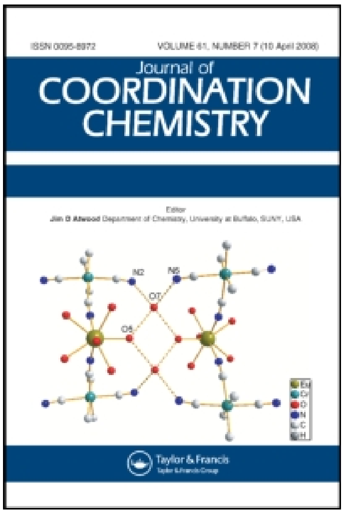

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A novel interdigitating metal-organic architecture showing the double edge-containing (4,4)topology based on the eight-connected Mn_4 tetramer

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A novel interdigitating metal-organic architecture showing the double edge-containing (4,4)topology based on the eight-connected Mn_4 tetramer

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This article presents the structure of a tight stacking coordination polymer, $\{Mn_4(bpy)_2(H_2O)_2(HBT\ C)_4\}_n$, **1**, (bpy=4,4′-dipyridine, H_3BTC=1,3,5-benzenetricarboxylic acid), which is self-assembled from the combination of $MnCl_2$, H_3BTC and bpy ligands via hydrothermal synthesis, and which has been further characterized by IR, element analysis, TG-DTA, variable-temperature magnetic susceptibility measurements. The overall structure of polymer **1** is the 3D interdigitating arrangement, constructed from the eight-connected Mn_4 tetramer. Further, the magnetic measurements reveal that polymer **1** displays a weak antiferromagnetic behavior with $\theta = -3.36\,K$ between Mn(II) ions in the electronic configuration of d^5 high spin ($S = 5/2$).

Keywords: Double edge-containing (4,4) network; Bpy; H_3BTC; Antiferromagnetic coupling

1. Introduction

Metal-organic frameworks are interest because of various applications and intriguing topological forms [1]. From characterization of the networks, [2] the majority are based on three-, four-, and six-connected topologies in which d- and f-block ions act as nodes. Examples of five-, seven-, and eight-connected metal-organic coordination frameworks are extremely rare, [3, 4] as a result of limitations in the symmetry or steric hindrance. Recently, metal clusters with substituted single metal atoms have been used as nodes for high-connected metal-organic frameworks [5]. Compared with d- or f-block ions, metal-cluster-based nodes generally have larger sizes and more coordination sites but smaller steric hindrance when coordinated by organic ligands. Up to now, a connectivity larger than eight has been observed in a few metal-organic frameworks via this method, such as eight- [6] and twelve-connectivity [7, 8]. Herein, we report an example, exhibiting the 3D interdigitating arrangement with the double edge-containing (4,4) nets, constructed from the eight-connected secondary building units (SBUs) of a Mn_4 cluster.

Benzene-1,3,5-tricarboxylic acid (H_3BTC), a polydentate ligand, possesses several interesting characteristics: (i) it contains three carboxylic groups, which after partial or

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full deprotonation, can coordinate to the metal ions in a wide variety of coordination modes leading to high-dimensional structures; (ii) it can act as a hydrogen-bond acceptor or as a hydrogen-bond donor, depending on the number of deprotonated carboxylic groups; (iii) some carboxylic groups may not lie in the phenyl ring plane upon complexation to metal ions owing to geometrical constraints, thereby the ligand may link metal ions in different directions; (iv) the high symmetry may be helpful for crystal growth of the product formed.

On the other hand, the neutral, rigid bidentate bpy gives rise to a special structure [9].

Based on the above considerations, self-assembly between metal ions and H_3BTC in the presence of bpy is carried out to produce polymer **1**.

2. Experimental

2.1. *Materials and methods*

All reagents were bought from commercial sources and used without further purification. Analyses for C, H and N were carried out on a Perkin-Elmer analyzer. Thermal gravimetric analyses were completed on a NETZSCH TG 209 instrument. IR spectra (KBr pellets) were recorded in the 400–4000 cm^{-1} range using a Perkin-Elmer Spectrum One FTIR spectrometer.

2.2. *Synthesis of 1*

An aqueous mixture (10 ml) of $MnCl_2 \cdot 4H_2O$ (60 mg, 0.3 mmol), bpy (57.6 mg, 0.3 mmol), H_3BTC (252 mg, 1.2 mmol) and KOH (201.6 mg, 3.6 mmol) in a molar ratio of 1 : 1 : 4 : 12 was sealed and heated at 180°C for 3 days under autogenous pressure. After cooling to room temperature, yellow crystals (60% yield based on Mn) were collected by filtration, washed with distilled water and dried in air at room temperature. Elemental Anal. calcd (%) for $C_{28}H_{18}Mn_2N_2O_{13}$ **1**: C 48.02, H 2.59, N 4.00; found: C 48.10, H 2.63, N3.89. IR (KBr, cm^{-1}): 3647 v, 3463 s, 3073 m, 1720 v, 1698 v, 1683 v, 1611 vs, 1574 s, 1557 m, 1452 m, 1434 m, 1105 w, 816 s, 450 m.

2.3. *Crystallographic measurements on 1*

A yellow clear single crystal was selected for the diffraction analysis. Data collection was performed on a Bruker SMART 1000 CCD bidimensional detector using Mo-Kα radiation. Data were integrated and corrected for absorption using the Bruker programs SAINT, SADABS and SMART [10]. The structure of **1** was resolved by direct methods and refined using SHELXL-97. All non-hydrogen atoms were located first in difference Fourier maps, whereas hydrogen atoms were placed in calculated positions. Crystal data and experimental details are summarized in table 1. Selected bond lengths and angles are listed in table 2. CCDC number is 284695.

Table 1. Crystallographic data for **1**.

Compound	**1**
Chemical formula	$C_{28}H_{18}Mn_2N_2O_{13}$
M	700.32
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.8472(6)
b (Å)	10.8031(7)
c (Å)	12.5890(8)
α, β, γ (°)	94.0440°(10), 96.0490° (10), 93.2410°(10)
V (Å^3)	1325.68(14)
Z	2
Density (mg m^{-3})	1.754
Reflections collected/unique	7232/4610
S	1.064
Final R indices [$I > 2$ (I)] R indices	$R_1 = 0.0279$, $\omega R_2 = 0.0750$
(all data)	$R_1 = 0.0320$, $\omega R_2 = 0.0767$

Table 2. The selected bond lengths (Å) and angles (°) of **1**.

Mn(1)–O(10)#1	2.0565(15)	O(4)#2–Mn(1)-N(1)	137.92(6)
Mn(1)–O(13)	2.1113(16)	O(10)#1–Mn(1)–O(1)	85.61(6)
Mn(1)–O(2)	2.2192(14)	O(13)–Mn(1)–O(1)	96.19(7)
Mn(1)–O(4)#2	2.2545(14)	O(2)–Mn(1)–O(1)	55.81(5)
Mn(1)-N(1)	2.2670(18)	O(4)#2–Mn(1)–O(1)	71.76(5)
Mn(1)–O(1)	2.4391(15)	N(1)–Mn(1)–O(1)	149.70(6)
Mn(2)–O(8)#3	2.0798(15)	O(8)#3–Mn(2)–O(7)	100.07(6)
Mn(2)–O(7)	2.1362(15)	O(8)#3–Mn(2)–O(6)#3	98.07(7)
Mn(2)–O(6)#3	2.1634(15)	O(7)–Mn(2)–O(6)#3	92.01(6)
Mn(2)-0(l)	2.2077(15)	O(8)#3–Mn(2)–O(1)	92.70(7)
Mn(2)–O(9)#1	2.2503(14)	O(7)–Mn(2)–O(1)	86.55(6)
Mn(2)–O(4)#2	2.2719(14)	O(6)#3–Mn(2)–O(1)	169.22(6)
O(10)#1–Mn(1)–O(13)	178.15(7)	O(8)#3–Mn(2)–O(9)#1	89.61(6)
O(10)#1–Mn(1)–O(2)	90.53(6)	O(7)–Mn(2)–O(9)#1	170.32(6)
O(13)–Mn(1)–O(2)	90.84(6)	O(6)#3–Mn(2)–O(9)#1	86.84(6)
O(10)#1–Mn(1)–O(4)#2	91.86(6)	O(1)–Mn(2)–O(9)#1	92.79(6)
O(13)–Mn(1)–O(4)#	2 88.30(6)	O(8)#3–Mn(2)–O(4)#2	166.92(7)
O(2)–Mn(1)–O(4)#2	127.14(5)	O(7)–Mn(2)–O(4)#2	85.82(6)
O(10)#1–Mn(1)-N(1)	87.09(7)	O(6)#3–Mn(2)–O(4)#2	93.36(6)
O(13)–Mn(1)-N(1)	91.55(7)	O(1)–Mn(2)–O(4)#2	75.89(5)
O(2)–Mn(1)-N(1)	94.95(6)	O(9)#1–Mn(2)–O(4)#2	84.66(5)

Symmetry code: #1 x, $y+1$, z #2$x-1$, y, z #3 $-x+1$, $-y$, $-z+2$.

3. Results and discussion

3.1. *Crystal structure of 1*

Polymer **1** was obtained hydrothermally by the reaction of $MnCl_2$, bpy, H_3BTC, and KOH in water, the overall structure of which is the 3D interdigitating architecture constructed from the eight-connected SBUs of Mn_4 clusters. In an asymmetric unit, Mn2 adopts octahedral [MnO_6] coordination geometry, with equatorial positions occupied by O1, O4, O6 and O8 from $HBTC^{2-}$ dianions, while the remaining apical positions are occupied by O7 and O9 atoms of $HBTC^{2-}$ dianions. The Mn–O bond length spans the range of 2.0798–2.2719° with the slight alteration of 0.1921°.

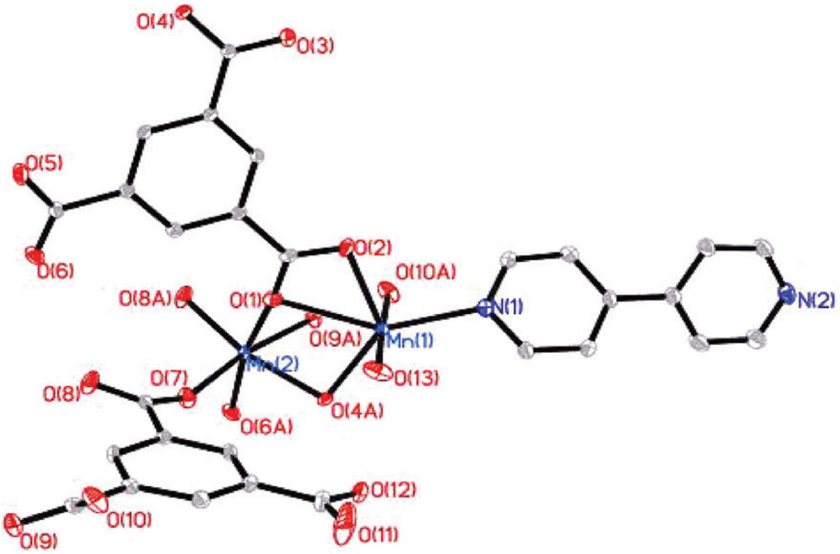

Figure 1. The asymmetric unit of **1**: all hydrogen atoms are omitted for clarity.

The distortion parameter 9.16×10^{-4} of the MnO_6 polyhedron with an average Mn–O distance 2.185 Å is calculated by using the formula of $\Delta = (1/N)\sum_{n=1,N}\{(d_n - \langle d\rangle)/\langle d\rangle\}^2$, in which the d_n and $\langle d\rangle$ is the single Mn–O and average Mn–O bond length, respectively [12]. Mn1 adopts the largely distorted $4+2$ coordination geometry in MnO_5N fashion, which is completed by O1, O2, O4, O10 atoms from $HBTC^{2-}$ dianions, $O13(H_2O)$, N1(bpy) atoms, and the Mn–O bond length obviously varies from 2.0565 to 2.4391° with the bigger alteration of 0.3826°. The distortion parameter 3.03×10^{-3} of the MnO_5N polyhedron is calculated with the average Mn–O distance 2.225°. Further investigations show that all the Mn–O lengths are comparable with that observed in the previously reported Mn-containing compounds [13]. In addition, the $HBTC^{2-}$ dianions derived from the partly deprotonated H_3BTC perform tetradentate and hexadentate coordinated modes (these can be confirmed by *IR*: the bonds at 1720 and 1698 cm^{-1} are assigned to the uncoordinated and monodentate coordinated protonated carboxyl groups, respectively, the typical antisymmetric (1611 cm^{-1}) and symmetric (1557, 1452, and 1434 cm^{-1}) stretching bands with respective values of $\Delta = v_a(coo–) - v_s(coo-)$ clearly indicate the presence of chelate (54 cm^{-1}), bidentate (159 cm^{-1}) and monodentate (177 cm^{-1}) coordination modes of the carboxyl groups [11]). Furthermore, the bpy ligand, showing the large dihedral angle 32.57° between two pyridyl rings, plays a terminal coordinated role in ligating Mn1 atoms (figure 1). The Mn1 and Mn2 atoms are bridged by two μ_2–$O_{carboxylate}$ atoms, and one bidentate carboxyl group to lead to the Mn2 dimer with Mn–Mn distance of 3.522°, in which the Mn–O–Mn angle is 98.44° for Mn1–O1–Mn2 and 102.17° for Mn1–O4–Mn2. Further, based on two bridging bidentate carboxyl groups, the special Mn2 dimer can combine with another symmetry-related Mn2 dimer to give rise to the rhombic Mn4 tetramer with the Mn2–Mn2A distance of 4.911°, surrounded by eight $HBTC^{2-}$ dianions to furnish the final eight-connected SBU. (figure 2b, f) Unfortunately, the eight links only orient in four different directions and

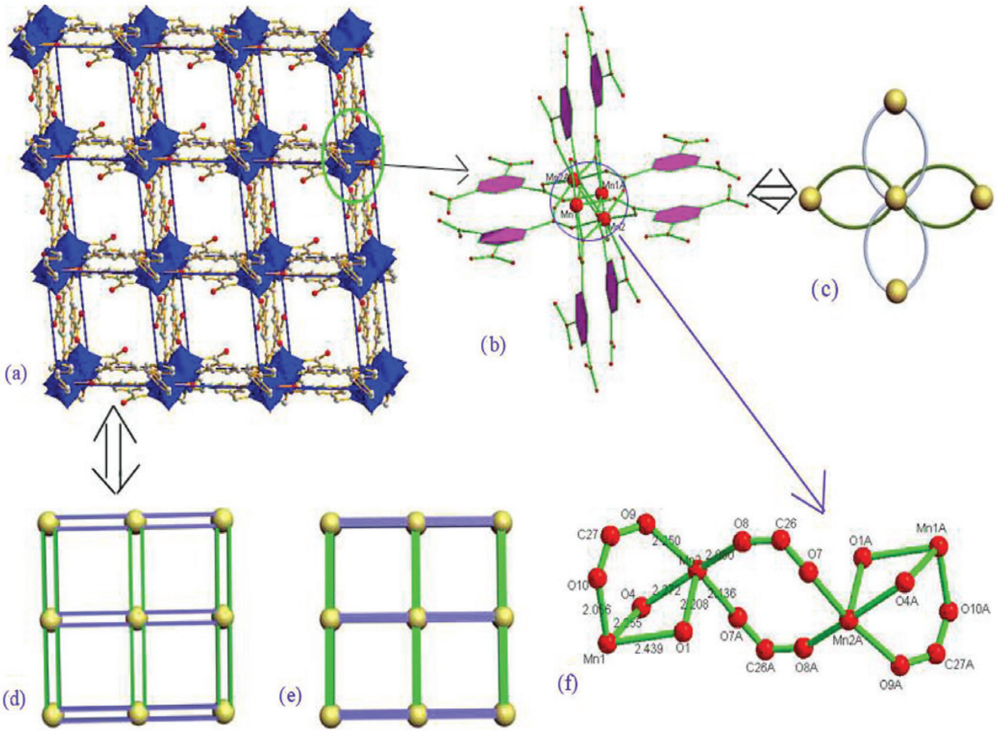

Figure 2. (a) View of the 2D (4,4) networks with double edges; (b) The eight-connected SBU of Mn4 tetramer; (c) Schematic description of the eight-connected SBU: oriented in four different directions and each pair of linkers chelated to another SBU; (d) Schematic description of the 2D (4,4) networks with double edges; (e) The common (4,4) networks; (f) The core of the eight-connected SBU of Mn4 tetramer.

each pair chelates to another SBU (figure 2c). Consequentially, each SBU can only connect to four adjacent SBUs to give rise to the 2D (4,4) networks with double edges of 1.0 nm rather than the 3D frameworks (figure 2a, d). As shown in figure 3, these 2D (4,4) nets are further arranged to construct the 3D interdigitating architecture in the ABAB stacking fashion, in which each (4,4) network is completed by two pyridyl rings from other (4,4) layers. This 3D interdigitating architecture is partly stabilized by typical hydrogen bonds: O5-H5 $\cdots$ N2/2.506 Å/159.66°, O12-H12 $\cdots$ O3/2.605Å/169.46°, O13-H13B $\cdots$ O2/2.660Å/174.59°, O13-H13A $\cdots$ O2/2.763Å/160.23°.

3.2. *TG-DTA, and magnetic characters of 1*

TG-DTA of **1** showed that the first loss occurs about 153°C, which is ascribed to the loss of coordinated water molecules. At the range of 153–450°C, there is no weight loss; after that, further weight loss is attributed to decomposition of polymer **1**. (See supporting information)

The magnetic properties of **1** were investigated over the temperature range 5–300 K in a field of 500 G. The observed $\chi_M T$ values of 9.26 $cm^3\,mol^{-1}\,K$ at 300 K is slightly smaller than the expected value of 9.92 $cm^3\,mol^{-1}\,K$ for a dinuclear Mn_2 complex with noninteracting metal ions ($g = 2.13$) in the electronic configuration of d^5 low spin

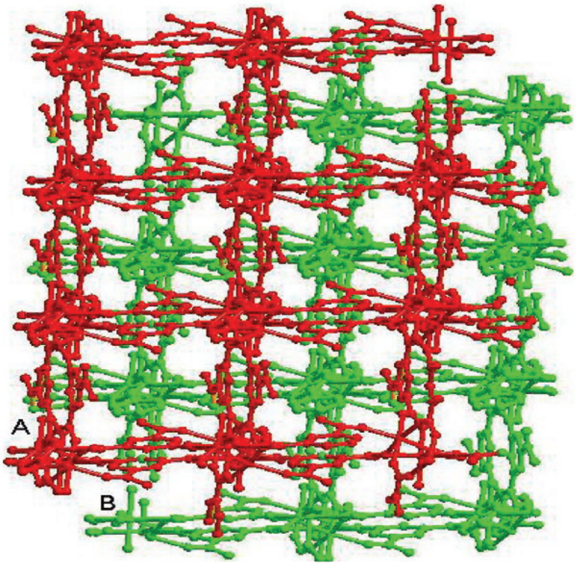

Figure 3. View of the 3D interdigitating architecture, stacking in ABAB fashion.

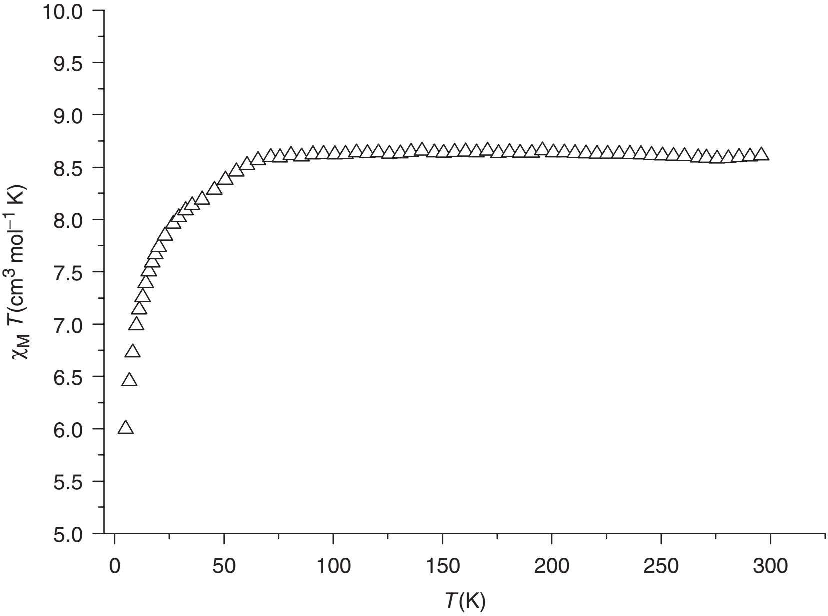

Figure 4. The $\chi_M T$ *vs.* T plot of 1.

($S = 5/2$) [15]. The $\chi_M T$ *versus* T plot shows that $\chi_M T$ of **1** increases to 9.36 cm^3 mol^{-1} K at 140 K upon cooling followed with a sharp decrease to 4.5 cm^3 mol^{-1} K at 5 K. The observed susceptibility data (5–300 K) were well fitted to the Curie–Weiss law ($\chi_M = C/(T - \theta)$) with $\theta = -3.36$ K, indicating weak antiferromagnetic interaction between metal ions (figure 4).

4. Conclusion

In this report, one novel metal–organic coordination polymer was obtained hydrothermally by reaction of $MnCl_2$, bpy, H_3BTC, and KOH in water. The overall structure of **1** is the 3D interdigitating architecture, constructed from the eight-connected SBUs of a Mn4 cluster. Compared with our reported case showing 3D networks, [14] the bpy ligands in **1** only adopt the terminal coordination to Mn leading to 2D (4,4) networks with double edges. In addition, polymer **1** has weak antiferromagnetic behavior with $\theta = -3.36\,K$ between Mn(II) ions in the electronic configuration of d^5 high spin ($S = 5/2$), which is comparable with that observed in other Mn4 clusters [13].

Supplementary material

The TG-DTA plot is included.

Acknowledgement

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