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Communication

A Two-Dimensional Octacyanomolybdate(V)-Based Ferrimagnet: {[Mn^{II}(DMF)$_4$]$_3$[Mo^V(CN)$_8$]$_2$}$_n$

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Treatment of [HNBu$_3$]$_3$[Mo^V(CN)$_8$] with manganese(II) *p*-toluene-sulfonate in *N,N′*-dimethylformamide (DMF) affords {[Mn^{II}(DMF)$_4$]$_3$-[Mo^V(CN)$_8$]$_2$}$_n$ (**1**) as a two-dimensional network. The structure of **1** consists of [*cis*-Mn^{II}(DMF)$_4$(μ-NC)$_2$]$^{2+}$ and [*trans*-Mn^{II}(DMF)$_4$(μ-NC)$_2$]$^{2+}$ units that are linked via cyanides to three-connected [Mo^V-(CN)$_5$(μ-CN)$_3$]$^{3-}$ centers in a 4:2:6 ratio, forming 12-membered rings. Magnetic measurements indicate that **1** is a ferrimagnet (T_N = 8 K) that exhibits frequency-dependent behavior in χ''. Heating of **1** affords an additional magnetic phase (T_N = 21 K) that is absent of linkage isomerism.

Cyanometalates are a versatile class of inorganic reagents that can be used to construct a variety of clusters and extended arrays of metal centers linked via cyanides.[1–6]

However, to prepare robust materials with predictable and tunable properties, it is crucial to control the self-assembly of precursors during synthesis. Well-defined cyanometalate precursors or building blocks that self-assemble with structures intact into a common structural archetype are necessary for constructing materials that exhibit tunable magnetic, optical, and electronic properties; this synthetic strategy allows for accurate magnetostructural correlations to be described.[1–3] Examples include single-molecule magnetic clusters[3a–e,7a] and single-chain magnetic,[3f–h] photomagnetic,[4] and room-temperature magnetic lattices.[2]

The diffuseness and radial extent of the 4d (Mo) and 5d (W) orbitals present in octacyanometalates are expected to afford enhanced π-back-bonding and superexchange efficiency, relative to first-row analogues. This suggests that octacyanometalates are promising building blocks for constructing clusters and networks that exhibit markedly different properties than known hexa- and heptacyanometalate analogues.[1–9]

Octacyanometalate clusters that exhibit single-molecule magnetic behavior, presumably because of single-ion anisotropy of the divalent Co^{II} centers present, were recently reported.[7a] These M^{II}[M^{II}(ROH)$_3$]$_8$[M^V(CN)$_8$]$_6$·nROH·mH$_2$O (R = Me, Et) clusters are typically prepared in alcoholic

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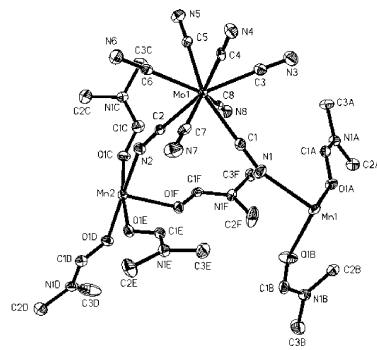‡ Virginia Polytechnic Institute and State University.
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media and are prone to rapid desolvation and aggregation under mild conditions.[7g] Consequently, we rationalized that N,N'-dimethylformamide (DMF) might be a more suitable donor ligand than alcohols for stabilizing the cluster framework. However, in a DMF solution, a series of magnetic chains of clusters, rather than the expected $\{M^{II}_9M^V_6\}$ clusters, are obtained. Tang and co-workers have previously reported that one-dimensional (1-D) $\{[M^{II}(DMF)_4][M^{II}(DMF)_2L_n]_2[M^V(CN)_8]_2\}_n$ (M^{II} = Mn, Co; L = bpy (n = 1), DMF (n = 2); M^V = Mo, W) networks exhibit "glassy", frequency-dependent, magnetic relaxation phenomena, despite the fact that the former contains isotropic spin centers.[8] In the present contribution, we describe recent efforts regarding the synthesis, crystallographic, spectroscopic, and magnetic properties of a new two-dimensional (2-D) structural archetype containing octacyanomolybdate(V) centers.

Treatment of manganese(II) p-toluenesulfonate[10] with tributylammonium octacyanomolybdate(V)[7f] in DMF readily affords $[Mn^{II}(DMF)_4]_3[Mo^V(CN)_8]_2$ (**1**), as a 2-D, crystalline network.[11] The infrared spectrum of **1** exhibits two ν_{CN} absorptions at 2156 (s) and 2143 (sh, w) cm^{-1}, which are comparable in energy to those found for $[HNBu_3]_3[Mo(CN)_8]$ (2141 cm^{-1}), suggesting that bridging and terminal cyanides are present.[12] Assuming that kinematic effects[12] are absent in **1**, we tentatively assign the bridging and terminal cyano stretching absorptions as 2156 and 2143 cm^{-1}, respectively.[4b,7e,8,9]

Compound **1** adopts a corrugated 2-D sheet structure that crystallizes in the monoclinic ($P2_1/n$) space group. The neutral network is composed of $[cis\text{-}Mn^{II}(DMF)_4(\mu\text{-}NC)_2]^{2+}$ and $[trans\text{-}Mn^{II}(DMF)_4(\mu\text{-}NC)_2]^{2+}$ units that are linked via cyanides to adjacent three-connected $[Mo^V(CN)_5(\mu\text{-}CN)_3]^{3-}$ centers in a 4:2:6 ratio; the asymmetric unit is illustrated in Figure 1. The 12-membered rings (Figure 2) are the basic units of construction for the lattice and have dimensions of ca. 24 (Mo1···Mo1D) × 9 Å (Mo1···Mo1A), with each offset by ca. 5 Å and linked via shared $trans\text{-}Mn^{II}(\mu\text{-}NC)_2$-(DMF)$_4$ units to adjacent $[Mo^V(CN)_8]^{3-}$ centers; the separation between adjacent ruffled sheets is ca. 7.0 Å (Mn···Mn). The average Mo^V−C bond lengths range from 2.161(3) to 2.168(3) Å, while the C−Mo^V−C bond angles range from

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Figure 1. Asymmetric unit of **1**. Thermal ellipsoids are at the 50% level, and all hydrogen and select carbon and nitrogen atoms are removed for clarity. Selected bond distances (Å) and angles (deg): N1−Mn1 2.235(3), N2−Mn2 2.246(3), Mo1−C1 2.164(3); C1−Mo1−C2 88.0(1), N2−Mn2−O1E 83.74(9).
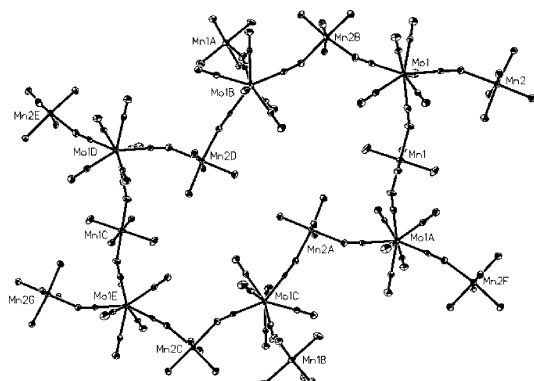
Figure 2. X-ray structure of **1** illustrating the 12-membered rings present. Thermal ellipsoids are at the 50% level, DMF ligands are truncated, and all hydrogen atoms are removed for clarity.
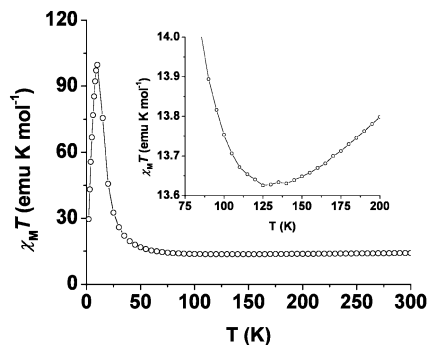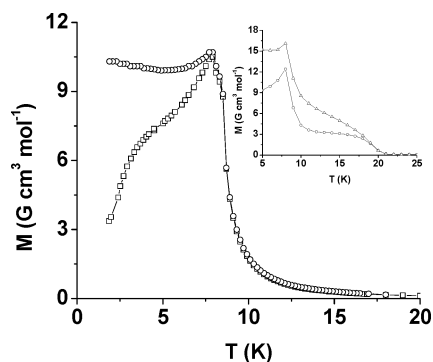

Figure 3. Temperature dependence of $\chi_M T$ for **1** (H_{dc} = 1 kG).

76.1(1) to 148.5(1)°; the Mo^V−C−N bond angles are nearly linear. The Mn^{II}−N and Mn^{II}−O bond distances are comparable to those in 1-D chains of $\{[Mn(DMF)_4][Mn(DMF)_2$-(bipy)]$_2[M^V(CN)_8]_2\}_n$ (M^V = Mo, W) stoichiometry.[8]

The temperature dependence of the $\chi_M T$ product for **1** suggests that the cyanide-bridged Mn^{II} and Mo^V centers are antiferromagnetically coupled. The room-temperature $\chi_M T$ value (14.15 emu K mol^{-1}) is close to the expected spin-only value (13.89 emu K mol^{-1}) for a 2:3 ratio of noninteracting isotropic Mo^V (S = $^1/_2$; g = 2) and high-spin Mn^{II} (S = $^5/_2$; g = 2) centers (Figure 3). The sign of the local exchange interactions can be deduced from the shape of the $\chi_M T$ vs T curve: for ferrimagnetic solids, there is often a shallow minimum above the magnetic ordering temperature due to short-range antiferromagnetic correlation interactions

Figure 4. Temperature dependence of the zero-field-cooled (○) and field-cooled (□) magnetization for **1** ($H_{dc} = 2$ G). Inset: Temperature dependence of the zero-field-cooled (○) and field-cooled (△) magnetization for heated (350 K) samples of **1** ($H_{dc} = 2$ G).

that compensate spins.[13] For **1**, a shallow minimum is observed at 125 K, suggesting that it is likely a ferrimagnet. As the temperature is lowered further, the $\chi_M T$ product monotonically increases, reaching a maximum value of 99.68 emu K mol^{-1} at 14.2 K. Below this temperature, $\chi_M T$ again decreases, affording a minimum value of 29.61 emu K mol^{-1} at 1.8 K; we postulate that the decreasing values of $\chi_M T$ below ca. 10 K are due to saturation effects. Furthermore, fitting of the χ_M^{-1} vs temperature data, via the Curie–Weiss expression, affords a negative Weiss constant (-10.36 K), confirming that local antiferromagnetic interactions are present.

The field dependence of the magnetization verifies that **1** is a ferrimagnet. At 70 kG and 2 K, the experimental saturation magnetization value for **1** is 71.1 kG cm^3 mol^{-1} and is close to the value expected (72.61 kG cm^3 mol^{-1}; $g = 2$ assumed) for an antiferromagnetically coupled Mn$^{II}_3$Mo$^V_2$ lattice (Figure S3 in the Supporting Information). Compound **1** also exhibits a closed hysteresis loop with a small coercive field, consistent with the presence of isotropic metal centers (Figure S4 in the Supporting Information).

Surprisingly, subsequent ac susceptibility measurements indicate that χ'' is frequency-dependent for **1** (Figure S2 in the Supporting Information). However, the χ'' peak is unsymmetrical and broadened and is similar in shape to that reported by Li and co-workers for a 1-D octacyanotungstate-(V) network of [Mn^{II}(bpy)(DMF)$_2$]$_2$[Mn(DMF)$_4$][W^V(CN)$_8$]$_2$.[8] The unsymmetrical χ'' peak suggests that more than one magnetic phase is present and/or **1** is unstable under the conditions of the measurement.[7f]

To probe this assumption, zero-field-cooled and field-cooled magnetization measurements were collected on freshly crushed crystalline samples of **1**, at an applied dc magnetic field of 2 G, between 2 and 350 K (Figure 4). Initially, fresh samples of **1** exhibit long-range magnetic order below ca. 8 K, but when samples are heated to 350 K, an additional magnetic phase ($T_N \sim 21$ K) becomes apparent

(inset of Figure 3); repeating the dc susceptibility measurements at an applied field of 1 kG affords an apparent $T_N = 21$ K. Moreover, the contribution of the high-temperature magnetic phase to the total magnetization appears to increase with respect to time, even when samples are stored at room temperature under an argon atmosphere in the absence of light for several weeks; similar behavior is also observed for other 1- and 2-D octacyanometalate lattices.[7e]

The infrared spectra of **1** also change as a function of heating (350 K), in argon or under a dynamic vacuum. With prolonged heating, the coordinated DMF $\nu_{C=O}$ stretching absorption (1650 cm^{-1}) slowly decreases, while the ν_{CN} absorption (2156 cm^{-1}) grows in intensity; we propose that heated samples still contain Mo^V–CN–Mn^{II} linkages and that no linkage isomerism has occurred (e.g., Mo^V–NC–Mn^{II}).[7] Furthermore, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Figures S5 and S6 in the Supporting Information) measurements suggest that the DMF ligands are somewhat labile. Low-field magnetization measurements also indicate that a new magnetic phase is introduced upon heating. The lower apparent decomposition temperature, suggested in magnetic studies, is probably due to samples being measured under vacuum. Additionally, attempts to isolate and structurally characterize the putative, partially desolvated phase, via recrystallization of heated solid samples or products (microcrystals and amorphous material) obtained via thermolysis of **1** in DMF (350 K), consistently met with failure. We propose that desolvation and possibly aggregation (intersheet) likely occurs in **1**.

We have described the synthesis, structural, infrared, and magnetic characterization of a new ferrimagnetic 2-D octa-cyanomolybdate(V) lattice. Coordinated DMF appears to limit the number of cyano linkages formed during the self-assembly of reactants, affording extended lattices rather than discrete molecular clusters. The network appears to be unstable with respect to desolvation above room temperature, as judged from infrared, TGA, DSC, and magnetic measurements, suggesting that the coordinated DMF ligands are somewhat labile. A subsequent report will describe the preparation and transformation of 1-D chains of clusters into 2-D networks that are isomorphous to **1**.

Supporting Information Available: X-ray crystallographic data (CIF format), synthetic details, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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