A Three-dimensional Manganese(II) 1,2,4-Benzenetricarboxylate Hydroxide Framework with Mn–O Inorganic Sheets: Hydrothermal Synthesis and Crystal Structure

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Utilizing unsymmetrical 1,2,4-benzenetricarboxylate (1,2,4-BTC) as a ligand, a complex [$Mn_{2.5}$(1,2,4-BTC)-$(OH)_2(H_2O)$] was synthesized by hydrothermal reaction and characterized by single crystal X-ray diffraction. The coordination polymer crystallizes in the triclinic space group $P\bar{1}$, with cell parameters a = 5.7702(5), b = 8.0269(6), c = 12.1378(9) Å, α = 88.000(1)°, β = 81.493(1)°, γ = 88.569(1)°, and Z = 2. In the the crystal, there are Mn–O–Mn sheets which are further connected through the 1,2,4-BTC ligands into a 3D framework, which is rare in the coordination chemistry originating from transition metal ions and unsymmetrical polycarboxylates.

Key words: Hydrothermal Reaction, Inorganic Sheets, Three-dimensional Framework, Bidentate Bridging Mode

Introduction

The rational design and preparation of metal-organic coordination frameworks with distinctive structures has currently become of interest, mainly originating from the intriguing architectures and the myriad of potential applications, such as gas storage, molecular recognition, heterogeneous catalysis, magnetism, and nonlinear optics [1 – 7]. Up to date, many coordination polymers have been constructed with bidentate or multidentate polycarboxylates as building blocks, due to their structural rigidity and versatile bonding or bridging modes [8]. A series of coordination polymers assembled from transition metal ions and symmetrical polycarboxylates, such as 1,3,5-benzenetricarboxylate, 1,4-benzenedicarboxylate, and 1,2,4,5-benzenetetracarboxylate (BTC) have been widely investigated [8 – 15]. However, in contrast to the large number of coordination polymers built from symmetrical polycarboxylates, reports on the polymers constructed from unsymmetrical polycarboxylates and divalent metals are rarely documented [16 – 22]. The topologies of the resulting coordination polymers mainly depend on the appropriate selection of ligands and the choice of reaction parameters, such as temperature, pH value, and the ratio of metal ion to ligand [23, 24]. On the basis of the aforementioned considerations, we synthesized a unique three-dimensional manganse-1,2,4-BTC coordination polymer [$Mn_{2.5}$(1,2,4-BTC)$(OH)_2(H_2O)$] under hydrothermal conditions. As far as we know, this is only the second manganese-1,2,4-BTC coordination architecture, the first being [$Mn_3(C_9H_3O_6)_2(C_{10}H_8N_2)_2$-$(H_2O)_2$] with a 2D structure reported in 2001 [19].

Experimental Section

General methods

All chemicals utilized were of reagent grade and used as purchased without purification. Infrared spectra were recorded from KBr pellets in the range of 400 – 4000 cm^{-1} on a Shimadzu 8400S-FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer.

Synthesis of [$Mn_{2.5}$(1,2,4-BTC)$(OH)_2(H_2O)$]

Complex [$Mn_{2.5}$(1,2,4-BTC)$(OH)_2(H_2O)$] was synthesized by hydrothermal reaction of $MnCl_2 \cdot 4H_2O$ (0.5 mmol), 1,2,4-BTC (0.25 mmol), $N(C_2H_5)_3$ (7.2 mmol), and 10 mL of H_2O in a 15 mL Teflon-lined stainless steel vessel. The vessel was kept at 160 °C for 96 h, and then cooled at a rate of 0.2 °C/min to r. t. The product was washed with alcohol and water and dried in the open atmosphere. Brown block crystals were obtained with a yield of 62 % based on Mn. – IR (KBr pellet): ν = 3421(br), 1612(s), 1492(m), 1398(s), 1259(w), 1178(m), 1135(m), 1076(s), 850(m), 823(w), 800(w), 777(s), 705(sh), 671(m), 555(m), 505(s) cm^{-1}. – Analysis for $C_9H_7Mn_{2.5}O_9$ (396.50): calcd. C 27.26, H 1.78; found C 27.53, H 1.83.

Table 1. Crystal structure and refinement data for compound $[Mn_{2.5}(1,2,4\text{-BTC})(OH)_2(H_2O)]$.

Empirical formula	$C_9H_7Mn_{2.5}O_9$
Formula weight	396.50
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal size, mm^3	$0.4 \times 0.3 \times 0.1$
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	5.7702(5)
b, Å	8.0269(6)
c, Å	12.1378(9)
α, deg	88.000(1)
β, deg	81.493(1)
γ, deg	88.569(1)
Volume, Å^3	555.55(8)
Z	2
D_{calcd}, g cm^{-3}	2.370
$F(000)$, e	391
θ range for data collected, deg	2.54 – 28.17
Limiting indices	$-7 \le h \le 6$, $-8 \le k \le 10$, $-15 \le l \le 16$
Reflections collected/unique	3527/2567
R_{int}	0.0410
Data/parameters	2567/203
GOF on F^2	0.946
$R1/wR2$ $[I \ge 2\sigma(I)]$	0.028/0.058
$R1/wR2$ (all data)	0.036/0.061
$\Delta\rho_{\text{min / max}}$, e Å^{-3}	−0.54/0.42

Crystal structure determination

The X-ray single crystal diffraction data of $[Mn_{2.5}(1,2,4\text{-BTC})(OH)_2(H_2O)]$ were collected on a Bruker Smart CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 293 K. The structure was solved through Direct Methods and refined on F^2 by full-matrix least-squares methods employing SHELXL-97 [25]. All non-hydrogen atoms were refined anisotropically. The crystallographic data and details of refinement are given in Table 1. Selected bond lengths and angles are summarized in Table 2.

CCDC688338 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Table 2. Bond lengths (Å) and angles (deg) for $[Mn_{2.5}(1,2,4\text{-BTC})(OH)_2(H_2O)]$[a].

$Mn(1)\text{-}O(8)^{\#2}$	2.1796(18)	$O(3)\text{-}Mn(1)\text{-}O(7)^{\#3}$	89.24(6)
$Mn(1)\text{-}O(8)^{\#1}$	2.1796(18)	$O(3)^{\#7}\text{-}Mn(1)\text{-}O(7)^{\#3}$	90.76(6)
$Mn(1)\text{-}O(3)$	2.2039(16)	$O(7)\text{-}Mn(1)\text{-}O(7)^{\#3}$	180.00(9)
$Mn(1)\text{-}O(3)^{\#3}$	2.2039(16)	$O(6)^{\#4}\text{-}Mn(2)\text{-}O(7)$	103.83(7)
$Mn(1)\text{-}O(7)$	2.2146(16)	$O(6)^{\#4}\text{-}Mn(2)\text{-}O(8)^{\#1}$	93.97(7)
$Mn(1)\text{-}O(7)^{\#3}$	2.2146(17)	$O(7)\text{-}Mn(2)\text{-}O(8)^{\#1}$	83.60(7)
$Mn(2)\text{-}O(6)^{\#4}$	2.0630(18)	$O(6)^{\#4}\text{-}Mn(2)\text{-}O(1)^{\#5}$	94.74(7)
$Mn(2)\text{-}O(8)^{\#1}$	2.1817(18)	$O(7)\text{-}Mn(2)\text{-}O(1)^{\#5}$	103.47(7)
$Mn(2)\text{-}O(1)^{\#5}$	2.2151(17)	$O(8)^{\#1}\text{-}Mn(2)\text{-}O(1)^{\#5}$	167.11(7)
$Mn(2)\text{-}O(9)^{\#6}$	2.490(2)	$O(6)^{\#4}\text{-}Mn(2)\text{-}O(9)$	102.28(7)
$Mn(2)\text{-}O(7)$	2.1141(18)	$O(7)\text{-}Mn(2)\text{-}O(9)$	151.64(7)
$Mn(2)\text{-}O(9)$	2.2233(19)	$O(8)^{\#1}\text{-}Mn(2)\text{-}O(9)$	83.74(7)
$Mn(3)\text{-}O(3)$	2.1697(17)	$O(4)^{\#8}\text{-}Mn(2)\text{-}O(9)$	85.14(7)
$Mn(3)\text{-}O(5)^{\#4}$	2.0587(19)	$O(6)^{\#4}\text{-}Mn(2)\text{-}O(9)^{\#6}$	171.44(7)
$Mn(3)\text{-}O(4)^{\#7}$	2.1541(17)	$O(7)\text{-}Mn(2)\text{-}O(9)^{\#6}$	81.83(7)
$Mn(3)\text{-}O(7)$	2.1611(18)	$O(8)^{\#1}\text{-}Mn(2)\text{-}O(9)^{\#6}$	93.05(7)
$Mn(3)\text{-}O(8)$	2.1328(18)	$O(1)^{\#5}\text{-}Mn(2)\text{-}O(9)^{\#6}$	77.55(7)
$O(8)^{\#2}\text{-}Mn(1)\text{-}O(8)^{\#1}$	180.00	$O(9)\text{-}Mn(2)\text{-}O(9)^{\#6}$	73.63(8)
$O(8)^{\#2}\text{-}Mn(1)\text{-}O(3)$	90.01(7)	$O(5)^{\#4}\text{-}Mn(3)\text{-}O(8)$	132.78(8)
$O(8)^{\#1}\text{-}Mn(1)\text{-}O(3)$	89.99(7)	$O(5)^{\#4}\text{-}Mn(3)\text{-}O(1)^{\#7}$	92.04(7)
$O(8)^{\#2}\text{-}Mn(1)\text{-}O(3)^{\#3}$	89.99(7)	$O(8)\text{-}Mn(3)\text{-}O(1)^{\#7}$	92.94(7)
$O(8)^{\#1}\text{-}Mn(1)\text{-}O(3)^{\#3}$	90.01(7)	$O(5)^{\#4}\text{-}Mn(3)\text{-}O(7)$	93.82(7)
$O(3)\text{-}Mn(1)\text{-}O(3)^{\#3}$	180.00	$O(8)\text{-}Mn(3)\text{-}O(7)$	86.73(7)
$O(8)^{\#2}\text{-}Mn(1)\text{-}O(7)$	98.66(7)	$O(1)^{\#7}\text{-}Mn(3)\text{-}O(7)$	172.30(7)
$O(8)^{\#1}\text{-}Mn(1)\text{-}O(7)$	81.34(7)	$O(5)^{\#4}\text{-}Mn(3)\text{-}O(2)$	117.05(7)
$O(3)\text{-}Mn(1)\text{-}O(7)$	90.76(6)	$O(8)\text{-}Mn(3)\text{-}O(2)$	110.14(7)
$O(3)^{\#3}\text{-}Mn(1)\text{-}O(7)$	89.24(6)	$O(1)^{\#7}\text{-}Mn(3)\text{-}O(2)$	85.94(7)
$O(8)^{\#1}\text{-}Mn(1)\text{-}O(7)^{\#3}$	81.34(7)	$O(7)\text{-}Mn(3)\text{-}O(2)$	86.95(7)
$O(8)^{\#1}\text{-}Mn(1)\text{-}O(7)^{\#3}$	98.66(7)		

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x+1$, y, z; $^{\#2}$ $-x-1$, $-y+1$, $-z$; $^{\#3}$ $-x$, $-y+1$, $-z$; $^{\#4}$ $-x$, $-y+1$, $-z-1$; $^{\#5}$ x, $y+1$, z; $^{\#6}$ $-x$, $-y+2$, $-z$; $^{\#7}$ $-x-1$, y, z; $^{\#8}$ x, $y-1$, z.

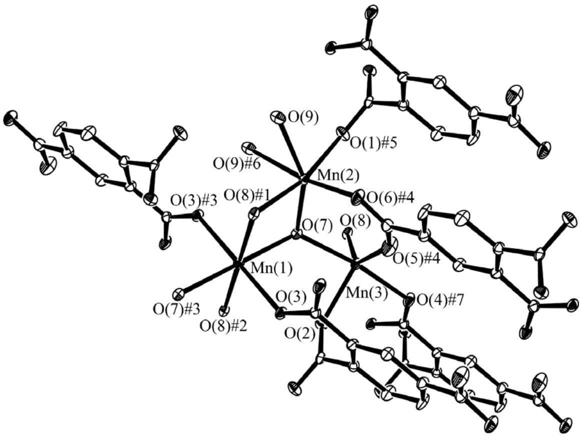

Fig. 1. Details of the coordination environments of the Mn atoms in $[Mn_{2.5}(1,2,4\text{-BTC})(OH)_2(H_2O)]$ (for the symmetry code used, see Table 2).

The single crystal X-ray diffraction experiment of compound $[Mn_{2.5}(1,2,4\text{-BTC})(OH)_2(H_2O)]$ has shown that the complex is a three-dimensional framework assembled from Mn–O inorganic layers and 1,2,4-BTC ligands. There are three types of Mn atoms in the asymmetric unit of the crystal. Mn(1) coordinates with two carboxylate oxygen atoms from 1,2,4-BTC units and two pairs of hydroxyl oxygen atoms which are related by inversion, resulting in the formation of an approximately regular octahedral coordination geometry. Mn(2) is linked to two carboxylate oxygen atoms

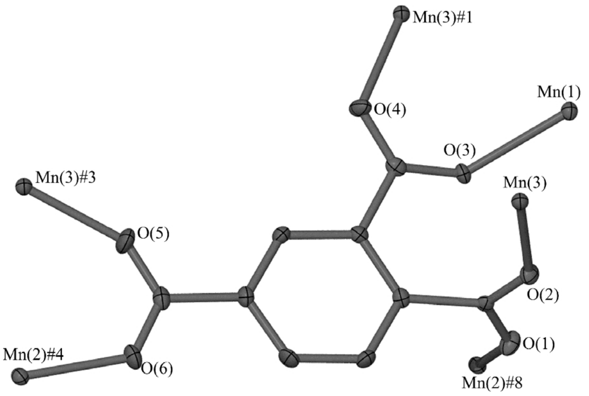

Fig. 2. Coordination mode of the 1,2,4-BTC ligands in [$Mn_{2.5}$(1,2,4-BTC)$(OH)_2(H_2O)$].

(O(6)$^{\#4}$, O(1)$^{\#5}$; for symmetry operations see Table 2), two hydroxyl oxygen atoms (O(7), O(8)$^{\#1}$), and two aqua oxygen atoms (O(9), O(9)$^{\#6}$) related by a center of inversion, thus creating a distorted octahedral coordination geometry with O(1)$^{\#5}$, O(7), O(8)$^{\#1}$, O(9) comprising the equatorial plane and O(6)$^{\#4}$, O(9)$^{\#6}$ occupying the apical sites. However, Mn(3) adopts a distorted trigonal bipyramidal coordination environment and is linked to three carboxylate oxygen atoms (O(3),O(4)$^{\#7}$,O(5)$^{\#4}$) and two hydroxyl oxygen atoms (O(7), O(8)) (Fig. 1). In the Mn(3)–O trigonal bipyramid, O(4)$^{\#7}$and O(7) hold the apical positions, and O(3), O(8), O(5)$^{\#4}$ constitute the equatorial plane. All three carboxylate groups of the 1,2,4-BTC unit exhibit bidentate coordination. Each 1,2,4-BTC unit connects six Mn atoms: one Mn(1) atom, three Mn(3) atoms related to each other by the symmetry operations $x+1, y, z$; $-x, -y+1$; $-z-1$, and two Mn(2) atoms related by a center of inversion (Fig. 2).

The most interesting feature of the complex is the presence of a Mn–O sheet in the framework. All edge-sharing polyhedra of Mn(2)and Mn(2)$^{\#6}$ are generated through O(9), O(9)$^{\#6}$ atoms. These polyhedra are connected with octahedra of Mn(1)–O by sharing O(7) and O(8)$^{\#1}$, so that Mn–O zig-zag chains are formed along the *b* axis. Along the *a* axis, these inorganic chains are linked with each other *via* trigonal bipyramids of Mn(3)–O, resulting in the formation of a Mn–O–Mn sheet (Fig. 3). On the other hand, along the *a* axis, Mn(1)–O octahedra are linked through trigonal bipyramids of Mn(3)–O *via* the O(7)–Mn(3)–O(8) and O(7)$^{\#2}$–Mn(3)$^{\#2}$–O(8)$^{\#2}$ bridging modes, which also builds a Mn–O chain. The chains are joined together through a series of edge-sharing polyhedra of Mn(2)–O along the crystallographic *b* axis, which also are constituents of the Mn–O layer. The Mn–O–Mn layers are linked *via* 1,2,4-BTC units to give a three-dimensional framework. To our best knowledge, in the architectures assembled from transition metal ions and

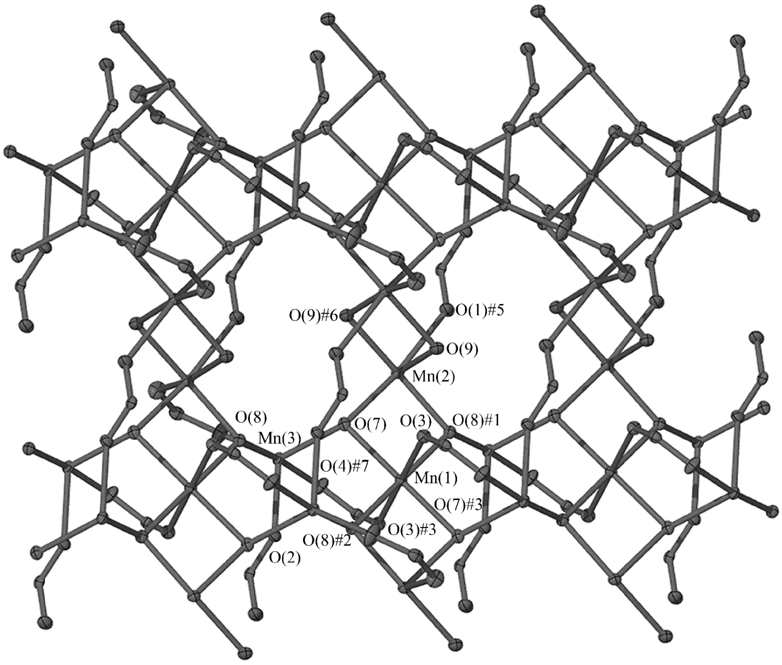

Fig. 3. An infinite Mn-O-Mn layer in [$Mn_{2.5}$(1,2,4-BTC)$(OH)_2(H_2O)$] along the crystallographic *ab* plane (benzene ring, O(5)$^{\#4}$ and O(6)$^{\#4}$ atom of the carboxylate group omitted for clarity).

the 1,2,4-BTC ligand reported in the literature there is only one example with a 3D framework featuring Cd–O–Cd sheets [22].

Summary

In summary, we have successfully prepared a three-dimensional coordination polymer [$Mn_{2.5}$(1,2,4-BTC)$(OH)_2(H_2O)$] by reacting $MnCl_2 \cdot 4H_2O$ with 1,2,4-benzenetricarboxylic acid in the presence of a base under hydrothermal conditions. In the framework of the crystal, there are Mn–O–Mn sheets (Fig. 3), which are further connected through the 1,2,4-BTC ligands. Each of the three carboxylate functions exhibits a bidentate bridging mode (Fig. 2).

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