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

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Received September 7, 2005

Treatment of [HNBu$_3$]$_2$[Mo$(\text{CN})_8$] with manganese(II) p-toluenesulfonate in $N,N'$-dimethylformamide (DMF) affords ([Mn$^\text{II}$(DMF)$_4$]$_2$-[Mo$^\text{V}$(CN)$_8$])$_2$ (1) as a two-dimensional network. The structure of 1 consists of cis-Mn$^\text{II}$ (DMF)$_4$(μ-NC)$_2$ and trans-Mn$^\text{II}$ (DMF)(μ-NC)$_2$ units that are linked via cyanides to three-connected $\text{Mo}^\text{V}$- (CN)$_2$(μ-CN)$_3$ centers in a 4:2:6 ratio, forming 12-membered rings. Magnetic measurements indicate that 1 is a ferrimagnet \( (T_N = 8 \text{ K}) \) that exhibits frequency-dependent behavior in $\chi'$. Heating of 1 affords an additional magnetic phase \( (T_N = 21 \text{ K}) \) 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. These M$^\text{II}$[M$^\text{II}$(ROH)$_3$]$^8$[M$^\text{V}$(CN)$_8$]$^6$ clusters 3a,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 $\pi$-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$^\text{II}$ centers present, were recently reported.7a These M$^\text{II}$(M$^\text{II}$(ROH)$_3$)$^8$(M$^\text{V}$(CN)$_8$)$^6$-nROH+nH$_2$O \( (R = \text{Me, Et}) \) clusters are typically prepared in alcoholic solutions.

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 

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Published on Web 04/26/2006

Inorganic Chemistry, Vol. 45, No. 11, 2006

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10.1021/ic0515251 CCC: $33.50
media and are prone to rapid desolvation and aggregation under mild conditions. 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 donors ligand than alcohols for stabilizing the cluster framework.

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 with tributylammonium octacyanomolybdate(V) in DMF readily affords [Mn(DMF)₄][MoV(CN)₈]₂ (I), as a 2-D, crystalline network. The infrared spectrum of I exhibits two νCN absorptions at 2156 (s) and 2143 (sh, w) cm⁻¹, which are comparable in energy to those found for [HNBu₃]₃[MoV(CN)₈] (CN)₈⁻ (2141 cm⁻¹), suggesting that bridging and terminal cyanides are present. Assuming that kinematic effects are absent in I, we tentatively assign the bridging and terminal cyano stretching absorptions as 2156 and 2143 cm⁻¹, respectively.

Compound I adopts a corrugated 2-D sheet structure that crystallizes in the monoclinic (P2₁/m) space group. The neutral network is composed of [cis-Mn(DMF)₄(μ-CN)]²⁻ and [trans-Mn(DMF)₄(μ-CN)]²⁺ units that are linked via cyanides to adjacent three-connected [MoV(CN)₈(μ-CN)]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-Mn(DMF)₄(μ-CN)⁻, MoV(CN)₈(μ-CN)⁻ units to adjacent [MoV(CN)₈]⁺ centers; the separation between adjacent ruffled sheets is ca. 7.0 Å (Mn⋯Mn). The average MoV⁻C bond lengths range from 2.161(3) to 2.168(3) Å, while the C–MoV⁻C bond angles range from 107.6(1) to 148.5(1)°; the MoV⁻C–N bond angles are nearly linear. The Mn⁵⁻N and Mn⁵⁻O bond distances are comparable to those in 1-D chains of [[Mn(DMF)₄][Mn(DMF)₂]-bipy]₂⁺[Mo(V)₃(CN)₈]₂⁻ (M⁵⁰ = Mo, W) stoichiometry.

The temperature dependence of the χMT product for I suggests that the cyanide-bridged Mn⁵⁺ and Mo⁵⁺ centers are antiferromagnetically coupled. The room-temperature χMT 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 nitrogen atoms in the octacyanomolybdate(V) core. The temperature dependence of χMT vs T curve: for ferrimagnetic solids, there is often a shallow minimum above the magnetic ordering temperature due to short-range antiferromagnetic correlation interactions.
that compensates spins.\textsuperscript{13} For \textbf{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\textsuperscript{-1} at 14.2 K. Below this temperature, $\chi_M T$ again decreases, affording a minimum value of 29.61 emu K mol\textsuperscript{-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 $\chi_M T$ 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 \textbf{1} is a ferrimagnet. At 70 kG and 2 K, the experimental saturation magnetization value for \textbf{1} is 71.1 kG cm\textsuperscript{3} mol\textsuperscript{-1} and is close to the value expected (72.61 kG cm\textsuperscript{3} mol\textsuperscript{-1}; \(g = 2\) assumed) for an antiferromagnetically coupled Mn\textsuperscript{II}Mo\textsuperscript{V} lattice (Figure S3 in the Supporting Information). Compound \textbf{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 $\chi''$ is frequency-dependent for \textbf{1} (Figure S2 in the Supporting Information). However, the $\chi''$ 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\textsuperscript{II}(bpy)(DMF)\textsubscript{2}][Mn(DMF)\textsubscript{4}][W\textsuperscript{V}(CN)\textsubscript{8}]\textsubscript{2}.\textsuperscript{8} The unsymmetrical $\chi''$ peak suggests that more than one magnetic phase is present and/or \textbf{1} is unstable under the conditions of the measurement.\textsuperscript{37}

To probe this assumption, zero-field-cooled and field-cooled magnetization measurements were collected on freshly crushed crystalline samples of \textbf{1}, at an applied dc magnetic field of 2 G, between 2 and 350 K (Figure 4). Initially, fresh samples of \textbf{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.\textsuperscript{7e}

The infrared spectra of \textbf{1} also change as a function of heating (350 K), in argon or under a dynamic vacuum. With prolonged heating, the coordinated DMF $v_C=O$ stretching absorption (1650 cm\textsuperscript{-1}) slowly decreases, while the $v_{CN}$ absorption (2156 cm\textsuperscript{-1}) grows in intensity; we propose that heated samples still contain Mo\textsuperscript{V}−CN−Mn\textsuperscript{II} linkages and that no linkage isomerism has occurred (e.g., Mo\textsuperscript{V}−NC−Mn\textsuperscript{II}).\textsuperscript{7f} 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 \textbf{1} in DMF (350 K), consistently met with failure. We propose that desolvation and possibly aggregation (intersheet) likely occurs in \textbf{1}.

We have described the synthesis, structural, infrared, and magnetic characterization of a new ferrimagnetic 2-D octacyanomolybdate(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 \textbf{1}.

Acknowledgment. S.M.H. gratefully acknowledges the donors of Petroleum Research Fund (PRF 38388-G3), funded by the American Chemical Society, the University of Kentucky Summer Faculty Research Fellow, and the National Science Foundation Research Experience for Undergraduates (Grant CHE-0097668) programs for financial support. We are indebted to the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign for use of their magnetometer facility. G.T.Y. thanks the National Science Foundation (Grant CHE-0210395) for financial support.

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. IC0515251