

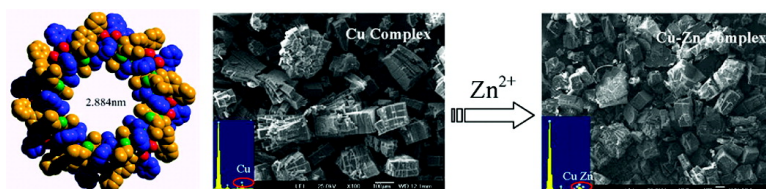
Communication

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Cation Exchange Induced Tunable Properties of a Nanoporous Octanuclear Cu(II) Wheel with Double-Helical Structure

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Porous coordination compounds with helical structures¹ have attracted increasing attention in recent research activities by reason that the helix is a central structural motif for biomacromolecules in nature and helical natural products always have fascinating fruitful functions.² Meanwhile, the helix has its own unique preponderance for the application in environment and chemical engineering. However, most of the reported helical architectures are a 1D infinite chain, and/or 2D and 3D net-like frameworks constructed from an infinite geared chain.³ Very few available examples concentrated on cyclic structures exist,⁴ especially on double-helical wheels with a large opening.

Herein, we employ a clinical medicine, *telmisartan*, as a flexible ligand, to react with copper sulfate to produce a double-helical octanuclear Cu(II) wheel with a 2.88 nm diameter. It should be notable that cyclic copper wheels⁵ containing pores greater than 2.0 nm have hardly been touched on because large-opening metal–organic frameworks with double-helical cyclic structures are indeed very hard to achieve.

Insertion and exchange of cations can be used to decorate compounds from one crystalline material to another. This could be achieved by immersing some crystals into the aqueous solution of a certain metal salt and generating the replacement of cations. As one very powerful and promising strategy for the synthesis and design of solid materials, much attention has been paid to varying the composition, size, and shape of a wide range of nanocrystals.⁶ For example, Kanatzidis and Long et al. reported the cation exchange in the open frameworks,⁷ and the intraframework cation exchange process was reported by Clearfield, Iwamura, and Koga et al.⁸

Previous efforts of our group were accumulated on the central metal ion exchange and sorption of metal ferrocenyl sulfonates.⁹ We believe that central metal ion exchange can be served as a powerful method to modify properties of crystalline materials by varying central metal ions. In this work, central copper ions in the double-helical octanuclear Cu(II) wheel compound are partially replaced by bivalent zinc and cobalt ions and fully exchanged by trivalent iron ions. The comparative experiments on catalysis properties, antitumor activity, and H₂ sorption of **1** and its Zn²⁺ and Co²⁺-exchanged products are listed in this work.

Crystals of [Cu₈L₁₆] (**1**) (HL = 4'-[4-methyl-6-(1-methyl-1H-benzimidazolyl-2-group)-2-*n*-propyl-1H-benzimidazolyl methyl]) were obtained via the reaction of CuSO₄·5H₂O with medicine *telmisartan* in the mixture solution of DMF and ethanol at room temperature for approximately a month. The phase purity of bulk products was confirmed from powder X-ray diffraction and element analysis. Single-crystal X-ray diffraction study indicates that **1** crystallizes in cubic space group *P4/ncc* (number 130) and shows

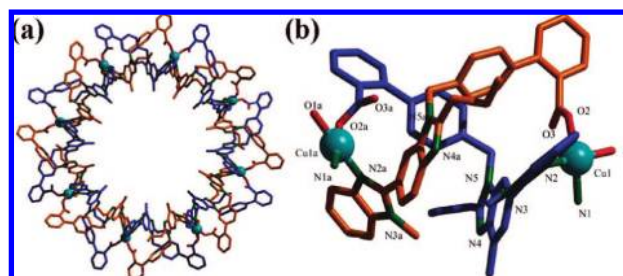


Figure 1. Ball-and-stick (a) view of double-helical octanuclear Cu(II) wheel; building blocks (b) of complex **1**. Cu atoms are shown as cyan, O red, N green, C blue and yellow. (Hydrogen atoms were deleted for clarity.)

a double-helical octanuclear Cu(II) wheel structure with a large opening (Figure 1). This wheel contains eight essential copper ions, and each copper ion lies in the center of a little irregular quadrilateral and coordinates with two bridging oxygen atoms from two carboxylate groups and two bridging nitrogen atoms from two benzoimidazole groups.

In the wheel, two chains overlap with each other to produce a double-helical structure. The separation between two neighboring copper atoms alternatively are by 10.9178(15) and 11.0685(12) Å. The wheel diameter, which is defined as the distance between two symmetry related opposing copper atoms, is 28.84 Å. Notably, this aperture is much larger than the reported octanuclear Cu(II) wheels.⁵ It is worth noting that the flexible joint, the methylene group, plays a vital role in the formation of this double-helical macrocyclic structure. The change of dihedral angles can be accomplished through the rotation of methylene groups, which is responsible for the formation of a helical backbone. On the other hand, the formation of such large pores should be recurred to the assistance of the rigid body of this medical ligand. Along the *b* axis, these octanuclear Cu(II) wheels are parallel to each other because eight copper atoms in the same wheel are nearly coplanar. The distance between two adjacent wheels is 16.74 Å.

To ascertain the tunable properties induced by cation-exchange-induced single-crystal-to-single-crystal transformation between the octanuclear Cu(II) wheel and its cation-exchanged products, we investigated the process of central metal ion exchange. Zinc ion-exchanged crystal [Zn_{1.6}Cu_{6.4}L₁₆], **2**, was achieved by immersing the big crystals of as-synthesized **1** into the aqueous solution of 50 mg/mL zinc nitrate for 5 days. Figure 2a and 2b give the typical SEM images of the as-prepared octanuclear Cu(II) wheel and its zinc-exchanged product, respectively. Clearly, **2** keeps the original shape of **1** entirely. Compared with **1**, only the color of **2** turns pale (Figure 2b). A single crystal photo (Figure 2c) and powder X-ray diffraction analysis (Figure 2d) confirm that single-crystal-to-single-crystal transformations induced by cation exchange have occurred, resulting in a Zn–Cu complex. Compound **2** was carefully

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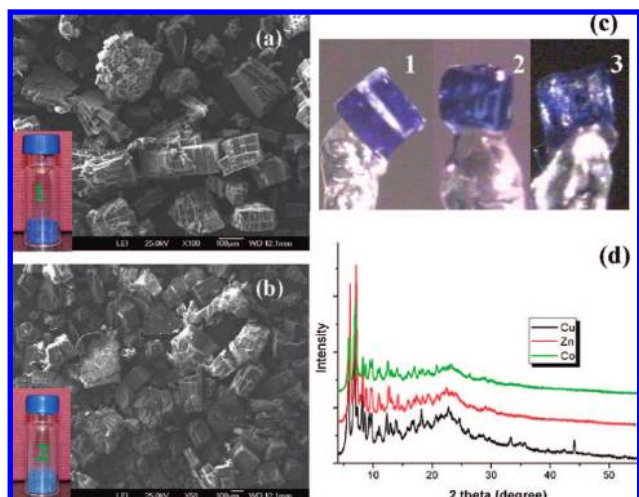


Figure 2. (a) Typical SEM images of as-prepared **1**; (b) Zn^{2+} -exchanged product from **1**; (c) Single crystal photos of **1**, Zn^{2+} -exchanged **2**, and Co^{2+} -exchanged **3**; (d) PXRD patterns of as-synthesized **1**, **2**, and **3**.

analyzed by using an atomic sorption spectrophotometer; the contents of zinc and copper are 20.81 and 79.19%, respectively. These results agree well with the element analysis, ICP, and energy dispersive X-ray spectroscopy (EDS). Similar to **2**, cobalt ion-exchanged crystal [$\text{Co}_{1.2}\text{Cu}_{6.8}\text{L}_{16}$], **3**, could also be prepared by immersing the big crystals of as-synthesized **1** into the aqueous solution of 50 mg/mL cobalt nitrate for 5 days. **3** also inherits the crystal shape of **1**. The contents of cobalt and copper are 14.97 and 86.03%, respectively, which were measured by atomic sorption and evidenced by element analysis, ICP, and EDS. We can not find any dissociative zinc and cobalt ions in **2** and **3**, which can also be proven by XPS analysis. Obviously, it is the coordination ability of the in-going metal ions toward organic ligands that controls the reaction process of central metal ion exchange. If the coordination ability of the in-going metal ions is close to or roughly similar to that of central metal ions, the cation-exchanged products will preserve the original structure to a great extent, as in the case of compounds **2** and **3**.

Subsequently, we study the catalysis properties of the octanuclear Cu(II) and its cation-exchanged products **2** and **3**. In their crystal structures, nanometer-sized tunnels are constructed through the arrangement of these macrocyclic architectures. Consequently, these structures can accommodate large amounts of organic molecules freely and make catalysis reaction feasible. We find that **1** shows high selectivity to oxidative self-coupling catalysis of 2,6-di-*tert*-butylphenol at air atmosphere under 30 °C. Interestingly, central metal ion-exchanged products **2** and **3** also give analogous selectivity to this reaction. Transparent red bulk single crystals of 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (DPQ) could be obtained directly by using a small quantity of compounds **1**, **2**, or **3** as catalysts. The yields of DPQ are 74.3% for **1**, 71.8% for **2**, and 72.1% for **3**. This means that small amounts of central metal ion exchange have a little influence on the catalysis activities for oxidation of 2,6-di-*tert*-butylphenol. Then we find **1** and its Zn-exchanged product **2** show different antitumor properties. The IC₅₀

value of **1** for the cell lines EC109 is 57.07 $\mu\text{g}/\text{mL}$ and that of **2** is 107.7 $\mu\text{g}/\text{mL}$, indicating that **1** is much more sensitive to these cell lines than those of **2**. It is reported that the copper-based drugs have been evidenced to exhibit higher antineoplastic potency than cisplatin for in vitro and in vivo studies of several tumor cell lines, which might be caused by its unpaired electrons.¹⁰ In addition, a significant application to porous polymeric complexes is gas sorption.¹¹ Herein, hydrogen sorption isotherm measurements of **1** and its cation-exchanged products **2** and **3** are performed by monitoring the volumetric change as a function of relative pressure. H_2 sorption for the three complexes shows large differences, and the data are 6.38 for **1** and 40.78 $\text{cm}^3_{\text{STP}}/\text{g}$ for **3**, respectively. Clearly, central metal ion exchange can also be used to modify the gas sorption properties of porous polymeric complexes.

Thus, central metal ion exchange might be regarded as a powerful and effective method to modify properties of crystalline materials only by varying central metal ions under moderate conditions.

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Supporting Information Available: Experimental Section, crystallographic data, IR spectra, PXRD patterns, XPS, TG analysis, hydrogen sorption, and SEM images for **1–3**, and the cytotoxicity of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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