Single-Molecule Magnets

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Surface Modification of a Six-Capped Body-Centered Cube Ni_9W_6 Cluster: Structure and Single-Molecule Magnetism**

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Research on single-molecule magnets (SMMs) has attracted intensive attention because of the intriguing physical properties associated with the quantum tunneling of magnetization effects and their potential applications in high-density information storage.[1] Since the slow magnetization relaxation in $[\mathrm{Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4}]$ (Mn12ac) was discovered, much effort has been made to fabricate metal–oxido clusters with the aim of generating properties analogous to those of the archetypical Mn_{12} cluster.[2,3] Recently, a giant Mn_{84} cluster with a diameter of around 4 nm that exhibits SMM behavior was characterized structurally and magnetically.[4] Despite the high nuclearity of the Mn_{84} supramolecular nanotube, its ground state (S) and energy barrier (U_{eff}) remain relatively small compared with the Mn12ac cluster.[4]

Alternatively, cyanides are frequently utilized for the construction of high-spin molecules because of their structural and magnetic predictability.[5] To attain SMMs with cyanides, it would be a rational approach to combine $[\mathrm{M(CN)}_p\mathrm{L}_q]^{n-}$ ($\mathrm{M}=\mathrm{Fe^{III}}$, $\mathrm{Mn^{III}}$; L = polydentate ligand) or $[\mathrm{M'(CN)}_x\mathrm{L}_y]^{m-}$ ($\mathrm{M'}=\mathrm{Mo^{III}}$, $\mathrm{Re^{II}}$) units as building blocks with magnetic anisotropy sources. In fact, when a metal ion with single-ion anisotropy is incorporated into a cluster, the magnetization at low temperatures relaxes slowly in some cases.[6,7] Given that U_{eff} is proportional to $S^2|D|$ for an integral spin state (D is the axial zero-field splitting parameter of a cluster), it is appropriate to seek high-spin clusters with negative values of D for the purpose of obtaining SMMs with increased values of U_{eff}. Sizable high-spin ground states were established in octacyanidometallate-based $\mathrm{M_9M'_6}$ ($\mathrm{M}=\mathrm{Mn^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Co^{II}}$; $\mathrm{M'}=\mathrm{Mo^{V}}$, $\mathrm{W^{V}}$) clusters with spins up to $S=51/2$.[8] In view of their high-spin ground states, the $\mathrm{M_9M'_6}$ systems are good candidates for SMMs only if they have negative D values. For example, the judicial choice of the $\mathrm{Co^{II}}$ ion as an anisotropic source has led to unique examples of SMM behavior.[9] However, the disadvantage of $\mathrm{M_9M'_6}$ analogues prepared to date is that they are air- and moisture-sensitive as a result of the facile loss of surface solvent molecules. In this context, we have attempted to achieve a stable analogue with SMM character by varying the typical molecular structures of the clusters. Herein we report the synthesis, structure, and magnetic properties of an air-stable Ni_9W_6 bimetallic complex whose surface is modified by 2,2′-bipyridine (bpy). Interestingly, the ligand substitution on the cluster surface breaks the overall molecular symmetry and as a result induces SMM characteristics.

The layering of $\mathrm{(Bu_4N)_3[W(CN)_8]}$ in MeCN onto $\mathrm{[Ni(bpy)(H_2O)_4](SO_4)\cdot 2\,H_2O}$ in water afforded yellow crystals of **1** in a yield of 8%. The IR spectrum shows that the characteristic CN vibrations of **1** are evident at 2183w and 2150w $\mathrm{cm^{-1}}$, which are somewhat higher than those of the precursor $[\mathrm{W(CN)_8}]^{3-}$ (2141w, 2130w, and 2123w (sh) $\mathrm{cm^{-1}}$). This observation is essentially associated with CN groups acting as bridges in **1**.[10]

The molecular structure of **1** (Figure 1), analyzed by X-ray crystallography, can be described as an octahedral core consisting of a Ni center linked by CN groups to six peripheral W atoms and face-capped by eight Ni atoms. It is thus a body-centered cube of Ni atoms with each of the tetragonal faces capped with six W moieties. Four of the CN groups of $[\mathrm{W(CN)_8}]^{3-}$ are connected to Ni atoms on the surface [mean Ni–W = 5.31(2) Å] and one to the central Ni ion [mean Ni–W = 5.35(2) Å]. Each peripheral Ni coordination sphere is

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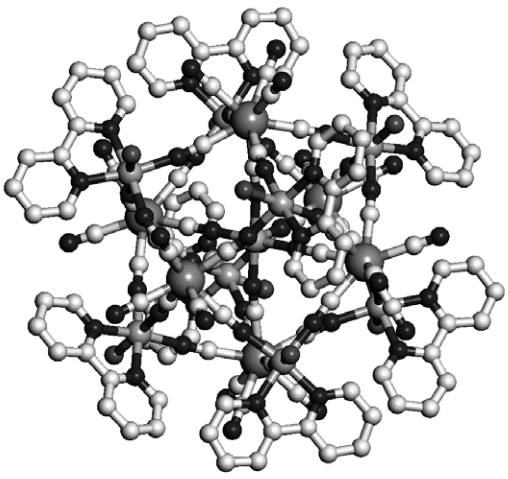

Figure 1. Molecular view of the Ni_9W_6 cluster. Progressively darker shades of gray represent C, Ni, W, O, and N, respectively.

also occupied by one water molecule and one bpy ligand, which is comparable with other $M_9M'_6$ clusters in which three coordination sites are filled by labile MeOH or EtOH molecules.[8,9] All the reported $M_9M'_6$ clusters tend to decompose upon exposure to air, so magnetic measurements were conducted cautiously in frozen solvent or liquid paraffin. The surface modification by the capping ligand bpy engenders the stability of sample in air as a result of the stronger binding affinity of bpy to the Ni center. Moreover, the coordination of bpy to the Ni ions on the molecular surface gives rise to an increase in the separation between clusters. The shortest distance between intercluster metal ions is 7.921 Å, which is significantly longer (by about 1 Å) than those within the $M_9M'_6$ clusters (see the Supporting Information).[8,9] The increased intercluster distance would preclude magnetic interactions between clusters and promote single-molecule magnetism.

The cryomagnetic properties were measured at $H = 1000$ G and $T = 1.8$–300 K (Figure 2). The $\chi_m T$ value of 15.11 $cm^3 K mol^{-1}$ at 300 K is slightly larger than the spin-only value (11.25 $cm^3 K mol^{-1}$) expected for nine noninteracting Ni ($S_{Ni} = 1$) and six W ($S_W = 1/2$) ions. As the temperature is lowered, $\chi_m T$ increases slowly and then abruptly reaches a maximum of 207.6 $cm^3 K mol^{-1}$ at 9 K. This behavior demonstrates the presence of ferromagnetic interactions among the magnetic centers. The sharp drop in $\chi_m T$ below the apex temperature can be attributed to zero-field splitting of a Ni^{II} ion. The magnetic interactions between nearest magnetic neighbors was assessed by employing the Curie–Weiss equation [$\chi_m = C/(T-\theta)$], which gave values of $C = 12.2$ $cm^3 K mol^{-1}$ and $\theta = 58.2$ K. The positive value of θ supports the hypothesis that ferromagnetic couplings between the spins of the Ni and W centers are mediated by the CN linkage.

The field-dependent magnetization (see the Supporting Information) reveals that the magnetization data at 1.8 K is saturated rapidly to 24.7 $N\beta$ at 7 T. The fast rise in magnetization in the low-field regime indicates the existence of a dominant ferromagnetic interaction, which is confirmed by the Brillouin curve with $g = 2.06$ for the uncoupled spins of nine Ni^{II} and six W^V atoms. The $M(H)$ data at 1.8 K can be reproduced well with a Brillouin curve calculated with $S = 12$ for each cluster, which shows that a ferromagnetic ground state exists with $S = 12$. The ferromagnetic interactions between Ni^{II} and W^V through the CN bridges can be understood in terms of orbital considerations. The W 5d orbital forms π overlap with the CN bridge, whereas the Ni e_g orbitals are linked through σ bonds to the CN ligand.[10,11] Consequently, the corresponding magnetic orbitals are orthogonal to each other and ferromagnetic interactions result.[12]

The magnetizations were measured in the temperature range 1.8–4 K at several magnetic fields to probe the onset of zero-field splitting (see the Supporting Information). The reduced magnetization versus H/T plots do not superimpose, which suggests appreciable zero-field splitting. The ac magnetic susceptibility was collected at $H_{dc} = 0$ G, $H_{ac} = 5$ G, and with various frequencies to examine the magnetic nature further. The in-phase (χ'_m; see the Supporting Information) and out-of-phase (χ''_m; Figure 3) components are dependent on the oscillating frequency. The maxima (T_{max}) in $\chi'_m(T)$ shift toward higher temperature with increasing frequency (f). A quantity of the frequency-dependent shifts of T_{max}, defined as $\Delta T_{max}/[T_{max}\Delta(\log f)]$, was found to be 0.13, which is substan-

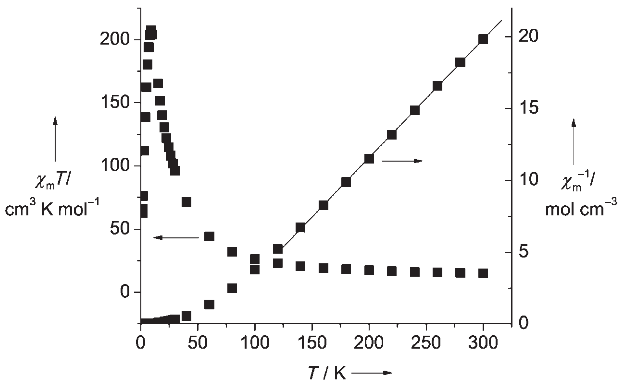

Figure 2. Plot of the temperature dependence of $\chi_m T$ and χ_m^{-1} with a fit to the Curie–Weiss equation (solid line).

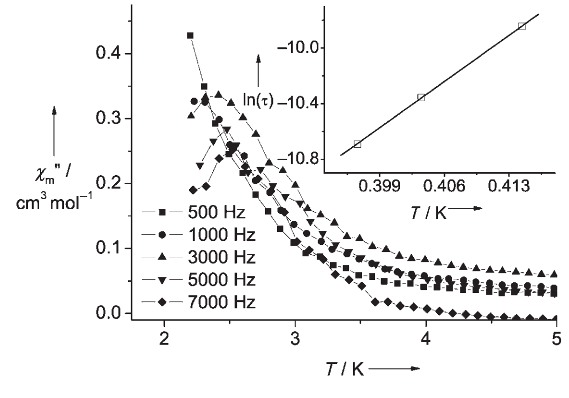

Figure 3. Plot of the out-of-phase term χ''_m versus temperature at the indicated oscillation frequencies. The solid line in the inset denotes a least-squares fit of the data to the Arrhenius equation.

tially larger than those of canonical spin glasses.[13] The obtained quantity designates that the present compound behaves as a superparamagnet. The slow relaxation of the magnetization was evaluated by investigating the variation of the maxima in $\chi''_m(T)$ with the Arrhenius law [$\tau = \tau_0\exp(U_{eff}/k_BT)$; τ_0 is the relaxation attempt frequency]. The least-squares fit gives parameters of $\tau_0 = 1.5\times10^{-13}$ s and $U_{eff} = 33.0\ \mathrm{cm}^{-1}$, which are consistent with SMMs.[6,7,9] The zero-field parameter D is estimated to be approximately $-0.23\ \mathrm{cm}^{-1}$, derived from the relationship $U_{eff} = S^2|D| = 33.0\ \mathrm{cm}^{-1}$, which is consistent with a Ni-based SMM.[14] This feature demonstrates that **1** exhibits SMM properties, which is surprising in that $Ni_9M'_6$ clusters show no χ''_m signal in zero dc field when the surface of the cluster is coordinated by MeOH molecules.[8c] The substitution of two MeOH molecules bound to each peripheral Ni coordination sphere with bpy lowers the molecular symmetry of the clusters, which is reflected in the change of crystal systems from a monoclinic ($C2/c$) to a triclinic space group ($P\bar{1}$). Hence, the surface modification plays a crucial role in reducing the structural symmetry and thus likely enhancing magnetic anisotropy, which eventually leads to such SMM behavior.

In summary, we have prepared an air-stable high-spin Ni_9W_6 cluster ($S = 12$) that displays ferromagnetic interactions between Ni^{II} and W^V ions bridged by CN groups. The symmetry-breaking ligand replacement with bpy into the spherical cluster gives rise to increased magnetic anisotropy and SMM behavior. This result shows that substitution of chelating ligands into symmetric entities should be an excellent strategy to facilitate structural anisotropy and thus magnetic anisotropy for SMMs with high spin-reversal energy barriers.

Experimental Section

In the dark $(Bu_4N)_3[W(CN)_8]$ (0.10 mmol) in MeCN was layered on top of $[Ni(bpy)(H_2O)_4]\cdot(SO_4)\cdot2H_2O$[15] (0.15 mmol) in water. Yellow crystals of $[Ni\{Ni(bpy)(H_2O)\}_8\{W(CN)_8\}_6]\cdot41H_2O$ suitable for X-ray crystallography grew after several days. The crystals were air-dried to yield $[Ni\{Ni(bpy)(H_2O)\}_8\{W(CN)_8\}_6]\cdot23H_2O$ (**1**) in 8% yield. The chemical composition of **1** was checked by elemental and thermogravimetric analysis. Elemental analysis (%) calcd for $C_{128}H_{126}N_{64}Ni_9O_{31}W_6$: C 32.79, H 2.71, N, 19.12; found: C 32.42, H 2.47, N 18.72.

Elemental analyses were performed at the Elemental Analysis Service Center of Sogang University. Infrared spectra were obtained from KBr pellets with a Bomen MB-104 spectrometer. Magnetic susceptibility data for **1** were measured with MPMS-7 (dc data) and PPMS (ac data) susceptometers. Diamagnetic corrections were estimated from Pascal's tables.

Crystal data for **1**: $C_{128}H_{162}N_{64}Ni_9O_{49}W_6$, $M_r = 5012.71$, triclinic, space group $P\bar{1}$, $a = 18.3936(6)$, $b = 19.6124(6)$, $c = 30.4162(10)$ Å, $\alpha = 90.7410(10)$, $\beta = 105.5680(10)$, $\gamma = 113.6290(10)°$, $V = 9593.0(5)$ Å^3, $Z = 2$, $D_{calcd} = 1.735\ \mathrm{g\,cm^{-3}}$, $\mu = 4.527\ \mathrm{mm^{-1}}$, $T = 130$ K, 159090 reflections collected, 47147 unique ($R_{int} = 0.1204$), $R1 = 0.0542$, $wR2 = 0.0990$ [$I > 2\sigma(I)$]. CCDC-606405 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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