

[M₆M'₄] Cage Compounds with Chiral Bidentate Ligands

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Summary: Two decanuclear cyanide-bridged cage compounds were synthesized through the combination of chiral bidentate ligand-capped transition metal building blocks with hexacyanometalate ions, and their structural and magnetic properties were investigated.

Keywords: chiral; cyanide-bridged; magnetism; polynuclear complexes; supramolecular structures

Introduction

Discrete cyanide-bridged polynuclear complexes have been reported to show a wide range of magnetic/electronic properties.^[1-11] Cyanide ligands can coordinate *via* their nitrogen and carbon donor groups to form approximately linear bridges between neighbouring metal centres and act as potent mediators of magnetic and electronic exchange. The cyanide nitrogen atom acts as a relatively weak field ligand, and thus stabilizes metal ions in their high-spin states, whereas the carbon donor is a strong field ligand and stabilizes low spin metal centres. The foregoing structural and electronic features aid the chemist in the rational synthesis of functional materials, and as a result, many research groups are actively pursuing the development of cyanide-bridged clusters and their physical properties.^[12-17] Molecular squares based on cyanide-bridges have proven to be one of the most intensely researched families of discrete cyanide compounds.^[18] Some of the published square complexes have shown magnetic multi-bistabilities, such as in the tetranuclear iron square, reported by our group, in which the iron(II) ions displayed spin crossover behaviour.^[19]

Cobalt-iron heterometallic square molecules have shown multi-bistabilities derived from the transition between the paramagnetic Fe(III)_{LowSpin}-Co(II)_{HighSpin} phase and the diamagnetic Fe(II)_{LowSpin}-Co(III)_{LowSpin} phase, where the states can be switched between by the application of external stimuli, such as temperature and light irradiation.^[20,21] Heterometallic nickel-iron square clusters have also been shown to act as single molecule magnets.^[22] Our current research is focussed upon the synthesis and physical properties of extended cyanide-bridged molecular species, such as in our recent investigations of the battery-type properties of an octanuclear cubic molecule comprised of mixed-valence iron ions,^[23] and the magnetic properties of two crown-shaped tetradecanuclear heterometallic cyanide-bridged compounds.^[24] Against this background, our aim is to synthesize a new family of discrete cyanide-bridged compounds with unique structural topology. Using a chiral bidentate ligand, enantiomeric nickel-iron decanuclear cyanide-bridged cage molecules, (Et₄N)₂[Ni(L^{RorS})₂]₆[Fe(CN)₆]₄·n(solv.) (L^{RorS} = N-(2-pyridylmethylene)-(RorS)-1-phenylethylamine), were synthesized and ferromagnetic interactions were shown to be operative between metal centers.^[25] In this work, cyanide-bridged cage analogues constructed using different chiral ligands, counter ions and transition

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metals were examined. The decanuclear nickel-iron cage compound, $(Et_4N)_2\{[Ni(L^{R-naph})_2]_6[Fe(CN)_6]_4\}_2\{[Ni(L^{R-naph})_2]_2[Fe(CN)_6]_2\}$ (**1**), was synthesized using the new chiral ligand *N*-(2-pyridylmethylene)-(*R*)-1-naphthylethylamine, while a second, homometallic decanuclear cage compound $(Me_4N)_3\{[Co(L^S)_2]_6[Co(CN)_6]_4\}[Co(CN)_6]$ (**2**), was synthesized by changing the metal source and counter ions. Their structural and magnetic properties are discussed herein.

Experimental Part

Synthesis of **1**

The reaction of 2-pyridine carbaldehyde (107 mg, 1.0 mmol) and *R*-(+)-1-(1-naphthyl)-ethylamine (171 mg, 1.0 mmol) with $NiCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol) in methanol (20 ml) afforded a green reaction mixture. After stirring for a few minutes, the solvents were removed by evaporation. The obtained green powder, $[Ni-L^{R-naph}]$, was collected and used as a precursor in the synthesis of complex **1**. To a methanolic solution (20 ml) of $[Ni-L^{R-naph}]$ (65 mg) was added $(Et_4N)_3\{[Fe(CN)_6]\}$ (60 mg, 0.1 mmol) in methanol (20 ml). The resulting red solution was left to stand for several days. Red needle crystals of $(Et_4N)_2\{[Ni(L^{R-naph})_2]_6[Fe(CN)_6]_4\}_2\{[Ni(L^{R-naph})_2]_2[Fe(CN)_6]_2\} \cdot 80H_2O \cdot 51MeOH$ (**1** · 80H₂O · 51MeOH) were obtained and collected by suction filtration, then air dried. Found: C, 58.63; H, 5.22; N, 13.60, Calcd. for $C_{580}H_{648}N_{118}O_{80}Ni_{14}Fe_{10}$ (**1** · 80H₂O): C, 58.38; H, 5.47; N, 13.85. IR (KBr, cm⁻¹): 2142 ($\nu_{C\equiv N}$), 2113 ($\nu_{C\equiv N}$), 1641 ($\nu_{C=N}$), 1599 ($\nu_{C=N}$).

Synthesis of **2**

Synthesis of **2** was performed by a 'one-pot' reaction, using a different synthetic approach to that employed in the synthesis of **1**. To a methanolic solution (10 ml) of $CoCl_2 \cdot 6H_2O$ (238 mg, 1.0 mmol) was added 2-pyridine carbaldehyde (214 mg, 2.0 mmol) and *S*-(-)-1-phenylethylamine (242 mg, 2.0 mmol) in methanol (10 ml), $K_3[Co(CN)_6]$ (332 mg, 1.0 mmol) and Me_4NCl (220 mg, 2.0 mmol)

were dissolved into 20 ml of water. The methanolic mixture was layered gently onto the water layer, and diffused for several days to afford orange prisms of $(Me_4N)_3\{[Co(L^S)_2]_6[Co(CN)_6]_4\}[Co(CN)_6] \cdot 38H_2O$ (**2** · 38H₂O). The crystals were collected by suction and air-dried. Found: C, 54.93; H, 5.22; N, 17.48, Calcd. for $C_{210}H_{250}N_{57}O_{23}Co_{11}$ (**2** · 23H₂O): C, 54.96; H, 5.49; N, 17.40. IR (KBr, cm⁻¹): 2153 ($\nu_{C\equiv N}$), 2127 ($\nu_{C\equiv N}$), 1641 ($\nu_{C\equiv N}$), 1598 ($\nu_{C=N}$).

X-Ray Structural Analyses

Single crystal X-ray diffraction quality crystals of **1** and **2** were removed from their respective mother liquors and glued on to the tip of a glass capillary. Data collection was performed using a Bruker Smart APEX I system at 100 K. After data collection, the first 50 frames of data were recollected to establish that the crystal had not deteriorated during the data collection. The data frames were integrated using the SAINT program and merged to give a unique data set for structure determination. SHELXS included in the Bruker package was used to determine the structure by direct methods. Subsequent Fourier difference processing and refinement allowed location of all non-H atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were fixed at calculated positions and refined using a riding model. Crystallographic and refinement details are given in Table 1.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre with data numbers of CCDC-869522 for **1** and 869523 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road Cambridge CB21EZ, UK (Fax: +44 (123) 336-033; E-mail: deposit@ccdc.cam.ac.uk).

Physical Measurements

Magnetic susceptibility data were collected under an applied magnetic field of 500 Oe using a Quantum Design MPMS5-XL SQUID magnetometer.

Table 1.

Crystal parameters and refinement details for **1** and **2**

Complex	1 ·80H ₂ O·51MeOH	2 ·38H ₂ O
Empirical formula	C ₆₃ H ₈₃ N ₁₁ Ni ₁₄ Fe ₁₀ O ₁₃ ₁	C ₂₀₆ H ₂₆₈ N ₅₆ O ₃₈ Co ₁₁
Formula weight	13548.25	4784.99
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Cubic
Space group	P2 ₁	F23
Unit cell dimensions	$a = 21.955(10)$ Å $b = 55.166(20)$ Å $c = 27.316(10)$ Å $\beta = 90.80(1)$ °	$a = 28.287(6)$ Å $b = 28.287(6)$ Å $c = 28.287(6)$ Å –
Volume	33081(21) Å ³	22635(8) Å ³
Z	2	4
Density (calcd.)	1.390	1.404
Absorption coefficient	0.692	0.866
F(000)	14612	9988
Crystal size	0.45 × 0.21 × 0.15 mm ³	0.45 × 0.45 × 0.45 mm ³
Theta range for data collection		
Index ranges	$-28 \leq h \leq 27$ $-71 \leq k \leq 53$ $-35 \leq l \leq 34$ 0.041(10)	$-35 \leq h \leq 36$ $-36 \leq k \leq 30$ $-35 \leq l \leq 36$ –0.01(4)
Flack's parameter		
Reflections collected	200127	34010
Independent reflections	105812	4310
R	0.0933	0.0751
Goodness-of-fit on F^2	0.895	0.917
Max and Min El. Diff eÅ ^{–3}	1.695 and –0.691 eÅ ^{–3}	0.516 and –0.240 eÅ ^{–3}

Results and Discussion

Structural Characterization of 1

Compound **1** crystallizes in the monoclinic space group $P2_1$. The asymmetric unit

contains two cage moieties, each encapsulating one tetraethylammonium cation, and one anionic square complex (Figures 1 and 2). The cage moieties consist of six $[\text{Ni}(\text{L}^{\text{R-naph}})_2]^{2+}$ and four $[\text{Fe}(\text{CN})_6]^{3-}$ frag-

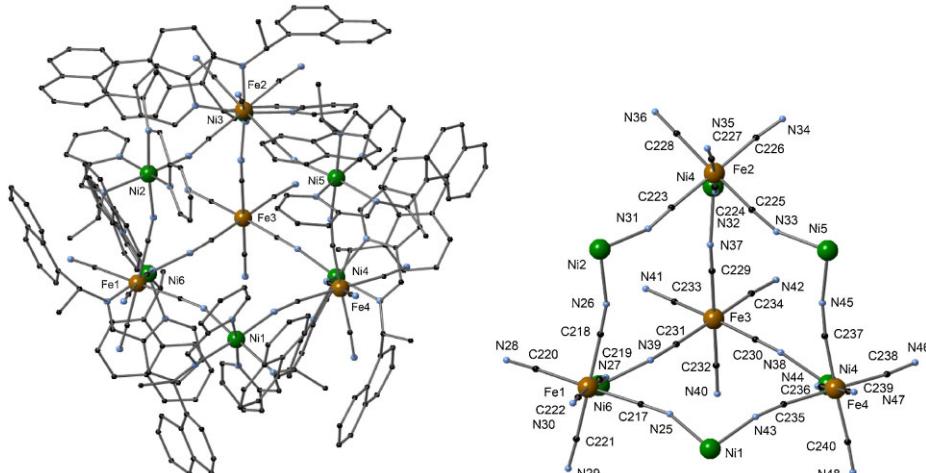
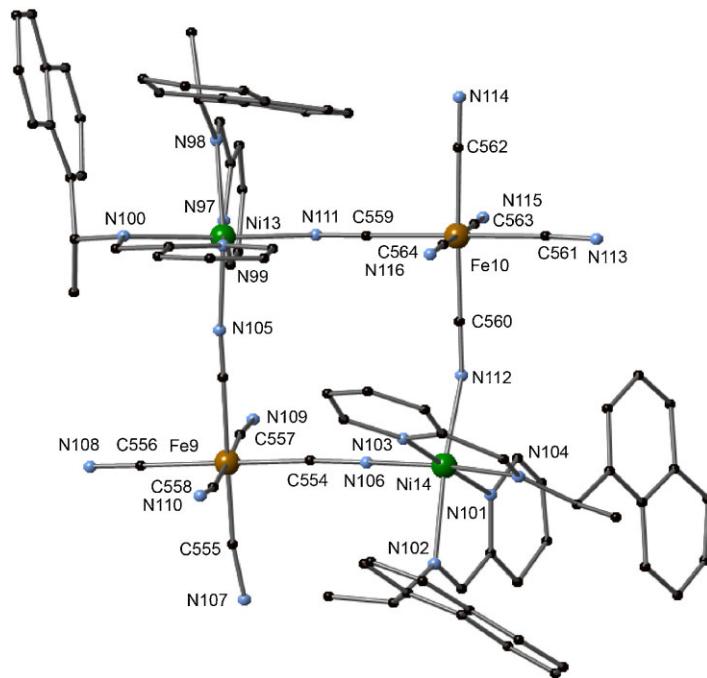


Figure 1.

The cationic cage component of **1** (left) and its core connectivity with capping ligands removed (right). The tetraethylammonium cations, hydrogen atoms and lattice solvent molecules were excluded for clarity. Fe centres in ochre; Ni green; N blue; C grey.

**Figure 2.**

The anionic square component of **1**. Cations, hydrogen atoms and lattice solvent molecules were excluded for clarity. Fe centres in ochre; Ni green; N blue; C grey.

ments, where the valences of the metal ions were assigned by charge balance and coordination bond lengths (Table 2). In $[\text{Ni}(\text{L}^{\text{R-naph}})^2]^{2+}$ the nickel ion is coordinated by two bidentate ligands, $\text{L}^{\text{R-naph}}$, and the residual *cis* sites are occupied by two nitrogen atoms from cyanide groups of

neighbouring $[\text{Fe}(\text{CN})_6]^{3-}$ units. Three of the cyanide groups in the $[\text{Fe}(\text{CN})_6]^{3-}$ units form bridges to Ni centres, while the remaining three cyanide groups located in the *fac*- sites act only as capping ligands. The core structure of the Fe-CN-Ni cluster is based on a highly symmetric adamantane-like cage framework constructed around one encapsulated tetraethylammonium cation. All bidentate $\text{L}^{\text{R-naph}}$ ligands coordinated to the nickel ions are involved in π - π stacking interactions between their naphthyl moieties and the pyridine groups of neighbouring ligands on the same nickel site. As a result, all nickel ions have Λ -type enantiomeric conformation, if the two cyanide ligands are considered as one bidentate group. The cage molecule contains six +2 and four -3 units, and therefore, the cluster would be neutral but for the encapsulated tetraethylammonium cation which renders the cage unit a 1+ cation.

The anionic square molecule consists of two $[\text{Ni}(\text{L}^{\text{R-naph}})^2]^{2+}$ moieties and two

Table 2.
Coordination bond lengths (\AA) for **1** and **2**

Complex 1			
Ni1-N _{ave.}	2.096	Ni2-N _{ave.}	2.095
Ni3-N _{ave.}	2.107	Ni4-N _{ave.}	2.107
Ni5-N _{ave.}	2.085	Ni6-N _{ave.}	2.092
Ni7-N _{ave.}	2.111	Ni8-N _{ave.}	2.099
Ni9-N _{ave.}	2.097	Ni10-N _{ave.}	2.108
Ni11-N _{ave.}	2.097	Ni12-N _{ave.}	2.111
Ni13-N _{ave.}	2.114	Ni14-N _{ave.}	2.082
Fe1-C _{ave.}	1.959	Fe2-C _{ave.}	1.959
Fe3-C _{ave.}	1.937	Fe4-C _{ave.}	1.960
Fe5-C _{ave.}	1.962	Fe6-C _{ave.}	1.949
Fe7-C _{ave.}	1.956	Fe8-C _{ave.}	1.958
Fe9-C _{ave.}	1.938	Fe10-C _{ave.}	1.957
Complex 2			
Co1-N(1)	2.126(7)	Co1-N(2)	2.212(6)
Co1-N(3)	2.097(8)	Co2-C(15)	1.858(12)
Co1-C(16)	1.879(12)	Co3-C(18)	1.88(2)

$[\text{Fe}(\text{CN})_6]^{3-}$ units, alternately bridged by cyanide ions to form a square core structure. The Ni ions have octahedral geometries with six nitrogen donor atoms from two bidentate $\text{L}^{\text{R-naph}}$ ligands and two cyanide groups. Two of the $[\text{Fe}(\text{CN})_6]^{3-}$ cyanide groups coordinate to the nickel ions and the other four cyanide groups act as capping ligands. In contrast to the cage moiety, the nickel ions have Δ -type conformations. The four metal ions are located on the same plane. The square has a net charge of -2 and thus behaves as a counter-anion in the crystal structure of **1**.

Structural Characterization of **2**

Complex **2** has a similar cage structure to **1** (Figure 3). However, the molecular symmetry is quite different. **2** crystallizes in the cubic space group $F\bar{2}3$. The asymmetric unit contains one twelfth of the decanuclear cluster $(\text{Me}_4\text{N})_3\{[\text{Co}(\text{L}^{\text{S}})_2]_6[\text{Co}(\text{CN})_6]_4\}[-\text{Co}(\text{CN})_6]$ (**2**): half of a $[\text{Co}(\text{L}^{\text{S}})_2]$ unit, one third of a $[\text{Co}(\text{CN})_6]^{3-}$ unit (in the cage), one twelfth of the $[\text{Co}(\text{CN})_6]^{3-}$ counteranion, one twelfth of the Me_4N^+ cation (encapsulated by the cage) and one-sixth of the Me_4N^+ cation (outwith the cage). The valences of the metal ions were

determined by charge balance and coordination bond lengths (Table 2). The cobalt ions of the $[\text{Co}(\text{L}^{\text{S}})_2]^{2+}$ unit lie on a two fold axis. The cobalt ion of the lattice $[\text{Co}(\text{CN})_6]^{3-}$ counteranion and the nitrogen atom of the encapsulated Me_4N^+ cation are both located on the intersections of three two fold axes. The Co ions of the $[\text{Co}(\text{L}^{\text{S}})_2]^{2+}$ units have octahedral coordination environments with six nitrogen donors in the same manner as those in **1**, and exhibit Δ -type geometry. Four $[\text{Co}(\text{CN})_6]^{3-}$ moieties bridge six $[\text{Co}(\text{L}^{\text{S}})_2]^{2+}$ units to afford a cage structure, encapsulating one Me_4N^+ cation. The bond lengths suggest that the cobalt ions of the $[\text{Co}(\text{L}^{\text{S}})_2]^{2+}$ units are divalent while those of the $[\text{Co}(\text{CN})_6]^{3-}$ moieties are trivalent. In **2**, a $[\text{Co}(\text{CN})_6]^{3-}$ complex acts as a lattice counterion and is compensated for by two further Me_4N^+ cations in the lattice.

The average distance between Ni ions located on opposite corners of the cage in **1** is 11.392 Å, compared to 11.100 Å between Co^{II} ions in **2**. The framework of **2** is smaller than that of **1** due to the difference in size between the Me_4N and Et_4N cation (Figure 4). This implies that the guests may template the cage formation. The cage

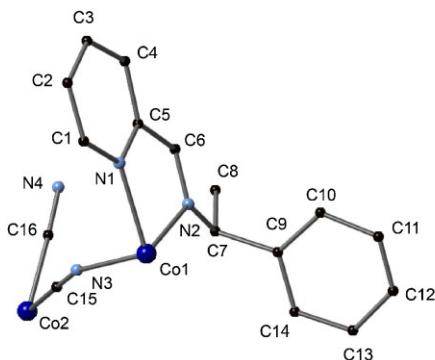
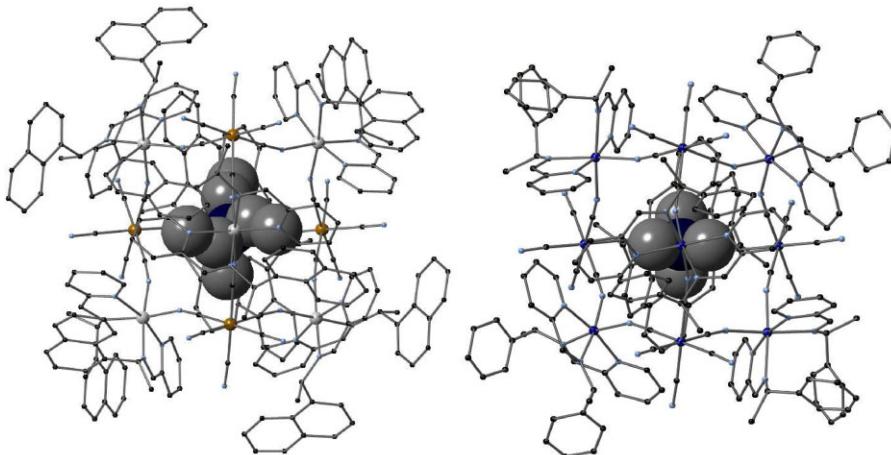


Figure 3.

The asymmetric unit (left) and core cage structure of **2** (right). The encapsulated tetramethyl ammonium cation, lattice counterions, solvent molecules and hydrogen atoms were excluded for clarity. Co centers in navy blue; N blue; C grey. Symmetry Code, #1: +x, -y, -z; #2: +y, +z, +x; #3: +z, +x, +y; #4: -z, -x, +y; #5: -y, +z, -x; #6: -x, -y, +z.

**Figure 4.**

Encapsulated ammonium cations in **1** (left) and **2** (right).

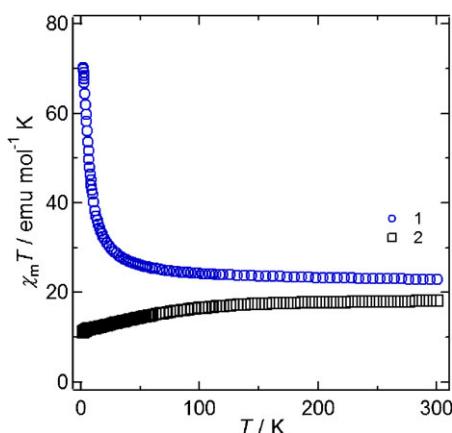
shrinking is exemplified by the M–NC bond angles (M=Ni or Co). In **1**, the average coordination angle (Ni–NC) is 158°, but in **2**, the bond angle (Co–NC) is reduced to 155°.

Magnetic Properties of **1** and **2**

The magnetic susceptibilities for **1** and **2** were measured in the temperature range of 1.8–300 K (Figure 5). The $\chi_m T$ value for **1** at 300 K was 22.962 emu mol⁻¹ K, larger than the value expected from the sum of the uncorrelated spins of fourteen Ni(II) ions and ten Fe(III)_{LowSpin} ions (17.75 emu

mol⁻¹ K, $g=2.00$). However, taking into account the large g factor associated with Ni ions, the observed value is reasonable and correlates with an effective g value of 2.27. As the temperature was lowered, the $\chi_m T$ values gradually rose until the temperature reached 25 K, after which they abruptly increased, reaching a maximum of 70.134 emu mol⁻¹ K at 2.2 K. **1** consists of three ferromagnetically coupled clusters: two Ni₆Fe₄ cages and one Ni₂Fe₂ square, which have $S_T=8$ and 3 spin ground states, respectively. The spin only values of $S_T=8$ and 3 clusters are estimated to 36.0 emu mol⁻¹ K and 6.00 emu mol⁻¹ K, respectively. The observed maximum $\chi_m T$ value is close to that expected for the three magnetically isolated ferromagnetic clusters (78.0 emu mol⁻¹ K). The ferromagnetic interactions between Ni and Fe ions originate from the strict orthogonality of their magnetic orbitals.

In the case of **2**, the $\chi_m T$ value at 300 K was 18.148 emu mol⁻¹ K, which is larger than the theoretical value predicted for the sum of six uncorrelated $S=3/2$ spins (11.25 emu mol⁻¹ K, $g=2.0$). **2** consists of four diamagnetic Co(III)_{LowSpin} ions and six paramagnetic Co(II)_{HighSpin} ions, which display significant spin-orbital coupling contribution. Therefore, the $\chi_m T$ value was expected to show deviation from the

**Figure 5.**

Plots of $\chi_m T$ versus T for **1** (○) and **2** (□).

spin only value. The $\chi_m T$ values gradually decreased as the temperature was lowered, reaching a minimum value of 11.172 emu mol⁻¹ K at 1.8 K. This magnetic behaviour can be understood as the typical magnetic susceptibility of six isolated Co(II) paramagnetic centres.

Conclusion

We synthesized a new family of cage compound comprising chiral mononuclear units with supporting bidentate ligands and hexacyanometallates. A decanuclear nickel-iron cage compound, $(Et_4N)_2\{[Ni(L^{R-naph})_2]_6[Fe(CN)_6]_4\}_2\{[Ni(L^{R-naph})_2]_2[Fe(CN)_6]_2\}$ (**1**), and a decanuclear cobalt cage compound, $(Me_4N)_3\{[Co(L^S)_2]_6[Co(CN)_6]_4\}[Co(CN)_6]$ (**2**), were obtained. The compounds have similar cage structures derived from M-CN-M' linkages, however, the constituent counter anions and cations are different. Cryomagnetic studies revealed **1** to show ferromagnetic interactions between Ni and Fe ions in both the cage and square molecules, and **2** to display paramagnetic behaviour due to the Co(II) centres. These results imply that it is possible to develop various molecular modifications in this decanuclear cage system, such as the use of different ligands, counter ions, guest molecules, and combinations of metal ions. Efforts towards the construction of multifunctional switching molecules based on these systems are on going, and our early experiments confirm that the related cobalt-iron decanuclear cage compounds display electron-transfer-coupled spin transition (ETCST).

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