Single-molecule magnet behavior in three cyano-bridged heterometallic Fe$^{III}$–Ni$^{II}$ clusters†

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One trinuclear and two tetranuclear cyanide-bridged Fe$^{III}$–Ni$^{II}$ complexes were synthesized via treatment of a tricyanometallate with divalent Ni salts in the presence of 1-butylimidazole, 2,2-bipyrimidyl and 1,10-phenanthroline, respectively. Magnetic property studies demonstrated that the three complexes exhibit single-molecule magnet behavior as a result of strong intracluster ferromagnetic coupling and weak intercluster magnetic interactions.

Introduction

The design and synthesis of single-molecule magnets (SMMs), exhibiting slow magnetic relaxation, have attracted extensive attention due to their potential applications in high-density information storage and quantum computation. To date, various strategies have been reported to obtain SMMs. Among them, one efficient synthetic approach is to utilize metalocyanate building blocks as multidentate ligands and linkers. The cyano group can efficiently transmit magnetic interactions between multifarious transition-metal ions. In addition, the linear bridging mode of the cyano group enables chemists to reasonably predict the nature of the exchange interactions in some cases. Therefore, metalocyanate building blocks have been extensively employed. Among them, the use of [Fe$^{III}$L(CN)$_3$]$^-$ (L = tridentate ligand) as the metalocyanate building block has produced various discrete polynuclear complexes and 1D assemblies, and some of them are promising SMMs. Moreover, the presence of the intermolecular magnetic interactions, even if very weak, is supposed to suppress the slow relaxation of SMMs. One efficient approach to decrease the intermolecular magnetic interactions is to enhance the steric hindrance by introducing bulky building blocks and ancillary ligands into the molecules. Based on the above strategy, we chose the bulky [Fe$^{III}$(CN)$_3$]$^-$ as the building block, and the bulky 1-butylimidazole, 2,2-bipyrimidyl and 1,10-phenanthroline were adopted as ancillary ligands. With rational design, we succeeded in synthesizing three new cyano-bridged heterometallic Fe$^{III}$–Ni$^{II}$ clusters: [Tp*Fe$^{III}$((CN)$_3$)$_2$Ni$^{II}$(1-butylimidazole)$_4$CH$_3$OH (PzTp = tetraakis(pyrazolyl)borate) (1), [(Tp*)Fe$^{III}$(CN)$_3$)$_2$Ni$^{II}$(2,2-bipyrimidyl)$_2$BF$_4$·2CH$_3$OH·2H$_2$O (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) (2) and [(Tp)Fe$^{III}$(CN)$_3$]$_2$Ni$^{III}$(1,10-phenanthroline)$_2$ClO$_4$·H$_2$O (Tp = hydrotris(pyrazolyl)borate) (3). Herein, we reported the synthetic, single crystal structures, and SMM behavior of complexes 1–3.

Results and discussion

Crystal structures of complexes 1–3

Complex 1 was synthesized by a diffusion method in a test tube. Single-crystal X-ray diffraction analyses revealed that 1 crystallized in the triclinic space group P1. The crystal structure consists of neutral [Fe$^{III}$(Tp*TP)(CN)$_3$]$_2$Ni$^{II}$(1-butylimidazole)$_4$ clusters and uncoordinated methanol molecules located between the clusters. In the trinuclear cluster, the [Fe$^{III}$(Tp*TP)(CN)$_3$]$_2$$^-$/anion acts as a monodentate ligand through one of its three cyano groups toward a central [Ni$^{II}$(1-butylimidazole)$_4$]$^{2+}$/unit, while each [Ni$^{II}$(1-butylimidazole)$_4$]$^{2+}$/unit is linked to two [Fe$^{III}$(Tp*TP)(CN)$_3$]$_2$$^-$/units, yielding a neutral centrosymmetric trinuclear [Fe$^{III}$(Tp*TP)(CN)$_3$]$_2$Ni$^{II}$(1-butylimidazole)$_4$/molecular structure. Three metal centers were in a linear array with a Fe–Ni–Fe angle of 180º, which is illustrated in Fig. 1. Within the trinuclear cluster, there is one crystallographically independent iron center (Fe1) and one crystallographically independent nickel center (Ni1). The Fe1 center is located in a distorted FeC$_2$N$_4$ octahedral coordination environment with three cyano carbon atoms and three nitrogen atoms from the Tp*TP. The Fe1–C bond lengths are 1.895(5)–1.934(4) Å, and the Fe1–N distances are 1.959(3)–1.981(4) Å, respectively, which are in good agreement with those observed in the related low-spin Fe$^{III}$ tricyanide complexes. The Fe–C=N linkage is close to linearity with a bond angle of 174.7(4)º, whereas the Ni1...
center has distorted N₆ octahedral coordination surrounding constructed by two cyano nitrogen atoms and four nitrogen atoms from 1-butylimidazole ligands. The NiI–N distances are 2.074(3)–2.117(4) Å, and the C≡N–Ni angle (167.9(4)°) slightly deviates from linearity. Selected bond lengths and angles for I are listed in Table S1.† The intracluster Fe⋯Ni and Fe⋯Fe distances are 5.100(1) and 10.201(1) Å, respectively. The nearest intercluster Fe⋯Ni, Ni⋯Ni and Fe⋯Fe distances are 8.730(1), 10.522(1) and 7.681(1) Å, respectively.

Complex 2 crystallized as a centrosymmetric tetranuclear cluster in the triclinic space group P1. The crystal structure comprises of four components: one tetranuclear square \([\{(\text{Tp})\text{Fe}^{III}(\text{CN})_3\}^2\text{Ni}^{II}_2\text{Fe}^{III}\text{(CN)}_3\}^2\] unit, two tetrafluoroborate anions, two methanol molecules, and two solvent water molecules, which are depicted in Fig. 2a. Within the square, each \([\text{Fe}^{III}(\text{Tp})(\text{CN})_3]^-\) fragment is alternatively connected with two \([\text{Ni}(2,2\text{-bipyrimidyl})_2]^{2+}\) units through two of its three cyano groups, forming a centrosymmetric \(\text{Fe}_2(\mu\text{-CN})\text{Ni}_2\) tetranuclear square structure. The four metal centers are perfectly coplanar in the tetranuclear cluster. The remaining one terminal cyano group is perpendicular to the plane. Each iron center shows a distorted octahedral coordination geometry with three cyano carbon atoms and three nitrogen atoms from the Tp*. The Fe1–C bond lengths are 1.924(8)–1.948(8) Å, and the Fe1–N distances are 1.995(6)–2.011(6) Å, respectively, which are in good accordance with those reported for the other low-spin FeIII species. The Fe–C≡N angles fall in the range of 173.6(6)°–178.5(7)°, which are close to linearity. Each nickel center is six-coordinated with two cyano nitrogen atoms and four nitrogen atoms from two bidentate 2,2′-bipyrimidyl ligands, resulting in a distorted NiN₆ octahedral coordination configuration. The NiI–N distances are in the range of 2.040(7)–2.114(6) Å. The C≡N–NiI angles depart from linearity and range between 165.5(6)° and 174.6(6)°. Selected bond lengths and angles for 2 are presented in Table S2.† In addition, hydrogen-bonding interactions are found between the nitrogen atoms of terminal cyanato, water molecules, the F atoms of tetrafluoroborate anions, and the C atoms of 2,2′-bipyrimidyl ligands, with a N⋯O distance of 3.088(6) Å, C⋯F distances varying from 2.990(2) to 3.261(2) Å, a C≡N distance of 3.508(1) Å, and a C⋯O distance of 3.200(3) Å (Fig. S1†). Furthermore, the neighboring clusters are joined together by intercluster hydrogen bonds, forming a one-dimensional chain structure (Fig. S2†). The Fe⋯Ni separations in the square are 5.086(2) and 5.116(2) Å, and the diagonal Ni⋯Ni and Fe⋯Fe separations are 6.887(2) and 7.526(2) Å, respectively. The nearest intersquare Fe⋯Ni, Ni⋯Ni, and Fe⋯Fe separations are 10.185(3), 9.101(2) and 8.828(2) Å, respectively, indicating that the intersquare magnetic interactions are very weak.

The crystal structure of 3 is similar to that of 2. It is composed of one tetranuclear square \([\{(\text{Tp})\text{Fe}^{III}(\text{CN})_3\}^2\text{Ni}^{III}_2(\text{1,10-phenanthroline})_4\}^{2+}\) unit, two solvent water molecules, and two perchlorate anions (Fig. 2b). The tetranuclear square unit consists of two \([\text{Fe}^{III}(\text{Tp})(\text{CN})_3]^-\) units and two \([\text{Ni}^{III}(\text{1,10-phenanthroline})_2]^{2+}\) units. The two moieties bridged each other through cyano groups, yielding a centrosymmetric tetranuclear square structure. In the square, the four metal ions are coplanar. The coordination environment of each metal ion is a distorted octahedral geometry. The six coordination sites of the iron center are occupied by three nitrogen atoms from Tp and three cyano carbon atoms. The Fe1–C bond lengths are 1.910(5)–1.928(6) Å, and the Fe1–N distances are 1.961(5)–1.972(4) Å, respectively, which is characteristic of the low-spin FeIII ion. These Fe1–C and Fe1–N bond lengths are very close to those found in the related tetranuclear complexes. The Fe–C≡N angles are almost linear with bond angles of 177.9(5)–179.5(4)°, while the nickel center is coordinated to two cyano nitrogen atoms and four nitrogen atoms from two bidentate 1,10-phenanthroline ligands. The NiI–N distances range between 2.041(4) and 2.110(4) Å, being similar to those seen in 2. The values of the C≡N–Ni angles are 167.2(4)°–170.3(3)°. Selected bond lengths and angles for 3 are listed in Table S3.† Moreover, there exist π–π stacking interactions between the adjacent pyrazolyl rings, and aromatic rings of the adjacent 1,10-phenanthroline ligands. The closest separation of pyrazolyl rings is 3.512(1) Å, while the closest separation of aromatic rings is 3.508(1) Å (Fig. S3†). Furthermore, the hydrogen-bonding interactions are found between water molecules and carbon atoms, with a C⋯O distance of 3.460(4) Å. The Fe⋯Ni distances within the square are 5.081(1) Å, and the diagonal...
Ni...Ni and Fe...Fe distances are 7.104(1) and 7.266(1) Å, respectively. The shortest intersquare Fe...Ni, Ni...Ni, and Fe...Fe distances are 9.827(1), 8.690(1) and 7.609(1) Å, respectively.

Magnetic studies

The temperature-dependent magnetic susceptibilities (χ) of 1 were measured under 1000 Oe in the temperature range of 2–300 K (Fig. 3a). The χT value at 300 K was 2.57 cm³ mol⁻¹ K per Fe₂Ni unit, which is larger than the spin-only value for two magnetically isolated low-spin FeIII ions (S = 1/2, g = 2.0) and one magnetically isolated high-spin NiII ion (S = 1/2, g = 2.0). As the temperature decreased, the χT value gradually increased to a maximum value of 6.9 cm³ mol⁻¹ K at 7.5 K; this behavior displays that ferromagnetic interactions dominate in 1. The maximum value of 6.9 cm³ mol⁻¹ K is larger than the theoretical value for the magnetically isolated trinuclear compounds with S = 2. This may come from intermolecular ferromagnetic interactions. Below 7.5 K, the χT value sharply decreases and reaches a value of 5.22 cm³ mol⁻¹ K at 2 K, which could be attributed to the zero-field splitting and/or weak intercluster antiferromagnetic interactions. In the temperature range of 10–300 K, the magnetic susceptibility data are fitted to the Curie–Weiss law with a Curie constant C of 2.54 cm³ mol⁻¹ K and a Weiss constant θ of 6.14 K. The positive Weiss constant further confirms the ferromagnetic behavior of 1. Moreover, the ferromagnetic behavior is also supported by the field-dependent magnetization measured at 1.8 K (Fig. S4†). As the applied magnetic field is increased, the magnetization first increases rapidly, and then reaching a maximum value of 4.2Nμ at 50 kOe, which is close to the saturated value for two low-spin FeIII ions and one high-spin NiII ion. It should be noted that no hysteresis is observed at 1.8 K. In addition, the plots of zero field-cooled magnetization (ZFCM) and field-cooled magnetization (FCM) under a field of 100 Oe show irreversibility below 4.5 K, indicating the occurrence of spontaneous magnetization at low temperatures (Fig. S5†).

To investigate the dynamics of the magnetization of 1, the alternating current (ac) magnetic susceptibility was measured as a function of both the temperature and frequency (Fig. 3b). The in-phase (χ′) and out-of-phase (χ″) showed apparent frequency dependency, as was observed in the related SMMs. Meanwhile, there are noticeable peaks in the χ′ and χ″ data from 4 to 10 K, which moved to higher temperature with increasing frequency. The frequency-dependent behavior precluded a three-dimensional ordering. Moreover, the parameter Φ (Φ = (ΔT/Tp) Δ(⟨log ν⟩)), where ν is the frequency and Tp is the peak temperature of χ″) was used to distinguish between the glass and superparamagnetism. The calculated value of 0.13 is out of range for the spin-glass but lies in the expected range for a superparamagnet, and thus rules out the possibility of spin-glass behavior. On the basis of these data, the relaxation times were estimated and fitted to the Arrhenius law of τ = τo exp(Δ/kB) (τo = 2πν), where τ, τo, ν and Δ/kB represent relaxation time, pre-exponential factor, frequency and relaxation energy barrier, respectively. The best fitting gives a pre-exponential factor of τo = 1.03 × 10⁻⁹ s and a corresponding relaxation energy barrier of Δ/kB = 106.2 K (Fig. 3c). The above results suggest that the intermolecular magnetic interactions did not suppress the spin relaxation of the molecule. However, the energy barrier is higher than similar types of SMM due to the intermolecular ferromagnetic interactions. These values are in good agreement with those reported values for typical SMMs (usually >10⁻¹² s). This analysis demonstrates the presence of a SMM behavior in 1.

The temperature-dependent magnetic susceptibilities of 2 and 3 are presented in Fig. 4. At 300 K, the χT products were 3.54 and 3.63 cm³ mol⁻¹ K for 2 and 3, respectively. From 300 to 70 K, the χT product is practically constant and increases rapidly to a maximum value of 13.89 and 6.55 cm³ mol⁻¹ K at 7 K for 2 and 9 K for 3, respectively. Such a magnetic behavior indicates the presence of an intramolecular ferromagnetic coupling between FeIII and NiII ions through the cyano-bridges. The maximum value of 13.89 cm³ mol⁻¹ K for 2 is

![Fig. 3](image-url) (a) Temperature-dependent magnetic susceptibilities of 1 in the temperature range of 2–300 K under an applied field of 1000 Oe. (b) Temperature dependence of the real part and the imaginary part of the ac susceptibility of 1 in a zero dc field and a 3.5 Oe ac field. (c) The plot of ln(2fiμ) versus 1/Tp⁻¹ of 1, where μ is the frequency and Tp is the peak temperature of χ″. The solid line represents the least-squares fit of the experimental data to the Arrhenius equation.

![Fig. 4](image-url) (b) Temperature-dependent magnetic susceptibilities of 2 (a) and 3 (b) in the temperature range of 2–300 K under an applied field of 1000 Oe. Inset: hysteresis loop of 2 (a) and 3 (b) at 1.8 K.
larger than the theoretical value for the magnetically isolated tetracene compounds with $S = 3$. This may come from intermolecular ferromagnetic interactions. As the temperature further decreased, the $\chi T$ product abruptly decreases to 10.23 and 3.32 cm$^3$ mol$^{-1}$ K for 2 and 3 at 2 K, respectively. This may be due to the presence of the zero-field splitting and/or weak intercluster antiferromagnetic interactions. The best fitting of the magnetic susceptibility data with the Curie-Weiss law in 20–300 K for 2 and 3, respectively, gave $C = 3.49$ cm$^3$ mol$^{-1}$ K and $\theta = 6.62$ K for 2, and $C = 3.50$ cm$^3$ mol$^{-1}$ K and $\theta = 4.72$ K for 3. The positive Weiss constant further indicates the ferromagnetic coupling between the Fe$^{III}$ and Ni$^{II}$ ions. In addition, the ferromagnetic behavior is also in accordance with the field-dependent magnetization of 2 and 3 at 1.8 K (Fig. S6†).

As the applied magnetic field is increased, the isothermal magnetization increases linearly at low fields, reaching a value of 6.32 and 6.46 cm$^3$ mol$^{-1}$ for 2 and 3, respectively, at 50 kOe, which is close to the theoretical value for two low-spin Fe$^{III}$ ions and two high-spin Ni$^{II}$ ions. A magnetization hysteresis loop is observed at 1.8 K (Fig. 4, inset) with values of the remnant magnetization ($M_r$) and coercive field ($H_c$) of 1.0 N/$\beta$ and 1200 Oe for 2, and 0.12 N/$\beta$ and 400 Oe for 3, respectively. It should be noted that the coercive field of 2 is much larger than that in 3 in addition, the plots of ZFCM and FCM under a field of 100 Oe (Fig. S7†) show irreversibility below 4.6 K for 2, and below 4.0 K for 3, respectively, indicating the occurrence of spontaneous magnetization at low temperatures.

To probe the dynamics of the magnetization of 2 and 3, the ac magnetic susceptibility was measured under a 3.5 Oe ac field (Fig. 5). The frequency dependency characteristics of $\chi'$ and $\chi''$ can be observed below 5 K for 2, and below 4 K for 3, respectively. Meanwhile, the peaks in the $\chi'$ and $\chi''$ data are shifted to higher temperatures with increasing frequency. The frequency-dependent characteristics rule out a three-dimensional ordering, and are consistent with the slow magnetic relaxation exhibited by a SMM or spin-glass. However, the value of calculated $\Phi$ is 0.11 for 2, and 0.17 for 3, respectively, which lies in the range expected for a SMM, and thus eliminate the possibility of a spin-glass behavior. The value of estimated $\tau_c$ is $2.34 \times 10^{-11}$ s for 2 and $6.42 \times 10^{-9}$ s for 3, and the corresponding relaxation energy barrier $\Delta/k_B$ is 64.3 K for 2, and 24.5 K for 3, respectively (Fig. 5, inset). These values are in good accordance with those reported values for typical SMMs (usually $>10^{-12}$ s), which indicates that 2 and 3 exhibit SMMs behavior.

Investigation of the magnetic properties of the three cyanobridged heterometallic Fe$^{III}$–Ni$^{II}$ complexes reveals ferromagnetic interactions between the Fe$^{III}$ and Ni$^{II}$ ions, which is easily rationalized in terms of the strict orthogonality of the magnetic orbitals of the low-spin Fe$^{III}$ and Ni$^{II}$ ions.$^{11-13}$ In comparison to Tp*, the steric hindrance between Tp and the ancillary ligand in 3 is smaller than that of 2, resulting in shorter distances between the intercluster metal ions, and there exist $\pi-\pi$ stacking interactions and hydrogen-bonding interactions in 3. While in 2, only weak hydrogen-bonding interactions are observed. The dynamic susceptibility measurements are clearly illustrative of the SMM behavior. The intramolecular ferromagnetic coupling is rather visible as the main feature, while low temperature details are assignable to the local anisotropy on Ni(ii) sites and possibly intermolecular interactions. The slow relaxation of the magnetization is not suppressed by the intercluster interactions. Although many Fe–Ni polynuclear complexes have been reported, few of them show magnetic hysteresis.$^{14}$ These results indicate that the enhancement of the steric hindrance to minimize the intercluster magnetic interactions and introduction of an appropriate ancillary ligand and building block to tune the magnetic interactions may play an important role in the formation of SMMs.

Conclusions

In conclusion, we have synthesized three new cyanobridged mixed-valence heterometallic Fe$^{III}$–Ni$^{II}$ complexes. The magnetic studies demonstrate that 1–3 exhibit ferromagnetic interactions between Fe$^{III}$ and Ni$^{II}$ ions, and SMM behavior. The present work focuses on taking advantage of the steric hindrance effect to decrease the intermolecular interactions to obtain SMMs.

Experimental

Materials and methods

All organic solvents and materials used for the synthesis were of reagent grade and used without further purification. Bu4N-[Fe(pzTp)(CN)$_3$], Bu4N[Fe(Tp*)(CN)$_3$] and Bu4N[Fe(Tp)(CN)$_3$] were prepared according to the literature method.$^{15}$ Elemental analyses (C, H, and N) were carried out using an Elementar Vario EL III analyzer. Magnetic measurements

![Fig. 5](image-url)
were performed using a Quantum Design SQUID (MPMS XL-7) magnetometer. The magnetic susceptibilities of microcrystalline samples of 1-3 were measured, and the powder X-ray diffraction analysis confirmed their purity (Fig. S8†). A correction was made for the diamagnetic contribution prior to the data analysis.

**Synthesis of** $\text{[}[\text{pzTp}]\text{Fe}^{III}(\text{CN})_{3}]\_2\text{Ni}^{II}(1\text{-butylimidazolide})_4\cdot\text{CH}_3\text{OH}$ (1). A 6.0 mL aqueous solution of Ni(BF$_4$)$_2$·6H$_2$O (0.05 mmol) was placed at the bottom of a test tube, a mixture of methanol and water (1:1, v/v, 6 mL) was gently layered on the top of the solution, and then a 6.0 mL methanol solution of Bu$_4$N[Fe(pzTp)(CN)$_3$] (0.1 mmol) and 1-butylimidazolide (0.2 mmol) was carefully added as the third layer. Six hours later, red crystals appeared and were collected and dried in air after quickly being washed with water. Yield: 62% based on Ni(BF$_4$)$_2$·6H$_2$O. Anal. calcld (%) for C$_{59}$H$_{74}$B$_2$NiFe$_2$N$_{36}$O$_{10}$: C, 50.02; H, 5.38; N, 29.59; Found (%): C, 50.14; H, 5.42; N, 29.73.

**Synthesis of** $\text{[(Tp*)Fe}^{III}(\text{CN})_{3}]\_2\text{Ni}^{II}(2\text{-bipyrimidyl})_2\text{BF}_4\cdot2\text{CH}_3\text{OH}·\text{H}_2\text{O}$ (2). A 3.0 mL methanol solution of Bu$_4$N[Fe(Tp*)(CN)$_3$] (0.1 mmol) and 2,2-bipyrimidyl (0.1 mmol) was placed at the bottom in one side of an H-shaped tube, and a 3.0 mL aqueous solution of Ni(BF$_4$)$_2$·6H$_2$O (0.05 mmol) was introduced into the other side. Then, 12 mL of methanol was layered over the solutions on both sides to provide a diffusion pathway. Crystallization required ten weeks, yield: 55% based on Ni(BF$_4$)$_2$·6H$_2$O. Anal. calcld (%) for C$_{72}$H$_{56}$B$_2$Cl$_2$Fe$_2$Ni$_2$O$_{10}$: C, 48.79; H, 3.14; N, 20.78; Found (%): C, 48.58; H, 4.28; N, 20.61.

**Synthesis of** $\text{[(Tp)Fe}^{III}(\text{CN})_{3}]\_2\text{Ni}^{II}(1\text{-10-phenanthroline})_4\cdot2\text{ClO}_4\cdot2\text{H}_2\text{O}$ (3). Complex 3 was prepared in the same way as for 2, except using Bu$_4$N[Fe(Tp)(CN)$_3$] (0.1 mmol) and 1,10-phenanthroline (0.1 mmol) to replace Bu$_4$N[Fe(pzTp)(CN)$_3$] and 2,2-bipyrimidyl, respectively. Red crystals appeared after nine weeks, yield: 52% based on Ni(BF$_4$)$_2$·6H$_2$O. Anal. calcld (%) for C$_{72}$H$_{56}$B$_2$Cl$_2$Fe$_2$Ni$_2$O$_{15}$: C, 48.79; H, 3.14; N, 20.78; Found (%): C, 48.94; H, 3.19; N, 20.61.

**Crystallography**

The data were collected at a temperature of 296 K using a Bruker Smart APEX II X diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on $F^2$ by using full-matrix least-squares methods with SHELXTL-97.16 For complexes 1–3, all non-hydrogen atoms and part solvent water molecules were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically and fixed isotropic thermal parameters. The crystal data and details of the structure refinement for complexes 1–3 are summarized in Table S4†.

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**Notes and references**


