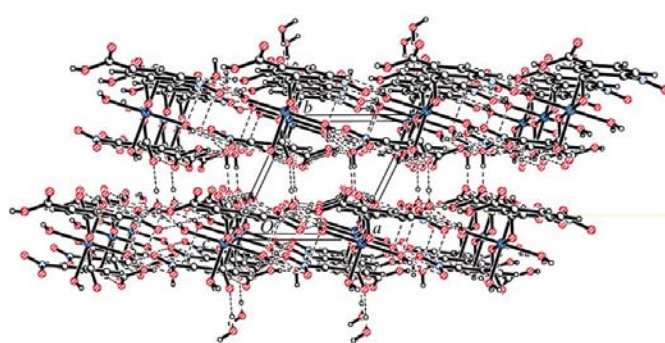


Figure 4
The crystal packing of (I), viewed down the *c* axis. Dashed lines indicate hydrogen bonds.

the water tetramer of $(D_2O)_4$ in the gas phase (Cruzan *et al.*, 1996), and longer than in other tetrameric clusters reported previously (2.77 – 2.94 \AA ; Supriya & Das, 2003; Long *et al.*, 2004; Zuhayra *et al.*, 2006; Tao *et al.*, 2004; Ye *et al.*, 2005). However, it is shorter than that observed in 1,4,7,10-tetraazacyclododecane trihydrate (3.004 \AA ; Pal *et al.*, 2003). Two of the water molecules in the cyclic tetramers of (I) bind to the Mn^{II} ions, resulting in an infinite metal–water chain along the *a* axis. To the best of our knowledge, such cyclic water clusters containing metal–water chains are not common (Turner *et al.*, 2004; Ghosh & Bharadwaj, 2003; Ye *et al.*, 2004; Liu & Xu, 2005; Li *et al.*, 2006). Another remarkable feature is that the two-dimensional structure is assembled into a three-dimensional network (Fig. 4) by the water tetramers through metal–water chains, indicating that the cyclic water tetramer plays a crucial role in the formation of the three-dimensional network.

Experimental

A solution of $MnSO_4$ (0.0151 g , 0.10 mmol) in water (5 ml) was added dropwise with constant stirring to an aqueous solution (5 ml) of 4-nitrobenzene-1,3-dicarboxylic acid (0.0211 g , 0.1 mmol). The resulting mixture was then transferred to a Teflon-lined stainless steel vessel, which was sealed and heated to 403 K for 72 h , then cooled to room temperature. The reaction mixture was filtered and single crystals were obtained from the filtrate after it had been allowed to stand at room temperature for a few days.

Crystal data

$[\text{Mn}(\text{C}_8\text{H}_4\text{NO}_6)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$	$V = 557.4 (5) \text{ \AA}^3$
$M_r = 583.28$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.738 \text{ Mg m}^{-3}$
$a = 7.355 (4) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.965 (4) \text{ \AA}$	$\mu = 0.69 \text{ mm}^{-1}$
$c = 11.056 (6) \text{ \AA}$	$T = 273 (2) \text{ K}$
$\alpha = 73.827 (8)^\circ$	Block, colorless
$\beta = 83.588 (7)^\circ$	$0.24 \times 0.22 \times 0.20 \text{ mm}$
$\gamma = 63.647 (7)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	2863 measured reflections
φ and ω scans	1957 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1741 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.852$, $T_{\max} = 0.875$	$R_{\text{int}} = 0.019$
	$\theta_{\max} = 25.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.1749P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.084$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.04$	$\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
1957 reflections	$\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$
171 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.331 (13)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Mn1—O1 ⁱ	2.1493 (17)	Mn1—O8	2.2060 (18)
Mn1—O1	2.1494 (17)	O1—C1	1.249 (3)
Mn1—O7 ⁱ	2.1815 (19)	O2—C1	1.239 (3)
Mn1—O7	2.1815 (19)	O3—C8	1.317 (2)
Mn1—O8 ⁱ	2.2060 (17)	O4—C8	1.211 (2)

Symmetry code: (i) $-x, -y + 2, -z + 1$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H3 \cdots O9 ⁱⁱ	0.82	1.79	2.608 (2)	175
O7—H7A \cdots O9	0.86	1.99	2.829 (2)	167
O8—H8A \cdots O4 ⁱⁱⁱ	0.85	1.88	2.725 (2)	173
O9—H9A \cdots O7 ^{iv}	0.86	2.43	3.155 (3)	143
O9—H9B \cdots O2 ^v	0.85	1.82	2.665 (3)	168

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

H atoms attached to C atoms were placed at calculated positions ($C-H = 0.93 \text{ \AA}$) and allowed to ride on their parent atoms [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. H atoms attached to O atoms were located in a difference map and refined as riding in their as-found positions ($O-H = 0.82-0.86 \text{ \AA}$), with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

The authors are grateful to the National Natural Science Foundation of China (grant Nos. 20371009 and 20171008) and the Foundation for the Key Laboratory of Radiopharmaceuticals (Beijing Normal University) supported by the Ministry of Education (grant No. 0502).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3055). Services for accessing these data are described at the back of the journal.

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