The step-wise assembly of an undecanuclear heterotrimetallic cyanide cluster†

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The step-wise assembly of the high nuclearity cluster, $\{[Ni^{II}(H_2O)_5]_6[Co^{III}(tmphen)_2]_3[Fe^{II}(CN)_6]_2\}^{13+}$, is achieved by treating $\{[Co(tmphen)_2]_3[Fe(CN)_6]_2\}$ with six equivalents of $Ni(ClO_4)_2$ in aqueous MeOH.

The discovery that discrete molecules with high spin ground states can behave as nanoscale magnets has led to heightened interest in the rational synthesis of polynuclear metal clusters. Since the initial discovery of Single-Molecule Magnet (SMM) behavior for the dodecanuclear complex, $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$,[1–3] the majority of magnetic clusters reported in the literature are based on metal-oxide cores equipped with capping ligands.[4,5] While this strategy has generated a fascinating array of clusters containing as many as 84 metal centers,[6] it does not easily lend itself to predicting the nuclearity or geometry of the resulting product. Since the thermal energy barrier to magnetization reversal is a combination of total spin (S) and uniaxial anisotropy (D), a general lack of synthetic control over the cluster reaction constitutes a disadvantage for realizing a systematic approach to developing SMMs with higher blocking temperatures.

An alternative method for preparing high spin molecules, which attempts to circumvent the aforementioned issue, is to prepare cyanide-bridged clusters from reactions of cyanometalate anions with metal complexes whose ligand environment precludes the formation of extended arrays. This approach has led to the isolation of high-nuclearity molecules with diverse geometries and unusually high ground state spin values.[7–11] A particularly important feature of many of these compounds is the presence of terminal cyanides that can be used for subsequent coordination of additional paramagnetic metal centers. Unfortunately, such a building block approach is often precluded by the instability of these molecules in solution. Recent results from our laboratories, however, indicate that trigonal bipyramidal cyanide-bridged molecules such as $\{[Co(tmphen)_2]_3[Fe(CN)_6]_2\}$ (**1**) (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline), retain their structural integrity in solution.[12,13] This compound serves as a convenient precursor for higher nuclearity clusters owing to the presence of six terminal cyanide ligands that can coordinate up to six additional metal ions (Fig. 1). Herein we report the first example of the successful use of this approach to prepare an undecanuclear cluster, *viz.*, $\{[Ni^{II}(H_2O)_5]_6[Co^{III}(tmphen)_2]_3[Fe^{II}(CN)_6]_2\}[ClO_4]_{13}$, (**2**) (Fig. 2).

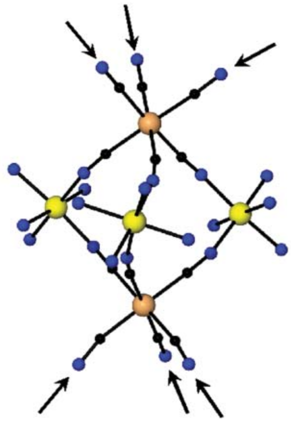

Fig. 1 Color PovRay plot of **1**[12] with arrows highlighting the six terminal sites available for coordination of metal ions. Color scheme: Fe: Orange; Co: Yellow; N: Blue (C and H atoms of tmphen ligands coordinated to Co ions have been removed for the sake of clarity).

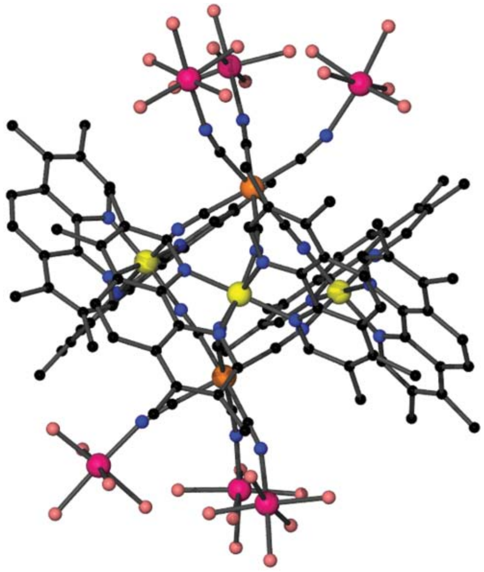

Fig. 2 Color PovRay plot of **2**. Color scheme: Fe: Orange; Co: Yellow; Ni: Magenta; O: Pink; N: Blue (H atoms have been removed for the sake of clarity).

The preparation of **2** first requires the isolation of red crystals of **1** *via* the slow diffusion of MeCN solutions of $[(18\text{-crown-}6)K]_3[Fe(CN)_6]$ and $[Co(tmphen)_2(H_2O)_2](NO_3)_2$.[13] The crystalline product **1** is then treated with $[Fc](PF_6)$ in MeOH to generate the

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† Electronic supplementary information (ESI) available: the infrared spectrum and magnetization data for **2**. See http://www.rsc.org/suppdata/cc/b4/b418698b/

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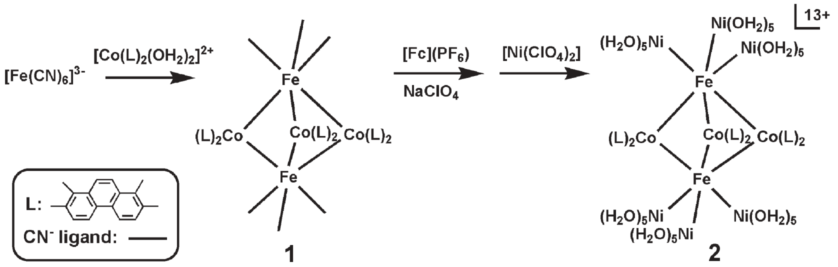

Scheme 1 Synthetic scheme depicting the stepwise assembly of **2**.

oxidized analogue of **1**, and subsequently combined with an excess of $Ni(ClO_4)_2$ in $MeOH/H_2O$ (Scheme 1).[14] Slow evaporation of the reaction mixture over a 1 week time period yields X-ray quality blue needles of $\mathbf{2}\cdot 17H_2O$ (Fig. 2). The molecular geometry of **2** was verified by single-crystal X-ray diffraction techniques to contain the original trigonal bipyramidal core of **1**, in which cyanide ligands span the three Co ions in the equatorial positions and two Fe ions occupy the axial sites. The three remaining CN^- ligands coordinated to each Fe ion are each connected to $[Ni(H_2O)_5]^{2+}$ moieties. The Co ions are coordinated to two *cis*-tmphen ligands in addition to the N-end of two CN^- ligands, with bond distances that are in accord with trivalent Co ions (Co–N = 1.866(5)–1.948(6) Å).[13,15,16] Each octahedral Ni ion is coordinated to the N-end of the terminal CN^- ligands (Ni–NC = 1.991(5)–1.998(6) Å), with the remaining coordination sites occupied by H_2O molecules (Ni–OH_2 = 2.030(7)–2.104(9) Å). The $\{Co(tmphen)_2\}^{3+}$ units in each cluster all exhibit the same chirality, but the unit cell contains both enantiomers which leads to a non-centrosymmetric space group (R-3c). At 97,600 Å^3, the volume of the unit cell is extremely large for a molecular species, and contains 18 molecular units, 13 $(ClO_4)^-$ anions and disordered interstitial solvent molecules modeled as 17 H_2O molecules. The solvent and anions are located in the large channels that are formed between the cluster units (Fig. 3), the anions in close proximity to the $\{Ni(OH_2)_5\}^{2+}$ units.

The oxidation states of the Co^{III} and Ni^{II} ions were identified based on their respective metrical parameters, while the Fe centers were indirectly deduced to be trivalent based on charge balance considerations. Infrared (IR) spectroscopy in the $\nu(CN^-)$ region (1950–2250 cm^{-1}) was recorded to further examine the oxidation state assignments of **2**. The terminal cyanide ligands of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ exhibit stretching modes at 2105 and 2065 cm^{-1}, respectively, and are shifted to higher energies when spanning two metal centers. The Fe^{II}–CN–Co^{III}_{LS} connectivity is typically observed at 2116–2133 cm^{-1} in 3D Prussian blue analogues, while Fe^{III}–CN–Co^{III}_{LS} is found at the higher energy range, 2153–2169 cm^{-1}.[17–19] A survey of Co/Fe trigonal bipyramidal structural analogues revealed IR bands at *ca.* 2065, 2104, and 2138 cm^{-1}.[13] The lowest energy band is assigned to the terminal Fe^{II}_{LS}–$CN_{terminal}$ mode, whereas the high-energy stretches are attributed to bridging CN^- ligands in the Fe^{II}_{LS}–CN–Co^{III}_{HS} and Fe^{II}_{LS}–CN–Co^{II}_{HS} bond structures. The complex, $\{[Ni^{II}(tmphen)_2]_3[Fe^{III}(CN)_6]_2\}$,[11] exhibits a terminal CN^- stretching mode at 2108 cm^{-1}, and two signals at 2114 cm^{-1} and 2150 cm^{-1} attributed to the bridging CN^- ligands. Utilizing these data to assign the IR spectrum of the title compound, **2**, the single bridging mode observed at 2103 cm^{-1} is interpreted as a superposition of the Fe^{II}–CN–Co^{III} and Fe^{II}–CN–Ni^{II} bonding modes. Furthermore, there is no evidence of terminal CN^- stretching modes indicating that all available CN^- coordination sites of **1** are bound to Ni(II) ions.

Variable temperature magnetic susceptibility measurements were performed on crushed single crystals of **2** at 1000 G from 300 K to 1.8 K (Fig. 4). The r.t. $\chi_m T$ value of ~7 emu K mol^{-1} is in reasonable agreement with the expected spin-only value of 6.0 emu K mol^{-1} for diamagnetic LS Co^{III} ions and LS Fe^{II} ions, and six octahedral Ni^{II} ions (S = 1). The $\chi_m T$ product is essentially

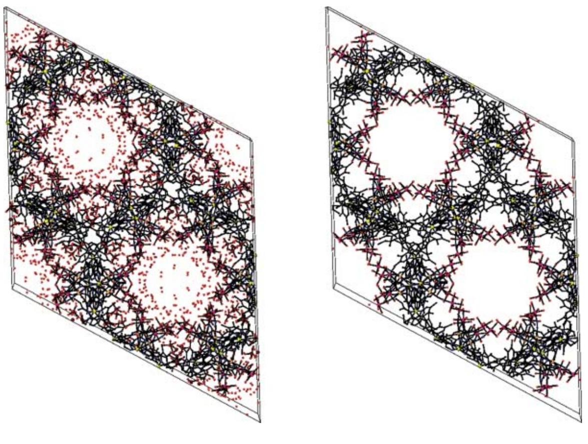

Fig. 3 Packing diagrams of compound **2** viewed along the c-axis. *Right*: The interstitial H_2O and ClO_4 molecules have been omitted to emphasize the large channels that run parallel to the c-axis.

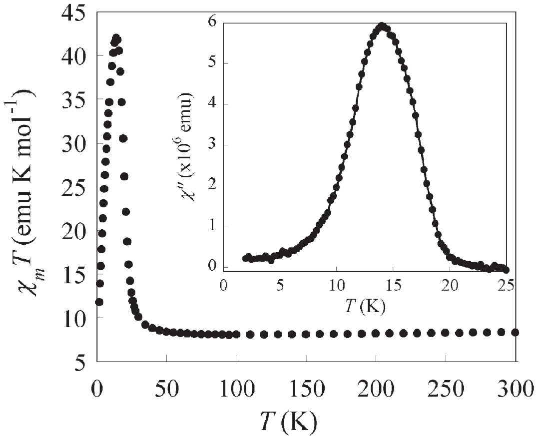

Fig. 4 The thermal variation of $\chi_m T$ *versus* temperature for **2** at H = 1000 G. *Inset*: The out-of-phase (χ'') AC susceptibility signal for **2** (1000 Hz).

invariant down to 50 K, after which temperature $\chi_m T$ increases to a maximum of 42 emu K mol^{-1} at 10 K, followed by a sharp decrease down to 1.8 K. This magnetic behavior is an indication that the compound is undergoing long-range ferromagnetic ordering at temperatures below *ca.* 25 K. This conclusion was confirmed by the presence of an out-of-phase (χ_m'') AC susceptibility (1000 Hz) signal at $T \sim 22$ K (Fig. 4, *inset*). The peak maximum of the χ_m''signal did not exhibit a frequency dependence, thus SMM behavior is not operative for this system.

The fact that magnetic ordering is observed at such a high temperature for a molecular species is puzzling, as there are no extended covalent interactions between clusters and the closest intermolecular metal ion interactions are > 8.1 Å (Ni···Ni). One possibility that was considered is a contamination of **2** with the known Co^{II}/Fe^{III} Prussian-blue 3-D phase (also blue in color), but this was ruled out on the basis of the fact that this material orders at $T \sim 16$ K.[17–19] The Ni^{II}/Fe^{III} PB solid (which is brown) exhibits ordering at $T \sim 22$ K,[20] but samples of blue crystals of **2** were viewed under a microscope and there was no evidence of a brown powder impurity nor did a bulk sample of **2** exhibit a powder diffraction pattern indicative of a face-centered cubic by-product. To be as careful as possible in selecting only *bona fide* crystals of **2** for magnetic studies, all the crushed single crystals that were used for the SQUID sample were first screened on a CCD diffractometer to verify the unit cell parameters. Given the aforementioned facts, the most reasonable explanation for the magnetic ordering is that the clusters, which are capped only by water molecules at the Ni^{II} sites and which co-crystallize with a large quantity of interstitial solvent, undergo desolvation and condensation to an extended phase.[21]

The title compound is an important addition to the field of cyanide-based clusters, as it represents a "proof-of-concept" for the building block approach to new molecules with unusual geometries and more than two types of metal spin centers. Such a synthetic strategy is convenient for accessing high spin molecules with the potential to exhibit superparamagnetic-like behavior. Efforts to introduce other types of metal capping units with less labile ligands than water molecules are currently underway. These studies will allow for the systematic exploration of a range of spin states and single-ion anisotropies and will help us to further ascertain the origin of the magnetic ordering for samples of $\{[Ni^{II}(H_2O)_5]_6[Co^{III}(tmphen)_2]_3[Fe^{II}(CN)_6]_2\}[ClO_4]_{13}$, **2**. Finally, an investigation into how the magnetic properties of **2** are affected by external stimuli are currently under investigation, as the diamagnetic Co^{III}–NC–Fe^{II} framework makes this complex a prime candidate for photo-magnetic behavior.‡§[19,22]

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Notes and references

‡ **2**·17H$_2$O: $C_{108}H_{190}Co_3Fe_2N_{24}Ni_6O_{99}$, M_w = 4510 g/mol, hexagonal, *R*-3*c*, a = 56.06(3) Å, c = 35.87(5) Å, V = 97600(100) Å^3, Z = 18, T = 110(2) K, ρ_{calc} = 1.351 g cm^{-3}, μ = 1.110 mm^{-1}, λ = 0.71073 Å, 1379 parameters and 278 restraints for 25124 independent reflections with $I > 4\sigma(I)$ gave $R1$ = 0.1197, $wR2$ = 0.3202. CCDC 258474. See http://www.rsc.org/suppdata/cc/b4/b418698b/ for crystallographic data in CIF or other electronic format.

§ Infrared (IR) spectrum of **2** was measured as a Nujol mull placed between KBr plates on a Nicolet 740 FT-IR spectrometer. DC and AC magnetic susceptibility measurements were recorded with a Quantum Design SQUID magnetometer MPMS-XL.

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