

一类六核三价铁簇化物的合成及结构表征

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摘要: 选择 3 种不同尺寸含氮配体(哌嗪、咪唑和三氮唑)与三羟甲基丙烷(H₃tmp)和 FeCl₃ 采用溶剂热反应合成 3 例六核 Fe(III) 化合物: (C₅H₁₄N₂)[Fe₆(μ₆-O)Cl₆(tmp)₄]·2H₂O·CH₃OH (**1**)、(C₃H₅N₃)₂[Fe₆(μ₆-O)Cl₆(tmp)₄] (**2**) 和 (C₄H₈N₃)₃(C₂H₄N₃)[Fe₁₂(μ₆-O)₂Cl₁₂(tmp)₈]·3CH₃OH (**3**), 并对它们的结构进行表征。发现三元醇配体有利于合成高核金属簇。3 个化合物具有相同的阴离子簇 [Fe₆(μ₆-O)Cl₆(tmp)₄]²⁻。通过晶体学参数, 元素分析, 红外等手段证实, 在化合物 **1** 和 **3** 的体系中, 氮杂环配体经历了 N-和 C-烷基化反应。

关键词: 六核铁簇; 晶体结构; 抗衡离子

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Syntheses and Structures Characterization of a Family of Hexanuclear Iron(III) Clusters

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Abstract: Solvothermal reactions of 1,1,1-tris(hydroxymethyl)propane (H₃tmp) and FeCl₃ by using different counter ions resulted in three hexanuclear iron(III) clusters (C₅N₂H₁₄)[Fe₆(μ₆-O)Cl₆(tmp)₄]·2H₂O·CH₃OH (**1**), (C₃N₂H₅)₂[Fe₆(μ₆-O)Cl₆(tmp)₄] (**2**), and (C₄N₃H₈)₃(C₂N₃H₄)[Fe₁₂(μ₆-O)₂Cl₁₂(tmp)₈]·3CH₃OH (**3**), whose structures were characterized. The tripodal alcohols ligands are very useful in constructing high-nuclearity metal clusters. In all cases, similar anionic cluster [Fe₆(μ₆-O)Cl₆(tmp)₄]²⁻ is formed by six Fe(III) ions, four tmp³⁻ ligands, one center O²⁻ ion, and six Cl⁻ ions. Within the system of compounds **1** and **3**, the nitrogen-containing heterocyclic ligands experience N- and C-alkylation reactions, which is validated by the crystallographic parameters, elemental analyses, and IR. CCDC: 980726, **1**; 980727, **2**; 980728, **3**.

Keywords: hexanuclear iron(III) clusters; crystal structure; counter ions

0 Introduction

The polynuclear transition metal clusters have attracted numerous attention since they simultaneously display pleasing architectural aesthetics and fascinating magnetic properties^[1-6]. The investigation of such magnetic materials is helpful in understanding the magnetio-structural correlations and provides a

fertile platform for the research of the attractive magnetic characteristics, such as ferromagnetic ordering^[7], antiferromagnetic ordering^[8], ferrimagnetic ordering^[9-11], spin-canting^[12-13], metamagnetic transition^[14], spin-glass^[15-17], spin-flop^[18-20], and spin-frustrated^[21-23], etc^[24-26]. Although there is great success made in the practice, the design and synthesis of such materials still remain an elusive goal and a major challenge to systema-

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tically study the structure-property relationship^[27]. To obtain a magnetic polynuclear cluster, incorporation of paramagnetic transition-metal ions with appropriate multidentate chelating ligands is a general strategy. In this respect, we chose Fe(III) ion, with $S=5/2$, as the paramagnetic center due to the exchange anisotropy and the large spin ground state achieved^[28-30]. As for the main organic ligand, we selected tripodal alcohol ligand, *i.e.*, 1,1,1-tris(hydroxymethyl)propane (abbreviated H₃tmp), which is a very attractive candidate for the construction of multinuclear clusters, due to its flexibility and diverse coordination modes as well as superexchange capacity reflected in interesting magnetic properties^[31]. It is well known that nitrogen-containing heterocyclic groups generally act as a role of bridging ligands, due to their strong σ -electron donors to metals^[32-33]. Furthermore, they can also perform counter cations because they are weak base and prone to protonate. Therefore, we have concentrated our efforts on the combination of nitrogen-containing heterocyclic ligands, which act as assistant role, with Fe(III)-H₃tmp system to explore the structures and investigate the resultant magnetic properties.

In this paper, we have successfully assembled and investigated three hexanuclear compounds, (C₅N₂H₁₄)[Fe₆(μ_6 -O)Cl₆(tmp)₄]·2H₂O·CH₃OH (**1**), (C₃N₂H₅)₂[Fe₆(μ_6 -O)Cl₆(tmp)₄] (**2**), and (C₄N₃H₈)₃(C₂N₃H₄)[Fe₁₂(μ_6 -O)₂Cl₁₂(tmp)₈]·3CH₃OH (**3**). These three compounds possess different protonated nitrogen-containing heterocyclic counter cations, despite the same [Fe₆(μ_6 -O)Cl₆(tmp)₄]²⁻ core. Within the system of compounds **1** and **3**, the nitrogen-containing heterocyclic ligands experience N- and C-alkylation reactions, which is validated by the crystallographic parameters, elemental analyses, and IR.

1 Experimental

1.1 Reagents and physical measurements

All chemicals and solvents were of reagent grade and used as commercially purchased without further purification.

Infrared spectra (400~4 000 cm⁻¹) were measured on a Perkin-Elmer Fourier transform infrared (FTIR)

spectrophotometer using KBr pellets (Fig.S1, Supporting information). The elemental analyses (C, H and N) were performed on a Perkin-Elmer Model 240C elemental analyzer. The Fe and Cl elemental contents were determined by the Leaman inductively coupled plasma (ICP) spectrometer. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TG-7 analyzer in flowing nitrogen atmosphere from room temperature to 800 °C with a heating rate of 10 °C·min⁻¹. Powder X-ray diffraction (PXRD) measurements were assessed on a Siemens D5005 diffractometer with Cu K α ($\lambda=0.154\ 184\ \text{nm}$) in 2θ range of 5°~50° at room temperature. The XRD accelerating voltage and emission current were 40 kV and 30 mA, respectively.

1.2 Syntheses of complexes 1~3

1.2.1 Synthesis of (C₅N₂H₁₄)[Fe₆(μ_6 -O)Cl₆(tmp)₄]·2H₂O·CH₃OH (**1**)

A mixture of FeCl₃ (0.049 g, 0.3 mmol), H₃tmp (0.027 g, 0.2 mmol), piperazine (0.026 g, 0.3 mmol), and methanol (15 mL) was placed in a 20 mL Teflon-lined autoclave and heated under autogenous pressure at 120 °C for 72 h. Then, the autoclave was cooled to ambient temperature at 3 °C·h⁻¹. Block-shaped red crystals of **1** were collected in ~80% yield (based on Fe). Anal. Calcd. for C₃₀H₆₆Cl₆Fe₆N₂O₁₆(%): C, 28.62; H, 5.25; N, 2.23; Fe, 26.64; Cl, 16.91. Found(%): C, 28.98; H, 5.14; N, 2.33; Fe, 26.51; Cl, 17.11. IR (KBr, cm⁻¹): 3 489 (m), 2 966 (m), 2 914 (m), 2 868 (m), 1 623 (w), 1 472 (m), 1 453 (m), 1 398 (w), 1 356 (w), 1 304 (w), 1 198 (w), 1 111 (s), 1 034 (s), 941 (s), 771 (w), 593 (m), 527 (s), 473 (m), 437 (w).

1.2.2 Synthesis of (C₃N₂H₅)₂[Fe₆(μ_6 -O)Cl₆(tmp)₄] (**2**)

A mixture containing FeCl₃ (0.081 g, 0.5 mmol), H₃tmp (0.027 g, 0.2 mmol), imidazole (0.014 g, 0.2 mmol), and methanol (15 mL) was heated in a Teflon-lined autoclave at 120 °C for 72 h and then allowed to cool to room temperature at the rate of 3 °C·h⁻¹. Needle-like red crystals of **2** were obtained in ~85% yield (based on Fe). Anal. Calcd. for C₃₀H₅₄Cl₆Fe₆N₄O₁₃(%): C, 29.36; H, 4.41; N, 4.57; Fe, 27.34; Cl, 17.35. Found(%): C, 29.05; H, 4.66; N, 4.39; Fe, 27.84; Cl, 17.64. IR (KBr, cm⁻¹): 3 148 (m), 2 972 (m), 2 915 (m), 2 868 (m), 1 585 (m), 1 472 (m), 1 455 (w), 1 399 (w),

1 303 (w), 1 199 (w), 1 110 (s), 1 033 (s), 990 (w), 941 (s), 821 (w), 794 (w), 771 (w), 755 (w), 628 (m), 591 (m), 528 (s), 474 (m), 438 (w).

1.2.3 Synthesis of $(C_4N_3H_8)_3(C_2N_3H_4)[Fe_{12}(\mu_6-O)_2Cl_{12}(tmp)_8] \cdot 3CH_3OH$ (**3**)

A mixture of $FeCl_3$ (0.081 g, 0.5 mmol), H_3tmp (0.041 g, 0.3 mmol), triazole (0.138 g, 2 mmol), and methanol (15 mL) was heated in Teflon-lined autoclave at 140 °C for 72 h. After the autoclave was cooled to room temperature at 3 °C·h⁻¹, red block-shaped crystals of **3** were afforded (Yield: 75% based on Fe). Anal. Calcd. for $C_{65}H_{128}Cl_{12}Fe_{12}N_{12}O_{29}$ (%): C, 29.59; H, 4.856; N, 6.37; Fe, 25.43; Cl, 16.14. Found(%): C, 28.31; H, 4.921; N, 6.12; Fe, 25.49; Cl, 16.78. IR (KBr, cm⁻¹): 3 464 (w), 3 075 (m), 2 964 (m), 2 911 (m), 2 866 (m), 1 628 (w), 1 584 (m), 1 470 (m), 1 452 (m), 1 398 (m), 1 302 (w), 1 198 (w), 1 165 (w), 1 112 (s), 1 038 (s), 942 (s), 771 (w), 733 (w), 659 (w), 625 (m), 592 (m), 526 (s), 473 (m).

1.3 Details of X-ray crystallography

Single-crystal X-ray diffraction data for complexes **1**~**3** were measured on a Bruker SMART APEX CCD area detector diffractometer using graphite monochro-

ated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ nm$) at room temperature. Structure solution (direct methods) and the refinement of full-matrix least-squares were carried out using the SHELXTL software package^[34]. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to carbon and nitrogen atoms were placed in geometrically calculated positions. For complex **1**, the hydrogen atoms on the non-coordinated MeOH molecule, that is O(14), and on water molecules, that are O(1W) and O(2W), were not located. The atoms C(30), O(14), O(1W) and O(2W) were found disordered over two sites. For complex **2**, the atom C(1) was highly disordered over two sites. For complex **3**, the hydrogen atom on one non-coordinated MeOH molecule, that is O(14), was not located. The atoms C(13) and C(14) were highly disordered over two sites. The protonated degrees of all the counter cations are according to the charge balance. Crystallographic and refinement details for all compounds are summarized in Table 1. Selected bond lengths and angles are listed in Table S1~S3.

CCDC: 980726, **1**; 980727, **2**; 980728, **3**.

Table 1 Crystallographic data and structure refinement for complexes **1**~**3**

	1	2	3
Formula	$C_{30}H_{66}Cl_6Fe_6N_2O_{16}$	$C_{30}H_{54}Cl_6Fe_6N_4O_{13}$	$C_{65}H_{128}Cl_{12}Fe_{12}N_{12}O_{29}$
Formula weight	1 257.8	1 225.8	2 635.6
Space group	$Pbca$	$R\bar{3}c$	$P\bar{1}$
Crystal system	Orthorhombic	Trigonal	Triclinic
a / nm	1.960 1(7)	2.746 9(3)	1.136 1(2)
b / nm	1.922 3(7)	2.746 9	1.144 3(2)
c / nm	2.550 4(9)	3.546 7(4)	2.195 5(4)
$\alpha / (^\circ)$			96.408(2)
$\beta / (^\circ)$			101.976(3)
$\gamma / (^\circ)$			112.667(2)
V / nm^3	9.610(6)	23.176(3)	2.517 8(8)
Z	8	18	1
$D_c / (g \cdot cm^{-3})$	1.731	1.576	1.738
$F(000)$	5 117.2	11 155.9	1 348
θ range / $(^\circ)$	1.60~25.04	1.48~25.00	1.94~25.21
Unique reflns (R_{int})	8 506 (0.069 5)	4 555 (0.051 2)	9 078 (0.024 3)
$R_1^a, wR_2^b [I > 2\sigma(I)]$	0.043 9, 0.116 8	0.044 5, 0.146 4	0.051 7, 0.117 7
R_1^a, wR_2^b (all data)	0.082 3, 0.139 1	0.060 3, 0.156 3	0.099 4, 0.148 7
GOF on F^2	1.072	1.09	1.027

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o^2)]^{1/2}$; $w = 1/\sigma(F_o)^2$.

2 Results and discussion

2.1 Synthesis

Complex **1** was prepared by the solvothermal reaction of FeCl_3 , H_3tmp , and piperazine in a 3:2:3 molar ratio in MeOH at 120 °C for 72 h. Interestingly, the piperazine ligand in such system experienced N-alkylation reaction to form methyl substituent piperazine (abbreviated as L_1). Complex **3** was synthesized by the solvothermal reaction of FeCl_3 , H_3tmp , and triazole in a 5:3:20 molar ratio in MeOH at 140 °C for 72 h. Part of triazole in such system went through C- and N-alkylation reactions to form dimethyl substituent triazole (abbreviated as L_2). The reasons for such N/C-alkylation reactions in the systems **1** and **3** are unclear due to the complexity under the solvothermal condition. Complex **2** was obtained by the reaction of FeCl_3 with H_3tmp and imidazole in a 5:2:2 molar ratio in MeOH at 120 °C for 72 h.

2.2 X-ray crystal structures

Single-crystal X-ray diffraction results of **1~3** reveal that each compound possesses same anionic structure unit composed of $[\text{Fe}_6(\mu_6\text{-O})\text{Cl}_6(\text{tmp})_4]^{2-}$ core (Fig.1), which exhibits marked similarities to previously reported compounds contained 1,1,1-tris(hydroxymethyl)ethane (H_3thme)^[35-36]. In the anionic core, the ligand H_3tmp possesses the level of deprotonation tmp^{3-} and adopts the $\eta^2:\eta^2:\eta^2:\mu_3$ coordinated mode^[31]. The central $\mu_6\text{-O}$ approximately locates in the center of an octahedron formed by six $\text{Fe}(\text{III})$ atoms. The Fe ions are all in +3 oxidation state, as determined from a combination of charge balance considerations, inspection of bond lengths, and BVS calculations^[37-39]. Each Fe atom exhibits distorted octahedral geometry, which coordinates to four oxygen atoms from two different tmp^{3-} ligands, one $\mu_6\text{-O}$ atom, and terminal chloride atom. It is worth notice that the charge balance is provided by the protonated nitrogen-containing heterocyclic cations. These counter cations provide not only the charge balance but also the hydrogen bond interactions to glue the counterpart of the structure. More structural details involving the packing patterns and the intracuster/intercluster distances are discussed as

follows. The ellipsoid for the complexes **1~3** are shown in Fig.2~4, respectively.

Compound **1** crystallizes in the orthorhombic system $Pbca$. The asymmetric unit consists of one $[\text{Fe}_6(\mu_6\text{-O})\text{Cl}_6(\text{tmp})_4]^{2-}$ unit, one doubly-protonated L_1 ligand, one non-coordinated methanol molecule, and two non-coordinated water molecules. The bond distances of Fe-O (0.197 2~0.227 7 nm) and Fe-Cl (0.226 6~0.229 4 nm) are similar to those reported $[\text{Fe}_6]$ cluster

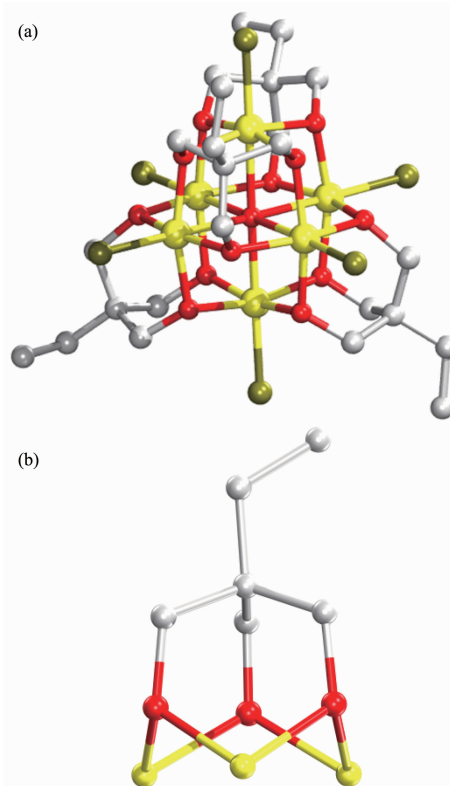


Fig.1 (a) Anion unit $[\text{Fe}_6(\mu_6\text{-O})\text{Cl}_6(\text{tmp})_4]^{2-}$ of complex **1**;
(b) Bridging mode of the tmp^{3-} ligand

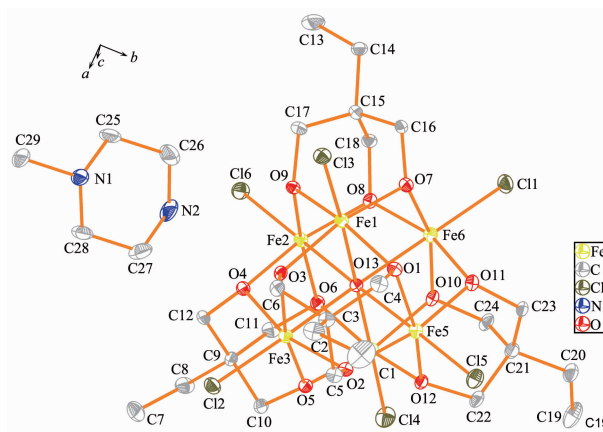
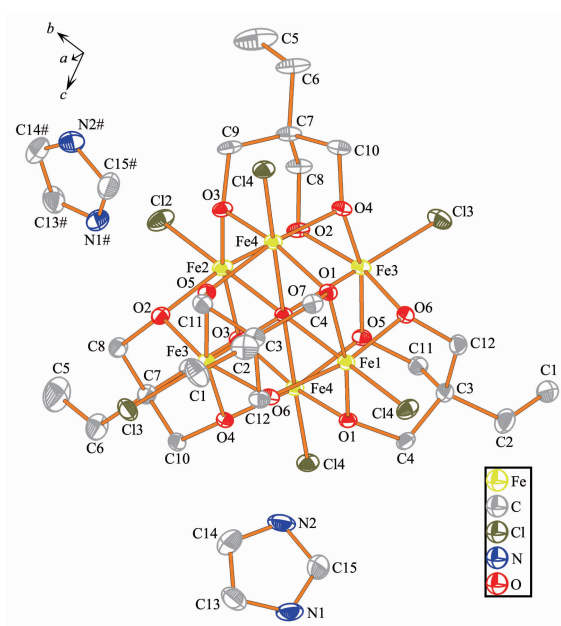


Fig.2 Ellipsoid for the complex **1** with probability of 30%



Symmetry codes: #1: $-1+x, y, z$

Fig.3 Ellipsoid for the complex **2** with probability of 30%

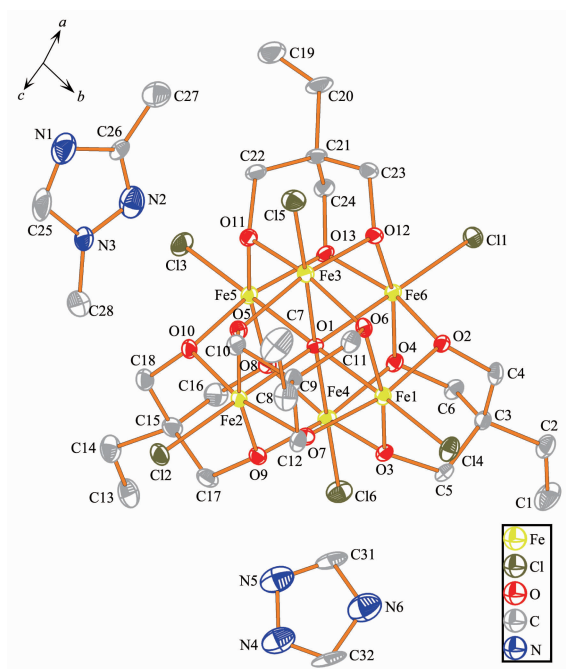


Fig.4 Ellipsoid for the complex **3** with probability of 30%

containing H_3thme ligand^[35-36]. The intracluster $Fe \cdots Fe$ distances are observed in the range of 0.315 4~0.322 3 nm (Fig. S2a).

Compound **2** belongs to the trigonal system $R\bar{3}c$. The asymmetric unit consists of half of $[Fe_6(\mu_6-O)Cl_6(tmp)_4]^{2-}$ unit, and one mono-protonated imidazole cation.

The Fe-O and Fe-Cl bond distance is in the range of 0.198 2~0.230 1 nm and 0.224 7~0.228 7 nm, respectively. The intracluster $Fe \cdots Fe$ distances fall in the range of 0.318 5~0.321 9 nm (Fig.S2b). The $[Fe_6]$ units within the lattice of **2** connect to each other into a hydrophobic channel along c axis.

Compound **3** crystallizes in triclinic system $P\bar{1}$. The asymmetric unit consists of one $[Fe_6(\mu_6-O)Cl_6(tmp)_4]^{2-}$ unit, one and half of mono-protonated L_2 ligands, half of mono-protonated triazole ligand, one and half of non-coordinated methanol molecules. The Fe-O and Fe-Cl bond distance is in the range of 0.198 0~0.228 2 nm and 0.227 1~0.230 6 nm, respectively. The intracluster $Fe \cdots Fe$ distances are within the range of 0.316 9~0.321 7 nm (Fig.S2c).

2.3 Thermal stability and PXRD analysis of 1~3

The thermogravimetric analyses (TGA) were performed to investigate the thermal stabilities of compounds **1~3** (Fig.S3). The TGA trace of compound **1** exhibits a weight loss of 5.13% from room temperature to 200 °C corresponding to the release of lattice water and methanol molecules (Calcd. 5.41%). Then two continuous weight loss steps are attributed to the loss of the counter-cation and the anion $[Fe_6]$ core. The remaining 37.84% above 735 °C corresponds to the final product of Fe_2O_3 (Calcd. 38.09%). The TGA profile of **2** does not lose any weight below 110 °C indicating there are no solvent molecules in the lattice. Then the weight loss is attributed to the gradual decomposition of the counter-cation and ligands. Finally, a plateau region is observed from 443 to 800 °C. The final residue of 38.95% corresponds to the formation of Fe_2O_3 (Calcd. 39.08%). Compound **3** displays the first weight loss of approximately 3.76% from room temperature to 144 °C corresponding to the release of three methanol molecules (Calcd. 3.64%). And then, the release of the counter-cation and the decomposition of organic ligands occur through several continuous weight loss steps after 200 °C. The final residuals were not characterized, which may be owing to the corrosive reactions of the final residuals with the TGA baskets made of Al_2O_3 ^[40]. Viewing from the trend of the TGA curve, it is known that the decom-

posing process is not achieved at the operating temperature limit (800 °C) of our instrument.

The phase purity is confirmed by powder X-ray diffraction (PXRD) at room temperature. The experimental patterns of **1**~**3** are in fairly good agreement with the simulated ones generated from single-crystal diffraction data (Fig.S4~S6).

3 Conclusions

In summary, the use of different counter ions has led to the synthesis of a family of hexanuclear iron(III) clusters **1**~**3**. They have same anionic $[\text{Fe}_6(\mu_6\text{-O})\text{Cl}_6(\text{tmp})_4]^{2-}$ core structures and different counter cations. The improved magnetic properties are in progress.

Supporting information is available at <http://www.wjhxxb.cn>

References:

- [1] Milway V A, Tuna F, Farrell A R, et al. *Angew. Chem. Int. Ed.*, **2013**,**52**:1949-1952
- [2] Mannini M, Pineider F, Danieli C, et al. *Nature*, **2010**,**468**: 417-421
- [3] Engelhardt L P, Muryn C A, Pritchard R G, et al. *Angew. Chem. Int. Ed.*, **2008**,**47**:924-927
- [4] Xiang S C, Hu S M, Sheng T L, et al. *J. Am. Chem. Soc.*, **2007**,**129**:15144-15146
- [5] Han S D, Song W C, Zhao J P, et al. *Chem. Commun.*, **2013**, **49**:871-873
- [6] ZHAO Su-Qin(赵素琴), GU Jin-Zhong(顾金忠). *Chinese J. Inorg. Chem.*(无机化学学报), **2016**,**32**(9):1611-1618
- [7] Seki H, Hosaka Y, Saito T, et al. *Angew. Chem. Int. Ed.*, **2016**,**55**:1360-1363
- [8] Fondo M, Doejo J, Garcia-Deibe A M, et al. *CrystEngComm*, **2016**,**18**:6673-6682
- [9] Zhang Y J, Liu T, Kanegawa S, et al. *J. Am. Chem. Soc.*, **2009**, **131**:7942-7943
- [10] Ohba M, Kaneko W, Kitagawa S, et al. *J. Am. Chem. Soc.*, **2008**,**130**:4475-4484
- [11] Numata Y H, Inoue K, Baranov N, et al. *J. Am. Chem. Soc.*, **2007**,**129**:9902-9909
- [12] Zheng Y Z, Tong M L, Xue W, et al. *Angew. Chem.*, **2007**, **119**:6188-6192
- [13] Tian J M, Li W L, Li B, et al. *Chem. Eur. J.*, **2013**,**19**:5097-5103
- [14] Wöhlert S, Boeckmann J, Wriedt M, et al. *Angew. Chem. Int. Ed.*, **2011**,**50**:6920-6923
- [15] Ouellette W, Prosvirin A V, Whitenack K, et al. *Angew. Chem. Int. Ed.*, **2009**,**48**:2140-2143
- [16] Mahata P, Natarajan S, Panissod P, et al. *J. Am. Chem. Soc.*, **2009**,**131**:10140-10150
- [17] Ting L X, Yi W X, Xin Z W, et al. *Adv. Mater.*, **2006**,**18**: 2852-2856
- [18] Folven E, Scholl A, Young A, et al. *Nano Lett.*, **2012**,**12**: 2386-2390
- [19] Pekala M, Wolff-Fabris F, Fagnard J F, et al. *J. Magn. Magn. Mater.*, **2013**,**335**:46-52
- [20] Zhao J P, Zhao R, Yang Q, et al. *Dalton Trans.*, **2012**,**41**: 4852-4858
- [21] Yoshida H, Yamaura J-i, Isobe M, et al. *Nat. Commun.*, **2012**,**3**:860-864
- [22] Kenneth R P, Masaki A. *Nat. Chem.*, **2011**,**3**:758-759
- [23] Aidoudi F H, Aldous D W, Goff R J, et al. *Nat. Chem.*, **2011**, **3**:801-806
- [24] Lennartson A, Bond A D, Piligkos S, et al. *Angew. Chem. Int. Ed.*, **2012**,**51**:11049-11052
- [25] Hoshino N, Iijima F, Newton G N, et al. *Nat. Chem.*, **2012**, **4**:921-926
- [26] Miller J S. *Chem. Soc. Rev.*, **2011**,**40**:3266-3296
- [27] Bi Y F, Wang X T, Liao W P, et al. *J. Am. Chem. Soc.*, **2009**,**131**:11650-11651
- [28] Sanudo E C, Font-Bardia M, Solans X, et al. *New J. Chem.*, **2011**,**35**:842-848
- [29] Kershaw Cook L J, Kulmaczewski R, Mohammed R, et al. *Angew. Chem. Int. Ed.*, **2016**,**55**:4327-4331
- [30] Li Z Y, Ohtsu H, Kojima T, et al. *Angew. Chem. Int. Ed.*, **2016**,**55**:5184-5189
- [31] Brechin E K. *Chem. Commun.*, **2005**:5141-5153
- [32] Yang F, Li B, Xu W, et al. *Inorg. Chem.*, **2012**,**51**:6813-6820
- [33] WU Xiao-Shuo(吴小说), WANG Peng-Fei(汪鹏飞), LU Peng-Peng(路朋朋), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2016**,**32**(9):1667-1675
- [34] Sheldrick G M. *SHELXS-97* and *SHELXL-97*, University of Göttingen, Germany, **1997**.
- [35] Batchelor L J, Shaw R, Markey S J, et al. *Chem. Eur. J.*, **2010**,**16**:5554-5557
- [36] Jiang G Q, Bai J F, Xing H, et al. *Cryst. Growth Des.*, **2006**, **6**:1264-1266
- [37] Dobson K D, McQuillan A J. *Spectrochim. Acta Part A*, **1999**, **55**:1395-1405
- [38] Sun Z, Gantzel P K, Hendrickson D N. *Inorg. Chem.*, **1996**, **35**:6640-6641
- [39] Liu W, Thorp H H. *Inorg. Chem.*, **1993**,**32**:4102-4105
- [40] Song J L, Yi F Y, Mao J G. *Cryst. Growth Des.*, **2009**,**9**: 3273-3277