

Structure of *catena-diaquatetrakis* (μ_2 -3,5-dinitrobenzoato-*O,O'*-manganese(II))

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Abstract

The structure of the title compound, $[\text{Mn}(\mu_2\text{-C}_7\text{H}_3\text{N}_2\text{O}_6)_2(\text{H}_2\text{O})_2]_n$ (**I**), has been determined at 150 K. The complex **I** forms 1-D polymeric chains connecting Mn^{2+} through bridging 3,5-dinitrobenzoate ligands. The Mn^{2+} ion is hexacoordinated to four oxygen atoms of bridging 3,5-dinitrobenzoate ligands and two water molecules. The molecules of **I** are connected through multicentered O–H···O hydrogen bonds, weak C–H···O interactions and π - π stacking interactions.

Keywords: manganese, X-ray, polymeric structure, hydrogen bonds

Introduction

The coordination polymers, which can be used as materials for heterogenous catalysis, physical adsorption of gases, non-linear optic materials, luminescent materials or magnetic materials represent a growing area of crystal engineering (Janiak, 2003; James, 2003). Although some manganese(II) carboxylates have been studied, the crystal structures of polymeric manganese(II) 3,5-dinitrobenzoate have not yet been well documented (Guo et al., 2007, Wang et al., 2007, 2010). The aim of this paper is to report an X-ray structure of the polymeric $[\text{Mn}(\mu_2\text{-C}_7\text{H}_3\text{N}_2\text{O}_6)_2(\text{H}_2\text{O})_2]_n$ complex.

Experimental

Synthesis

Manganese(II) carbonate (1.03 g) was mixed in water ($V = 50$ mL) with 3,5-dinitrobenzoic acid (3.82 g) in molar ratio 9:18. This mixture was stirred for 5 days resulting in a dark-brown suspension. The dark-brown precipitate was then filtered off and the mother liquor of pale-yellow colour was left to crystallize. Yellow, needle-like crystals of the title compound were separated from the mother liquor after 2 months.

Table 1. Experimental details.

Chemical formula	$C_{14}H_{10}MnN_4O_{14}$
M_r	513.20
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	150
a, b, c (Å)	25.907(3), 4.705(1), 18.312(2)
β (°)	124.17(3)
V (Å ³)	1846.7(5)
Z	4
Radiation type	Mo K_α
μ (mm ⁻¹)	0.81
Crystal size (mm)	0.48 × 0.23 × 0.15
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan SADABS (Bruker, 2008)
T_{min}, T_{max}	0.698, 0.889
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6024, 2050, 1735
R_{int}	0.023
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.029, 0.077, 1.09
No. of reflections	2050
No. of parameters	151
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.32, -0.23
CCDC	846177

X-ray Crystallography

Crystal data and conditions of data collection and refinement are reported in Table 1. Data collection and cell refinement were carried out using diffractometer Bruker KAPPA APEXII

CCD (Bruker, 2008) at 150 K with graphite monochromated Mo K α radiation. The semi-empirical absorption corrections were applied using multi-scan method. The structures were solved by direct methods using SIR-97 (Altomare et al., 1999) and refined by the full-matrix least-squares procedure with SHELXL-97 (Sheldrick, 2008). Geometrical analyses were performed with SHELXL-97. The structures were drawn with XP in SHELXTL (Sheldrick, 2008).

Results and discussion

The crystal structure of the title compound at 295 K has already been reported (Yang et al., 2001). The crystal structure of the complex **I** has been redetermined at 150 K. The complex has been prepared by a different method (see experimental section) as reported previously (Yang et al., 2001). The title complex exhibits a one-dimensional coordination polymeric chain, shown in Fig. 1. Each Mn²⁺ ion is located at an inverse center and coordinated by two aqua ligands [Mn1–O1W = 2.1734(12) Å] and four carboxylate oxygen atoms [Mn1–O1 = 2.1211(11) Å and Mn1–O2 = 2.2313(11) Å] from four bridging 3,5-dinitrobenzoate ligands in trans positions in a nearly idealized octahedron with O–Mn–O bond angles in the range of 84.32(5)–95.68(5)°. All Mn1–O bond distances of **I** at 150 K are longer by 0.01 Å than those determined at 295 K. The molecular structure is stabilized by intramolecular hydrogen bonds between coordinated water molecules and coordinated carboxylate O atoms of 3,5-dinitrobenzoate ligands [O1W–H1W...O1ⁱⁱ (Symmetry code: (ii) x, y+1, z) with O...O distance of 2.801(2) Å.

Each pair of Mn atoms are bridged by two 3,5-dinitrobenzoate ligands to form infinite linear chains with the Mn...Mn distance being 4.71 Å. The structure of **I** exhibits at 295 K a shorter Mn...Mn distance being of 4.66 Å (Yang et al., 2001). The crystal structure of two dimensional coordination polymers [Mn₂(μ_2 -C₇H₃N₂O₆)₄(μ_2 -4,4'-bipyridine)]_n (**II**) (Wang et al., 2010) consists of similar linear chains connected through bridging 4,4'-bipyridine ligands. The N atoms of coordination polyhedron in **II** are oriented in *trans* positions. The Mn...Mn separation in crystal structure of **II** is 5.08 Å. On the other hand, the crystal structures of [Mn(μ_2 -C₇H₃N₂O₆)₂(μ_2 -2,2'-bipyridine)]_n (**III**) (Guo et al., 2007) and [Mn(μ_2 -C₇H₃N₂O₆)₂(μ_2 -1,10-phenanthroline)]_n (**IV**) (Wang et al., 2007) show *zigzag* one-dimensional coordination polymers. The N atoms of coordination polyhedron in both complexes (**III,IV**) are oriented in *cis* positions. In the complex **III**, Mn...Mn separation within the coordination polymer exists

in two different and alternating distances, being of 4.79 and 4.34 Å, respectively. A similar situation exists for complex IV, with distances being of 4.77 and 4.42 Å.

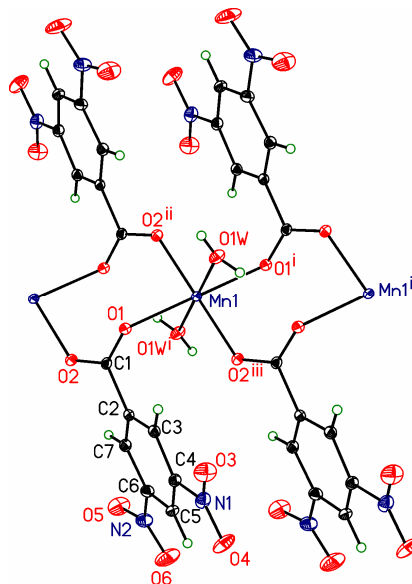


Fig. 1. Perspective view of I, with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms have been omitted for clarity.

Table 2. Selected geometric parameters (Å, °).

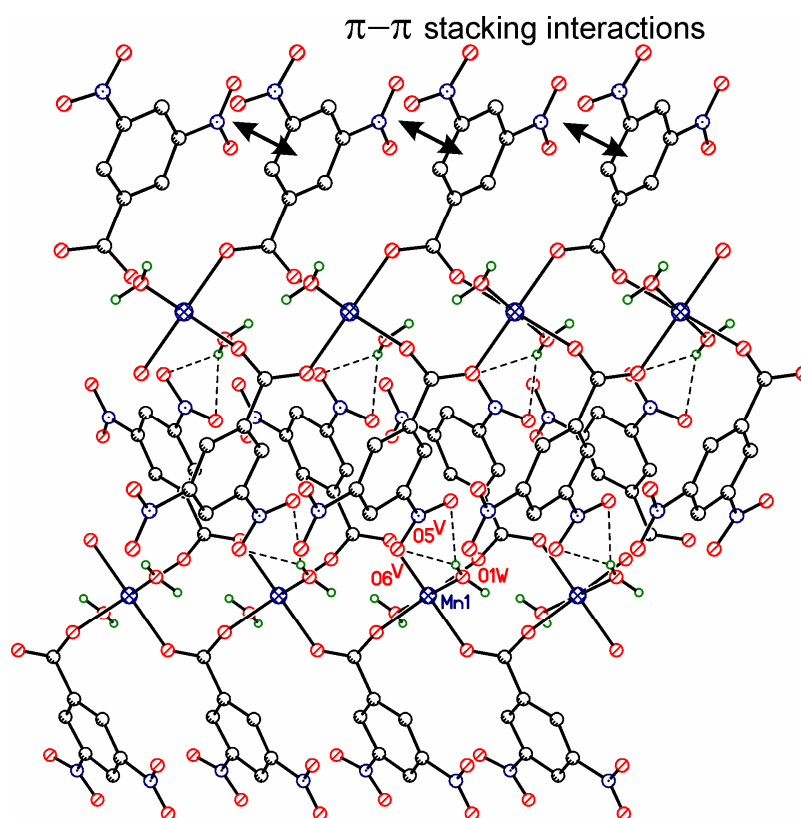
Mn1—O2 ⁱ	2.1211(13)	Mn1—O1W	2.1734(12)
Mn1—O2 ⁱⁱ	2.1211(13)	Mn1—O1 ⁱⁱⁱ	2.2313(11)
Mn1—O1W ⁱⁱⁱ	2.1734(12)	Mn1—O1	2.2313(11)
O2 ⁱ —Mn1—O2 ⁱⁱ	180.00	O1W ⁱⁱⁱ —Mn1—O1 ⁱⁱⁱ	95.68(5)
O2 ⁱ —Mn1—O1W ⁱⁱⁱ	88.67(5)	O1W—Mn1—O1 ⁱⁱⁱ	84.32(5)
O2 ⁱⁱ —Mn1—O1W ⁱⁱⁱ	91.33(5)	O2 ⁱ —Mn1—O1	89.34(4)
O2 ⁱ —Mn1—O1W	91.33(5)	O2 ⁱⁱ —Mn1—O1	90.66(4)
O2 ⁱⁱ —Mn1—O1W	88.67(5)	O1W ⁱⁱⁱ —Mn1—O1	84.32(5)
O1W ⁱⁱⁱ —Mn1—O1W	180.00	O1W—Mn1—O1	95.68(5)
O2 ⁱ —Mn1—O1 ⁱⁱⁱ	90.66(4)	O1 ⁱⁱⁱ —Mn1—O1	180.00
O2 ⁱⁱ —Mn1—O1 ⁱⁱⁱ	89.34(4)		

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

Table 3. Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$D-H\cdots A$ (°)
O1W—H1W \cdots O1 ⁱ	0.84	2.09	2.801(2)	142
O1W—H2W \cdots O5 ⁱⁱ	0.84	2.32	3.074(2)	150
O1W—H2W \cdots O6 ⁱⁱ	0.84	2.37	3.112(2)	147
C5—H5 \cdots O4 ⁱⁱⁱ	0.95	2.71	3.637(3)	167

Symmetry code(s): (i) $x, y+1, z$; (ii) $x-1/2, -y+3/2, z-1/2$; (iii) $-x+1/2, -y+5/2, -z+1$.

**Fig. 2.** The two 1-D chains connecting through O–H \cdots O hydrogen bond in crystal structure.

The 1-D coordination chains are linked through multicentered O–H \cdots O hydrogen bonds (Desiraju & Steiner, 1999; Jeffrey, 1997; Gilli & Gilli, 2009) to 3-D hydrogen bonding frameworks (Fig. 2). The multicentered hydrogen bonds are localized between coordinated water molecules and one of two nitro groups of 3,5-dinitrobenzoate ligands of neighbouring 1-D chains (Fig. 2) [O1W–H2W \cdots O5^v and O1W–H2W \cdots O6^v (Symmetry code: (v) $x-1/2, -y+3/2, z-1/2$) with O \cdots O distances of 3.074(2) and 3.112(2) Å, respectively]. The hydrogen

bonds are also supplemented by C5–H5 \cdots O4^{vi} hydrogen bonding interactions (Symmetry code: (vi) $-x+1/2, -y+5/2, -z+1$) with C \cdots O distance of 3.637(3) Å in R₂²(10) supramolecular synthons (Bernstein et al., 1995) (Fig. 3) and π - π stacking interactions (Janiak, 2000) between two 3,5-dinitrobenzoate ligands. The 3,5-dinitrobenzoate ligands are stacked through benzene rings and one nitro group. The distances between aromatic ring and nitro groups of two stacked 3,5-dinitrobenzoate ligands are in the range 3.29–3.37 Å (Fig. 3).

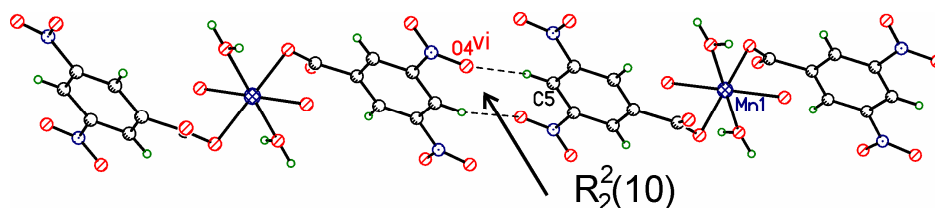


Fig. 3. The C–H \cdots O interactions between two chains of **I**.

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