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Protein-Sized Chiral Fe$_{168}$ Cages with NbO-Type Topology

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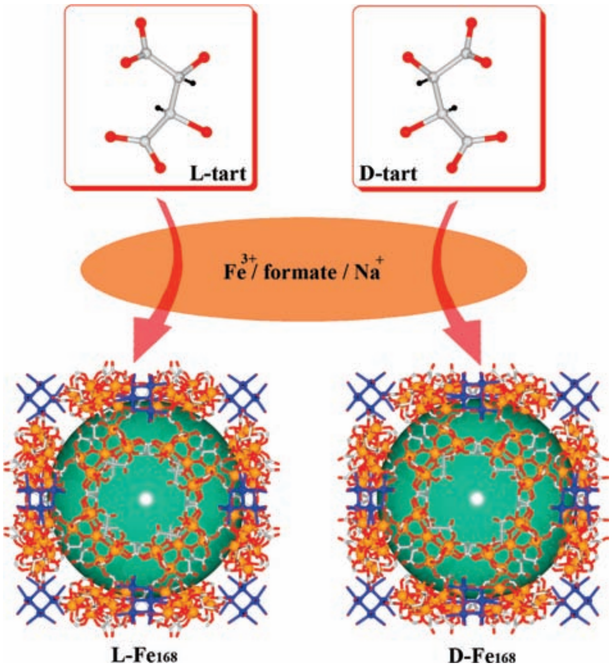
In recent years, design and synthesis of the molecule-based protein-sized complexes are of great interest due to their potential applications in chemical bionics, catalysis, energy storage, and multifunctional materials.[1−4] In this research field, Müller et al. have discovered a series of fascinating polyoxomolybdate complexes that can simulate cellular function or behave as quantum spin systems.[1] Further, Christou and others have shown a versatile Mn chemistry that can isolate various polynuclear Mn complexes from Mn$_3$ clusters to a unique Mn$_{84}$ giant wheel.[2] Interestingly, many of these complexes exhibit single-molecule magnet properties.[2] Ferric systems represent another attractive family of polynuclear aggregates mainly because of their potential applications in bionics models, magnetic properties, and catalysis.[5−8] In most of the cases, the preparation of giant ferric aggregates is highly dependent on the assistance of the alkoxide- and carboxylate-based ligands. Based on this strategy, we have obtained two nanosized chiral {Fe$_{28}$} wheels by the introduction of L- or D-tartrate ligands into an Fe^{3+}/acetate system.[9] Recently, Liu et al. discovered that the nanosized Mo/W oxide wheels can be self-assembled into huge hollow vesicles in aqueous solution with cations acting as "glue" between negatively charged wheels.[10] Following aforementioned works, we postulated that the cations could also play similar roles in self-assembling nanosized {Fe$_{28}$} wheels into huge hollow cages. Furthermore, considering the potential steric hindrance of the acetate ligands in combination with the countercations with {Fe$_{28}$} wheels, the acetate was replaced by the formate in the synthesis. In this work, the introduction of L-tartrate and D-tartrate into the Fe^{3+}/formate system in the presence of a large amount of Na$^+$ cations led to the isolation of two unprecedented protein-sized chiral Fe$_{168}$ cages (Scheme 1) with a NbO-type topology:

$Na_{96}[Na_{24}Fe_{168}(\text{L-Tart})_{96}(\mu_3\text{-O})_{48}(HCOO)_{144}]\cdot 310H_2O$ (**L-Fe$_{168}$**)

$Na_{96}[Na_{24}Fe_{168}(\text{D-Tart})_{96}(\mu_3\text{-O})_{48}(HCOO)_{144}]\cdot 310H_2O$ (**D-Fe$_{168}$**).

Single crystal X-ray diffraction analyses[11] reveal that both compounds contain a cage-like Fe$_{168}$ basic unit, consisting of 6 homochiral wheel-like {Fe$_{28}$} building blocks and 12 cubane-like {Na$_4$} linking units (Scheme 1, Figures 1, S1, and S2). In the Fe$_{168}$ cage, each {Fe$_{28}$} wheel coordinates to four crystallographically identical {Na$_4$} motifs via eight carboxyl ligands. Furthermore, each {Na$_4$} node links to two {Fe$_{28}$} wheels at a right angle, leading to the protein-sized NbO-type Fe$_{168}$ cage (Figures 1, S1, and S2). The dimensions of the ferric cage are ca. 38.7 × 38.7 × 38.7 Å (Figure S1c), and the diameter of the inner spherical cavity is ca. 29.1 Å. In this cage, six {Fe$_{28}$} wheels are equivalent and each of them are composed of 28 hexacoordinated Fe^{3+} centers linked by 8 μ_3-O bridges, 16 tartrate linkers, and 24 formate ligands. The {Fe$_{28}$} wheel contains a cross-like inner cavity with the shortest and longest diameters of ca. 8.5 and 11.5 Å, respectively (its external diameter is ca. 26.5 Å and the thickness is ca. 8.5 Å; Figure S2). Furthermore, each {Fe$_{28}$} wheel can also be viewed as four equivalent {Fe$_7$} fragments connected by four tartrate linkers (Figure S3). In the {Fe$_7$} unit, the central Fe(1) is sandwiched by two {Fe$_3$} fragments (Figure S4). Ultimately, the {Fe$_{28}$} wheels are connected by {Na$_4$} linkers into a 3D NbO-type open framework (Figures 1d and

Scheme 1. Schematic View of the Synthetic Route To Obtain **L-Fe$_{168}$** and **D-Fe$_{168}$** (Fe, O, Na, and C Are Gold, Red, Blue, And Gray Spheres, Respectively)



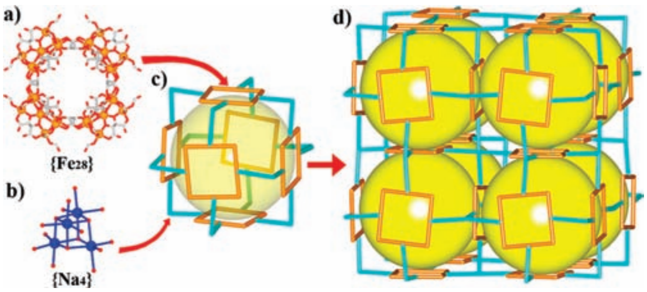


Figure 1. (a) {Fe$_{28}$} wheel; (b) {Na$_4$} linker; (c) NbO-type Fe$_{168}$ cage; (d) 3D NbO-type open framework in **L-** and **D-Fe$_{168}$**.

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S7−S9). The void space of the crystal structure is occupied by Na^+ cations and interstitial water molecules. PLATON analysis shows that the free volume is ~34.5% of the crystal volume (64 428.9 Å^3 out of the 186 999.0 Å^3 per unit cell volume). Thermogravimetric analysis indicates the presence of ca. 310 water molecules in the 3D framework. The chiroptical activities of both enantiomers were determined by circular dichroism (CD) spectroscopy (Figure S10). The magnetic properties of the two enantiomers have also been studied. As expected, they are identical with the error bar of the measurement revealing extremely strong antiferromagnetic interactions between Fe^{3+} spins as already shown in the $\{Fe_{28}\}$ wheel (Figure S11).[9]

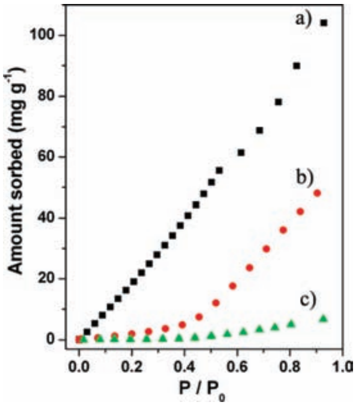

Figure 2. Sorption isotherm of alcohols at 298 K for **L-Fe$_{168}$**: (a) methanol ($P_0 = 168$ mbar), (b) ethanol ($P_0 = 78$ mbar), and (c) 1-butanol ($P_0 = 8.2$ mbar).

The adsorption isotherms of alcohols are measured at 298 K for **L-Fe$_{168}$**. Before the measurement, the crystalline sample was soaked in methanol for 48 h and then evacuated at 308 K to remove the guest solvent molecules. As shown in Figure 2, the amount of methanol sorption increases with a P/P_0 increase. The sorption amount reaches 104 mg/g at $P/P_0 = 0.9$, indicating the methanol molecules enter into the bulk material.[12,13] As for ethanol and 1-butanol, the sorption amounts increase suddenly after $P/P_0 > 0.4$ and reach 48.1 mg/g for ethanol and 6.67 mg/g for 1-butanol at $P/P_0 = 0.9$, respectively. The sorption amounts of alcohols decrease in the order of methanol > ethanol >1-butanol. The X-ray powder diffraction patterns of the as-synthesized, evacuated, and alcohol-exchanged solids are almost identical to the calculated pattern from single-crystal diffraction data (Figure S13). Only diffraction peak intensities and widths show some variations, revealing that the removal of the guest molecules does not lead to a host-framework transformation.[12] Additionally, the alcohol-guest sorption at liquid−solid phase has also been investigated and confirmed by ^{1}H NMR (Figure S14; see Supporting Information).

In summary, the introduction of L- and D-tartrate ligands into the Fe^{3+}/formate/Na^+ system leads to the isolation of a pair of protein-sized enantiomerically pure chiral Fe_{168} cages with a 3D NbO-type open framework that exhibits an alcohol-guest sorption property. Further research will focus on the sorption of other hydrophilic or hydrophobic organic solvent molecules as well as the potential enantioselective separation of racemic solvents.

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Supporting Information Available: X-ray crystallographic files for **L-Fe$_{168}$** and **D-Fe$_{168}$** in CIF format, Experimental Section, additional structural figures, and physical characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystal data at 150(2) K: **L-Fe$_{168}$**: Space group F_{432}, $a = 57.185(3)$ Å, $V = 186\,999(18)$ Å^3, $M = 39\,226.20$, $Z = 4$, $\rho = 1.393$ g m^{-3}, $\mu = 1.384$ mm^{-1}, $F(000) = 78\,664$, Flack parameter $= 0.01(2)$, $R_1(wR_2) = 0.0616$ (0.1430) and $S = 0.960$ for 13 524 reflections with $I > 2\sigma(I)$. **D-Fe$_{168}$**: Space group F_{432}, $a = 57.1261(17)$ Å, $V = 186\,425(10)$ Å^3, $M = 39\,226.20$, $Z = 4$, $\rho = 1.398$ g m^{-3}, $\mu = 1.388$ mm^{-1}, $F(000) = 78\,664$, Flack parameter $= -0.03(2)$, $R_1(wR_2) = 0.0596$ (0.1570) and $S = 1.084$ for 13 870 reflections with $I > 2\sigma(I)$. CCDC 705618 for **L-Fe$_{168}$** and 723962 for **D-Fe$_{168}$**.

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