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A cyano-bridged $Fe^{II}Re^{IV}(CN)_2$ cluster incorporating two high-magnetic anisotropy building units

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ABSTRACT

The pentagonal bipyramidal high-spin iron(II) complex, $[(\mathrm{TPA}^{2C(O)NHtBu})\mathrm{Fe}(\mathrm{CF_3SO_3})]^+$, is shown to exhibit a high-anisotropy ground state, with fits to dc magnetization data providing an axial zero-field splitting parameter of $D = -7.9\ \mathrm{cm^{-1}}$. The utility of this compound as a building unit is demonstrated, as its reaction with $[\mathrm{ReCl_4(CN)_2}]^{2-}$ affords the cyano-bridged dinuclear cluster $(\mathrm{TPA}^{2C(O)NHtBu})\mathrm{FeReCl_4(CN)_2}$. dc magnetic susceptibility measurements reveal intracluster ferromagnetic exchange interactions between $\mathrm{Fe^{II}}$ and $\mathrm{Re^{IV}}$ centers, with $J = +3.0\ \mathrm{cm^{-1}}$, giving rise to a spin ground state of $S = 7/2$. Moreover, fits to dc magnetization data obtained for the FeRe cluster show the presence of strong axial anisotropy, with $D = -2.3\ \mathrm{cm^{-1}}$. Finally, variable-frequency ac susceptibility measurements reveal the onset of slow magnetic relaxation at low temperature, suggesting that the FeRe cluster is a single-molecule magnet.

1. Introduction

The past two decades have seen the preparation and characterization of numerous molecules that relax their magnetization slowly upon removal of an applied magnetic field at low temperature [1]. This slow magnetic relaxation arises due to the presence of a negative axial zero-field splitting (D) and a non-zero spin ground state (S), which together give rise to an energy barrier to spin relaxation. The magnitude of this barrier can be quantified according to the expressions $U = S^2|D|$ for integer spin systems and $U = (S^2 - 1/4)|D|$ for half-integer spin systems. Molecules that exhibit this slow dynamic behavior, known as single-molecule magnets, have attracted considerable attention, as they could find use in applications such as high-density information storage or quantum computing [2].

One strategy for constructing single-molecule magnets hinges on use of the cyanide ligand to bridge paramagnetic metal centers [3]. Indeed, cyanide preferentially connects only two metal centers in a nearly linear geometry, thus imparting a significant degree of structural control to the synthesis of multinuclear cyano-bridged complexes. The ability to direct the formation of such assemblies lends itself to a building block approach, wherein a mononuclear cyanometalate complex is allowed to react with a secondary metal complex that features at least one open coordination site. Additionally, the building unit should bear a high-spin ground state and strong magnetic anisotropy. Toward this end, we recently reported the synthesis of a new cyanometalate complex, $[\mathrm{ReCl_4(CN)_2}]^{2-}$, which features an $S = 3/2$ ground state and an axial zero-field splitting parameter of $D = -14.4\ \mathrm{cm^{-1}}$ [4].

Ideally, the spin and anisotropy of the secondary metal complex will also be maximized, and the exchange between the two metal centers will be dominated by ferromagnetic interactions. High-spin iron(II) serves as a promising candidate for this purpose, as it features an $S = 2$ ground state that often displays extraordinarily strong axial anisotropy [5]. However, a ligand must be employed that will preserve a high-spin ground state for the $\mathrm{Fe^{II}}$ ion while not quenching orbital angular momentum. Exemplifying this strategy, a recent report introduced an amide-functionalized tris(pyridyl)amine ligand, 6,6′-(pyridin-2-ylmethylazanediyl)bis(methylene)bis(*N*-tert-butylpicolinamide), and its appendage to iron(II) to give the pentagonal bipyramidal $S = 2$ complex $[(\mathrm{TPA}^{2C(O)NHtBu})\mathrm{Fe}(\mathrm{CF_3SO_3})]^+$ [6]. We were interested in the potential of this complex to exhibit strong uniaxial anisotropy, considering the unquenched orbital angular momentum associated with an approximate $e_1^3e_2^2a_1^1$ electronic configuration,[1] as well as the possibility to generate a multinuclear cluster via displacement of the labile $\mathrm{SO_3CF_3}^-$ ligand. Herein, we report an investigation of the magnetic axial anisotropy in $[(\mathrm{TPA}^{2C(O)NHtBu})\mathrm{Fe}(\mathrm{CF_3SO_3})]^+$. Moreover, we demonstrate the utility of this complex as a building unit, through its reaction with $[\mathrm{ReCl_4(CN)_2}]^{2-}$ to give the dinuclear coordination cluster $(\mathrm{TPA}^{2C(O)NHtBu})\mathrm{FeReCl_4(CN)_2}$. For this cluster, dc susceptibility measurements disclose the presence of intracluster ferromagnetic exchange coupling. In addition, fits to magnetization data show strong uniaxial anisotropy of the ground state. Finally, ac susceptibility measurements reveal the presence of slow magnetic relaxation, consistent with single-molecule magnet behavior.

2. Synthesis and characterization

2.1. General considerations

Unless otherwise stated, manipulations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using Schlenk techniques under a nitrogen atmosphere. The compounds $(\mathrm{Bu_4N})_2[\mathrm{ReCl_4(CN)_2}]\cdot 2\mathrm{DMA}^{4a}$ (DMA = *N*,*N*-dimethylacetamide) and $[(\mathrm{TPA}^{2C(O)NHtBu})\mathrm{Fe}(\mathrm{CF_3SO_3})](\mathrm{CF_3SO_3})^6$ were prepared as previously reported. The compound $(\mathrm{Bu_4N})_2[\mathrm{ReCl_4(CN)_2}]\cdot$ 2DMA was desolvated by heating in vacuo at 40 °C for 12 h to give $(\mathrm{Bu_4N})_2[\mathrm{ReCl_4(CN)_2}]$. Acetonitrile was sparged and dried using VAC Solvent Purification modules, then stored over 4 Å molecular sieves, prior to use.

2.2. Magnetic measurements

Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer. Measurements were obtained for finely ground microcrystalline powders (30.8 mg for $[(\mathrm{TPA}^{2C(O)NHtBu})\mathrm{Fe}(\mathrm{CF_3SO_3})](\mathrm{CF_3SO_3})$ and 11.9 mg for $(\mathrm{TPA}^{2C(O)NHtBu})\mathrm{FeReCl_4(CN)_2}\cdot 2\mathrm{MeCN}$) restrained in a frozen eicosane matrix within polycarbonate capsules. dc susceptibility data were collected in the temperature range 1.8–300 K under a dc field of 1000 Oe. dc magnetization data were collected in the temperature range 1.8–10 K at fields of 1, 2, 3, 4, 5, 6, and 7 T. Ac susceptibility data were collected in the frequency range 10–1488 Hz at temperatures of 1.74, 1.90, 2.10, 2.30, 2.50, and 2.90 K, with an oscillating field of 4 Oe. dc susceptibility data were corrected for diamagnetic contri-

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[1] Derived considering approximate C_{5v} symmetry.

Table 1
Crystallographic data for $(TPA^{2C(O)NHtBu})FeReCl_4(CN)_2 \cdot 2MeCN$.

Formula	$C_{34}H_{42}Cl_4FeN_{10}O_2Re$
Formula weight	1006.62
T (K)	139
Space group	$C2/c$
Z	4
a (Å)	36.624(4)
b (Å)	9.9266(11)
c (Å)	24.733(3)
β (°)	117.182(5)
V (Å^3)	7998.6(15)
d_{calc} (g/cm^3)	1.313
R_1 (wR_2) (%)	6.10 (14.33)

butions from the sample holder and eicosane, as well as for the core diamagnetism of each sample (estimated using Pascal's constants).

2.3. X-ray crystallography

A single crystal of $(TPA^{2C(O)NHtBu})FeReCl_4(CN)_2 \cdot 2MeCN$ was coated with Paratone-N oil and mounted on a Kaptan loop. The crystal was then quickly transferred to a Bruker MICROSTAR diffractometer and cooled in a stream of nitrogen gas. Preliminary cell data were collected, giving a unit cell consistent with the triclinic Laue group for the compound, using the APEX2 [7] program package. The unit cell parameters were later refined against all data. A full hemisphere of data was collected for the compound. The crystal showed no significant decay during data collection. Data were integrated and corrected for Lorentz and polarization effects using SAINT [8] and were corrected for absorption effects using SADABS [9].

The space group assignment was based upon systematic absences, E-statistics, and successful refinement of the structure. The structure was solved by direct methods and expanded through successive difference Fourier maps. They were refined against all data using the SHELXTL program [10]. Thermal parameters for all non-hydrogen, non-solvent atoms were refined anisotropically. Table 1 summarizes the unit cell and structure refinement parameters for $(TPA^{2C(O)NHtBu})FeReCl_4(CN)_2$.

2.4. Other physical methods

Infrared spectra were obtained on a Perkin–Elmer Spectrum 100 Optica FTIR spectrometer equipped with an attenuated total reflectance accessory (ATR). Elemental analyses were carried out at the Microanalytical Facility at the College of Chemistry, University of California, Berkeley.

2.5. $(TPA^{2C(O)NHtBu})FeReCl_4(CN)_2 \cdot 2MeCN$

A solution containing $(Bu_4N)_2[ReCl_4(CN)_2]$ (23 mg, 0.027 mmol) in CH_3CN (3 mL) was added dropwise to a solution containing $[(TPA^{2C(O)NHtBu})Fe(CF_3SO_3)](CF_3SO_3)$ (23 mg, 0.026 mmol) in CH_3CN (3 mL) to form a purple solution. Upon standing, dark purple needle-like crystals, suitable for X-ray diffraction, formed from the solution. The crystals were collected on a 0.22 μm nylon filter and washed with Et_2O (3 × 1 mL) to give 18 mg (69%) of product. IR: ν_{CN} 2125 cm^{-1}. *Anal.* Calc. for $C_{34}H_{42}Cl_4FeN_{10}O_2Re$: C, 40.57; H, 4.21; N, 13.91. Found: C, 40.57; H, 4.15; N, 13.75%.

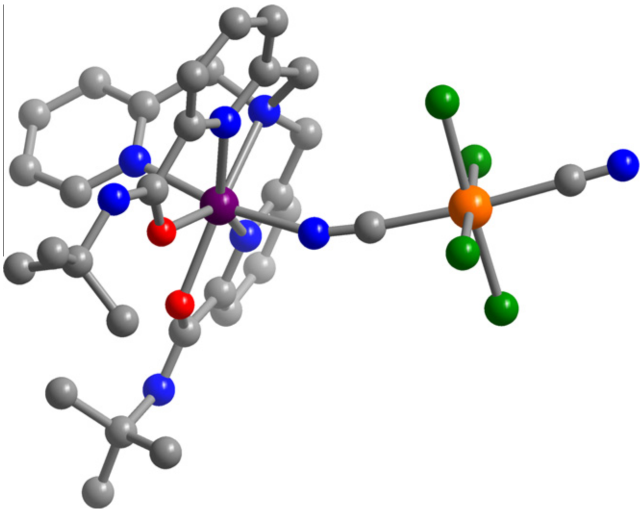

Fig. 1. Crystal structure of the dinuclear cluster $(TPA^{2C(O)NHtBu})FeReCl_4(CN)_2$. Orange, purple, green, gray, and blue spheres represent Re, Fe, Cl, C, and N atoms, respectively; H atoms are omitted for clarity. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Synthesis and structural analysis

Reaction of $[(TPA^{2C(O)NHtBu})Fe(CF_3SO_3)](CF_3SO_3)$ with an equimolar amount of $[ReCl_4(CN)_2]^{2-}$ in acetonitrile afforded dark purple needle-like crystals of $(TPA^{2C(O)NHtBu})FeReCl_4(CN)_2$ suitable for single-crystal X-ray analysis. The structure of this compound (see Fig. 1) consists of a dinuclear cluster, wherein a $[ReCl_4(CN)_2]^{2-}$ unit is bridged through one cyanide ligand to a $[(TPA^{2C(O)NHtBu})Fe]^{2+}$ fragment. The octahedral coordination environment of the Re^{IV} center does not deviate significantly from that observed for $(Bu_4N)_2[ReCl_4(CN)_2] \cdot 2DMA$ [4]. The Fe^{II} center resides in a pentagonal bipyramidal coordination environment, with the pentagonal plane consisting of an N_3O_2 cavity provided by the amine nitrogen

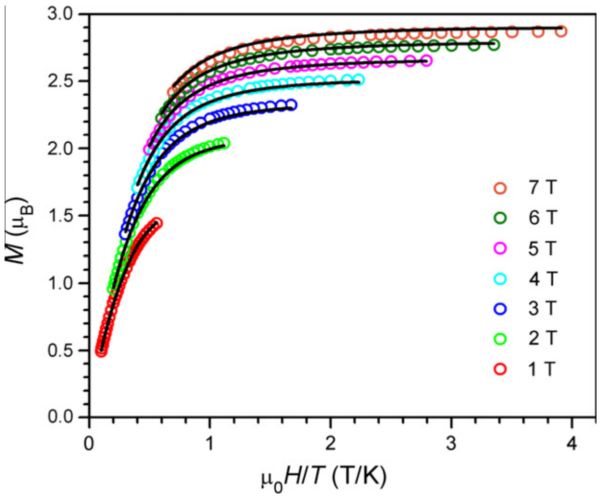

Fig. 2. Low-temperature magnetization data for the pentagonal bipyramidal compound $[(TPA^{2C(O)NHtBu})Fe(CF_3SO_3)](CF_3SO_3)$, collected under various dc fields. Solid black lines represent fits to the data, giving $D = -7.9$ cm^{-1} and $|E| = 2.2$ cm^{-1}.

and oxygen and nitrogen atoms from two amide-functionalized pyridine ligands, and the axial sites occupied by the nitrogen end of a bridging cyanide and a non-functionalized pyridine ligand. Similar to that observed for the Re^{IV} center, the bond distances and angles involving the Fe^{II} center do not deviate significantly from those observed in the mononuclear parent unit, $[(TPA^{2C(O)NHtBu})Fe^{II}]^{2+}$ [6]. Whereas the structure features a Re–C–N angle of 174.712(8)°, the Fe–N–C angle is significantly more bent at 156.918(9)°. Such a deviation from linearity is common through the nitrogen end of cyanide, and likely results here from crystal packing and steric constraints imposed by the bulky $TPA^{2C(O)NHtBu}$ ligand [4,11]. Finally, the FeRe clusters are well-separated, with a closest intermolecular metal–metal contact of 7.926 Å between Re^{IV} and Fe^{II} centers.

3.2. Magnetic properties

To assess the magnetic anisotropy of $[(TPA^{2C(O)NHtBu})Fe(CF_3SO_3)](CF_3SO_3)$, low-temperature magnetization data were collected at various fields. As shown in Fig. 2, the resulting plot of reduced magnetization features a series of non-superimposable isofield curves. This splitting of the curves demonstrates qualitatively the presence of significant anisotropy. To quantify this effect, the data were modeled according to the following zero-field splitting spin Hamiltonian:

$$\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + g_{iso}\,\mu_B\,\mathbf{S}\cdot\mathbf{H}$$

Fits to the data obtained using ANISOFIT 2.0 [12] provide axial and transverse zero-field splitting parameters of $D = -7.9\ cm^{-1}$ and $|E| = 2.2\ cm^{-1}$, with $g = 2.11$. Here, the strong uniaxial anisotropy likely arises due to the presence of an e_1^3 orbital set, which gives rise to unquenched orbital angular momentum and thus magnetic anisotropy. Indeed, several other studies have reported strong uniaxial zero-field splitting for molecules possessing an e^3 configuration, both in trigonal pyramidal [5g,5h] and pentagonal bipyramidal [13] geometries.

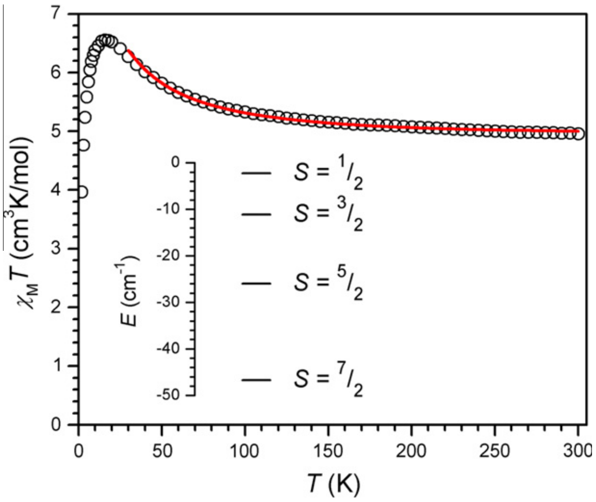

Fig. 3. Variable-temperature dc magnetic susceptibility data, collected for $(TPA^{2C(O)NHtBu})FeReCl_4(CN)_2{\cdot}2MeCN$ under a 1000 Oe applied field. The solid red line represents a fit to the data, giving $J = +3.0\ cm^{-1}$. Inset: Spin ladder showing energies of spin states in the FeRe cluster, as calculated from the fit of the dc susceptibility data. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

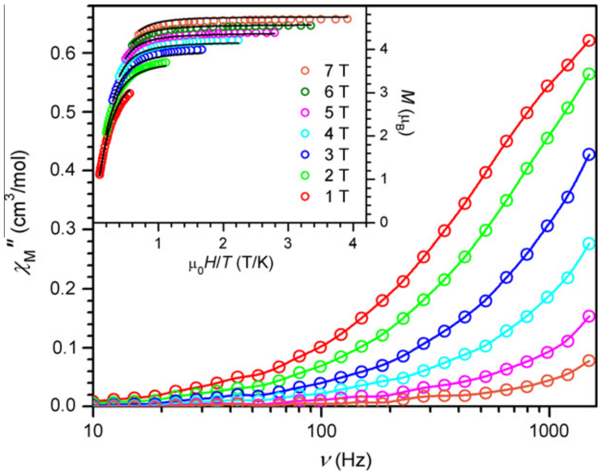

Fig. 4. Variable-frequency out-of-phase ac magnetic susceptibility data for $(TPA^{2C(O)NHtBu})FeReCl_4(CN)_2{\cdot}2MeCN$, collected at temperatures of 1.74 (red), 1.90 (green), 2.10 (blue), 2.30 (turquoise), 2.50 (magenta), and 2.90 (orange) K. Inset: Low-temperature magnetization data for the FeRe cluster, collected at various fields. Solid black lines represent fits to the data, giving $D = -2.3\ cm^{-1}$. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

To probe the magnetic exchange interactions in the FeRe cluster, dc magnetic susceptibility data were collected under an applied field of 1000 Oe. The resulting plot of $\chi_M T$ versus T is shown in Fig. 3. At 300 K, $\chi_M T = 4.96\ cm^3\ K/mol$, slightly higher than the expected value of $\chi_M T = 4.28\ cm^3\ K/mol$ for magnetically isolated Fe^{II} ($S = 2$, $g = 2.00$) and Re^{IV} ($S = 3/2$, $g = 1.65$) centers. As the temperature is lowered from 300 K, the data begin a monotonic rise, reaching a maximum value at 16 K of $\chi_M T = 6.56\ cm^3\ K/mol$. This rise with decreasing temperature is indicative of ferromagnetic exchange between Fe^{II} and Re^{IV} centers within each cluster molecule. To quantify this exchange, the data were modeled according to the following spin Hamiltonian:

$$\hat{H} = -2J(\hat{S}_{Fe}\cdot\hat{S}_{Re})$$

A fit to the data in the temperature range 30–300 K using MAGFIT 3.1 [14] provided an exchange constant of $J = +3.0\ cm^{-1}$, with $g = 1.96$. Below 16 K, the data undergo a downturn, likely due to zero-field splitting of the spin ground state. Notably, $\chi_M T$ falls short of the expected value of $\chi_M T = 7.88\ cm^3\ K/mol$ for an $S = 7/2$ ground state, likely due to a combination of zero-field splitting and low-lying spin excited states. Indeed, considering the spin state energies corresponding to $J = +3.0\ cm^{-1}$ and the Hamiltonian provided above, the $S = 5/2$ first excited state is separated from the $S = 7/2$ ground state by only $20.8\ cm^{-1}$ (see inset of Fig. 3).

To further investigate the magnetic anisotropy in the FeRe cluster, low-temperature magnetization data were collected (see inset of Fig. 4). The resulting non-superimposable isofield curves were modeled according to the following Hamiltonian:

$$\hat{H} = D\hat{S}_z^2 + g_{iso}\,\mu_B\,\mathbf{S}\cdot\mathbf{H}$$

Fits to the data provide an axial zero-field splitting parameter of $D = -2.3$ cm^{-1}, with $g = 1.84$. We note that expanding the Hamiltonian to include an E term does not improve the fit quality. In addition, the discrepancy in g value between this measurement and the dc susceptibility measurement likely arises due to subtle effects of the diamagnetic correction. Nevertheless, in view of this result, in conjunction with the high-spin $S = 7/2$ ground state observed for the mononuclear Fe$^{\mathrm{II}}$ complex, variable-frequency ac susceptibility measurements were carried out to test the possibility of slow magnetic relaxation. Indeed, as shown in Fig. 4, the out-of-phase ac susceptibility exhibits a shoulder that shifts to higher frequency with increasing temperature, demonstrating the onset of single-molecule magnet behavior at low temperature. The presence of only shoulders, rather than well-defined peaks, precludes any quantitative determination of the overall relaxation barrier. Notably, though, the barrier falls well short of 28 cm^{-1}, the theoretical maximum barrier obtained from the expression $U = (S^2 - 1/4)|D|$. This discrepancy is likely the result of quantum tunneling of the magnetization, which enables relaxation through energy levels where $|M_S| < 7/2$.

4. Conclusions

The foregoing results present an examination of the magnetic anisotropy in the recently reported high-spin pentagonal bipyramidal complex $[(\mathrm{TPA}^{2\mathrm{C(O)NH}t\mathrm{Bu}})\mathrm{Fe(CF_3SO_3)}]^{+}$. In addition, we demonstrate the utility of this complex as a building unit for magnetic materials, by virtue of its reaction with $[\mathrm{ReCl_4(CN)_2}]^{2-}$ to generate the cyano-bridged dinuclear cluster $(\mathrm{TPA}^{2\mathrm{C(O)NH}t\mathrm{Bu}})\mathrm{FeReCl_4(CN)_2}$. dc magnetic data obtained for the FeRe cluster reveal ferromagnetic coupling between Fe$^{\mathrm{II}}$ and Re$^{\mathrm{IV}}$ centers, giving rise to a high-anisotropy $S = 7/2$ ground state. Finally, the observed high-spin and uniaxial magnetic anisotropy are shown to give rise to slow magnetic relaxation in the cluster, as evidenced by a frequency-dependent signal in the out-of-phase ac magnetic susceptibility. Future efforts will focus on incorporating $[(\mathrm{TPA}^{2\mathrm{C(O)NH}t\mathrm{Bu}})\mathrm{Fe}]^{2+}$ units into higher-nuclearity metal clusters in an attempt to access new single-molecule magnets with higher relaxation barriers.

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Appendix A. Supporting information available

CCDC 791230 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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