

A rectangular Ni–Fe cluster with unusual cyanide bridges†

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An asymmetric polycyanide iron complex, $K_2[Fe^{III}(L1)(CN)_4](MeOH)$ (HL1 = 2,2'-(1*H*-pyrazole-3,5-diyl)bis-pyridine), was synthesized and its complexation compatibility with nickel ions was examined. Two kinds of enantiomeric nickel–iron squares were obtained in the presence of a chiral bidentate capping ligand. The compounds display unusual cyanide bridge geometry and have ferromagnetic interactions between nickel and iron ions.

The cyanide group is a valuable unit for the construction of molecular assemblies with magnetic and electronic interactions between metal ions because it can form linear bridges between neighbouring metal centres. Cyanometallates are well known in the literature, and can form coordination bonds to transition metal ions through their terminal N donor atoms.¹ Many examples of functional cyanide-bridged molecular assemblies have been reported.² Indeed, molecular magnets such as single-molecule magnets (SMMs) and single chain magnets (SCMs), the properties of which are reliant upon the interactions mediated by cyanide bridges, can be controllably constructed following modular approaches to molecular design with cyanometallate units.^{3,4} For example, combinations of building units with two or three free cyanide groups can often lead to the synthesis of square type $[M_2M'_2]$ molecules.⁵ Such discrete molecules have been shown to display dynamic spin transition phenomena such as multi-spin crossover behaviour and electron-transfer-coupled spin transitions (ETCST).⁶ The development of new polycyano building blocks may be important for the generation of novel functional molecular systems. Therefore, we have focussed on the syntheses of polycyano iron complexes with a polynucleating ligand. In this work, the bis-bidentate ligand, 3,5-bis(2-pyridyl)pyrazolate (HL1), was chosen as the capping ligand and a novel tetracyanoferrate complex was developed. Using the tetracyano iron complex as a building block, two cyanide-bridged

tetranuclear nickel–iron complexes were synthesized and their magnetic properties were investigated.

The tetracyanoferrate complex, $K_2[Fe^{III}(L1)(CN)_4](MeOH)$ (1·MeOH), was synthesized by the reaction of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in boiling water with HL1 and KCN.† Single crystal X-ray analysis of 1·MeOH reveals that the pyrazolate group of the ligand is deprotonated and coordinates to one iron and one potassium ion which occupy the two bidentate sites of L1 (Fig. 1). The second potassium ion connects neighbouring complexes through the CN groups. 1 forms a one-dimensional network structure linked by potassium ions.§ The combination of the tetracyanoferrate complex 1 with $NiCl_2 \cdot 6H_2O$ and the

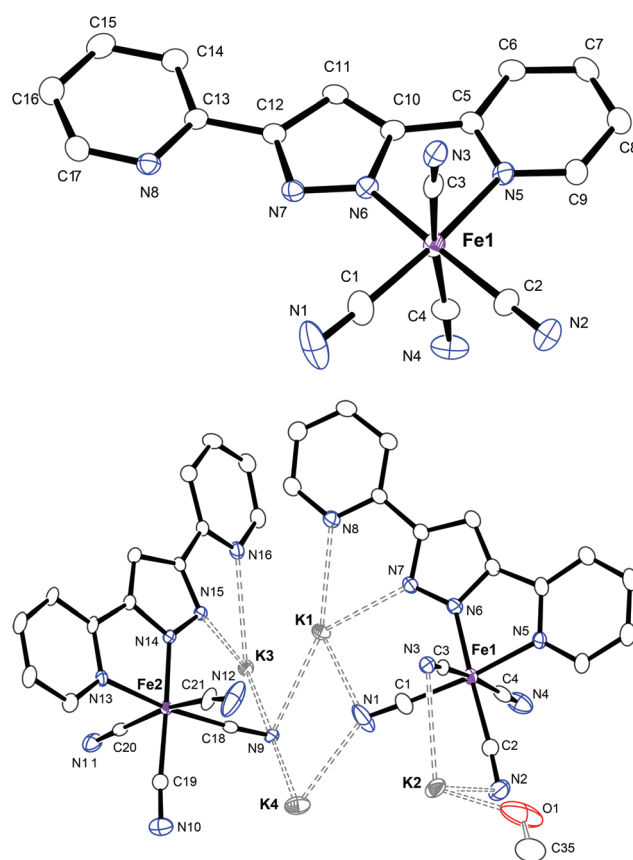


Fig. 1 Molecular structure of **1**. (top) Tetracyanoferrate moiety, (bottom) asymmetric unit. Fe centres in purple; K grey; N blue; O red; C white. Lattice solvent molecules were excluded for clarity.

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chiral bidentate ligand $L2^R$ ($L2^R = N$ -(2-pyridylmethylene)-(R)-1-phenylethylamine) yielded a tetranuclear heterometallic complex, $\{[Ni(L2^R)]_2[Fe(L1)(CN)_4]_2\} \cdot 6H_2O \cdot 2MeOH$ ($2 \cdot 6H_2O \cdot 2MeOH$). The corresponding enantiomer **3** was prepared by the same method using $L2^S$ ($L2^S = N$ -(2-pyridylmethylene)-(S)-1-phenylethylamine).

X-ray structural analysis revealed that **2** and **3** were enantiomers. Complex **3** comprises two nickel ions, two chiral ligands and two tetracyanoferrate moieties, forming rectangular molecules with Ni–NC–Fe bridges, with the complex molecule located on a two-fold axis of symmetry. The nickel ion has an octahedral N_6 coordination geometry with donor atoms from the bidentate chiral ligand, the bidentate site of **1** and two cyanide groups, also from **1**. Thus the building unit, **1**, behaves simultaneously as a tridentate capping group and as a bridging ligand. Two nitrogen atoms (N9 and N10) of the supporting chiral ligand coordinate to the Ni1 atom, along with three nitrogen atoms (N1, N7, and N8) from **1**, in which the N7 and N8 donor atoms belong to the bidentate site of L1. Interestingly, the cyanide nitrogen atom N1 bridges between Ni and Fe ions in an unusual manner: with an (Ni1–N1–C1) angle of $105.0(3)^\circ$ in **2** and $104.8(3)^\circ$ in **3**. To the best of our knowledge, the sharpest Ni–N≡C angle reported in a cyanide-bridged square complex is $147.8(2)^\circ$,⁷ while the sharpest reported in any species was in a dinuclear nickel complex displaying coordination angles of 111.2 – 112.9° .⁸ The presented compounds thus contain the most acute Ni–N≡C angles observed to date (Fig. 2).

Magnetic susceptibility data for $2 \cdot 11H_2O$ and $3 \cdot 11H_2O$ were collected in the temperature range of 1.8–300 K under an applied magnetic field of 500 Oe (Fig. 3 and S2†). The $\chi_m T$ value for **3** was $3.43 \text{ emu mol}^{-1} \text{ K}$ at 300 K, larger than the value ($2.75 \text{ emu mol}^{-1} \text{ K}$) expected for the sum of the uncorrelated spins of two Ni(II) ions and two Fe(III) ions. These discrepancies are explained by the large g values of the nickel and iron ions.⁹ As the temperature was lowered, the $\chi_m T$ value of **3** increased, reaching a maximum of $5.04 \text{ emu mol}^{-1} \text{ K}$ at 9.0 K, followed by a steep decrease to $4.24 \text{ emu mol}^{-1} \text{ K}$ at 1.8 K. The temperature dependence of the magnetic susceptibility data suggests that ferromagnetic interactions between nickel and iron ions are operative through the cyanide and pyrazolate bridges. The magnetic behaviour was analyzed for both samples with a Heisenberg spin model of $H = -2J_1 S_{Fe1}(S_{Ni1} + S_{Ni1*}) - 2J_2 S_{Fe1*}(S_{Ni1} + S_{Ni1*})$ for the data above 10 K, using julX.¹⁰ In this simulation, intermolecular interactions based on a molecular field approximation zJ' ($\chi = \chi_0/[1 - \chi_0(2zJ'/Ng^2\mu_B^2)]$) were considered. The obtained best fit parameters for **2** and **3** were $g_{Fe} = 2.31, 2.31, g_{Ni} = 2.18, 2.10, J_1 = +7.2, +7.0 \text{ cm}^{-1}, J_2 = +4.2, +4.0 \text{ cm}^{-1}$, and $zJ' = -1.5 \text{ K}, -1.7 \text{ K}$, respectively. The zJ' parameters imply intermolecular magnetic interactions, but also include contributions from the magnetic anisotropy present in the system. The ferromagnetic arrangement of the spins leads to a spin ground state of $S_T = 3$. Neither **2** nor **3** showed any out of phase response in their ac magnetic susceptibility, suggesting they were not SMMs.

We synthesised a novel tetracyanoferrate building unit, using which two heterometallic nickel–iron rectangular complexes were obtained. The orientation of the cyanide group on the iron site led to very unusual Ni–N≡C bonding angles in **2** and **3**. The investigation into the coordination behaviour of **1** showed

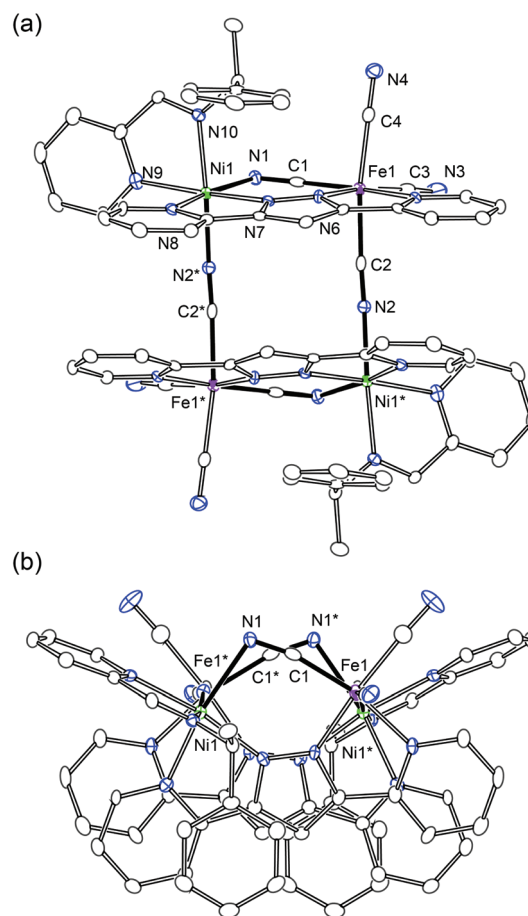


Fig. 2 ORTEP diagrams of complex **3**. (a) Top view, (b) side view. Selected bond angles: Ni1–N1–C1 $104.8(3)^\circ$, Ni1*–N2–C2 $170.2(4)^\circ$ (symmetry code: *, $-x + 1, -y + 1, z$).

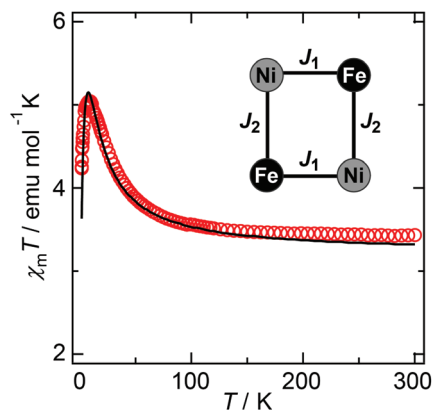


Fig. 3 $\chi_m T$ versus T plots for **3**. The solid line indicates the theoretical value (see text).

that it tends to coordinate metal ions in a tridentate manner by adding a cyanide donor to the typically bidentate pyrazole–pyridine binding site, and can bridge to additional metal ions *via* its free cyanide groups. It is expected that **1** may be used to generate magnetic one-dimensional networks due to its charge of -2 and its four perpendicular cyanide ligands. This work will be

extended to investigate the combination of **1** with other transition metals and supporting ligands.

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Notes and references

‡ $K_2[Fe^{III}(L1)(CN)_4](MeOH)$ (1·MeOH): To a suspension of HL1 (3.8 g, 17 mmol) in boiling water (100 cm³), $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (3.9 g, 10 mmol) was added. After stirring for a few minutes, a large excess of KCN (9.77 mg, 150 mmol) was added as a solid to the resultant dark red mixture. After boiling and stirring for a few minutes, the reaction mixture was filtered. The orange filtrate was cooled down to r.t. and left to stand for one day, after which time unreacted ligands had precipitated. The mixture was filtered again and left to stand undisturbed. After a few days, yellow microcrystals of the crude product were obtained. The yellow microcrystals were re-crystallized from methanol/*n*-butanol to afford purple needle crystals of $\{[K_2Fe^{III}(L1)(CN)_4]_2(MeOH)\} \cdot MeOH$ (1·MeOH). Anal. calcd for 1·MeOH $C_{18}H_{13}N_8FeK_2O_1$: C, 44.00; H, 2.67; N, 22.80. Found: C, 43.71; H, 2.58; N, 22.70%.

{ $[Ni(L^2R)]_2[Fe(L1)(CN)_4]_2 \cdot 11H_2O$ (2·11H₂O): To an aqueous solution (5 cm³) of **1** (31.88 mg, 0.06 mmol) was added a mixture of $NiCl_2 \cdot 6H_2O$ (14.26 mg, 0.06 mmol), 2-pyridine carbaldehyde (5.7 μL, 0.06 mmol) and *R*-phenylethylamine (7.6 μL, 0.06 mmol) in methanol (5 cm³). After stirring for a few seconds, the resulting solution was filtered and left for a few days after which purple crystals were obtained. The crystals were filtered and recrystallized from methanol yielding purple platelet crystals of $\{[Ni(L^2R)]_2[Fe(L1)(CN)_4]_2 \cdot 6H_2O \cdot 2MeOH$ (2·6H₂O·2MeOH). They were collected by suction filtration and dried in air. Anal. calcd for 2·11H₂O $C_{62}H_{88}N_{20}Ni_2Fe_2O_{11}$: C, 49.70; H, 4.57; N, 18.70. Found: C, 49.79; H, 4.43; N, 18.57%.

{ $[Ni(L^2S)]_2[Fe(L1)(CN)_4]_2 \cdot 11H_2O$ (3·11H₂O): Complex 3·11H₂O was prepared by the same method as **2**, using *S*-phenylethylamine. Anal. calcd for 3·11H₂O $C_{62}H_{88}N_{20}Ni_2Fe_2O_{11}$: C, 49.70; H, 4.57; N, 18.70. Found: C, 50.00; H, 4.50; N, 18.53%.

§ Crystal data for **1**: $C_{36}H_{26}N_{16}Fe_2K_4O_2$, $M_r = 982.83$, monoclinic, $P2_1/c$, $a = 8.408(4)$, $b = 20.572(10)$, $c = 24.726(13)$ Å, $\beta = 99.789(7)$, $V = 4215(4)$ Å³, $Z = 4$, $d = 1.549$ g cm⁻³, $\mu = 1.138$ mm⁻¹, $F(000) = 1992$, GOF = 0.954. A total of 25 983 reflections were collected, 9551 of which were unique ($R_{int} = 0.1217$). R_1 (wR_2) = 0.0740 (0.1833) for 563 parameters and 9551 reflections ($I > 2\sigma(I)$). Crystal data for 2·6H₂O·2MeOH: $C_{64}H_{46}N_{20}Ni_2Fe_2O_8$, $M_r = 1452.33$, orthorhombic, $P2_12_12$, $a = 13.334(2)$, $b = 20.437(3)$, $c = 11.9421(18)$ Å, $V = 3254.5(9)$ Å³, $Z = 2$, $d = 1.482$ g cm⁻³, $\mu = 1.078$ mm⁻¹, $F(000) = 1484$, GOF = 1.043, Flack parameter of $x = -0.004(14)$. A total of 18 523 reflections were collected, 7251 of which were unique ($R_{int} = 0.0412$). R_1 (wR_2) = 0.0395 (0.0979) for 444 parameters and 7251 reflections ($I > 2\sigma(I)$). Crystal data for 3·6H₂O·2MeOH: $C_{64}H_{44}N_{20}Ni_2Fe_2O_8$, $M_r = 1450.31$, orthorhombic, $P2_12_12$, $a = 13.319(2)$, $b = 20.390(3)$, $c = 11.9344(18)$ Å, $V = 3241.0(8)$ Å³, $Z = 2$, $d = 1.486$ g cm⁻³, $\mu = 1.082$ mm⁻¹, $F(000) = 1480$, GOF = 1.002, Flack parameter of $x = -0.017(15)$. A total of 20 217 reflections were collected, 7363 of which were unique ($R_{int} = 0.0511$). R_1 (wR_2) = 0.0498 (0.1003) for 444 parameters and 7363 reflections ($I > 2\sigma(I)$). The intensity data were collected on a Bruker SMART APEX diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Direct methods were used to solve the structure and to locate the heavy atoms using the SHELXL-97 program package. The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. Routine Lorentz polarization corrections and an absorption correction were applied. CCDC 883725–883727 for **1**–**3**, respectively.

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