

Notes

Coordination Polymers: Structural Transformation from Two to Three Dimensions through Ligand Conformation Change

Zhan Shi, Lirong Zhang, Shan Gao, Guoyu Yang, Jia Hua, Lu Gao, and Shouhua Feng*

Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, People's Republic of China

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Introduction

Coordination polymers with open framework structures,¹ which bridge the molecular and atomic solids, possess potential functions such as enantiomer separation, chiral synthesis, ligand exchange, and selective catalysis.² Their network topologies based on molecular building blocks are usually controlled and modified by the selection of the coordination geometry of the central metal, the structural chemistry of organic ligands, the character of solvent used, and the ratio of metal salt to organic ligand. Recent efforts in this field are mostly focused on the design and synthesis of novel coordination polymers by using

* To whom correspondence should be addressed. Fax: +86-431-5671974. E-mail: shfeng@mail.jlu.edu.cn.

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Table 1. Crystallographic Data for 1 and 2

empirical formula	C ₁₄ H ₁₁ N ₂ O _{4.5} Mn	C ₁₉ H ₁₆ N ₃ O ₅ Mn
a, Å	7.706(6)	11.6612(14)
b, Å	9.509(6)	8.6480(10)
c, Å	10.236(11)	18.493(2)
α, deg	97.58(4)	90.0
β, deg	106.08(4)	102.037(2)
γ, deg	108.936(17)	90.0
V, Å ³	661.0(9)	1824.0(4)
Z	2	4
fw	334.19	421.29
space group	P $\bar{1}$ (no. 2)	P2 ₁ /c (no. 14)
temp, °C	20(2)	20(2)
λ, Å	0.71073	0.71073
ρ _{calc} , g/cm ³	1.679	1.534
μ, cm ⁻¹	1.021	0.761
R1, ^a [I > 2σ(I)]	0.0454	0.0376
wR2, ^b [I > 2σ(I)]	0.1203	0.0661

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

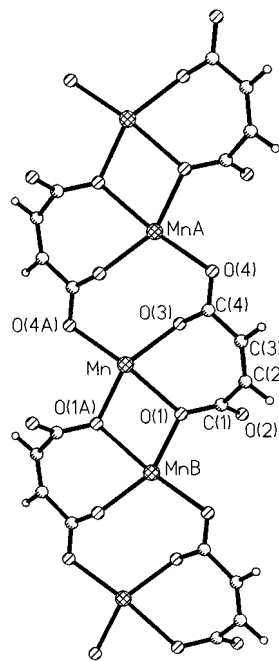


Figure 1. View of zigzag [Mn(maleate)]₈ chain in 1.

neutral donor ligands (i.e., 4,4'-bipyridine, pyrimidine, pyrazine),³ strictly anionic ligands (i.e., carboxylate),⁴ and their combination.⁵ For example, some Mn-containing coordination polymers have been synthesized by the use of 4,4'-bipyridine.⁶ However, the control of dimensionality of coordination polymers is still challenging.⁷ Here, we report the synthesis and single-crystal structures of two novel coordination polymers with mixed ligands of 4,4'-bipyridine and maleate/fumarate, {[Mn(maleate)-(μ-4,4'-bipy)]·0.5(H₂O)}_∞ (**1**) and {[Mn(fumarate)(μ-4,4'-bipy)-(H₂O)]·0.5(4,4'-bipy)}_∞ (**2**) (bipy = bipyridine). Our study

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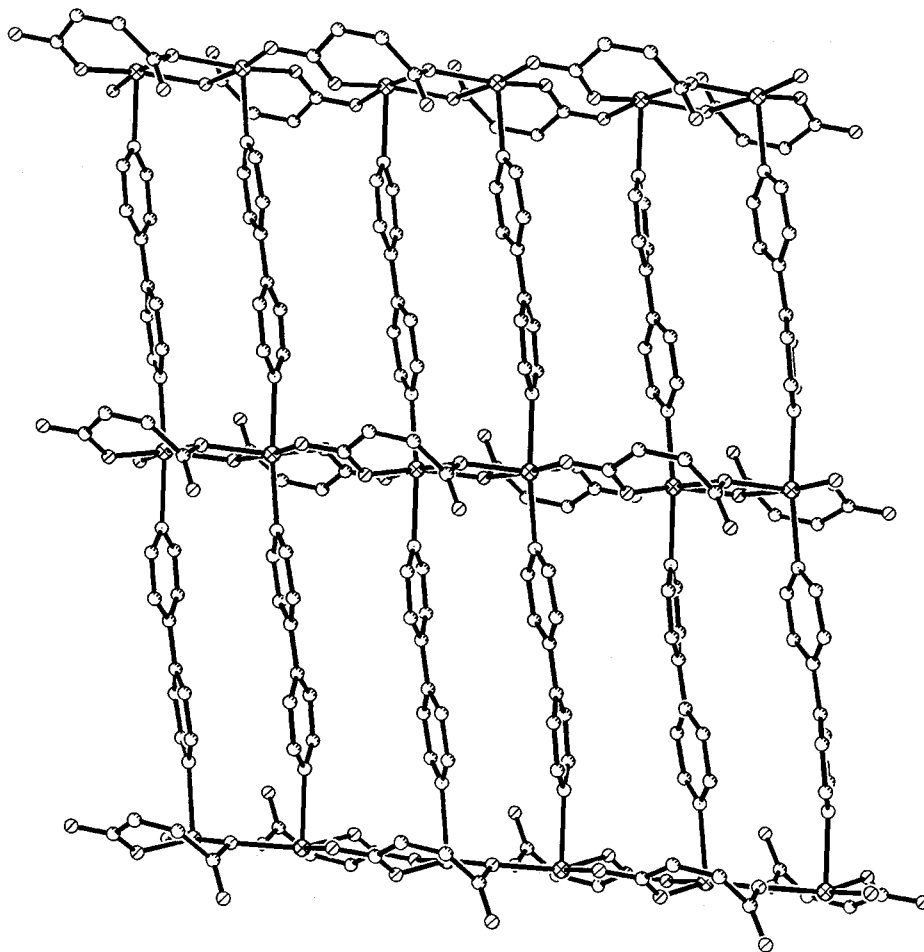


Figure 2. View of layered structure of **1** along [011].

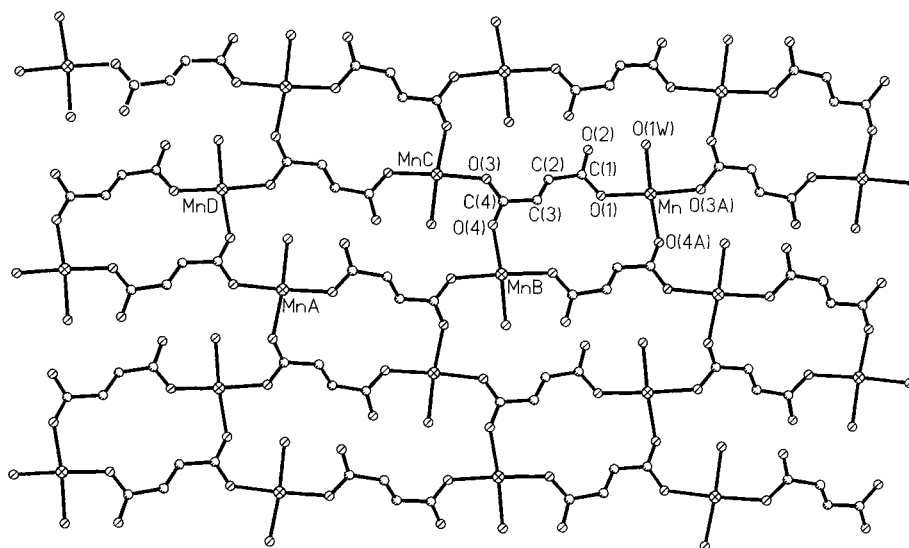


Figure 3. View of $[\text{Mn}(\text{fumarate})(\text{H}_2\text{O})]_n$ layer in **2** along the a axis.

reveals a structural transformation from two dimensions (compound **1**) to three dimensions (compound **2**) through conformation change of the carboxylate ligand.

Experimental Section

Syntheses. In a typical synthesis, $\text{C}_4\text{H}_4\text{O}_4$ (maleic acid or fumaric acid) (0.116 g, 1 mmol) and NaOH (0.080 g, 2 mmol) were added in a mixed solution of H_2O (10 mL) and methanol (10 mL), and then $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.198 g, 1 mmol) and $4,4'$ -bipy $\cdot 2\text{H}_2\text{O}$ (0.192 g, 1 mmol) were

added with stirring. The reaction mixture was allowed to crystallize at room temperature for 3 days to give yellow crystal **1** or light-yellow crystal **2**. Anal. Calcd (found) for **1**: C, 50.32 (50.14); H, 3.32 (3.25); N, 8.38 (8.25). Anal. Calcd (found) for **2**: C, 54.17 (54.02); H, 3.83 (3.74); N, 9.97 (9.83).

X-ray Crystallography. Crystals of **1** and **2** suitable for single-crystal X-ray diffraction with sizes $0.120 \text{ mm} \times 0.070 \text{ mm} \times 0.040 \text{ mm}$ and $0.170 \text{ mm} \times 0.040 \text{ mm} \times 0.040 \text{ mm}$ were selected, respectively. Structural analyses for **1** and **2** were performed on a Siemens SMART CCD diffractometer with graphite-monochromated

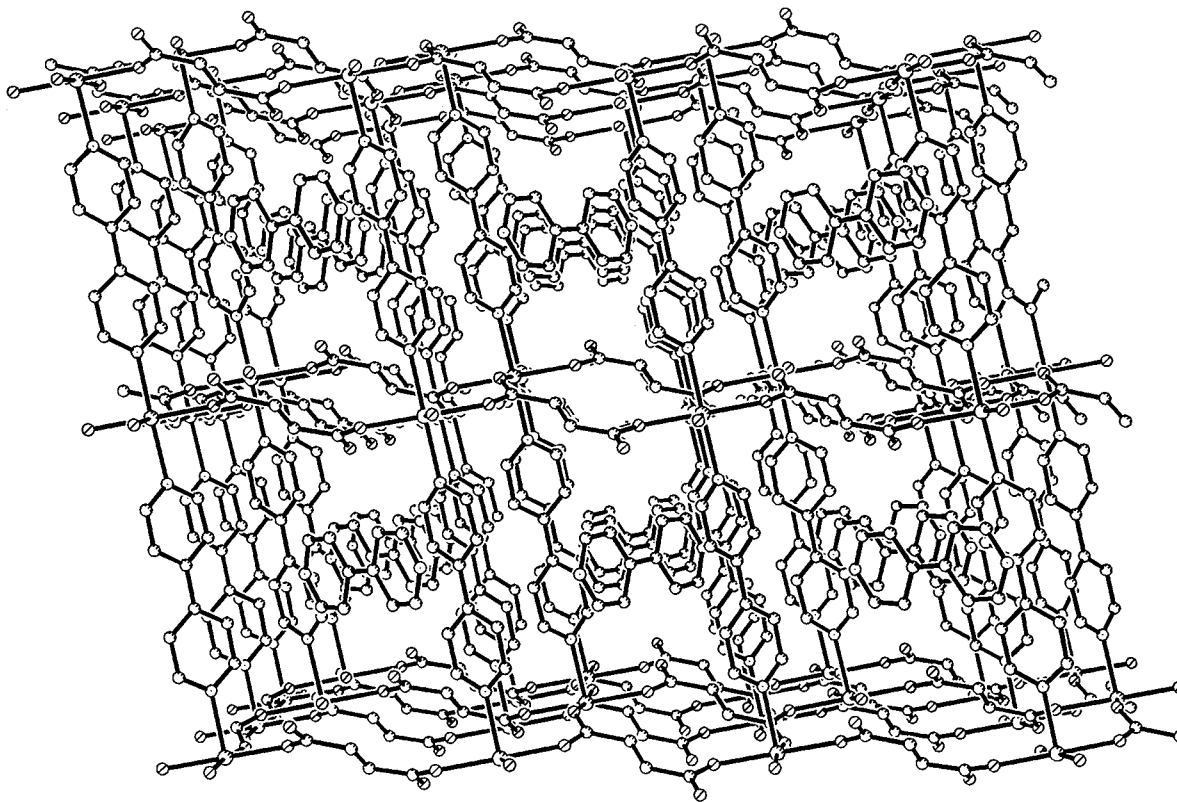


Figure 4. View of the packing structure of **2** along the *b* axis.

Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The structures were solved by direct methods followed by Fourier difference syntheses using the SHELXTL package. Crystal parameters and details of the data collection and refinement are given in Table 1 (for full details see Supporting Information).

Results and Discussion

In the crystal structure of **1**, the manganese centers are interlocked by maleate ligands, giving zigzag $[\text{Mn}(\text{maleate})]_{\infty}$ infinite chains as shown in Figure 1. The manganese is six-coordinated in a compressed octahedral environment. Two pyridyl nitrogen donors occupy the axial positions with Mn–N distances of 2.292 and 2.336 Å. The equatorial plane is defined by four oxygen donors from different carboxylate groups with three shorter Mn–O distances of 2.129 to 2.181 Å and one longer Mn–O distance of 2.337 Å. Two carboxylate groups of maleate ligands have two coordination modes. In the first mode the carboxylate group acts as a monatomic bridge linked two manganese ions. This mode appears in a few examples.⁸ Another oxygen atom (O(2)) forms a hydrogen bond with a crystal water molecule with an O(2)⋯O(1w) distance of 2.790 Å. In the second mode it serves as a bidentate ligand to bridge two manganese centers. Two carboxylate groups of maleate chelate one Mn ion to form a seven-membered ring. Accordingly, two carboxylate groups in the second mode (–O(3)–C(4)–O(4)–) bridge two Mn ions (Mn, Mn(A)) to form an eight-membered ring (Mn–Mn(A) distance is 4.348 Å). Two first-mode carboxylate groups bond to Mn ions, forming a four-membered ring (Mn–Mn(B) distance is 3.563 Å). As a result, a zigzag chain along the *a* axis is generated in a sequence of seven-, eight-, seven-, and four-membered rings. This zigzag chain is linked by μ -4,4'-bipy to form a 2-D network as shown in Figure

2. The pyridine rings of 4,4'-bipy linking two Mn ions are twisted by 25.0°. The bridged Mn–Mn distance along μ -4,4'-bipy is 11.732 Å. Since there are two Mn–Mn distances in the $[\text{Mn}(\text{maleate})]_{\infty}$ chains, the differences of grid dimensions of 4.348 Å \times 11.732 Å and of 3.563 Å \times 11.732 Å in the layers are obvious. The stacking of such layers along the *c* axis generates structure **1**.

In crystal structure **2**, the geometry environment around the Mn(II) is octahedral, the same as **1**. The four oxygen atoms define the equatorial positions, whereas two nitrogen atoms of bridging μ -4,4'-bipy ligands occupy the axial ones. Three oxygen atoms are from three different carboxylate groups, and the central Mn ions cannot be chelated by two carboxylates in this case because of the trans conformation of fumarate. Another oxygen is from a coordination water (Mn–O(1w) distance is 2.183 Å). The coordination water is hydrogen-bonded to the O(2) and O(3) ($-x, -y + 1, -z + 2$). The axial Mn–N distances of 2.276 and 2.282 Å are longer than those of the equatorial Mn–O bonds. The coordination of the two carboxylate groups of the fumarate ligands is also different: (1) as a monodentate ligand to bind a metal ion; (2) as a bidentate ligand to bridge two manganese centers, which is already encountered in the structure **1**. Two fumarates bridge two Mn ions (Mn, Mn(B)) to form a 14-membered ring (Mn–Mn(B) distance is 7.461 Å). Four Mn ions (Mn(A), Mn(B), Mn(C), and Mn(D)), two carboxylate groups of fumarate, and two fumarate ligands form a 22-membered ring. As a result, a $[\text{Mn}(\text{fumarate})(\text{H}_2\text{O})]_{\infty}$ layer is formed along the *bc* plane by an alternative arrangement of a 22-membered ring and a 14-membered ring (see Figure 3). The difference in the conformation of fumarate from maleate as described in structure **1** is the key to forming the layer and contributing to the structural transformation from 2-D (structure **1**) to 3-D (structure **2**). The μ -4,4'-bipy ligands link the $[\text{Mn}(\text{fumarate})(\text{H}_2\text{O})]_{\infty}$ layers together to construct a 3-D network

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structure (Figure 4). The pyridine rings in the μ -4,4'-bipy ligands are nearly coplanar (the interplanar angle is 5.7°). The bridged Mn–Mn distance along the μ -4,4'-bipy is 11.661 Å. It is noteworthy that 4,4'-bipy guest molecules are clathrated in the host cavity and stabilized by π – π stacking. The ratio of guest 4,4'-bipy to μ -4,4'-bipy is 1:2 in structure **2**.

Conclusions

It has been noted that all previous syntheses use such ligands because they freely adopt either cis or trans conformations⁹ (e.g., 1,2-bis(4-pyridyl)ethane and 2,2'-bi-1,6-naphthyridine) or a combination of cis and trans conformations (e.g., 3,3'-dicyano-diphenylacetylene). Accordingly, the resulting coordination polymers contain these ligands in all-cis, all-trans, or mixed cis and trans conformations. In our study we aim for the rational

synthesis of the coordination polymer with a ligand in a single conformation (either cis or trans). The respective selection of maleate and fumarate as ligands led to the difference in coordination features to Mn ions due to the variation in bonding directions to Mn ion. Two carboxylates of a maleate molecule can chelate an Mn ion, resulting in the formation of 1-D [Mn(maleate)]_∞ chains, whereas those of the fumarate molecule link different Mn ions, leading to the formation of 2-D [Mn(fumarate)(H₂O)]_∞ layers. One-dimensional [Mn(maleate)]_∞ chains connect with 4,4'-bipy to form 2-D layers; 2-D [Mn(fumarate)(H₂O)]_∞ layers and 4,4'-bipy give a 3-D open framework. Therefore, the conformation change of the carboxylate ligand indicates the structural transformation from two dimensions (structure **1**) to three dimensions (structure **2**).

Supporting Information Available: Two figures showing ORTEP representations of **1** and **2**; two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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