

From 1D to 3D Single-Crystal-to-Single-Crystal Structural Transformations Based on Linear Polyanion $[\text{Mn}_4(\text{H}_2\text{O})_{18}\text{WZnMn}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{4-}$

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S Supporting Information

ABSTRACT: A 1D anionic polyoxometalate, $[\text{Mn}_4(\text{H}_2\text{O})_{18}\text{WZnMn}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{4-}$, undergoes 1D to 3D single-crystal-to-single-crystal structural transformations that are induced by transition-metal cations (Co^{2+} and Cu^{2+}) and solvent molecules. These solid materials present interesting catalytic activity for the oxidative aromatization of Hantzsch 1,4-dihydropyridines that is dependent on the inserted heterogeneous metal cations.

Solid materials based on polyoxometalates (POMs) have received considerable contemporary attention because of their interesting topological architectures and properties and have potential applications in diverse fields of catalysis, medicine, and magnetics.^{1–4} A general method for the construction of solid POMs is “one-pot” reaction. However, their compositions and framework structures cannot be precisely controlled.⁵ Recently, “step-by-step aggregation” technology was proven to be a more efficient method for the synthesis of functional solid POMs.^{6,7} Particularly, single-crystal-to-single-crystal (SCSC) structural transformation often results in interesting materials that cannot be obtained by a traditional synthesis method.⁸

The sandwich-type POMs $[\text{WM}\{\text{M}'(\text{H}_2\text{O})\}_2(\text{MW}_9\text{O}_{34})_2]^{12-}$ ($\text{M} = \text{Zn}^{2+}$ and Co^{2+} ; $\text{M}' = \text{Co}^{2+}$, Mn^{2+} , and Cu^{2+} , etc.) have a functional $\text{WM}'\text{M}'$ ring belt between two $\{\text{B}-\alpha\text{-MW}_9\text{O}_{34}\}$ units.⁹ We have used them as functional building blocks to construct a series of solids that present interesting catalytic properties.¹⁰ However, the framework structures of these compounds are confined as 1D linear networks or discrete clusters. To further understand the coordination ability of $[\text{WM}\{\text{M}'(\text{H}_2\text{O})\}_2(\text{MW}_9\text{O}_{34})_2]^{12-}$, we have synthesized a 1D anionic chain network of $[\text{H}_3\text{O}]_4[\text{Mn}_4(\text{H}_2\text{O})_{18}]\text{WZnMn}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2 \cdot 18\text{H}_2\text{O}$ (**1**) by using $[\text{WZn}\{\text{Mn}^{\text{II}}(\text{H}_2\text{O})\}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ ($\{\text{Zn}_3\text{Mn}_2\text{W}_{19}\}$) as building blocks and Mn^{II} ions as connecting nodes. Induced by heterogeneous transition-metal cations (Co^{2+} and Cu^{2+}) and solvent molecules, solid **1** was transformed into two interesting 3D solid frameworks $\{[\text{M}_2(\text{H}_2\text{O})_6][\text{Mn}_4(\text{H}_2\text{O})_{16}][\text{WZn}(\text{Mn}(\text{H}_2\text{O})_2)(\text{ZnW}_9\text{O}_{34})_2]\} \cdot 10\text{H}_2\text{O}$ [$\text{M} = \text{Co}^{\text{II}}$ (**2**) and Cu^{II} (**3**)] in an SCSC structural transformation fashion.

The reaction of $\{\text{Zn}_3\text{Mn}_2\text{W}_{19}\}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ at 80 °C for 1 day afforded light-brown crystals of **1**. Single-crystal X-ray diffraction (XRD) analysis revealed that compound **1** crystallizes in the triclinic $P\bar{1}$ space group, which consists of

1D polyanionic chains based on $\{\text{Zn}_3\text{Mn}_2\text{W}_{19}\}$ anions that are linked by Mn^{II} cations.¹¹ Considering that there is no sodium cation in the crystal lattice of **1** based on elemental analysis and structural study, we have used hydronium cations to keep the charge balance. The $\{\text{Zn}_3\text{Mn}_2\text{W}_{19}\}$ unit acts as a hexadentate ligand to coordinate six Mn^{II} cations through six terminal oxygen atoms of six $\{\text{WO}_6\}$ octahedra (Figure 1a). According

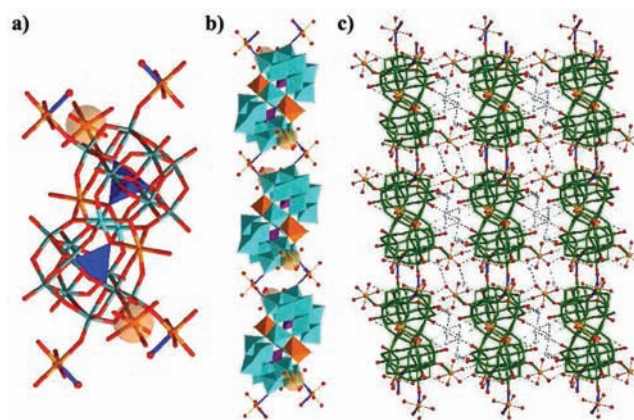


Figure 1. (a) Ball-and-stick and polyhedral representations of the polyoxoanion $[\text{Mn}_4(\text{H}_2\text{O})_{18}\text{WZnMn}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{4-}$ in **1**. (b) Side view of the 1D polyanionic chain of $[\text{Mn}_4(\text{H}_2\text{O})_{18}\text{WZnMn}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{4-}$ (the terminal Mn^{II} sites are highlighted as superimposed balls). (c) View of the 3D supramolecular framework of **1** (hydrogen bonds are shown as dotted lines).

to the coordination environments, there are two kinds of octahedrally coordinated Mn^{II} cations. The first kind serves as a connecting node, which coordinates to two terminal oxygen atoms of two $\{\text{Zn}_3\text{Mn}_2\text{W}_{19}\}$ units and four aqua ligands. The second kind terminates on the $\{\text{Zn}_3\text{Mn}_2\text{W}_{19}\}$ unit, and the octahedral coordination environment is furnished by five water molecules. The $\{\text{Zn}_3\text{Mn}_2\text{W}_{19}\}$ units are linked by Mn^{II} cations to form a 1D linear network (Figure 1b). The polymeric chains are further held together by extensive hydrogen bonding to form a 3D supramolecular network (Figure 1c). Thermogravimetric analysis (TGA) showed that a weight loss of 12.0% occurred between 30 and 340 °C, corresponding to the loss of water molecules (expected 12.8%).

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The motile anionic chains and substitutable hydronium cations make it possible to insert heterogeneous transition-metal cations in the crystal lattice of **1**. Because water molecules can prompt movement of the polymeric chains, a crucial step is how to extract out the lattice water molecules without destroying the single crystallinity of **1**. When the crystals were submersed in methanol, compound **1** lost its crystallinity very quickly. However, compound **1** can retain its crystallinity for 1 week in a mixed solvent of water and methanol ($V_{\text{H}_2\text{O}}:V_{\text{MeOH}} = 1:1$). On the basis of this finding, we submersed the freshly prepared crystals of **1** in a mixture of cobalt nitrate, water, and methanol at 50 °C for 3 days. The color of the resulting crystalline solid of compound **2** changed to red while monitored by optical microscopy. Under identical reaction conditions, when cobalt nitrate was replaced by copper(II) nitrate, a crystalline sample of compound **3** was isolated as green crystals.

Single-crystal XRD analysis revealed that compounds **2** and **3** are isomorphous and crystallize in the triclinic $P\bar{1}$ space group.¹¹ Herein we only discuss the crystal structure of **2** in detail. Compared with the crystal structure of **1**, the linear skeleton is retained in **2**. The Mn^{II} sites were assigned according to their original positions in compound **1**, while the additional metal sites between the polymeric chains were assigned to Co^{II} cations in compound **2** (Figure 2). It is

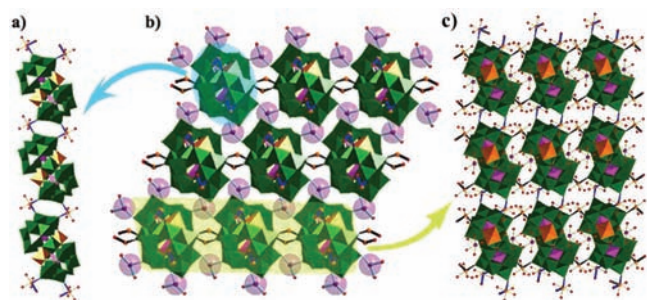


Figure 2. (a) 1D polyanionic chain of $[\text{Mn}_4(\text{H}_2\text{O})_{18}\text{WZnMn}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{4-}$ in **2**. (b) View of the 3D framework structure of **2**, showing the linkage between the polymeric chains (Co^{II} sites are highlighted as superimposed balls, and water ligands are omitted for clarity). (c) Top view of the lamellar network in **2**.

interesting that one aqua ligand of the second manganese cation was substituted by a terminal oxygen atom of the neighboring chain. As a result, the chains are joined together by the Mn^{II} cations to form a lamellar network. The inserted Co^{II} cation coordinates to three oxygen atoms of three chains and three aqua ligands in a distorted octahedral geometry, which further links up the lamellar networks to form the 3D solid framework of **2**.

Elemental analysis has revealed that there is only a trace of Mn^{II} cations (0.37%) in the plasma after SCSC transformation from **1** to **2**, which should be from the surface Mn^{II} cations that are replaced by abundant ambient Co^{II} cations.^{9,10b} We speculate that the transformation from **1** to **2** should be a synergistic movement of the polymeric chains and Mn^{II} cations, while the transportation of Co^{II} cations is controlled by diffusive equilibrium. The movement of the polymeric chain is evident from the reduction of the distance between the neighboring chains [from 12.614(1) to 11.889(1) Å along the a axis and from 13.939(1) to 12.271(1) Å along the b axis]. The

unit cell volume decreases 14.6% [from 2536.3(1) Å³ for **1** to 2165.5(1) Å³ for **2**], and the distance between the terminal Mn^{II} cation and the tungsten atoms of two neighboring chains decreases from 5.06(1) Å in **1** to 3.77(2) Å in **2**. Single-crystal structural analysis and TGA revealed that eight water molecules in the formula unit were lost after SCSC structural transformation. The SCSC framework transformation was further confirmed by comparing the powder XRD patterns of compounds **1** and **2**.

Catalysts that contain heterogeneous metal cations often present excellent catalytic activity because of the synergistic effect.¹² Because Hantzsch 1,4-dihydropyridines (DHPs) and their derivatives are an important class of bioactive molecules,^{13,14} we have chosen the oxidative aromatization of Hantzsch DHPs to evaluate the catalytic activity of compounds **1–3**.

When a mixture of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (DHP-a) and 30% H_2O_2 in THF was heated at 60 °C for 6 h under stirring, the product yield is 40.9% (Table 1, entry 1). When **1**, **2** or **3** was added into the reaction

Table 1. Catalytic Oxidation of Dihydropyridines to Pyridine Derivatives^a

entry	substrate	R	catalyst	yield (%) ^b
1	DHP-a	H		40.9
2	DHP-a	H	1	65.0
3	DHP-a	H	2	>99.9
4	DHP-a	H	3	43.8
5	DHP-b	CH_3	2	60.7
6	DHP-c	Ph	2	82.5
7	DHP-d	2-Fury	2	86.4
8	DHP-d	H	2	97.6 ^c

^aDHP (0.05 mmol), catalyst (10 mol %), and 30% H_2O_2 (0.2 mmol) in THF were stirred at 60 °C for 6 h. ^bDetermined by GC. ^cThe sixth cycle.

mixture, the product yield increased (Table 1, entries 2–4). It is worth noting that DHP-a almost quantitatively transformed into the aromatized product in the presence of **2** (Table 1, entry 3). Catalyst **2** also prompted the oxidation of a range of DHPs for the formation of corresponding pyridine derivatives with satisfied yields (Table 1, entries 5–7).

After **2** was suspended in THF at 60 °C for 6 h under stirring, DHP-a and 30% H_2O_2 were added into the hot filtrate. After the mixture was heated at 60 °C for another 6 h under stirring, gas chromatography (GC) analysis showed that the product yield is identical with that of the background reaction, which thus demonstrates the heterogeneous catalytic nature of **2**. Catalyst **2** can be simply recovered by filtration, which was reused for the successive run without deterring the catalytic activity (Table 1, entry 8). The catalytic results of compound **2** are slightly inferior to that of the homogeneous cobalt acetate in the literature.¹⁴ However, a stoichiometric rather than a catalytic amount of the homogeneous catalyst was used for the oxidization of Hantzsch DHPs. These results indicate that the catalytic activity can be fine-tuned by synergizing the functionalities of multiple metal sites in a POM-based solid.

In summary, we have constructed a POM-based solid by using $\{\text{Mn}_2\text{Zn}_3\text{W}_{19}\}$ as a building block and Mn^{II} cation as a connecting node. Compound **1** undergoes interesting 1D to 3D SCSC structural transformations that are induced by heterogeneous metal cations and solvent molecules. The gradual loss of water molecules in the crystal lattice plays a very important role for SCSC structural transformations. This work should provide a new pathway for the synthesis of high-dimensional solid POMs with modulated functionality for potential applications.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental procedures, additional figures, a table, and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Crystal data for **1**: $\text{H}_{88}\text{Mn}_6\text{O}_{110}\text{W}_{19}\text{Zn}_3$, $M = 5867.60$, triclinic, $a = 12.6138(4) \text{ \AA}$, $b = 13.9393(4) \text{ \AA}$, $c = 16.8356(5) \text{ \AA}$, $\alpha = 82.597(2)^\circ$, $\beta = 73.703(3)^\circ$, $\gamma = 63.213(3)^\circ$, $V = 2536.32(13) \text{ \AA}^3$, space group $P\bar{1}$, $Z = 1$, $\mu = 22.975 \text{ mm}^{-1}$, $R1 = 0.0896$, $wR2(F^2) = 0.2254$, and $S = 1.338$. Crystal data for **2**: $\text{H}_{68}\text{Co}_2\text{Mn}_6\text{O}_{102}\text{W}_{19}\text{Zn}_3$, $M = 5837.30$, triclinic, $a = 11.8890(11) \text{ \AA}$, $b = 12.2712(8) \text{ \AA}$, $c = 16.2733(14) \text{ \AA}$, $\alpha = 77.537(7)^\circ$, $\beta = 87.576(7)^\circ$, $\gamma = 69.196(7)^\circ$, $V = 2165.5(3) \text{ \AA}^3$, space group $P\bar{1}$, $Z = 1$, $\mu = 57.031 \text{ mm}^{-1}$, $R1 = 0.0673$, $wR2(F^2) = 0.1643$, and $S = 1.025$. Crystal data for **3**: $\text{H}_{68}\text{Cu}_2\text{Mn}_6\text{O}_{102}\text{W}_{19}\text{Zn}_3$, $M = 5846.52$, triclinic, $a = 11.9163(14) \text{ \AA}$, $b = 12.2608(12) \text{ \AA}$, $c = 16.2768(15) \text{ \AA}$, $\alpha = 77.604(8)^\circ$, $\beta = 87.472(8)^\circ$, $\gamma = 69.13(1)^\circ$, $V = 2168.9(4) \text{ \AA}^3$, space group $P\bar{1}$, $Z = 1$, $\mu = 54.551 \text{ mm}^{-1}$, $R1 = 0.1271$, $wR2(F^2) = 0.2747$, and $S = 1.357$.
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