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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 ($N(CH_2CH_2OH)_3$, *tea*H_3), a tripodal ligand having been recently used for synthesizing polynuclear species,[11,13] and formate $HCOO^-$, the smallest and simplest carboxylate of small stereohindrance, 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 $\{[Fe_8O_3(tea)(teaH)_3(HCOO)_6]_8(HCOO)_{12}\}(ClO_4)_{12}\bullet 3CH_3OH\bullet 36H_2O$ (**Fe_{64}**) (*tea* $= N(CH_2CH_2O)_3{}^{3-}$ and *tea*H $= N(CH_2CH_2O)_2\text{-}(CH_2CH_2OH)^{2-}$). 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 wheel[17] and the large magnetocaloric effect in an Fe_{14} cluster.[18]

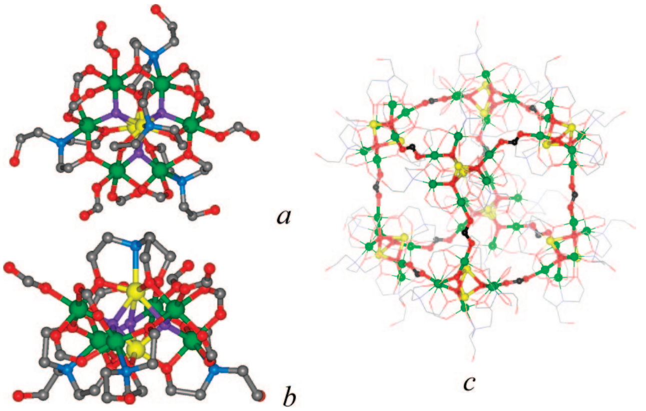

Figure 1. The structure of Fe_{64} cubic cage. (a and b) Top and side view of the Fe_8 corner. Atomic scheme: Fe, large green (peripheral) and yellow (central) spheres; O, small red and purple (the three μ_4-O^{2-}) spheres; N, blue spheres; C, gray spheres. (c) The cubic cage with the corner Fe_8O_3 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.

Fe_{64} 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 *tea*H^{2-}, and 60 $HCOO^-$, thus a total of 180 components. The cubic cage consists of eight corners of octanuclear $[Fe^{III}{}_8O_3(tea)(teaH)_3(HCOO)_6(HCOO)_{3/2}]$ unit (Fe_8, Figure 1a,b) with a propeller-like Fe_8O_3 core, linked further by 12 *anti-anti* formato ions as the edges of the cube (Figure 1c). The Fe_8 corner possesses similar structure to $[Fe_8O_3(O_2CPh)_9\text{-}(tea)(teaH)_3]\cdot MeCN$ 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 μ_4-O^{2-}, and each μ_4-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 $[Fe_4(\mu_4\text{-}O)]$ tetrahedra sharing the central Fe−Fe axis of the core. The Fe^{3+} ions are further linked by ligands, *tea*$^{3-}$, *tea*H^{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 atom of the *tea*$^{3-}$ connects one upper peripheral Fe^{3+} ion. However, each lower peripheral Fe^{3+} ion is chelated by one *tea*H^{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 (Fe•••Fe 2.994 Å), edge-sharing between the central and peripheral Fe^{3+} ions (Fe•••Fe 2.988−3.132 Å), apex-sharing between the central and peripheral Fe^{3+} ions (Fe•••Fe 3.638−3.902 Å), and apex-sharing between the peripheral Fe^{3+} ions (Fe•••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 Fe•••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 stereohindrance of $HCOO^-$ ligand[14] 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 benefitial 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

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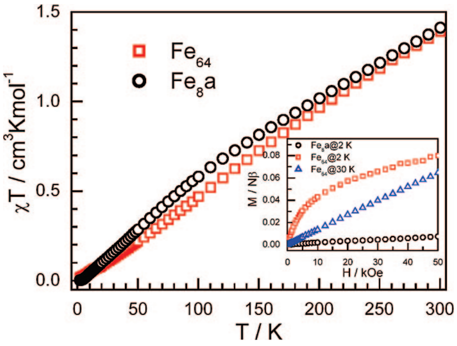

Figure 2. χT versus T plots under 1 kOe field, and M versus H plots (inset) for **Fe$_{64}$** and **Fe$_8$a**. Data are for one Fe^{3+}.

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 Fe•••Fe separation is 8.61 Å.

In a different preparation using Fe^{3+} source, we obtained the compound of $[Fe_8O_3(tea)(teaH)_3(HCOO)_9]\{[(CH_3CH_2)_3NH+]-(ClO_4^-)\}_3(H_2O)_{0.5}$ (**Fe$_8$a**), in quite a high yield (SI). The compound consists of discrete neutral octanuclear $[Fe_8O_3(tea)(teaH)_3(HCOO)_9]$ molecules, with similar molecular structure (Figure S2 in SI) to the Fe$_8$ corner of the Fe$_{64}$ cage. The shortest intercluster Fe•••Fe separation is 7.05 Å. However, several attempts to prepare **Fe$_{64}$** from Fe^{3+} source were unsuccessful (SI).

The magnetic study of **Fe$_{64}$** was performed on carefully selected small crystals of **Fe$_{64}$** but still containing a very small amount of impurity of the ferrimagnetic $[Fe_3(HCOO)_6]$(solvent)[19] and weak ferromagnetic $Fe(HCOO)_2\cdot 2H_2O$[20] probably (SI). As depicted in Figure 2, at 300 K, the χT value is 1.39 cm^3 mol^{-1} K per Fe^{3+}, significantly lower than the value of 4.375 cm^3 mol^{-1} 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 cm^3 mol^{-1} 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 $[Fe_3(HCOO)_6]$(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 $Fe(HCOO)_2\cdot 2H_2O$ 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 Nβ per Fe^{3+} even at 50 kOe, far below the saturation value expected (5 Nβ 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 Nβ per Fe^{3+} at 50 kOe. The magnetic behavior of the Fe$_{64}$ cage is similar to the related discrete octanuclear species[16] 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 **Fe$_{64}$** versus 80 K of **Fe$_8$a** 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$_8$a** which contains discrete neutral octanuclear species only. Both **Fe$_{64}$** and **Fe$_8$a** 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 stereohindrance 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 **Fe$_{64}$** and **Fe$_8$a**, 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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