ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2018, Vol. 44, No. 7, pp. 432–438. © Pleiades Publishing, Ltd., 2018.

Ferromagnetic Behavior of an Uncommon Trinuclearcopper(II) Coordination Polymer Based on Tartarate and 1,2-bis(4-Pyridyl)ethane Linker[1]

E. H. Zhou[a, b], B. H. Li[c], H. R. Zhong[c], H. D. Zeng[c], J. X. Zhang[c], J. Q. Liu[c, *], M. M. Luo[c], Y. Y. Wang[d], and J. C. Jin[a, b, **]

[a] *Anhui Provincial Laboratory of Biomimetic Sensor and Detecting Technology, West Anhui University, Anhui, 237012 P.R. China*

[b] *West Anhui Health Vocational College, Anhui, 237012 P.R. China*

[c] *Dongguan Key Laboratory of Drug Design and Formulation Technology, Key Laboratory of Research and Development of New Medical Materials of Guangdong Medical University, School of Pharmacy, Guangdong Medical University, Dongguan, 523808 P.R. China*

[d] *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry and Materials Science, Northwest University Xi'an, 710069 P.R. China*

**e-mail: jianqiangliu2010@126.com*

***e-mail: jcjgd2017@126.com*

Received September 18, 2017

Abstract—A new Cu(II) based metal-organic framework (MOF) having formula $[Cu_3(H_2Tar)(Tar)(H_2O)(Bpa)] \cdot 3H_2O$ (**I**) (H_4Tar = tartaric acid, Bpa = 1,2-bis(4-pyridyl)ethane) has been characterized by elemental analysis, FT-IR spectra, thermal analysis, and single-crystal X-ray diffraction (CIF file CCDC no. 1575136). In **I**, the Cu(II) center are connected by four symmetry-related tartrate ligands into a 2D layer encapsulating trinuclear cluster, which are further bridged by Bpa molecules into a 3D framework. Complex **I** exhibits strong ferromagnetic behavior between metal centers.

Keywords: magnetism, Cu(II) MOF, tartaric acid

DOI: 10.1134/S1070328418070072

ITRODUCTION

Polynuclear copper carboxylate chemistry is a new realm of research that has attracted scientists from multi-disciplinary areas, including biochemistry, material science, magnetochemistry and so on [1–5]. In recent years more attention on this class of compounds has been extensively investigated due to their potential applications with particular focus on their magnetic properties [6–11]. Conceivably, exploring new preparative approach towards the synthesis of high nuclearity copper complexes is thus of great appeal not only for the discovery of integrated new compounds but also as a means of construction types of related species so that structure-property relation would be further evolved. Polycarboxylates are widely employed to magnetic exchange pathways between the metal ions because of their abundant coordinated fashions, which can transmit magnetic coupling interactions to different degrees [6]. However, some interesting magnetic behaviors (such as long-range magnetic ordering) need spin carriers of shorter separation via short linkages. Hydroxyl polycarboxylates act as perfect candidates in designing extended magnetic networks [12–14]. For instance, $\{[KCo_3(Hbd)(HHbd)(H_2O)_2]\} \cdot 8H_2O$ (H_4Hbd = citric acid) displays a novel 3D canted antiferromagnetic porous network [15]. In this context, we chose a simple and in expensive tartaric acid ligand source, because it has versatile coordination modes and may stabilize new cluster in the crystallization process. Moreover, tartaric acid is an important component in detergents and cleaners because it has high binding potential for transition metal ions. For consumer product applications, it is often preceded to phosphate due to health or environmental concerns [16–18].

Generally, a Cu^{2+} ion with d^9 configuration tends to form a 4 + 1 or 4 + 2 coordination geometry thanks to a strong Jahn–Teller effect [19]. This flexibility of the coordination sphere for Cu^{2+} ion is prone to allow variations of the orientation and symmetry of the molecular orbital. The Cu^{2+} ion describing its unpaired electron (magnetic orbital) per centre is the

[1] The article is published in the original.

Table 1. Crystallographic data and structure refinements for **I**

Parameter	Value
Formula weight	741.05
Temperature, K	291(2)
Crystal system	Monoclinic
Space group	$P2_1$
a, Å	10.2056(9)
b, Å	7.9516(7)
c, Å	18.2418(16)
β, deg	101.4540(10)
V, Å^3; Z	1450.9(2); 2
ρ_{calcd}, kg/m^3	1.696
μ, mm^{-1}	2.253
Scan mode	ω-Scan technique
θ Range for data collection, deg	2.28–25.50
Reflections collected/unique	8614/5050
Reflections with $I > 2\sigma(I)$	4050
R_{int}	0.0473
Goodness-of-fit on F^2	1.022
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0397$, $wR_2 = 0.0965$
R indices (all data)	$R_1 = 0.0480$, $wR_2 = 0.0984$
Largest diff. peak and hole, e Å^{-3}	0.095 and −0.552

simplest case of the magnetic exchange without orbital contribution, which is a priori easier to understand than others, hence playing the role of model [20–22]. However, except in very few cases, it seems extremely diffcult to control the value of these structural parameters during the synthetic process [23–25].

Herein, we report our results for the polynuclear copper-tartrate system and magnetic characterization of the microporous polymers, namely $[Cu_3(H_2Tar)(Tar)(H_2O)(Bpa)] \cdot 3H_2O$ (**I**) (H_4Tar = tartaric acid, Bpa = 1,2-bis(4-pyridyl)ethane). In **I**, four symmetry-related tartrate ligands encapsulating trinuclear cluster are extended to adjacent four trinuclear clusters, Bpa molecules used as pillars link the copper-cluster layer into a 3D microporous framework. Interestingly, complex **I** exhibits strong ferromagnetic behavior.

EXPERIMENTAL

Materials and physical measurements. All commercially available solvents and reagents for synthesis were of reagent grade and used as received without further purification. FT-IR spectra (KBr pellets) were recorded as solid phase samples on a FT-IR 170SX (Nicolet) spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Thermogravimetric (TG) curves were measured on a NETZSCH STA 449C microanalyzer at a heating rate of 5°C min^{-1} from room temperature to 500°C under nitrogen atmosphere. The powder X-ray diffraction (PXRD) were recorded on a Pigaku D/Max 3III diffractometer. The magnetic measurements for **I** were carried out on crystalline samples with a MagLab System 2000 magnetometer in a magnetic field up to 1 kOe.

Synthesis complex I. A water–methanol solution (15 mL, v : v = 1 : 5) of $Cu(NO_3)_2 \cdot 8H_2O$ (0.25 mmol), sodium tartrate (0.16 mmol), Bpa (0.092 mmol), NaOH (0.04 mmol) and KI (0.005 mol) was sealed in a 25 mL Teflon-lined stainless steel container, which was heated to 150°C for 96 h. After the sample was cooled to room temperature at a rate of 2°C h^{-1}. Blue crystals were obtained in ~52% yield based on Cu.

For $C_{20}H_{26}N_2O_{16}Cu_3$			
Anal. calcd., %	C, 32.41	H, 3.53	N, 3.78
Found, %	C, 32.50	H, 3.48	N, 3.71

FT-IR (KBr; ν, cm^{-1}): 3489 v.s, 1608 m, 1551 s, 1508 w, 1426 m, 1386 m, 1089 m, 879 m.

X-ray structure determination. X-ray diffraction data were collected on a BRUKER SMART APEX-CCD diffractometer with MoK_α radiation (λ = 0.71073 Å) at 298(2) K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXL-97 program package [26]. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced in calculatedpositions and were allocated one overall isotropic thermal parameter, some of the hydrogen atoms of the water molecules were located from different Fourier maps. The crystallographic data for **I** are listed in Table 1, selected bond lengths and angles are presented in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1575136); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Single-crystal X-ray analysis of **I** reveals a 3D framework. Figure 1 shows the asymmetric unit of **I** consists of three independent Cu^{2+} cations, two Tar

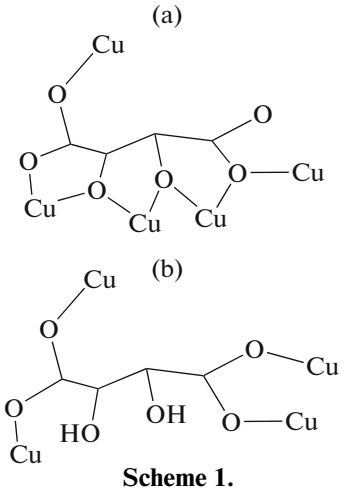
Table 2. Selected bond lengths (Å) and angles (deg) for complex **I***

Bond	*d*, Å	Bond	*d*, Å
		I	
Cu(1)–O(2)	1.913(4)	Cu(1)–O(11)	1.942(4)
Cu(1)–O(8)	1.944(4)	Cu(1)–O(4)	1.947(4)
Cu(1)–O(13)	2.488(5)	Cu(2)–O(6)	1.920(4)
Angle	ω, deg	Angle	ω, deg
		I	
O(2)Cu(1)O(11*A*)	168.2(2)	O(4)Cu(1)O(8)	179.7(2)
O(8)Cu(1)O(13)	94.3(2)	O(6)Cu(2)O(12*A*)	174.7(2)
O(4)Cu(2)N(2)	172.7(2)	O(12)Cu(2)O(13)	89.3(2)
O(1)Cu(3)O(7)	173.7(2)	O(2)Cu(3)N(2*B*)	165.8(2)
O(7)Cu(3)N(1)	93.2(2)	O(1)Cu(3)O(1)	84.7(2)

* Symmetry codes: (*A*) $-1+x, y, -1+z$; (*B*) $-1-x, -1/2+y, -z$.

and H_2Tar ligands (Scheme 1), one Bpa ligand, one coordinated water and three lattice water molecules.

Coordination modes of tartrate ligand in **I** are given below.



Scheme 1.

The Scheme correlates with the Fig. 1 clearly, the (a) matches with the below part of ligand, the above part matches with the (b). Although Cu(1) and Cu(2) atoms adopt distorted trigonal-bipyramidal geometries, the coordinated environments are very different. The Cu^{2+} ion is coordinated by two oxygen atoms from two hydroxy groups of one Tar ligand, two oxygen atoms from two neighboring bidentated-bridging carboxylate groups of H_2Tar ligands, and one oxygen atom from a μ_2-H_2O molecule. While Cu(2) is formed by one hydroxy oxygen atom and one carboxylic oxygen atom from one Tar ligand, one oxygen atom of bidentated-bridging carboxylate group, one sharing oxygen atom of μ_2-H_2O molecule, and one nitrogen atom from one Bpa ligand. The Cu(3) center lies in distorted square-pyramidal surroundings, defined by one hydroxy oxygen and one carboxylic oxygen atoms from one Tar ligand, two oxygen atoms from adjacent bidentated-bridging carboxylate groups of H_2Tar ligands, and one nitrogen atom from the other Bpa ligand. The Cu–O distances range from 1.913(4) to 2.678(6) Å, and the OCuO bond angles vary from

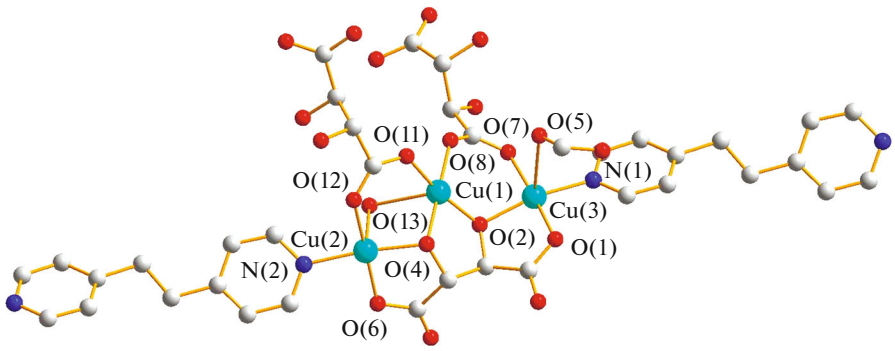


Fig. 1. Perspective view of the trinuclear unit of **I** showing the atom numbering.

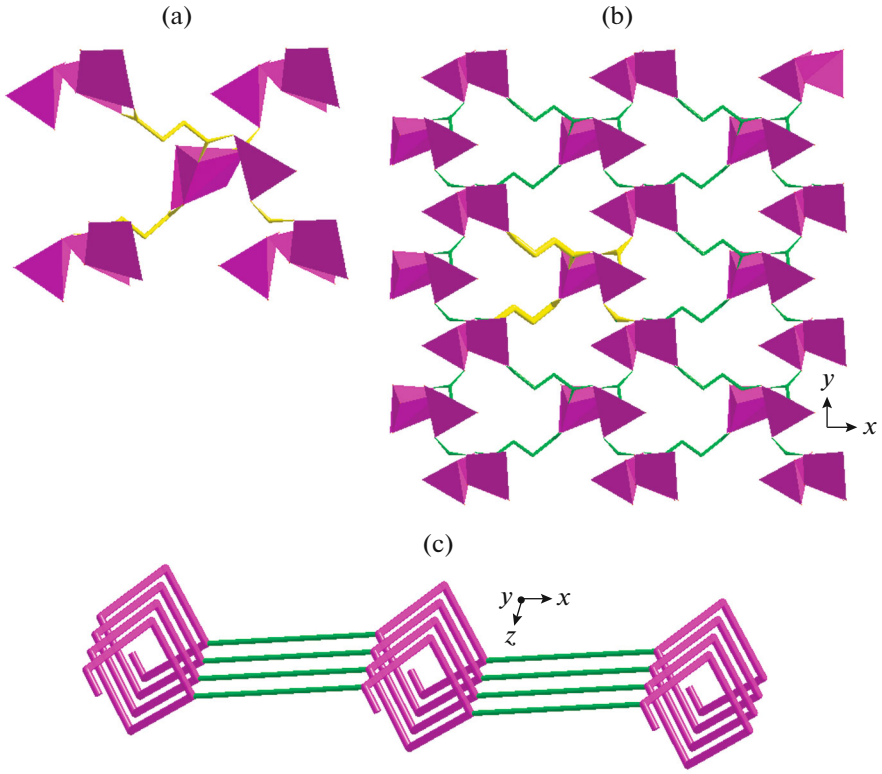


Fig. 2. Schematic view of a trinuclear copper cluster and its adjacent four copper clusters (a) and a perspective viewing of (4,4) cluster layer (b) in complex **I**; 2D framework of **I** showing its helical layer (c).

85.68(16)° to 179.72(18)° (Table 2). All parameters are similar with polymers of carboxylate [27].

Trinuclear copper cluster further binds to adjacent four trinuclear clusters (Fig. 2a). The framework of alternating trinuclear copper-tartrate cluster and tetrahedral copper nodes can be described as an infinite 2D (4,4) layer along z axis (Fig. 2b). Strikingly, the copper clusters and tartrate form microporous channels, which are hollow and do not contain encapsulated guest molecules along y axis. These copper clusters are linked up via tartrate ligands to give rise to eight-shaped helical chains. It should be noted that all helices have the same handedness in the same layer (Fig. 2c). This can be interpreted by the more flexible configuration of this tartrate ligand. Another interesting aspect of the structure is that the 2D layers are connected by Bpa ligands through the axial positions of both Cu(2) and Cu(3) centers in subunits to form a 3D double pillared-layer structure (Fig. 3). The whole structure can rationally be described as a 3D porous framework with open channels, and guest water molecules occupy the channels.

Magnetic measurements were performed on samples containing a collection of very small block single crystals with random orientations. The magnetic susceptibility of complex **I** was measured in the range 2–300 K. For complex **I**, the $\chi_M T$ value at room temperature (300 K) was 1.236 cm^3 K mol^{-1}, little higher than the expected spin-only value for three noninteracting Cu^{2+} ion (1.125 cm^3 K mol^{-1}). Upon lowering the temperature, the magnetic moment ($\chi_M T$) gradually augments from 1.236 cm^3 K mol^{-1} at 300 K to reach a maximum of 1.907 cm^3 K mol^{-1} at 22.1 K (Fig. 4a), which indicates ferromagnetic interactions between copper ions. The plot of χ_M^{-1} versus T for complex **I** obeys the Curie–Weiss law $\chi_M = C/(T - \theta)$, giving C = 1.22 emu K mol^{-1} and θ = 8.1 K (Fig. 4b). The positive θ value confirms the ferromagnetic exchange interaction between copper atoms with $S = 1/2$ spins. The fit of the susceptibility data has been carried out using Hamiltonian and the formula proposed by Sinn [28].

$$\chi_M = \frac{Ng^2(\mu_B)^2}{4K(T-\theta)} \frac{1+5e^{\frac{3J}{KT}}}{1+e^{\frac{3J}{KT}}}. \quad (1)$$

A least-square fit of the data to the equation (1) yields the values of θ = 0.41, J = +27.8 cm^{-1}, g = 2.04 and $R = 1.863 \times 10^{-4}$ (where R is defined as $\sum\left(\left(\chi_M^{obs} - \chi_M^{calc}\right)^2 / \left(\chi_M^{obs}\right)^2\right)$. This indicates the presence of ferromagnetic interactions. Most of the tricopper compounds previously observed exhibit antiferro-

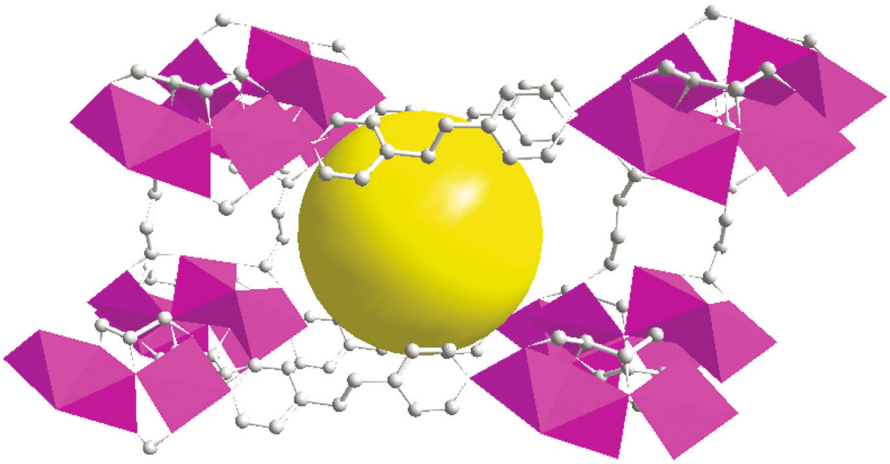


Fig. 3. The 3D porous network of viewed along the *x* axis in complex **I**. The polyhedrons represent copper clusters, the Bpa ligands represent white pillars. The ball represents an oblate spheroid at the center of cavity, its radius is 5 Å.

magnetic interactions [29, 30], ferromagnetic interactions were reported in some μ_3-oxo and μ_3-hydroxo tricopper complexes [31–33].

To study the stability of the polymers, TG analysis of complex **I** was performed (Fig. 5). TG diagrams of **I** indicate two main steps of weight losses. The weight loss begins at 20°C and is completed at 132°C. The observed weight loss of 10.1% is corresponding to the loss of the crystallization water molecule (calcd. 9.7%). The second weight loss occurs in the range 200–450°C, which can be attributed to the elimination of TAR and Bpa ligands (obsd. 11.2%, calcd. 10.7%) (Fig. 5).

Additionally, to confirm the phase-pure and the stable framework of compound **I**, the original sample and dehydrated sample were characterized by PXRD at room temperature. The pattern that was simulated from the single-crystal X-ray data of compound **I** was in good agreement with those that were observed (Fig. 6), thus compound **I** was obtained as a single

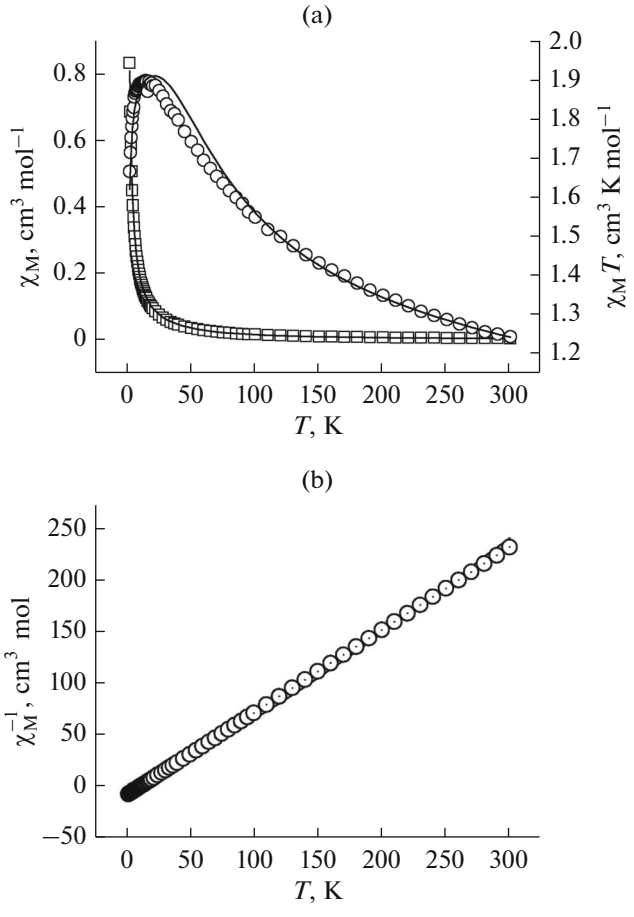


Fig. 4. Thermal variation of χ_M(□) and $\chi_M T$ (○) (a) and plots of $1/\chi_M$ versus T (b) for complex **I**.

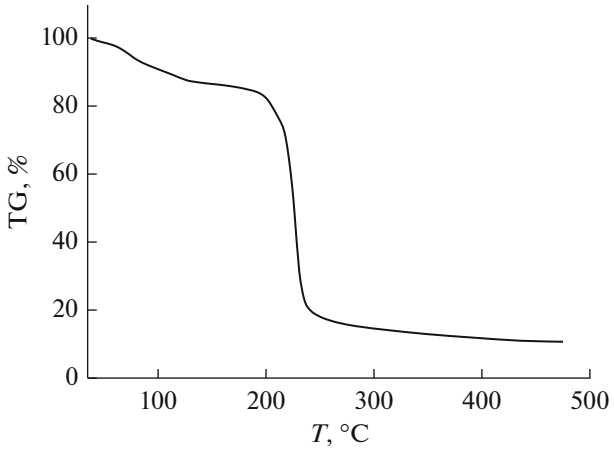


Fig. 5. Thermogravimetric curve of **I**.

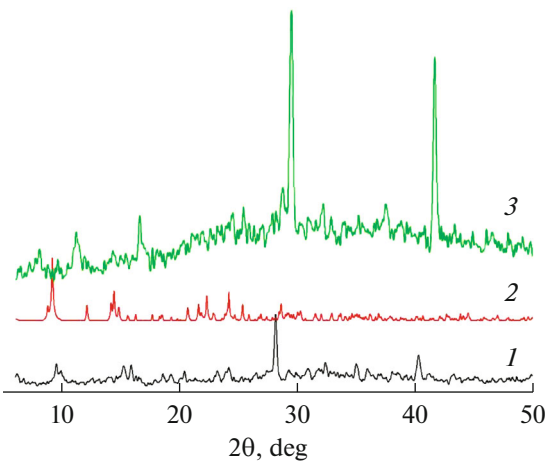


Fig. 6. Comparison of PXRD patterns of the simulated pattern from the single-crystal structure determination (*1*), as-synthesized product (*2*), the desolvated (*3*).

phase. For compound **I**, after heating at 135°C for 4 h, the guest water molecule was removed (the evacuated frameworks are defined as **I'**). The PXRD pattern of **I'** is similar to compound **I**, although minor differences can be seen in the positions, intensities, and widths of some peaks (Fig. 6), which indicates that the framework of compound **I** is retained after the removal of the guest molecule.

Thus, we have successfully isolated a new coordination polymer constructed from tartrate (Tar) and N-donor co-ligand. Interestingly, Tar acts as a perfect ligand in the self-assembly because of its moderate length, flexibility and five discrete metal-binding sites. The new design idea depicted in this paper may be a promising technique for the construction of other intriguing organic-inorganic hybrid coordination polymers, and further efforts on this perspective are underway.

ACKNOWLEDGMENTS

This work was partially supported by the grants from Innovative Entrepreneurial Training Plan of undergraduates in Guangdong Province (nos. 201710571012, 201710571019, 2017105710116, 201710571060), the Public Research and Capacity Building Projects of Department of Guangdong Province (no. 2017A010103022), Natural Science Foundation of Guangdong Province (no. 2017A030313079) and Science Foundation funded project of Guangdong Medical University (Z2016001 and M2016023), and financial support from the NSF of China (no. 21401143); the Anhui Provincial Natural Science Foundation (no. KJ2016B02); the Anhui provincial quality project (no. 2016jyxm1089), the Excellent Young Support Program of Anhui Province (gxygZD20170703 and gxyqZD2017073). Thanks for Dr. Yanling Li, Prof. Michel Verdaguer and Dr. Eliseo Ruiz for kind suggestion and discussion.

REFERENCES

1. Kahn, O., *Molecular Magnetism*, New York: VCH, 1993.
2. Braga, D., Grepioni, F., and Desiraju, G.R., *Chem. Rev.*, 1998, vol. 98, p. 1375.
3. Ferrer, S., Haasnoot, J.G., Reedijk, J., et al., *Inorg. Chem.*, 2000, vol. 39, p. 1859.
4. Liu, J.C., Guo, G.C., Huang, J.S., et al., *Inorg. Chem.*, 2003, vol. 42, p. 235.
5. Cage, B., Cotton, F.A., Dalal, N.S., et al., *J. Am. Chem. Soc.*, 2003, vol. 125, p. 5270.
6. Gojon, E., Gaillard, J., Latour, J.M., et al., *Inorg. Chem.*, 1987, vol. 26, p. 2047.
7. Murphy, B.P., *Coord. Chem. Rev.*, 1993, vol. 124, p. 63.
8. Haasnoot, J.G., *Coord. Chem. Rev.*, 2000, vol. 200, p. 131.
9. Bian, H.D., Xu, J.Y., Gu, W., et al., *Polyhedron*, 2003, vol. 22, p. 2927.
10. Doyle, R.P., Julve, M., Lloret, F., et al., *Dalton Trans.*, 2006, p. 2081.
11. Miller, J.S., *Dalton Trans.*, 2006, p. 2742.
12. Chui, S.S.Y., Lo, S.M.F., Charmant, J.P.H., et al., *Science*, 1999, vol. 283, p. 1148.
13. Konar, S., Zangrando, E., Drew, M.G.B., et al., *Dalton Trans.*, 2004, p. 260.
14. Konar, S., Mukherjee, P.S., Zangrando, E., et al., *Angew. Chem. Int. Ed.*, 2002, vol. 41, p. 1561.
15. Xiang, S.C., Wu, X.T., Zhang, J.J., et al., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 16352.
16. Murrie, M., Teat, S.J., Stoecki-Evans, H., et al., *Angew. Chem. Int. Ed.*, 2003, vol. 42, p. 4653.
17. Thushari, S., Cha, J.A.K., Sung, H.H.-Y., et al., *Chem. Commun.*, 2005, p. 5515.
18. Zhang, X.M., Hou, J.J., and Wu, H.S., *Dalton Trans.*, 2004, p. 3437.
19. Julve, M., Verdaguer, M., Kahn, O., et al., *Inorg. Chem.*, 1983, vol. 22, p. 368.
20. Carranza, J., Grove, H., Sletten, J., et al., *Eur. J. Inorg. Chem.*, 2004, p. 4836.
21. Julve, M., Verdaguer, M., Gleizes, A., et al., *Inorg. Chem.*, 1984, vol. 23, p. 3808.
22. Gleizes, A., Julve, M., Verdaguer, M., et al., *J. Chem. Soc., Dalton Trans.* (*1972–1999*), 1992, p. 3209.
23. Zhang, X.-M., *Coord. Chem. Rev.*, 2005, vol. 249, p. 1201.
24. Hennigar, T.L., MacQuarrie, D.C., Losier, P., et al., *Angew. Chem. Int. Ed.*, 1997, vol. 36, p. 972.
25. Zhou, Y.X., Shen, X.Q., Liu, H.L., et al., *Syn. React. Inorg. Met.*, 2006, vol. 36, p. 563.

26. Sheldrick, G.M., *SHELXL-97, Program for Structure Determination and Refinement,* Göttingen: Univ. of Göttingen, 1997.
27. Duan, L.M., Xie, F., Chen, X.Y., et al., *Cryst. Growth Des.*, 2006, vol. 6, p. 1101.
28. Butcher, R.J. and O'Connor, C.J.E., *Sinn. Inorg. Chem.*, 1981, vol. 20, p. 537.
29. Bailey, N.A., Fenton, D.E., Moddy, R., et al., *J. Chem. Soc., Dalton Trans.* (*1972–1999*), 1988, p. 2817.
30. Angaroni, A., Ardizzoiz, G.A., Beringhelli, T., et al., *Dalton Trans.*, 1990, p. 2817.
31. Suh, M.P., Han, M.Y., Lee, J.H., et al., *J. Am. Chem. Soc.*, 1998, vol. 120, p. 3819.
32. Tong, M.L., Wu, Y.M., Tong, Y.X., et al., *Eur. J. Inorg. Chem.*, 2003, p. 2385.
33. Lin, J.G., Zang, S.Q., Tian, Z.F., et al., *CrystEngComm*, 2007, vol. 9, p. 915.