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## Divalent Metal Ions Modulated Strong Frustrated M(II)-Fe(III)<sub>3</sub>O (M= Fe, Mn, Mg) Chains with Metamagnetism Only in Mixed Valence Iron Complex

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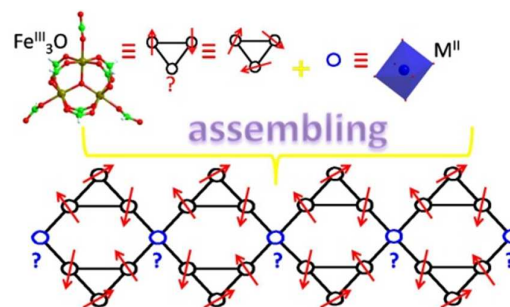
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Linking the magnetic frustrated triangle Fe<sup>III</sup><sub>3</sub>O units by divalent metal ions (M<sup>II</sup>= Fe<sup>II</sup> for 1, Mn<sup>II</sup> for 2) gives isostructural 1D spin chains. Strong antiferromagnetic interactions were found in these complexes with significant frustrations but very interesting ferrimagnetic like transition and metamagnetism were found in mixed valence 1. By comparing the magnetic behaviours with isostructural complex 3 (with M<sup>II</sup> = Mg<sup>II</sup>), it is proposed that the spins of Fe<sup>II</sup> ions and Mn<sup>II</sup> ions have ferromagnetic and antiferromagnetic contribution respectively.

Low dimensional magnetic materials are attracting much attention for their amazing properties such as single chain magnets, spin peierls, spin ladders metamagnetism and magnetic frustrations.<sup>1</sup> Among them spin frustration in one-dimensional complexes is of particular interest for their quantum spin behaviour. Among the strategies<sup>2</sup> developed to realize frustration complexes, using frustration units as building blocks in the process of assembly is the promising approach.<sup>3</sup> Thus, assembling of preformed isolated magnetic frustrated polymetallic clusters into a correlated 1D spin sequence has become a quite desired target for chemists. Variation of the connectivity, size, kinds of spin center of the building blocks as well as the entity as linker between them allows us to gain the control over the topology of the resulting complexes and tune the desired physical properties of the final materials.

As versatile frustrated building blocks, the triangular Fe<sup>III</sup>-carboxylate trimeric units [Fe<sup>III</sup><sub>3</sub>(μ<sub>3</sub>-O)(μ-OOCR)<sub>6</sub>]<sup>+</sup> have been well utilized to generate various magnetic architecture like 1D chain,<sup>4</sup> 2D "star"<sup>3b</sup> and *hnb* layer<sup>3c</sup> and *eta-c4* interpenetrating 3D framework<sup>3d</sup>. The successful examples provided an effective way to connect the triangular units by coordinated bonds via spin centre rather than the covalent bonds via carboxylate, which lead to strong magnetic coupling between the triangular units. Furthermore, using another spin carrier to link the triangular units by coordinated bonds would bring heterospin complexes with novel coupling sequence. In the heterospin system, some attractive phenomena such as intramolecular redox induced by charge transition, photo switchable valence tautomerism and ferromagnetic interactions derived from double exchange would be presented.<sup>5</sup> In this work, frustrated triangles [Fe<sup>III</sup><sub>3</sub>(μ<sub>3</sub>-O)(μ-OOC)<sub>6</sub>]<sup>+</sup> constructed by the smallest carboxylate formate and divalent metal ions Fe<sup>II</sup> were linked by formate anions to give a magnetic chain (NH<sub>4</sub>)<sub>2</sub> [{Fe<sup>III</sup><sub>3</sub>(μ<sub>3</sub>-O)(HCO<sub>2</sub>)<sub>6</sub>]<sub>2</sub>{Fe<sup>II</sup>(H<sub>2</sub>O)<sub>2</sub>(HCO<sub>2</sub>)<sub>6</sub>}] (1). And by a persistent effort the divalent metal ions in 1 was replaced by Mn<sup>II</sup> ions producing



**Scheme 1** The 1D chain constructed from frustrated triangle units and divalent metal ions.

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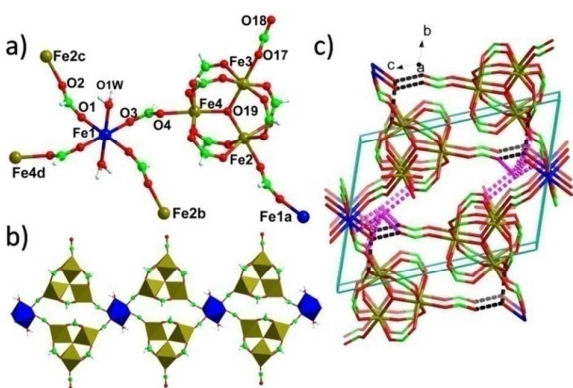
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complex  $(\text{NH}_4)_2\{[\text{Fe}_3^{\text{III}}(\mu_3\text{-O})(\text{HCO}_2)_6]_2\{\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2(\text{HCO}_2)_6\}\}$  (**2**) (Scheme 1). The mixed valence **1** and heterometallic **2** are very rare among comprehensive explored metal formates with diversified properties.<sup>6</sup> Magnetic analysis indicated an overall strong antiferromagnetic interactions with remarkable magnetic frustration was found in **1** and at low temperature a ferrimagnetism like behaviour and metamagnet characters were presented. While in **2** only frustrated antiferromagnetic interactions were found. In order to comprehend the different magnetism of two complexes, an isostructural complex with divalent diamagnetic metal ions  $\text{Mg}^{\text{II}}$   $(\text{NH}_4)_2\{[\text{Fe}_3^{\text{III}}(\mu_3\text{-O})(\text{HCO}_2)_6]_2\{\text{Mg}^{\text{II}}(\text{H}_2\text{O})_2(\text{HCO}_2)_6\}\}$  (**3**) was synthesized. By comparing the magnetic behaviours of the three complexes, magnetism modulated by the divalent metal ion was illustrated remarkably.

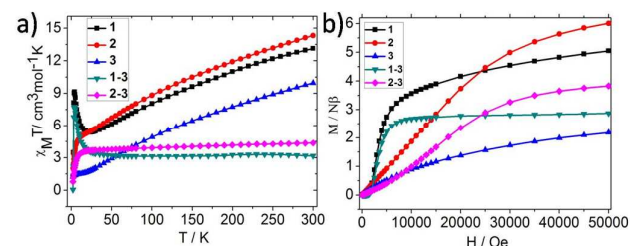
Complex **1** was synthesized by the solvothermal reaction of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in  $\text{HCOOH}$  with urea saturation at  $140^\circ\text{C}$  for 2 days. It is very similar with the synthesis condition of the *eta-c4* framework, and in that case, the acetate acid with urea saturation was used.<sup>3d</sup> Compared with the *eta-c4* framework, in **1** for the oxidation-reduction activity of the formate, some  $\text{Fe}^{\text{III}}$  ions were *in-situ* reduced to  $\text{Fe}^{\text{II}}$ , which lead to a distinct 1D structure compared with the acetate complex with the same charge-balancer or template ammonium. Attempts to obtain **2** and **3**, in which the  $\text{Fe}^{\text{II}}$  ions will be replaced by  $\text{Mn}^{\text{II}}$  and  $\text{Mg}^{\text{II}}$ , by adding the divalent metal sates  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in the solvothermal reaction of **1** is failed. In order to suppress the reduction of the  $\text{Fe}^{\text{III}}$  ions, we try other synthesis method, and by a persistent effort we obtained **2** and **3** by microwave-assisted synthesis, in which the low reaction temperature of  $90^\circ\text{C}$  and short reaction time within two hours may avoid the reduction reaction of  $\text{Fe}^{\text{III}}$  ions. And it is worth noticing that the attempts to obtain **1** by microwave-assisted synthesis within two hours at  $90^\circ\text{C}$  and  $140^\circ\text{C}$  were fruitless, which indicated that the reduction reaction of  $\text{Fe}^{\text{III}}$  ions was suppressed under such microwave-assisted reaction.



**Fig.1** a) Coordination mode of the metal ions and linkage of the formate anions in **1**, with symmetry codes: <sup>a</sup> -1+x, -1+y, z; <sup>b</sup> -x, -y, -z; <sup>c</sup> 1+x, 1+y, 1+z; <sup>d</sup> 1-x, 1-y, -z. b) The polyhedron view of the 1D chain in **1**. c) 3D supermolecular network connected by the H-bonds (dashed line in pink and black).  $\text{Fe}^{\text{III}}$  in dark yellow,  $\text{Fe}^{\text{II}}$  in blue, O in red, C in green, N in pink and H in white but omitted in c) for clarity.

The structures of the three complexes are isomorphic 1D chain structure containing one  $[\text{Fe}_3^{\text{III}}(\mu_3\text{-O})(\mu\text{-OOCH})_6]^+$  cation, a half  $\text{M}^{\text{II}}$  ion, three formate anions, one water and one ammonium cation in the asymmetry units. Therefore, the structure of **1** was described in details. In **1**, the  $[\text{Fe}_3^{\text{III}}(\mu_3\text{-O})(\mu\text{-OOCH})_6]^+$  cation was coordinated by three formate anions through the unsaturated coordinated positions of the Fe2, Fe3 and Fe4, which lead to an anionic molecule aggregate (Fig. 1a). In the aggregate, the  $\text{Fe}^{\text{III}}\text{-O}$  bond lengths are in the range of 1.905(6)-2.062(6)Å. The coordinated bonds of the  $\mu_3\text{-O}$  (O19) are shorter than that of the formate. The divalent Fe1 ion in the special position, is coordinated by four formates and two water molecules with bond lengths 2.123(6)-2.160(6) Å, and the coordinated bond lengths of Fe1 are much longer than the bond lengths of other metal centres in **1**. Bond valence calculation gives 2.02, 3.01, 3.05 and 2.95 for Fe1 to Fe4, which approved the valence state of the metal ion in **1**.<sup>7</sup> Three formate anions occupy the unsaturated coordinated positions of the  $\text{Fe}^{\text{III}}$  ions in  $[\text{Fe}_3^{\text{III}}(\mu_3\text{-O})(\mu\text{-OOCH})_6]^+$  cation featuring different coordination modes. The formate containing O17 acted as a monodentate ligand to coordinate to Fe3; the second formate in *anti,anti* mode coordinated to Fe2c and Fe1, while the last formate coordinated to Fe4 and Fe1 in *syn,anti* mode. In that way, double formate triangles  $[\text{Fe}_3^{\text{III}}(\mu_3\text{-O})(\mu\text{-OOCH})_6]^+$  cations were stringed together by the  $\text{Fe}^{\text{II}}$  ions coordinated with formate ligands to give a 1D chain (Fig. 1b). The chain is anionic and ammonium (pink in Fig. 1c) acts as a charge-balancer. The chains are connected by H-bonds between the coordinated water, monodentate formate and ammonium to form a 3D supermolecular network (Fig.1c). Compared with the *eta-c4* framework,<sup>3d</sup> the trimeric units in **1** are connected to  $\text{Fe}^{\text{II}}$  ions by *syn,anti* and *anti,anti* formates, however, in the *eta-c4* framework the trimeric units are connected to each other by *anti,anti* acetate anions.

The coordinated bond lengths in **2** and **3** are different from those in **1**, especially the coordinated bond lengths of divalent metal positions. In **2** the Mn-O bonds lengths are in the range of 2.19(2)-2.23(3) Å, while the Mg-O bonds lengths is in the scope of 2.076 (2)-2.095(2) Å. The bond length reflects the difference of the coordinated radius of the three types of divalent metal ions. In general, in metal formates the bond length of  $\text{Mn}^{\text{II}}\text{-O}$  is longer than that of  $\text{Fe}^{\text{II}}\text{-O}$ , while  $\text{Mg}^{\text{II}}\text{-O}$  bond lengths is the shortest.<sup>8</sup> To further confirm the replacement of the  $\text{Fe}^{\text{II}}$  ion by  $\text{Mn}^{\text{II}}$  and  $\text{Mg}^{\text{II}}$  in **2** and **3**, UV-vis spectrum of the three complexes in bulk sample were investigated (Fig. S1). It is clear to find that a typical intervalence charge-transfer absorption band in 550-1000 nm for classic II mixed-valence iron (II,III) complexes is observed in **1**,<sup>3d,6c,9</sup> while those bands are absent in **2** and **3**. That indicated the  $\text{Fe}^{\text{II}}$  ion in **1** was replaced by  $\text{Mn}^{\text{II}}$  and  $\text{Mg}^{\text{II}}$  in **2** and **3**.

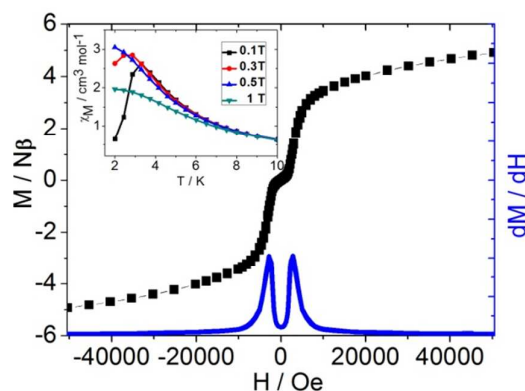


**Fig. 2** a)  $\chi_M T$  vs.  $T$  plots of **1**, **2** and **3**. b) Field-dependent magnetization plots of **1**, **2** and **3**. **1-3** and **2-3** stand for the difference of the corresponding magnetic data between **1/2** and **3**.

The temperature dependence of the magnetic susceptibilities of **1**, **2** and **3** were measured from 2 to 300 K in an applied magnetic field of 1000 Oe (phase purity confirmed by XRPD, see Fig. S2). The plots of  $\chi_M T$  versus  $T$  (normalized to  $M^{\text{II}}(\text{Fe}_3^{\text{III}}\text{O})_2$  unit) are shown in Fig. 2. The observed  $\chi_M T$  values at 300 K are 13.24, 14.33 and 9.96  $\text{cm}^3 \text{mol}^{-1} \text{K}$  for **1**, **2** and **3**, respectively. Moreover, the value of  $\chi_M T$  at 300 K of six fully spin-decoupled  $\text{Fe}^{\text{III}}$  ions with  $S = 5/2$  is 26.25  $\text{cm}^3 \text{mol}^{-1} \text{K}$ , and the  $\chi_M T$  values in the three complexes are much smaller than the corresponding spin-only systems. This discrepancy should be mainly attributed to the significant antiferromagnetic couplings between the three high-spin  $\text{Fe}^{\text{III}}$  ions in the oxo-bridged clusters. The data above 150 K obey the Curie–Weiss law, yielding  $C = 21.44 \text{ cm}^3 \text{mol}^{-1} \text{K}$  and  $\vartheta = -189.65 \text{ K}$  for **1**,  $C = 22.67 \text{ cm}^3 \text{mol}^{-1} \text{K}$  and  $\vartheta = -178.62 \text{ K}$  for **2**,  $C = 21.99 \text{ cm}^3 \text{mol}^{-1} \text{K}$  and  $\vartheta = -365.74 \text{ K}$  for **3** (see Fig. S3). The difference of the  $\vartheta$  value reflects the contribution of the  $M^{\text{II}}$  ions. The  $\vartheta$  values of **1** and **2** are larger than that of **3** for the magnitude of the magnetic interactions between  $\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{II}}/\text{Mn}^{\text{II}}$  ions are less than the counterpart between the  $\text{Fe}^{\text{III}}$  ions in the triangle. The large negative  $\vartheta$  values indicate very strong antiferromagnetic interaction in **1-3**. It is worth noticing that, not like that of **2** and **3**, on cooling the  $\chi_M T$  plots of **1** has an increase at about 25 K before finally dropping, which is the typical behaviour of ferrimagnetism or spin canting.<sup>10</sup> An obvious peak in the  $\chi_M$  vs.  $T$  plot of **1** suggested an antiferromagnetic transition between the ferrimagnetic like chains in **1** at low temperature (Fig. S4). Different from that of **1**, there is no peak in the  $\chi_M$  vs.  $T$  plots of **2** and **3**, which exclude the long-range magnetic order above 2 K. Thus, the spins in **2** and **3** are highly frustrated. For the diamagnetic ion  $\text{Mg}^{\text{II}}$ , the magnetism of **3** reflects the nature of the isolated triangle clusters. Furthermore, the magnetic interactions between the  $\text{Fe}^{\text{III}}$  ions in the triangle clusters are far more than those between the  $\text{Fe}^{\text{III}}\text{-M}^{\text{II}}$  ions in **1** and **2**. It is possible to comprehend the contribution of the  $M^{\text{II}}$  ions to the whole magnetism by deducting that of the triangle clusters (denoted as  $\chi_M T(\mathbf{1}) - \chi_M T(\mathbf{3})$  and  $\chi_M T(\mathbf{2}) - \chi_M T(\mathbf{3})$ ). It is obvious to see the ferromagnetic contribution of the  $\text{Fe}^{\text{II}}$  ions, but antiferromagnetic contribution of the  $\text{Mn}^{\text{II}}$  ions. From the bond valence calculations, UV spectrum of **1**, we found that **1** is a classic II type of mixed-valence complex rather than a valence delocalization complex, thus the double exchange in **1** seems impossible. More important the frustrated nature of the triangle in the chains makes it hard to obtain satisfied spin configurations in a single direction. The random magnetic anisotropy of the  $\text{Fe}^{\text{II}}$  ions may be responsible for the proportion of ferromagnetic contribution in **1**.<sup>11</sup> The field-dependent magnetization plot of **1** was registered with a small field step and increased quickly with the field, which also supported there was ferromagnetic contribution in **1**. The contribution of the  $\text{Fe}^{\text{II}}$  ions calculated as  $M(\mathbf{1}) - M(\mathbf{3})$  is shown in Fig. 2b, which gives a saturated value of 2.9  $N\beta$ , lower than 4.0  $N\beta$  for a high spin  $\text{Fe}^{\text{II}}$  ions due to the significant role of anisotropy. The contribution of the  $\text{Mn}^{\text{II}}$  ions calculated as  $M(\mathbf{2}) - M(\mathbf{3})$  display the typical antiferromagnetism. In a recent review, Zheng, *et al.* developed a symbol approach to classify molecular magnetic materials, and according to this approach the symbols of **1**, **2** and **3**

are  $M^{1-3}U^1S^1$ ,  $M^1U^1S^1$ ,  $M^0U^0S^1$ , which reflect the magnetic difference of **1-3**.<sup>12</sup>

The step in the magnetization of **1** reveals metamagnetic transitions, which is more evident in the hysteresis loop and the first derivative plots of **1** at 2 K. As the magnetic field increased from zero, the slope of magnetization curve, initially, is small, that is typical for an antiferromagnet. When increasing the field to the critical value  $H_c \approx 3 \text{ kOe}$ , a sharp upraise of magnetization was observed. The metamagnetic nature was also confirmed by the  $\chi_M$  vs  $T$  plots under different fields in 2-15K, in which notable peaks of the  $\chi_M$  under low external fields were found but vanished in high field. Recently, slow magnetic relaxation was found in the same metamagnetic chains with an external field near  $H_c$ .<sup>13</sup> The reciprocal temperature dependence of  $\ln(\chi_M T)$  at 0.1 T and 0.5 T for **1** shows a linear range in 8-20 K, suggesting **1** is an Ising-chain (Fig. S5). However, no components of  $\chi''$  signals were observed even at an applied field of 0.4 T (Fig. S6). The large interchain magnetic interactions and lack of enough Ising anisotropy may be responsible for the absence of slow magnetic relaxation in **1**.



**Fig. 3** The hysteresis loop and the first derivative plots of **1** at 2 K. Insert: the  $\chi_M$  vs  $T$  plots under different fields in 2-10K.

In conclusion, a mixed valence 1D chain complex **1** and isostructural heterometallic complex **2** was constructed by using formate ligands to link frustrated triangle  $[\text{Fe}_3^{\text{III}}(\mu_3\text{-O})(\mu\text{-OCH})_6]^+$  and divalent metal  $\text{Fe}^{\text{II}}$  and  $\text{Mn}^{\text{II}}$  ions. According to the Weiss constants, antiferromagnetic interactions with remarkable frustration were presented in **1** and **2**. However, on further cooling at low temperature they feature distinct magnetic behaviours, and a ferrimagnetism like behaviour and metamagnet characters were found in **1**. By comparing the magnetism of the two complexes with the isostructural complex **3** in which the  $M^{\text{II}}$  ions is used with diamagnetic  $\text{Mg}^{\text{II}}$  ions, it is found that the magnetism of the complexes is modulated by divalent metal ions, and  $\text{Fe}^{\text{II}}$  ions have ferromagnetic contribution, while the  $\text{Mn}^{\text{II}}$  ions have antiferromagnetic ones. The successes of this work suggested that it is an effective way to obtain diverse magnetic materials by assembling isolated magnetic frustrated polymetallic clusters into polymeric complexes through another spin carrier. This work was supported by NSFC of China 21471112, 20801041 and Q.L. Wu thanks the National Undergraduate training programs for innovation and entrepreneurship 201310060029.



## Notes and references

<sup>††</sup>A mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O (5 mmol) and formate acid solution 10 mL saturated with urea was sealed in a Teflon-lined stainless steel vessel, heated at 140°C for 2 days under autogenous pressure, and then cooled to room temperature. Dark brown crystals of **1** were harvested in about ~30% yield based on FeCl<sub>3</sub>·6H<sub>2</sub>O. Complexes **2** and **3** were obtained by microwave-assisted synthesis: a mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O (6 mmol) and MnCl<sub>2</sub>·4H<sub>2</sub>O (2 mmol) or MgCl<sub>2</sub>·6H<sub>2</sub>O (2 mmol) in formic acid solution 15 mL saturated with urea was heated at 90 °C for two hours under autogenous pressure, and then cooled to room temperature. Crystals of **2** and **3** were harvested in about ~30% yield based on FeCl<sub>3</sub>·6H<sub>2</sub>O.

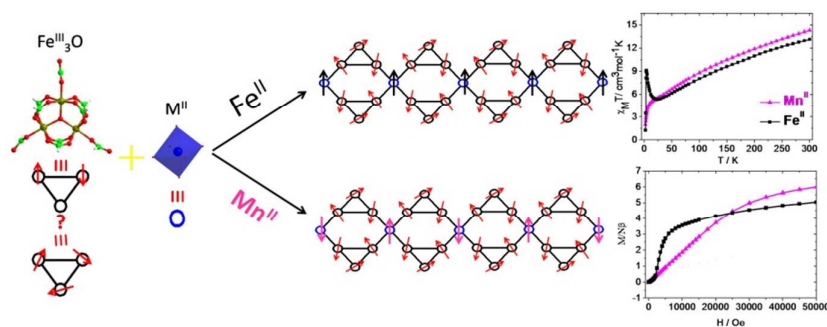
<sup>§</sup>Crystal data for **1**, C<sub>18</sub>H<sub>30</sub>Fe<sub>7</sub>N<sub>2</sub>O<sub>40</sub>: *M* = 1305.39, *P*-1, *a* = 6.8366 (14) Å, *b* = 10.967 (2), *c* = 14.884 (3) Å,  $\alpha$  = 111.35 (3)°,  $\beta$  = 97.42 (3)°,  $\gamma$  = 92.39 (3)°, *V* = 1026.0 (4) Å<sup>3</sup>, *Z* = 1, *D*<sub>c</sub> = 2.113 Mg/m<sup>3</sup>, 8745 reflections collected *R*<sub>1</sub> = 0.0884, *wR*<sub>1</sub> = 0.1908. Crystal data for **2**, C<sub>18</sub>H<sub>30</sub>Fe<sub>6</sub>MnN<sub>2</sub>O<sub>40</sub>: *M* = 1304.48, *P*-1,  $\sigma$  = 6.8216 (14) Å, *b* = 10.968 (2), *c* = 14.889 (3) Å,  $\alpha$  = 111.34 (3)°,  $\beta$  = 97.28 (3)°,  $\gamma$  = 92.22 (3)°, *V* = 1026.3 (4) Å<sup>3</sup>, *Z* = 1, *D*<sub>c</sub> = 2.111 Mg/m<sup>3</sup>, 7750 reflections collected *R*<sub>1</sub> = 0.1391, *wR*<sub>1</sub> = 0.2700. Crystal data for **3**, C<sub>18</sub>H<sub>30</sub>Fe<sub>6</sub>MgN<sub>2</sub>O<sub>40</sub>: *M* = 1273.85, *P*-1,  $\sigma$  = 6.8025 (14) Å, *b* = 10.887 (2), *c* = 14.826 (3) Å,  $\alpha$  = 111.43 (3)°,  $\beta$  = 97.52 (3)°,  $\gamma$  = 92.24 (3)°, *V* = 1008.8 (4) Å<sup>3</sup>, *Z* = 1, *D*<sub>c</sub> = 2.097 Mg/m<sup>3</sup>, 8751 reflections collected *R*<sub>1</sub> = 0.0350, *wR*<sub>1</sub> = 0.0832. Elemental analysis (%) calcd for **1**, C<sub>18</sub>H<sub>30</sub>Fe<sub>7</sub>N<sub>2</sub>O<sub>40</sub>(1305.34): C 16.56, H 2.32, N 2.15%; found for **1**: C 16.21, H 2.62, N 1.96%; calcd for **2**, C<sub>18</sub>H<sub>30</sub>Fe<sub>6</sub>MnN<sub>2</sub>O<sub>40</sub>(1304.43): C 16.57, H 2.32, N 2.15%; found for **2**: C 16.37, H 2.17, N 2.36%; calcd for **3**, C<sub>18</sub>H<sub>30</sub>Fe<sub>6</sub>MgN<sub>2</sub>O<sub>40</sub>(1273.80): C 16.97, H 2.37, N 2.20%; found for **3**: C 16.73, H 2.06, N 2.49%. CCDC: 1402020-1402022 for **1-3**.

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## Synopsis

## Divalent Metal Ions Modulated Strong Frustrated M(II)-Fe(III)<sub>3</sub>O (M= Fe, Mn, Mg) Chains with Metamagnetism Only in Mixed Valence Iron Complex

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Using divalent ion Fe<sup>II</sup> and Mn<sup>II</sup> to link the frustrated Fe(III)<sub>3</sub>O units generated two isostructural chains with distinct magnetic behaviour: frustrations and metamagnetism in mixed valence complex but only magnetic frustrations in heterometallic one.