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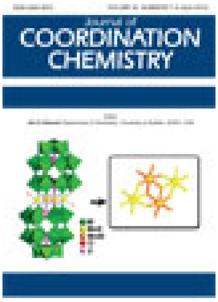

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Synthesis, structural characterization, and properties of an entangled metal-organic framework based on a flexible dicarboxylate and a rigid N-donor

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Synthesis, structural characterization, and properties of an entangled metal–organic framework based on a flexible dicarboxylate and a rigid N-donor

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Self-assembly of manganese acetate with 1,3-bis(4-carboxy-phenoxy)propane (H_2bcp) and 1,2-bis(4-pyridyl)ethene (bpe) under solvothermal conditions yielded a polymer $\{[Mn_2(bcp)_2(bpe)(DMF)]\}_n$ (**1**), which shows 2-D → 3-D inclined interpenetration with polyrotaxane character. The magnetic behavior of **1** shows antiferromagnetic exchange between Mn magnetic centers.

Keywords: Interpenetration; Structure; Magnetism; Coligand

1. Introduction

Coordination polymers with entangled structures have attracted attention for intriguing molecular topologies and properties. Among various types of entanglements, interpenetration of 2-D and 3-D networks has been studied [1, 2]. Usually, the origin of entanglement can be ascribed to the presence of large free voids in a single network [3]. Long ligands lead to larger voids that may result in high-fold interpenetrating structures. Thus, one effective way to increase the number of interpenetrating folds is to extend the length of the ligand sustaining the framework [4]. For some time, we have been interested in the synthesis and characterization of entangled metal–organic frameworks (MOFs) containing the organic dicarboxylates 4,4′-oxybis(benzoic acid) (H_2oba) and 1,2-bis(4-carboxy-phenoxy)ethane (H_2bce) [5]. For these two types of flexible dicarboxylates, the segment of –O–X–O– chains are different with respect to the relative orientation of CH_2 groups. Herein, we extend the segment of –O–X–O– and employ a new ligand 1,3-bis(4-carboxy-phenoxy)propane (H_2bcp) to sustain structures

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of MOFs. Employment of H_2bcp, Co(II), and bpp (1,3-bis(4-pyridyl)propane leads to an unexceptional sextuple-stranded molecular braid. However, control of product architectures still remains a challenge due to the fact that self-assembly is frequently influenced by the type and spatial disposition of the ligand-binding site, assisting ligand, stereoelectronic preferences of the metal ion, and other factors [6].

We continue our investigation and chose H_2bcp as a bridging ligand to react with Mn(II) in the presence of rigid N-donor (bpe). A new polymer, $\{[Mn_2(bcp)_2(bpe)(DMF)]\}_n$ (**1**), was obtained under mild conditions. The polymer exhibits 2-D → 3-D inclined interpenetration with polyrotaxane character. The magnetic behavior of **1** exhibits antiferromagnetic exchange between Mn centers.

2. Materials and instruments

All reagents were purchased from commercial sources and used as received. Infrared (IR) spectra were recorded with a Perkin-Elmer Spectrum One spectrometer from 4000 to 400 cm^{-1} using KBr pellets. Thermogravimetric analysis (TGA) were carried out with a Mettler–Toledo TA 50 in dry dinitrogen (60 $mL\,min^{-1}$) at a heating rate of 5°C min^{-1}. Magnetic susceptibility data of powdered sample in parafilm were measured on an Oxford Maglab 2000 magnetic measurement system from 300 to 1.8 K and at field of 1KOe.

2.1. *X-ray crystallography*

Single-crystal X-ray diffraction analysis of **1** was carried out on a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using φ/ω scan technique at room temperature. The intensities were corrected for Lorentz and polarization effects as well as for empirical absorption based on multi-scan techniques; all structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [7]. Absorption corrections were applied by using multi-scan program SADABS [8]. The hydrogen atoms of organic ligands were placed in calculated positions and refined riding on attached atoms with isotropic thermal parameters 1.2 times those of their carriers. All disordered atoms O9, O10, C25, C26, and C27 in **1** display occupancies of 0.65 and 0.35. Twelve restraints were applied during refinement of the structure including distance restraint (dfis) and thermal restraints (isor, delu, and eadp) for some unreasonable atoms. Table 1 shows crystallographic data of **1**. Selected bond distances and angles are listed in table 2.

2.2. *Synthesis of the complex*

2.2.1. $\{[Mn_2(bcp)_2(bpe)(DMF)]\}_n$ (1). A mixture of $Mn(OAc)_2 \cdot 4H_2O$ (0.1 mmol), H_2bcp (0.1 mmol), bpe (0.1 mmol), H_2O (8 mL), CH_3OH (3 mL), and several drops of DMF (1 mL) was prepared. The pH of the resulting solution was adjusted to 6 using dilute NaOH (0.1 mol L^{-1}) and kept at 150°C for 72 h in a sealed Teflon-lined stainless

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Table 1. Crystal data and structure refinement information for **1**.

Empirical formula	$C_{86}H_{80}Mn_4N_4O_{26}$
Formula weight	1805.30
Temperature (K)	298(2)
Crystal system	Triclinic
Space group	$P-1$
Unit cell dimensions (Å, °)	
a	12.404(2)
b	13.840(3)
c	14.651(4)
α	114.405(4)
β	96.809(4)
γ	110.871(3)
Volume (Å^3)	2033.1(8)
Calculated density (g cm^{-3})	1.475
F(000)	932
Reflections collected	7094
Unique reflections	10,200 [R(int) = 0.033]
Goodness-of-fit on F^2	1.038
Final R indices [$R^{a,b}(I > 2\sigma(I))$]	$R_1 = 0.0487$, $wR_2 = 0.0955$
R indices (all data)	$R_1 = 0.1103$, $wR_2 = 0.1058$

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $^bwR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Mn1–O1	2.219(3)	Mn1–O7	2.184(3)
Mn1–O12	2.133(3)	Mn1–O13	2.171(3)
Mn1–O6#1	2.198(3)	Mn2–O2	2.088(3)
Mn2–O8	2.109(3)	Mn2–O11	2.117(3)
Mn2–N1	2.224(3)	Mn2–O5#1	2.123(3)
O–Mn1–O7	125.90	O5–Mn2–O11	145.44
O6–Mn1–O12	158.65(10)	O13–Mn1–O17	146.89(12)
O12–Mn1–O13	87.20(11)	O1–Mn1–O6	147.58(10)
O2–Mn2–O8	177.87(11)	O7–Mn1–O13	146.89(12)
O8–Mn2–N1	90	O2–Mn2–O11	90

Symmetry code: 1: $1 + x, 1 + y, z$.

steel vessel (25 mL) under autogenous pressure. The solution was then cooled to room temperature at a rate of 5°C h^{-1} to yield a very fine pale yellow crystalline product **1**. Yield: 40%. $C_{86}H_{80}Mn_4N_4O_{26}$ (1805.30). Calcd: C, 57.22; H, 4.47; N, 3.10. Found: C, 57.26; H, 4.51; N, 3.23. IR (KBr, cm^{-1}): 3350(m), 2998(w), 2238(m), 1652(vs), 1638(m), 1521(m), 1432(vs), 1245(m), 1088(w), 919(w), 778(m), 661(m). CCDC: 854094.

3. Results and discussion

3.1. *$\{[Mn_2(bcp)_2(bpe)(DMF)]\}_n$ (1)*

The results of crystallographic analysis revealed that the asymmetric unit of **1** contains two crystallographically unique Mn(II), two bcp, one bpe, and one

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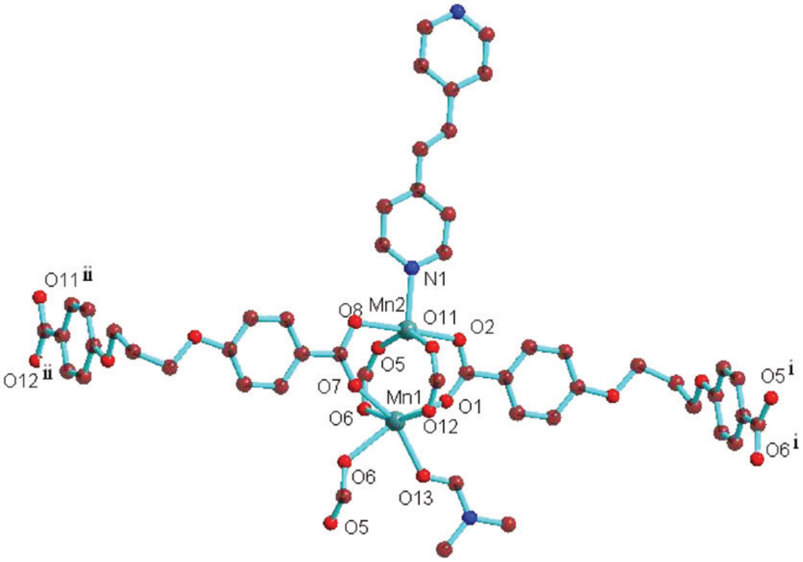

Figure 1. The coordination geometries of the metal centers [($^{\text{i}}$) $x-1$, $y-1$, z; ($^{\text{ii}}$) $x+1$, $y+1$, z].

coordinated DMF (figure 1). Mn(1) in each tetranuclear unit lies on an inversion center and is coordinated by four carboxylate oxygen atoms from four bcp ligands and one oxygen atom from DMF to give a square pyramid. The terminal Mn(2) is coordinated by four carboxylate oxygen atoms from four bcp ligands and one nitrogen atom from bpe to give a square pyramid. Two types of bcp with $(k^1\text{–}k^1)\text{–}(k^1\text{–}k^1)\text{–}\mu_4$ and $(k^1\text{–}\mu_2)\text{–}(k^1\text{–}k^1)\text{–}\mu_4$ link Mn(II)'s to give a tetra-stranded chain. With this chain, two Mn(I) ions and Mn(2) ions are bridged by six carboxylates to form a tetrametallic unit $[Mn_4(RCO_2)_6]$. Such tetrametallic set is quite rare. Adjacent chains are pillared by bpe with bis-bidentate coordination to generate a sheet, showing a window with dimensions 14.93×20.18 Å (figure 2a). Pairs of sheets interpenetrate in a 2-D → 3-D inclined fashion [1a], as shown in figure 2(b). The interpenetration is such that each metal-bcp loop has a bpe from the other net passing through it.

Another fascinating feature of **1** is that a tetra-stranded chain exists in the 2-D sheet (figure 2b). The bcp ligands link Mn1 and Mn2 into two types of left- and right-handed helical chains. The sheets individually can be described as having (4,4) topology based on the connection, however, the description simplifies the loops into a single linkage and, thus, becomes inadequate for describing the interpenetration. From a topological view, if each $[Mn_4(RCO_2)_6]$ is considered as a 6-connected node, bcp is considered as a 2-connected node, and bpe is considered as connector then the structure of **1** is a 2-D (2,2,6)-connected net with $\{4^2.6^8.8.10^4\}\{4\}_2$ topology (figure 2c). In **1**, a pair of $[Mn_2(bcp)_2]$ loops is threaded by one bpe as rod from an adjacent layer. The reported $M_2(L)_2$ or $M_4(L)_2$ loop only contains two or four metal centers and two organic ligands [9]. To the best of our knowledge, this is the first example of a (2,2,6)-connected network exhibiting such polyrotaxane character.

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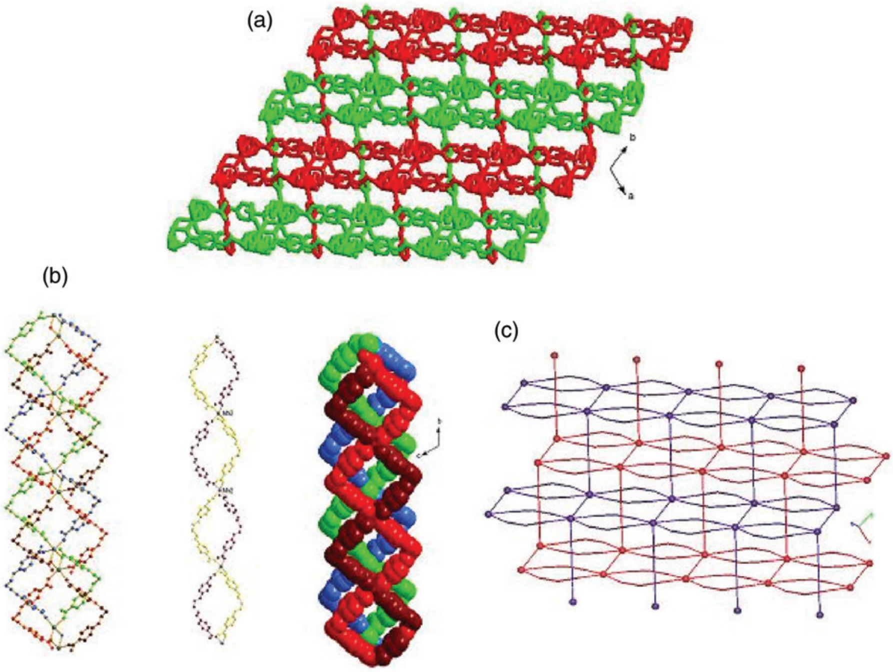

Figure 2. The structure of **1**: (a) view of the unusual interlocked frameworks; (b) perspective view of quadruple-stranded helical chain; (c) schematic view of such new interlocked nets.

3.2. *Comparison of related compounds*

The connectivity of MOFs is strongly related to the type of carboxylate ligand. The following discussion gives a qualitative explanation for this (scheme 1). Although oba and bcp are both flexible dicarboxylate linkers, there are significant differences. The bcp can assume a more flexible character due to the extended length of the –O–X–O segment. Thus, to some extent, the bcp can more meet the coordinative preference of the metal center. When bcp was introduced into the Mn-bpe system, we obtained a 2-D → 3-D inclined network containing polyrotaxane character. The polymer $\{[Mn(oba)(bpe)]\cdot H_2O\}_n$ has a threefold Pcu-type topological structure [5c]. When Mn(II) and oba are selected to react with bipy a new compound $\{[Mn(oba)(bipy)]\cdot bipy\}_n$ was prepared in which the solid displays a 3-D microporous MOF with free bipy in the channels [10]. When we chose bce that bears appreciably less length of –X–O–X– introduced into the Co-bpe system, the compound $\{[Co_2(bce)_2(bpe)_2(H_2O)_2]\cdot H_2O\cdot CH_3CN\}_n$ is composed of a 3-D unusual self-interpenetrating net [5e]. Furthermore, a new polymer $[Co(oba)(bpe)]_n$ also shows threefold interpenetrating framework with Pcu-type topology [11]. LaDuca *et al.* [12] reported $\{[Co(oba)(dpa)]\cdot H_2O\}_n$, which is an intriguing self-catenated 2-D layer motif with very rare non-diamond topology. Therefore, the different topological networks and entanglement observed in the compounds are caused by the different lengths of dicarboxylate and coligands (scheme 1). Many metal complexes based on dicarboxylates and N-donors, such as benzene-1,4-dicarboxylate and 2 -(3-pyridyl)-imidazo[4,5-f]1,10-phenanthroline,

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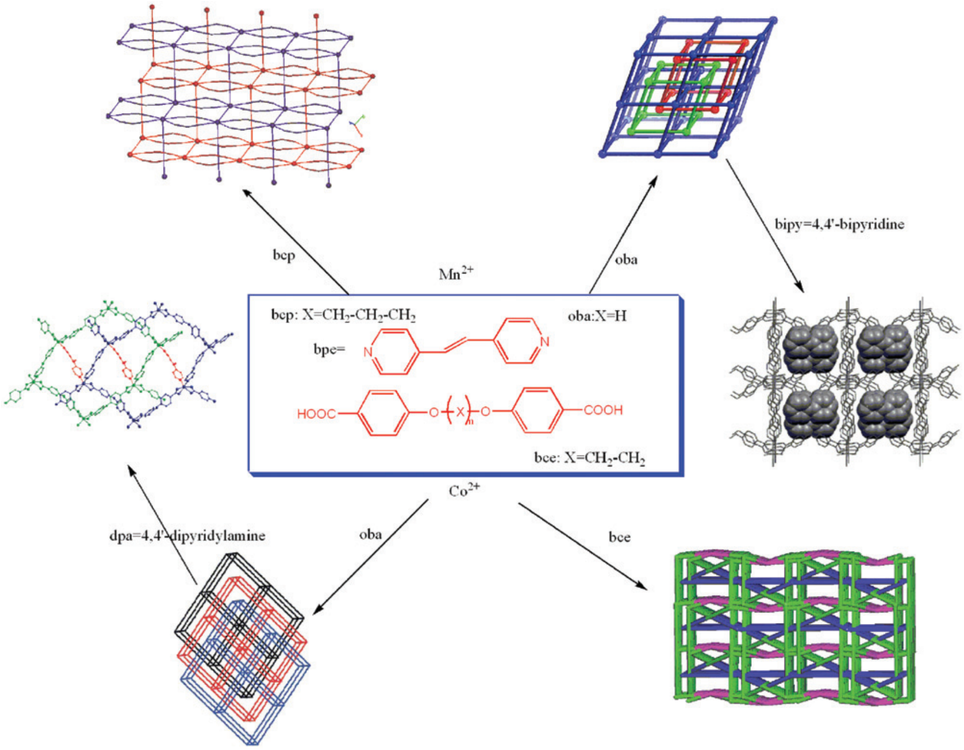

Scheme 1. Schematic view of entangled topologies containing flexible dicarboxylates and N-donor coligands.

have also been reported [13]. Wang *et al.* [13d] reported two new Mn(II) complexes consisting of rigid dicarboxylate and chelating N-donor. Both complexes exhibit 1-D chain and further extend into 3-D supramolecular structures by hydrogen-bonding and aromatic stacking interactions.

3.3. *Thermogravimetric analyses*

To study the stability of the polymer, TGA of **1** was performed (Supplementary material). The TGA diagram of **1** shows two weight loss steps. The first began at 160°C and was completed at 220°C. The observed weight loss of 4.5% corresponds to loss of coordinated DMF (Calcd 4.1%). The second weight loss of 78.6% between 230°C and 819°C corresponds to loss of bcp and bpe (Calcd 74.9%).

In order to confirm the phase purity of **1**, the original sample was characterized by X-ray powder diffraction (XRPD). The XRPD experimental and simulated patterns of **1** (Supplementary material) show peak positions in agreement with each other, demonstrating that the crystal structures are representative of the bulk materials. Differences in intensity may be from preferred orientation of the powder samples.

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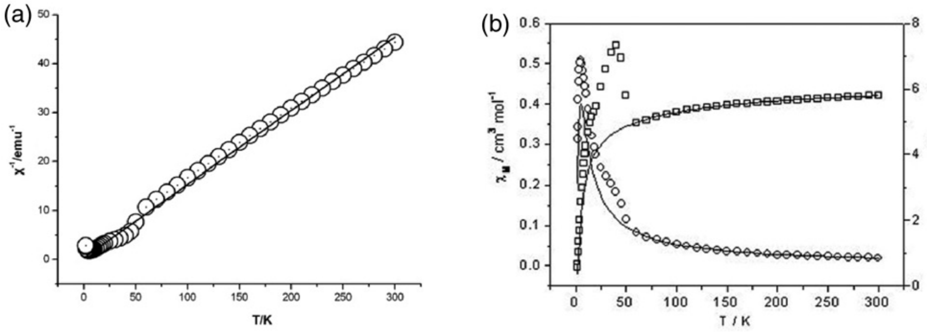

Figure 3. Plots of $\chi_{\mathrm{M}}T$, χ_{M}, and χ_M^{-1} *vs.* T for **1**; solid lines represent fits to the data.

3.4. *Magnetic property*

The variable temperature magnetic susceptibilities were measured from 1.8 K to 300 K at 1000 Oe for **1**. The magnetic data of **1** is displayed in figure 3, plotted as the thermal variation of $\chi_{\mathrm{M}}T$, χ_{M}, and $1/\chi_{\mathrm{M}}$. The $\chi_{\mathrm{M}}T$ *versus* T plot has a value of $6.85\,\mathrm{cm^3\,mol^{-1}\,K}$, which is less than the spin-only value ($8.74\,\mathrm{cm^3\,mol^{-1}\,K}$) for $S = 5/2$ per formula unit [14]. χ_{M}^{-1} obeys the Curie–Weiss law with a Weiss constant of $\theta = -1.19\,\mathrm{K}$. The negative θ value is indicative of a dominant antiferromagnetic interaction between Mn^{2+} centers. The magnetic data of **1** were fitted using the following simple phenomenological equation [15]:

$$\chi_{\mathrm{M}}T = A\exp(-E_1/kT) + B\exp(-E_2/kT).$$

The least-squares analysis ($R = 1.7 \times 10^{-4}$), shown as solid lines in figure 3, led to the parameters $A = 0.95\,\mathrm{cm^3\,mol^{-1}\,K}$, $E_1/k = 115.15\,\mathrm{K}$, $B = 5.23\,\mathrm{cm^3\,mol^{-1}\,K}$, and $E_2/k = 4.81\,\mathrm{K}$. Here, $A + B$ equals the Curie constant, and E_1 and E_2 represent the "activation energies," corresponding to spin–orbit coupling and magnetic exchange interactions. The positive value E_2/k corresponding to spin coupling $J < 0$ shows antiferromagnetic exchange between Mn magnetic centers. A new complex $[\mathrm{Mn(H_2bptc)(2,2'\text{-}bpy)2}]\cdot 2\mathrm{H_2O}$ ($\mathrm{H_4bptc}$ = biphenyl-2,5,2′,5′-tetracarboxylic acid and 2,2′-bpy = 2,2′-bipyridine) also shows weak antiferromagnetic interaction [16]. In a 2-D complex $\{[\mathrm{Mn_2(DBT)(DMF)_4}]\cdot 2\mathrm{H_2O}\}_n$ (DBT = 3,6-dinitro-1,2,4,5-benzenetetracarboxylate anion), there exist two kinds of coordination environments for Mn(II), each DBT coordinates four Mn(II) ions by four carboxylates and in this way a 2-D sheet was constructed with very weak antiferromagnetic coupling between Mn(II) ions [17].

4. Conclusion

A new entangled MOF of a "V" shape ligand 1,3-bis(4-carboxy-phenoxy)propane ($\mathrm{H_2bcp}$) with Mn(II) in the presence of rigid N-donor has been synthesized under solvothermal condition and structurally characterized by X-ray diffraction. The compound shows 2-D → 3-D inclined interpenetration with polyrotaxane character.

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The magnetic behavior shows that **1** exists as antiferromagnetic exchange between Mn magnetic centers. Further efforts are underway in our laboratory to explore the construction of the coordination chemistry of bcp ligand.

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