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COMMUNICATION

A cyano-bridged tubular coordination polymer with dominant ferromagnetic interactions

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It is a challenge to synthesize porous tubular coordination polymer with magnetic properties. Utilizing $[\text{Fe}^{\text{II}}(\text{bipy})(\text{CN})_4]^{2-}$ (bipy = 2,2'-bipyridine) as the building block to react with Mn^{2+} , we successfully synthesized a cyano-bridged tubular coordination polymer with dominant ferromagnetic interactions. The inner surface of the heterometallic tube is hydrophilic, whereas the outer surface is hydrophobic. The framework is stable up to 320 °C and can adsorb N_2 and CO_2 . Ferromagnetic interactions were transmitted via the diamagnetic N–C–Fe^{II}–C–N species between Mn^{2+} ions in the tube.

The study of coordination polymer has attracted considerable attention due to their fascinating structures and potential applications in various fields.¹ It is known that metal–organic coordination polymer comprise both metal ions and organic ligands, providing the possibility of fabricating multifunctional materials in which more than two different physical properties coexist or interact synergistically.² The structures and properties of metal–organic coordination polymer can be modified by choosing functional metal atoms and ligands, which can be synthesized by rational designs based on molecular engineering.³ Inert and rigid building block is a good candidate to provide directional assembly with controllable structures and physical properties. Hence, metalocyanates have been the subject of extensive research because metalocyanate building blocks are inert and stable molecules that can act as ligands for metal complexes.⁴ The linear bridging mode of the cyano group allows a stepwise approach for preparing complexes with predictable architectures. Moreover, the nature of the exchange interaction via the cyanide bridge enables chemists to reasonably predict the spin of the ground state and the magnitude of the magnetic anisotropy in some cases.⁵ However, it is still a challenge to synthesize cyano-bridged tubular coordination polymer with magnetic properties. To solve this problem, we proposed using $[\text{Fe}^{\text{II}}(\text{bipy})(\text{CN})_4]^{2-}$ as a building block to directional assembly with paramagnetic Mn^{2+} ion, providing the magnetic properties for the synthesis of tubular coordination polymer. Here, a novel cyano-bridged tubular compound $\{[\text{Fe}^{\text{II}}(\text{bipy})(\text{CN})_4]\text{Mn}^{\text{II}}(\text{H}_2\text{O})\} \cdot \text{H}_2\text{O}$ (**1**) was synthesized, wherein ferromagnetic interactions dominate in the framework.

Moreover, **1** shows high thermal stability and can adsorb N_2 and CO_2 .

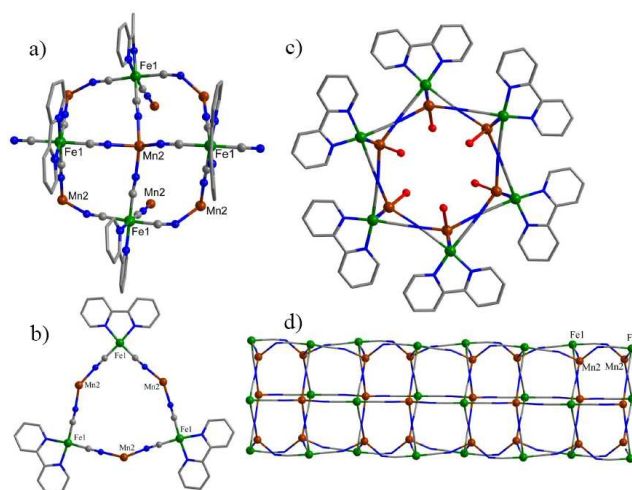


Figure 1 (a) Coordination environment of Fe and Mn centers in **1**. (b) The hexanuclear Fe_3Mn_3 unit in the ab plane. (c) Tube diagram of **1** along the c axis. (d) Side view of the tube structure. H and O atoms have been omitted for clarity (Fe green, Mn brown, C gray, N blue).

1 was synthesized by the reaction of $\text{K}_2[\text{Fe}^{\text{II}}(\text{bipy})(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ and $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in water. Crystallization required several weeks. Single-crystal X-ray diffraction analyses at 296 K revealed that **1** crystallized in the trigonal space group $R\bar{3}$, presenting an infinite tubular structure with a 1D hexagonal channel along the c direction (Figure S1). The structure is made up of neutral $\{[\text{Fe}^{\text{II}}(\text{bipy})(\text{CN})_4]\text{Mn}^{\text{II}}(\text{H}_2\text{O})\} \cdot \text{H}_2\text{O}$ and non-coordinated solvate water molecules. In **1**, one Fe^{II} (Fe1) and one Mn^{II} (Mn2) are crystallographically independent, and their coordination environments are shown in Figure 1. The Fe1 center is coordinated by four cyanide carbon atoms and two nitrogen atoms of bidentate 2,2'-bipyridine, forming a distorted FeC_4N_2 octahedral coordination environment. Selected bond lengths and angles are presented in Table S1. The Fe–C bond lengths are 1.886(4)–1.929(4) Å and the

Fe–N distances are 1.985(3)–1.995(3) Å, which is in good agreement with those observed for the low-spin Fe^{II} in an octahedral coordination environment.⁶ The Fe–C≡N linkages are almost linear with bond angles of 171.5(3)–177.9(3)°, whereas, the Mn2 center is located in a distorted square pyramidal environment with four cyanide nitrogen atoms and an oxygen atom from coordinated water molecules. The Mn–N and Mn–O bond lengths are 2.115(4)–2.166(3) Å and 2.363(3) Å, respectively, which is similar to those observed in the related complexes.^{4d} The axial Mn–N≡C bond angles deviate distinctly from linearity with bond angles of 140.4(3)° and 159.0(3)°. The equatorial Mn–N≡C bond angles are closer to linearity with bond angles of 175.4(3)° and 175.7(3)°. As shown in Figure 1a, each [Fe^{II}(bipy)(CN)₄]²⁻ unit acts as a tetradentate bridging ligand to four manganese(II) ions through its four cyanide groups in the equatorial/axial(2:2) positions, while each manganese(II) ion is connected to four [Fe^{II}(CN)₄(bipy)]²⁻ units. The N≡C–Fe–C≡N plane related to the axial cyano groups is almost perpendicular to the Mn–N≡C–Fe plane related to the equatorial cyano groups by a dihedral angle of 89.7°. The equatorial Fe–Mn distances are 5.158(2) and 5.168(2) Å, and the axial Fe–Mn distances are 4.860(2) and 5.130(2) Å. As shown in Figure 1b, in the *ab* plane, three Fe^{II} ions and three Mn^{II} ions are alternately bridged by six cyano groups, forming a hexanuclear Fe₃Mn₃ unit. Interestingly, three Fe^{II} ions and three Mn^{II} ions construct a regular triangle with an edge of 9.821(2) Å and 7.403(2) Å, respectively. Within the tube, the hydrogen bonding interactions were formed between the coordinated water molecules with donor acceptor distance O1...O1 ≈ 2.760(6) Å. In addition, six metal ions of the Fe₃Mn₃ units are nearly coplanar with a mean deviation of 0.34 Å. Moreover, along the *c* axis, the Fe^{II} and Mn^{II} ions are alternately bridged by axial cyano groups. In this manner, all the hexanuclear Fe₃Mn₃ units are assembled alternately to form an infinite 1D tubular structure with a hexagonal channel. After removed all water molecules, the tube has an internal 1D channel with a diameter of 2.4 Å, excluding the van der Waal radii of the surface atoms (Figure 1c). The tube comprises six identical sides, and each side runs along the *c* direction like a distorted ladder structure (Figure 1d). Each coordination tube is surrounded by six neighboring identical coordination tubes with a distance of 16.82(2) Å between the centers of the two closest tubes (Figure S1). The non-coordinated water molecules reside in the tubular cavity, and the potential void volume, calculated by PLATON, was 11.8% if the water molecules were removed.

The temperature-dependent magnetic susceptibilities (χ) of **1** were measured in the temperature range of 2–300 K under a 1000 Oe field (Figure 2a). At 300 K, the χT value was 4.43 cm³mol⁻¹K per FeMn unit. As the temperature decreased, the χT values gradually increased to a maximum value of 9.14 cm³mol⁻¹K at 2 K. This behavior indicates that ferromagnetic interaction dominates in this system. In the temperature range of 2–300 K, the magnetic susceptibility data are fitted to the Curie–Weiss law with a Curie constant *C* of 4.4 cm³mol⁻¹ K and a Weiss constant θ of 0.34 K. This *C* value is in agreement with a magnetically isolated manganese(II) ion. The positive Weiss temperature further confirms the dominant ferromagnetic interaction in this temperature region. Moreover, the ferromagnetic coupling is also supported by the field dependence of magnetization for **1** at 1.8 K,⁷ as shown in Figure 2b. As the applied magnetic field increases, the isothermal magnetization increases almost linearly at low fields and reaches a saturation value of 5.0 *N* β at 50 kOe, which corresponds to the predicted saturation value (5.0 *N* β for one Mn^{II}, assuming *g* = 2.00) for an *S* = 5/2 magnetically isolated high-spin manganese(II) ion. The magnetization of **1** is significantly higher than the Brillouin curve corresponding to non-interacting *S*_{Mn} spins (*S* = 5/2), confirming ferromagnetic

interactions in **1** (Figure 2b). It has been reported that the N–C–Fe^{II}–C–N species can transmit ferromagnetic interactions between Fe^{III} (*S* = 5/2) ions although the magnetic exchange through diamagnetic anions is weak.⁸ Moreover, the hydrogen bonding can transmit ferromagnetic interactions.⁹ We measured the magnetic properties of the dehydrated sample to determine the ferromagnetic interactions were transmitted via the diamagnetic N–C–Fe^{II}–C–N species or hydrogen bonding. It was found that the magnetic properties of **1** and dehydrated sample were very similar. Because there are no hydrogen bonding in the dehydrated sample, the ferromagnetic interactions should be transmitted via the diamagnetic N–C–Fe^{II}–C–N species between Mn^{II} ions in **1** and dehydrated sample.

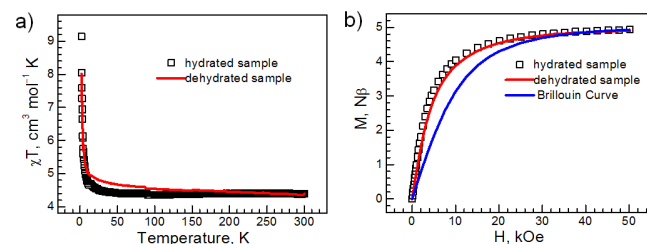


Figure 2(a) Temperature-dependent magnetic susceptibilities of **1** and dehydrated sample in the temperature range of 2–300 K under an applied field of 1000 Oe. (b) Field dependence of magnetization for **1** and dehydrated sample at 1.8 K. The blue solid line is the calculated Brillouin Curve of the isolated Mn²⁺ ion.

Thermal gravimetric analysis (TGA) of the crystalline sample powder of **1** was performed in the temperature range of 25–800°C under a N₂ atmosphere (Figure S2). The initial mass loss of 9.3% in the temperature range 25°C to approximately 110 °C in the TGA data corresponds to the loss of all coordinated water molecules and solvent water molecules (calculated as 8.9%), which is consistent with the single crystal data. A plateau is observed from 110 to 320°C, indicating that **1** has high thermal stability until 320°C. Above 320°C, **1** shows a rapid weight loss due to the decomposition of the framework. The powder X-ray diffraction patterns of **1** and dehydrated **1** are almost identical (Figure S3), indicating that the framework is stable after removal of the water molecules, implying that dehydrated **1** has excellent thermal stability. This stability provided an opportunity for probing the gas adsorption properties of dehydrated **1**.

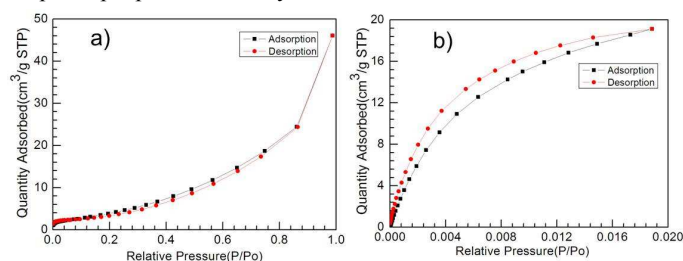


Figure 3(a) Adsorption/desorption isotherms of N₂ at 77 K. (b) Adsorption/desorption isotherms of CO₂ for dehydrated **1** at 273 K.

The gas adsorption properties of dehydrated **1** for N₂ at 77 K and CO₂ at 273 K were evaluated (Figure 3). The maximum uptake of N₂ for dehydrated **1** is 46.03 cm³g⁻¹ at 77 K and 1 atm, with a reversible type I behavior, confirming the microporous nature of dehydrated **1**.¹⁰ The Brunauer–Emmett–Teller (BET) surface area of dehydrated **1**, calculated from the maximum of the N₂ adsorption isotherm, is estimated to be 10.49 m² g⁻¹ with a pore volume of 0.069 cm³ g⁻¹. This small pore volume is reasonable because dehydrated **1** has only 1D channel along the *c* axis.¹¹ Interestingly, the CO₂ sorption isotherms for dehydrated **1** also exhibited typical type I isotherms with a steep initial increase at low pressures and saturation at higher

pressures, and with a slight hysteresis on desorption.¹² The type I isotherms observed with abrupt adsorption at very low pressures are common for microporous materials. The presence of hysteresis may contribute to the existence of intercrystalline voids or the diffusion of CO₂ inside the pores appears to experience some restrictions.¹³ There is no significant CO₂ uptake for dehydrated **1**, and the adsorption amount is only 19.13 mL g⁻¹ at 273 K. These are comparable to the uptake capacities of some highly porous zeolitic imidazolate frameworks, which are in the range 19–55 mL g⁻¹ under the same conditions.¹⁴

Conclusions

In summary, we have successfully constructed a novel tubular coordination polymer with dominant ferromagnetic interactions in the tube using metalocyanate as a building block. The inner surface of the tube is hydrophilic, whereas the outer surface is hydrophobic. The magnetic tubular coordination polymer exhibits permanent porosity for gas sorption of CO₂ and N₂, providing a strategy to synthesize multi-functional materials.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Experimental details, XRD spectra, X-ray crystallographic file in CIF format for **1**, Tables S1, Figures S1-S2 and CCDC number of 1(994569) are provided. See DOI:10.1039/c000000x/

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Utilizing $[\text{Fe}^{\text{II}}(\text{bipy})(\text{CN})_4]^{2-}$ as the building block to react with Mn^{II} , we successfully synthesized a tubular coordination polymer with dominant ferromagnetic interactions. Moreover, the framework shows high thermal stability.

