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Chiral Materials

Enantiomerically Pure Chiral {Fe$_{28}$} Wheels**

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Chirality is a remarkable property that is found in daily life, but it also plays an important role in various functional materials.[1] The introduction of chirality into molecular materials can create, adjust, or change their functionality, inducing potential applications in nonlinear optics, enantioselective catalysis, chiral medicine, and chiral magnetism.[2] An effective strategy to synthesize chiral molecular materials is the use of chiral ligands as structure-directing reagents.[3–5] Many high-dimensional chiral framework materials have been obtained based on this strategy;[3,4] however, nanoscale chiral polynuclear metal complexes are unexplored to date,[5] as most of these chiral aggregates usually crystallize in a racemic mixture or undergo rapid racemization in solution.[5b] Ferric systems represent an important subfamily of polynuclear aggregates, and attract much attention owing to their relevance as model complexes for protein active sites[6] and as molecular species with unusual magnetic properties.[7] To date, a series of polynuclear ferric aggregates with nuclearities including 6, 7, 8, 9, and up to 22, and a very recent {Fe$_{64}$} aggregate have been reported,[8–11] but compounds with chiral features were rarely observed, especially by X-ray diffraction.[12] Numerous synthetic efforts indicate that the preparation of ferric aggregates is highly dependent on the assistance of the alkoxide- and carboxylate-based ligands. We thus postulated that it should be possible to prepare chiral ferric complexes by choosing a ligand containing alkoxide and carboxylate groups along with chiral carbon atoms. Following this strategy, chiral tartaric acid is one of the best candidates as it contains both alkoxide and carboxylate groups. Herein, L-(+)-tartaric acid and D-(−)-tartaric acids have been used to obtain the first two enantiomerically pure ferric chiral aggregates:

$K_2Na_{18}[Fe_{28}(\mu_3\text{-}O)_8(\text{L-(}-\text{)-tart})_{16}(CH_3COO)_{24}]\cdot 29\,H_2O$ (L-**1**)

$K_2Na_{18}[Fe_{28}(\mu_3\text{-}O)_8(\text{D-(}+\text{)-tart})_{16}(CH_3COO)_{24}]\cdot 29\,H_2O$ (D-**1**)

The L-**1** and D-**1** enantiomers were prepared in good yield by the reaction of L-(+)- or D-(−)-tartaric acid with iron(III) nitrate in a pH 4.5 buffer solution. Compounds L-**1** and D-**1** crystallize in the orthorhombic chiral space group I_{222}.[13] Single-crystal X-ray diffraction analyses reveal that the two compounds are enantiomers and have a chiral wheel-type structure (Figure 1 a,b). The anionic ferric wheel $[Fe_{28}(\mu_3\text{-}O)_8(tart)_{16}(CH_3COO)_{24}]^{20-}$, {Fe$_{28}$}, consists of 28 six-coordinate iron(III) centers linked by 8 μ_3-oxido bridges, 16 L-(−)-

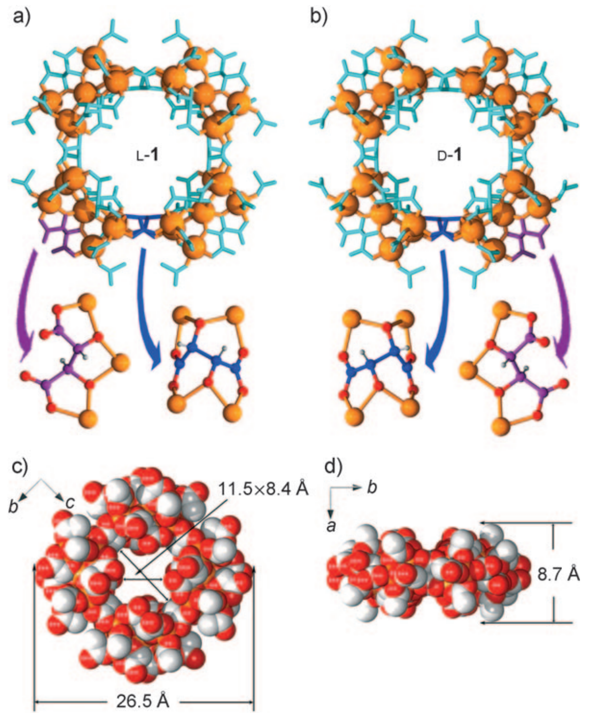

Figure 1. Ball-and-stick representations of a) L-**1** b) D-**1** (upper views; Fe orange spheres, C cyan, hydrogen atoms omitted for clarity) and two coordination modes for L-(−)-tartrate in L-**1** and for D-(+)-tartrate in D-**1** (lower views; O red, H gray). c), d) Space-filling representations of the {Fe$_{28}$} wheel. Fe orange, O red, C gray, hydrogen atoms omitted for clarity.

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or D-(+)-tartrate linkers, and 24 acetate ligands. The {Fe$_{28}$} wheel contains a cross-like inner cavity with the shortest and longest diameters of circa 8.4 Å and 11.5 Å, respectively; its external diameter is about 26.5 Å and the thickness is circa 8.7 Å (Figure 1 c,d). The Fe−O bond lengths are in the range 1.859(7)–2.081(7) Å for L-**1** and 1.857(8)–2.075(8) Å for D-**1**. The {Fe$_{28}$} wheel can also be viewed as four {Fe$_7$} fragments connected by four tartrate linkers (Figure 2).

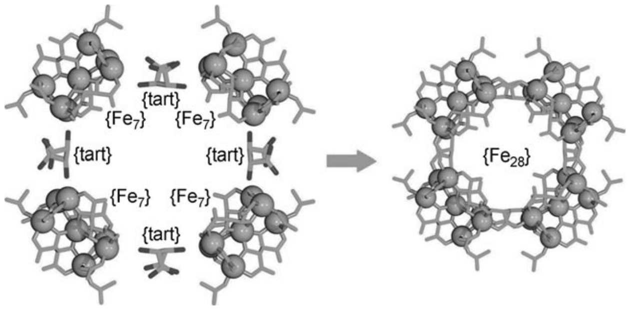

Figure 2. Ball-and-stick representation of the basic building blocks and their connection modes in the {Fe$_{28}$} aggregate. Fe orange, C cyan, O red.

In the {Fe$_7$} unit (Supporting Information, Figure S1 and S2), the central atom Fe(1) is sandwiched by two {Fe$_3$} fragments. It is noteworthy that five tartrate ligands in the {Fe$_7$} moiety adopt two kinds of coordination modes: three act as a tetradentate ligand linking three iron centers of a {Fe$_7$} unit (purple in Figure 1 a,b, and Supporting Information, Scheme S1) and the two others act as a hexadentate ligand connecting four iron centers derived from two different {Fe$_7$} units (blue in Figure 1 a,b). Based on these coordination modes, four {Fe$_7$} moieties are connected by four tartrate ligands into the {Fe$_{28}$} wheel. In the packing arrangement, all of the {Fe$_{28}$} aggregates are parallel to each other and are linked by potassium and sodium ions into a three-dimensional supramolecular framework (Supporting Information, Figure S3 and S4).

To examine the chiroptical activities and stabilities of both enantiomers in solution, the circular dichroism (CD) of compounds L-**1** and D-**1** in a pH 4.5 buffer solution were investigated (Figure 3). The CD spectra of L-**1** and D-**1** are mirror images and demonstrate conclusively that the two compounds are enantiomers. Compared with the CD data of L-(+) and D-(−) tartaric acid (Figure 3, inset), the spectra of L-**1** and D-**1** exhibit totally different Cotton effects. In fact, the tartrate-induced L-**1** and D-**1** complexes show optical rotation that is opposite to free L-(+)- and D-(−)-tartaric acid. Furthermore, the spectra of L-(+) and D-(−)-tartaric acid molecules exhibit only a single Cotton effect at 244 nm, whereas the spectra of L-**1** and D-**1** exhibit Cotton effects at 245, 298, 448, 463, and 554 nm. Such induced circular dichroism further confirms that the chirality of the tartaric acid ligands has been transferred to the whole {Fe$_{28}$} aggregates.[14] The CD and UV/Vis spectra (Supporting Information, Figure S5 and S6) of the two compounds do not change with time, indicating that both compounds are stable in the pH 4.5 buffer solution.

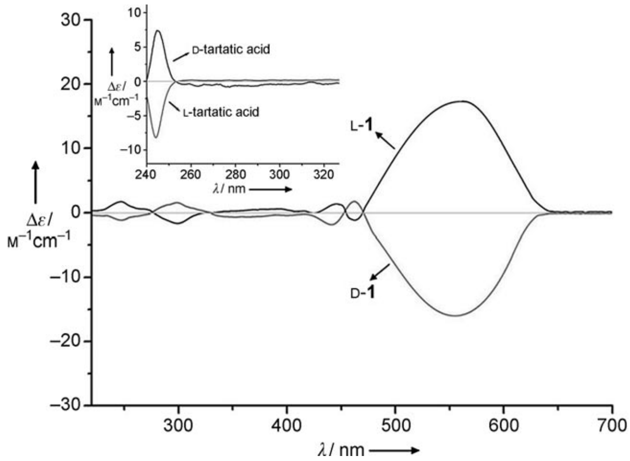

Figure 3. CD spectra of L-**1** and D-**1** in pH 4.5 in a 0.4 M NaOAc/HOAc buffer solution. Inset: CD spectra of L-(+)- and of D-(−)-tartaric acid.

The Mössbauer spectrum of a crystalline sample of L-**1** at room temperature exhibits a single quadrupole doublet with an isomer shift of 0.39 mm s^{-1} and a quadrupole splitting of 0.88 mm s^{-1} (Supporting Information, Figure S12). These characteristics are the unambiguous signature of high-spin iron(III) ions.[9e] The solid-state magnetic behavior of L-**1** and D-**1** have also been investigated and are identical within the margin of error for the two enantiomerical forms (Supporting Information, Figure S13 and S14). At room temperature, the χT products are 34.0 and 32.8 cm^3 K mol^{-1} for L-**1** and D-**1**, respectively, which are much lower than the expected value (122 cm^3 K mol^{-1}) for the presence of 28 uncoupled iron(III) ions ($S = 5/2$, $C = 4.375$ cm^3 K mol^{-1}) taking into account an g value of 2.0. This result suggests the presence of strong antiferromagnetic interactions between iron(III) spins, probably within the {Fe$_7$} core. This assumption is confirmed by the fast decrease of the χT product with a lowering of the temperature. At 1.8 K, χT reaches 0.2 and 1.4 cm^3 K mol^{-1} for L-**1** and D-**1** respectively, which is in agreement with an $S = 0$ ground state for the {Fe$_{28}$} aggregates. The field dependence of magnetization at low temperatures confirms the presence of strong antiferromagnetic interaction and a singlet ground state, as no saturation and a low magnetization value are observed.

In summary, we have obtained the first two enantiomerically pure chiral ferric aggregates using chiral tartrate ligands. The CD spectra of D-**1** and L-**1** reveal a significant induced optical activity of the paramagnetic {Fe$_{28}$} wheels. The successful synthesis of the largest homochiral ferric aggregates provides not only new examples of enantiomerically pure architectures, but also suggests a new route for the design and synthesis of chiral polynuclear metal complexes with functionalities induced by chirality.

Experimental Section

L-**1**: An $Fe(NO_3)_3 \cdot 6H_2O$ aqueous solution (1 M, 8 mmol, 8 mL) was diluted in a sodium acetate/acetic acid buffer solution (pH 4.5, 0.4 M NaOAc/HOAc, 30 mL) to yield solution A. An aqueous solution of $Gd(NO_3)_3 \cdot 6H_2O$ (0.1 M, 0.8 mmol, 8 mL,) and L-(+)-tartaric acid

(4.6 mmol, 0.70 g) were added in another NaOAc/HOAc buffer solution (pH 4.5, 0.4 M, 30 mL), and the mixture was boiled for 10 min to yield solution B. Solution B was then added to solution A, and an aqueous solution of K_2CO_3 (2 M, 6 mL) was added to the mixture of A and B. The resulting solution was heated at 95 °C for 12 h and then filtered. Brown block crystals of L-**1** were isolated after one week (yield 72% based on Fe). Elemental analysis (%) calcd for $C_{112}H_{162}Fe_{28}K_2Na_{18}O_{181}$: C 20.8, H 2.53, Fe 24.2, K 1.21, Na 6.41; found: C 20.6, H 2.31, Fe 23.9, K 1.01, Na 6.51. IR (KBr pellet): $\tilde{\nu} =$ 1655 (m), 1559 (m), 1419 (m), 1374 (m), 1106 (w), 1033 (m), 976 (m), 806 (m), 669 (s), 617 (w), 545 (w) cm^{-1}.

D-**1** was prepared in a similar fashion to L-**1** except that D-(−)-tartaric acid was used instead of L-(+)-tartaric acid (yield 70% based on Fe). Elemental analysis (%) calcd for $C_{112}H_{162}Fe_{28}K_2Na_{18}O_{181}$: C 20.8, H 2.53, Fe 24.2, K 1.21, Na 6.41; found: C 20.5, H 2.66, Fe 23.8, K 1.06, Na 6.37. IR (KBr pellet): $\tilde{\nu} = 1653$ (m), 1557 (m), 1421 (m), 1373 (m), 1106 (w), 1035 (m), 976 (m), 806 (m), 668 (s), 619 (w), 546 (w) cm^{-1}.

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[13] Crystal data: L-**1**: $C_{112}H_{162}Fe_{28}K_2Na_{18}O_{181}$, $M_r = 6460.24$, orthorhombic, space group I_{222}, $a = 18.189(4)$, $b = 25.046(5)$, $c = 33.451(7)$ Å, $V = 15239(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.408\ g\,cm^{-3}$, R_1 (wR_2) = 0.0696 (0.1786), Flack parameter = 0.01(2) and $S =$ 0.931 for 13206 reflections with $I > 2\sigma(I)$. D-**1**: $C_{112}H_{162}Fe_{28}K_2Na_{18}O_{181}$, $M_r = 6460.24$, orthorhombic, space group I_{222}, $a = 18.168(4)$, $b = 25.041(5)$, $c = 33.018(7)$ Å, $V =$ 15022(5) Å^3, $Z = 2$, $\rho_{calcd} = 1.428\ g\,cm^{-3}$, R_1 (wR_2) = 0.0792

(0.2014), Flack parameter = 0.02(3) and $S = 0.987$ for 12789 reflections with $I > 2\sigma(I)$. Data collection was performed at 150(2) K on a Rigaku R-axis Rapid IP diffractometer with graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å) and an image plate. The structures of L-**1** and D-**1** were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 crystallographic software package. CCDC-695269 and CCDC-695270 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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