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A cyano-bridged $Mn^{II}Mo^{V}$ bimetallic ferrimagnet with a novel moniliform structure†

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$\{[Mn(bipy)_2(DMF)_2]_2[Mo(CN)_8]_2[Mn(DMF)_4]\}_\infty$, a novel one-dimensional moniliform cyano-bridged Mn(II)-Mo(V) bimetallic ferrimagnet, exhibits long-range magnetic ordering below 2.8 K.

Continuous attention has been paid to the design and synthesis of molecular magnetic materials exhibiting spontaneous magnetization in the past decade. Hexacyanometalate ions, acting as good building units, have been successfully utilized to obtain a large number of one-, two-, and three-dimensional cyano-bridged assemblies with high magnetic ordering temperatures and interesting architectures.[1,2] Recently, there is ongoing interest in using 4d/5d metal-containing paramagnetic anions $[Mo^{III}(CN)_7]^{4-}$, $[M^{V}(CN)_8]^{3-}$ (M = Mo or W) as building blocks to construct molecular magnetic material for their diffuse orbitals and various geometrical structures,[3–5] following the pioneering work of Kahn's group.[3] These flexible species may be used as versatile synthons to construct a variety of architectures or networks with novel topological structures and interesting magnetic properties. So far, only a few such bimetallic assemblies based on $[M^{V}(CN)_8]^{3-}$ have been studied structurally and magnetically and they show intriguing magnetic properties.[4,5] For instance, the discrete Mn_9Mo_6 giant-spin cluster, $\{Mn^{II}_9[Mo^{V}(CN)_8]_6\cdot 24CH_3OH\}\cdot 5CH_3OH\cdot 2H_2O$, is the highest ground-state molecule with $S_T = 51/2$ to date, in which the magnetic exchange interaction between the neighboring Mn^{II} and Mo^{V} is ferromagnetic.[4] Very recently, the origin of ferromagnetism in these complexes has been analyzed within the Anderson superexchange theory by Chibotaru *et al.*[5] To the best of our knowledge, cyano-bridged bimetallic 1-D, 2-D or 3-D infinite coordination polymers using the $[Mo^{V}(CN)_8]^{3-}$ anion as precursor have not been reported until now. Herein we describe the synthesis, structure, ESR and magnetic properties of a novel one-dimensional moniliform cyano-bridged coordination polymer, $\{[Mn^{II}(bipy)_2(DMF)_2]_2[Mo^{V}(CN)_8]_2[Mn^{II}(DMF)_4]\}_\infty$ (**1**)‡, where bipy is 2,2′-bipyridine and DMF is *N*,*N*-dimethylformamide.

Single-crystal X-ray diffraction§ shows that the product is a neutral, one-dimensional infinite polymer with a novel moniliform structure. The asymmetric unit of the structure consists of a $[Mo^{V}(CN)_8]^{3-}$ moiety connected to two different types of Mn^{II} centers by cyanide bridges (Fig. S1, ESI). The Mo1 atom is coordinated by eight C–N groups with Mo–C distances ranging from 2.132(4) to 2.151(4) Å in a distorted bicapped trigonal prism geometry. The two Mn atoms are all in a slightly distorted octahedral geometry. For Mn1, the equatorial sites are occupied by four nitrogen atoms, N4, N7, N9 and N10, with an average Mn–N distances of 2.213 Å, while the apical positions are occupied by two oxygen atoms (O1, O2) from two DMF molecules. The other Mn atom (Mn2), localized at the center of inversion, is coordinated to four oxygen atoms (O3, O4, O3B, and O4B) from four DMF molecules which occupy the equatorial sites and two nitrogen atoms (N1, N1B) from two adjacent $Mo(CN)_8$ units at the axial positions (Fig. 1). Each $Mo^{V}(CN)_8$ group connects three Mn atoms (Mn1, Mn1A and Mn2) *via* three cyano bridges (C1–N1, C4–N4 and C7A–N7A) with the $Mn–N_{CN}$ distance ranging from 2.181(3) to 2.251(3) Å. As a result, Mo, Mn1A, Mo1A and Mn1 are linked by the cyano bridges (C4–N4, C7–N7, C4A–N4A and C7A–N7A) to form a four-metallic 12-atom rhombic cycle, $Mn_2Mo_2(CN)_4$, while Mn2 links the cycles in a *trans* mode through Mo1–C1–N1–Mn2–N1B–C1B–Mo1B linkages to form a 1-D infinite moniliform or rosary-like chain, running along one of the diagonal directions of the *b* and *c* axes. The nearest interchain distances for Mo1 ··· Mn1 and Mo1 ··· Mn2 are equal to 8.46 and 11.93 Å, respectively. The one-dimensional chains are further joined together to form layer structures *via* π–π stack interactions which exist between two adjacent interchain aromatic rings of 2,2′-bipyridine, face–face distance of 3.93 Å (Fig. 1).

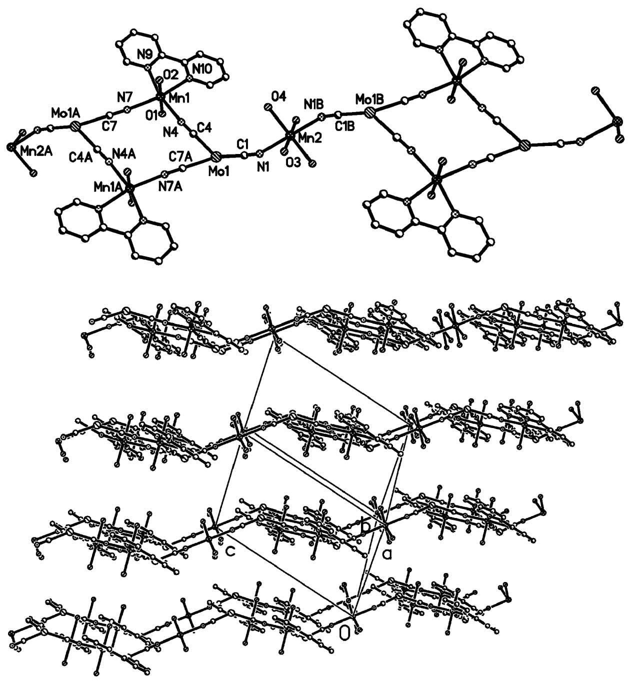

Fig. 1 (Top) A segment of the one-dimensional infinite moniliform structure. (Bottom) Projection of **1** showing the layer structure. The H atoms, C and N atoms of the coordinated DMF molecules and the non-bridged cyanides are omitted for clarity. Symmety operators: A: −*x*, −*y* + 1, −*z* − 1; B: −*x*, −*y*, −*z*.

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† Electronic supplementary information (ESI) available: ORTEP plot of the asymmetric unit of **1**; X-band ESR spectrum of **1** in DMF solution at 110 K; temperature dependence of field-cooled magnetization (*H* = 500 Oe) for **1** and field dependence of magnetization of **1** measured at 1.8 K. See http://www.rsc.org/suppdata/dt/b2/b205197b/

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The X-band ESR spectrum for **1** in frozen DMF solution at 110 K exhibits a six-line hyperfine pattern with $g_{\parallel}^{Mn}$ = 2.008 ($A_{\parallel}^{Mn}$ = 95.6 G) at the center field (Fig. S2, ESI), which is typical of a Mn(II) complex with an octahedral coordination environment. Additionally, there is another signal with g_{Mo} = 1.993 at the center field, which corresponds to Mo^V ions in an axially symmetric coordination environment. At the half field, a weak signal was detected at g_{hf} = 4.286, which demonstrates an exchange interaction between the adjacent Mn^{II} and Mo^V atoms in the complex.

The dc variable-temperature (2–300 K) magnetic susceptibility of **1** has been measured on a crystalline sample in a field of 5 kOe. A plot of $\chi_M T$ *vs.* T is shown in Fig. 2, where χ_M is the magnetic susceptibility per Mn_3Mo_2 unit. The $\chi_M T$ value at room temperature is *ca.* 13.84 cm^3 K mol^{-1} (10.52 μ_B), which is slightly smaller than the spin-only value (13.875 cm^3 K mol^{-1}, 10.534 μ_B) for three high-spin Mn(II) (S = 5/2) and two Mo(V) (S = 1/2) centers with g = 2.0. As T is lowered, $\chi_M T$ decreases smoothly, and reaches a minimum value of 12.40 cm^3 K mol^{-1} (9.96 μ_B) around 60 K. Upon further cooling, the value of $\chi_M T$ increases rapidly, reaching a sharp maximum value of 45.55 cm^3 K mol^{-1} (19.09 μ_B) at 4.8 K. The minimum in the $\chi_M T$ *vs.* T curve indicates ferrimagnetic behavior with a Mn^{II}–Mo^V antiferromagnetic interaction, and the maximum value in the curve, much larger than the above-mentioned spin-only value, suggests the occurrence of long-range magnetic ordering. Below 4.6 K, the value of $\chi_M T$ decreases abruptly, which may be due to the interchain antiferromagnetic interactions or saturation effects. The magnetic susceptibility in the range 50–260 K obeys the Curie–Weiss law [based on $1/\chi_M = (T - \theta)/C$, inset in Fig. 2] with a negative Weiss constant, θ, of −9.70 K, which also indicates an intramolecular antiferromagnetic coupling between the adjacent Mn(II) and Mo(V) ions through the cyano bridges. The Curie constant, C, is equal to 13.90 cm^3 K mol^{-1}, close to the expected value of 13.875 cm^3 K mol^{-1} with g = 2.0.

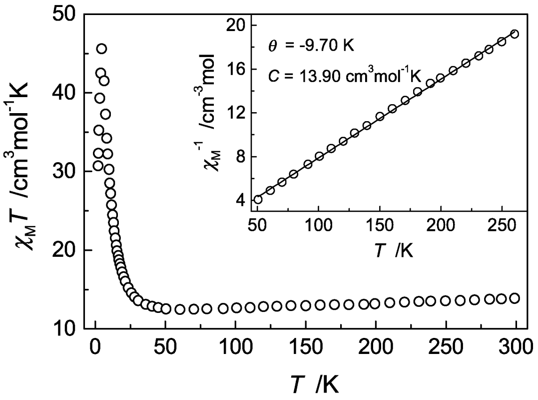

Fig. 2 Plot of $\chi_M T$ (per Mn_3Mo_2) *vs.* T for **1** in the range 2–300 K. Inset: temperature dependence of $1/\chi_M$. The solid line indicates the best fit obtained by the Curie–Weiss law.

The field-cooled magnetization (FCM) curve measured in a low field of 500 Oe shows a rapid increase in M at *ca.* 3.2 K, implying the occurrence of spontaneous magnetization at this point (Fig. S3, ESI). The onset of a long-range magnetic phase transition is further confirmed by the temperature dependence of the ac magnetic susceptibility displayed in Fig. 3. The real part of the ac magnetic susceptibility, χ'_M, has a maximum at *ca.* 2.8 K for a frequency of 111 Hz, suggesting that the T_C of **1** is about 2.8 K.

The field dependence of the magnetization (0–70 kOe) measured at 1.8 K shows a sharp increase with applied field and rapid increase of the magnetization, as expected for a magnet, reaching 13.01 $N\beta$ per Mn_3Mo_2 at 9.5 kOe, very close to the expected S_T = 13/2 value of 13 $N\beta$ for a ferrimagnetic Mn^{II}_3-Mo^V_2 (5/2 × 3 − 1/2 × 2 = 13/2) system (Fig. S4, ESI). The magnetization increases further above 9.5 kOe as the spins begin to deviate from antiferromagnetic coupling and align with the applied field. A hysteresis loop at 1.8 K was observed with a very small coercive field of less than 10 Oe, typical of a soft magnet.

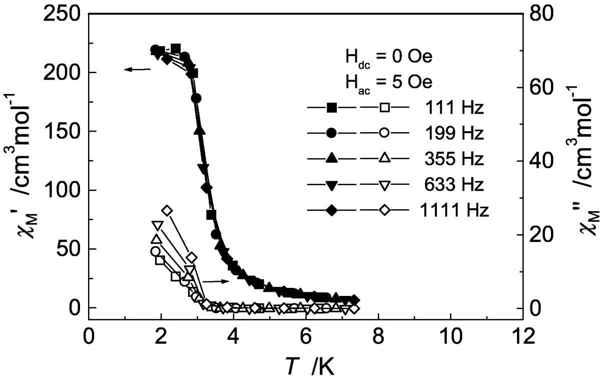

Fig. 3 Real (χ_M') and imaginary (χ_M'') ac magnetic susceptibilities in zero applied dc field and an ac field of 5 Oe at different frequencies for **1**.

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Notes and references

‡ Preparation of **1**: $K_3[Mo(CN)_8]\cdot H_2O$ (1.118 g, 1.0 mmol) was added to a solution of $MnCl_2\cdot 4H_2O$ (0.297 g, 1.5 mmol) and 2,2′-bipy (0.468 g, 3.0 mmol) in *N*,*N*-dimethylformamide (DMF; 10 ml) with stirring to give a pale-yellow solution, which was filtered and layered with isopropyl alcohol. Brown block crystals of **1** were obtained in 48% yield after several days. Calc. for $C_{60}H_{72}N_{28}O_8Mn_3Mo_2$ (**1**): C, 43.15; H, 4.34; N, 23.48; Mn, 9.87. Found: C, 43.02; H, 4.26; N, 23.67; Mn, 10.03%. IR data (cm^{-1}, KBr disk): $\nu_{C\equiv N}$ 2178 (m), 2158 (m).

§ Crystal data for **1**: M_r = 1670.16, triclinic, space group $P\bar{1}$, a = 10.639(3), b = 12.986(3), c = 15.920(4) Å, α = 78.124(4), β = 75.429(5), γ = 66.418(4)°, V = 1937.2(9) Å^3, Z = 1, D_c = 1.432 g cm^{-3}, μ(Mo-Kα)= 0.857 mm^{-1}. Data were collected on a Bruker Apex SMART CCD system equipped with monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. The structures were solved by direct methods and refined on F^2 using the SHELXTL suite of programs.[6] Except for the disordered carbon and nitrogen atoms of the coordinated DMF molecules (C19, C20, C21, C22, C23, C24, C26 and C29), the majority of the non-H atoms were refined anisotropically. 7812 reflections measured, 5793 unique (R_{int} = 0.0198) which were used in all calculations. The final $R1$ and $wR2$ are 0.0401 and 0.1098 with $I > 2\sigma(I)$, respectively. CCDC reference number 183396. See http://www.rsc.org/suppdata/dt/b2/b205197b/ for crystallographic data in CIF or other electronic format.

1 See, for example: T. Mallah, S. Thiébaut, M. Verdaguer and P. Veillet, *Science*, 1993, **262**, 1554; S. Ferlay, T. Mallah, R. Quahes, P. Veillet and M. Verdaguer, *Nature (London)*, 1995, **378**, 701.

2 See, for example: M. Ohba, N. Usuki, N. Fukita and H. Ōkawa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1795 and references therein; K. Inoue, H. Imai, P. S. Ghalsasi, K. Kikuchi, M. Ohba, H. Ōkawa and J. V. Yakhmi, *Angew. Chem., Int. Ed.*, 2001, **40**, 4242; H.-Z. Kou, S. Gao, J. Zhang, G.-H. Wei, G. Su, R. K. Zheng and X. X. Zhang, *J. Am. Chem. Soc.*, 2001, **123**, 11809 and references therein.

3 J. Larionova, R. Clérac, J. Sanchiz, O. Kahn, S. Golhen and L. Ouahab, *J. Am. Chem. Soc.*, 1998, **120**, 13088; J. Larionova, O. Kahn, S. Golhen, L. Ouahab and R. Clérac, *J. Am. Chem. Soc.*, 1999, **121**, 3349; A. Kaur Sra, M. Andruh, O. Kahn, S. Golhen, L. Ouahab and J. V. Yakhmi, *Angew. Chem., Int. Ed.*, 1999, **38**, 2606.

4 J. Larionova, M. Gross, M. Pilkington, H. Andres, H. Stoeckli-Evans, H. U. Güdel and S. Decurtins, *Angew. Chem., Int. Ed.*, 2000, **39**, 1605.

5 L. F. Chibotaru, V. S. Mironov and A. Ceulemans, *Angew. Chem., Int. Ed.*, 2001, **40**, 4429 and references therein.

6 G. M. Sheldrick, SHELXTL, Siemens Analytical X-Ray Instruments, Madison, WI, 1997.