

# [N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>[Mn(H<sub>2</sub>O)]<sub>3</sub>[Mo(CN)<sub>7</sub>]<sub>2</sub>·2H<sub>2</sub>O: A New High *T<sub>c</sub>* Cyano-Bridged Ferrimagnet Based on the [Mo<sup>III</sup>(CN)<sub>7</sub>]<sup>4-</sup> Building Block and Induced by Counterion Exchange

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**Abstract:** The title compound was synthesized by slow diffusion of aqueous solutions containing K<sub>4</sub>[Mo(CN)<sub>7</sub>]·2H<sub>2</sub>O, [Mn(H<sub>2</sub>O)<sub>6</sub>](NO<sub>3</sub>)<sub>2</sub>, and [N(CH<sub>3</sub>)<sub>4</sub>]Cl. The compound crystallized in monoclinic space group *C2/c*, *a* = 25.8546(14), *b* = 12.3906(7), *c* = 13.5382(7) Å, β = 116.4170(10)°, *Z* = 4, *R* = 0.0353, *wR2* = 0.0456. The Mo<sup>III</sup> site is surrounded by six -C-N-Mn linkages and one terminal cyano group in a distorted capped-prism fashion. There are two pentahedral Mn<sup>II</sup> sites in the structure, both with four -N-C-Mo link-

ages and one water molecule. The anisotropic three-dimensional structure consists of connected corrugated grid-like sheet layers parallel to the *bc* plane. Tetramethylammonium counterions ([N(CH<sub>3</sub>)<sub>4</sub>]<sup>+</sup>) located between these layers seem to induce their distortion. The three-dimensional organization may also be viewed as interconnected octag-

onal channels propagated along the *c* axis. The void space of these channels is occupied by coordinated and crystallized water molecules. Temperature and field dependence of the magnetization in both the dc and ac modes have been measured on polycrystalline sample. These investigations have revealed that the compound ordered ferrimagnetically at *T<sub>c</sub>* = 86 K, with a small hysteresis effect. These findings have been compared to those reported previously for three- and two-dimensional materials of the same family.

**Keywords:** cyanides · ferrimagnet · heptacyanometalate · magnetic properties · molybdenum

## Introduction

In the past ten years, numerous bimetallic cyano-bridged molecular based networks have been synthesized and have aroused a great deal of interest for their possible applications in molecular electronics, electron-transfer processes, and as molecular magnets.<sup>[1]</sup> Indeed, the observation of ferro- and ferrimagnetic ordering at relatively high and even room temperatures has been established for several hexacyanometalate-based materials that possess a Prussian Blue type structure.<sup>[2]</sup> The use of 4d and 5d metal ions in new cyano-bridged networks opens many possibilities in the field of

molecular magnetism.<sup>[3]</sup> The more remarkable potential offered by these new building blocks is their capability to accept larger coordination spheres and, therefore, to allow the design of new architectures with efficient and original physical properties. As a matter of fact, octacyanometalate building blocks of Mo(IV),<sup>[4]</sup> Mo(V),<sup>[5a,b]</sup> W(IV),<sup>[4d-i]</sup> W(V),<sup>[5b-e]</sup> and Nb(IV)<sup>[5b,6]</sup> have recently been extensively used in order to obtain coordination materials that present fascinating magnetic<sup>[5a-d]</sup> and photomagnetic properties.<sup>[4a,b,d,h,i]</sup> On the other hand, heptacyanometalate units have received less attention.<sup>[7-9,4b]</sup> In contrast to the hexa- and octacyanometalate building blocks, which potentially are able to form highly symmetrical lattices, the geometry of the heptacyanometalates motif can lead to the formation of low-symmetry extended networks. This characteristic is an important feature for designing high-temperature molecular magnets with interesting anisotropic magnetic properties. As a result, three-dimensional coordination polymers [Mn<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>]-[Mo<sup>III</sup>(CN)<sub>7</sub>]<sub>n</sub>·*n*H<sub>2</sub>O (*n* = 4 and *n* = 4.75 for the α and β phases, respectively) have provided the first structural evidence of cyano-bridged formation by heptacyanides.<sup>[7]</sup> These compounds have long-range magnetic ordering below 51 K and detailed physical studies performed on single crystals reveal many peculiarities, such as the presence of several magnetically ordered phases and spin-reorientation phenomenon. However, the nature and coordination sphere of metal

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ions are not the only parameters needed to design new cyano-bridged architectures. During the synthesis, we discovered that the introduction of counterions can affect the topology and dimensionality of the network and, therefore, strongly influenced the magnetic properties.<sup>[8, 10]</sup> As illustrated by  $K_2[Mn_3(H_2O)_6][Mo(CN)_7]_2 \cdot 6H_2O$ , the presence of two  $K^+$  ions leads to a new 3:2 stoichiometry of the magnetic building blocks ( $Mn^{2+}:[Mo(CN)_7]^{4-}$ ) and to a two-dimensional structure which orders at 39 K.<sup>[8]</sup> Large organic counterions such as tetramethylammonium ( $[N(CH_3)_4]^+$ ) were initially chosen to increase the interlayer distance of the network obtained with  $K^+$  ion. As it turns out, the size but more probably the nature of  $N(CH_3)_4^+$  has a specific and unexpected influence on the structural organization of this system. We report here the crystal structure and the magnetic properties of a new seven-coordinate cyano-bridged molecular magnet,  $[N(CH_3)_4]_2[Mn(H_2O)]_3[Mo(CN)_7]_2 \cdot 2H_2O$  (**1**), which has the highest ordering temperature for compounds of its family.

## Results and Discussion

Under argon atmosphere, the slow diffusion in an H-shaped tube of two aqueous solutions containing  $K_4[Mo(CN)_7] \cdot 2H_2O$ <sup>[11]</sup> and  $[Mn(H_2O)](NO_3)_2$ , in presence of  $N(CH_3)_4Cl$ ,

**Abstract in French:** Le composé  $[N(CH_3)_4]_2[Mn(H_2O)]_3[Mo(CN)_7]_2 \cdot 2H_2O$  a été synthétisé par diffusion lente de solutions aqueuses contenant respectivement  $K_4[Mo(CN)_7] \cdot 2H_2O$ ,  $[Mn(H_2O)](NO_3)_2$  et  $[N(CH_3)_4]Cl$ . Le matériau obtenu cristallise dans le groupe d'espace monoclinique  $C2/c$ ,  $a = 25.8546(14)$ ,  $b = 12.3906(7)$ ,  $c = 13.5382(7)$  Å,  $\beta = 116.4170(10)^\circ$ ,  $Z = 4$ ,  $R = 0.0353$ ,  $wR2 = 0.0456$ . La sphère de coordination du  $Mo^{III}$  est composée de six -C-N-Mn liens et d'un groupe cyano terminal dans une géométrie distordue de type prisme à base pyramidale. La structure possède deux sites  $Mn^{II}$  indépendants de symétrie pentagonale, tous deux possèdent une sphère de coordination composée de quatre liens -N-C-Mo et d'une molécule d'eau. La structure tri-dimensionnelle est anisotrope, elle consiste en des plans parallèles au plan  $bc$  et inter-connectés par des atomes de Mn. Ces plans peuvent être vus comme des grilles ondulées à maille carrée. Les atomes de Mn et de Mo sont répartis alternativement sur chacun des nœuds du réseau bi-dimensionnel. Le contre-ion tétraméthylammonium,  $N(CH_3)_4^+$ , est localisé entre ces plans, semblant induire leur distorsion. L'organisation tri-dimensionnelle peut aussi être décrite par un réseau inter-connecté de canaux octogonaux se propageant suivant l'axe  $c$ . Ces pores sont remplis par des molécules d'eau de coordination et d'insertion. Les dépendances en température et en champ magnétique de l'aimantation en mode  $dc$  et  $ac$  ont été mesurées sur un échantillon poly-cristallin. Ces études ont montré que le composé  $[N(CH_3)_4]_2[Mn(H_2O)]_3[Mo(CN)_7]_2 \cdot 2H_2O$  s'ordonne ferrimagnétiquement à  $T_c = 86$  K, avec un petit effet d'hystérésis en champ magnétique à 1.8 K. Les résultats exposés dans ce manuscrit seront comparés à ceux déjà publiés sur des composés tri et bi-dimensionnels appartenant à cette famille de matériau.

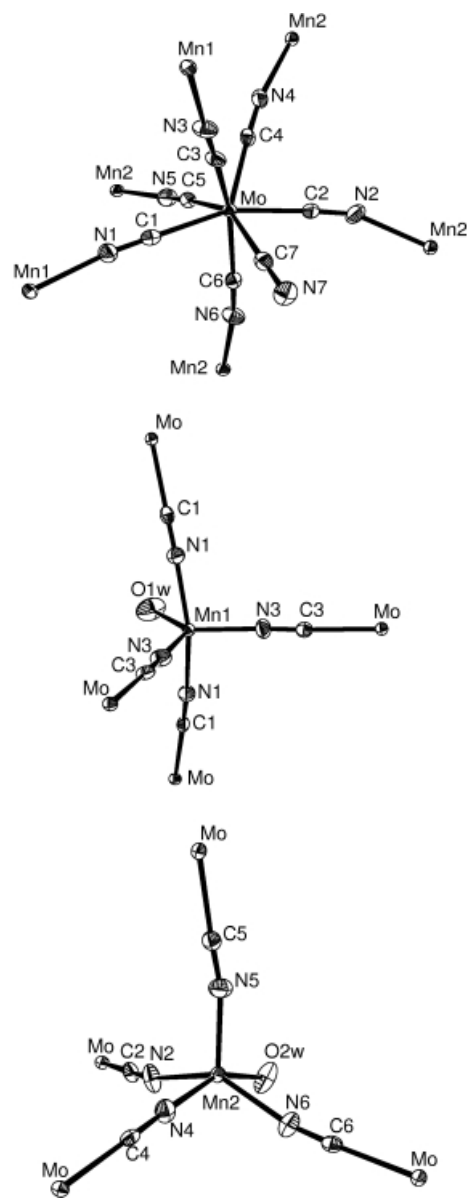


Figure 1. ORTEP drawings of local coordination environments of Mo, Mn1, and Mn2 sites.

leads to dark green crystalline elongated plates. Single-crystal X-ray diffraction studies revealed that **1** has an unexpected three-dimensional network. The structure has one molybdenum site and two manganese sites, Mn1 and Mn2, as shown in Figure 1. The molybdenum atoms are surrounded by four -N-C-Mn2 linkages, two -N-C-Mn1 linkages, and a terminal (C7–N7) cyano group. The Mo–C bond lengths range from 2.109(5) to 2.185(5) Å, with a mean value of 2.147 Å. All of the Mo–C–N bond angles are relatively close to 180°, they range from 173.0(4) to 178.8(4)°. In contrast, the Mn–N–C bond angles deviate significantly from 180°, they range from 157.8(4) to 177.6(4)°. An interesting point of this structure is the sevenfold coordination at the  $Mo^{III}$  site. Among the large number of possible polyhedra with seven vertices,<sup>[12]</sup> only three of them suffice to describe the established elements of structure in sevenfold coordination, namely, the pentagonal

bipyramid ( $D_{3h}$ ), the capped trigonal prism ( $C_{2v}$ ), and the monocapped octahedron ( $C_{3v}$ ). The versatility of the  $[\text{Mo}(\text{CN})_7]^{4-}$  building block is illustrated by  $\text{K}_4[\text{Mo}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  and  $\text{NaK}_3[\text{Mo}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$  in which the  $[\text{Mo}(\text{CN})_7]^{4-}$  moiety adopts two different symmetries: a capped trigonal prism and a pentagonal bipyramid, respectively.<sup>[11]</sup> In the case of **1**, the geometry of the Mo site may be viewed as a distorted capped trigonal prism (Figure 1). The Mn1 and Mn2 atoms are surrounded by four -N-C-Mo linkages and one water molecule. The Mn–N bond lengths range from 2.080(4) to 2.157(4) Å, and the Mn1–O and Mn2–O bond lengths are 2.237(7) and 2.284(4) Å, respectively. Both Mn1 and Mn2 sites are in unusual pentahedral geometry, which can be viewed as a slightly distorted trigonal bipyramid ( $D_{3h}$ ) for Mn1, and as a distorted square-based pyramid ( $C_{4v}$ ) for Mn2 (Figure 1).

The three-dimensional organization of this compound is relatively complicated. The basic structural unit may be described as a noncentrosymmetrical cyano-bridged lozenge motif,  $\{\text{Mo}-\text{C}4-\text{N}4-\text{Mn}2-\text{N}6-\text{C}6-\text{Mo}-\text{C}2-\text{N}2-\text{Mn}2-\text{N}5-\text{C}5\}$  (I), and its inverse,  $\{\text{Mo}-\text{C}2-\text{N}2-\text{Mn}2-\text{N}5-\text{C}5-\text{Mo}-\text{C}4-\text{N}4-\text{Mn}2-\text{N}6-\text{C}6\}$  (II). These motifs alternate and connect through C6–N6 bridges to form distorted bent ladders running along the  $[011]$  direction. These ladders are linked to each other by C4–N4 and C2–N2 bridges to form a corrugated gridlike sheet layer parallel to the  $bc$  plane (Figure 2). In this plane across a cyano bridge, the Mo–Mn2 separations range from 5.267(4) to 5.421(4) Å. It is worth noting that the  $[\text{N}(\text{CH}_3)_4]^+$  counterions are located between the gridlike layers parallel to the  $bc$  plane and, in effect, their presence seems to initiate the distortion of these layers. Two parallel sheets are connected by  $\{\text{Mn}1(\text{C}1\text{N}1)_2(\text{C}3\text{N}3)_2(\text{H}_2\text{O})\}$  units to form a three-dimensional network (Figure 3). Each  $\{\text{Mn}1(\text{CN})_4(\text{H}_2\text{O})\}$  unit is linked to four Mo atoms (two belonging to each of two sheets), leading to chains made of corner-sharing lozenges,  $\{\text{Mo}-\text{C}1-\text{N}1-\text{Mn}1-\text{C}3-\text{N}3\}_2$ , running along the  $c$  direction. The Mo–Mn1 separations across the cyano-bridge are equal to 5.470 and 5.404 Å.

The three-dimensional organization of the whole structure may also be described as interconnected octagonal pores ( $\approx 10$  Å diameter) propagated along the  $c$  axis (Figure 4). In the void space of these channels, four non-coordinated water molecules (O3W) and four other water molecules coordinated to Mn2 ions (O2W) participate to a hydrogen-bonded water cluster. The molecules of water (O1W) coordinated to Mn1 ions do not participate to this hydrogen-bonded entity.

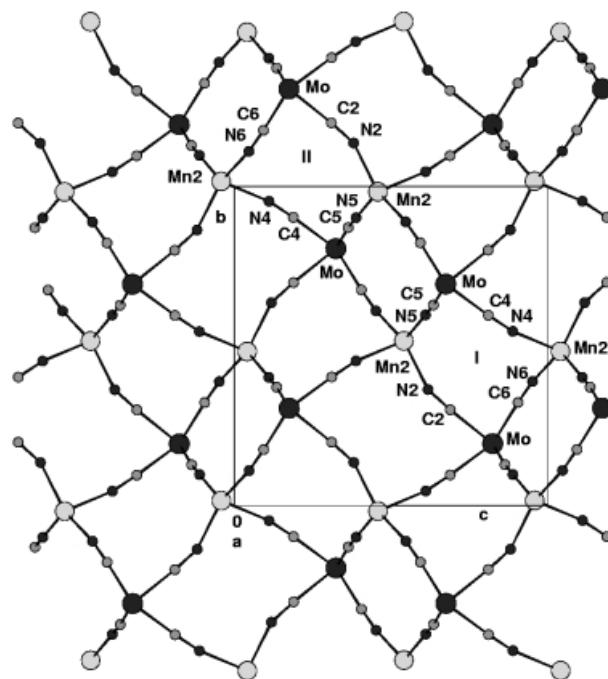


Figure 2. A view of the structure in the  $bc$  plane showing a corrugated gridlike plane. Mn1 atoms, hydrogen atoms, and solvents molecules have been omitted for clarity.

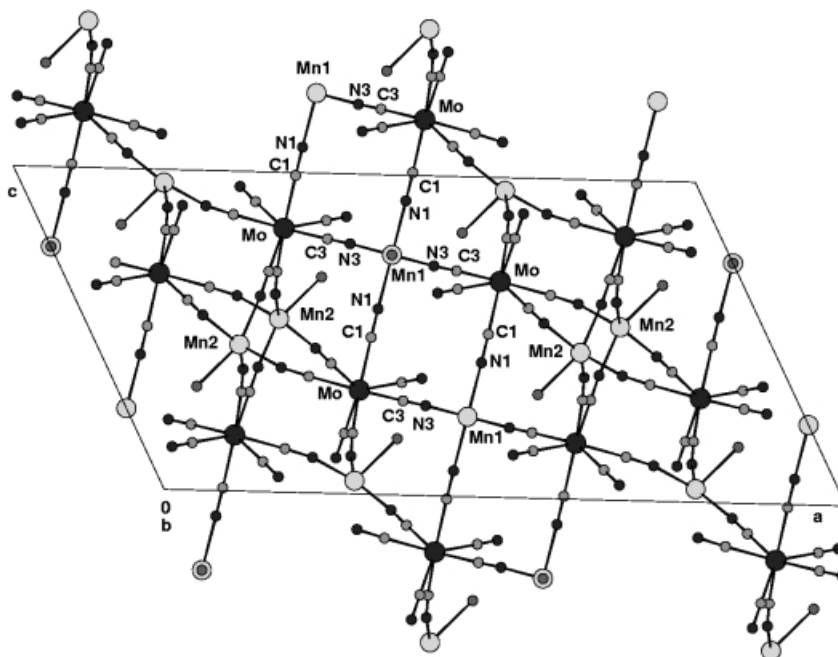


Figure 3. A view of the structure in the  $ac$  plane emphasizing the  $\{\text{Mn}1(\text{C}1\text{N}1)_2(\text{C}3\text{N}3)_2(\text{H}_2\text{O})\}$  connection between two parallel gridlike planes. Hydrogen atoms and solvents molecules have been omitted.

The temperature dependence of the magnetic susceptibility ( $\chi_M$ ) for a polycrystalline sample of **1** is reported in Figure 5. Above 100 K,  $\chi_M$  can be fitted to the Curie–Weiss law ( $\chi_M = C/(T - \theta)$ ) with  $C = 13.4 \text{ emu K mol}^{-1}$  and  $\theta = +89 \text{ K}$  (inset of Figure 5). The Curie constant is close to the expected value for three  $\text{Mn}^{2+}$  ( $S = 5/2$ ) and two  $\text{Mo}^{3+}$  ( $S = 1/2$ ) uncoupled spins ( $C_{\text{theor}} = 13.9 \text{ emu K mol}^{-1}$ ). The positive sign of the Weiss constant reveals that ferromagnetic interactions are

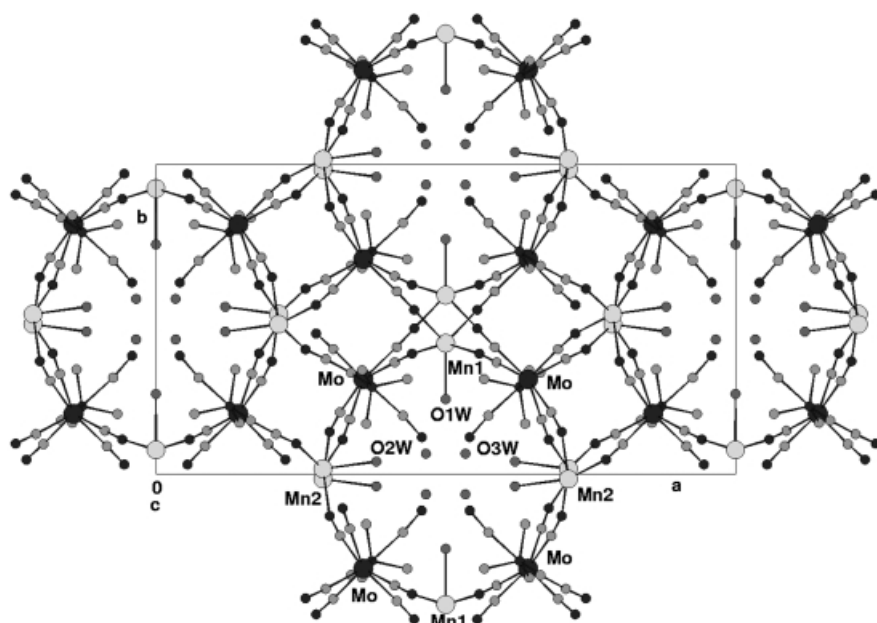


Figure 4. Global view of the crystal structure of **1** in the *ab* plan. Hydrogen atoms have been omitted for clarity.

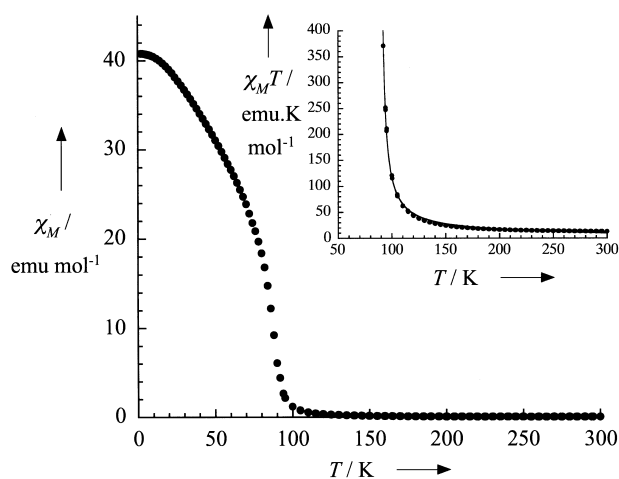


Figure 5. Temperature dependence of  $\chi_M$  for **1** at 1 kOe. Inset: Temperature dependence of  $\chi_M T$  above 100 K fitted to the Curie–Weiss law (solid line).

dominating. Below 100 K,  $\chi_M$  deviates from the Curie–Weiss behavior and undergoes an abrupt increase suggesting the onset of a magnetic ordering. As expected for a magnet, the first magnetization at 1.8 K increases rapidly from 0 to  $7 \mu_B$  below 1 kOe, then slowly reaches  $12.5 \mu_B$  at 50 kOe (Figure 6). A hysteresis loop of the magnetization is also observed at 1.8 K with a coercive field of 200 Oe (inset Figure 6). At high fields, the magnetization is close to the saturation value of  $13 \mu_B$  expected for antiferromagnetic  $\text{Mn}^{2+}$ – $\text{Mo}^{3+}$  interactions (ferromagnetic interactions should lead to a saturation value of  $17 \mu_B$ ). It is worth noting this unusual situation where the  $\text{Mn}^{2+}$ – $\text{Mo}^{3+}$  interactions are clearly antiferromagnetic and the Weiss constant is positive. It is well known that the Weiss constant reflects the sum of all magnetic interactions (through bridging ligands or/and through space).<sup>[13]</sup> Therefore to explain our results, we suggest that first neighbor antiferromagnetic  $\text{Mn}^{2+}$ – $\text{Mo}^{3+}$  interactions may be dominated by second neighbor  $\text{Mn}^{2+}$ – $\text{Mn}^{2+}$  and  $\text{Mo}^{3+}$ – $\text{Mo}^{3+}$  ferromagnetic

exchanges.<sup>[8c]</sup> This result highlights the possible importance of these second neighbor magnetic interactions in the understanding of  $\text{Mn}^{2+}/[\text{Mo}(\text{CN})_7]^{4-}$  systems. The in-phase ( $\chi'_M$ ) and out-of-phase ( $\chi''_M$ ) components of the ac magnetic susceptibility of **1** are shown in Figure 7. Confirming the presence of a magnetic ordering,  $\chi'_M$  exhibits a peak located around 83 K and  $\chi''_M$  becomes different from zero at the critical temperature, 86 K. No significant frequency dependence (between 1 and 1500 Hz) is observed for the  $\chi'_M$  and  $\chi''_M$  responses. Therefore, the dc and ac susceptibility measurements support the occurrence of a ferrimagnetic ordering at 86 K in compound **1**.

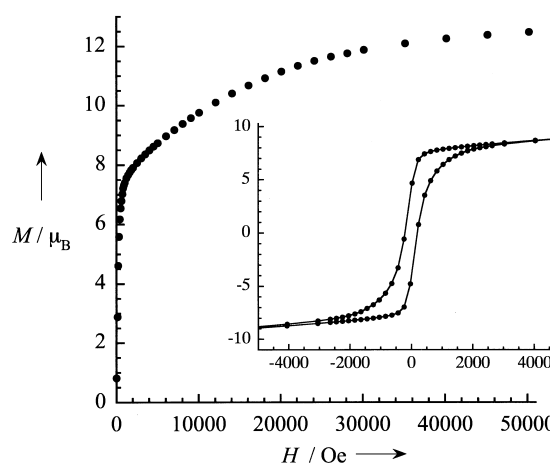


Figure 6. Field dependence of the first magnetization  $M$  for **1** at 1.8 K. Inset: hysteresis loops at 1.8 K.

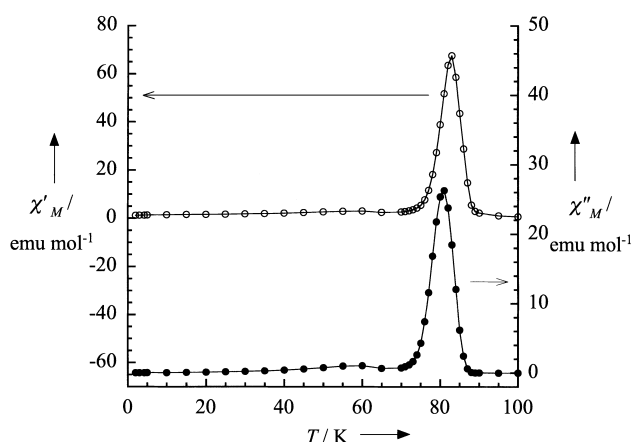


Figure 7. Temperature dependence of  $\chi'_M$  and  $\chi''_M$  in zero external field at 125 Hz.

## Conclusion

The  $\text{Mn}^{2+}/[\text{Mo}(\text{CN})_7]^{4-}$  system<sup>[7,8]</sup> highlights perfectly the structural versatility and diversity of the magnetic properties of materials that contain heptacyanomolybdenum(III) as a building block. We shown here that the introduction of  $[\text{N}(\text{CH}_3)_4]^+$  precludes the formation of the three-<sup>[7]</sup> and two-dimensional<sup>[8]</sup> structures observed previously. Indeed, a new “porous” three-dimensional network is observed which exhibits the highest critical temperature observed for magnetic ordering in the  $\text{Mn}^{2+}/[\text{Mo}(\text{CN})_7]^{4-}$  family. In our quest of new, high  $T_c$  anisotropic magnets, we are currently in progress to investigate new materials based on heptacyanometalate building blocks and their combinations with different metal- and counterions.

## Experimental Section

**Synthesis:** Compound **1** was obtained by slow diffusion in an H-shaped tube under argon atmosphere of two deoxygenated  $10^{-4}\text{M}$  aqueous solutions containing  $\text{K}_2[\text{Mo}(\text{CN})_7] \cdot 2\text{H}_2\text{O}^{[11]}$  and  $[\text{Mn}(\text{H}_2\text{O})_6](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , respectively, in the presence of  $10^{-4}\text{M}$  of  $\text{N}(\text{CH}_3)_4\text{Cl}$ . After few months, dark green crystals with an elongated plate shape formed. The compound was slightly air sensitive.

**Magnetic measurements:** Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer. Measurements on one single crystal and two polycrystalline samples lead to the same results. The data was corrected for the sample holder and the diamagnetism contributions calculated from the Pascal's constants.<sup>[14]</sup>

**Crystal structure determination:** Crystal data for **1** ( $\text{C}_{22}\text{H}_{34}\text{N}_{16}\text{O}_5\text{Mn}_3\text{Mo}_2$ ):  $M_w = 959.36$ , monoclinic, space group  $C2/c$ ,  $a = 25.8546(14)$ ,  $b = 12.3906(7)$ ,  $c = 13.5382(7)$  Å,  $\beta = 116.4170(10)^\circ$ ,  $V = 3884.1(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 193(2)$  K,  $\rho_{\text{calcd}} = 1.641$  mg mm<sup>-3</sup>,  $\lambda(\text{MoK}\alpha) = 0.71073$  Å, CCD diffractometer,  $F(000) = 1908$ ,  $\mu = 1.628$  mm<sup>-1</sup>, 5320 reflections collected, 3637 of which were unique ( $R_{\text{int}} = 0.0413$ ). The structure was solved by direct methods (SIR92)<sup>[15a]</sup> followed by Fourier synthesis, and refined on  $F^2$  (SHELX-97).<sup>[15b]</sup> All non-hydrogen atoms were refined anisotropically. The final refinement gave  $R = 0.0353$ ,  $wR2 = 0.0456$  [ $I > 2\sigma(I)$ ],  $\text{GOF} = 0.773$ . CCDC-167332 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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