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Communication

Step-by-step synthesis of one Fe₆ wheel and two Fe₁₀ clusters derived from multidentate triethanoamine ligandSui-Jun Liu,^a Song-De Han,^a Ji-Min Jia,^a Li Xue,^a Yu Cui,^a Shu-Ming Zhang,^b and Ze Chang^{a*}

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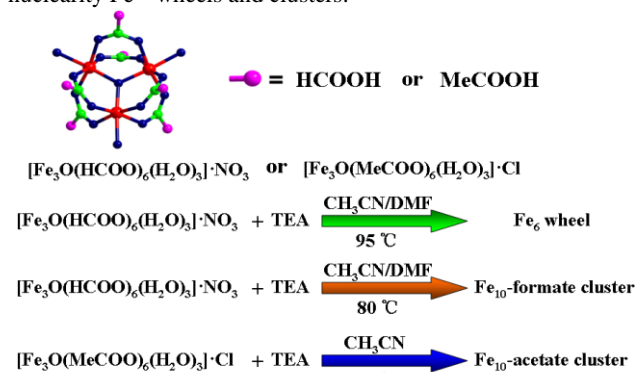
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One Fe₆ wheel and two Fe₁₀ clusters were obtained with step-by-step strategy. With Fe₃O precursors, the title wheel and cluster complexes were synthesized by reacting with triethanolamine. Magnetic investigation indicates that the Fe₆ wheel shows strong antiferromagnetic behavior.

Over the past two decades, cluster complexes and coordination polymers based on metal clusters have taken much attention and current research in the field was focused on the design of functional molecular magnetic materials and metal-organic frameworks.¹ Especially, the polynuclear metal wheels and clusters are being extensively researched because of their fascinating structures and interesting magnetic properties.² As the pioneer of functional molecular magnetic materials, a Mn₁₂ cluster with slow magnetic relaxation and hysteresis effects has been reported, which was found to have implications for fundamental science and potential applications in information storage and quantum computing at the molecular level.³ Encouraged by the widely prospect of single-molecule magnets (SMMs), high nuclearity Fe^{III} wheels and clusters, as potential SMMs, have attracted more and more attention and the investigation of them has been an active field in recent years.⁴ Up to now, several Fe^{III} wheels and clusters with the number of ions ranging from 6 to 18 have been reported.⁵ Though more examples of Fe^{III} wheels and clusters are required for the understanding of their magnetic phenomena, it is still a great challenge to realize the targeted synthesis of metal wheels and clusters.⁶

It has been reported that many methods have been utilized to construct high-nuclearity Fe^{III} complexes.⁷ Among the various methods, step-by-step method, with different precursors for the assembly of Fe^{III} wheels and clusters, has been proved to be efficient.⁸ One of the most successful synthetic procedures to polynuclear iron clusters relies on the reaction of classic Fe₃O precursors {[Fe₃O(RCO₂)₆(H₂O)₃]·X} with other bridging-chelating ligands under ambient conditions.⁹ Notably, X[−] could be various counteranions and have potential chelating abilities. In our previous work, [Fe₃O(PhCO₂)₆(H₂O)₃]·PhCO₂ and [Fe₃O(C₆H₁₁CO₂)₆(H₂O)₃]·C₆H₁₁CO₂ have been used to synthesize Fe₁₂Ln₄ clusters and Fe₂₀ cluster based coordination polymers, respectively.¹⁰ These results indicates that the [Fe₃O]⁷⁺ core of the trinuclear iron complex could serve as building block for the construction of higher-nuclearity species. However, the exact nuclearity and structure of the products depend on several factors, such as synthetic temperature and counteranions type.

Additionally, some cases reported indicate that the use of Fe₃O precursors in solvothermal reactions may introduce OH[−] and O^{2−} during the reaction process, which could benefit the formation of clusters.¹¹ Therefore, the combination of Fe₃O precursors and solvothermal method is favourable for constructing high-nuclearity Fe^{III} wheels and clusters.



Scheme 1. Synthetic routes for complexes 1-3.

On the other hand, triethanoamine (TEA) as an exceptional candidate for the synthesis of low-dimensional structures including wheels and clusters possessing both N and O donors with various coordination modes, has been rarely used for the construction of multinuclear iron wheels and clusters.¹¹ In this work, we used TEA for the construction of iron wheels and clusters. Herein, we report the synthesis, structures and magnetic properties of one Fe₆ wheel and two Fe₁₀ clusters, namely { [Fe^{III}₆(TEA)₆] · 9H₂O } (1), { [Fe^{III}₁₀(μ₄-O)(μ₃-O)₂(TEA)₆(HCOO)₆] · H₂O } (2) and { [Fe^{III}₁₀(μ₄-O)(μ₃-O)₂(TEA)₆(CH₃COO)₂Cl₄] · CH₃CN · CH₃OH · H₂O } (3), resulted from the reaction of different precursors and TEA. To obtain desired discrete structures, different counteranions and synthetic conditions have been investigated, and it was found that the properties of the counteranions introduced, specifically their coordination ability with metal centres, could determine the structures of resulted compounds.¹²

The reactions of [Fe₃O(HCOO)₆(H₂O)₃]·NO₃ and TEA in MeCN/DMF under 95 °C in glass vial and 80 °C in teflon-lined autoclave conditions led to yellow crystals of Fe₆ wheel and reddish-brown crystals of Fe₁₀-formate clusters, respectively. When [Fe₃O(HCOO)₆(H₂O)₃]·NO₃ were replaced by [Fe₃O(MeCOO)₆(H₂O)₃]·Cl, another Fe₁₀-acetate cluster was

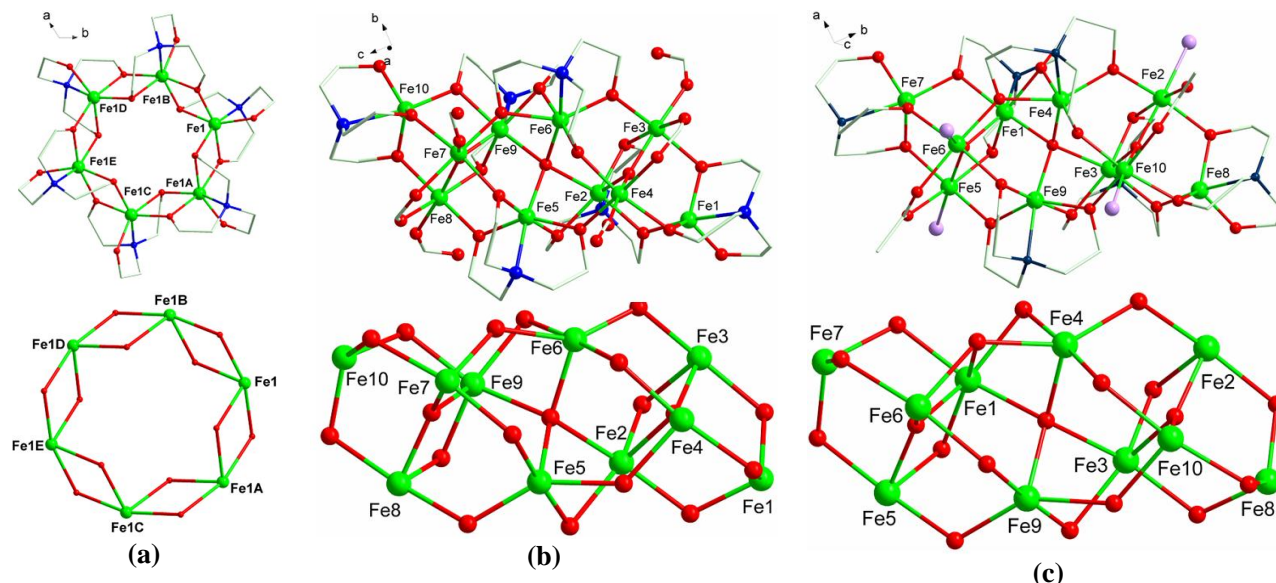


Fig. 1 Views of (a) the molecular structure of Fe₆ wheel (symmetry codes: A: $x-y, x, -z+1$; B: $y, -x+y, -z+1$; C: $-y, x-y, z$; D: $-x+y, -x, z$; E: $-x, -y, -z+1$); (b) the molecular structure of **2** and the core of Fe₁₀; (c) the molecular structure of **3** and the core of Fe₁₀.

obtained (Scheme 1).[‡] Therefore, the stronger coordination ability of Cl[−] than NO₃[−] has contribution to the unique structure of the Fe₁₀-acetate cluster.

Crystallographic studies reveal that complexes **1–3** crystallize in *P*-3 c 1 of trigonal system, *C*2/*c* of monoclinic system and *P*2₁/*n* of monoclinic system, respectively. Complex **1** has a similar structure with that of the reported [Fe₆(tea)₆]-6MeOH and {Na[Fe₆(tea)₆]}Cl reported previously,¹³ thus herein the structure of **1** is described briefly. The asymmetric unit of **1** consists of one Fe^{III} ion, one TEA ligand and one and half lattice water. Each Fe^{III} ion is located in the six coordinated environment with one nitrogen and five oxygen atoms from TEA. Every two Fe^{III} ions are bridged by two oxygen atoms to form the Fe₆ wheel (Fig. 1a).

The structure of **2** comprises ten crystallographically independent Fe atoms in a closed, cage-like conformation. The Fe^{III} centers exhibit two types of coordination geometry of six-coordinated distorted octahedral (FeO₅N and FeO₆) and five-coordinated distorted trigonal bipyramidal (FeO₄N, Fe1 and Fe10). Interestingly, Fe2 and Fe9 are important junctions to form [Fe₁₀(μ₄-O)₂(μ₃-O)(μ₂-O)₁₆]⁷⁺ core. Fe2 connects two different cage-like structures composed of Fe2, Fe5, Fe6, Fe9 (Structure A) and Fe1, Fe2, Fe3, Fe4 (Structure B), respectively. Another one cage-like structure composed of Fe7, Fe8, Fe9 and Fe10 (Structure C) and A is linked by Fe9. Further, the TEA ligands and formates chelate and bridge Fe^{III} ions of Fe₁₀ core to give complex **2** (Fig. 1b).

As shown in Fig. 1c, complex **3** consists of ten Fe^{III} centers, two μ₄-O anions, one μ₃-O anion, six TEA ligands, two acetate anions, four chloride ions and three guest molecules including CH₃CN, CH₃OH and H₂O. Similar to that of **2**, the Fe^{III} centers in **3** exhibit two different kinds of coordination geometries: slightly distorted five-coordinated trigonal bipyramidal (FeO₄N for Fe7 and Fe8), and distorted six-coordinated octahedra (FeO₅N for Fe1, Fe3, Fe4 and Fe9 and FeO₅Cl for Fe2, Fe5, Fe6 and Fe10). However, differ from **2**, four coordinated chloride ions were incorporated to replace four carboxylate anions to occupy the

coordination sites. A closer look at the structure of **3** reveals that the central μ₄-O anion is the key point for the formation of Fe₁₀ cluster by forming one rectangle and two cage-like architectures with Fe^{III} ions. Each cage consists of four Fe^{III} ions, one μ₃-O^{2−} and three μ₂-O^{2−} ions (Fig. 1c). The ten iron centers are further supported by six TEA ligands and two acetate anions. The slight differences of Fe₃O precursors (different coordination abilities of counteranions) and synthetic conditions (including synthetic temperature and pressure) result in the distinct structures.

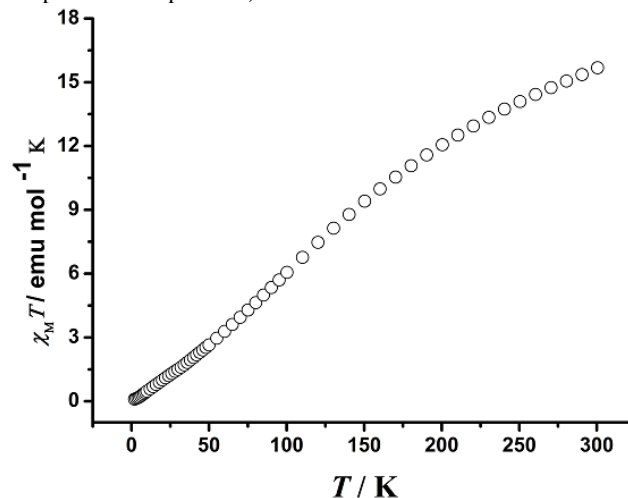


Fig. 2 Temperature dependence of magnetic susceptibilities in the form of $\chi_M T$ (°) at an applied field of 500 Oe for **1**.

To further study the magnetic properties of the obtained complexes, magnetic measurements were planned to carry out. However, since complexes **2** and **3** are not very stable, only the properties of complex **1** were investigated. All the experiments were carried out on crushed crystalline sample and its phase purity was confirmed by X-ray powder diffraction (see Fig. S1, ESI). The temperature-dependent magnetic susceptibility of **1** was investigated in the range of 2–300 K with a 500 Oe applied field (Fig. 2). The $\chi_M T$ product of **1** at room temperature is 15.68

emu mol⁻¹ K, which is significantly below the spin-only value 26.3 emu mol⁻¹ K for six non interacting Fe^{III} ions, indicating strong antiferromagnetic exchange interactions. And the $\chi_M T$ value decreases linearly with decreasing temperature to a minimum value of 0.11 emu mol⁻¹ K at 2.0 K, indicating an $S = 0$ ground state. This plot is indicative of the occurrence of a weak antiferromagnetic interaction between the iron ions in **1**. The magnetization vs. field (M vs. H) curve (at 2 K) for **1** is shown in Fig. S3 (ESI). The magnetization increases slowly and tends to a value of 0.08 N β at 70 kOe, far from the theoretical saturated value, confirming again the strong antiferromagnetic coupling between the Fe^{III} ions in **1**.

The magnetic result of **1** is consistent with those Fe₆ wheels and other Fe^{III} wheels with even iron centers reported previously.¹⁴ All the even Fe^{III} wheels have spin singlet ground state as a result of antiferromagnetic exchange interactions between adjacent Fe^{III} ions and result in antiparallel arrangement of spin around the ring.¹³ As aforementioned and to the best of our knowledge, even Fe^{III} wheels could exhibit strong antiferromagnetic behaviour.

In conclusion, by using two similar Fe₃O precursors as Fe^{III} ion sources, one Fe₆ wheel and two Fe₁₀ clusters have been obtained under solvothermal conditions. Step-by-step strategy was successfully employed to construct discrete complexes, which is applicable to the assembly of other related high-nuclearity iron wheels and clusters. Magnetic measurements indicate that **1** shows strong antiferromagnetic behavior with $S = 0$ ground state. Furthermore, the multidentate TEA as an important chelate-bridged ligand is favorable to synthesize much more complicated and fantastic frameworks with possible interesting magnetic properties.

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[†]Electronic Supplementary Information (ESI) available: crystallographic data in CIF or other electronic format see DOI: 10.1039/C3DTXX00000X

‡Synthesis of **1**: A mixture of a solution of [Fe₃O(HCOO)₆(H₂O)₃]·NO₃ (0.05 mmol, 0.285 g) in MeCN (6 mL), TEA (1 mL) and DMF (1 mL) was sealed in a 10 mL glass vial, and heated to 95 °C for 3 days then slowly cooled to 20 °C in 12 h. Small yellow crystals were obtained and the vial was allowed to stand undisturbed for three days to obtain large yellow crystals. Yield: ca. 45% based on Fe. Element analysis (%): Calcd. for C₃₆H₉₀Fe₆O₂₇N₆: C 31.46, H 6.60, N 6.12; found: C 31.62, H 6.22, N 6.22.

Synthesis of **2**: A mixture of a solution of [Fe₃O(HCOO)₆(H₂O)₃]·NO₃ (0.05 mmol, 0.285 g) in MeCN (10 mL), TEA (one drop) and DMF (2~8 drops) was sealed in a 23 mL teflon-lined autoclave, and heated to 80 °C for 2 days then slowly cooled to 20 °C in 12 h. Reddish-brown crystals were collected with a yield of ca. 25% based on Fe. Element analysis (%):

Calcd. for C₄₂H₈₀Fe₁₀N₆O₃₄: C 28.47, H 4.55, N 4.74; found: C 28.63, H 4.54, N 5.11.

Synthesis of **3**: A mixture of a solution of [Fe₃O(CH₃COO)₆(H₂O)₃]·Cl (0.16 mmol, 0.1 g) in MeCN (10 mL) and TEA (one drop) was stirred and sealed in a 23 mL teflon-lined autoclave, then heated to 80 °C for 2 days then slowly cooled to 20 °C in 12 h. Brown crystals were collected with a yield of ca. 27% based on Fe. Element analysis (%): Calcd. for C₄₃H₈₇Fe₁₀N₇O₂₇Cl₄: C 28.15, H 4.78, N 5.34; found: C 26.97, H 5.29, N 4.70.

§Crystal data for **1** (C₃₆H₉₀Fe₆N₆O₂₇): $M_r = 1374.24$, trigonal, space group $P\bar{3}c1$, $a = 13.6451(19)$, $b = 13.6451(19)$, $c = 17.203(3)$ Å, $\gamma = 120^\circ$, $V = 2773.9(8)$ Å³, $Z = 2$, $\rho = 1.645$ g cm⁻³, $\mu = 1.615$ mm⁻¹, $F(000) = 1440$, 22296 reflections measured, 1638 unique ($R_{int} = 0.0668$), $R_1 = 0.0593$, $wR_2 = 0.1388$ [$>2\sigma(I)$]. Crystal data for **2** (C₄₂H₈₀Fe₁₀N₆O₃₄): $M_r = 1771.62$, monoclinic, space group $C2/c$, $a = 37.09(2)$, $b = 11.390(7)$, $c = 29.307(16)$ Å, $\beta = 90.0100(10)^\circ$, $V = 12379(13)$ Å³, $Z = 8$, $\rho = 1.901$ g cm⁻³, $\mu = 2.369$ mm⁻¹, $F(000) = 7248$, 45224 reflections measured, 10909 unique ($R_{int} = 0.1679$), $R_1 = 0.0991$, $wR_2 = 0.1801$ [$>2\sigma(I)$]. The monoclinic with beta approximately 90° may emulate orthorhombic and the use of "twin" restraint instruction surmounts twinning. To make the displacement parameters be more reasonable, "isor", "simu" and "sadi" instructions were used to refine the crystallographic data. Crystal data for **3** (C₄₃H₈₇Fe₁₀N₇O₂₇Cl₄): $M_r = 1834.50$, monoclinic, space group $P2_1/n$, $a = 11.154(2)$, $b = 29.642(6)$, $c = 21.965(4)$ Å, $\beta = 104.05(3)^\circ$, $V = 7045(2)$ Å³, $Z = 4$, $\rho = 1.730$ g cm⁻³, $\mu = 2.224$ mm⁻¹, $F(000) = 3752$, 51294 reflections measured, 12401 unique ($R_{int} = 0.1248$), $R_1 = 0.0811$, $wR_2 = 0.2013$ [$>2\sigma(I)$]. CCDC reference numbers for **1-3**: 972470-972472.

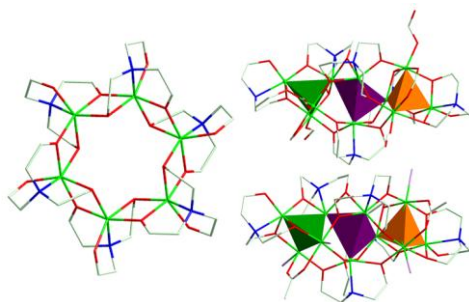
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Graphic Abstract

Step-by-step synthesis of one Fe₆ wheel and two Fe₁₀ clusters derived from multidentate triethanoamine ligand

Sui-Jun Liu,^a Song-De Han,^a Ji-Min Jia,^a Li Xue,^a Yu Cui,^a Shu-Ming Zhang,^b and Ze Chang^{a*}



One Fe₆ wheel and two Fe₁₀ clusters based on multidentate triethanolamine have been prepared and characterized. Step-by-step strategy was used to construct target complexes. Magnetic analyses indicate that the Fe₆ wheel exhibits strong antiferromagnetic behavior with $S = 0$ ground state.