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Chiral Hexanuclear Ferric Wheels

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S *Supporting Information*

ABSTRACT: The homochiral iron(III) wheels $[Fe_6\{(S)\text{-pedea}\}_6Cl_6]$ and $[Fe_6\{(R)\text{-pedea})\}_6Cl_6]$ [(*R*)- and (*S*)-**2**; pedea = phenylethylaminodiethoxide] exhibit high optical activities and antiferromagnetic exchange. These homochiral products react with each other, producing the centrosymmetric, crystallographically characterized $[Fe_6\{(S)\text{-pedea}\}_3\{(R)\text{-pedea}\}_3Cl_6]$ diastereomer [(*RSRSRS*)-**2**]. ^{1}H NMR and UV–vis studies indicate that exchange processes are slow in both homo- and heterochiral systems but that, upon combination, the reaction between (*R*)- and (*S*)-**2** occurs quickly.

Polynuclear coordination compounds attract great research attention because of their relevance to bioinorganic chemistry,[1] their potential as nanoscale magnets,[2] and the inherent challenge of controlling their formation.[3] An important subclass of these materials are the many metallacycles formed by transition metals and alcoholato/carboxylato ligands, spanning nuclearities from 6 to 84 and exhibiting a wide range of magnetic characteristics.[4−9] For iron, a large family of antiferromagnetic (AF) hexanuclear wheels[5,6] is complemented by several cyclic heptanuclear single-molecule magnets (SMMs)[7] and larger metallacycles and cages containing up to 64 iron nuclei;[1c,8] yet so far only one system has been reported incorporating chiral ligands.[9]

Motivated by recent interest in chiral magnetic materials,[10,11] we are using ligands based on 1-phenylethylamine to introduce optical activity to magnetic coordination compounds.[12] Here, the *N,N*-diethanolato derivatives (*R*)- and (*S*)-pedea (pedea = phenylethylaminodiethoxide; Figure 1) form the first homochiral $\{Fe_6\}$ wheels. As well as demonstrating strong chirality transfer, the chiral ligands enable observation (by isolation/detection of diastereomers[13]) of a sterically driven rearrangement reaction between wheels of opposite chirality.

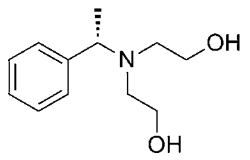

Figure 1. (*S*)-1-phenylethylamine-derived ligand (*S*)-H_2pedea [(*S*)-**1**] in its protonated form.

The reaction of enantiomerically pure ligands with anhydrous $FeCl_3$ produces the $[Fe_6(\text{pedea})_6Cl_6]$ ferric wheels (*R*)- and (*S*)-**2** in yields of up to 35% (see the Supporting Information, SI). Formation of these cyclic products was confirmed by mass spectrometry, elemental analysis, ^{1}H NMR, IR, UV–vis, and circular dichroism (CD). However, crystals suitable for study by X-ray diffraction were not obtained. Ultimately, cocrystallization of (*R*)- and (*S*)-**2** from dichloromethane (DCM)/tetrahydrofuran (THF) mixtures produced measurable crystals of the centrosymmetric diastereomer (*RSRSRS*)-$[Fe_6(\text{pedea})_6Cl_6]$ [(*RSRSRS*)-**2**; yield 7%], indicating that the homochiral *R* and *S* wheels undergo a racemizing rearrangement reaction. (*RSRSRS*)-**2** can be obtained in higher yields (13% overall) by the direct reaction of the ligand racemate (*R*/*S*)-**1** with $FeCl_3$. Initially, a ca. 44% yield of crude racemic (*R*/*S*)-**2** is obtained, shown by ^{1}H NMR to contain a mixture of heterochiral diastereomers (see the SI), from which (*RSRSRS*)-**2** alone crystallizes.

(*RSRSRS*)-**2**·2DCM·9THF crystallizes in $P\bar{1}$, with the *S* and *R* stereocenters alternating around the ring (Figure 2a). Consequently, the wheel has one face presenting exclusively *S* stereocenters and another presenting exclusively *R* stereocenters (Figure 2b). All six Fe^{III} centers have a distorted octahedral geometry comprising one N donor, four μ_2-alkoxo O donors, and a chloro ligand. Importantly, Fe⋯Fe distances [avg. 3.218(1) Å] and magnetically relevant Fe−O−Fe angles [106.1(1)−108.0(1)°] are larger than those in directly comparable published species (ca. 3.16−3.19 Å and 105°).[5,6e]

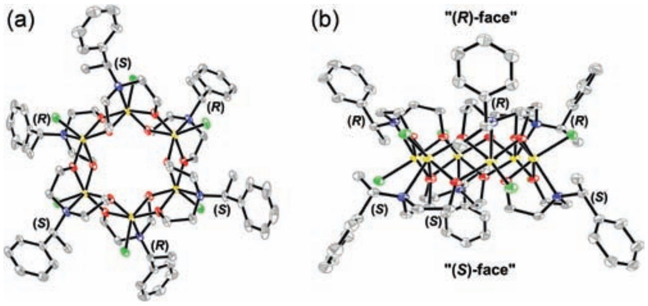

Figure 2. Structure of (*RSRSRS*)-**2** (ADP ellipsoids are drawn at 30% probability level). (a) View showing the alternation of *R* and *S* stereocenters around the wheel. (b) Resulting "(*R*)-face" and "(*S*)-face". Color code: Fe, yellow; C, gray; O, red; N, blue; Cl, green; H, omitted.

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This ring expansion appears to alleviate a steric clash as the chloro ligands in (*RSRSRS*)-**2** fit tightly between the methyl and CH groups of adjacent pedea ligands. The (*R*/*S*)-pedea alternation also helps to reduce steric repulsion as the closest pedea···Cl contact is made by the CH group [H5···Cl1 ≈ 2.68 Å; C5···Cl1 = 3.274(4) Å]. Inverting the stereochemistry of any ligand would switch the proton and methyl positions, causing an even closer contact between the bulkier methyl and chloro groups. Evidence for the influence of steric repulsion on this system is also seen in the consistently higher yields obtained for crude (*R*/*S*)-**2** compared to the homochiral wheels (see the SI for details).

UV−vis measurements on the $\{Fe_6\}$ wheels in DCM show a strong absorption peaking at $\lambda \approx 280$ nm in the homochiral species and 297 nm in (*RSRSRS*)-**2** (Figure S3 in the SI). This is assigned to pedea N/O → Fe^{III} ligand-to-metal charge transfer (LMCT). Therefore, the change in λ_{max} between the homochiral species and (*RSRSRS*)-**2** suggests differences in their Fe^{III} coordination spheres, caused by the steric factors discussed above. CD measurements on (*R*/*S*)-**2** indicate that the pedea N,O,O chelator strongly transfers chirality to the Fe^{III} center due to observation of very strong Cotton effects at wavelengths where the ligands are inactive (Figure 3). These Cotton effects at around 275 and 350 nm, associated with LMCT processes, are among the highest peak molar ellipticities ($\Delta\varepsilon = \pm 17$ mol^{-1} L cm^{-1}) reported for a chiral magnetic compound.[14]

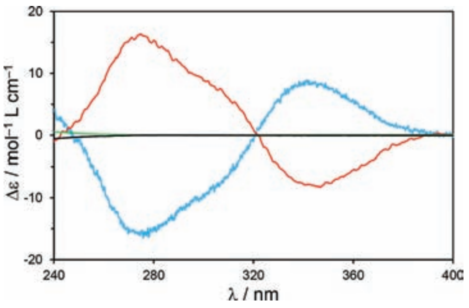

Figure 3. CD spectra of the H_2pedea ligands (*S*)-**1** (green) and (*R*)-**1** (black) and the homochiral $[Fe_6(pedea)_6Cl_6]$ wheels (*S*)-**2** (red) and (*R*)-**2** (light blue) in DCM at 298 K.

The solid-state magnetic properties of (*S*)-**2** and (*RSRSRS*)-**2** are very similar, showing AF behavior between 2.0 and 290 K ($B = 0.1$ T) and $S = 0$ ground states (Figure 4). In both, the room temperature $\chi_m T$ values (11.84 and 12.38 cm^3 K mol^{-1}) are well below the spin-only value of 26.25 cm^3 K mol^{-1} for six noninteracting Fe^{3+} ions, consistent with strong AF coupling. This is typical of $\{Fe_6\}$ wheels, whose AF exchange energies depend on Fe−O−Fe angles.[6] The low temperature increases in χ_m can be accounted for by monomeric $S = {}^5/_2$ impurities. An isotropic Heisenberg-type exchange model implemented in *CONDON 2.0*[15] (including an impurity level ρ; see the SI) gives $J = -14.34$ cm^{-1}, $g_{iso} = 1.998$, and $\rho = 1.0(3)\%$ for (*S*)-**2**. For (*RSRSRS*)-**2**, $J = -13.71$ cm^{-1}, $g_{iso} = 1.998$, and $\rho = 2.0(3)\%$. The coupling is considerably larger than the value of -8.1 cm^{-1} reported for a diethanolamine-based $\{Fe_6\}$ wheel,[6e] consistent with the extended Fe···Fe distances and wider Fe−O−Fe angles in (*RSRSRS*)-**2**. The slightly stronger AF coupling for (*S*)-**2** therefore suggests that its Fe···Fe distances and Fe−O−Fe angles are, on average, even larger than those of (*RSRSRS*)-**2**, a consequence of the increased pedea/Cl steric repulsions expected in the homochiral compound.

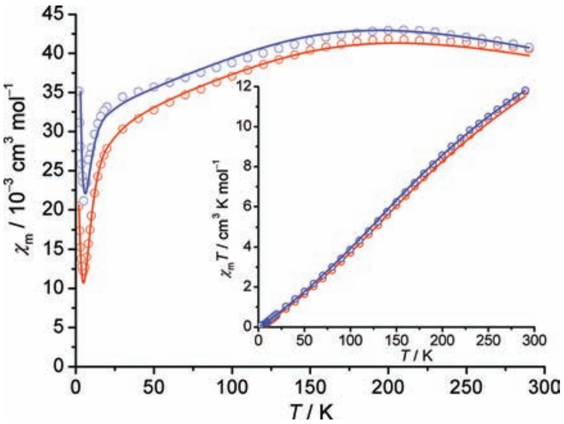

Figure 4. Temperature dependence of the molar susceptibility χ_m. Inset: $\chi_m T$ vs T for (*S*)-**2** (red) and (*RSRSRS*)-**2** (blue). Experimental data: circles. Least-squares fits: solid lines.

Elongated Fe···Fe distances are also likely to be responsible for the reaction of (*R*)- and (*S*)-**2** to form heterochiral products, including (*RSRSRS*)-**2**. We followed the reaction of (*R*)- and (*S*)-**2** by UV−vis in DCM, exploiting the ca. 10 nm red shift in λ_{max} between the homochiral species and crude (*R*/*S*)-**2** (see the SI). Over ca. 6 h, λ_{max} red-shifted by 4 nm, and the peak absorbance fell by ca. 12% (8% in the first 60 min), suggesting a reaction between the two wheels to form heterochiral species, with destructive side reactions causing a decrease in the absorbance. (*S*)-**2** alone showed no red shift and a much smaller absorbance decrease (<2% after 4.5 h), showing that the changes in the mixed solution do not simply result from spontaneous decomposition.

Previous ^1H NMR studies on $\{Fe_6\}$ wheels indicated fully associated species, with no evidence for exchange processes.[6a,b] Our ^1H NMR measurements confirm that exchange processes in the heterochiral wheels are slow on the NMR time scale (Figures S5−S7 in the SI): spectra of the diastereomerically mixed (*R*/*S*)-**2** and diastereomerically pure (*RSRSRS*)-**2** in CD_2Cl_2 are clearly different from each other, and the peaks in (*R*/*S*)-**2** do not coalesce upon heating to 65 °C in C_6D_6. In the case of rapid exchange, the spectra of (*RSRSRS*)-**2** and the mixture (*R*/*S*)-**2** would be the same. Furthermore, over the course of 14 days, the spectrum of (*R*/*S*)-**2** shows little change in the relative intensities of the peaks (and hence the mixture of diastereomers present), indicating that the mixture is equilibrated, or that exchange reactions between the mixture of species are very slow. ^1H NMR measurements on (*S*)-**2** in CD_2Cl_2 show 11 resonances at 293 and 308 K, indicating that (*S*)-**2** is mostly associated with the NMR time scale (Figure 5): a [Fe(pedea)Cl] monomer could present a maximum of nine signals. Therefore, exchange processes also appear to be slow in the homochiral wheels. Upon cooling to 263 K, the signals downfield of 8 ppm broaden while other resonances sharpen to reveal several additional small shoulders. This sharpening may be explained by slowing of the molecular motions of the wheel and by slowing or elimination of any minor ligand and/or monomer exchange processes. Further cooling results in paramagnetic signal broadening as the maximum in χ_m (at around 190 K) is approached.

Combining the ^1H NMR results, we conclude that (i) any exchange processes are very slow on the NMR time scale and

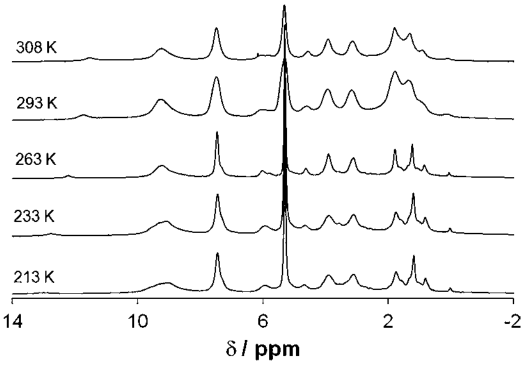

Figure 5. Variable-temperature ^{1}H NMR spectra of (*S*)-**2** at 400 MHz and 8.8×10^{-3} M in CD_2Cl_2.

both hetero- and homochiral wheels are largely associated; and (ii) (*R*)- and (*S*)-**2** are clearly disfavored because of their absence from the (*R*/*S*)-**2** mixture. Therefore, the rapid changes observed by UV−vis upon mixing (*R*)- and (*S*)-**2** suggest that dissociated fragments, present in a low concentration, attack the sterically destabilized homochiral wheels, producing heterochiral products. The slow changes observed thereafter indicate that equilibration of the initial heterochiral products to the mixture seen in (*R*/*S*)-**2** is slow.

In summary, we have synthesized the first homochiral hexanuclear ferric wheels using easily accessible chiral diethanolamine ligands. The steric bulk of the ligand results in a strong chirality transfer to the homochiral wheels but also destabilizes them so that they react with each other to produce mixed diastereomers, even though exchange processes are slow on the NMR time scale. This provides the first evidence that $\{Fe_6\}$ wheels can undergo exchange processes in solution and demonstrates the potential of chiral ligands not only for the synthesis of multiproperty materials, but also to monitor the self-assembly processes in coordination clusters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, further spectra, a synthetic and structural discussion, and a CIF file for (*RSRSRS*)-**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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