

Cyanide-Limited Complexation of Molybdenum(III): Synthesis of Octahedral $[\text{Mo}(\text{CN})_6]^{3-}$ and Cyano-Bridged $[\text{Mo}_2(\text{CN})_{11}]^{5-}$

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Received November 21, 2001

The use of molecular precursors in assembling solids with potentially adjustable magnetic properties has developed into an area of intense research.¹ Only a few of the materials produced thus far, however, have been shown to exhibit bulk magnetic ordering at room temperature.^{2,3} Prominent among these are Prussian blue analogues such as $\text{V}[\text{Cr}(\text{CN})_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$ ($T_N = 315$ K) and $\text{KV}[\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ ($T_N = 376$ K) prepared via reaction of $[\text{Cr}(\text{CN})_6]^{3-}$ with a variety of V^{II} salts.³ Indeed, numerous related solids containing the octahedral complex $[\text{Cr}(\text{CN})_6]^{3-}$ have been found to behave as magnets with relatively high ordering temperatures.⁴ Moreover, by carefully regulating composition, these compounds can be invested with a range of unique magnetic and magneto-optical properties.⁵ A possible means of enhancing the utility of such materials by increasing their ordering temperatures is through the incorporation of second- or third-row transition metal ions, for which the more diffuse, higher-energy valence d orbitals are expected to lead to stronger magnetic exchange coupling. Recently, this effect has been demonstrated with the substitution of Mo^{III} for Cr^{III} in molecular metal–cyanide clusters.⁶ To attempt analogous replacements in Prussian blue-type solids, we have pursued the synthesis of octahedral $[\text{Mo}(\text{CN})_6]^{3-}$.

Owing to its size, molybdenum tends to form cyanide complexes with coordination numbers of greater than six. To date, the structures of four homoleptic species have been verified crystallographically: pentagonal bipyramidal $[\text{Mo}(\text{CN})_7]^{3-/4-}$ and dodecahedral $[\text{Mo}(\text{CN})_8]^{3-/4-}$.⁸ Although previous studies have claimed syntheses of $[\text{Mo}(\text{CN})_6]^{3-/4-}$, the authenticity of these products is unlikely in view of the limited characterization data available and comparisons with the results presented below.⁹ Here, we report that octahedral coordination of Mo^{III} can be achieved simply by restricting the amount of cyanide available upon complex formation.

An efficient preparation of $[\text{Mo}(\text{CN})_6]^{3-}$ takes advantage of the low solubility of its Li^+ salt in DMF. Under a dinitrogen atmosphere, solid $\text{LiCN} \cdot \text{DMF}^{10}$ (0.89 g, 8.4 mmol) was added to a solution of $\text{Mo}(\text{CF}_3\text{SO}_3)_3^{11}$ (0.46 g, 0.84 mmol) in 10 mL of DMF. After stirring for 2 days, the resulting precipitate was collected by filtration, and washed with successive aliquots of DMF (2×1 mL) and THF (3×5 mL). Subsequent drying under dinitrogen afforded 0.32 g (54%) of $\text{Li}_3[\text{Mo}(\text{CN})_6] \cdot 6\text{DMF}$ (**1**) as a tan solid.¹² The compound is highly soluble in methanol and water, but decomposes in the presence of dioxygen, initially forming $[\text{Mo}(\text{O})(\text{CN})_5]^{3-}$.¹³

Diffusion of THF into a dilute solution of **1** in DMF produced pale brown block-shaped crystals suitable for X-ray analysis.¹⁴ The structure of the $[\text{Mo}(\text{CN})_6]^{3-}$ complex (Figure 1) closely approaches O_h symmetry, with C–Mo–C and Mo–C–N angles near 90° and 180° , respectively. At 2.181(3) Å, its Mo–C distances are comparable to those observed in $[\text{Mo}(\text{CN})_7]^{4-}$ (2.157–2.164 Å),^{7b} and, expectedly, longer than the Cr–C distances of 2.08(2) Å in $[\text{Cr}(\text{CN})_6]^{3-}$.¹⁵

The spectral and magnetic properties of $[\text{Mo}(\text{CN})_6]^{3-}$ confirm a

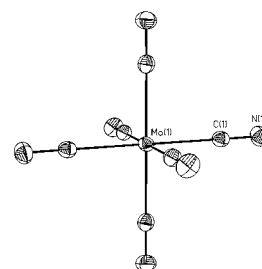


Figure 1. Structure of the octahedral $[\text{Mo}(\text{CN})_6]^{3-}$ complex in **1**; ellipsoids are drawn at the 40% probability level. The molecule resides on a $\bar{3}$ symmetry site in the crystal. Selected interatomic distances (Å) and angles (deg): Mo(1)–C(1) 2.181(3), C(1)–N(1) 1.160(3), C(1)–Mo–C(1) 88.8–(1), 91.2(1), Mo(1)–C(1)–N(1) 179.8(7).

t_{2g}^3 electron configuration. As measured by SQUID magnetometry, the effective magnetic moment of **1** at 295 K is $3.80 \mu_B$, consistent with an $S = 3/2$ ground state where $g = 1.96$. The diffuse reflectance UV-vis spectrum of solid **1** closely matches its absorption spectrum in DMF,¹² suggesting—as do results from mass spectrometry—that the octahedral complex remains intact in solution. The absorption spectra feature bands at 406 and 359 nm, which can be assigned to the transitions ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and ${}^4T_{1g} \leftarrow {}^4A_{2g}$, respectively. On the basis of these assignments, the ligand field parameters for $[\text{Mo}(\text{CN})_6]^{3-}$ are $\Delta_o = 24\,800 \text{ cm}^{-1}$ and $B = 247 \text{ cm}^{-1}$. Thus, its d orbital splitting energy is greater than that of $[\text{MoCl}_6]^{3-}$ ($\Delta_o = 19\,200 \text{ cm}^{-1}$),¹⁶ but, surprisingly, is less than that observed for $[\text{Cr}(\text{CN})_6]^{3-}$ ($\Delta_o = 26\,600 \text{ cm}^{-1}$).¹⁵ The latter result can be construed as indicating that the enhancement in metal–cyanide π -bonding upon replacing Cr^{III} with Mo^{III} is overwhelmed by a diminution in the metal–cyanide σ -bonding.¹⁷

Further limiting the cyanide available for complex formation leads to cyano-bridged species, such as $[\text{Mo}_2(\text{CN})_{11}]^{5-}$. Under a pure dinitrogen atmosphere, solid $(\text{Et}_4\text{N})\text{CN}^{18}$ (0.92 g, 5.9 mmol) was added to a solution of $\text{Mo}(\text{CF}_3\text{SO}_3)_3^{11}$ (0.58 g, 1.1 mmol) in 50 mL of DMF. Stirring for 2 days generated a light green precipitate, which was collected by filtration, and dissolved in 10 mL of a 1:1 mixture of DMF and methanol. Diffusion of THF into the solution gave 0.35 g (52%) of $(\text{Et}_4\text{N})_5[\text{Mo}_2(\text{CN})_{11}] \cdot 2\text{DMF} \cdot 2\text{MeOH}$ (**2**)¹⁹ as green plate-shaped crystals suitable for X-ray analysis.¹⁴

Figure 2 depicts the structure of the $[\text{Mo}_2(\text{CN})_{11}]^{5-}$ complex, which, to our knowledge, is without precedent in metal–cyanide chemistry. Here, two octahedrally coordinated Mo^{III} centers are linked through a μ -cyanide bridge. The two sets of terminal cyanide ligands directed perpendicular to the bridging axis are almost perfectly eclipsed, such that the molecule approximates C_{4v} symmetry. While the mean Mo–C distance involving terminal cyanides is 2.19(1) Å, a shorter distance of 2.125(5) Å is observed for Mo(1)–C/N(1). This, together with the slightly elongated C–N distance of 1.187(10) Å for the bridging cyanide ligand, suggests an increase in molybdenum–cyanide π -bonding upon bridge formation.²⁰

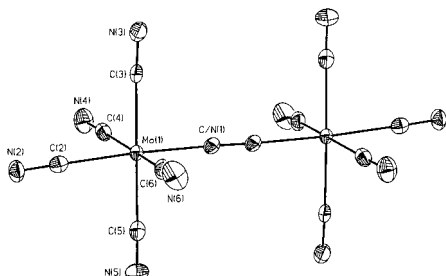


Figure 2. Structure of the dinuclear $[\text{Mo}_2(\text{CN})_{11}]^{5-}$ complex in **2**; ellipsoids are drawn at the 40% probability level. The molecule resides on a crystallographic inversion center, such that the carbon and nitrogen atoms of the bridging cyanide ligand cannot be distinguished. Selected interatomic distances (\AA) and angles (deg): Mo(1)–C/N(1) 2.125(5), Mo(1)–C(2) 2.176(6), Mo(1)–C(3) 2.201(6), Mo(1)–C(4) 2.193(6), C/N(1)–C/N(1') 1.187(10), C(2)–N(2) 1.159(7), C(3)–N(3) 1.144(7), C(4)–N(4) 1.154(8), Mo(1)⋯Mo(1') 5.4371(8), C/N(1)–Mo(1)–C(2) 177.1(2), C/N(1)–Mo(1)–C(3) 89.9(2), Mo(1)–C/N(1)–C/N(1') 178.0(6), Mo(1)–C(2)–N(2) 178.7(5), Mo(1)–C(3)–N(3) 177.5(5).

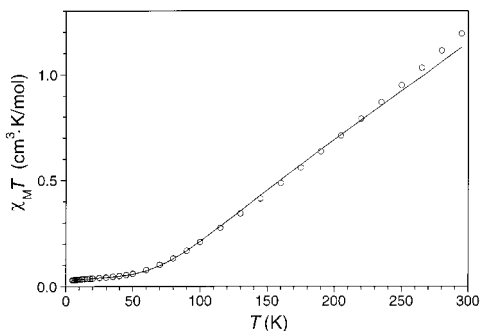


Figure 3. Magnetic behavior of **2**, as measured in an applied field of 1000 G using a SQUID magnetometer. The solid line represents an approximate fit to the data, calculated with $J = -113 \text{ cm}^{-1}$, $g = 2.33$, $\text{TIP} = 475 \times 10^{-6} \text{ cgs/mol}$, and $P = 0.026$.²²

The magnetic behavior of compound **2** (Figure 3) reveals strong antiferromagnetic coupling between the two Mo^{III} centers. At 295 K, $\chi_M T$ is $1.193 \text{ cm}^3 \text{K/mol}$, well below the value of $3.75 \text{ cm}^3 \text{K/mol}$ predicted for two uncoupled $S = 3/2$ ions with $g = 2.00$. As the temperature is lowered, $\chi_M T$ decreases steadily, beginning to plateau around 50 K, and then approaching the value of zero expected for an $S = 0$ ground state. The residual moment of $\chi_M T = 0.031 \text{ cm}^3 \text{K/mol}$ at 5 K is attributed to the presence of a small amount of an unidentified paramagnetic impurity that could not be removed through successive recrystallizations. An approximate fit to the data, obtained using MAGFIT 3.1²¹ and an exchange Hamiltonian of the form $\hat{H} = -2J\hat{S}_{\text{Mo}(1)}\hat{S}_{\text{Mo}(2)}$, gave $J = -113 \text{ cm}^{-1}$ and $g = 2.33$.²² Thus, the diffuse, high-energy 4d orbitals of the Mo^{III} centers lead to the strongest magnetic coupling yet measured through a cyanide bridge, eclipsing the previous record of $J = -88 \text{ cm}^{-1}$ observed for $[\text{Cu}_2(\text{tren})_2(\mu\text{-CN})]^{3+}$.²³

It is anticipated that the molybdenum–cyanide complexes disclosed here will be of utility in the synthesis of new molecule-based magnets. Efforts to incorporate them in Prussian blue-type solids are currently underway.

Acknowledgment. This research was supported by NSF Grants No. CHE-0072691 and CHE-0111164, the Camille and Henry Dreyfus Foundation, and the Alfred P. Sloan Foundation. We thank Mr. M. P. Shores for experimental assistance, Ms. J. J. Sokol and Prof. J. K. McCusker for helpful discussions, Prof. D. N. Hendrickson for supplying software used to fit the magnetic susceptibility data, and Prof. A. M. Stacy for use of the SQUID magnetometer.

Supporting Information Available: Tables of crystal data, structure solution and refinement parameters, atomic coordinates, bond

lengths and angles, and anisotropic thermal parameters for **1** and **2** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) Characterization of **1**: Absorption spectrum (DMF): $\lambda_{\text{max}} (\epsilon_M)$ 278 (1959), 291 (4023), 359 (798), 406 (483), 650 (sh) nm. IR: ν_{CN} 2115 (s) cm^{-1} . $\mu_{\text{eff}} = 3.80 \mu_B$ at 295 K. ES[−]MS (DMF/MeOH) m/z 268 ($[\text{Li}_2[\text{Mo}(\text{CN})_6]^-]$). Anal. Calcd for $\text{C}_{24}\text{H}_{42}\text{Li}_3\text{MoN}_{12}\text{O}_6$: C, 40.52; H, 5.95; N, 23.63. Found: C, 40.23; H, 5.83; N, 23.34.
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- (14) Crystal and refinement parameters for **1**: $\text{C}_{24}\text{H}_{42}\text{Li}_3\text{MoN}_{12}\text{O}_6$, $T = 160 \text{ K}$, $R3c$, $Z = 6$, $a = 13.5285(3) \text{ \AA}$, $c = 35.8530(2) \text{ \AA}$, $V = 5682.7(2) \text{ \AA}^3$, $d_{\text{calc}} = 1.247 \text{ g/cm}^3$, $R1 = 0.0426$, $wR2 = 0.1231$. **2**: $\text{C}_{50}\text{H}_{122}\text{Mo}_2\text{N}_{18}\text{O}_4$, $T = 153 \text{ K}$, $P1$, $Z = 1$, $a = 10.6037(2) \text{ \AA}$, $b = 11.9623(3) \text{ \AA}$, $c = 15.2316(1) \text{ \AA}$, $\alpha = 96.627(1)^\circ$, $\beta = 107.770(1)^\circ$, $\gamma = 94.860(1)^\circ$, $V = 1821.82(6) \text{ \AA}^3$, $d_{\text{calc}} = 1.227 \text{ g/cm}^3$, $R1 = 0.0604$, $wR2 = 0.1642$. Data were collected on a Siemens SMART diffractometer using graphite monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation, and were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using SHELXTL 5.0. In the structure of **2**, atoms of the bridging cyanide ligand were assigned an occupancy of 0.5C + 0.5N.
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- (19) Characterization of **2**: Absorption spectrum (1:1 DMF/MeOH): $\lambda_{\text{max}} (\epsilon_M)$ 289 (7100), 308 (sh), 329 (sh), 357 (15000), 401 (6200), 515 (5), 538 (12), 552 (19), 568 (17), 584 (38), 602 (17), 618 (58), 639 (18), 657 (88), 681 (19), 699 (63), 732 (42) nm. IR: ν_{CN} 2196 (w), 2092 (s) cm^{-1} . $\mu_{\text{eff}} = 3.09 \mu_B$ at 295 K. Cyclic voltammogram (DMF): $E_{1/2}([\text{Mo}_2(\text{CN})_{11}]^{5-}) = -2.202 \text{ V}$ ($\Delta E_p = 112 \text{ mV}$) versus $\text{CpFe}/\text{CpFe}^+$. ES[−]MS (1:1 DMF/MeOH): m/z 1000 ($\{(\text{Et}_4\text{N})_4[\text{Mo}_2(\text{CN})_{11}]^-\}$). Anal. Calcd for $\text{C}_{50}\text{H}_{122}\text{Mo}_2\text{N}_{18}\text{O}_4$: C, 52.90; H, 9.18; N, 18.82. Found: C, 52.79; H, 9.33; N, 18.55.
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JA0175901