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Magnetic Properties

A Docosanuclear $\{Mo_8Mn_{14}\}$ Cluster Based on $[Mo(CN)_7]^{4-}$**

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One of the recent strategies being explored for obtaining molecular magnets with enhanced properties is the incorporation of heavier transition metals from the 4d and 5d metal ions.[1–3] A central player in this area of research is the cyanide ligand, which can be used to prepare mixed metal clusters with unusual properties.[4] Of particular interest is the fact that cyanide molecules containing 4d or 5d ions or combinations of them with 3d ions have been predicted to behave as single-molecule magnets (SMMs) with higher blocking temperatures T_B than those based on 3d ions. They are also expected to exhibit properties such as anisotropic magnetic exchange interactions.[5]

A main driving force for the high activity in cyanide magnetism is that the use of cyanometalates in reactions with metal ions equipped with capping ligands present several advantages, such as control over the sign of magnetic interactions in most cases and also predictable structures based on the building block approach. Magnetic anisotropy can be conveniently introduced by choosing the appropriate preformed 4d or 5d cyanometalate anion. The observation of SMM behavior with 4d and 5d metal ions with oxygen-type bridging ligands is limited to only one case,[6] but there are a number of SMMs from the heavier congeners of Groups 6 and 7 with the precursors $[(Me_3tacn)Mo^{III}(CN)_3]$,[7] $[Mo^{V}(CN)_8]^{3-}$,[8,9] $[W^{V}(CN)_8]^{3-}$,[8–10] $[Re^{IV}(CN)_7]^{3-}$,[11] and $[(triphos)Re^{II}(CN)_3]^{-}$.[12]

In contrast to the widely investigated anion $[Mo^{V}(CN)_8]^{3-}$,[2,8,9] the heptacyanomolybdate derivative $[Mo^{III}(CN)_7]^{4-}$ has received much less attention in the molecular magnetism field, presumably because of the synthetic challenges in the preparation and handling of this anion. Unlike the hexa- and octacyanometalates, the $[Mo^{III}(CN)_7]^{4-}$ anion favors low-symmetry extended structures with pronounced magnetic anisotropy.[1,13] The results of theoretical investigations have suggested that $[Mo(CN)_7]^{4-}$ will be useful for the design of SMMs with high T_B values as a result of its strong anisotropic exchange properties.[5] Despite such promising predictions, magnetic materials based on $[Mo(CN)_7]^{4-}$ are relatively scarce, with the exception of the pioneering work of Kahn and co-workers, and subsequent studies by several other research groups, who prepared a number of two- and three-dimensional magnets with the $[Mo(CN)_7]^{4-}$ and Mn^{II} ions.[1,13] The only other reports are an amorphous compound with iron(II)[14] and two microcrystalline materials with vanadium(II) and nickel(II).[15] To our knowledge, no discrete clusters based on $[Mo(CN)_7]^{4-}$ have been reported.

Given the aforementioned considerations, we recently devoted efforts to the preparation of mixed-metal molecules that contain the $[Mo(CN)_7]^{4-}$ building block. Herein, we report the first discrete compound based on $[Mo(CN)_7]^{4-}$, namely $[Mn(dpop)(H_2O)_2]_2[\{Mo(CN)_7\}_8\{Mn(dpop)\}_{10}\{Mn(dpop)(H_2O)\}_4]\cdot x\,H_2O$ (**1**; dpop = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12.3.1]octadeca-1(18),2,12,14,16-pentaene). The cluster contains the largest number of paramagnetic centers and the highest spin ground state among the cyanide-bridged clusters reported to date.

Compound **1** was prepared by slow diffusion of aqueous solutions of $[Mo(CN)_7]^{4-}$ and $[Mn(dpop)(H_2O)_2]^{2+}$ under a nitrogen atmosphere. The anaerobic atmosphere is crucial to the success of the reaction because the $[Mo^{III}(CN)_7]^{4-}$ ion is easily oxidized to $[Mo^{IV}(CN)_8]^{4-}$, resulting in the mixed-valence two-dimensional material $[\{Mn(dpop)\}_6\{Mo^{III}(CN)_7\}\{Mo^{IV}(CN)_8\}_2]\cdot 19.5\,H_2O$.[16] Although the authors of reference [16] reported that the oxidization was inevitable even under strictly anaerobic conditions, we found **1** could be synthesized in a moderate yield.

Compound **1** is an ionic compound with two $[Mn(dpop)(H_2O)_2]^{2+}$ cations and one docosanuclear $[\{Mo(CN)_7\}_8\{Mn(dpop)\}_{10}\{Mn(dpop)(H_2O)\}_4]^{4-}$ anion in the unit cell; the center of the cluster is located on an inversion center (Figure 1).[17] In the asymmetric unit, there are 4 Mo^{III} and 8 Mn^{II} centers, all being heptacoordinated with distorted pentagonal bipyramidal geometries. Among the 4 $[Mo(CN)_7]^{4-}$ units, one of them (Mo1) is connected to 4 Mn^{II} ions; two (Mo2 and Mo3) are bridged to 3 Mn^{II} ions, and the other (Mo4) bridges only 2 Mn^{II} centers. For Mo2, Mo3, and Mo4, all of the bridging CN^{-} groups are in equatorial positions. In the case of Mo1, the distortion from a pentagonal bipyramid is pronounced, and one of the axial CN^{-} groups also bridges to a Mn^{II} center, Mn6 (Supporting Information, Figure S1).

The Mo–C bond lengths range from 2.05 to 2.20 Å, and the Mo-C-N bond angles range from 173 to 180°. According to their connectivity, the eight crystallographically unique Mn^{II} centers can be divided into three categories: the countercation (Mn8), terminal units (Mn6 and Mn7), and bridging units (Mn1–Mn5). The $Mn-N_{CN}$ bond lengths range from 2.22 to 2.34 Å, and the $Mn-N_{CN}-C_{CN}$ bond angles deviate significantly from linearity, ranging from 144 to 160° (Supporting Information, Table S1).

The large $\{Mo_8Mn_{14}\}$ cluster can be roughly described as a buckled $\{Mo_6Mn_6\}$ loop spanned by two $\{Mo_3Mn_2\}$ cross-links

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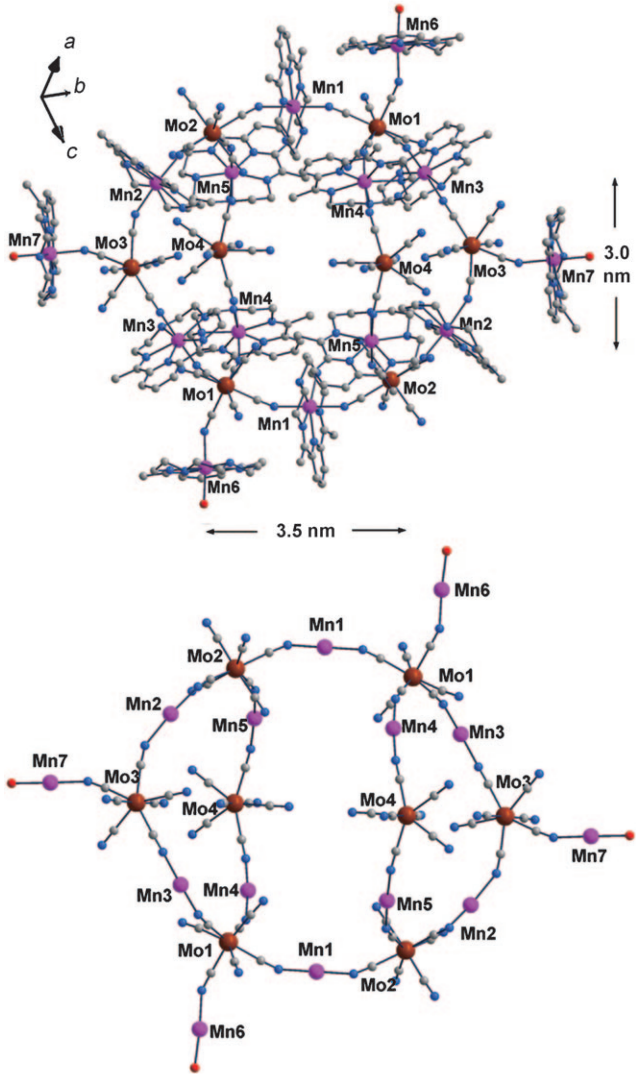

Figure 1. Depiction of the complete (top) and skeletal backbone (bottom) of the anion in **1**. The cations, interstitial water molecules, and hydrogen atoms have been omitted for clarity.

and four terminal Mn^{II} units arranged symmetrically around the perimeter. The $\{Mo_6Mn_6\}$ wheel and the $\{Mo_3Mn_2\}$ cross-links are involved in the sequences (Mo1-Mn1-Mo2-Mn2-Mo3-Mn3)$_2$ and Mo1-Mn4-Mo3-Mn5-Mo2, respectively. The intra-cluster Mo–Mn distances are in the range of 5.28 to 5.47 Å. When viewed from the side, the $\{Mo_6Mn_6\}$ unit has the appearance of a chair conformation for the outer ring with two $\{Mo_3Mn_2\}$ cross-links spanning opposite sides of the chair (Supporting Information, Figure S2). Including the terminal Mn^{II} units, the molecule is approximately 3.0 × 3.5 nm in size, which is by far the largest cyanide-bridged metallamacrocycle reported to date,[18] and contains the most paramagnetic centers among the known cyanide-bridged clusters. Two previously reported higher-nuclearity molecules with cyanide ligands are known, namely $\{Cr_{12}Ni_{12}\}$ and $\{Cr_{14}Ni_{13}\}$,[19] but in these molecules, the nickel(II) centers are diamagnetic.

The choice between adopting the closed structure found in **1** versus an open-framework solid results from subtle factors. The bridging CN^- groups in the Mo_8Mn_{14} molecules are all in the equatorial position of $[Mo(CN)_7]^{4-}$, a situation that leads to C_{bridge}-Mo-C_{bridge} angles in the range 142.3–147.5°, which are ideally suited to form the closed loop. The Mn-N_{CN}-C_{CN} bending is also important for the formation of a cyclic molecule, as found for example in the case of a reported $\{Mn_6Fe_6\}$ wheel structure.[18] The clusters and the cations are interconnected to each other with hydrogen bonds and also $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions involving interstitial H_2O molecules (Supporting Information, Figure S3). These weak interactions no doubt influence the magnetic properties of **1**, as discussed in the following section.

The magnetic susceptibility data for **1** measured under a direct-current (dc) field of 1000 Oe from 2 to 300 K are depicted as $\chi_m T(T)$ and $\chi_m^{-1}(T)$ plots in Figure 2. Upon cooling, the $\chi_m T$ value decreases slowly from 75.2 (300 K) to 74.0 $cm^3 mol^{-1} K$ (150 K), and then increases slowly until about 25 K, at which temperature it begins to increase abruptly to 658.2 $cm^3 mol^{-1} K$ at 5 K with a further decrease to 2 K. A fitting of the data above 140 K to the Curie–Weiss law gives $C = 74.9\ cm^3 mol^{-1} K$ and $\theta = -3.8$ K. The room-temperature $\chi_m T$ and the C values are close to the spin-only value of 73.0 $cm^3 mol^{-1} K$ for 8 low-spin Mo^{III} ($S = 1/2$) and 16 high-spin Mn^{II} ($S = 5/2$) with $g = 2.0$. Owing to the complicated structure of **1**, the low symmetry environments of both the Mn^{II} and Mo^{III} ions, and the anisotropy of Mo^{III}, it is not possible to estimate the coupling constant between the Mo^{III} and Mn^{II} centers. The negative θ value and the decrease in $\chi_m T$ above 150 K suggest that antiferromagnetic interactions are dominant, consistent with literature reports.[13] The complications arising from the strong anisotropy of $[Mo(CN)_7]^{4-}$ are supported by theoretical predictions.[5] As an illustration of the inherent difficulty in interpreting these data, we note that some of the $Mn^{II}[Mo^{III}(CN)_7]^{4-}$ compounds were first reported as ferromagnets because of the observed positive θ values, but were later revealed to be ferrimagnets on the basis of neutron diffraction data.[13a,c]

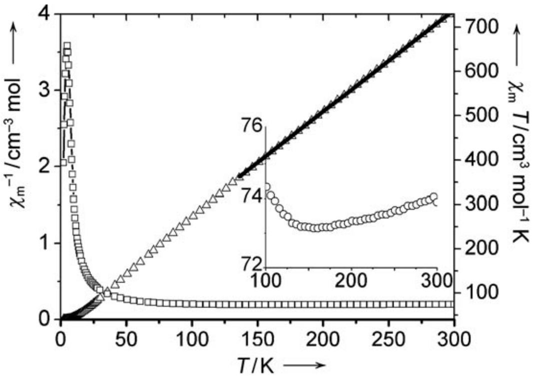

Figure 2. Temperature dependence of $\chi_m T$ (□) and χ_m^{-1} (△) for **1**. Inset: $\chi_m T$ curve between 100 to 300 K. $C = 74.9\ cm^3 mol^{-1} K$, $\theta = -3.8$ K.

The abrupt increase of $\chi_m T$ below 25 K is a feature that warranted further investigation. The temperature dependence of the field-cooled (FC), zero-field-cooled (ZFC), and the remnant magnetization (RM) were measured in a dc field of 10 Oe (Figure 3). The ZFC data exhibits a peak and

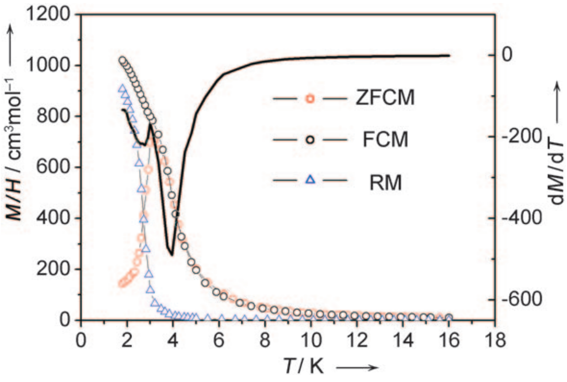

Figure 3. Temperature dependence of ZFCM, FCM, RM, and dM/dT of the FCM data for **1**. $H = 10$ Oe.

diverges from the FC curve at about 3.6 K; the remnant magnetization vanishes above 4.0 K, as indicated by the derivative dM/dT for the FC magnetization data. These results suggest that the compound either undergoes long-range ordering or slow magnetic relaxation, such as that found for glassy magnets or SMMs. The isothermal magnetization M at 1.8 K increases rapidly at low fields and then increases steadily with $H > 10$ kOe to reach a near saturation value of 76.2 μ_B at 70 kOe. A discernible hysteresis loop at 1.8 K was observed with a remnant magnetization $M_R = 18.5\ \mu_B$ and a coercive field $H_c = 180$ Oe (Figure 4). The $M(H)$ curve fits well with the Brillouin curve for one $S = 31$ and two $S = 5/2$ centers ($g = 2.1$), and the Weiss constant $\theta = -3.8$ K is in accord with the antiferromagnetic magnetic interaction.[20] These data support a giant ground-state spin value of $S = 31$ for the Mo_8Mn_{14} cluster arising from antiparallel alignment of the spins on the Mo^{III} and Mn^{II} centers. Although there are several examples with higher spin ground states in the manganese oxide family of clusters,[21] compound **1** has the largest spin ground state for a cyanide-bridged cluster.[22] Reduced magnetization data (Supporting Information, Figure S4) indicate anisotropy in the system, but it was not possible to fit the data because of the complexity of the system.

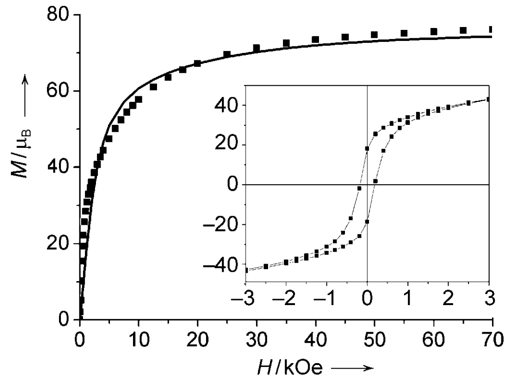

Figure 4. Field dependence of the magnetization data for **1** at 1.8 K. The line represents the Brillouin function. Inset: the hysteresis loop measured at 1.8 K.

To further characterize the ground state at low temperature, alternating-current (ac) susceptibility data under a zero dc applied field at different frequencies were measured (Figure 5). The in-phase signals χ_m' have a shape reminiscent of the ZFC magnetization data, with a peak at about 4 K. The out-of-phase signals χ_m'' begin to take on a non-zero value at about 4.5 K, with a steady increase to a maximum near 3.4–3.6 K, followed by a slow decrease. A very small frequency dependence for both the χ_m' and χ_m'' data was observed. The temperature of the peaks T_p in χ_m' changes from 3.6 to 4.0 K, with frequencies from 1 Hz to 1000 Hz. The shift parameter $\phi = (\Delta T_p/T_p)/\Delta(\log f)$ is approximately 0.035, which is close to a typical value for a spin glass but much smaller than expected for a superparamagnet, such as a SMM.[23]

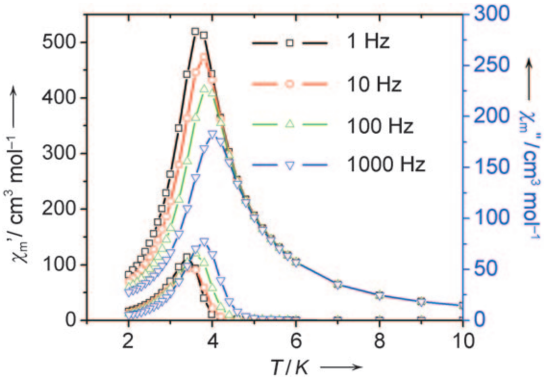

Figure 5. Temperature dependence of the ac susceptibility (χ_m': black vertical axis, χ_m'': blue vertical axis) for **1** at different frequencies under $H_{ac} = 3$ Oe and $H_{dc} = 0$ Oe.

By considering all the points discussed above, we conclude that compound **1** is a magnet with glassy behavior. The magnetic interactions between the anionic clusters are most likely facilitated by hydrogen bonding through the disordered water molecules and the isolated $[Mn(dpop)(H_2O)_2]^{2+}$ cations, whose ability for effecting magnetic coupling has been documented in the literature.[24] Dipole–dipole interactions between the anionic cluster and the manganese(II)-containing cations is also possible. The glassy behavior is reasonable owing to the large number of disordered water molecules in the crystals.

In summary, an anionic nanosize docosanuclear heterometallic Mo_8Mn_{14} cluster has been prepared and fully characterized. This is the first molecular magnet cluster based on the $[Mo(CN)_7]^{4-}$ building unit. Moreover, the metal core contains 22 paramagnetic centers, a record for cyanide clusters, and exhibits the largest ground-state spin value ($S = 31$) for a cyanide molecule reported to date. We are currently investigating other materials that incorporate the $[Mo(CN)_7]^{4-}$ anion with building blocks containing 3d metal centers, such as vanadium(II), chromium(II), and iron(II) to probe the role of the metal ions in determining the properties of this fascinating new class of compounds.

Experimental Section

All experiments were performed under a N_2 atmosphere. Dark red single crystals of **1** were obtained by slow diffusion in a thin single tube of two deoxygenated aqueous solutions of $K_4[Mo(CN)_7]\cdot 2H_2O$[25] (23 mg in 2 mL of H_2O) and $[Mn(dpop)(H_2O)_2]Cl_2\cdot 4H_2O$[26] (25 mg in 2 mL of H_2O). Yield: 30 mg, 51%. Anal. calcd (%) for **1**, $C_{296}H_{432}N_{136}O_{32}Mn_{16}Mo_8$: C 44.44, N 23.39, H 5.47, O 6.62; found: C 44.14, N 23.65, H 5.41, O 6.36. IR (KBr): 2066, 2037 cm^{-1} ($C\equiv N$). The elemental analysis indicates less water than was located in the structure owing to facile loss of water from the dry crystals. The same set of samples was used for the magnetic measurements (SQUID) and the TGA analysis to estimate the number of water molecules in the sample (Supporting Information, Figure S5; 16.5% weight loss, about 86 interstitial H_2O molecules).

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[17] Crystal data for **1**: $C_{296}H_{576}N_{136}O_{104}Mn_{16}Mo_8$, triclinic, $P\bar{1}$, $a = 22.007(4)$, $b = 22.702(4)$, $c = 24.218(4)$ Å, $\alpha = 106.557(2)$, $\beta = 110.939(2)$, $\gamma = 98.059(3)°$, $V = 10429(3)$ Å^3, $Z = 1$, $T = 110$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). $R_1 = 0.1069$ for 2410 parameters and 17114 unique reflections with ($I > 2\sigma(I)$) and $\omega R_2 = 0.3149$ for all 36566 reflections with GOF = 0.994. After SQUEEZE/PLATON was used to remove the disordered water molecules in the structure, $R_1 = 0.0837$ for 2062 parameters and 16481 unique reflections with ($I > 2\sigma(I)$) and $wR_2 = 0.2240$ for all 36676 reflections with a GOF = 0.929. CCDC 752446 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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