

Ferromagnetically Coupled Chiral Cyanide-bridged $\{\text{Ni}_6\text{Fe}_4\}$ Cages

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Enantiomeric, ferromagnetically coupled decanuclear $\{\text{Ni}_6\text{Fe}_4\}$ cages with adamantane-like cores were synthesized around templating tetraethylammonium cations, as shown by crystallographic analysis and CSI-MS, and their homochiral nature was confirmed by circular dichroism measurements.

In recent years functional molecules have helped to underpin dramatic developments in the field of nano-scale materials. Nano-capsules are a class of molecular materials in which the functionality can be precisely defined (especially in the case of supramolecular inclusion complexes / sensors), as it is possible to engineer specific spaces for reactions to occur, under the dynamic conditions associated with host/guest systems.[1-4] Polynuclear transition metal complexes are interesting potential candidates to form cage compounds as the cage itself may be endowed with a large spin ground state and negative magnetic anisotropy resulting in quantum magnetism that could give rise to physical phenomena.[5] It goes without saying that design plays a critical role in the development of these clusters, particularly as we are now gaining an understanding of how precise control of magnetic properties can be achieved through subtle alterations in ligand structure.[6] The introduction of chirality into a system can result in interesting optical and magneto-optical properties as well as ferroelectricity, as a result of the asymmetric dipole moment.[7,8] Further, in the field of chiral magnetism, unique properties such as magneto-chiral dichroism have been reported,[9] and the synergy between multiple physical properties may be the key to developing novel functionality.[10] To date, we have reported large (nano-scale) molecular-based magnetic systems, and their quantum properties and multi-stabilities have been discussed.[11] In order to combine the physical properties derived from the introduction of ligands that allow chiral complexes and cages to form, with molecular magnetism, we must focus on the rational synthesis of chiral complexes with high spin ground states, where all metal centers have the same absolute configuration with respect to their coordination environment. Herein, we report the syntheses, structures and magnetic properties of two ferromagnetically coupled decanuclear complexes with chiral cage structures, obtained in the course of synthesising functional materials which exhibit both magnetic properties and chirality.

The reaction of 2-pyridine carbaldehyde, R-phenyl ethyl amine and nickel chloride hexahydrate in a 2:2:1 ratio in methanol gives rise to the chiral nickel precursor

complex $[\text{Ni}(\text{L}^{\text{R}})_2\text{Cl}_2]$ (**1R**, $\text{L}^{\text{R}} = N$ -(2-pyridylmethylene)-(R)-1-phenylethylamine) and the chiral $\{\text{Ni}_6\text{Fe}_4\}$ decanuclear complex, $(\text{Et}_4\text{N})[\text{Ni}(\text{L}^{\text{R}})_2]_6[\text{Fe}(\text{CN})_6]_4(\text{PF}_6)\cdot 22\text{H}_2\text{O}\cdot 26\text{CH}_3\text{OH}$ (**2R**) was obtained by the reaction of **1R** with $(\text{Et}_4\text{N})_3[\text{Fe}(\text{CN})_6]$ and NH_4PF_6 in $\text{MeOH}/\text{H}_2\text{O}$. The corresponding enantiomers **1S** and **2S** were prepared by the same method using L^{S} ($\text{L}^{\text{S}} = N$ -(2-pyridylmethylene)-(S)-1-phenylethylamine) in place of L^{R} .

The structure of **1R**, which was obtained by recrystallization, contains a dinuclear unit and a mononuclear unit, and can be described as $[\text{Ni}_2\text{Cl}_2(\text{L}^{\text{R}})_4][\text{NiCl}_2(\text{L}^{\text{R}})_2]\text{Cl}_2\cdot 3\text{MeOH}$ (Figure 1S). Each nickel ion adopts an octahedral coordination environment, coordinated by four nitrogen atoms from two bidentate L^{R} ligands and two chloride ions. There are π - π stacking interactions between the pyridyl and phenyl rings of the two chiral ligands. Consequently, all nickel ions have Λ -type coordination geometry. Likewise, when L^{S} was used, a homo chiral **1S** complex with Δ -type configuration was obtained. Both **1R** and **1S** crystallized in the chiral space group, $P1$, as confirmed by the Flack parameters; 0.009(8) for **1R** and 0.000(11) for **1S**, respectively.

The structure of the chiral decanuclear $\{\text{Ni}_6\text{Fe}_4\}$ cage **2R** derived from the homochiral precursor **1R** is shown in Figure 1. Four nitrogen atoms from two ligand molecules and the nitrogen atoms from two cyano groups coordinate to the nickel ions, resulting in octahedral coordination environments. The $[\text{Ni}(\text{L}^{\text{R}})_2]$ units are connected to the $[\text{Fe}(\text{CN})_6]^{3-}$ units via the nitrogen atoms of *fac*- CN^- ligands, so that each nickel center is associated with two iron ions, and each iron center has bridges to three nickels. **2R** consists of six $[\text{Ni}(\text{L}^{\text{R}})_2]^{2+}$ and four $[\text{Fe}(\text{CN})_6]^{3-}$ units to form a neutral decanuclear cyanide-bridged cage with an adamantane-like metal arrangement. It is worthy to note that the adamantane-like motif is a new variation among reported discrete cyanide-bridged clusters.[12] All six nickel ions exhibit identical Λ -type absolute configuration as in **1R** due to the π - π stacking between neighboring ligands. One tetraethylammonium cation is captured by the cage as a template and one hexafluorophosphate ion exists in the lattice as a counter anion. The intracluster separations between nickel and iron ions range from 5.030 to 5.070 Å, and the shortest metal-metal intermolecular distance is 10.454 Å between Ni ions. When using the homochiral enantioisomer nickel complex **1S**, the corresponding homochiral **2S** decanuclear complex with Δ -type nickel configuration was formed (Figure S2). These absolute structures were confirmed on the basis of the Flack parameters; 0.09(2) for **2R** and 0.057(17) for **2S**. The structural incarceration of the templating tetraethylammonium cation is confirmed by CSI-MS measurements carried out at 20 °C, which show that the cage exists as a dication in solution with the formula $[(\text{Et}_4\text{N})\text{X}[\text{Ni}(\text{L}^{\text{S}})_2]_6[\text{Fe}(\text{CN})_6]_4]^{2+}$ for both homochiral species **2R** and **2S**, where X = H, Na,

K (Figure 2 and S3).[13]

Similar synthetic methods have been used to generate numerous cyanide-bridged networks using bidentate diamine ligands.[14] For example, two-dimensional bimetallic networks $[\text{Ni}(\text{diamine})_2]_2[\text{Fe}(\text{CN})_6]\text{X}$ (diamine = 1,2-propanediamine or 1,1-dimethylethylenediamine, X = Cl^- , ClO_4^- , PF_6^-), were synthesized by almost the same synthetic method as the present compounds with the exception of the ligand and the base used. It is suggested that the chiral bidentate ligands L^{S} and L^{R} stabilize a cis-form mononuclear intermediate in solution due to their π - π stacking in the synthesis of **2R** and **2S**, thus disfavoring the formation of extended network structures.

Magnetic susceptibility measurements for a powdered sample of **2R** were performed in the temperature range of 1.8 – 300 K. The $\chi_{\text{m}}T$ value at 300 K is 9.84 emu mol⁻¹ K, which is larger than the value expected for six uncorrelated Ni(II) ions and four low-spin Fe(III) ions (7.5 emu mol⁻¹ K, $g = 2.00$). The $\chi_{\text{m}}T$ values gradually increased as the temperature was lowered, reaching a maximum value of 34.81 emu mol⁻¹ K at 2.2 K. This behaviour is an indication that the magnetic interactions between the metal ions are ferromagnetic, as expected due to the orthogonality of the e_{g} magnetic orbitals of the Ni(II) ions and the $t_{2\text{g}}$ magnetic orbitals of the low-spin Fe(III) ions. The Curie–Weiss plot gave a positive Weiss constant ($C = 9.67$ emu mol⁻¹ K and $\theta = +5.11$ K in the range of 50-300K), which suggested relatively strong ferromagnetic interactions in operation between metal ions. Plots of the magnetization data at 1.8 K as a function of the applied magnetic field up to 5 T are shown in Figure 3 (inset). The $M/N\beta$ values increased with increasing magnetic field strength, and did not show saturation up to 5 T, which corresponds to the existence of zero-field splitting due to the low structural symmetry derived from the adamantane-like metal arrangement. The value of magnetization at 5 T is close to the expected value for $S_{\text{T}} = 8$. To examine the nature of the ground states and zero-field splitting, variable field magnetization measurements were carried out in 1-5 T fields in the range of 1.8-4.0 K (Figure S4). The nonsuperposition of the isolated lines confirms the existence of significant zero-field splitting due to the molecular structure having pseudo tetrahedral symmetry. The reduced magnetization data in the 1.8-2.4 K and 2-5 T ranges were fitted assuming a $S_{\text{T}} = 8$ ground state with $g = 2.00$ and $D/k_{\text{B}} = -0.28$ K for **2R**. The Δ -type enantiomer **2S** shows similar ferromagnetic interactions (Figures S5,S6), which are confirmed by the positive Weiss constant ($C = 10.04$ emu mol⁻¹ K and $\theta = +4.54$ K in the range of 50-300K) and the magnetization behaviour (reduced magnetization data were fitted with $S_{\text{T}} = 8$, $g = 2.00$ and $D/k_{\text{B}} = -0.29$ K). To confirm the sign and magnitude of the D value, high-field EPR measurements at low temperature will be required.

UV-vis spectra in acetonitrile for both **2R** and **2S** were collected, showing absorption peaks at 900 nm and 415 nm, which were assigned to the $d-d$ transitions of Ni(II) ions and charge transfer from cyanide to Fe(III) centers, respectively (Figure S7). Circular dichroism measurements for **2R** and **2S** were performed in acetonitrile and KCl pellets (Figure 4 and S8). Well-defined peaks confirm the enantiomeric nature of these complexes. **2R** and **2S** gave mirror-symmetrical CD spectra, providing evidence of the homochiral nature of both.

In conclusion, we have obtained novel homochiral decanuclear nickel-iron cyanide bridged complexes with an $S_T = 8$ ground state due to ferromagnetic interactions between nickel and iron ions. The homochiral nature of the structures was confirmed crystallographically by the Flack parameters and through CD spectrometry. Various combinations of other transition metal ions and polycyanometallates with chiral ligands, which can induce absolute structures, may lead to multifunctional nanoclusters displaying both chirality and interesting magnetic properties. Moreover, specific cage structures may lead to selective-recognition of chiral molecules and the magnetic field effect on the host/guest complexes will be investigated.

Notes and references

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$[\text{NiCl}_2(\text{L}^{\text{R}})_2]$ (**1R**) : $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (3.56 g, 15 mmol) in methanol (25 ml) was added to 2-pyridine carbaldehyde (3.21 g, 30 mmol) and R-phenyl ethyl amine (3.64 g, 30 mmol) in methanol (50 ml). The resulting light green solution was allowed to evaporate and crystalline green solid $[\text{NiCl}_2(\text{L}^{\text{R}})_2]$ (**1R**) formed. Yield 8.434 g (92 %). Since the resulting green precipitate had deliquescent, the dried precipitate was used for the following syntheses of **2R**. Light-green square plates were recrystallized from

methanol by ether diffusion. Anal. calcd. (found) for (C₈₄H₁₀₄N₁₂Cl₆Ni₃O₁₀) : C, 55.11 (55.36); H, 5.73 (5.71); N, 9.18 (9.10).

[[NiCl₂(L^R)₂] (**1S**): **1S** was obtained by the same synthetic approach as **1R** with L^S in place of L^R. Yield 8.711 g (92 %). Anal. calcd. (found) for (C₈₄H₁₁₀Cl₆N₁₂Ni₃O₁₃): C, 53.53 (53.34); H, 5.88 (5.76); N, 8.92 (8.90).

(Et₄N)[Ni(L^R)₂]₆[Fe(CN)₆]₄(PF₆)·22H₂O·26CH₃OH (**2R**) : A methanol-H₂O mixed solution (20 ml) of **1R** (55 mg) and NH₄PF₆ (64 mg, 0.4 mmol) was diffused to (Et₄N)₃[Fe(CN)₆]₄ (60 mg, 0.1 mmol) in methanol (20 ml) at 5 °C and light-brown hexagonal plates of (Et₄N)[Ni(L^R)₂]₆[Fe(CN)₆]₄(PF₆)·22H₂O (**2R**) were obtained. Yield ca. 90%. Anal. calcd. (found) for C₂₀₀H₁₇₆N₄₉F₆P₁Fe₄Ni₆·22(H₂O): C, 54.81 (54.18); H, 5.06 (5.10); N, 15.66 (15.85).

(Et₄N)[Ni(L^S)₂]₆[Fe(CN)₆]₄(PF₆)·22H₂O·28CH₃OH (**2S**): obtained by the same synthetic approach as **2R**, but using **1S** instead of **1R**. Yield ca. 90 %. Anal. calcd. (found) for C₂₀₀H₁₇₆N₄₉F₆P₁Fe₄Ni₆·22(H₂O) : C, 54.81 (54.54); H, 5.06 (5.01); N, 15.66 (16.02).

X-ray structural analysis of **1R**: light-green square plates, 0.40×0.40×0.32 mm³, C₈₇H₉₆N₁₂Cl₆Ni₃O₃, M = 1746.53, triclinic, *P*1 (No.1), *T* = 200 K, *a* = 10.3057(17), *b* = 14.806(2), *c* = 15.877(3), *α* = 107.701(2), *β* = 107.261(2), *γ* = 99.251(2), *V* = 2118.6(6) Å³, *Z* = 1, *D*_{calcd.} = 1.369 gm⁻³, final *R*1 = 0.0273 (*I* > 2σ(*I*)), *wR*2 = 0.0721 (all data), GOF = 1.024, Flack parameter = 0.009(8). Non-H atoms were refined anisotropically for all data sets. H atoms were added with ideal geometry.

X-ray structural analysis of **1S**: light-green square plates, 0.50×0.20×0.18 mm³, C₈₇H₉₆N₁₂Cl₆Ni₃O₃, M = 1746.53, triclinic, *P*1 (No.1), *T* = 200 K, *a* = 10.3220(17), *b* = 14.819(3), *c* = 15.883(3), *α* = 107.650(3), *β* = 107.289(2), *γ* = 99.278(3), *V* = 2124.6(6) Å³, *Z* = 1, *D*_{calcd.} = 1.365 gm⁻³, final *R*1 = 0.0385 (*I* > 2σ(*I*)), *wR*2 = 0.0908 (all data), GOF = 1.001, Flack parameter = 0.000(11).

X-ray structural analysis of **2R**: brown hexagonal plates, 0.50×0.50×0.05 mm³, C₂₃₁H₃₃₂F₄Fe₄N₄₉Ni₆O₄₁P₆, M = 4362.48, trigonal, *P*3 (No.143), *T* = 200 K, *a* = 19.567(5), *c* = 35.123(13), *V* = 11646(6) Å³, *Z* = 2, *D*_{calcd.} = 1.460 gm⁻³, final *R*1 = 0.0811 (*I* > 2σ(*I*)), *wR*2 = 0.1979 (all data), GOF = 0.875, Flack parameter = 0.09(2). HKL file was processed with SQUEEZE to eliminate disordered solvent molecules for **2R** and **2S**.

X-ray structural analysis of **2S**: brown hexagonal plates, 0.50×0.50×0.05 mm³, C₂₃₃H₃₄₀F₆Fe₄N₄₉Ni₆O₄₃P, M = 5236.17, trigonal, *P*3 (No.143), *T* = 200 K, *a* = 19.574(3), *c* = 35.075(9), *V* = 11638(4) Å³, *Z* = 2, *D*_{calcd.} = 1.494 gm⁻³, final *R*1 = 0.0684 (*I* > 2σ(*I*)), *wR*2 = 0.1556 (all data), GOF = 0.780, Flack parameter = 0.057(17).

CCDC 756354, 756355, 756356, 756357 for **1R**, **1S**, **2R**, **2S** respectively.

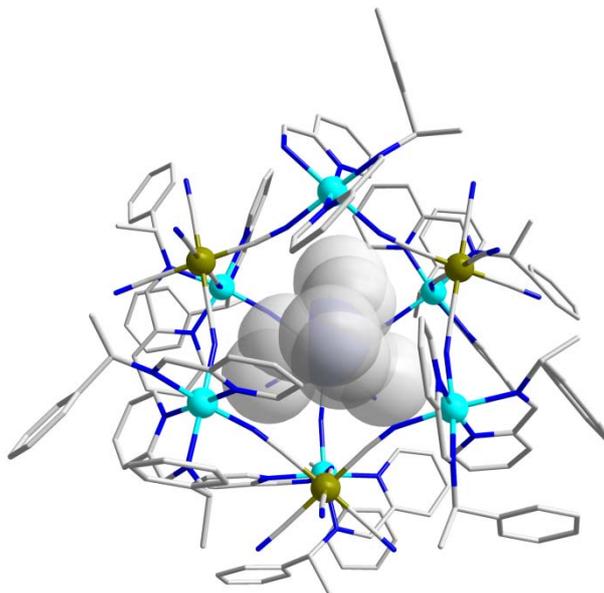
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Graphical Abstract



Chiral Cages: Two enantiomerically pure decanuclear mixed metal R/S- $\{\text{Ni}_6\text{Fe}_4\}$ cage clusters, comprising cyano-bridged nickel (II) and iron (III) ions in an adamantane-like core arrangement with capping chiral ligands, were synthesized. Their homochiral nature was confirmed by crystallography and CD measurements, while magnetic studies showed all interactions were ferromagnetic, resulting in $S=8$ ground states.

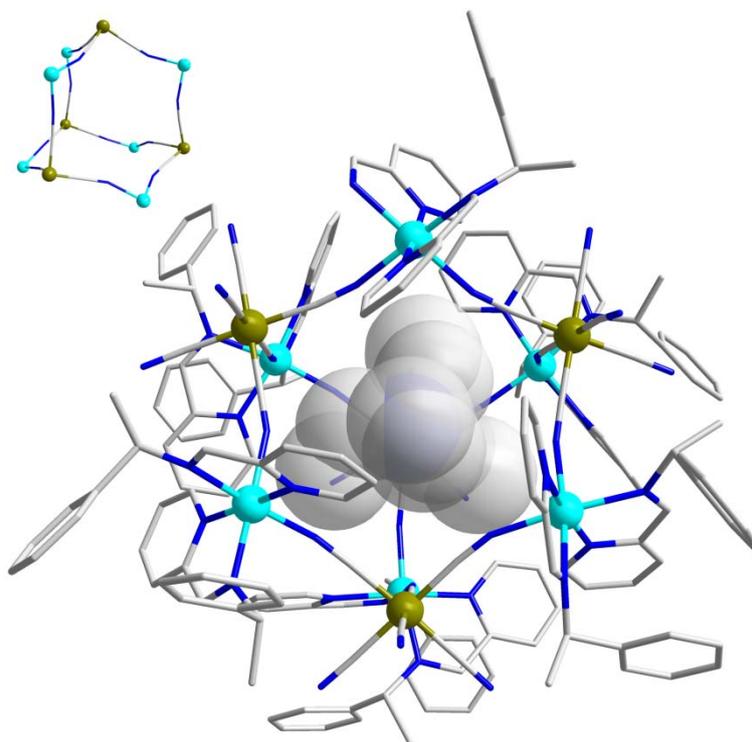


Figure 1: Molecular structure of **2R**. Colour code: C grey, N light blue, Ni green, Fe brown. Inset: the adamantane-like core.

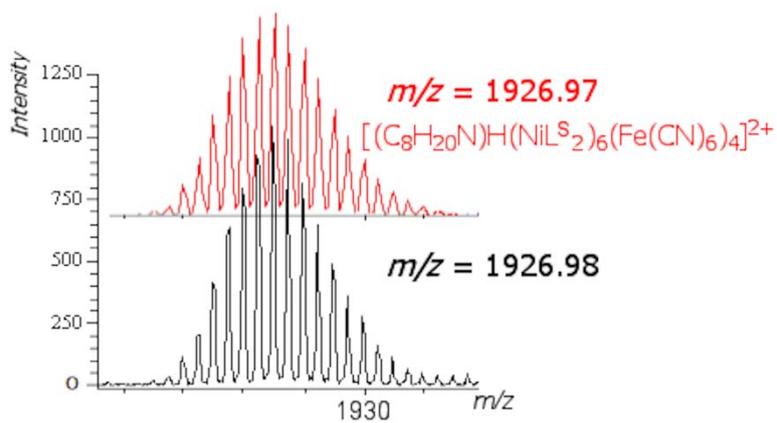


Figure 2: CSI-MS spectra of **2S**, showing the primary cluster peak observed (black) and the assignment (red).

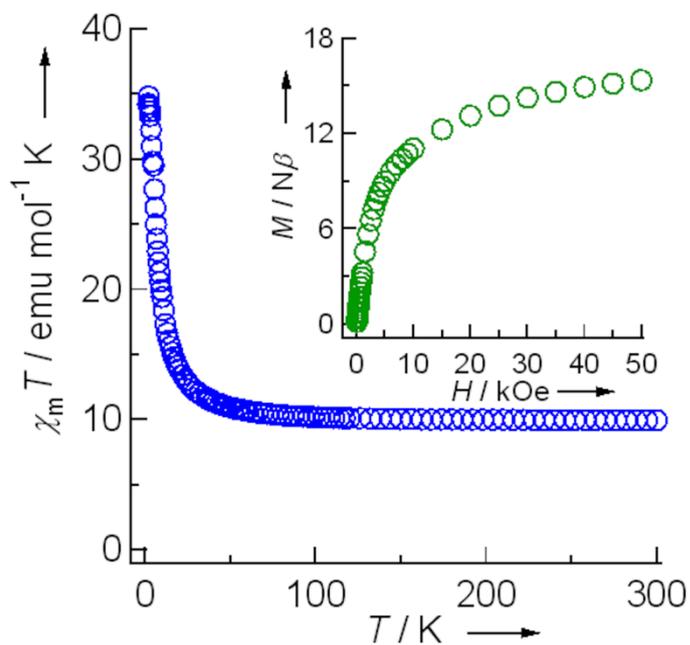


Figure 3: Plot of $\chi_m T$ vs. T of **2R** at applied field of 500 Oe. Inset: Field dependence of the magnetization at 1.8 K.

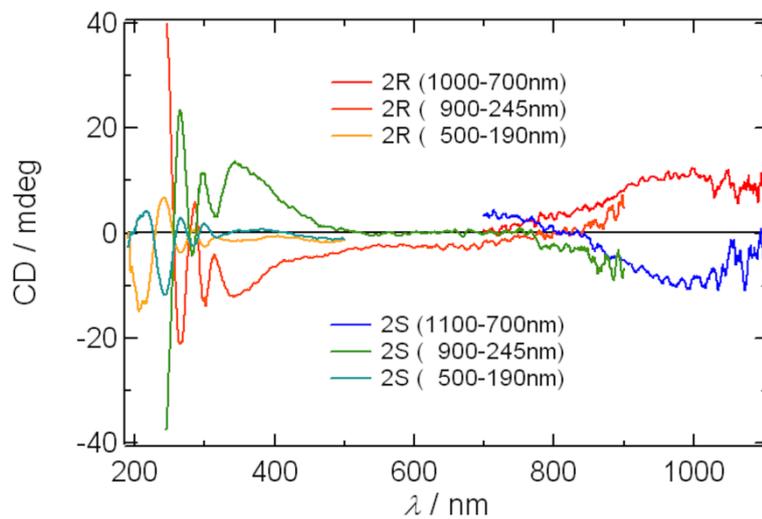


Figure 4: CD data obtained from a transparent disk with a radius of 5 mm made from a mixture of crystalline **2R** (or **2S**) and KCl (see ESD).