

酸性离子液调控下咪唑硫酸四铁簇合物和铁-DMSO 配合物的合成

罗倩倩¹ 林和春^{*1} 罗春花¹ 张媛媛¹ 彭 晖^{1,2}

(¹ 华东师范大学信息学院, 极化材料与器件教育部重点实验室, 上海 200141)

(² 山西大学光学协作创新中心, 太原 030006)

摘要: FeCl₂ 与酸性离子液在乙醇中反应制备得到咪唑硫酸铁簇合物 [HMIM]₂[Fe₂O(SO₄)₃(DMSO)₂]·0.5DMSO (**1**) 和 [HPIM]₄[Fe₄O₂(SO₄)₆(DMSO)₄]·2MeCN (**2**), 该类簇合物为四核铁簇 Fe₄(O)₂(SO₄)₆(DMSO)₄ 结构, 4 个 Fe 原子通过中心 μ₃-O 桥、硫酸根上的 μ₂-O 和 μ₃-O 桥连接, 形成共平面结构, 中间的四核铁簇为 -4 价, 4 个质子化的咪唑正离子起电荷平衡作用。该簇合物的晶体结构属于三斜晶系中的 *P* $\bar{1}$ 空间群。变温磁化率测试表明该簇合物具有强的反铁磁性。但在类似的反应条件下, FeCl₃ 在酸性离子液反应没有得到类似的簇合物, 而是得到 DMSO 配合物 [FeCl₂(DMSO)₄][EtSO₄]·DMSO (**3**)。

关键词: 铁簇合物; 开放框架; 酸性离子液; 反铁磁性

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Syntheses of Imidazole Template Fe₄ Sulfate Clusters and Iron-DMSO Complex Mediated by Brønsted Acid Ionic Liquids

LUO Qian-Qian¹ LIN He-Chun^{*1} LUO Chun-Hua¹ ZHANG Yuan-Yuan¹ PENG Hui^{1,2}

(¹Key Laboratory of Polar Materials and Devices, Ministry of Education, East China Normal University, Shanghai 200141, China)

(²Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan 030006, China)

Abstract: Imidazole template iron sulfate clusters, [HMIM]₂[Fe₂O(SO₄)₃(DMSO)₂]·0.5DMSO (**1**) and [HPIM]₄[Fe₄O₂(SO₄)₆(DMSO)₄]·2MeCN (**2**), were synthesized via the reaction of FeCl₂ with Brønsted acidic ionic liquid [HRIM][HSO₄] using ethanol as solvent. The clusters crystallize in triclinic with a space group *P* $\bar{1}$. The core contains 4 iron atoms, which are coplanar connected by the central μ₃-O bridge, μ₂-O and μ₃-O bridge of SO₄ groups. Protonated imidazoliums are the counter cations for the balance of charges of the core. Variable temperature magnetic susceptibility measurements of the Fe₄ sulfate clusters reveal weak antiferromagnetic exchange interactions between the metal centers. In contrast, the reaction of FeCl₃ under the similar experimental conditions didn't produce the similar cluster structure, whereas iron-DMSO complex [FeCl₂(DMSO)₄][EtSO₄]·DMSO (**3**) was obtained. CCDC: 1495092, **1**; 1495093, **2**; 1495086, **3**.

Keywords: polynuclear ferric cluster; open-framework; brønsted acidic ionic liquid, antiferromagnetic

Polynuclear ferric complexes have attracted continuing interest mainly due to their aesthetically fascinating structures and unique properties. They may represent biomimetic models for the iron oxide/

hydroxide core of the iron storage protein ferritin^[1-4], and can sometimes exhibit unusual and occasionally novel magnetic properties, with some of them even being examples of single molecule magnets (SMMs)^[5-13].

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*通信联系人。E-mail: hclin@ee.ecnu.edu.cn

Polynuclear ferric complexes with primarily oxygen and nitrogen based ligation have been designed and prepared including Fe_4 , Fe_6 , Fe_7 , Fe_8 , Fe_{11} , Fe_{14} , Fe_{12} , Fe_{16} , Fe_{19} , Fe_{22} and others^[13-29].

The open-framework sulfates combining transition metals and organic groups have attracted a great interest due to their fascinating structure diversities and potential applications as functional materials^[30-32]. Several organically template iron sulphates^[33-40] directing by diamines or 1,4-diazabicyclo[2.2.2]octane have been reported with linear and layered structures. In our recent work, we have reported the interreaction of metal salts with ionic liquids to find the anion exchange reactions of BF_4^- or PF_6^- based ionic liquids with titanium or zirconium alkoxide to form $[\text{Ti}(\text{OH})_6]^{2-}$ or $[\text{Zr}(\text{OH})_6]^{2-}$ complexes^[41]. Furthermore, imidazole template metal sulfates with zero dimensional monomeric structure or one dimensional metal-organic frameworks were synthesized (HMIM=protonated 1-methylimidazolium)^[42]. In this article, we investigated the reactions of FeCl_2 or FeCl_3 with Brnsted acidic ionic liquids. Two imidazole template Fe_4 sulfate clusters with interesting magnetic properties were achieved for the reaction of FeCl_2 . In contrast, the iron DMSO complex $[\text{FeCl}_2(\text{DMSO})_4][\text{EtSO}_4] \cdot \text{DMSO}$ was obtained with the reaction of FeCl_3 under the similar reaction conditions.

1 Experimental

1.1 Materials and methods

All reagents were commercially available and used without further purification. Elemental analyses (C, H, N) were carried out with a Vario EL III elemental analyzer. FTIR spectra measurements were performed on Nexus 670 IR spectrometer by using KBr pellets in the region of 4 000~400 cm^{-1} . The variable-temperature magnetic susceptibility data were recorded on a Quantum Design PPMS-9 magnetometry in a field of 0.1 T and 3.0~300.0 K. TGA/DTA curves were obtained by using STA449 F3 Jupiter simultaneous thermo-analyzer in N_2 at a heating rate of 10 $\text{K} \cdot \text{min}^{-1}$ from room temperature to 800 $^\circ\text{C}$.

Single-crystal XRD data of the crystals were

collected with a Bruker APEX-II CCD diffractometer with graphite-monochromatic $\text{Mo } K\alpha$ radiation ($\lambda = 0.071\,073\,\text{nm}$). All the structures were solved by direct methods (SHELXS-97 program^[43]) and refined by full-matrix least-squares on F^2 (SHELXL-97 program^[43]) using Olex2 software^[44]. Hydrogen atoms were added geometrically and refined using the riding mode.

CCDC: 1495092, **1**; 1495093, **2**; 1495086, **3**.

1.2 Syntheses of the complexes

Synthesis of $[\text{HMIM}]_2[\text{Fe}_2\text{O}(\text{SO}_4)_3(\text{DMSO})_2] \cdot 0.5\text{DMSO}$ (**1**). $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.50 g, 2.5 mmol) was added to a solution of $[\text{HMIM}][\text{HSO}_4]$ (0.90 g, 5 mmol) in ethanol (20 mL). Green precipitates were generated slowly under the stirring. The reaction mixture was refluxed for 4 h. After cooling to the room temperature, ethanol was removed by rotary evaporation to give rise to dark brown solids. The obtained solids were dissolved in DMSO (dimethyl sulfoxide) at 90 $^\circ\text{C}$ and filtered. The clear solution in a vessel was kept under MeCN atmosphere to grow crystals. Dark brown flake crystals suitable for SXRD analysis were collected after 2 days. Anal. Calcd. for $\text{C}_{13}\text{H}_{29}\text{Fe}_2\text{N}_4\text{O}_{15.55}\text{S}_{5.5}(\%)$: C, 20.06; H, 3.76; N, 7.20. Found(%): C, 20.66; H, 4.34; N, 8.01. Main IR bands(cm^{-1}): 3 423 (s), 3 416 (s), 2 963 (m), 1 636 (s), 1 585 (s), 1 551 (w), 1 420 (w), 1 280 (w), 1 224 (s), 1 139 (s), 1 076 (s), 995 (s), 941 (m), 832 (w), 761 (w), 623 (m), 601 (m), 475 (w). The product has been identified with single-crystal X-ray diffraction.

Synthesis of $[\text{HPIM}]_4[\text{Fe}_4\text{O}_2(\text{SO}_4)_6(\text{DMSO})_4] \cdot 2\text{MeCN}$ (**2**). The synthesis procedure was similar to **1**. The MeCN solvate molecules probably escaped from crystals during drying under high vacuum. Elemental analysis, TGA and FTIR were based on formula $(\text{HPIM})_4\text{Fe}_4\text{O}_2(\text{SO}_4)_6(\text{DMSO})_4$. Anal. Calcd. for $\text{C}_{32}\text{H}_{68}\text{Fe}_4\text{N}_8\text{O}_{30}\text{S}_{10}(\%)$: C, 24.19; H, 4.31; N, 7.05. Found(%): C, 23.91; H, 4.64; N, 7.07. Main IR bands (cm^{-1}): 3 430 (s), 2 970 (m), 1 636 (m), 1 580 (m), 1 547 (w), 1 402 (w), 1 221 (s), 1 139 (s), 1 080 (m), 990 (m), 946 (m), 832 (w), 599 (w), 542 (m), 478 (w). The product has been identified with single-crystal X-ray diffraction.

Synthesis of $[\text{FeCl}_2(\text{DMSO})_4][\text{EtSO}_4] \cdot \text{DMSO}$ (**3**). FeCl_3 (0.41 g, 2.5 mmol) was added to the mixed

solution of [HMIM][HSO₄] (0.90 g, 5 mmol) and ethanol (20 mL) under magnetic stirring and refluxed (90 °C) for 4 h. The black mixture gradually turned into brown during the reaction. The solvent was removed by rotary evaporation to generate a dark brown liquid. The liquid was resolved in DMSO and filtered to grow crystals in the refrigerator. Yellow flake crystals were collected from the solution after a few days. Anal. Calcd. for C₁₀H₂₉Cl₂FeO₈S₅(%): C, 21.28; H, 5.18. Found (%): C, 20.91; H, 5.52. Main IR bands (cm⁻¹): 3 434 (s), 3 114 (s), 2 834(s), 2 517 (m), 2 135 (w), 1 794 (w), 1 635 (s), 1 579 (m), 1 541 (s), 1 400 (w), 1 239 (m), 940 (w), 775 (w), 688 (w), 582 (w), 419 (s), 400 (s). The product has been identified with single-crystal X-ray diffraction.

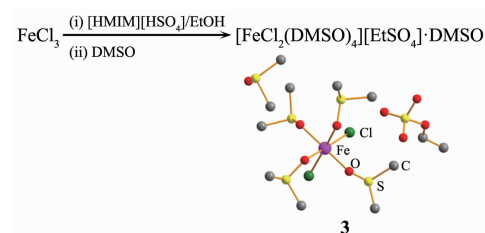
2 Results and discussion

2.1 Synthesis

Green precipitates were first generated within a few minutes after the addition of FeCl₂·4H₂O to an ethanol solution of [HMIM][HSO₄]. After removing ethanol by rotary evaporation, the colour of precipitates changed from green to dark brown. The obtained solid did not dissolve in most common organic solvent, such as acetone, acetonitrile, DMF or THF, but it did dissolve in DMSO to produce a clear brown solution. The solution was kept under MeCN atmosphere to grow single crystals. Finally, dark brown flake crystals were obtained, which were identified as [HMIM]₂[Fe₂O(SO₄)₃(DMSO)₂]·0.5DMSO (**1**) by the single X-ray diffraction method (Scheme 1). It is compelling to find that Fe(II) has been oxidized to

Fe(III) to produce an imidazole template Fe₄ sulfate cluster. Under the similar reaction conditions, [HPIM]₄[Fe₄O₂(SO₄)₆(DMSO)₄]·2MeCN (**2**) was obtained as well.

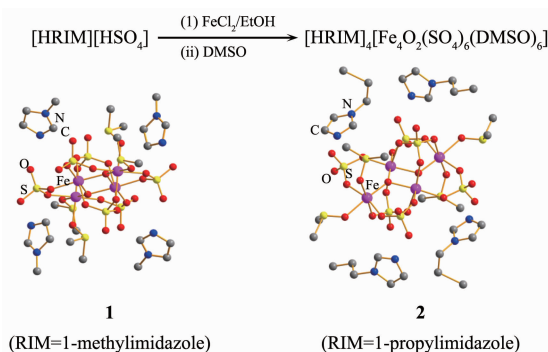
To see whether FeCl₃ can also carry out the similar reaction, we underwent the similar reaction of FeCl₃ with [HMIM][HSO₄] in ethanol. Anhydrous FeCl₃ was added to the solution of [HMIM][HSO₄] in ethanol. The black mixture gradually turned into brown during the reaction. The solvent was removed by rotary evaporation to generate a dark brown liquid. This phenomenon differed from the reaction of FeCl₂, where brown solids were obtained. The liquid was then resolved in DMSO to grow crystals. Imidazole template complex was not formed, however, yellow flake crystals [FeCl₂(DMSO)₄][EtSO₄]·DMSO (**3**) were achieved, where four DMSO molecules coordinate to one iron atom, and one Cl⁻ is substituted by EtSO₄⁻. EtSO₄⁻ probably was generated by the reaction of EtOH with HSO₄⁻ under this special reaction condition^[45]. Cations [FeCl₂(DMSO)₄]⁺ were balanced by the EtSO₄⁻ anions.



Scheme 2 Formation of complex **3** mediated by [HMIM][HSO₄]

2.2 Crystal structure

Table 1 summarizes the crystallographic data for complexes **1**~**3**. Complexes **1** and **2** are the products of the reactions of [HRIM][HSO₄] with FeCl₂ in ethanol, which crystallize in triclinic with a space group *P* $\bar{1}$. They have the similar structural fragment and contain the tetranuclear [Fe₄(O)₂(SO₄)₆(DMSO)₄] core template by imidazole derivatives. The Fe₄ core structure is shown in Fig.1. The core contains four Fe atoms, two μ_3 -O, four μ_2 -SO₄, two μ_3 -SO₄, and four DMSO molecules. Four Fe atoms are coplanar connected by the central μ_3 -O bridge and μ_2 -O and μ_3 -O bridge of SO₄ groups. The μ_3 -oxo-bridged [Fe₃(μ_3 -O)]₄ fragment presents as a pyramidal geometry. Two SO₄



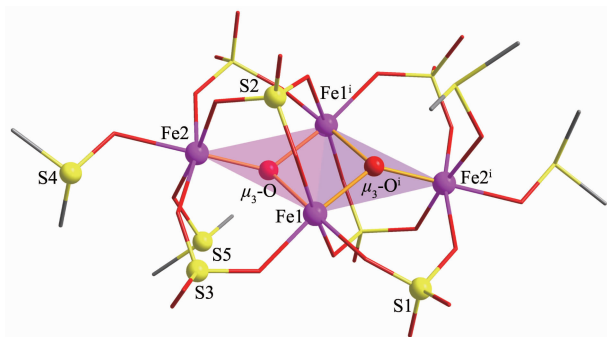
Scheme 1 Reactions of FeCl₂ with [HRIM][HSO₄] in ethanol

Table 1 Crystal data and details of structural determination for 1~3

Complex	1	2	3
Formula	C ₁₃ H ₂₉ Fe ₂ N ₄ O _{15.55} S _{5.5}	C ₃₆ H ₇₄ Fe ₄ N ₁₀ O ₃₀ S ₁₀	C ₁₂ H ₃₅ Cl ₂ FeO ₉ S ₆
Formula weight	777.43	1 671.15	642.57
Temperature / K	149.99	293.0	173.0
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> / nm	1.145 43(9)	1.183 46(4)	0.902 2(3)
<i>b</i> / nm	1.233 65(10)	1.293 31(4)	1.204 7(4)
<i>c</i> / nm	1.278 07(10)	1.367 12(4)	1.359 3(5)
α / (°)	105.002(3)	64.862 0(10)	84.34(2)
β / (°)	101.184(3)	71.101 0(10)	71.31(2)
γ / (°)	110.623(3)	70.121 0(10)	77.811(17)
<i>V</i> / nm ³	1.549 3(2)	1.741 40(10)	1.367 2(8)
<i>Z</i>	2	1	2
<i>D_c</i> / (g·cm ⁻³)	1.666	1.594	1.561
μ / mm ⁻¹	11.609	10.097	10.845
<i>F</i> (000)	798.0	864.0	670.0
Data, restraint, parameter	4 760, 65, 398	6 326, 1, 433	5 018, 0, 290
GOF on <i>F</i> ²	1.191	1.051	1.044
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.091 8, 0.234 4	0.070 3, 0.196 5	0.052 4, 0.132 6
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.107 8, 0.249 6	0.075 9, 0.200 8	0.055 5, 0.135 2

groups act as tridentate bridging ligands coordinated to Fe atoms on the two [Fe₃(μ₃-O)]₄ fragments, and the other four SO₄ groups engage in O,Oⁱ-bridging within the tetracenter. DMSO groups act as mono-dentate ligands coordinated to Fe2 and Fe2ⁱ atoms. In the asymmetric unit of **1**, protonated imidazoliums are the counter cations for the balance of charges of the Fe(III) core [Fe₂O(SO₄)₃(DMSO)]²⁻ anion.

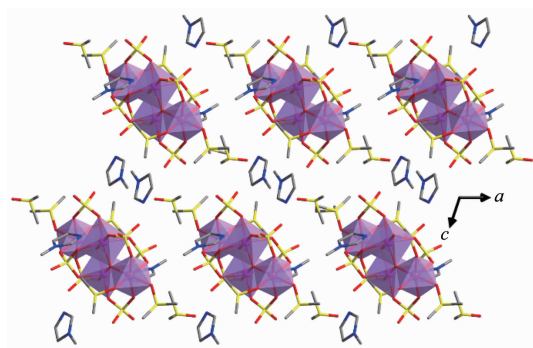
The selected bond distances and angles are listed in Table S1~S3. For complex **1**, the distances of Fe1-(μ₃-O) and Fe1-(μ₃-O)ⁱ equal to 0.195 0(5) nm and



Fe, pink; C, grey; N, blue; O, red; S, yellow; Symmetry code: ⁱ -*x*, 1-*y*, 1-*z* for **1**; ⁱ 1-*x*, 1-*y*, 1-*z* for **2**

Fig.1 Structure fragment of the coordination clusters

0.196 0(4) nm, respectively, while Fe2-(μ₃-O) distances are slight shorter with 0.186 9(5) nm. Fe1-(μ₃-O)-Fe1ⁱ angles (91.9(2)°) are almost equal to (μ₃-O)-Fe1-(μ₃-O)ⁱ angles (88.1(2)°). They are close to the right angle so that the four atoms Fe1, Fe1ⁱ, and two (μ₃-O) atoms form a nearly perfect square face which exerts a *trans* to Fe2 and Fe2ⁱ with respect to the [Fe₂O₂] plane. Four Fe atoms are coplanar to form a rhombic plane, where Fe1-Fe2-Fe1ⁱ and Fe2-Fe1-Fe2ⁱ angles are 48.243(30)° and 131.757(44)°, respectively. It is different to the oxygen-based ligation Fe₄ clusters^[25-26,46], where cubic plane is often seen. Two Fe2-O_{DMSO} distances are separately 0.204 6(5) and 0.211 0(6) nm. Four Fe1-O_{sulfate} distances vary from 0.198 0(5) to 0.208 8(5) nm while three Fe2-O_{sulfate} distances fall in the range of 0.200 5(5)~0.203 9(5) nm. The Fe1-Fe1ⁱ distance (0.281 0(2) nm) is much shorter than the Fe1-Fe2 distance (0.346 31(11) nm). The coordinated DMSO groups are partly disordered. [HMIM]⁺ cations lay in the lattice without any interaction with the main structure as shown in the crystal packing view of complex **1** (Fig.3). Complex **2** has the almost same

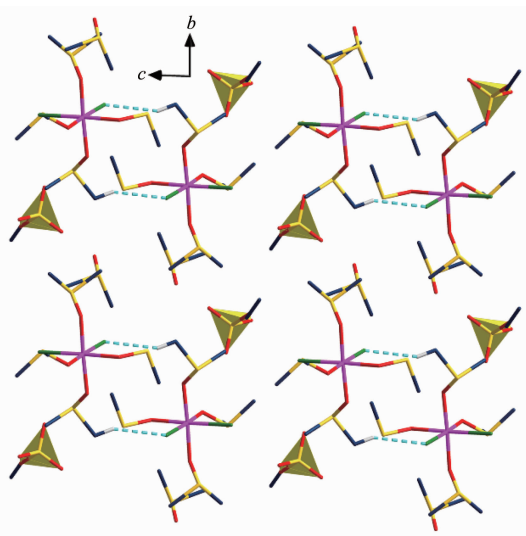


H atoms are omitted for clarity; Fe, pink; C, grey; N, blue; O, red; S, yellow

Fig.2 Perspective packing view of the crystal structure of complex **1** along *b* axis

core structure parameters with complex **1** except the variation of alkyl groups on imidazole rings and existing different solvent molecules in the lattice as shown in Table S2. The crystal packing views of complexes **2** are presented in Fig.S1.

The reaction of FeCl_3 in $[\text{HMIM}][\text{HSO}_4]$ led to the formation of $[\text{FeCl}_2(\text{DMSO})_4][\text{EtSO}_4] \cdot \text{DMSO}$ (**3**). Complex **3** crystallizes in triclinic with a space group $P\bar{1}$. Fe atom is bonded to two chlorine atoms and four oxygen atoms from four DMSO leading to a distorted octahedral geometry. Distances of Fe-O bonds fall in the range of 0.200 3(3)~0.202 4(3) nm. Fe-Cl bond lengths are ~0.235 nm. DMSO solvent molecules are



H atoms are omitted for clarity; Fe, pink; C, grey; N, blue; O, red; S, yellow; Cl, green

Fig.3 View of the crystal structure of complex **3** along *c* axis showing hydrogen bonds $\text{C-H}\cdots\text{Cl}$

disordered. Anion $[\text{EtSO}_4]^-$ resides in the side of $[\text{FeCl}_2(\text{DMSO})_4]^+$. $[\text{FeCl}_2(\text{DMSO})_4]^+$ is connected to each other with $\text{C-H}\cdots\text{Cl}$ with 0.283 nm length (Fig.3).

2.3 Thermal behaviour

The TGA curves for the obtained complexes **1~3** are shown in Fig.4. The decomposition of complex **1** undergoes in three steps. DMSO groups are firstly decomposed in the range of 28~300 °C (Obsd. 62.3%, Calcd. 62.1%). The second weight loss process in the 300~540 °C range is ascribed to the releasing of four $[\text{HMIM}]^+$ and three SO_3 (Obsd. 23.3%, Calcd. 22.5%). With the increasing of the temperature, the complex is further decomposed and the total weight loss observed is 81.1%. The remaining weight of 18.9% is assigned as Fe_2O_3 (Calcd. 20.4%). For complex **2**, free solvent molecules are firstly lost in the range of 28~300 °C, and then, four imidazonium cations and four SO_4^{2-} are further decomposed in the range of 400~700 °C to give rise to the remaining weight of Fe_2O_3 . For complex **3**, there is a dramatically weight loss in the range of 28~190 °C, which is attributed to the losses of four DMSO molecules (Obsd. 50.8%, Calcd. 51.2%). The second weight loss process occurring in the range of 189~316 °C is related to the losses of chloride anions and one DMSO molecule. The third stage in the 316~507 °C is due to the loss of anion $[\text{EtSO}_4]^-$.

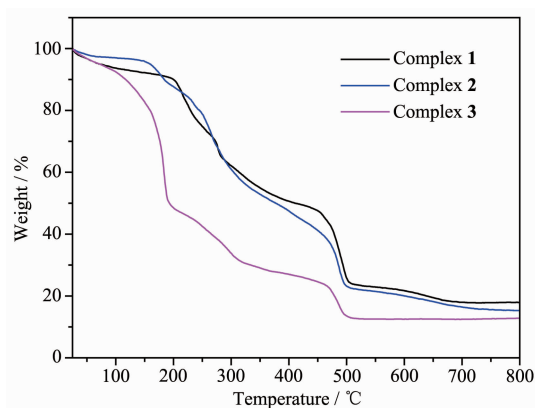


Fig.4 TGA curves for complexes **1~3**

2.4 Magnetic analysis

Molar magnetic susceptibility (χ_M) data were collected on powered polycrystalline samples of **1** and **2** in a 0.1 T field in the 3.0~300 K range. The data of **1** and **2** are depicted as $\chi_M T$ versus *T* in Fig.5. As

shown in Fig.5, $\chi_M T$ monotonously decreases with decreasing temperature from $2.15 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ (for **1**) and $3.22 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ (for **2**) at 300 K to $0.13 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ (for **1**) and $0.33 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ (for **2**) at 3 K. The 300 K values are much less than the spin-only ($g=2.0$) value of $17.5 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ for four non-interacting Fe(III) ions, indicating the presence of strong antiferromagnetic exchange interactions with the Fe_4 complexes, leading to a singlet ($S=0$) ground state. This behaviour is analogous to that of other Fe_4 clusters with primarily oxygen-based ligand^[25-26,46].

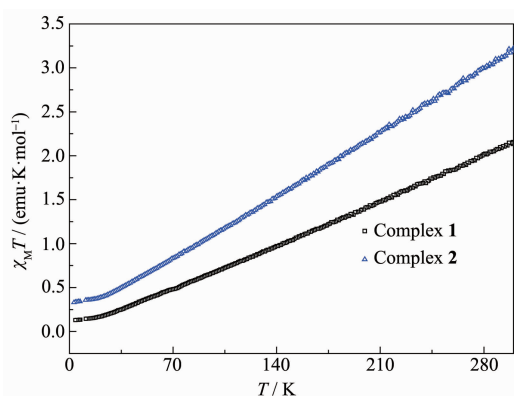


Fig.5 Plots of $\chi_M T$ vs T for complexes **1** and **2**

3 Conclusions

In summary, imidazole template Fe_4 sulfate clusters were synthesized via the reactions of FeCl_2 with Brnsted acidic ionic liquids $[\text{HRIM}][\text{HSO}_4]$ with ethanol as solvent. In contrast, the reaction of FeCl_3 under the similar reaction conditions did not lead to the similar cluster structure, and the imidazole free iron complex $[\text{FeCl}_2(\text{DMSO})_4][\text{EtSO}_4] \cdot \text{DMSO}$ (**3**) was produced. The clusters contain the tetranuclear $[\text{Fe}_4(\mu_3\text{-O})_2(\mu_2\text{-SO}_4)_6(\text{DMSO})_4]$ core, and protonated imidazoliums are the counter cations for the balance of charges of the core. Variable temperature magnetic susceptibility measurements of the Fe_4 sulfate clusters reveal that the complexes possess strong antiferromagnetic exchange interactions between the metal centres.

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

References:

- [1] Nair V S, Hagen K S. *Inorg. Chem.*, **1992**,**31**:4048-4050
- [2] Taft K L, Papaefthymiou G C, Lippard S J. *Inorg. Chem.*, **1994**,**33**:1510-1520
- [3] Frank P, DeTomaso A, Hedman B, et al. *Inorg. Chem.*, **2006**, **45**:3920-3931
- [4] Taft K, Papaefthymiou G, Lippard S. *Science*, **1993**,**259**:1302-1305
- [5] Gomez-Coca S, Ruiz E, Kortus J. *Chem. Commun.*, **2009**: 4363-4365
- [6] Ruiz E, Cano J, Alvarez S. *Chem. Eur. J.*, **2005**,**11**:4767-4771
- [7] Petukhov K, Bahr S, Wernsdorfer W, et al. *Phys. Rev. B*, **2007**,**75**:064408
- [8] Benelli C, Cano J, Journaux Y, et al. *Inorg. Chem.*, **2001**,**40**: 188-189
- [9] Schlegel C, Slagereen J, Manoli M, et al. *Polyhedron*, **2009**, **28**:1834-1837
- [10] Zhu Y Y, Guo X, Cui C, et al. *Chem. Commun.*, **2011**,**47**: 8049-8051
- [11] Rigamonti L, Piccioli M, Malavolti L, et al. *Inorg. Chem.*, **2013**,**52**:5897-5905
- [12] Jeon I R, Park J G, Xiao D J, et al. *J. Am. Chem. Soc.*, **2013**,**135**:16845-16848
- [13] Nachtigall O, Kusserow M, Clérac R, et al. *Angew. Chem. Int. Ed.*, **2015**,**54**:10361-10364
- [14] Koumoussi E S, Routzomani A, Nguyen T N, et al. *Inorg. Chem.*, **2013**,**52**:1176-1178
- [15] Bagai R, Daniels M R, Abboud K A, et al. *Inorg. Chem.*, **2008**,**47**:3318-3327
- [16] Alborés P, Rentschler E. *Inorg. Chem.*, **2008**,**47**:7960-7962
- [17] Stamatatos T C, Boudalis A K, Sanakis Y, et al. *Inorg. Chem.*, **2006**,**45**:7372-7381
- [18] Casey C P, Guan H. *J. Am. Chem. Soc.*, **2009**,**131**:2499-2507
- [19] Jones L F, Low D M, Helliwell M, et al. *Polyhedron*, **2006**, **25**:325-333
- [20] Ferguson A, Thomas L H, Murrie M. *Polyhedron*, **2013**,**52**: 227-233
- [21] Ferguson A, McGregor J, Brechin E K, et al. *Dalton Trans.*, **2009**:9395-9397
- [22] Masello A, Sanakis Y, Boudalis A K, et al. *Inorg. Chem.*, **2011**,**50**:5646-5654
- [23] Rajaraman G, Cano J, Brechin E K, et al. *Chem. Commun.*, **2004**:1476-1477
- [24] Mitchell K J, Abboud K A, Christou G. *Inorg. Chem.*, **2016**, **55**:6597-6608

- [25]Taguchi T, Stamatatos T C, Abboud K A, et al. *Inorg. Chem.*, **2008**,**47**:4095-4108
- [26]Mulyana Y, Nafady A, Mukherjee A, et al. *Inorg. Chem.*, **2009**,**48**:7765-7781
- [27]Murali M, Nayak S, Costa J S, et al. *Inorg. Chem.*, **2010**,**49**:2427-2434
- [28]TIAN Ju-Mei(田菊梅), CUI Zheng(崔正), ZHANG Jing-Ping(张景萍). *Chinese J. Inorg. Chem.*(无机化学学报), **2017**,**33**(9):1625-1630
- [29]WANG Ming(汪明), PAN Qun-Hui(潘群慧), SHEN Tao(沈涛), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2005**,**21**(9):1296-1300
- [30]Choudhury A, Krishnamoorthy J, Rao C N R. *Chem. Commun.*, **2001**:2610-2611
- [31]MasPOCH D, Ruiz-Molina D, Veciana J. *Chem. Soc. Rev.*, **2007**,**36**:770-818
- [32]Natarajan S, Mandal S. *Angew. Chem. Int. Ed.*, **2008**,**47**:4798-4828
- [33]Yahyaoui S, Rekik W, Nali H, et al. *J. Solid State Chem.*, **2007**,**180**:3560-3570
- [34]Behera J N, Rao C N R. *Chem. Eur. J.*, **2006**,**1**:742-750
- [35]Paul G, Choudhury A, Sampathkumaran E V, et al. *Angew. Chem. Int. Ed.*, **2002**,**41**:4297-4300
- [36]Behera J N, Rao C N R. *Inorg. Chem.*, **2006**,**45**:9475-9479
- [37]Fu Y, Xu Z, Ren J, et al. *Cryst. Growth Des.*, **2007**,**7**:1198-1204
- [38]Dan M. *J. Mol. Struct.*, **2004**,**706**:127-131
- [39]Paul G, Choudhury A, Rao C N R. *Chem. Mater.*, **2003**,**15**:1174-1180
- [40]Calligaris M. *Coord. Chem. Rev.*, **2004**,**248**:351-375
- [41]Lin H, de Oliveira P W, Huch V, et al. *Chem. Mater.*, **2010**,**22**:6518-6523
- [42]Luo Q Q, Lin H C, Zhang Y Y, et al. *Inorg. Chim. Acta*, **2016**,**447**:32-37
- [43]Sheldrick G M. *Acta Crystallogr. Sect. A: Found. Crystallogr.*, **2008**,**A64**:112-122
- [44]Dolomanov O V, Bourhis L J, Gildea R J, et al. *J. Appl. Crystallogr.*, **2009**,**42**:339-341
- [45]Evans P N, Albertson J M. *J. Am. Chem. Soc.*, **1917**,**39**:456-461
- [46]Murali M, Nayak S, Costa J S, et al. *Inorg. Chem.*, **2010**,**49**:2427-2434