Variations in Topology and Magnetic Properties of Hepta- and Octacyanometallates of Molybdenum with Manganese (II)

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Variations in Topology and Magnetic Properties of Hepta- and Octacyanometallates of Molybdenum with Manganese (II)

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Treatment of $[(dpop)Mn(H_2O)_2]Cl_2 \cdot 2H_2O$ (dpop = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12.3.1]octadeca-1(18),2,12,14,16-pentaene) with $K_4[Mo(CN)_7] \cdot 2H_2O$ under varied synthetic conditions afforded four different compounds: $\{[Mn(dpop)]_4[(dpop)Mn(H_2O)]_2[Mo^{III}(CN)_7]_3 \cdot 27H_2O\}_n$ (**1**),
[10] $[(dpop)Mn(H_2O)][Mo^{III}(CN)_7][Mn(dpop)]_3[Mo^{IV}(CN)_8] \cdot 29H_2O\}n$ (**2**), $\{[(dpop)Mn(H_2O)]_2[Mo^{IV}(CN)_8]_2 - [Mn(dpop)]_4Mo^{III}(CN)_7] \cdot 12H_2O\}_n$ (**3**), and $[(dpop)Mn(H_2O)]_2[Mo^{IV}(CN)_8] \cdot 9H_2O$ (**4**). Compound **1** contains only $[Mo^{III}(CN)_7]^{4-}$ anions and exhibits a corrugated two-dimensional layered architecture. The structure of **2** with a 1:1 ratio of $Mo^{III}:Mo^{IV}$ is best described as a ladder-like chain composed of $[Mo^{III}(CN)_7]^{4-}$-based pentanuclear $[Mo^{III}Mn^{II}_4]$ fragments which are further linked by *in situ* produced
[15] $[Mo^{IV}(CN)_8]^{4-}$ anions. In the case of **3**, $[Mn_8Mo_8]$ rings containing bent $[Mo^{III}Mn^{II}_2]$ fragments are extended into a two-dimensional layer with the ratio of $[Mo(CN)_7]^{4-}:[Mo(CN)_8]^{4-}$ being 1:2. Compound **4** exhibits a bent trinuclear structure in which two CN⁻ groups of $[Mo(CN)_8]^{4-}$ function as μ_2-bridges to $[Mn(dpop)(H_2O)]^{2+}$ fragments. Magnetic studies suggest significant antiferromagnetic coupling interactions occur between Mo(III) and Mn(II) ions while, not surprisingly, interactions between the
[20] Mn(II) ions through diamagnetic $[Mo^{IV}(CN)_8]^{4-}$ anions are negligible. Compound **1** exhibits ferrimagnetic ordering below 3.0 K whereas **2** shows the signature of single molecule magnet behavior with slow relaxation of the magnetization and an effective energy barrier (U_{eff}) of 8.1 K.

Introduction

The field of molecular magnetism has expanded rapidly over the [25] past few decades into a diverse and exciting research enterprise with promising potential applications for high density storage media as well as quantum computing.[1] Among the coordination compounds being pursued for their rich magnetic, spectroscopic and physical properties are those with cyanide ligands.[2] The [30] cyanide bridge is well-known in magnetism for providing a short (≈ 5.0 Å) and effective pathway for superexchange between metal ions. A large number of cyanide-bridged complexes have been reported over the past fifteen years that exhibit a wide range of behavior including room-temperature magnetism,[3] spin-[35] crossover,[4] single-molecule magnetism (SMMs),[5] single-chain magnetism (SCMs),[6] and photomagnetism.[7]

In recent years molecular magnets based on 4d and 5d metal ions have received increasing attention due to the existence of strong spin-orbit coupling and anisotropic magnetic exchange, [40] with the $[Mo^{III}(CN)_7]^{4-}$ anion being one of the most promising precursors reported thus far.[2e] This heptacyanometalate anion is an excellent building block to construct a variety of compounds with novel topological structures due to its flexibility in adopting different geometries, *e.g.*, pentagonal bipyramid (D_{5h}), mono-[45] capped octahedron (C_{3v}), and capped trigonal prism(C_{2v}) and the

presence of multiple binding sites.[8] Moreover, both theoretical and experimental investigations have demonstrated that the pentagonal symmetry of the $[Mo^{III}(CN)_7]^{4-}$ anion can lead to a high degree of anisotropy for targeting high-T_B SMMs.[5g, 9]

[50] The synthesis of $K_4[Mo(CN)_7] \cdot 2H_2O$ was first reported in 1932[10] but compounds based on the $[Mo^{III}(CN)_7]^{4-}$ anion remain quite scarce, presumably because of its high sensitivity to air and light which leads to challenges in handling. To date, only a limited number of heterometallic Mo^{III}-M^{II} magnets, with M = [55] Mn^{II} being the most studied, have been reported beginning with the pioneering studies by Kahn[11] and co-workers in the 1990s with several other research groups adding to the literature in more recent years.[12-21] Magnetic interactions through the $\{Mn^{II}$-NC-$Mo^{III}\}$ unit were found to be antiferromagnetic (AF), and as a [60] result, ferrimagnetic ordering at temperatures up to 106 K were observed. Self-assembly reactions of $[Mo(CN)_7]^{4-}$ and the aquated cation $[Mn(H_2O)_6]^{2+}$ led to two thermodynamically stable pseudo-dimorphic three-dimensional (3-D) frameworks *viz*., $[Mn_2(H_2O)_5][Mo(CN)_7] \cdot nH_2O$ (n = 4 for α, n = 4.75 for the β-[65] phase), which order ferrimagnetically at T < 51 K.[12] The introduction of different cations into the chemistry resulted in many new topologies with interesting magnetic properties. For example, $[N(CH_3)_4]_2[Mn(H_2O)_3][Mo(CN)_7] \cdot 2H_2O$[13] and $[NH_4]_2Mn_3(H_2O)_4[Mo(CN)_7]_2 \cdot 4H_2O$[14] exhibit different 3-D [70] frameworks with cavities, either cubic or larger pores, with

Table 1. Crystallographic data for **1 - 4** at 100(2) K.

Compound	1	2	3	4
Formula	$C_{111}H_{150}Mn_6Mo_3N_{51}O_6$	$C_{75}H_{94}Mn_4Mo_2N_{35}O$	$C_{113}H_{166}Mn_6Mo_3N_{53}O_{14}$	$C_{38}H_{68}Mn_2MoN_{18}O_{11}$
Formula Weight	2912.20	1913.44	3108.36	1158.89
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1$/c	P-1	$C\,2$/c	$C\,2$/c
R_{int}	0.0421	0.0203	0.0536	0.0338
a [Å]	20.831(4)	15.518(3)	40.845(8)	16.957(3)
b [Å]	21.372(4)	17.430(4)	17.007(3)	14.646(3)
c [Å]	45.279(12)	21.899(4)	24.632(5)	22.159(4)
α [°]	90	93.07(3)	90	90
β [°]	117.11(2)	109.74(3)	120.68(3)	104.91(3)
γ [°]	90	109.00(3)	90	90
V [Å³]	17943(7)	5181.6(18)	14715(5)	5318.0(18)
Z	4	2	4	4
ρ_{calcd} [mgm^{-3}]	1.045	1.221	1.393	1.417
F(000)	5762	1946	6292	2312
Crystal size[mm^{-1}]	0.32 × 0.26 × 0.22	0.26 × 0.18 × 0.14	0.24 × 0.18 × 0.16	0.18 x 0.15 x 0.10
$\mu(Mo_{k\alpha})$ [mm^{-1}]	0.661 mm^{-1}	0.761 mm^{-1}	0.816 mm^{-1}	0.768 mm^{-1}
Measured refl.	138965	54804	55078	23275
unique refl.	24757	21104	9936	4232
No. of parameters	1593	1063	878	320
GOF	1.030	1.050	1.064	1.101
$R1^{[a,b]}$	0.1051	0.0541	0.0424	0.0380
$wR2^{[a,c]}$	0.2561	0.1516	0.1177	0.1199

[a] $I \geq 2\sigma(I)$: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

ordering temperatures of 86 K and 53 K, respectively whereas a 2-D layer instead of a 3-D architecture is observed for $K_2[Mn_3(H_2O)_6][Mo(CN)_7]_2 \cdot 6H_2O$[15] ($T_c$ = 39 K).

The use of chelating co-ligands for the Mn^{II} ions is effective for tuning the structures as well as obtaining single crystals. In 2003, Sutter *et a*l reported two structurally related 3-D ferrimagnets with $[Mn_2(tea)Mo(CN)_7] \cdot H_2O$ (75K) and $[Mn_2(tea)Mo(CN)_7]$ (106 K) by using triethanolamine (tea).[16] Later, by employing a chiral co-ligand N,N-dimethylalaninol (HL, R- and S-), the same group obtained a family of chiral magnets of general formula $[\{Mn(HL)(H_2O)\}_2Mn\{Mo(CN)_7\}_2] \cdot 2H_2O$ that crystallize in an open framework 3-D structure and exhibit reversible switching behavior of the magnetic ordering (T_c = 85 K ↔ 106 K) upon dehydration and rehydration.[17] A one pot reaction of $MnCl_2 \cdot 4H_2O$, triazacyclononane (tacn) and $K_4[Mo(CN)_7] \cdot 2H_2O$ led to a new material that behaves as a ferromagnet below 90 K with the proposed formula of $[Mn(tacn)]_2[Mo(CN)_7] \cdot 5H_2O]$ although the structure is not known.[18] Finally, it should also be mentioned that Ohkoshi's group recently prepared the first vanadium $[Mo^{III}(CN)_7]$ based ferrimagnet, namely $V^{II}_2[Mo^{III}(CN)_7](pyrimidine)_2 \cdot 4.5H_2O$, with the fairly high Curie temperature of 110 K whose structure was confirmed by its isomorphous $Mn^{II}_2[Mo^{III}(CN)_7]$-(pyrimidine)$_2 \cdot 2H_2O$ analog which orders at the much lower temperature of T_c = 47 K.[19]

The ligand 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12.3.1]octadeca-1(18),2, 12,14,16-pentaene (dpop, **Scheme 1**) is a planar macrocyclic ligand first introduced into this chemistry in 1999 by Kahn's group. The reaction of Mn(dpop)Cl$_2$·4H$_2$O and K$_4$[Mo(CN)$_7$]·2H$_2$O in
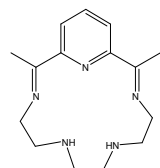
Scheme 1. ligand dpop.

deoxygenated water afforded the 2-D mixed-valence complex $[Mn(dpop)]_6[Mo^{III}(CN)_7][Mo^{IV}(CN)_8] \cdot 19.5H_2O$ that exhibits long-range ferromagnetic ordering below 3 K.[11e] Although the

authors reported that oxidization was inevitable even under strictly anaerobic conditions, our group recently managed to isolate the first example of a pure compound with the dpop ligand by following the same procedure but with a 1:1 molar ratio of the starting materials. The product is the salt $[Mn(dpop)(H_2O)_2]_2[\{Mo^{III}(CN)_7\}_8\{Mn(dpop)_{10}\}][Mn(dpop)(H_2O)_2]_4] \cdot xH_2O$, which contains the largest number of paramagnetic centers and the highest spin ground state (S = 31) among polynuclear cyanide-bridged compounds.[21] Treatment of the above reaction with mixed solvents of methanol and water and a Mn:Mo molar ratio of 2:1, however, afforded the new 3-D ferrimagnet $\{[Mn(dpop)]_3[Mn(dpop)(H_2O)][Mo^{III}(CN)_7]_2 \cdot 13.5H_2O\}_n$ (T_c = 3 K). Remarkably, this compound undergoes a single-crystal to single-crystal transformation to the new network polymer $\{[Mn(dpop)]_2[Mo^{III}(CN)_7] \cdot 2H_2O\}_n$ with a higher blocking temperature (24 K).[22] Encouraged by these interesting results, we continued our research of this highly adaptive system by adjusting the reaction solvents and synthetic conditions which led to the isolation of $\{[Mn(dpop)]_4[Mn(dpop)(H_2O)]_2$-$[Mo^{III}(CN)_7]_3 \cdot 27H_2O\}_n$ (**1**), $[Mn(dpop)]_3[Mn(dpop)(H_2O)]$-$[Mo^{III}(CN)_7][Mo^{IV}(CN)_8] \cdot 29H_2O\}_n$ (**2**), $\{[Mn(dpop)]_4$-$[Mn(dpop)(H_2O)]_2[Mo^{IV}(CN)_8]_2[Mo^{III}(CN)_7] \cdot 12H_2O\}_n$ (**3**) and $[Mn(dpop)(H_2O)]_2[Mo^{IV}(CN)_8] \cdot 9H_2O$ (**4**). Herein, we present their syntheses, structures and magnetic properties.

Experimental Section

General. All chemicals and solvents are of reagent grade quality and used without further purification. The reagents $[Mn(dpop)(H_2O)_2]Cl_2$[23] and $K_4[Mo(CN)_7] \cdot 2H_2O$[10] were prepared as described in the literature. All experiments were performed under a nitrogen atmosphere and in the dark. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQUID magnetometer from 2 to 300 K in a magnetic field of 2000 G. The samples were prepared in the glove box and sealed in NMR tubes. The diamagnetic

contributions of all constituent atoms were subtracted by the use of Pascal's constants.

Synthesis of 1. Both $[Mn(dpop)(H_2O)_2]Cl_2$ (63.5 mg, 0.125 mmol) and $K_4[Mo(CN)_7]\cdot 2H_2O$ (30.0 mg, 0.0625 mmol) were
5 dissolved in a 3 mL mixed solution of $CH_3OH:H_2O = 2:1$, respectively, and then layered on each side of a U-tube with 8 mL of H_2O as a buffer at the bottom. Dark block crystals of **1** were obtained after a week by diffusion in a U-tube; yield 26%.

Synthesis of 2. A 1 mL aliquot of H_2O as a buffer was layered on
10 top of a 1 mL solution of H_2O: DMSO = 2:1 (v/v) containing $K_4[Mo(CN)_7]\cdot 2H_2O$ (9.4 mg, 0.02 mmol) in a single tube and then $[Mn(dpop)(H_2O)_2]Cl_2$ (20.3 mg, 0.04 mmol) in 1 mL of CH_3OH: $H_2O = 2:1$ (v/v) was carefully layered on top. Dark red cubic crystals of **2** were obtained after a week in the sealed single
15 tube; yield 37%.

Synthesis of 3. Dark red rhombus crystals of **3** were obtained after a month by slow diffusion in an H-tube following a similar procedure as reported in the literature;[12] yield: 58%.

Synthesis of 4. Orange needle-like crystals of **4** were obtained
20 following the same procedure as for **1**, except that oxygen was introduced accidentally; yield: 81%.

X-ray Crystallographic Studies. Diffraction intensities for complexes **1-4** were collected on a computer controlled Bruker Apex-II CCD diffractometer equipped with graphite-
25 monochromated Mo-K_α radiation (0.71073 Å) by using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the *SHELXS-97* and *SHELXL-97* programs.[24] Anisotropic thermal
30 parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were
35 incorporated. The program SQUEEZE/PLATON was used to remove the disordered water molecules for **1** and **2**. The number of interstitial water molecules was estimated by TGA analyses for **1** and **2**. Further details of the crystal structure determination have been deposited to the Cambridge Crystallographic Data Centre as
40 supplementary publication. CCDC deposition numbers 973467 for **1**, 973468 for **2**, 973469 for **3** and 973470 for **4** contain the full crystallographic data for this paper.

Results and Discussion

X-ray Crystallographic Studies.

45 A summary of the crystallographic and refinement data are listed in Table 1. The Mn(II) ions in the title compounds are hepta-coordinate with a slightly distorted pentagonal bipyramidal geometry. The macrocyclic ligand dpop provides five equatorial nitrogen donors for the Mn^{II} ions. Only two different Mn^{II}
50 environments were found, namely $[(dpop)Mn(NC)_2]$ and $[(dpop)Mn(NC)(H_2O)]$. The former type serves as a μ_2 bridge with two cyanide nitrogen atoms in the apical sites, whereas the latter unit serves as a terminal node with one cyanide nitrogen atom and one coordinated water molecule in the apical positions.
55 All Mo^{III} ions exist as the $[Mo(CN)_7]^{4-}$ anion and adopt a pentagonal bipyramidal geometry, whereas the Mo^{IV} ions exist in the form of the $[Mo(CN)_8]^{4-}$ anion and adopt a square

antiprismatic geometry.
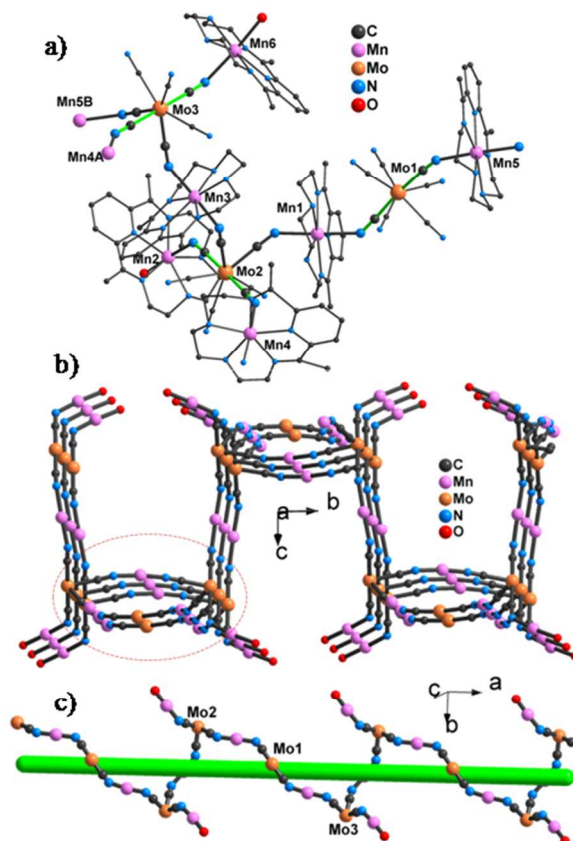
60 **Fig. 1**. a) Asymmetric unit b) depiction of the skeletal backbone of the 2-D layer and c) helical chain of **1**. The terminal cyanide groups, dpop ligands, interstitial water molecules and hydrogen atoms have been omitted for the sake of clarity.

65

$\{[Mn(dpop)]_4[(dpop)Mn(H_2O)]_2[Mo^{III}(CN)_7]_3\cdot 27H_2O\}_n$ **(1).**
Compound **1** crystallizes in the monoclinic space group $P2_1$/c. The asymmetric unit of $\{[Mn(dpop)]_4[Mn(dpop)(H_2O)]_2\text{-}[Mo^{III}(CN)_7]_3\}$ is shown in Fig. 1a. There are three different
70 $[Mo^{III}(CN)_7]^{4-}$ units with Mo1 being connected to two Mn^{II} ions via its axial CN^- ligands (N1, N5) whereas both Mo2 and Mo3 centers are linked to four Mn^{II} ions through cyanide groups in a μ_4-mode, two in the axial positions (N8, N12 for Mo2 and N15, N19 for Mo3, respectively) and the other two in *ortho*-1,2
75 equatorial positions (N11, N13 for Mo2 and N16, N17 for Mo3, respectively). For the six crystallographically independent Mn^{II} ions, each of the Mn2 and Mn6 ions in the $[Mn(dpop)(H_2O)]^{2+}$ terminal nodes are coordinated to one water molecule and linked to one $[Mo^{III}(CN)_7]^{3-}$ anion. The other Mn^{II} ions that function as
80 μ_2-nodes are bonded to two Mo^{III} ions through cyanide linkages along the axial direction. Thus, a 2_1 helical cyanide-bridged Mn-Mo alternate chain is formed along the *a* axis with the repeat unit [-Mn5-Mo1-Mn1-Mo2^{Mn2}-Mn3-Mo3^{Mn6}]. (Fig. 1c) Each chain is further linked to another two through μ_2 [Mn(dpop)]$^{2+}$ (Mn2)
85 nodes to form corrugated 2-D layers (Fig. 1b) that stack along the *c* direction into a 3-D structure connected via H-bonds between water molecules and terminal cyanide groups and π-π stacking interactions between the neighboring pyridine rings of [dpop]. TGA analysis was used to estimate the number of water

molecules in **1** (Supporting Information, Fig. S1. A 13.78% weight loss corresponds to ~27 crystallized H_2O molecules per $Mo_3^{III}Mn_6^{II}$ unit.)

The Mo-C-N bond angles range from 173.6(13) to 178.6(13)° and the bent cyanide Mn-N-C bond angles range from 133.4(9) to 151.3(13)°. The Mo-Mn separations are in the range 5.119(27) – 5.368(4) Å.
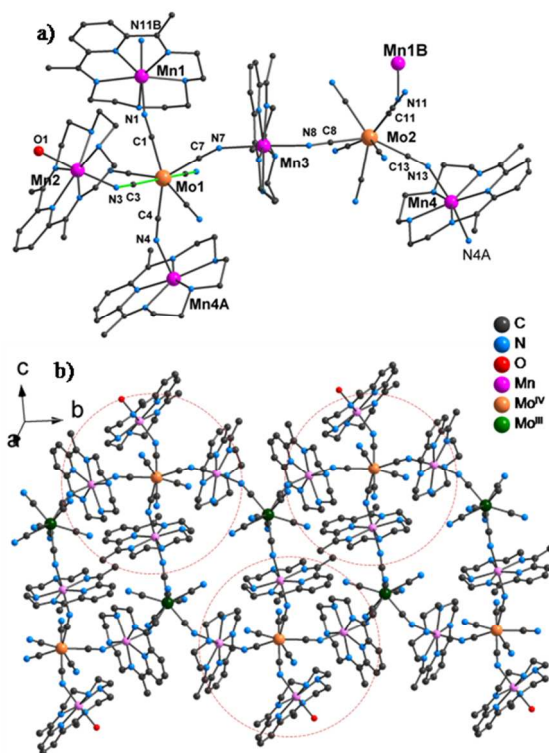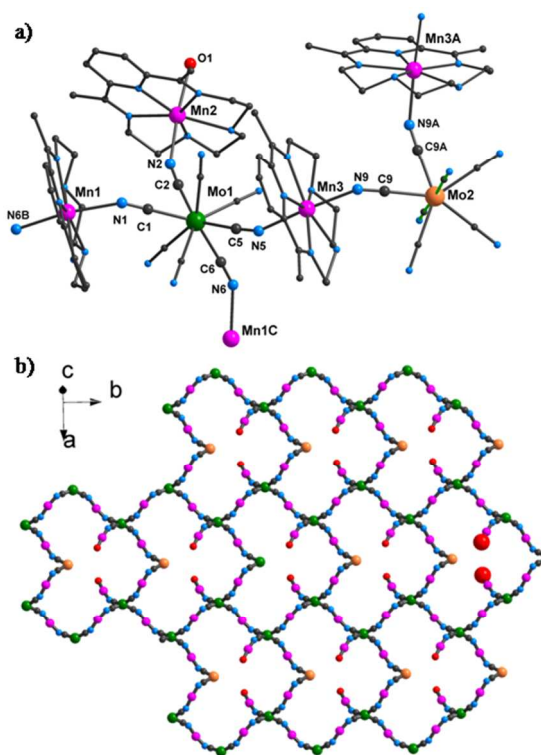

Fig. 2. The ball-and-stick view of a) asymmetric unit and b) the ladder-like chain with alternating $[Mo^{IV}(CN)_8]^{4-}$ and $[Mo^{III}Mn_4^{II}]$ fragments of **2**. The interstitial water molecules and hydrogen atoms have been omitted for the sake of clarity.

[(dpop)Mn(H₂O)][Mo^{III}(CN)₇][Mn(dpop)]₃[Mo^{IV}(CN)₈] ·29H₂O}ₙ (2). Compound **2** consists of neutral ladder-like chains of $\{[Mn(dpop)(H_2O)][Mo^{III}(CN)_7][Mn(dpop)]_3\text{-}[Mo^{IV}(CN)_8]\}_n$ and interstitial water molecules. As depicted in Fig. 2, the Mo1 site in the $[Mo^{III}(CN)_7]^{4-}$ unit is bonded to one $[Mn(dpop)(H_2O)]^{2+}$ moiety (Mn2) via one of its axial CN^- groups and another three $[Mn(dpop)]^{2+}$ units (Mn1, Mn3, and Mn4A) in the equatorial plane which leads to a pentanuclear $[Mo^{III}Mn_4^{II}]$ fragment. The Mo2 center in the $[Mo^{IV}(CN)_8]^{4-}$ unit adopts a square antiprismatic geometry and is linked to three $[Mn(dpop)]^{2+}$ fragments (Mn3, Mn4, Mn1B) through cyanide bridges. Thus, each $[Mo^{III}Mn_4^{II}]$ fragment is bound to three different diamagnetic $[Mo^{IV}(CN)_8]^{4-}$ units and each $[Mo^{IV}(CN)_8]^{4-}$ anion is connected to three $[Mo^{III}Mn_4^{II}]$ units to form a ladder-like chain along the *b* axis. The chains are organized into a 3-D motif through H-bonds between the terminal cyanide groups and the guest water molecules. The number of interstitial water molecules was estimated from TGA analysis (SI, Fig. S2; 21.5% weight loss, which is ~ 29 H_2O molecules per Mo_2Mn_4 unit).

The Mo^{III}-C-N bond angles range from 175.7(4) to 179.4(5)° and the cyanide Mn-N-C bond angles deviate significantly from

linearity, ranging from 143.0(3) to 156.0(4)°. The Mo^{III}-Mn^{II} separations are in the range 5.26(8) to 5.39(5) Å. The nearest Mn---Mn distance between the $[Mo^{III}Mn_4^{II}]$ fragments is 9.10(9) Å.

Fig. 3. The ball-and-stick view of a) the asymmetric unit and b) the depiction of the layer based on $[Mn_8Mo_8]$ rings of **3**. The interstitial water molecules and hydrogen atoms have been omitted for the sake of clarity.

{[(dpop)Mn(H₂O)]₂[Mo^{IV}(CN)₈]₂[Mn(dpop)]₄Mo^{III}(CN)₇] ·12H₂O}ₙ (3). Compound **3** crystallizes in the monoclinic space group *C*2/c. The structure (Fig. 3) was described previously in the literature.[11e] We are describing its isolation and characterization in this work only because the magnetic properties were reinvestigated and found to differ from what was reported. The basic unit of the structural topology is a ring of $[Mn_8Mo_8]$ with both Mo^{III} (Mo2) and Mo^{IV} (Mo1) ions that are extended to form a layer in the *ab* plane. It is important to note that Mo2 in the $[Mo^{III}(CN)_7]^{4-}$ unit is connected to two $[Mn(dpop)]^{2+}$ units through two *ortho*-1,2 equatorial CN^- groups[5g] to form bent $[Mo^{III}Mn_2^{II}]$ fragments that are well isolated from each other by the diamagnetic $[Mo^{IV}(CN)_8]^{4-}$ bridges with the nearest Mo---Mn distance being 13.60(1) Å. The Mn3-N9-C9 and Mo2-C9-N9 bond angles in the Mo−C−N−Mn linkage are 144.45(39) and 177.87(42)°, giving a separation of 5.38(4) Å between Mo2 and Mn3 ions.

[(dpop)Mn(H₂O)]₂[Mo^{IV}(CN)₈]·9H₂O (4). Compound **4** crystallizes in the monoclinic space group *C*2/c as the neutral cyanide-bridged trinuclear species $[Mn(dpop)(H_2O)]_2[Mo^{IV}(CN)_8]$ along with interstitial water molecules. (Fig. 4) The Mo^{IV} ion is located on a C_2 axis and is in a distorted square antiprismatic environment with an average Mo^{IV}-$C_{cyanide}$ bond distance of 2.17 Å that links two $[Mn(dpop)(H_2O)]^{2+}$ fragments through Mo1-C1-N1 = 178.2(3)°, Mn1-N1-C1 = 160.8(3)° to give a bent trinuclear structure. The angle Mn1-Mo1-Mn1A is highly acute at 129.4°.

The molecules pack into a 3-D arrangement through hydrogen bonds between the terminal CN⁻ groups and coordinated/interstitial H_2O molecules (N3⋯O1A = 2.852 Å; N3⋯O3A = 2.933 Å, N4⋯O4A = 2.814 Å, N2⋯O2A = 2.880 Å). The nearest intra- and inter-molecular Mn⋯Mn distances are 9.804(13) Å and 8.535(23) Å, respectively.
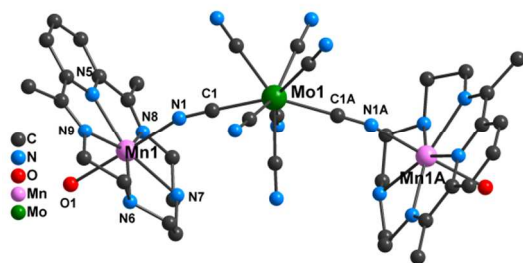

Fig. 4. Ball-and-stick view of the bent trinuclear of **4**.

The $K_4[Mo^{III}(CN)_7]$ salt is known to be unstable due to both light and air sensitivity and quickly decomposes in the presence of oxygen evidenced by a change in color from the olive of $[Mo(CN)_7]^{4-}$ to red within seconds. Additionally, $[Mo^{IV}(CN)_8]^{4-}$ anions are produced, presumably by disproportionation of $[Mo^{III}(CN)_7]^{4-}$ in the presence of light even under strictly anaerobic conditions, but this process is much slower and depends on the exposure level to light. Because of these factors, it is challenging to control the chemistry of the $[Mo^{III}(CN)_7]^{4-}$ anion but one can use empirically derived information to help optimize the synthetic conditions for one product over another including the diffusion rate, stoichiometry and choice of solvents. With these considerations in mind, the starting materials of $Mn(dpop)Cl_2 \cdot 4H_2O$ and $K_4[Mo(CN)_7] \cdot 2H_2O$ were combined under different synthetic procedures to produce four different compounds. All experiments were carried out in the dark and under a N_2 atmosphere. Compound **1** with only heptacyanomolybdate(III) was obtained from slow diffusion in a U-tube in less than a week. Compound **2** with the $Mo^{III}:Mo^{IV}$ ratio of 1:1 formed after diffusion in one week in a single tube along with added DMSO to slow down the crystallization. Compound **3**, containing two equivalents of $[Mo^{IV}(CN)_8]^{4-}$ and one equivalent of $[Mo^{III}(CN)_7]^{4-}$ was isolated after one month in an H-tube. Compound **4** with only $[Mo^{IV}(CN)_8]^{4-}$ ions as well as **3** are the result of the unintentional introduction of small amounts of oxygen and/or disproportionation as the time for crystallization is prolonged. These results, which were not anticipated, lead to extended networks with mixed paramagnetic and diamagnetic Mo cyanide building blocks which may be a useful way to isolate paramagnetic fragments that could behave as SMMs.

Magnetic Studies. The temperature dependence of the magnetic susceptibility data for **1** in the range of 2-300 K is shown in Fig. 5. The value of $\chi_m T$ (χ_m being the molar magnetic susceptibility per $[Mo^{III}_3 Mn^{II}_6]$ unit and T for the temperature) at 300 K is 26.2 cm³ K mol⁻¹, which is slightly lower than the spin-only value of 27.4 cm³ K mol⁻¹ calculated for six uncoupled high-spin Mn(II) (S = 5/2) and three low-spin Mo(III) (S = 1/2) ions assuming g = 2.0. Upon lowering the temperature, the $\chi_m T$ value decreases smoothly and reaches a minimum of 22.70 cm³ K mol⁻¹ at 95 K, and then sharply increases to a maximum of 189.95 cm³ K mol⁻¹

at 3.0 K followed by a rapid decrease to 148.47 cm³ K mol⁻¹ at 2 K. A fitting of the data above 95 K to the Curie-Weiss law gives C = 28.6 cm³ K mol⁻¹ and θ = -30.0 K. (Fig. S3) The negative θ value clearly indicate antiferromagnetic interactions between Mn^{II} and Mo^{III} spin centers. The field dependent magnetization (M) at 2.0 K increases quickly to near saturation suggesting long-range ferrimagnetic order. Indeed the value of 28.15 μ_B at 70 kOe is consistent with a ground state of S = 27/2 per $Mo_3^{III} Mn_6^{II}$ unit. (Fig. S4) Isothermal magnetization experiments performed at 1.8 K exhibit hysteresis with a small coercive field of 30 Oe and a remnant magnetization of 0.56 $N\mu_B$ (Fig. S5).
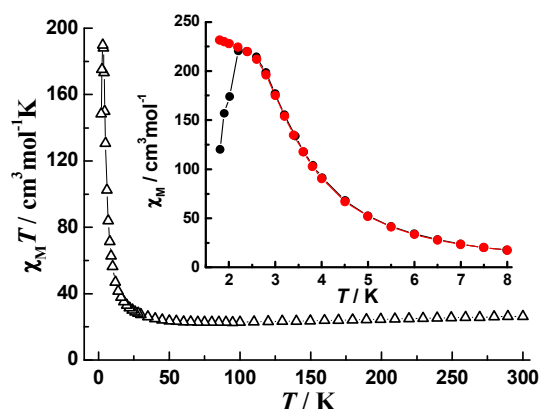

Fig. 5. The $\chi_M T$ vs. T plot of **1**; Inset, ZFCM and FCM plots.
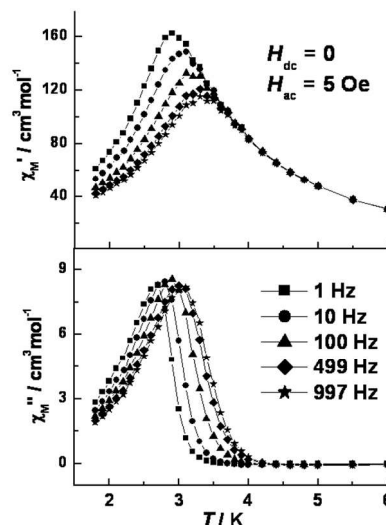
Fig. 6. The temperature dependence of the *AC* magnetic susceptibility data at different frequencies for **1**.

The zero-field-cooled magnetization (ZFC) and field-cooled magnetization (FC) data (Inset of Fig. 5) at a field of 10.0 Oe exhibits irreversibility below 2.2 K, consistent with the above isothermal magnetization. The AC susceptibility data obtained at different frequencies of 1-1339 Hz in a zero DC field showed peaks in both the in phase (χ_M') and the out-of phase (χ_M'') components. (Fig. 6) A small frequency dependence of the peaks in χ_M' and χ_M'' data was observed. The temperature T_p of the peaks in χ_M' shift from 2.9 to 3.3 K, with frequencies ranging from 1 Hz to 1339 Hz. The shift parameter $\gamma = (\Delta T_p/T_p)/\Delta(\log f)$ is

approximately 0.041, in the range of values typical for glassy magnetic behavior.[25] Glassiness can result from two main origins: (i) randomness (i.e., atom or bond disorder or defect in the crystal structure), and (ii) competing interactions.[25] In the present compound, the glassy behavior is reasonable owing to the large number of disordered water molecules in the crystals.

The variable temperature dependence of the magnetic susceptibility data for **4** (per [$Mo^{IV}Mn_2^{II}$] unit) was measured under a 2 kOe dc field from 2-300 K. (Fig. 9) The $\chi_M T$ value at 300 K is 8.59 cm^3 K mol^{-1}, consistent with the spin-only value of 8.75 cm^3 K mol^{-1} for two uncoupled high-spin M^{II} ions ($S = 5/2$) with $g = 2.0$. When the temperature is lowered, the $\chi_M T$ value remains essentially constant until 26 K after which temperature the value decrease to 8.32 cm^3 mol^{-1} K at 2.0 K possibly due to a weak antiferromagnetic interaction between the Mn^{II} ions. As the Mo^{IV} ion is diamagnetic, an appropriate Hamiltonian can be written as: $H = -2J S_1 \cdot S_2$, ($S_1 = S_2 = 5/2$), where J is the magnetic interaction between the Mn ions linked by the diamagnetic [$Mo^{IV}(CN)_8$]$^{4-}$ anion. Based on the Kambe's method,[26] the best fitting for the experimental data gave: $J = -1.46 \times 10^{-2}$ cm^{-1}, $g = 1.98$ and R $= 1.18 \times 10^{-5}$ (R $= (\Sigma(\chi_{obsd}-\chi_{calcd})^2/\Sigma(\chi_{obsd})^2)$). Such a small J value indicates that the interaction through the diamagnetic [$Mo^{IV}(CN)_8$]$^{4-}$ unit is negligible. The isothermal field dependent magnetization $M(H)$ measured at 2 K up to 70 kOe is typical for a system with two uncoupled Mn^{II} ions. (Fig. S6).

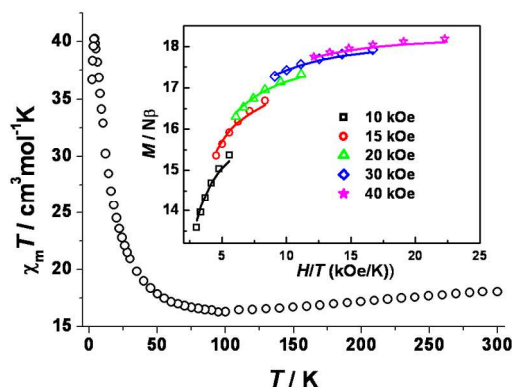**Fig. 7.** The $\chi_M T$ vs. T plot for **2**; Inset, M vs. H/T plots.

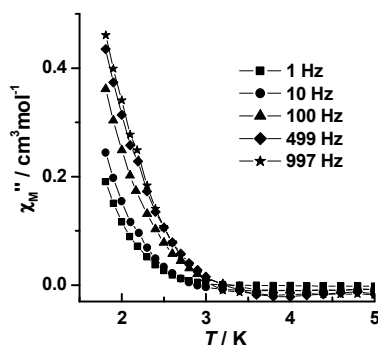The temperature dependence of $\chi_M T$ for **2** (per [$Mo^{III}Mn_4^{II}$] unit) in the range of 2 - 300 K is shown in Fig. 7. The value (18.06 cm^3 K mol^{-1}) of $\chi_M T$ at 300 K is consistent with the spin-

only value of 17.88 cm^3 K mol^{-1} for four uncoupled high-spin Mn^{II} ($S = 5/2$) ions and one Mo^{III} ($S = 1/2$) ion based on $g = 2.0$. As the temperature is lowered, the $\chi_M T$ value decreases smoothly to reach a minimum of 16.30 cm^3 K mol^{-1} at 95 K and then increases rapidly to a maximum of 40.27 cm^3 K mol^{-1} at 4.0 K, and finally decreases to 36.70 cm^3 K mol^{-1} at 2.0 K. A fitting of the data above 120 K to the Curie-Weiss law gives $C = 19.62$ cm^3 K mol^{-1} and $\theta = -26.7$ K. (Fig. S7) The negative θ value is in accord with antiferromagnetic interactions between the Mn^{II} and Mo^{III} ions. Due to the negligible interaction through the diamagnetic [$Mo^{IV}(CN)_8$]$^{4-}$ units, the magnetic topology of **2** can be considered to be well-isolated pentanuclear clusters of [$Mo^{III}Mn_4^{II}$] with the central Mo^{III} linked to four Mn^{II} ions through cyanide. The Hamiltonian $H = -2J \Sigma(S_1 \cdot S_i)$ ($S_1 = 1/2$, for Mo^{III}; $S_i = 5/2$ for Mn^{II}, $i = 2, 3, 4, 5$) was used but attempts to fit the data by MAGPACK[27] or PHI[28] did not succeed. The field dependent magnetization at 2.0 K increases steadily to reach a near saturation value of 18.44 μ_B at 70 kOe, which is in good agreement with the antiferromagnetic ground state of $S = 19/2$ per Mo$^{III}Mn_4^{II}$ unit. No hysteresis loop was observed down to $T = 1.8$ K (Figures S8 and S9).

Ac susceptibilities at different frequencies were measured with a 5.0 Oe ac field from 1.8-5.0 K under a zero static field (Fig. 8, S10). A beginning of frequency-dependent out-of-phase signals (χ_M'') was observed indicating that **2** is a SMM. Rough estimations of U$_{eff}$ = 8.0 K and $\tau_0 = 2.0 \times 10^{-6}$ s were extracted by fitting the experimental data at 1000 Hz based on a relative expression suitable for cluster compounds with only one characteristic relaxation process:[29] $\ln(\chi''/\chi') = \ln(\omega\tau_0)+Ea/(k_BT)$. These values are consistent with SMM behavior.[5]

Field dependent magnetization data (10–40 kOe) obtained in the range 1.8–3.3 K. (Inset of Fig. 7) exhibit non-superposition of the isofield lines which is an indication of anisotropy. The best fit of the data by ANISOFI 2.0[30] gave $g = 1.933$, $D = -0.09$ K and E $= 0.006$ K with R $= 6.2 \times 10^{-4}$ (R $= (\Sigma(\chi_{obsd}-\chi_{calcd})^2/\Sigma(\chi_{obsd}^2)$) for the ground state of S $= 19/2$ for the pentanuclear [$Mo^{III}Mn_4^{II}$] fragment. The U_{eff} of 8.1 K can be estimated based on $U = |D|(S^2-1/4)$, consistent with the AC data.
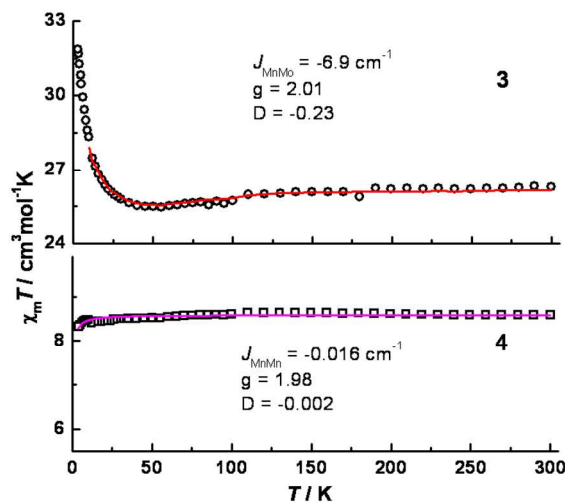

Fig. 9. The $\chi_M T$ (○ for **3**, and □ for **4**) vs. T plots. The solid lines are for the best fit using the PHI program.

The variable temperature (2 - 300 K) magnetic susceptibility of

3 (per $[Mo^{III}Mn^{II}_6]$ unit) is plotted in Fig. 9. The $\chi_M T$ value of 26.3 cm^3 K mol^{-1} at 300 K is agreement with the spin-only value of 26.6 cm^3 K mol^{-1} for six uncoupled high-spin Mn^{II} ($S = 5/2$) ions and one Mo^{III} ($S = 1/2$) ion for a $g = 2.0$. When the temperature is lowered, $\chi_M T$ decreases smoothly to a minimum of 25.47 cm^3 K mol^{-1} at 55 K and then increases rapidly to 31.87 cm^3 K mol^{-1} at 2 K, reflecting the ferrimagnetic nature of the material due to antiferromagnetic interactions between Mo^{III} and Mn^{II} spin centers. A fitting of the data to the Curie-Weiss law gives $C = 26.3$ cm^3 K mol^{-1} and $\theta = -0.04$ K (Fig. S11). The field dependent magnetization at 2.0 K increases steadily to reach a near saturation value of 28.3 μ_B at 70 kOe, consistent with a ground state of $S = 29/2$ per Mo^{III}Mn$^{II}_6$ unit (Fig. S12). No hysteresis loop was observed at above 1.8 K (Fig. S13). It should be mentioned that long range ordering below 3.0 K and ferromagnetic coupling between cyanide-bridged Mn(II) and Mo(III) ions in **3** was observed previously which we find to be surprising.[11e] Given the structure and the negligible interaction through the diamagnetic $[Mo^{IV}(CN)_8]^{4-}$ anions, **3** can be regarded as a trinuclear $[Mn^{II}Mo^{III}Mn^{II}]$ fragment and four isolated Mn^{II} ions. The Hamiltonian for such a trinuclear fragment is: $H = -2J(S_{Mn2}\cdot S_{Mn3}+S_{Mn2}\cdot S_{Mn3'})$, where J represents the interaction between Mo^{III} and Mn^{II} spins through the cyanide bridge. The molecular susceptibility (χ_M) by adding the contribution of the other four $[Mn(dpop)]^{2+}$ (χ_{Mn}) bridged by $[Mo^{IV}(CN)_8]^{4-}$ is the following:

$$\chi_M = \chi_{MoMn_2} + 4\chi_{Mn} = \chi_{MoMn_2} + \frac{4Ng^2\beta^2}{3kT}\left[S_{Mn}(S_{Mn}+1)\right]$$

By using the PHI program,[28] the best fitting for the experimental data above 10 K gives $J = -6.9$ cm^{-1}, $g = 2.0$ and $D_{Mo} = -0.23$ cm^{-1}. The resulting interaction between Mo^{III} and Mn^{II} ions through cyanide bridges is comparable to those previous ones based on $[Mo(CN)_7]^{4-}$ anions within the range of -5.7 to 12.4 cm^{-1}.[12-16]

Ac susceptibilities at different frequencies of 1-1339 Hz in a zero dc field were also measured in the range of 2.0 to 8.0 K (Fig. S14). No peaks were observed in the in-phase ac magnetic susceptibility (χ'), and the out-of-phase of ac magnetic susceptibility (χ'') signals are very weak, precluding 3-D magnetic ordering, spin-glass or SMM behavior above 1.8 K.

Conclusions

The chemistry of Mn(dpop)Cl$_2$·4H$_2$O and K$_4$[Mo(CN)$_7$]·2H$_2$O was investigated under different conditions and found to result in four compounds. Compound **1** with a corrugated 2-D layer structure exhibits ferrimagnetism below 3.0 K. The ladder-like chain structure of **2**, which can be regarded as pentanuclear $[Mo^{III}Mn_4^{II}]$ fragments linked by diamagnetic $[Mo^{IV}(CN)_8]^{4-}$ anions, displays SMM-like behavior. Compound **3** is also a 2-D architecture but the diamagnetic $[Mo^{IV}(CN)_8]^{4-}$ anion suppresses the propagation of magnetic interactions through the cyanide bridges between adjacent Mn^{II} ions resulting in paramagnetic behavior. Compound **4** is a trinuclear compound in which two CN$^-$ groups of $[Mo^{IV}(CN)_8]^{4-}$ function as μ_2-bridges to a $[Mn(dpop)(H_2O)]^{2+}$ fragment. These results demonstrate that the chemistry of $[Mo^{III}(CN)_7]^{4-}$ can lead to extended networks as well as isolated molecules depending on the nature of the synthetic conditions.

Notes and references

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† Electronic Supplementary Information (ESI) available: magnetic data for compounds 1-3. See DOI: 10.1039/b000000x/
‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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