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Article

Substantial Increase of the Ordering Temperature for {Mn^{II}/$Mo^{III}(CN)_7$}-Based Magnets as a Function of the 3d Ion Site Geometry: Example of Two Supramolecular Materials with $T_c = 75$ and 106 K

Stéfania Tanase,[†,‡] Floriana Tuna,[†,§] Philippe Guionneau,[†] Thierry Maris,[||] Guillaume Rombaut,[†] Corine Mathonière,[†] Marius Andruh,[‡] (the late) Olivier Kahn,[†,⊥] and Jean-Pascal Sutter*,[†]

Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS No. 9048, F-33608 Pessac, France, Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie No. 23, RO-70254 Bucharest, Romania, Institute of Physical Chemistry of the Romanian Academy, 70208 Bucharest, Romania, and Inorganic Chemistry Laboratory, Oxford OX1 3QR, United Kingdom

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Two molecule-based magnets, $[Mn_2(tea)Mo(CN)_7]\cdot H_2O$, **1**, and $[Mn_2(tea)Mo(CN)_7]$, **2** (tea stands for triethanolamine), formed with the 4d ion building block, $[Mo(CN)_7]^{4-}$, Mn^{II} ions, and an additional ligand, tea, have been prepared and structurally characterized by single-crystal X-ray analyses. Whereas **1** is obtained by a self-assembling process in solution, compound **2** is quantitatively formed through a smooth thermal treatment of **1**. Their magnetic properties revealed that these compounds exhibit magnetic ordering at $T_c = 75$ and 106 K respectively for compounds **1** and **2**. The difference for their critical temperature is attributed to the geometry of the coordination sphere of a Mn^{II} site found to be square-pyramidal for **1** and tetrahedral for **2**.

Introduction

Over the past two decades considerable efforts have been devoted to the preparation and studies of molecule-based magnets. Since the description of the two first compounds designed to exhibit a spontaneous magnetization below a critical temperature, T_c,[1,2] several such materials involving transition metals, lanthanide ions, or organic radicals as spin carriers have been reported.[3] The preparation of permanent magnets, i.e. materials for which T_c is above room temperature, however, remains a major challenge in this field. At present, only two compounds characterized by a magnetic order persistent above 300 K have been obtained. Both involve V^{II} ions and either organic radicals[4] or $[Cr(CN)_6]^{3-}$.[5,6] The latter belongs to the family of Prussian blue derivatives and corresponds to the compound with the highest ordering temperature as predicted from theoretical models based on the symmetry of the single occupied orbitals.[7,8]

Paramagnetic 4d and 5d metal ions have been envisaged only recently for the construction of molecule-based magnets.[9,10] Due to the more spatially extended d orbitals for these elements, stronger exchange interactions are anticipated between magnetic centers and, consequently, magnetic ordering at higher temperatures. For instance, three-dimensional networks built from cyanometalate derivatives of Mo^{III},[11,12] W^{V},[13] or Nb^{IV}[14] associated with Mn^{II} exhibit

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* To whom correspondence should be addressed. Fax: (33) 556 84 26 49. E-mail: jpsutter@icmcb.u-bordeaux.fr.

[†] UPR CNRS No. 9048.

[‡] University of Bucharest.

[§] Romanian Academy.

[||] Inorganic Chemistry Laboratory.

[⊥] Deceased.

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the characteristic features for magnets below temperatures around 50 K. Interestingly, the magnetic properties of Mo^{III} compounds were found to be modified through partial dehydration, leading to an increase of the T_c up to 65 K.[12] An even more pronounced effect has been observed for a bi-dimensional network of the same spin carriers for which the T_c augmented from 39 to 72 K after H_2O was released from the network.[15] Moreover, a related derivative with five coordinated Mn^{II} centers was recently described to order at 86 K.[16] These observations suggest that slight modifications of the lattice and/or the coordination spheres of the metal ions might have an important effect on the temperature at which the magnetic order occurs.

With this idea in mind we considered the possibility of controlling the conformations in such networks and consequently the magnetic properties by introducing a ligand into the coordination sphere of the M^{II} metal ion. In this report we describe our results obtained with triethanolamine (hereafter abbreviated tea) and the $\{Mn^{II}/Mo^{III}(CN)_7\}$-based magnetic network. Two compounds of formula $[Mn_2(tea)Mo(CN)_7]\cdot xH_2O$, **1** ($x = 1$) and **2** ($x = 0$), have been prepared and were found to exhibit a significantly increased T_c. The crystal structure analyses and magnetic features for both compounds are reported.

Results

Syntheses and Structural Features. (a) $[Mn_2(tea)Mo(CN)_7]\cdot H_2O$, 1. The reaction of $[Mo(CN)_7]^{4-}$, Mn^{II} ions, and tea in 1/2/1 ratio in H_2O at 50 °C afforded the green compound $[Mn_2(tea)Mo(CN)_7]\cdot H_2O$. Single crystals were grown by interdiffusion of solutions of these reagents in a H-shaped tube. The single-crystal X-ray structural determination revealed that **1** has a polymeric structure based on a network of $Mo(CN)_7$ units and Mn^{II} ions with the solvate molecule, H_2O, located in the void of the framework (Figure 1). Each $Mo(CN)_7$ building block is linked to Mn^{II} ions through its seven CN ligands, and each Mn^{II} center is connected to either three (Mn1) or four Mo units (Mn2) forming a three-dimensional framework. A peculiar feature of this structure is the two coordination geometry exhibited by the Mn^{II} ions. One Mn^{II} site, Mn1, is in a distorted octahedral environment formed by three MoCN→Mn linkages along with the N and two O atoms of the tea ligand (Figure 2). The second, Mn2, is in a square-pyramidal environment consisting of four MoCN→Mn linkages and one O atom from a hydroxyethyl arm of tea from a neighboring {Mn1(tea)} moiety. Each $Mo(CN)_7$ unit is connected to three octahedral Mn1 and four Mn2 centers. The coordination sphere for each metal center and their interconnections are depicted Figure 2. The crystal structure shows two close statistical disordered positions for four carbon atoms (C8, C9, C14, C13) of tea as well as for one oxygen (O3) and two nitrogen atoms (N8, N9) within the coordination sphere of Mn2 as a result of the ligand puckering. Only one position for these atoms is represented Figure 2.

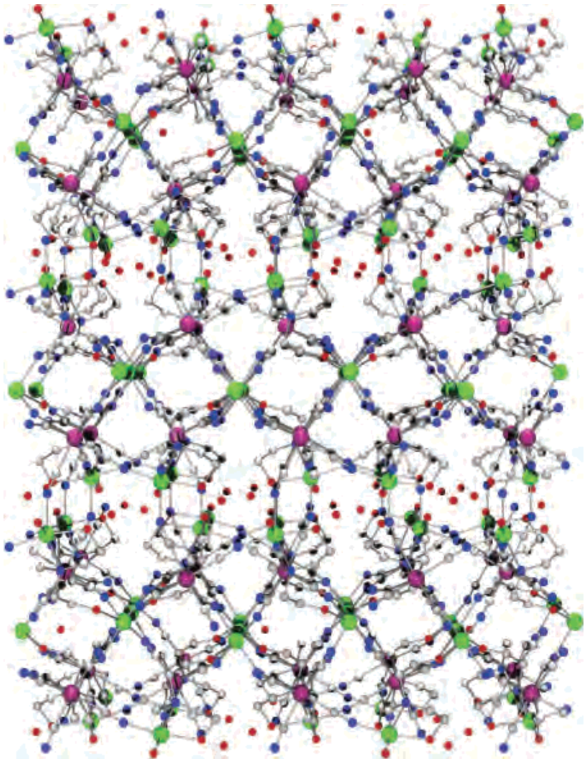

Figure 1. View of the 3-D network of $[Mn_2(tea)Mo(CN)_7]\cdot H_2O$ (**1**) along *b* (Mo, violet; Mn, green; N, blue; O, red, C, gray). H atoms are omitted.

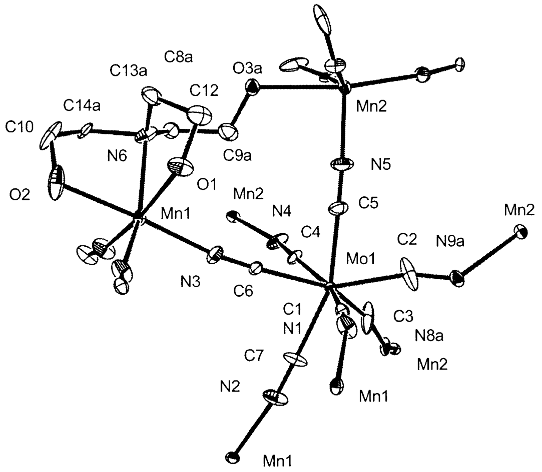

Figure 2. ORTEP plot (30% probability) of the coordination spheres for the metal ions in $[Mn_2(tea)Mo(CN)_7]\cdot H_2O$, **1**. Selected bond lengths (Å): Mo−C, 2.08(1)−2.167(9); Mn1−O, 2.248(8)−2.290(9); Mn1−N1, 2.161(9); Mn1−N2, 2.152(9); Mn1−N3, 2.190(9); Mn1−N6, 2.357(9); Mn2−O3b, 2.369(13); Mn2−N4, 2.122(9); Mn2−N5, 2.064(10). Hydrogen atoms and second statistical positions for b labeled atoms are omitted for clarity. (Symmetry codes are as follows: For 3, $^1/_2 + x$, $^1/_2 - y$, $-z$; for 4, $-x$, $^1/_2 + y$, $^1/_2 - z$; for 5, $-x$, $-y$, $-z$; for 6, $x - {}^1/_2$, y, $^3/_2 - z$; for 7, $^1/_2 - x$, $^1/_2 + y$, z.)

The geometry of the $Mo(CN)_7$ unit might be described as a slightly distorted capped trigonal prism. The Mo−C bond lengths are found between 2.08(1) and 2.167(9) Å (mean value, 2.134 Å), and the Mo−C−N angles range from 160.84

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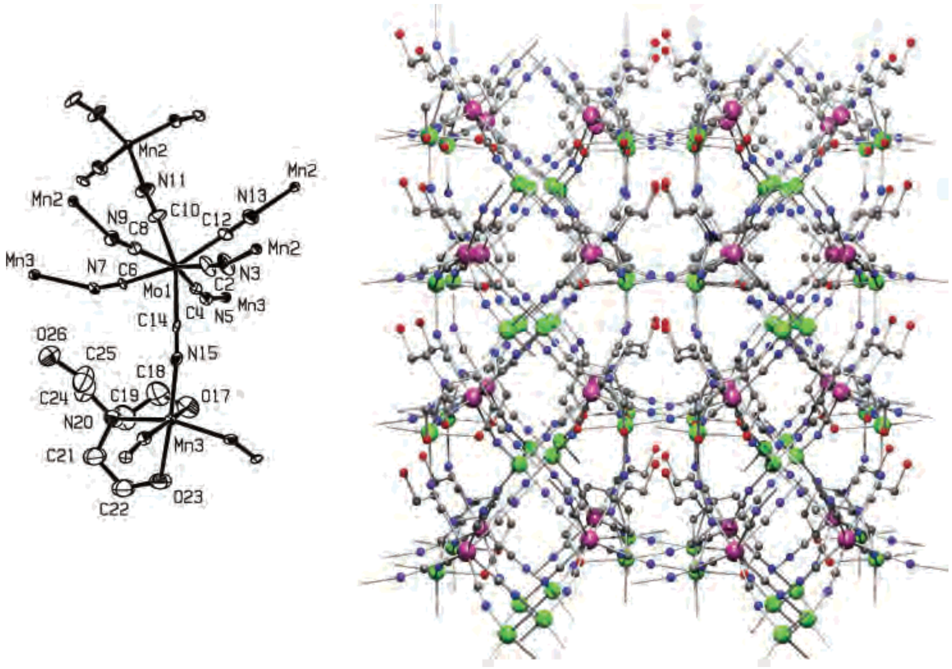

Figure 3. (Left) ORTEP plot (30% probability) of the coordination spheres for the metal ions in [Mn_2(tea)Mo$(CN)_7$], **2**. Selected bond lengths (Å) and angles (deg): Mo−C, 2.10(2)−2.176(14); Mn2−N3, 2.017(17); Mn2−N9, 2.076(15); Mn2−N11, 2.083(18); Mn2−N13, 2.065(16); Mn3−N5, 2.160(13); Mn3−N7, 2.234(13); Mn3−N15, 2.162(12); Mn3−O17, 2.207(12); Mn3−O23, 2.252(12); Mn3−N20, 2.349(11); Mn2−N3−C2, 168.5(17); Mn2−N9−C8, 161.7(14); Mn2−N11−C10, 175.0(17); Mn2−N13−C12, 173.7(15); Mn3−N5−C4, 160.2(11); Mn3−N7−C6, 153.5(11); Mn3−N15−C14, 162.9(11); Mo−C−N, 172.3(12)−179.0(15). (Right) View of the 3-D network of **2**, along *a* (Mo, violet; Mn, green; N, blue; O, red, C, gray). H atoms are omitted.

to 178.42° with a mean value of 172.14°. The Mn←NC bond lengths (see caption to Figure 2) of the octahedral Mn1 site range from 2.152(9) to 2.190(9) Å, whereas those of the square-pyramidal Mn2 center are shorter with 2.064(10) and 2.122(9) Å.[17] The related Mn−N−C angles range from 155.47 to 171.32°.

As mentioned above, [Mn_2(tea)Mo$(CN)_7$]·H_2O was also prepared by instantaneous reaction of the reagents in H_2O at 50 °C. The resulting powder consists of small plate-shaped crystals of micrometric size. The experimental powder X-ray pattern for a sample prepared following this procedure is compared Figure S1 (Supporting Information) to the pattern simulated from the atomic coordinates of the crystal structure of compound **1**. Both perfectly match, confirming that they correspond to the same compound.

(b) [Mn_2(tea)Mo$(CN)_7$], 2. In one of the slow diffusion setups used to crystallize compound **1**, a few crystals of a second compound, **2**, grew together with **1**. Except the solvate molecule, the chemical formula of compound **2**, [Mn_2(tea)Mo$(CN)_7$], appeared to be the same as that for **1**, but the magnetic features for both compounds were found to be very different (vide infra). The X-ray structure analysis performed on a single crystal of **2** revealed that the overall network resulting from the MoCN→Mn connections remains the same as that for **1**. But the Mn2 atom is now found in a slightly distorted tetrahedral environment consisting of four Mn−NC linkages (Figure 3); the O-atom (O26) from the tea arm no longer coordinates to Mn2. The second Mn^{II} site (Mn3) is in a distorted octahedral environment formed by three MoCN→Mn linkages along with the N and two O atoms of the tea ligand as for compound **1**. The released hydroxyethyl arms of the tea is located in the channel of the framework. A short distance is found between the O-atom (O26) of the free arm and a coordinated O-atom from a neighboring {Mn3(tea)} unit (O26···O17*, 2.750 Å), suggesting the existence of an OH···O hydrogen bond. The Mo−C bond lengths between 2.10(2) and 2.176(14) Å (mean value, 2.138 Å) are very similar to the one found for **1**. The Mo−C−N angles are close to linearity, ranging from 172.3(12) to 179.0(15)° with a mean value of 176.4°. Concerning the Mn←NC bond lengths (see caption to Figure 3), the mean value for the tetrahedral Mn2 center is 2.060 Å, and 2.185 Å for the octahedral Mn3 site. The related Mn−N−C mean angles are found at 158.5° for the Mn3 polyhedron and 169.7° for the Mn2 site. It can be mentioned that two other examples of tetrahedral Mn^{II} centers bound to N atoms of CN ligands in magnetic materials have been reported recently.[18−20]

The topological features of the frameworks for compounds **1** and **2** are very much the same and suggest that compound **2** could result from dehydration of compound **1**. When a sample of **1** was heated to 100 °C, the H_2O located in the channels of the framework was removed, yielding indeed compound **2**. A thermogravimetric study revealed the H_2O release to take place between 50 and 70 °C and indicated

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(17) Note: *The atoms with disordered positions are not considered, but the average values of bond lengths and angles obtained from their extreme positions are in the range of those found for the non-disordered positions.*

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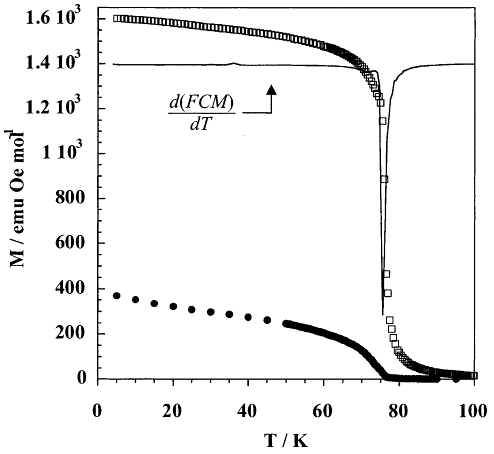

Figure 4. Field cooled magnetization (□, $H = 50$ Oe) and remnant magnetization (●) versus temperature for compound **1**. The solid line represents the derivative d(FCM)/d*T*.

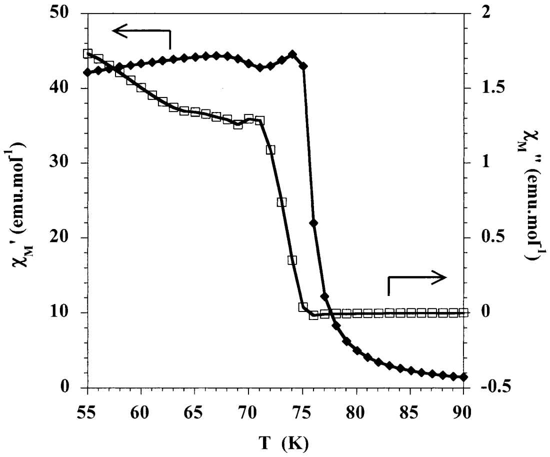

Figure 5. Temperature dependencies of the in-phase, χ'_M (◆), and out-of-phase, χ''_M (′), components at 10 Hz for $[Mn_2(tea)Mo(CN)_7]\cdot H_2O$, **1**.

no further weight loss below 200 °C (see Supporting Information). The IR spectrum for compound **2** shows an intense ν_{CN} band at 2090 cm^{-1} and a much weaker one at 2140 cm^{-1}, a feature similar to the one found for compound **1** for which the strong absorption is observed at 2092 cm^{-1} with a shoulder at 2080 cm^{-1} and the smaller band at 2142 cm^{-1}. A noticeable difference in the IR signatures for the two compounds was found for the bands of the tea moiety in the 700−1200 cm^{-1} energy domain. Upon dehydration, a simplification of the bands from a split set for **1** to a single set for **2** is observed (see Supporting Information). According to the IR data, the removal of the H_2O molecules induces structural modifications involving the tea ligand but the Mo−CN→Mn linkages remain unaffected by the solid-state process transforming **1** in **2**. The composition of a bulk sample of compound **2** obtained by thermal treatment of **1** has been checked by powder X-ray diffraction. The experimental pattern perfectly compares to the one simulated from the atomic coordinates for **2** (Figure S4), confirming that the process leads to a single species in quantitative yields. Finally, it may be noticed that compound **2** is perfectly stable; no back-transformation to **1** was observed over a period of 12 months in ambient conditions.

Magnetic Properties. (a) $[Mn_2(tea)Mo(CN)_7]\cdot H_2O$, 1. The magnetic properties of $[Mn_2(tea)Mo(CN)_7]\cdot H_2O$ were investigated and revealed that **1** behaves as a magnet below a temperature of 75 K. The temperature dependence of the field cooled magnetization (FCM) obtained for a polycrystalline sample recorded in a field of 50 Oe is depicted in Figure 4. A steep rise of the magnetization is observed when the temperature is decreased below 80 K, featuring long-range magnetic ordering. This is confirmed by the remnant magnetization (REM) which vanishes above 75 K (Figure 4). The critical temperature, $T_c = 75$ K, was determined from the FCM behavior as the extreme of the derivative d*M*/d*T*. The temperature dependence of $\chi_M T$, where χ_M is the molar magnetic susceptibility, is equal to 9.1 cm^3 K mol^{-1} at 300 K, a value corresponding to what is expected (9.15 cm^3 K mol^{-1}) for a low-spin Mo^{III} ($\mu_{eff} = 1.80\ \mu_\beta$)[21,22] and two Mn^{II} ($S = 5/2$, $g = 2$) ions in the Curie regime. Below this temperature, the value of $\chi_M T$ increases continually as T is lowered to ca. 80 K where a steep increase is observed.

The AC magnetic susceptibility behavior on temperature for **1** was measured with an oscillating field of 2 Oe for frequencies of 10 and 100 Hz in the absence of static field. The in-phase, χ'_M, and out-of-phase, χ''_M, responses obtained for 10 Hz are reported Figure 5; the same behavior was found for 100 Hz. The value for χ''_M become different from zero for temperatures below 75 K, confirming thus the occurrence of a magnetic order. For lower temperature, the values for both χ'_M and χ''_M remain in the range of those reached just below T_c; such a behavior suggests that **1** should display a feeble coercivity. The field dependence of the magnetization recorded at 5 K indicates that **1** reaches quickly a saturation magnetization of 8.8 Nβ (see Supporting Information) and revealed that the compound exhibits a weak coercivity (Hc = 70 Oe). This saturation magnetization value is consistent with antiferromagnetic interactions between the Mo^{III} and Mn^{II} ions; consequently compound **1** is a ferrimagnet. Our observation is in agreement with the results of a polarized neutron diffraction study performed on a compound formed with the same building blocks, i.e. Mo^{III}(CN)$_7$ and Mn^{II}, which established that the Mo^{III}/Mn^{II} exchange interaction through a CN linker was antiferromagnetic.[23]

(b) $[Mn_2(tea)Mo(CN)_7]$, 2. The magnetic properties for compound **2** were investigated in the temperature range 5−370 K and revealed dramatic changes. The magnetic ordering was now found to occur at 106 K, 31 K above T_c for **1** (Figure 6). The AC magnetic susceptibility behavior depicted in Figure 7 shows the out-of-phase component, χ''_M, to become different from zero below 107 K. These measurements have been performed at different frequencies ranging from 1 to 1000 Hz, and no significant dependence on frequency of oscillating field was observed. The field dependence of the magnetization obtained at 5 K for **2** revealed a larger coercivity with Hc = 200 Oe, the saturation

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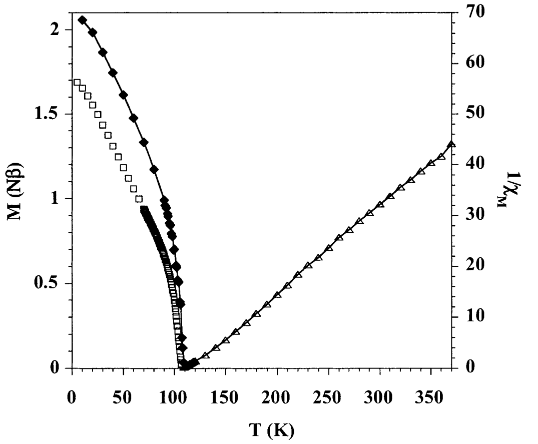

Figure 6. Temperature dependence of the magnetic behavior for **2** plotted as $1/\chi_M$ (△) above T_c and FCM (◆) and REM (□) below T_c ($H = 50$ Oe).

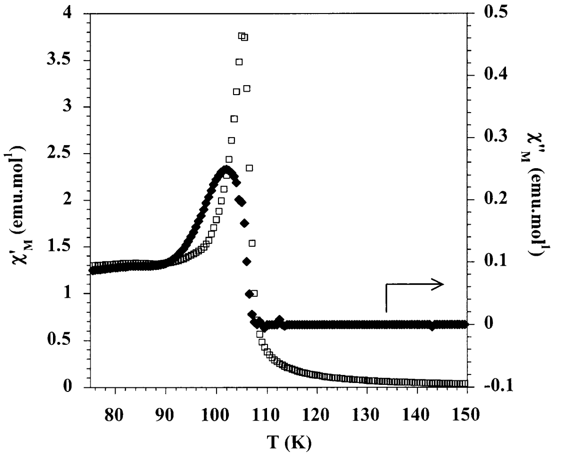

Figure 7. Temperature dependencies of the in-phase, χ'_M (◆), and out-of-phase, χ''_M (□), components at 10 Hz for $[Mn_2(tea)Mo(CN)_7]$, **2**.

magnetization being Ms = 8.7 Nβ (see Supporting Information).

Discussion

It is well-established that the temperature at which magnetic ordering occurs for an extended framework is strongly dependent on the spin carriers and the number of next-neighbors in exchange interaction with each magnetic center. The results gathered with the $[Mn_2(tea)Mo(CN)_7]\cdot xH_2O$ derivatives reported here show that, even for an isotropic metal ion such as Mn^{II}, the geometry of the coordination of the 3d metal ion may have a substantial influence on T_c of the supramolecular network as well. For instance, the subtle modifications of the Mo−CN→Mn network adapting the transformation of the Mn2 site from square pyramidal for **1** to tetrahedral for **2** led to a difference of 31 K for T_c. This difference might be rationalized in terms of bond lengths and angles. A comparison of the Mn2−N distances indicates a shortening of the bonds when going from the square-pyramidal arrangement of **1** to the tetrahedral site of **2**, the distances involving the octahedral Mn sites remaining similar for both compounds. Moreover, the corresponding Mn−N−C angles as well as the Mo−CN angles are closer to 180° for **2** than for **1**. The evolution of these geometric features between compounds **1** and **2** is in favor of a better overlap of the magnetic orbitals of the metal ions through those of the bridging ligand. This will result in an improved exchange interaction between the magnetic centers and, consequently, may account for the increase of T_c by 31 K for compound **2**.

One of the remarkable features for the $[Mn_2(tea)Mo(CN)_7]\cdot xH_2O$ derivatives is the significant increase of T_c as compared to the compounds $[Mn_2(H_2O)_5Mo(CN)_7]\cdot xH_2O$[11,12] made up with the same building blocks, i.e. Mn^{II} and $Mo^{III}(CN)_7$, in the same stoechiometry (2 to 1), but having T_c for 51 K. For all these compounds the connectivity between the spin carriers through CN bridges is the same; i.e. each Mo ion is linked to seven Mn ions, and the two distinct Mn centers are respectively connected to three (Mn1) and four (Mn2) Mo centers. Consequently, the main exchange pathways between the ions via the CN linkers are the same. The difference is found for the coordination geometry of the Mn^{II} sites, which all are octahedral for the $[Mn_2(H_2O)_5Mo(CN)_7]\cdot xH_2O$ compounds. The increase of T_c from 51 to 75 K and further to 106 K appears to be related to the coordination sphere of the Mn^{II} ions following the trend octahedral < square pyramidal < tetrahedral. This might be understood by the decrease of the Mn←NC bond length observed when going from an octahedral to a tetrahedral geometry as discussed above. For instance, for the derivative with T_c = 51 K the Mn←NC bond lengths are found between 2.158(4) and 2.242(4) Å, whereas for compound **2** with T_c = 106 K, those of the tetrahedral Mn2 site are much shorter with an average value of 2.060 Å. Consequently, the Mo−Mn exchange interaction is anticipated to be best for compound **2**. Using the mean field approximation,[24] an estimation of the average interaction parameter, *J*, between the Mn^{II} and Mo^{III} ions leads to $J = -8.8$ cm^{-1} for **1** and -12.4 cm^{-1} for **2**, a value twice as large as the one reported for the compounds with T_c = 51 K.[12]

A striking difference in the behavior of compounds **1** and **2** concerns the values of their magnetization at low temperatures; the magnetization for **2** is significantly increased with respect to compound **1**. For instance, a comparison of their FCM behavior reveals that the magnetization at 10 K (FCM, Figure 6) for **2** is 2 Nβ, whereas a value of 0.3 Nβ was obtained for **1** (FCM Figure 4) in the same conditions. This is rather surprising if we consider that their frameworks are very much the same. The origin of this difference might be found in the hydroxyethyl arm of the tea ligand which is coordinated to Mn2 for **1** but not longer for **2**. Thus for **1** two Mn^{II} ions are linked through a tea moiety, and, even if this linker is not a good pathway for exchange interaction, a weak interaction can exist between them. This may introduce some canting between the local moments and result in a smaller macroscopic magnetization as compared to **2**.

Concluding Remarks

The results reported herein show that a substantial increase of the critical temperature of a molecule-based magnet like

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those built from $[Mo(CN)_7]^{4-}$ and Mn^{II} can be expected through a modification of the local geometry of the 3d metal ion by means of an ancillary ligand like tea and/or dehydration by smooth thermal treatment. For the ferrimagnets $[Mn_2(tea)Mo(CN)_7]\cdot xH_2O$ ($x = 1$, **1**, or 0, **2**) described here, ordering temperatures of 75 and 106 K could be reached. The evolution of T_c for these supramolecular materials was found to be related to the local symmetry of the Mn^{II} sites and follows the trend T_c (octahedral) < T_c (square pyramidal) < T_c (tetrahedral). The increase of T_c is rationalized by an improved exchange interaction after the shortening of the $Mn\leftarrow NC$ bond as a function of the geometry of the coordination sphere of the 3d metal ion. These observations underline the importance of subtle geometrical considerations within the supramolecular lattice on the characteristics of molecule-based magnets.

It is interesting to compare the magnetic properties of the $\{Mn^{II}/Mo(CN)_7\}$ based magnets with a related compound, $[Mn_3\{Fe(CN)_6\}_2]\cdot 15H_2O$.[25] Indeed, both Fe and Mo cyanometalate units bear a local spin of $S = 1/2$, but whereas for the compound formed with the 3d ion derivative T_c is found at 9 K, the compounds with the 4d ion, Mo^{III}, are characterized by ordering temperatures above 50 K. For the compound described here, $[Mn_2(tea)Mo(CN)_7]$, T_c could even be driven up to 106 K, above liquid nitrogen temperature. This opens interesting perspectives in the use of 4d and 5d metal ions as building blocks for the preparation of high-T_c magnets.

Experimental Section

General Methods. All experiments were conducted in N_2 atmosphere; the solvent and reagent were degassed prior to use. Magnetic studies were performed on a Quantum Design MPMS 5S-SQUID magnetometer; the diamagnetic contribution for the compounds was estimated to -300×10^{-6} emu mol^{-1}.

Synthesis of $[Mn_2(tea)Mo(CN)_7]\cdot H_2O$ 1. (a) Method a. In a typical crystallization experiment in an H-shaped tube (total volume, ca. 60 mL) a solution of $[K_4Mo(CN)_7\cdot 2H_2O]$[26] (70 mg, 0.15 mmol) and tea (40 mg, 0.27 mmol) in H_2O was allowed to slowly diffuse into a H_2O solution of $[MnCl_2\cdot 4H_2O]$ (60 mg, 0.30 mmol). After a period of 3 weeks well-shaped dark green crystals (ca. 15 mg) were collected.

(b) Method b. A solution of $[Mn(NO_3)_2\cdot H_2O]$ (394 mg, 2.0 mmol) in H_2O (15 mL) was added dropwise to a solution of $[K_4Mo(CN)_7\cdot 2H_2O]$ (470 mg, 1.0 mmol) and tea (270 μL, 2 mmol) in H_2O (15 mL) at 50 °C. After 1 h of stirring, the olive-green precipitate was collected by filtration and washed with H_2O followed by EtOH and Et_2O, yielding 390 mg (70%) of microcrystalline **1**. IR (KBr, cm^{-1}): 3514 (w), 3490 (w), 3207 (w), 2975 (w), 2920 (w), 2854 (w), 2142 (m), 2092 (s), 1614 (w) 1216 to 882 (several small bands attributed to tea). Anal. Calcd (%) for $C_{13}H_{17}N_8O_4Mn_2Mo$: C, 28.13; H, 3.08; N, 20.18. Found: C, 27.5; H, 3.1; N, 19.2.

Synthesis of $[Mn_2(tea)Mo(CN)_7]$, 2. A sample of **1** was heated to 100 °C for ca. 1 h. IR (KBr, cm^{-1}): 3545, 3389 and 3225 (broad), 2977 (w), 2911 (w), 2858 (w), 2140 (w), 2090 (s), 1620 (w), 1057 (w), 1036 (w), 1016 (w), 986 (w) 884 (w).

Table 1. Selected Experimental and Crystal Data for the Studied Compounds

	$[Mn_2(tea)Mo(CN)_7]\cdot H_2O$, **1**	$[Mn_2(tea)Mo(CN)_7]$, **2**
formula	$C_{13}H_{17}Mn_2MoN_8O_4$	$C_{13}H_{15}Mn_2MoN_8O_3$
fw	555.15	537.15
cryst syst	orthorhombic	orthorhombic
space group	Pbca	$Pca2_1$
a (Å)	12.5269(4)	12.699(4)
b (Å)	12.0208(4)	12.134(2)
c (Å)	26.1327(4)	12.639(3)
V (Å^3)	3935.1(2)	1947.6(8)
Z	8	4
ρ_{calc} (g.cm^{-3})	1.867	1.832
λ (Å)	Mo Kα, 0.71073	Cu Kα, 1.54180
μ (mm^{-1})	1.928	15.87
collctd reflns	25 556	4382
indep reflns	4303	2095
R_{int}	0.07	0.06
refined params	314	245
refinement against	F^2	F
R^a	0.075	0.056
$R_{w2}(F^2)^a$	0.16	
$R_w(F)^a$		0.068

^{a} $R = (\sum||F_o| - |F_c||)/\sum|F_o$; $R_{w2}(F^2) = [(\sum w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]$; $R_w(F) = [(\sum w(F_o - F_c)^2)/(\sum w(F_o)^2)]^{1/2}$.

Solution and Refinement of the X-ray Structures. Experimental and crystal data are reported in Table 1.

(a) $[Mn_2(tea)Mo(CN)_7]\cdot H_2O$, 1. A plate-shaped green crystal, $0.16 \times 0.12 \times 0.02$ mm^3, was selected on a polarized microscope and measured on a Bruker-Nonius κ-CCD diffractometer, Mo Kα radiation, ϕ scans, 387 frames of 1°, 400 s/frame, θ range 4.2−27.1°, data completeness 99.1%. The structural determination by direct methods and the refinement of the atomic parameters based on full-matrix least squares on F^2 were performed using the SHELX-97[27] programs within the WINGX package.[28] The crystal structure shows two close statistical disordered positions for two nitrogen atoms (N8, N9) and one oxygen (O3) within the coordination sphere of Mn2 as well as for four carbon atoms of tea (C8, C9, C14, C13). Hydrogen atoms of tea were included in the model at geometrically idealized positions, while hydrogen atoms of water were localized on Fourier maps.

$[Mn_2(tea)Mo(CN)_7]$, 2. A plate-shaped green crystal, $0.20 \times 0.20 \times 0.02$ mm^3, was mounted on an Enraf-Nonius Mach-3 and cooled at 230 K, Cu Kα radiation, $\omega/2\theta$ scans, θ range 2.2−75°, 3% decay during data collection. The structural determination by direct methods and the refinement of the atomic parameters based on full-matrix least squares on F were performed using SIR92 and CRYSTALS.[29,30] All hydrogen atoms were included in the model at geometrically idealized positions.

X-ray Powder Patterns. The powder samples were investigated using a Philips PW 3040/00 X'PERT MPD device in Bragg−Brentano geometry using diffracted beam graphite monochromator Cu Kα radiation ($\lambda = 1.5406$ Å). Data were collected over the angular range $5° \leq 2\theta \leq 120°$ with a 0.02° step and a counting time of 40 s.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, X-ray powder patterns, IR spectra, and field dependence of the magnetization plots for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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