An unusual fluorite network constructed by dinuclear manganese and 5-carboxyl-1-carboxymethyl-3-oxidopyridimium[†]

Cai-Hong Zhan, Mei-Xiang Jiang, Yun-Long Feng* and Jian-Wen Cheng

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A novel manganese 5-carboxyl-1-carboxymethyl-3-oxidopyridinium (H₂L) metal–organic framework has been synthesized and characterized using single-crystal X-ray diffraction analysis. The structure can be considered as constructed of 2D layers consisting in left- and right-handed helical chains and further linked by L^{2-} ligands into a 3D (4,8)-connected fluorite network with a Schläfli symbol of $(4^{6})_2(4^{12}.6^{12}.8^{4})$. The magnetic susceptibility data are interpreted with the dimer law, yielding J and g values of 0.94(2) cm⁻¹ and 1.97(2). The exchange integral (J) indicates that there is a weak ferromagnetic interaction between two Mn²⁺ ions.

Introduction

The design and synthesis of novel metal-organic frameworks (MOFs) have developed rapidly in recent years not only for potential applications,¹ but also for their intriguing topology.² Consequently, a variety of coordination polymers with interesting and complicated architectures and topologies have been synthesized successfully. In these compounds, the metal ions generally serve for nodes while the ligands act as linkers. The "network topological approach" is an important and essential aspect of the analysis, comparison, and design of MOFs by reducing multidimensional structures to simple node-andconnection nets.3 Recent reviews on the network topologies illustrate this importance.4 Among the 3D network, three-, fourand six-connected topologies are commonly observed,⁵ examples of five-, seven-, and eight-connected MOFs remain relatively scarce. On the other hand, some MOFs with mixed-connected topologies such as Pt₃O₄, boracite, twisted boracite, PtS, rutile, pyrite and anatase have been reported.⁶ For example, (3,6)connected rutile nets have already been reported in Ln(pydc)(Hpydc) ($Ln = Sm, Eu, Gd; H_2pydc = pyridine-2,5$ dicarboxylic acid).⁷ The expanded rhombohedral Fe₂(SO₄)₃ structure with corner-sharing octahedron and tetrahedron derived from (4,6)-connected Al₂O₃ (α-alumina) topology were also reported.⁸ MOFs with binodal high-connected structures are extremely rare⁹ due to the limited coordination numbers of metal centers and steric hindrance issues of the organic ligands.7d Considering the limited number of coordination sites at the metal centers, our strategy is to use polynuclear metal units as the higher-connected nodes and ligands as lower-connected nodes to construct a 3D high-connected binodal net. Herein, we present a novel 3D MOF: [MnL(H₂O)]·H₂O, utilizing dinuclear manganese metal clusters as 8-connected node and

multicarboxylic bridging ligands as 4-connected node, which defines a rare case of a fluorite net (Scheme 1).

Experimental

MnCl₂·4H₂O (1.0 mmol, 0.1985 g), H₂L (1.0 mmol, 0.1982 g), 4,4'-bipyridine (0.25 mmol, 0.0390 g) (4,4'-bipy plays an important role in the reaction although it is not a spacer in the complex) and Na₂CO₃ (1.0 mmol, 0.1062 g) were mixed in 15 mL distilled water. Then the mixture was transferred into a Parr Teflon–lined stainless steel vessel (25 mL) and heated to 160 °C for 72 h. It was cooled to room temperature over 3 d. Yellow cube-shaped crystals of **1** were obtained and collected by filtration, washed with water, then dried in air, 67% yield (based on H₂L). IR (KBr cm⁻¹): 3213, 1620, 1572, 1486, 1453, 1389, 1340,



Scheme 1 Structure of the Mn(OR)₂Mn core

Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang, 321004, P. R. China

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Downloaded by University of Pennsylvania Libraries on 22 February 2013 Published on 11 September 2009 on http://pubs.rsc.org | doi:10.1039/B909889E 1315, 1136, 1053, 798, 785. Anal. Calc. for C₈H₉MnNO₇: C, 33.55; H, 3.15; N, 4.89. Found: C, 33.53; H, 3.17; N, 4.87%.

Elemental analysis was performed on a Perkin-Elmer 2400II elemental analyzer. IR spectra were measured in KBr pellets on a Nicolet 5DX FT-IR spectrometer. The thermogravimetric measurement was performed on a Netzsch STA449C apparatus with a heating rate of 10 °C min⁻¹ under an oxygen atmosphere. Variable temperature susceptibility measurement was carried out in the temperature range 1.9–300 K at a magnetic field of 5 kOe on powdered samples with a Quantum Design SQUID magnetometer on the MPMS-7 system. XRPD patterns were collected on a Philips PW3040/60 automated powder diffractometer, using Cu K α radiation ($\lambda = 1.542$ Å) with a 2 θ range of 5–50°

The single crystal diffraction data were collected on a Bruker APXE II diffractometer equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 296(2) K. Data intensity was corrected by Lorentz-polarization factors and empirical absorption. The structure was solved by direct methods and expanded with difference Fourier techniques. All nonhydrogen atoms were refined anisotropically. Except for the hydrogen atoms on oxygen atoms which were located from the difference Fourier maps and refined with distance restraints of O-H = 0.85(2) Å and H…H = 1.30(2) Å, the other hydrogen atoms were generated geometrically. All calculations were

 Table 1
 Crystal Data and Structure Refinement for the Complex

Empirical formula	C _o H _o MnNO ₇
Formula weight	286.10
Color	Yellow
Crystal system	Monoclinic
Space group	$P2_1/n$
alÅ	10.3259(1)
b/Å	9.1606(1)
c/Å	11.3351(1)
βl°	101.970(1)
V/Å ³	1048.89(2)
Ζ	4
$D_{\rm c}/\mu { m g~cm^{-3}}$	1.812
μ/mm^{-1}	1.283
<i>F</i> (000)	580
$\theta_{\min}, \theta_{\max} / ^{\circ}$	2.43, 27.48
Reflections collected/unique/Rint	8815/2389/0.0224
Observed Reflections $(I > 2\sigma(I))$	2150
Parameters refined	166
$S ext{ on } F^2$	1.042
$R, wR (I > 2\sigma(I))$	0.0232, 0.0618
R, wR (all data)	0.0266, 0.0639
max, min $\Delta \rho/e \ \text{\AA}^{-3}$	0.298, -0.260

Table 2 Selected Bond lengths (Å) and Angles($^{\circ}$) for the complex^{*a*}

performed using SHELXS-97 and SHELXL-97.¹⁰ Further details for structural analyses are summarized in Table 1, selected bond lengths and angles are listed in Table 2.

Results and discussion

Single-crystal X-ray diffraction analyses show that the title complex is monoclinic with $P2_1/n$ space group. The asymmetric unit consists of one Mn2+, one L2- ligand, one coordination water molecule and one lattice water molecule (Fig. 1). The Mn²⁺ ion is six-coordinated and has a slightly distorted octahedral coordination environment: three oxygen atoms from one flexible carboxyl group and two rigid carboxyl groups of three individual L^{2-} ligands, two phenolic oxygen atoms from two L^{2-} ligands, and one water molecule. The Mn-O bond lengths range from 2.099(1) to 2.218(1) Å (Table 2), which is in agreement with the ones reported for Mn²⁺ complexes with pyridinecarboxylic acids.11 Two crystallographically identical Mn2+ ions are linked by two phenolic oxygen atoms to give a dinuclear $\{Mn_2\}$ subunit in which the Mn…Mn distance is 3.372(3) Å. Two carboxyl groups of the L^{2-} ligand are fully deprotonated with a flexible carboxyl group in a monodentate mode and rigid carboxyl group in a bidentate mode.

The dinuclear $\{Mn_2\}$ subunits are joined by rigid carboxyl oxygen and phenolic oxygen atoms of L²⁻ ligands to form 1D chains. These two neighboring chains are further bridged via the flexible carboxyl oxygen atoms to generate double ladder chains. These double chains are interlinked by sharing dinuclear $\{Mn_2\}$ subunits to form two-dimensional (2D) networks. The remaining rigid carboxylic oxygen atoms adopt different coordination directions to complete the construction of the three-dimensional (3D) framework, as illustrated in Fig. 2, that is, one points outwards and the others point inwards. It is worth noting that there are alternate right- and left-handed helices in the 2D layer along the *b* axis with the pitches of 9.1606(1) Å, so the whole sheet does not show chirality. What is more, the double ladder chains include two different helices twining together and these twining helices link each other by dinuclear $\{Mn_2\}$ subunits. There are some examples of MOFs with left- and right-handed helical chains, most of these helice coordination polymers are alternately linked only via hydrogen bonds, π - π stacking interactions or covalent bonds.¹² The 2D helix layers are further connected by rigid carboxylic oxygen atoms to generate the final 3D structure (Fig. 3), which contains 1D channels with dimensions of about 4.9 \times 7.0 Å along the *b* axis. The lattice water

Bond	Distance	Angle	(°)	Angle	(°)
Mn(1)–O(4)#1	2.099(1)	O(4)#1-Mn(1)-O(1)	95.08(6)	O(5)#2–Mn(1)–O(5)#4	78.12(4)
Mn(1) - O(1)	2.128(1)	O(4)#1-Mn(1)-O(5)#2	167.74(4)	O(3)#3-Mn(1)-O(5)#4	173.54(4)
Mn(1) - O(5) #2	2.152(1)	O(1)-Mn(1)-O(5)#2	89.81(5)	O(4)#1-Mn(1)-O(1 W)	92.95(5)
Mn(1)–O(3)#3	2.181 (1)	O(4)#1-Mn(1)-O(3)#3	95.89(4)	O(1) - Mn(1) - O(1 W)	165.47(6)
Mn(1)–O(5)#4	2.191(1)	O(1) - Mn(1) - O(3) #3	82.19(5)	O(5)#2-Mn(1)-O(1 W)	84.78(5)
Mn(1)–O(1 W)	2.218(1)	O(5)#2-Mn(1)-O(3)#3	95.91(4)	O(3)#3-Mn(1)-O(1 W)	84.96(5)
		O(4)#1-Mn(1)-O(5)#4	89.93(4)	O(5)#4-Mn(1)-O(1 W)	91.96(5)
		O(1) - Mn(1) - O(5)#4	100.13(5)		~ /

^a Symmetry codes: (#1) -x + 5/2, y - 1/2, -z + 1/2; (#2) -x + 5/2, y + 1/2, -z + 1/2; (#3) x + 1, y, z; (#4) x + 1/2, -y + 5/2, z - 1/2.



Fig. 1 The coordination environment of Mn atoms. The symmetry codes for the generated atoms are the same as in Table 2.

molecules fill in the channels to provide additional hydrogen bonds for stabilizing the crystal structure (Fig. 4).

As shown in Fig. 5, each L²⁻ ligand is linked to four dinuclear {Mn₂} subunits to represent a 4-connected node (Fig. 5a), and each $\{Mn_2\}$ subunit serves for an 8-connected node by combining eight L²⁻ ligands (Fig. 5b), thus, a (4,8)-connected network is formed with a Schläfli symbol of $(4^6)_2(4^{12}.6^{12}.8^4)$ (Fig. 5c). The vertex symbol calculation using OLEX gives (4.4.4.4.4.4)for the 4-connected node and $(4.4.4.4.4.4.4.4.4.4.4.4.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.6_{2}.8_{2}.*.*)$ for the 8-connected node.13 The resulting binodal (4,8)-connected topology is a rare case of a fluorite net. To date, MOFs with such connectivity are extremely rare, only two MOFs with fluorite topology have been reported.¹⁴ One contains 8-connected {Cd₄} clusters and tetrahedral organic ligands,14a the other is constructed of 8-connected ligands and 4-connected metal nodes.14b Notably, the geometry of the 8-connected dinuclear $\{Mn_2\}$



Fig. 3 Schematic illustration of the 3D network of the title complex.

subunit is distorted as compared with the cubic geometry in the reported fluorite topology.¹⁰

The experimental and simulated XRPD patterns of title complex are shown in Fig. 6. Their peak positions are in good agreement with each other, indicating the phase purity of the product. The differences intensity may be due to the preferred orientation of the power sample.

Magnetic properties

From a magnetic point of view, the title complex can be considered as a dinuclear complex, where two metal ions are bridged by two phenolic oxygen atoms. The magnetic susceptibility of the title complex in the form of $\chi_m T vs. T$ is shown in Fig. 7. The experimental value at room temperature (8.56 cm³Kmol⁻¹) increases on decreasing the temperature, first slowly and then rapidly. This behavior is consistent with the presence of



Fig. 2 A 2D sheet of the title complex constructed by 1D left- and right-handed helical chains (the L^{2-} ligands in black orientate upward while in gray orientate downward).



Fig. 4 3D network of the title complex viewed down the *b* axis (left) and a space-filling model omitting the lattice water molecules for clarity (right) with channels of about 4.9×7.0 Å.



Fig. 5 (a) L^{2-} ligand regarded as an organic 4-connected node linked with four dinuclear metal units. (b) Inorganic 8-connected dinuclear metal units coordinated with eight L^{2-} ligands. (c) Schematic representation of the fluorite topology of the title complex.

a weak ferromagnetic interaction between the Mn^{2+} ions which is quite different from the reported complexes displaying antiferromagnetic behavior between Mn^{2+} ions linked by the oxygen bridge.¹⁵ A model with a spin-spin interaction Hamiltonian H = $-2JS_1S_2$ ($S_1 = S_2 = 5/2$) has been used in the simulation of



Fig. 6 Experimental (A) and simulated (B) XRPD spectra of title complex.

experimental susceptibilities using eqn (1): where *J* is the exchange coupling parameter between S_1 and S_2 , and N, g, μ_B , k, and *T* have their usual meaning. As shown in Fig. 5, the magnetic behavior of the complex can be well reproduced by eqn (1) using $J = 0.94(2) \text{ cm}^{-1}$, g = 1.97(2). The R ($R = \sum [(\chi_m T)_{calc} - (\chi_m T)_{expt}]^2 / \sum [(\chi_m T)_{expt}]^2$) are 6.82×10^{-5} . The exchange integral (*J*) indicates that there is a weak ferromagnetic interaction between two Mn²⁺ ions. The magnetic susceptibility obeys the Curie–Weiss law and a plot of $1/\chi_M$ versus *T* yields a straight line (inset of Fig. 5) with $C = 7.43 \text{ cm}^3 \text{ mol}^{-1}\text{K}$, $\theta = 6.99$. The positive Weiss constant θ further suggests a weak ferromagnetic interaction between Mn²⁺ ions.

Thermal analyses

To study the stability of the complex, thermogravimetric analytical (TG) studies were performed. The TG curve exhibits

$$\chi_{\rm m} = \frac{2Ng^2\mu_{\rm B}^2}{kT} \cdot \frac{\exp(2J/kT) + 5\exp(6J/kT) + 14\exp(12J/kT) + 30\exp(20J/kT) + 55\exp(30J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT) + 9\exp(20J/kT) + 11\exp(30J/kT)}$$
(1)



Fig. 7 Plot of the $\chi_M T$ vs T and $1/\chi_M$ vs T (inset) for the title complex.



Fig. 8 TG curve of the title complex.

two steps of weight loss (Fig. 8). The weight loss from 80 to 146 $^{\circ}$ C corresponds to the release of the lattice and coordination water molecule. The observed weight loss of 12.02% is in agreement with the calculated value of 12.58%. The second weight loss between 250 and 800 $^{\circ}$ C is attributable to the loss of all organic ligands.

Conclusion

In summary, we have synthesized a MOF by incorporating dinuclear $\{Mn_2\}$ cores and 5-carboxyl-1-carboxymethyl-3-oxidopyridimium ligands in the framework. The linkage between eight-connected $\{Mn_2\}$ nodes and four-connected liangds give an unusual fluorite topology. Variable temperature magnetic susceptibility indicates the existence of a weak ferromagnetic interaction between two Mn^{2+} ions.

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