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A Facially Capped Body-Centered Ni_9W_6 Cubane Modified with Sulfur-Containing Bidentate Ligands: Structure and Magnetic Properties

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A fully capped body-centered cubane cluster $[Ni_9(btz)_8(MeOH)_8\{W(CN)_8\}_6]\cdot 18H_2O\cdot 6MeOH$ (**1**) [btz = 2,2′-bi(4,5-dihydrothiazine)], whose periphery was modified with sulfur-containing bidentate ligands acting as potential anchoring sites to electrodes and substrates, was prepared. The geometric analyses around the W atoms revealed that W1 adopts a distorted dodecahedron, while the other W atoms are closer to a square-antiprism geometry than a dodecahedron. The magnetic studies of **1** reveal that ferromagnetic couplings are operative through CN bridges, generating an $S = 12$ ground state. It appears that magnetic anisotropy of a molecule is venerable to subtle structural variations.

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Introduction

The remarkable advances in methods integrating individual molecules into electrodes or substrates have provided insight into intrinsic physical characters.[1] For instance, the Kondo effects sometimes coupled with negative magnetoresistance were observed in single-molecule transitors where chemically well-defined molecules were incorporated.[2] In addition, magnetic states and their magnetic anisotropy of a cluster were qualitatively investigated by taking electron-tunneling spectra.[3] More recently, molecular electrodes with a localized spin were reliably constructed at the edge of a multilayer thin film pattern.[4] In this context, as far as chemical synthesis is concerned, the rational design of molecules possessing both favorable binding groups, which can self-organize into specific electrodes and substrates to ensure the grafting of the molecules on their surfaces, and large spins that can affect electron transports between electrodes, is highly sought.

The higher ground-state spins among cyanide-bridged clusters were found in octacyanatometalate-based dimetallic assemblies $[M'\{M(Sol)_3\}_8\{M(CN)_8\}_6]\cdot x\mathrm{Sol}\cdot yH_2O$ (M′ = Mn, Co, Ni; M = W, Mo; Sol = MeOH or EtOH).[5] We showed that the alcohol molecules on the parent Ni_9M_6 clusters can be replaced by the aromatic bidentate ligand 2,2′-bipyridine, allowing for the formation of modified stable clusters.[6]

Herein we present the synthesis, structure, and magnetic properties of a new cluster, $[Ni_9(btz)_8(MeOH)_8\{W(CN)_8\}_6]\cdot 18H_2O\cdot 6MeOH$ (**1**) [btz = 2,2′-bi(4,5-dihydrothiazine)]. It is noted that the cluster is composed of flexible bidentate ligands that carry thioether groups capable of serving as authentic anchoring points toward Au electrodes and substrates. It constitutes the first example of a sulfur-containing cluster with a large ground-state spin among the reported M'_9M_6 family. A magnetic relaxation was not observed in **1**, which is contrary to the Ni–W analogue chelated with bpy,[6a] designating that magnetic anisotropy of a molecule is very sensitive to subtle structural variations.

Results and Discussion

A reaction of $Ni(ClO_4)_2\cdot 6H_2O$, btz, and $(Bu_4N)_3[W(CN)_8]$ in a mixed solvent of MeOH/MeCN/H_2O afforded brown crystals of **1** in good yield. The Cl–O stretching vibrations in the IR spectra are absent. The characteristic IR bands for CN ligands are visible at 2150w, 2158w (sh), 2181w, and 2196w cm^{-1} for **1**, which are compared with the reference peaks of 2123w (sh), 2139w, and 2141w cm^{-1} for $(Bu_4N)_3[W(CN)_8]$. The shift of the peak positions toward higher frequencies evidently supports the presence of bridging CN groups. The observation in CN peak positions is related with the prevalent kinematic effect, which leads to restricted motion of CN groups, and electronic and geometric effects.[7]

The X-ray structure analysis shows that **1** crystallizes in the triclinic system with space group $P\bar{1}$. The overall struc-

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ture of **1** can be viewed as a body-centered Ni_9 cube facially capped with six W moieties (Figure 1). The W geometry deviates from the ideal symmetry of a square antiprism (SAPR, D_{4d}), dodecahedron (DD, D_{2d}), and bicapped trigonal prism (BTP, C_{2v}). The exact determination of the polyhedral shape around the W ions is of crucial importance, because the strength of the exchange coupling through the CN bridge is influenced by the actual shape of the $[M(CN)_8]^{3-}$ moiety.[8] We performed a continuous shape measure (CShM) analysis using the SHAPE program (Table 1).[9,10] In **1**, W1 adopts a distorted DD, while the other W atoms, which have large generalized interconversion coordinates (ϕ), are closer to the SAPR geometry than to DD. For comparison, the bpy-capped Ni–W analogue was analyzed by the same procedure (Table S1). Each W2, W3, and W6 atom can be viewed as a distorted DD, and W4 and W5 have shapes closer to SAPR than to DD. The W1 atom is midway between the SAPR and DD geometries. It is noticed that the parameters Δ for the deviation from the DD/SAPR interconversion path are relatively larger than those calculated for some octacyanatometalate-based systems.[8]

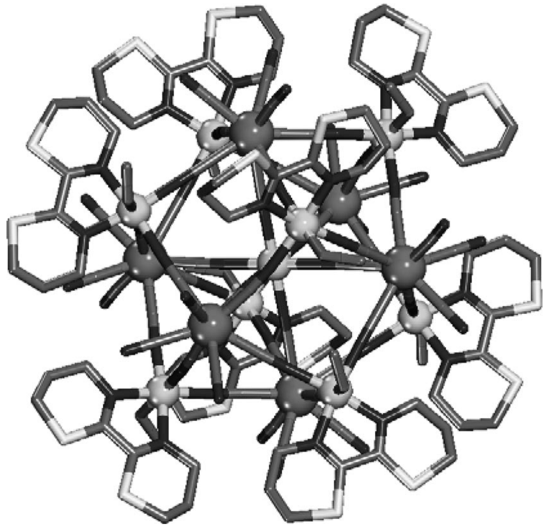

Figure 1. Molecular view of **1**. Progressively darker shades of gray represent S, Ni, C, W, O, and N, respectively.

Table 1. Results of the continuous shape measure analysis for **1**.[a]

Metal center	S_{SAPR}	S_{DD}	S_{BTP}	$\Delta_{(SAPR,DD)}$	$\phi_{(SAPR>DD)}$	$\phi_{(DD>SAPR)}$
W1	2.13	0.52	2.28	0.29	86%	43%
W2	1.15	1.42	1.66	0.34	64%	71%
W3	1.18	1.44	1.68	0.35	64%	71%

[a] S_{DD} is the shape measure relative to the dodecahedron, S_{SAPR} the shape measure relative to the square antiprism, S_{BTP} the shape measure relative to the bicapped trigonal prism, $\Delta_{(SAPR,DD)}$ indicates the deviation from the DD/SAPR interconversion path, and $\phi_{(SAPR>DD)}$ and $\phi_{(DD>SAPR)}$ the generalized interconversion coordinates. The sum $\phi_{(SAPR>DD)} + \phi_{(DD>SAPR)}$ is larger than 100% because of the nonzero value of $\Delta_{(SAPR,DD)}$.

The average W–C distance is 2.16(1) Å, and the bridging W–C–N angle is almost linear and ranges from 173.7 to 178.6° for **1**. The Ni–N–C(cyanide) angles are in the range of 170.8–176.3° for **1**. Five of eight CN ligands of $[W(CN)_8]^{3-}$ take part in coordination to one central and four peripheral Ni atoms, whereas the other CN groups remain uncoordinated. The average intracluster Ni–W distances in **1** are equal to 5.319(7) Å for the central Ni atom, and 5.34(2) Å for the peripheral Ni atoms, respectively, which fall in the usual ranges of octacyanatometalate-based dimetallic clusters.[5,6,11] The geometric environment of each terminal Ni ion in **1** corresponds to a distorted octahedron, consisting of three N atoms from bridging CN groups and two N atoms from btz, and one O atom from MeOH. In the crystal packing of **1** (Figure S1), no π–π interactions between clusters are present, because the chelated btz ligands on the clusters are not planar. The hydrogen bonds are formed among unbound CN ligands, lattice water molecules, and coordinated methanol molecules. The shortest intercluster metal–metal distance is 7.830 Å for **1**, which is larger than those of unsubstituted clusters but shorter than those of bpy-capped molecules.[5,6] This material is airstable because of the presence of the bidentate ligand btz chelating the Ni^{II} ions. It is also worth mentioning that the sulfur atoms of the btz ligands are oriented outward and potentially behave as anchoring sites to Au substrates and electrodes. This functionality may be utilized in immobilizing molecules on their surfaces to examine properties induced by the single molecules.[1]

The magnetic data of **1** at 1000 G in the temperature range of 2–300 K are displayed in Figure 2. The $\chi_m T$ value of 16.05 $cm^3 K mol^{-1}$ at 300 K is larger than the spin-only one (11.25 $cm^3 K mol^{-1}$) expected for nine non-interacting Ni ($S_{Ni} = 1$) and six W ions ($S_W = 1/2$) assuming $g = 2$, which implies the presence of an intramolecular ferromagnetic coupling, and similar to the Ni_9M_6 family capped with bpy.[5e,6] As the temperature is lowered $\chi_m T$ undergoes a gradual rise up to 89.72 $cm^3 K mol^{-1}$ at 10 K. The magnetic behavior definitely demonstrates the presence of ferromagnetic interactions among magnetic centers mediated by CN ligands, which are due to the orbital orthogonality between magnetic orbitals of spin centers. Further cooling below the peak temperature causes $\chi_m T$ to be reduced, which may be associated with the combined contributions from zero-field

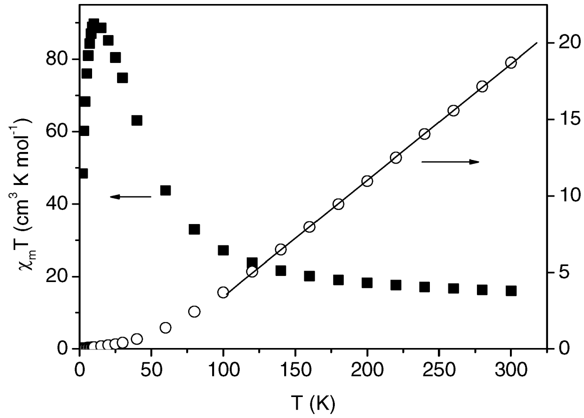

Figure 2. Plots of $\chi_m T$ (left) and χ_m^{-1} (right) at 1000 G of **1**. The solid line represents the best fit to the Curie–Weiss equation.

splitting, Zeeman effects under the applied field, and intermolecular magnetic interactions. The Curie–Weiss fitting in the high-temperature region ($T > 120$ K) affords a Weiss constant (θ) of 55.0 K, implying the presence of overall ferromagnetic couplings in **1**.

The $M(H)$ data were recorded at $T = 2$ K and $H = 0$–7 T (Figure 3). The magnetization curve of **1** increases very rapidly at low fields and reaches a saturation value of 26.3 Nβ at 7 T. The intracluster ferromagnetic couplings are confirmed by the fact that the experimental data in the entire field regime lie above the Brillouin curves derived from nine uncoupled S_{Ni} and six S_{W}. For **1**, the data points are fairly reproduced by the theoretical line of $S = S_{\mathrm{Ni}} + S_{\mathrm{W}} = 12$ with $g = 2.19$, suggesting that the ground state at 2 K is equal to $S = 12$, which agrees with the reported $\mathrm{Ni_9M_6}$ systems.[5e,6]

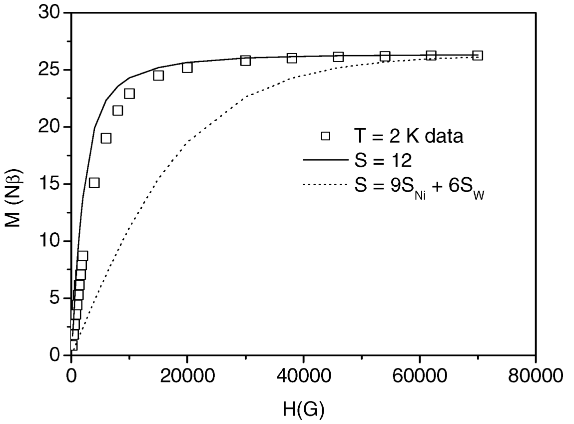

Figure 3. Plot of the magnetization (M) vs. H of **1** at 2 K. The solid and dotted lines are theoretically calculated curves with the Brillouin functions involving $S = 12$ and a set of uncoupled $9S_{\mathrm{Ni}}$ and $6S_{\mathrm{W}}$, respectively.

The reduced magnetization data of **1** at low temperatures (2–4 K) and high magnetic fields (1–7 T) were measured to determine the total-spin ground state and the zero-field splitting parameter (Figure 4). The obvious non-superimposition of isofield lines of **1** supports the existence of zero-field splitting. Because low-field data are more significantly governed by intermolecular magnetic interactions and/or the population of low-lying excited states,[12] we fitted the high-field data at $H = 4$–7 T using the Anisofit 2.0 program.[13] A best fit with an $S = 12$ ground state assuming no intercluster magnetic interactions provides values of $g = 2.19$, $D = 0.054\ \mathrm{cm^{-1}}$, and $E = 0.0003\ \mathrm{cm^{-1}}$, where D and E stand for the axial and rhombic zero-field splitting parameters. The resultant D value denotes that **1** possesses no signature of single-molecule magnet property requiring a uniaxial negative zero-field splitting parameter. In the ac magnetic susceptibility data (Figure S2), **1** exhibits no frequency dependence of the in-phase component (χ_m') and the out-of-phase term (χ_m''), which are in accordance with the positive D parameter.[5e] This is in contrast to the bpy-capped $\mathrm{Ni_9W_6}$ analogue, suggesting that the subtle structural variations arising from polyhedral shapes of W centers, bond lengths and angles in the bridging pathways probably affect the magnetic anisotropic nature of a molecule.[8]

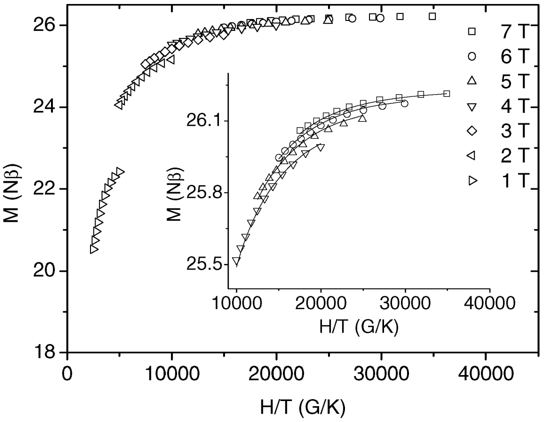

Figure 4. Plot of the reduced magnetization (M) vs. H/T of **1** at indicated magnetic fields. The solid lines in the inset present the best fits with $S = 12$ at $H = 4$–7 T.

Conclusions

We have prepared a cyanide-bridged cluster $\mathrm{Ni_9W_6}$ (**1**) illustrating a fully capped body-centered cubane structure. The alcohol molecules on the periphery of the parent clusters were successfully replaced by sulfur-containing bidentate ligands. The decoration of a cluster with groups having potential anchoring sites to specific electrodes and substrates might provide a way to immobilize individual molecules and study correlated single molecular properties. The adjustment of the magnetic anisotropy may be achieved by altering structural parameters to some extent.

Experimental Section

Materials: $\mathrm{(Bu_4N)_3[W(CN)_8]}$ and 2,2′-bi(4,5-dihydrothiazine) (btz) were prepared according to literature procedures.[14,15] All other chemicals and solvents in the synthesis were of reagent grade and used as received.

Physical Measurements: Elemental analyses for C, H, and N 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 data for **1** were collected by using Quantum Design SQUID magnetometers. Diamagnetic corrections of **1** were estimated from Pascal's Tables.

Preparation of Compound 1: A methanolic solution of $\mathrm{Ni(ClO_4)_2\cdot 6H_2O}$ (0.15 mmol) was mixed with btz (0.15 mmol) in MeOH to afford a yellow powder. The resulting mixture was redissolved by adding a small amount of MeCN. A solution of $\mathrm{(Bu_4N)_3[W(CN)_8]}$ (0.10 mmol) in MeCN/MeOH/$\mathrm{H_2O}$ mixed solvent was added to the $\mathrm{Ni^{II}}$ solution. The brown solution was filtered and left undisturbed for several days, producing yellow crystals. The air-dried product $\mathrm{[Ni_9(btz)_8(MeOH)_8\{W(CN)_8\}_6]\cdot 18H_2O}$ (**1**) was obtained in a yield of 76%. $\mathrm{C_{120}H_{164}N_{64}Ni_9O_{26}S_{16}W_6}$ (5063.32): calcd. C 28.5, H 3.26, N 17.7, S 10.1; found C 28.1, H 2.87, N 18.1, S 9.73. Attempts to characterize a cyanide-bridged Ni–Mo analogue with btz were unsuccessful.

Crystal Data for 1: $C_{126}H_{188}N_{64}Ni_9O_{32}S_{16}W_6$, M = 5255.85, triclinic, space group $P\bar{1}$, a = 17.1370(17), b = 18.6108(19), c = 19.2427(19) Å, α = 109.015(3), β = 113.529(3), γ = 98.628(4)°, V = 5034.5(9) Å^3, Z = 1, $\rho_{calcd.}$ = 1.734 g cm^{-3}, μ = 4.471 mm^{-1}, T = 130 K, 83889 reflections collected, 24668 unique (R_{int} = 0.0773), $R1$ = 0.0505, $wR2$ = 0.0945 [$I > 2\sigma(I)$]. CCDC-674134 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Relevant crystal structure and ac magnetic susceptibility data of **1**.

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