Inorg. Chem. **2004**, *43*, 6899–6901

Inorganic Chemistry
Communication

One-Dimensional Octacyanomolybdate-Based Cu(II)–Mo(V) Bimetallic Assembly with a Novel Rope-Ladder Chain Structure

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Received August 18, 2004

A new type of one-dimensional cyanide-bridged Cu(II)–Mo(V) bimetallic assembly, $[Cu(cyclam)]_3[Mo(CN)_8]_2\cdot 5H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), was prepared by self-assembling $Mo(CN)_8^{3-}$ and $Cu(cyclam)^{2+}$ ions in a 2:3 stoichiometric ratio. The overall molecular view is delineated as a novel rope-ladder chain structure. It displays a dominant ferromagnetic behavior within a pentanuclear Cu_3Mo_2 unit ($J_p = 3.88$ cm^{-1}). Interunit ferromagnetic interactions ($J_c = -0.03$ cm^{-1}) through a longer magnetic pathway of Cu–Mo and weak antiferromagnetic couplings ($zJ' = -0.46$ cm^{-1}) resulting from interchain interactions are obtained.

Molecule-based magnetic materials have received extensive attention because of their potential applications to magnetic devices.[1] In an effort to achieve magnetically interesting systems, hexacyanometalates with 3d metal ions have been one of successful building bricks. A great number of bimetallic compounds based on hexacyanometalates have already been reported.[2] In recent years, octacyanometalates, $[M(CN)_8]^{n-}$ (M = 4d or 5d metal ion), as another useful synthon for supramolecular architectures have been utilized to fabricate magnetic self-assemblies on account of their functionalities and high critical temperatures applicable to molecular magnets.[3] The coordination versatility of the molecular precursors depending on chemical environments resulted in cyanide-bridged bimetallic systems with discrete molecules, 1D chains, 2D sheets, or 3D network structures.[4−8] Among them, for instance, a few W(V)−M′ [M′ = Mn(II), Co(II), Ni(II), Cu(II)] compounds have been characterized structurally and magnetically, exhibiting intriguing properties.[4−7] Compared to these octacyanotungstate(V)-based complexes, examples of bimetallic assemblies including octacyanomolybdate(V) as a building brick are still extremely rare.[8] In the present paper, we report the synthesis, structure, and magnetic properties of a new 1D complex, $[Cu(cyclam)]_3[Mo(CN)_8]_2\cdot 5H_2O$ (**1**), with a novel rope-ladder chain structure, which is the first structural motif found in octacyanometalate-based bimetallic systems.

To an aqueous solution of $Cu(cyclam)(NO_3)_2$ (0.30 mmol) was added a methanolic solution of $(Bu_4N)_3[Mo(CN)_8]$ (0.20 mmol) with stirring. Immediately, crystalline product was precipitated in a yield of 62%. Pink-brown plate single crystals suitable for X-ray were obtained by layering the two solutions.[9] The three CN stretching frequencies in the IR spectrum for **1** are present at 2162w, 2149m (sh), and 2140s

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(9) Anal. Calcd: C, 37.1; H, 5.55; N, 26.3. Found: C, 37.3; H, 5.47; N, 26.0. IR data (cm^{-1}, KBr pellet): 3523, 3460 (s, OH stretching), 3261, 3199 (s, NH stretching), 2959, 2937, 2876 (m, CH stretching) 2162w, 2149m (sh), 2140m (CN stretching), 1637, 1605 (m, H_2O bending), 1481m, 1460s, 1431s, 1386s, 1334w, 1319w, 1296w, 1261w, 1244w, 1236w, 1130m, 1095s, 1068m, 1028m, 982s, 908w, 812w.

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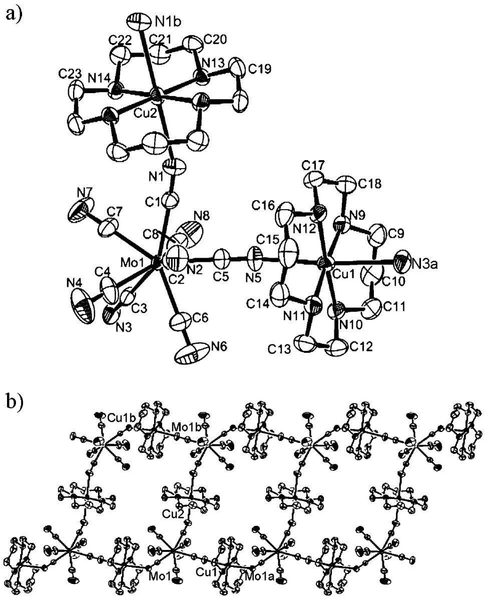

Figure 1. (a) ORTEP diagram showing the asymmetric unit and symmetry-related atoms along with the atom-labeling scheme. (b) 1D extended chain structure. Symmetry codes: a $= 1 + x, -1 + y, z$; b $= 1 - x, -y, 1 - z$.

cm^{-1}, which are higher than those (2140s and 2123m cm^{-1}) of the precursor $Mo(CN)_8^{3-}$. This demonstrates that the bands at 2162 and 2149 cm^{-1} can be assigned to bridging CN groups and the lowest band at 2140 cm^{-1} is related to free CN groups.

Figure 1a shows the crystal structure of **1** determined by single-crystal X-ray analysis.[10,11] The Mo center has an irregular square antiprism consisting of eight CN groups with an average Mo−C bond length of 2.156(10) Å. As expected from the IR data, three CN moieties are linked to neighboring Cu(II) ions, and the rest are left unbound. The geometry around a Cu atom can be described as axially elongated octahedral, because the four N atoms from cyclam constitute the basal plane while the apical positions are occupied by the N atoms from CN groups. The apical Cu−N distances are 2.514(3) Å for Cu1−N5 and 2.557(4) Å for Cu2−N1, which are compared to the longer distance of Cu1−N3a [a $= 1 + x, -1 + y, z$; 2.711(4) Å]. The axial distortion is definitely associated with the characteristic Jahn−Teller effect of Cu(II) ion.[8] The angles between central Cu(II) ions and coordinated CN ligands from Mo1 correspond to 160.6(3)° for Cu1−N5−C5 and 156.6(3)° for Cu2−N1−C1, whereas the Cu1−N3a−C3a angle is much more acute, 142.7(3)°. Four among the five water molecules in the unit cell are involved in hydrogen bonding to terminal CN groups and the other water molecule, with lengths spanning from 2.897 to 3.152 Å, which has another hydrogen bond to a NH group of cyclam with a distance of 2.992 Å. The overall molecular structure can be viewed as a rope-ladder chain (Figure 1b), which is reminiscent of the hexacyanometalate-based bimetallic assemblies $[Ni(en)_2]_3[M(CN)_6]_2{\cdot}2H_2O$ (en = ethylenediamine; M = Fe, Mn, Cr, Co) with the different bidentate chelating en ligand.[12] The Cu−Mo distances in the chain are in the range from 5.696 to 5.741 Å. The shortest interchain Mo1−Mo1, Cu1−Cu1, and Cu2−Cu2 separations are identical at 8.904(5) Å. The nearest Mo1−Cu1 and Mo1−Cu2 distances are equal to 7.683(4) and 7.517(4) Å, respectively.

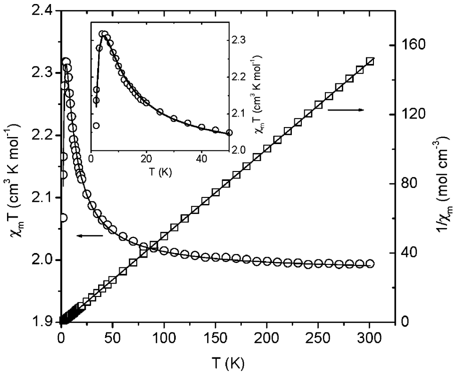

Figure 2. Plot of $\chi_m T$ and χ_m^{-1} vs T for **1**. The solid lines denote the best theoretical fits.

The cryomagnetic property of **1** is illustrated in Figure 2 in the form of $\chi_m T$ and χ_m^{-1} versus T. The $\chi_m T$ value of 1.99 cm^3 K mol^{-1} at 300 K is slightly larger than the spin-only value (1.88 cm^3 K mol^{-1}) expected for an uncoupled set of three Cu(II) ($S_{Cu} = {}^1/_2$) and two Mo(V) ($S_{Mo} = {}^1/_2$) ions. With decreasing temperature, $\chi_m T$ increases gradually and then abruptly, reaching a maximum of 2.32 cm^3 K mol^{-1} at 5 K, indicative of the presence of ferromagnetic interactions. Further cooling causes a sharp drop in $\chi_m T$, suggesting the existence of antiferromagnetic interactions. The inverse magnetic susceptibility data in the temperature range 5−300 K were fitted with the Curie−Weiss equation, providing parameters of $C = 1.99$ cm^3 K mol^{-1} ($g = 2.06$) and $\theta = 1.24$ K. The positive Weiss constant (θ) indicates that individual Cu(II) and Mo(V) spins interact ferromagnetically in the lattice.

To probe the nature of the magnetic exchange between the Cu(II) and Mo(V) magnetic centers, we examined the structural parameters of **1**. For Cu and apical N atoms from Mo1, the Cu−N bond lengths and Cu−N−C angles are similar to each other within 0.04 Å and 4°. In comparison, the bond length and angle regarding Cu1, N3a, and C3a are quite longer by about 0.2 Å and much sharper by around 16° than the aforementioned case. It is therefore reasonably assumed that magnetic interactions between Cu1−Mo1a via the CN bridge is much weaker than the other Cu−Mo couplings through the CN linkage.[13] On the basis of these criteria, we took into account a magnetic model for the

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(10) Crystal structure of **1**: $C_{23}H_{41}N_{14}O_{2.5}Cu_{1.5}Mo$, Fw = 744.95, triclinic, space group $P\bar{1}$, $a = 8.904(3)$, $b = 10.056(4)$, $c = 19.464(10)$ Å, $\alpha = 78.32(4)°$, $\beta = 83.15(3)°$, $\gamma = 69.71(3)°$, $V = 1598.5(12)$ Å^3, $Z = 2$, $D_{calc} = 1.548$ g cm^{-3}, $T = 293(2)$ K. The structure was solved and refined by least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the WinGX package.[11] H atoms were calculated at idealized positions. The O3 atom is disordered and assigned with a 0.5 occupancy factor. The final refinement on F^2 gave R1 = 0.0420 and wR2 = 0.1057 using 5813 reflections with the condition $I > 2\sigma(I)$.

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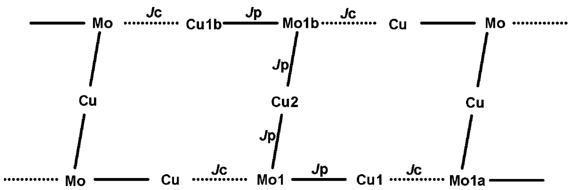

Figure 3. Schematic representation of magnetic exchange couplings in **1**. The solid lines stand for intrapentamer interactions (J_p), and the dotted ones for interpentamer interactions (J_c).

pentanuclear Cu1−Mo1−Cu2−Mo1b−Cu1b (b = 1 − *x*, −*y*, 1 − *z*) skeleton with the Hamiltonian $\mathbf{H} = -J_p(S_{Cu1}S_{Mo1} + S_{Mo1}S_{Cu2} + S_{Cu2}S_{Mo1b} + S_{Mo1b}S_{Cu1b}) + g\beta H(S_{Cu1} + S_{Mo1} + S_{Cu2} + S_{Mo1b} + S_{Cu1b})$. The expression for molar magnetic susceptibility of the pentamer can be described as $\chi_p = (Ng^2\beta^2/3kT)\{\sum_S S(S+1)(2S+1)\exp[-E(S)/kT]\}/\{\sum_S(2S+1)\exp[-E(S)/kT]\}$, where $E(S)$ represents eigenvalues of $\mathbf{H}$. To interpret the observed magnetic behavior, an approximate exchange coupling mechanism was adopted. As shown in Figure 3, we employed an infinite chain model by considering the pentamer unit (S_p) as a classical spin[14]

$$\chi_p = (Ng^2\beta^2/3kT)S_p(S_p + 1) \qquad (1)$$

$$\chi_c = [Ng^2\beta^2 S_p(S_p + 1)/3kT][(1 + u)/(1 - u)] \qquad (2)$$

where $u = \coth[J_cS_p(S_p + 1)/kT] - kT/J_cS_p(S_p + 1)$.

To assess interchain magnetic interactions, the molecular field correction is incorporated into the magnetic model for the chain of the pentamers, which is consequently represented as $\chi_m = \chi_c/(1 - zJ'\chi_c/Ng^2\beta^2)$. A best fit with this corrected magnetic susceptibility formula affords magnetic parameters of $g = 2.07$, $J_p = 3.88$ cm^{-1}, $J_c = 0.03$ cm^{-1}, and $zJ' = -0.46$ cm^{-1}. The measure of the goodness of fit R, defined as $R = \Phi/(n - k)$, where n is the number of data points, k is the number of parameters, and $\Phi = \Sigma_i[(\chi_mT)_i^{obs} - (\chi_mT)_i^{calc}]^2$, is equal to 7.0×10^{-5}. The curve calculated with these parameters provides satisfactory agreement with the experimental points as illustrated in Figure 2. The ferromagnetic coupling (J_p) between Cu(II) and Mo(V) within the pentamer is understood by the fact that the magnetic orbital ($d_{x^2-y^2}$) on Cu(II) atom directed toward four equatorial N atoms of cyclam is not likely to be efficiently delocalized on the empty π^* orbitals of the CN bridges, owing to the long bond distances that match in π symmetry with the d_{z^2} orbitals of adjacent Mo(V) atoms.[15] The overlap between magnetic orbitals through the CN bridges is thus minimal, leading to the ferromagnetic interaction. This is because, given the overall magnetic exchange (J_{total}) contributed from ferromagnetic (J_F) and antiferromagnetic (J_{AF}) components, J_{AF} proportional to overlap integral is negligible in this situation, allowing J_F to be dominant. For magnetic coupling between Cu1 and Mo1a, the tiny ferromagnetic interaction (J_c) is obtained because of the structural parameters of the longer pathway and more acute angle for Cu1−Mo1a in which magnetic communication is more ineffective compared to the shorter ones of Cu−Mo. The negative zJ' value, which accounts for the antiferromagnetic phenomenon observed below 5 K in Figure 2, arises from antiferromagnetic interchain interactions mediated by hydrogen bonds.

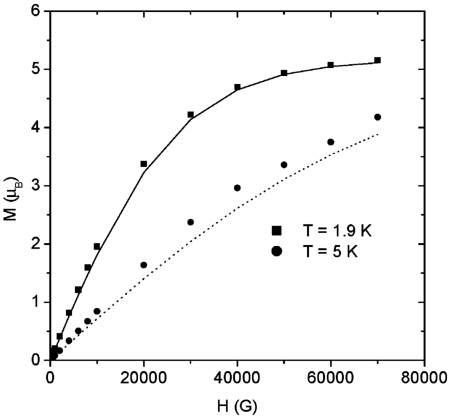

Figure 4. Field dependence of the magnetization of **1**. The solid and dotted lines illustrate the Brillouin curves for an independent set of three Cu(II) and two Mo(V) ions at 1.9 and 5 K, respectively.

Figure 4 represents the field dependence of the magnetization at 1.9 and 5 K. The magnetization curve at 1.9 K arrives at a saturation value of 5.15 μ_B in 7 T, which is consistent with the theoretical value (5.11 μ_B) calculated from the Brillouin function at $g = 2.07$ for an independent set of three Cu(II) and two Mo(V) spins. It is noticed that the measured data points reach saturation faster than the calculated curve, implying that a global ferromagnetic interaction in **1** is operative, in good agreement with the magnetic susceptibility result. The disparity between the data points and theoretical values is more pronounced at 5 K because the ferromagnetic interaction is prevalent at temperatures down to 5 K.

In summary, a 1D rope-ladder shaped Cu(II)−Mo(V) assembly bridged by CN ligands was synthesized and characterized using X-ray crystallography and magnetometry. Ferromagnetic interactions occur between Cu(II) and Mo(V) through CN bridges within and between the Cu_3Mo_2 pentamer units, while weak antiferromagnetic couplings are transmitted through hydrogen-bonding interactions between chains.

Acknowledgment. The present research is financially supported by Korea Research Foundation (Grant KRF-2003-003-C00073).

Supporting Information Available: Expression for the magnetic suceptibility of the pentameric unit. X-ray crystallographic file for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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