

一个具有温度补偿磁行为的分子基亚铁磁体:混合价甲酸铁铵

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摘要: 通过溶剂热的方法合成了一个具有 nia 拓扑结构混合价的甲酸铁铵盐,并对其进行了单晶结构和磁性表征,该化合物不仅在 $T_N=37.2$ K 以下显示亚铁磁体的性质,还在大约 28 K 出现温度补偿磁性行为。本文首次用分子场理论对该磁体的温度补偿行为和磁结构相关性进行了详细的讨论与分析。

关键词: 亚铁磁体; 甲酸配合物; 铁; 温度补偿

中图分类号: O614.81+1

文献标识码: A

文章编号: 1001-4861(2010)03-0385-06

Mixed Valence Iron Formate $\{[\text{NH}_4][\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CHOO})_6]\}_\infty$: A Molecule-Based Ferrimagnet Showing Temperature Compensation Behavior

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Abstract: A mixed valence iron formate $\{[\text{NH}_4][\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CHOO})_6]\}_\infty$ (**1**) with nia topology was prepared under solvothermal condition and structurally characterized by X-ray single crystal analysis. The results show that the title compound exhibits not only the ferrimagnetic nature with $T_N=37.2$ K, but also magnetization sign inversion at the so-called compensation temperature ~ 28 K. The ferrimagnetic properties with temperature compensation behavior corresponding to definite single crystal structure are, for the first time, discussed in detail by molecular field theory. CCDC: 725225.

Key words: ferrimagnet; formate complex; iron; temperature compensation

0 Introduction

Transition metal formates have attracted extensive attentions^[1-5], not only owing to the interest for discovery of novel metal-organic frameworks (MOFs)^[6-7], but also

to the smallest carboxylate bridges effectively mediating the magnetic coupling between the metal ions. Thereby, synthesis of versatile metal formate complexes is of great significance for the fundamental magnetic study and the development in new functional magnetic

收稿日期: 2010-01-15。收修改稿日期: 2009-01-20。

国家自然科学基金(No.20571013, 20771057, 20631030)、优秀博士论文作者专项资金(No.200733)和辽宁省教育厅基金(No.20060470)资助项目。

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materials^[2-4], for example porous magnet^[8].

Up to date, a large number of zero-, one-, two- and three-dimensional metal formate complexes have been reported^[1-6]. Even though the formate carboxylate are observed with various bridge modes^[5], the antiferromagnetic coupling is still found to prevail in the substances. Only in very few cases, ferromagnetic interaction is partially mediated by certain carboxylate groups that have given rise to magnetic ordering with remanent magnetization below the critical temperature^[3b,4a]. The ferrimagnetic behavior is observed frequently in formate compounds containing either different magnetic ions or only one type of magnetic ions but with different valence states or different crystallographic positions^[2]. And in some cases of the ferrimagnets, if a weak magnetic field (less than the field of coercivity) is applied, the total magnetization of a substance becomes zero and changes signs at a certain compensation temperature^[9] that may result in the compound functioning as a sensor (such as switch) in response to the temperature. The first metal formate observed with the temperature compensation behavior is $[\text{Ni}(\text{CHOO})_2 \cdot 2\text{H}_2\text{O}]_\infty$ ^[2], showing spin-canted magnetic properties. Here, we report in detail a mixed valence iron formate $\{[\text{NH}_4][\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CHOO})_6]\}_\infty$ (**1**) that behaves as a ferrimagnet below $T_N=37.2$ K and the magnetization sign inversion at a compensation temperature ~ 28 K. It should be noted that as we completed this paper writing, a research paper^[10] concerning with compound **1** was published but without any analysis on its complicated magnetic properties. To the best of our knowledge, there has been no detail discussion by molecular field theory on the ferrimagnet with temperature compensatoin behavior corresponding to definite single crystal structure.

1 Experimental

1.1 Materials and analyses

All reagents used were obtained from commerical sources without further purification. Magnetic measurements were performed on a Quantum Design MPMS XL-7 SQUID system for a crushed single crystal sample. The heat capacity was measured on PPMS. ⁵⁷Fe Mossbauer experiments were carried out by using a ⁵⁷Co/

Pd source on a constant-acceleration spectrometer. The transmission spectra were recorded at room temperature. The reported isomer shifts (IS) are relative to the centre of the α -Fe spectrum at room temperature^[11]. The Moss Winn3.0 programme was used to determine the Mössbauer parameters^[12].

1.2 Synthesis of 1

0.333 mmol (0.166 g) $[\text{Fe}^{\text{III}}_3\text{O}(\text{CHOO})_7 \cdot 2\text{H}_2\text{O}]$ ^[13] and 1 mmol (0.182 g) $[\text{Fe}(\text{CHOO})_2 \cdot 2\text{H}_2\text{O}]$ ^[14] were placed into a Teflon-lined autoclave (30 mL) and a mixed solvent containing 16 mL formic acid (88%) and *N,N*-dimethylformamide (DMF) was added. Then, the autoclave was sealed and heated at 130 °C for 24 hours. After cooling to room-temperature, the autoclave was opened and well crystallized black hexagonal prisms formulated as $[\text{NH}_4][\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CHOO})_6]$ (**1**) were separated by filtration and washed with formic acid (88%) (Yield: 52%). Elemental analysis: calcd. (%) for $\text{C}_6\text{H}_{10}\text{Fe}_2\text{O}_{12}\text{N}$: C 18.02, H 2.52, N 3.50; found: C 17.79, H 2.24, N 3.55.

1.3 Crystal structure determination

The data were collected on a Bruker SMART-APEX-II CCD diffractometer with Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). The structure was solved by direct methods and refined by full-matrix least-square techniques on F^2 using the SHELX program package. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were generated and included in the structure calculations with assigned isotropic thermal parameters but not refined. Crystal data: $\text{C}_6\text{H}_{10}\text{Fe}_2\text{O}_{12}\text{N}$, $M_r=399.84$, trigonal, space group $P\bar{3}1c$, $a=0.825\ 42(7)$ nm, $c=1.386\ 7(2)$ nm, $V=0.818\ 22(16)$ nm³, $Z=2$, $\rho_{\text{calcd}}=1.623$ g·cm⁻³, $F(000)=402$, μ (Mo $K\alpha$)= 1.825 mm⁻¹, $T=393$ K, 4 729 measured data, 698 unique, $R_{\text{int}}=0.025\ 3$, 622. $R_1=0.043\ 2$ for 622 observations of $I \geq 2\sigma(I)$, $wR_2=0.121\ 1$ for all data, GOF=1.083.

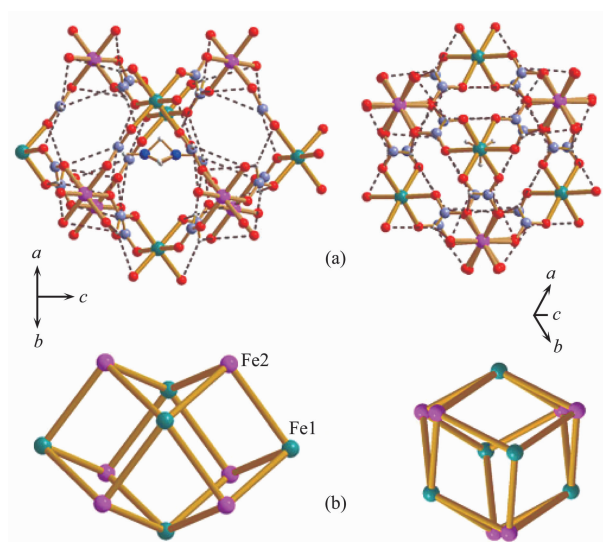
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2 Results and discussion

2.1 Structural description

Single crystal X-ray analysis reveals that compound **1** contains two unique iron atoms of different oxidation states (Fe1 and Fe2 correspond to Fe(II) and

Fe(III), respectively). They are six-coordinated with oxygen atoms (Fe(II)-O and Fe(III)-O bonds are 0.211 5 and 0.200 4 nm respectively) and are bridged by the anti-anti formate^[5] anions into a three-dimensional binodal 6-connected net of $(4^{12}, 6^3)$ $(4^9, 6^6)$ topology (nia topology) (Fig.1), in which the Fe(III) atoms site on the points of Schläfli symbol $(4^{12}, 6^3)$ while the Fe(II) atoms on the points of Schläfli symbol $(4^9, 6^6)$. Due to the ratio of Fe(II)/Fe(III)=1:1 in compound **1**, the binodal 6-connected net is, therefore, negative and charge-balanced with the ammonium cations that come from the hydrolysis of DMF molecules and reside in the 4^{12} -cages of the framework of **1** (Fig.1).



(a) Ball-and-stick diagram exhibiting the Formate intermolecular H···O bonds; (b) Topological view of the 4^9 -cage unit where the formic ligands are replaced by sticks

Ball colour representation: pink, Fe(III); green, Fe(II); red, O; indigo, C; blue, N; grey, H

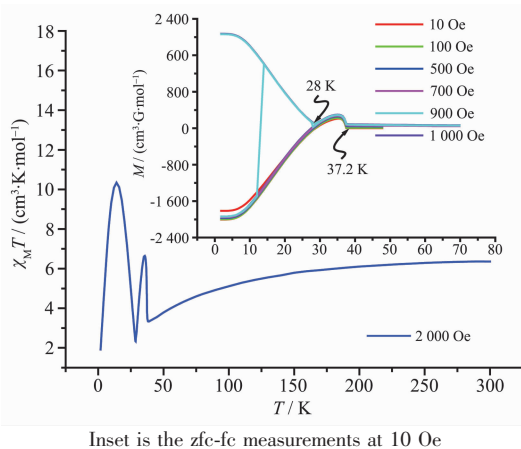
Fig.1 4^9 -cage unit of the nia-structural $[\text{NH}_4][\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CHOO})_6]_{\infty}$ (**1**)

The nia topology was primitively discovered in niccolite (NiAs) and is rarely found in other inorganic solids^[4c] and MOFs. The first discovered MOFs with the nia topology are iso-crystalline metal formates $[\text{dmenH}_2^{2+}][\text{M}_2(\text{HCOO})_6^{2-}]$ ($\text{M}=\text{Co}^{\text{II}}$ and Mn^{II} , $\text{dmenH}_2^{2+}=\text{N,N}'$ -dimethylethylenediammonium)^[4c] prepared by reaction of $\text{M}[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ with $[\text{dmenH}_2^{2+}][\text{CHOO}^-]_2$ where the $[\text{dmenH}_2^{2+}]$ was claimed as the template. Also as a metal formate with the nia topology, compound **1** is iso-structural, but not *iso*-crystalline, with the above-

mentioned metal formates (since the unit cell parameters and the charge-counter cations are different) and has stronger hydrogen-bonding interactions between oxygen and hydrogen atoms inter formate-ligands (OH distances within 0.264 ~0.286 nm). However, the hydrogen-bonding between the formate anions and the guest ammonium cations in compound **1** is not observed (therefore, NH_4^+ does not function as the template in **1**).

2.2 Magnetic property

The variable-temperature magnetic behaviour of compound **1** in 2 kOe shows that the susceptibility above 100 K obeys the Curie-Weiss law with $\chi_{\text{M}}T=6.36 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ (the effective moment, $\mu_{\text{eff}} \equiv (8\chi_{\text{M}}T)^{1/2}=7.13 \mu_{\text{B}}$) at 300 K. The obtained Curie constant, $C=7.26 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, is consistent with the theoretical value of $7.38 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ based on both high-spin Fe(II) and Fe(III) ions, and a negative Weiss constant, $\theta=-39.12 \text{ K}$, indicates a dominant antiferromagnetic coupling between iron ions. This result is agreeable with those of metal formate compounds with anti-anti formate bridges^[2,4,6,8]. However, the low-temperature susceptibility (Fig.2) shows great difference from those of metal formates reported in these literatures^[2,4,6,8]. Upon cooling, the $\chi_{\text{M}}T$ values slowly drop to $3.38 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at $\sim 37.2 \text{ K}$, then increase sharply to the first maximum of $6.72 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at $\sim 34.9 \text{ K}$, after that go abruptly down to a minimum at 28.00 K and then turn up, going abruptly to the maximum at $\sim 13.60 \text{ K}$. Finally, they decrease to $1.87 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 1.8 K . The first magnetic phase transition at $\sim 37.2 \text{ K}$ is indicative of the onset of a



Inset is the zfc-fc measurements at 10 Oe

Fig.2 Temperature dependence of magnetic properties of **1**

long-range spin ferrimagnetic ordering resulting from the antiferromagnetic coupling between the Fe(II) and Fe(III) ions. Support for this ferrimagnetic ordering T_N comes from the zero-field-cooling (zfc) and field-cooling (fc) magnetization (inset in Fig.2), the temperature dependencies of the in-phase, $\chi'(T)$, and out-of-phase, $\chi''(T)$ components of the AC susceptibility (Fig.3). The further specific heat measurements show a lambda-shape curve, the specific heat abrupt-increase upon cooling at around 37 K (Fig.4), that also indicate the long-range magnetic ordering being onset at this

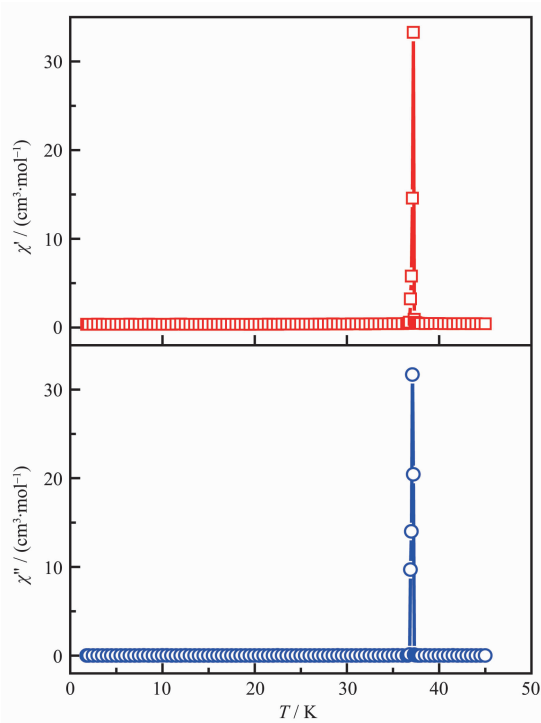


Fig.3 Plot of temperature dependence of AC susceptibility χ' (\square) and χ'' (\circ) obtained at $H_{dc}=0$ Oe, $H_{ac}=3$ Oe and $f=10$ Hz for $[\text{[NH}_4\text{][Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CHOO})_6\text{]}]$

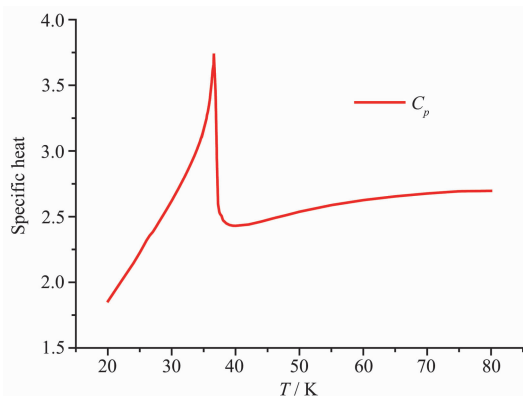


Fig.4 Specific heat measurement for compound **1**

temperature.

Below 28 K, compound **1** shows the very interesting magnetic phenomenon. For examining the nature of the possible second magnetic transition at ~ 28.00 K, the low-field magnetic properties of **1** were investigated. As shown in inset of Fig.2, zfc and fc magnetizations of **1** at 10, 100, 500 and 700 Oe are reversible and are increased from the negative to the positive passing through a zero value at ~ 28 K, a maximum at 35 K and a minimum at 37.2 K when warming up the system. It has been confirmed by AC measurements mentioned above that 37.2 K is the critical temperature T_N from ferrimagnetic ordering to paramagnetic phase. And all low-field magnetic behaviors indicate that compound **1** is a ferrimagnet with compensation temperature^[9], $T_{\text{com}}=28$ K. According to the structure of **1**, Fe(II) and Fe(III) ions are bridged by an *anti-anti* formate which mediates antiferromagnetic coupling^[13], further gives rise to two sublattices of Fe(II) and Fe(III) and forms two magnetic subsystems below spontaneous magnetic ordering temperature 37.2 K. The magnetizations of two anti-parallel spin systems compete with each other, leading to a complicated magnetic behavior, which depends on the magnitude of their S values and the magnetized extent of the spins. When their spin weights along external field are equal, the magnetization becomes zero at the compensation temperature.

Below 900 Oe, zfc and fc magnetizations are reversible, indicating that the competition of two sets of spins dominates the magnetic properties of **1** and the spins of Fe(II) phase is along the direction of the external field not strong enough to overcome the magnetic anisotropy of **1** for reversing the net spins, thus, to keep the magnetization negative below T_{com} . At 1 kOe and below T_{com} , zfc and fc magnetizations of **1** are nonreversible and enantimorphous on the ground of temperature axis. The positive fc magnetization value over a whole temperature range indicates that the field effect can dominate the net spins along the external field direction above 1 kOe. A jump on $M-T$ curve is observed with the external applied field of 900 Oe, indicating the critical field for overcoming the anisotropy and reversing the net spins.

The magnetic behaviour with temperature compensation can also be analyzed by molecular field theory with $S_{\text{Fe(II)}}=2$ and $S_{\text{Fe(III)}}=5/2$ ^[9d]. The molecular fields $H_{\text{Fe(II)}}$ and $H_{\text{Fe(III)}}$ acting on sublattice sites can be expressed as follows:

$$H_{\text{Fe(II)}}=H_0+nM_{\text{Fe(III)}}$$

$$H_{\text{Fe(III)}}=H_0+nM_{\text{Fe(II)}}$$

where H_0 is the external magnetic field, n is the molecular field coefficient relating to the coupling constant J , and $M_{\text{Fe(II)}}$ and $M_{\text{Fe(III)}}$ are the sublattice magnetization per unit volume for Fe(II) and Fe(III) sites, respectively. According to the treatment method reported by Ohkoshi^[9d], fitting M - T curve ($M=-M_{\text{Fe(III)}}+M_{\text{Fe(II)}}$) using a Brillouin function gives: $J=-4.4$ K, $S_{\text{Fe(II)}}=1.55$ and $S_{\text{Fe(III)}}=1.99$ as shown in Fig.5.

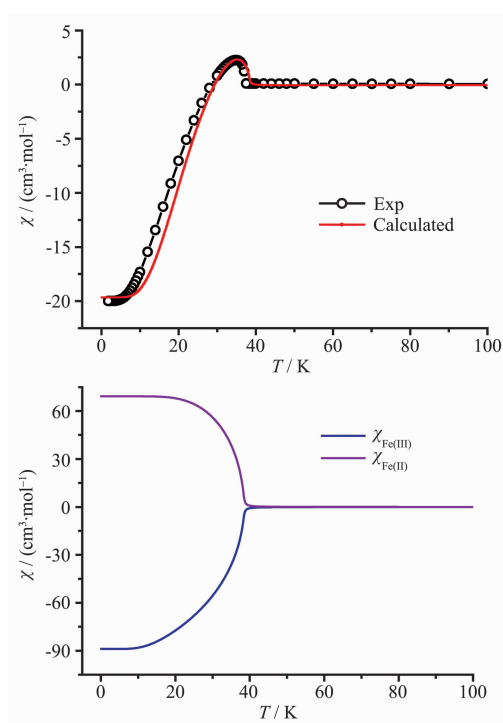
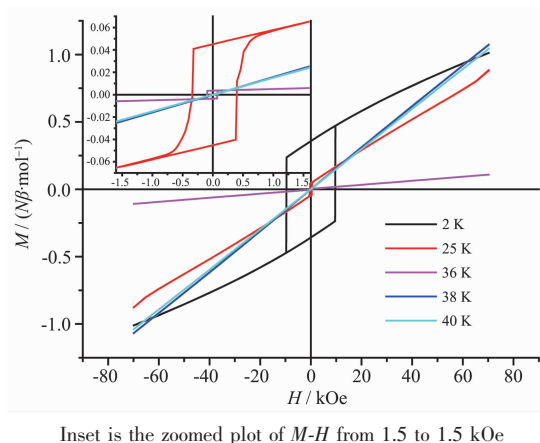


Fig.5 Calculated temperature dependence curves for two sublattices and total magnetization susceptibility for compound **1** based on molecular field theory at 100 Oe

Fig.6 illustrates a field dependence of the magnetizations for compound **1** at various temperatures. At 2 K, a hysteresis loop shows a remnant magnetization (M_r) of $0.36 N\beta \cdot \text{mol}^{-1}$ and a coercive field (H_c) of 9.7 kOe and the magnetization increases slowly under external field reaching $1.01 N\beta \cdot \text{mol}^{-1}$ in 70 kOe. This

observation testifies again the antiferromagnetic coupling between Fe(II) and Fe(III) ions. The linearly and sharply growing of the magnetization suggests that a strong magnetic anisotropy exists in compound **1** because the spins are difficultly magnetized along the hard direction even in high field. At 25 and 36 K, the hysteretic behaviour still could be observed with $M_r=0.045$ and $0.0036 N\beta \cdot \text{mol}^{-1}$, $H_c=0.34$ and 0.1 kOe, respectively. Above 38 K, hysteresis loop disappears and the magnetization is higher than those below this temperature at the same field, indicating that **1** has been in the paramagnetic phase. Thus, the magnetic investigations illustrated in Fig.6 have given a support for the magnetic phase transition between temperature 36 and 38 K.



Inset is the zoomed plot of M - H from 1.5 to 1.5 kOe
Fig.6 Field dependence of magnetization of compound **1** at various temperatures

⁵⁷Fe Mössbauer experiments were carried out for complex **1**. As shown in Fig.7, the spectrum consists of

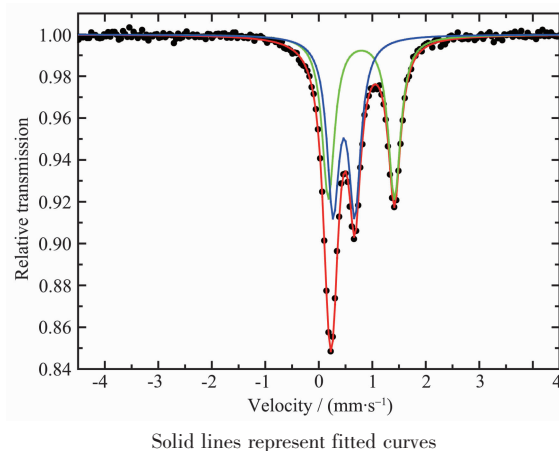


Fig.7 Mössbauer spectra of the compound **1** obtained at room temperature

two quadruple-split doublets assigned to the HS Fe(II) sites ($\delta=0.79(6) \text{ mm} \cdot \text{s}^{-1}$, $\Delta E_Q=1.23(6) \text{ mm} \cdot \text{s}^{-1}$) and HS Fe(III) sites ($\delta=0.47(0) \text{ mms}^{-1}$, $\Delta E_Q=0.40(7) \text{ mm} \cdot \text{s}^{-1}$) that are agreeable to the Mössbauer parameters for Fe(II) and Fe(III) formate and carboxylates reported in literature^[15]. The analysis of the band intensities gives $A_{\text{Fe(III)}}/A_{\text{tot}}=50.2$ and $A_{\text{Fe(II)}}/A_{\text{tot}}=49.8\%$, respectively, indicating the ratio of Fe(II)/Fe(III)=1 in compound **1** that is consistent with the results of the structural and magnetic studies.

In conclusion, a mixed valence iron formate **1** with nia topology was prepared under solvothermal condition and structurally characterized by X-ray single crystal analysis that exhibits not only the ferrimagnetic nature with $T_N=37.2 \text{ K}$, but also magnetization sign inversion at the compensation temperature of $\sim 28 \text{ K}$. The ferrimagnetic properties with temperature compensation behavior are, for the first time, discussed in detail by molecular field theory.

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