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A 64-Nuclear Cubic Cage Incorporating Propeller-like Fe^{III}_8 Apices and HCOO^- Edges

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High nuclearity clusters are currently of great interest, by virtue of their structural beauty and their important role in connecting micro to macro and quantum to classic regimes.^{1–10} While many such systems have been explored, for example, giant polyoxometalates,¹ giant metal-chalcogenide clusters,² inorganic fullerene-like molecules,³ lanthanide hydroxo compounds,⁴ and oxo-clusters containing both d- and f-block metals,⁵ those containing magnetic transition metals attract special and continuous attention regarding their rich magnetism such as high ground-state spin values,⁶ single molecular magnet (SMM)⁷ and coupled SMM behavior by weak linkages,⁸ and their promising applications for data storage,⁷ quantum computing,⁹ and spintronics.¹⁰ Various ligands, especially multipodal ones,¹¹ are widely employed in the syntheses of such high nuclearity species. However, many simple and popular ligands, like acetate, can also afford compounds of high nuclearity.¹² With these serendipities in mind, we are currently exploring the mixed-ligand system of triethanolamine ($\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, *teaH*), a tripodal ligand having been recently used for synthesizing polynuclear species,^{11,13} and formate HCOO^- , the smallest and simplest carboxylate of small steric hindrance, favoring both formation of metal-oxo clusters and further linkage of them.¹⁴ The outcome is, quite surprising and interesting, a large cubic cage consisting of 64 Fe^{3+} ions of $\{[\text{Fe}_8\text{O}_3(\text{tea})(\text{teaH})_3(\text{HCOO})_6](\text{HCOO})_{12}\} \cdot (\text{ClO}_4)_{12} \cdot 3\text{CH}_3\text{OH} \cdot 36\text{H}_2\text{O}$ (**Fe**₆₄) (*tea* = $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3^{3-}$ and *teaH* = $\text{N}(\text{CH}_2\text{CH}_2\text{O})_2 \cdot (\text{CH}_2\text{CH}_2\text{OH})^{2-}$). Fe^{3+} -oxo-based clusters have been continuously studied.^{15–18} They can display ground state of spin values from 0 up to 25 and pleasing physical properties such as the Néel vector tunneling of Fe_8 wheel¹⁷ and the large magnetocaloric effect in an Fe_{14} cluster.¹⁸

Fe₆₄ was obtained by a very slow crystallization procedure or reaction lasting 2 months (Supporting Information, SI). The structure analysis (SI) revealed a cubic cage (Figure 1) containing 64 Fe^{3+} ions, 24 O^{2-} , 8 *tea*^{3−}, 24 *teaH*^{2−}, and 60 HCOO^- , thus a total of 180 components. The cubic cage consists of eight corners of octanuclear $[\text{Fe}^{\text{III}}_8\text{O}_3(\text{tea})(\text{teaH})_3(\text{HCOO})_6](\text{HCOO})_{3/2}]$ unit (Fe_8 , Figure 1a,b) with a propeller-like Fe_8O_3 core, linked further by 12 *anti-anti* formate ions as the edges of the cube (Figure 1c). The Fe_8 corner possesses similar structure to $[\text{Fe}_8\text{O}_3(\text{O}_2\text{CPh})_9(\text{tea})(\text{teaH})_3] \cdot \text{MeCN}$ and related octanuclear compounds,¹⁶ and the Fe_8 moiety has been found in some high nuclearity clusters.^{15b} Its propeller-like core has two central axial Fe^{3+} ions bridged by three $\mu_4\text{-O}^{2-}$, and each $\mu_4\text{-O}^{2-}$ further bridges two peripheral Fe^{3+} ions in pair, one upper and one lower (Figure 1b), being one of the three blades of the propeller. The Fe_8O_3 core thus consists of three flattened $[\text{Fe}_4(\mu_4\text{-O})]$ tetrahedra sharing the central Fe–Fe axis of the core. The Fe^{3+} ions are further linked by ligands, *tea*^{3−}, *teaH*^{2−}, and HCOO^- . The upper axial Fe^{3+} ion is capped by one *tea*^{3−} via the N atom and the three alkoxide O atoms, thus this Fe^{3+} ion is 7-fold coordinated in a face-capped octahedron. Each alkoxide O

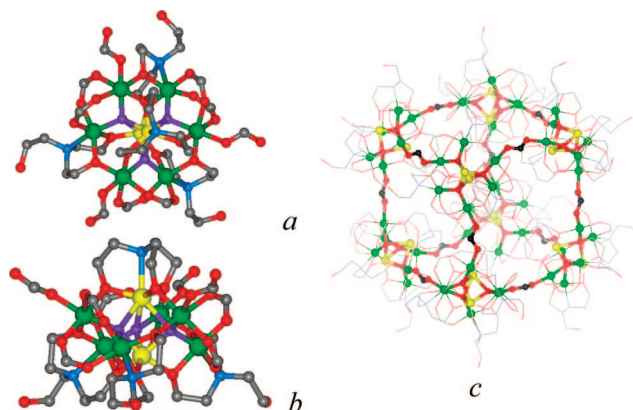


Figure 1. The structure of Fe_{64} cubic cage. (a and b) Top and side view of the Fe_8 corner. Atomic scheme: Fe, large green (peripheral) and yellow (central) spheres; O, small red and purple (the three $\mu_4\text{-O}^{2-}$) spheres; N, blue spheres; C, gray spheres. (c) The cubic cage with the corner Fe_8O_3 cores and HCOO^- edges highlighted (O red and C black) while other parts in thin sticks. H atoms, ClO_4^- anions, and lattice solvents are not included.

atom of the *tea*^{3−} connects one upper peripheral Fe^{3+} ion. However, each lower peripheral Fe^{3+} ion is chelated by one *teaH*^{2−} through its N atom and two alkoxide arm O atoms, of which one further links the lower central Fe^{3+} ion, and the other to one upper peripheral Fe^{3+} ion, leaving one alcohol arm free of coordination. Therefore, the lower axial Fe^{3+} ion is octahedrally coordinated by O atoms. In each blade, the two peripheral Fe^{3+} ions are bridged by two *syn-syn* HCOO^- ligands, and the upper peripheral Fe^{3+} ion is finally coordinated by one HCOO^- ligand, which is one edge connecting to other Fe_8 corner of the cube (Figure 1b,c). Each Fe_8 corner thus has three HCOO^- ligands to link the other three Fe_8 corners, and its central axis points to the cube center, with the *tea*^{3−} cap inside the cube. It is noted that the coordinate octahedra of Fe^{3+} ions are face-sharing for the two central axial Fe^{3+} ions ($\text{Fe} \cdots \text{Fe}$ 2.994 Å), edge-sharing between the central and peripheral Fe^{3+} ions ($\text{Fe} \cdots \text{Fe}$ 2.988–3.132 Å), apex-sharing between the central and peripheral Fe^{3+} ions ($\text{Fe} \cdots \text{Fe}$ 3.638–3.902 Å), and apex-sharing between the peripheral Fe^{3+} ions ($\text{Fe} \cdots \text{Fe}$ 3.270–3.539 Å). It could be estimated that the magnetic interaction within the Fe_8 corner should be strong or major. The $\text{Fe} \cdots \text{Fe}$ distances spanned by the *anti-anti* HCOO^- edge are 5.806–5.943 Å, and the cube has edges of 13.2 Å counting the separation between the outer axial Fe atoms of the corners. It is clear that the small steric hindrance of HCOO^- ligand¹⁴ allows the further linkage of the bulk Fe_8 units. The successful synthesis of the Fe_{64} cage reveals that the HCOO^- ligand is indeed beneficial for synthesizing species of high nuclearity. In the lattice, the cationic Fe_{64} cubic cages have their 3-fold axes parallel to the *c* axis, and form the hexagonal

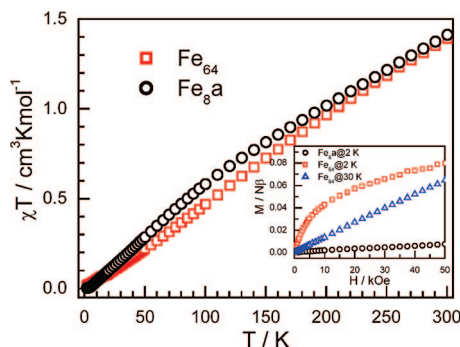


Figure 2. χT versus T plots under 1 kOe field, and M versus H plots (inset) for Fe_{64} and Fe_{8a} . Data are for one Fe^{3+} .

closest packing layer (Figure S1 in SI) along the ab plane, then these layers stack along the c direction in ABCABC style, with interstices occupied by ClO_4^- anions, lattice water and methanol, mostly disordered. The shortest intercage $\text{Fe}\cdots\text{Fe}$ separation is 8.61 Å.

In a different preparation using Fe^{3+} source, we obtained the compound of $[\text{Fe}_8\text{O}_3(\text{tea})(\text{teaH})_3(\text{HCOO})_9]\{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+](\text{ClO}_4^-)\}_3(\text{H}_2\text{O})_{0.5}$ (**Fe_{8a}**), in quite a high yield (SI). The compound consists of discrete neutral octanuclear $[\text{Fe}_8\text{O}_3(\text{tea})(\text{teaH})_3(\text{HCOO})_9]$ molecules, with similar molecular structure (Figure S2 in SI) to the Fe_8 corner of the Fe_{64} cage. The shortest intercluster $\text{Fe}\cdots\text{Fe}$ separation is 7.05 Å. However, several attempts to prepare **Fe₆₄** from Fe^{3+} source were unsuccessful (SI).

The magnetic study of **Fe₆₄** was performed on carefully selected small crystals of **Fe₆₄** but still containing a very small amount of impurity of the ferrimagnetic $[\text{Fe}_3(\text{HCOO})_6](\text{solvent})^{19}$ and weak ferromagnetic $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}^{20}$ probably (SI). As depicted in Figure 2, at 300 K, the χT value is $1.39 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ per Fe^{3+} , significantly lower than the value of $4.375 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ expected for the noninteracting high-spin Fe^{3+} ion ($S = 5/2$ and $g = 2.00$). It decreases almost linearly with lowering temperature to $0.016 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2.0 K. A broad maximum of the corresponding χ is observed at 170 K (Figure S3 in SI). The overall behavior is clearly indicative of strong antiferromagnetic interactions between the Fe^{3+} centers. The rise in χ values and a kink in χT around 16 K is due to the impurity of ferrimagnetic $[\text{Fe}_3(\text{HCOO})_6](\text{solvent})$ with critical temperature of 16.1 K,¹⁹ and further rise in χ values below 5 K might be due to the impurity of weak ferromagnetic $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ with critical temperature of 3.7 K.²⁰ The impurity is responsible for the rapid rise of the isothermal magnetization in the low field region at 2 K (Figure 2 inset). However, the very low value of $0.08 \text{ N}\beta$ per Fe^{3+} even at 50 kOe, far below the saturation value expected ($5 \text{ N}\beta$ per Fe^{3+} assuming $g = 2.00$), confirms the significant antiferromagnetic interactions within the material. The isothermal magnetization at 30 K, above the critical temperatures of the two assumed impurities, is linear and reaches only $0.06 \text{ N}\beta$ per Fe^{3+} at 50 kOe. The magnetic behavior of the Fe_{64} cage is similar to the related discrete octanuclear species¹⁶ possessing the same propeller-like Fe_8O_3 core. It is clear that in the Fe_{64} cage the antiferromagnetic interaction within the Fe_8 corner is strong and dominant, and the magnetic interaction between Fe_8 corners through the *anti-anti* HCOO^- edge is minor but it could have an effect on the magnetism. The higher peak temperature of 170 K of **Fe₆₄** versus 80 K of **Fe_{8a}** in temperature-dependent susceptibility (Figure S3 in SI) revealed that the *anti-anti* HCOO^- bridges in the Fe_{64} cage provide further significant interaction between the Fe_8 corners, compared to **Fe_{8a}** which contains discrete neutral octanuclear species only. Both **Fe₆₄**

and **Fe_{8a}** have $S = 0$ ground state as observed for many even-numbered Fe^{3+} -oxo-based clusters.^{15,16}

In conclusion, a high nuclearity cubic cage involving 64 Fe^{3+} ions has been successfully synthesized, and it displays strong antiferromagnetism. This demonstrates that the combination of the small steric hindrance HCOO^- and polypodal ligands can provide a new route to obtain high nuclearity magnetic clusters and/or further linkage of them, thus giving the opportunity to explore their beautiful structures and interesting magnetism.

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Supporting Information Available: An X-ray crystallographic file in CIF format for **Fe₆₄** and **Fe_{8a}**, a PDF file containing further information and Figures S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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