

Sheet-like of Mo^V–Sm^{III} assembly containing [Mo^V(CN)₈]³⁻ and Sm³⁺ ions as building blocks

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Abstract. The reaction of [Mo(CN)₈]³⁻ with Sm³⁺ and 2,2'-bipyridine (bpy) lead to a sheet-like bimetallic complex, {Sm(H₂O)₉[Sm₂(bpy)₂(OH)_{2.75}(NO₃)_{0.25}][Mo(CN)₈]₂}_n (**1**) in EtOH/H₂O mixture solvent. The complex **1** crystallizes in monoclinic, space group *C2/c*. The structural investigation denotes that the layers interaction with each other by π - π stacks and hydrogen bonds result in a 3D network, containing Sm(H₂O)₉³⁺ as guest molecules in the holes. The magnetic behaviour of the complex **1** has been studied.

Keywords. Cyano bridges; ferromagnetic coupling; π - π stacks; 3D network structure.

1. Introduction

There has been a growing interest in the preparation of molecule-based magnet in recent years.^{1–7} The 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 temperature and interesting architectures.^{8–11} Recently, octacyanometallate-based magnets have also drawn much attention. [M^V(CN)₈]³⁻ (M = Mo, W), etc. is a versatile class of building blocks that can adopt different spatial configurations, just as square antiprism (*D*_{4d}), dodecahedron (*D*_{2d}), and bicapped trigonal prism (*C*_{2v}). Because of their enhanced exchange interaction in bimetallic compounds based on large extended of *4d* or *5d* magnetic orbitals, [M^V(CN)₈]³⁻ (M = Mo and W) are a kind of good precursors in magnetic materials. Following the pioneering work of Kahn's group,^{12–14} 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. For example, M^V–Mn^{II}^{15–23}, M^V–Cu^{II}^{24–34}, M^V–Co^{II}^{35–38}, M^V–Ni^{II}^{39–41}, M^V₆Mn^{II}₉^{36,40–45} (M = Mo and W) bimetallic assemblies with a variety of extended structure, have been obtained. However,

the syntheses of complexes containing octacyanometallate(V) and lanthanide ions are still relatively challenging. To the best of our knowledge, metal assemblies based on [M^V(CN)₈]³⁻ (M = Mo or W) with lanthanide ions can take various geometries in the crystal structure, e.g. with one-dimensional (1D)^{46–51} and two-dimensional (2D)^{52,53} assemblies. Among these dimensionalities, there are only three complexes, [Tb^{III}(pzam)₃(H₂O)Mo^V(CN)₈]₂·H₂O⁴⁶ (pzam = pyrazine-2-carboxamide), {[Gd^{III}(DMF)₄(MeOH)₂][Mo^V(CN)₈]₂}_n⁵¹ and Tb^{III}(H₂O)₅[Mo^V(CN)₈]₂⁵³ based on anionic octacyanomolybdate(V) with rare earth ions. In search of new materials of *4d*–*4f* cyanide-bridged assemblies from [Mo(CN)₈]³⁻ building blocks, this paper details the synthesis, characterization, and magnetic properties of octacyanomolybdate(IV)-based complex with 2D sheet-like structure, {Sm(H₂O)₉[Sm₂(bpy)₂(OH)_{2.75}(NO₃)_{0.25}][Mo(CN)₈]₂}_n (**1**) (bpy = 2,2'-bipyridine).

2. Experimental

2.1 Materials and methods

The precursor (*n*-Bu₄N)₃[Mo^V(CN)₈]₂·2H₂O was prepared according to literature methods.⁵⁴ All other chemicals were reagent grade and can be used without further purification. Since the octacyanometalate ions have a tendency to decompose under irradiation

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tion, the synthesis of the complex was performed in a dark room at room temperature.

2.2 Preparation of $\{Sm(H_2O)_9[Sm_2(bpy)_2(OH)_{2.75}(NO_3)_{0.25}]/[Mo(CN)_8]_2\}_n$ (**1**)

To a solution of $Sm(NO_3)_3 \cdot 6H_2O$ (0.2 mmol, 88.9 mg) and $(n-Bu_4N)_3[Mo(CN)_8] \cdot 2H_2O$ (0.2 mmol, 147.8 mg) in EtOH/H₂O (1:1, 8 mL) was added a solution of bipyridine (0.6 mmol, 93.6 mg) in ethanol (2 mL). The reaction mixture was stirred for 5 min at room temperature, and then filtered. Slow evaporation of the filtrate led to the formation of yellow crystals. Yield: ca 28%. Anal Calcd for $C_{36}H_{36.50}Mo_2N_{20.50}O_{14}Sm_3$: C, 26.63; H, 2.27; N, 17.69%. Found: C, 26.58; H, 2.56; N, 17.56%. IR data (cm^{-1} , KBr pellets): 2120 $\nu(C\equiv N)$.

2.3 Physical measurements

Elemental analyses for C, H, and N were carried out on a Perkin-Elmer elemental analyzer (model 240). The infrared spectrum was obtained on a Bruker Tensor 27 Fourier transform infrared spectroscopy in the 4000–400 cm^{-1} region, using KBr pellets. Variable temperature magnetic susceptibilities were measured on SQUID magnetometer from 2.0 to

300 K in a magnetic field of 2000 Oe, and the diamagnetic corrections were applied by using Pascal's constants.

2.4 X-ray data collections and structure determinations

All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo–K α radiation ($\lambda = 0.71070 \text{ \AA}$). The empirical absorption corrections by semi-empirical from equivalents were carried out. The structure was solved by direct methods using the SHELXS-97 program⁵⁵ and refined with SHELXL-97⁵⁵ by full-matrix least-squares techniques on F^2 . All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically. Further details of the structure analysis are given in table 1.

3. Results and discussion

3.1 General properties

A bimetallic complex **1** has been synthesized, and fully characterized by elemental analysis, IR spectroscopy, and X-ray crystallography. The most feature

Table 1. Crystallographic data and structure refinement for **1**.

Empirical formula	$C_{36}H_{38.50}Mo_2N_{20.50}O_{14}Sm_3$
<i>F</i> w	1625.30
Temperature (K)	293(2)
λ (Å)	0.71070
Cryst. syst.	Monoclinic
Space group	$C2/c$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	25.784(2), 11.0630(10), 21.5080(18)
β (°)	123.864(8)
<i>V</i> (Å ³)	5094.4(7)
ρ (g/cm ³)	2.119
<i>Z</i>	4
μ (mm ⁻¹)	3.965
<i>F</i> (000)	3120
Crystal size (mm)	0.20 × 0.20 × 0.20
Theta range for data collection (°)	1.90 to 25.01
Limiting indices	$-30 \leq h \leq 30$, $-13 \leq k \leq 13$, $-25 \leq l \leq 25$
Reflections collected/unique	25234/4490 ($R_{int} = 0.0441$)
Completeness to theta = 25.01	100.0%
Max. and min. transmission	0.810 and 0.716
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4490/51/362
Goodness-of-fit on F^2	1.097
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0453$, $wR_2 = 0.1233$
<i>R</i> indices (for all data)	$R_1 = 0.0474$, $wR_2 = 0.1247$
Largest diff. peak and hole (e/Å ³)	2.200 and -4.200

Table 2. Selected bond lengths (Å) and angles (deg) for the complex **1**.

Mo(1)–C(4)	2.143(9)	Sm(1)–O(1)	2.461(5)
Mo(1)–C(7)#1	2.153(8)	Sm(1)–N(6)	2.492(7)
Mo(1)–C(2)	2.155(7)	Sm(1)–N(7)	2.507(7)
Mo(1)–C(6)#2	2.161(8)	Sm(1)–N(8)	2.509(7)
Mo(1)–C(1)	2.167(8)	Sm(1)–N(1)	2.525(7)
Mo(1)–C(8)#3	2.170(9)	Sm(1)–N(11)	2.564(6)
Mo(1)–C(3)	2.171(8)	Sm(1)–N(10)	2.568(7)
Mo(1)–C(5)	2.175(8)		
C(1)–Mo(1)–C(3)	77.7(3)	N(7)–C(7)–Mo(1)#5	176.7(7)
C(1)–Mo(1)–C(5)	143.2(3)	N(8)–C(8)–Mo(1)#3	176.7(8)
C(2)–Mo(1)–C(1)	74.5(3)	C(1)–N(1)–Sm(1)	155.1(6)
C(2)–Mo(1)–C(3)	72.4(3)	C(6)–N(6)–Sm(1)	152.4(6)
C(2)–Mo(1)–C(5)	130.1(3)	C(7)–N(7)–Sm(1)	157.7(6)
C(3)–Mo(1)–C(5)	131.4(3)	C(8)–N(8)–Sm(1)	167.9(7)
C(4)–Mo(1)–C(1)	71.2(3)	C(9)–N(10)–Sm(1)	120.7(5)
C(4)–Mo(1)–C(2)	132.9(3)	C(13)–N(10)–Sm(1)	122.0(5)
C(4)–Mo(1)–C(3)	128.2(3)	C(14)–N(11)–Sm(1)	121.9(5)
C(4)–Mo(1)–C(5)	72.4(3)	C(18)–N(11)–Sm(1)	119.6(5)
C(4)–Mo(1)–C(7)#1	142.0(3)	O(1)–Sm(1)–N(1)	73.4(2)
C(1)–Mo(1)–C(8)#3	89.4(3)	O(1)–Sm(1)–N(6)	77.0(2)
C(2)–Mo(1)–C(6)#2	140.7(3)	O(1)–Sm(1)–N(7)	75.30(19)
C(2)–Mo(1)–C(8)#3	71.3(3)	O(1)–Sm(1)–N(8)	79.5(2)
C(4)–Mo(1)–C(6)#2	76.4(3)	O(1)–Sm(1)–N(10)	144.1(2)
C(4)–Mo(1)–C(8)#3	76.9(3)	O(1)–Sm(1)–N(11)	148.38(19)
C(6)#2–Mo(1)–C(1)	98.5(3)	N(1)–Sm(1)–N(10)	80.8(2)
C(6)#2–Mo(1)–C(3)	68.3(3)	N(1)–Sm(1)–N(11)	138.0(2)
C(6)#2–Mo(1)–C(5)	78.1(3)	N(6)–Sm(1)–N(1)	78.1(2)
C(7)#1–Mo(1)–C(1)	146.6(3)	N(6)–Sm(1)–N(7)	77.0(2)
C(7)#1–Mo(1)–C(2)	75.9(3)	N(6)–Sm(1)–N(8)	147.3(2)
C(7)#1–Mo(1)–C(3)	79.0(3)	N(6)–Sm(1)–N(10)	73.5(2)
C(7)#1–Mo(1)–C(5)	69.6(3)	N(6)–Sm(1)–N(11)	109.0(2)
C(8)#3–Mo(1)–C(3)	143.6(3)	N(7)–Sm(1)–N(1)	143.5(2)
C(8)#3–Mo(1)–C(5)	77.2(3)	N(7)–Sm(1)–N(8)	75.3(2)
N(1)–C(1)–Mo(1)	172.6(7)	N(7)–Sm(1)–N(10)	116.5(2)
N(2)–C(2)–Mo(1)	178.3(7)	N(7)–Sm(1)–N(11)	76.0(2)
N(3)–C(3)–Mo(1)	178.9(7)	N(8)–Sm(1)–N(1)	116.2(2)
N(4)–C(4)–Mo(1)	177.1(7)	N(8)–Sm(1)–N(10)	135.3(2)
N(5)–C(5)–Mo(1)	178.8(7)	N(8)–Sm(1)–N(11)	80.7(2)
N(6)–C(6)–Mo(1)#2	175.3(7)	N(11)–Sm(1)–N(10)	63.1(2)

Symmetry codes: #1 $x, -y, z + 1/2$; #2 $-x + 1/2, -y - 1/2, -z + 1$; #3 $-x + 1/2, -y + 1/2, -z + 1$; #4 $-x, y, -z + 1/2$; #5 $x, -y, z - 1/2$

of the IR spectra concern the existence of 2120 cm^{-1} for **1**, which may be assigned to the characteristic CN^- stretching vibrations.⁵⁶

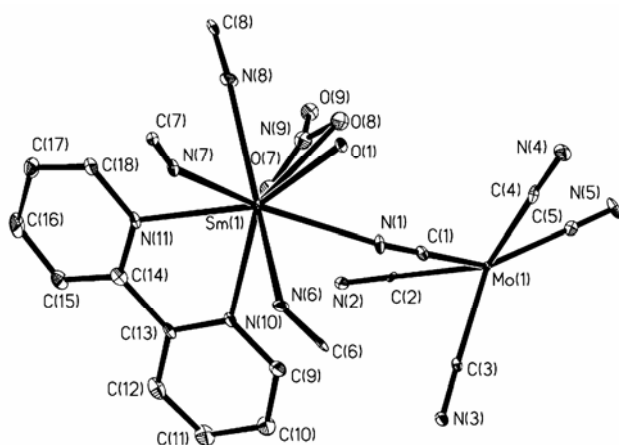
3.2 Structural description

X-ray single crystal analysis indicates that **1** crystallizes in monoclinic, space group $C2/c$, with $a = 25.784(2)$, $b = 11.0630(10)$, $c = 21.5080(18)$ Å, $\beta = 123.864(8)^\circ$. Selected bond lengths and angles are listed in table 2. ORTEP view of the basic unit of **1** is shown in figure 1. Crystal structure analysis of **1** reveals that **1** consists of a two-dimensional

(2D) cyano-bridged network, in which Sm^{III} and Mo^V ions are linked in alternating fashion, and the charge of which is balanced by the $[Sm(H_2O)_9]^{3+}$ cation. In the complex **1**, the four μ -CNs of $[Mo(CN)_8]^{3-}$ are bridged to Sm^{III} ions, respectively, and the other four are free. The Sm atom is surrounded by nitrogen atoms of four μ -CNs; one bpy ligand; and a disordered group $[NO_3^- (0.25\%) \text{ or } OH^- (0.75\%)]$, respectively. It is noticed that the bond angles of C–N–Sm are far from linearity with the angles of $155.1(6)^\circ$ [C(1)–N(1)–Sm(1)] and $152.4(6)^\circ$ [C(6)–N(6)–Sm(1)], respectively, while the angles of Mo–C–N are almost linear, ranging

Table 3. Selected H-bond lengths (Å) for the complex **1**.

Donor–H...Acceptor	D–H	H...A	A...D	D–H...A	Symmetry code
O(1)–H(1A)...N(5)	0.850	2.319	2.896	125.43	$x, -y, z - 1/2$
O(1)–H(1B)...O(4)	0.850	2.181	2.909	143.62	
O(1)–H(1B)...O(9)	0.850	2.366	2.868	118.32	$-x + 1/2, -y + 1/2, -z + 1$
O(1)–H(1B)...O(5)	0.850	2.657	3.284	131.69	
O(2)–H(2A)...N(2)	0.850	2.401	2.844	113.02	$-x + 1/2, -y + 1/2, -z + 1$
O(2)–H(2B)...N(2)	0.850	2.401	2.844	113.02	$x - 1/2, -y + 1/2, z - 1/2$
O(3)–H(3A)...N(5)	0.850	2.244	2.864	129.82	$x, -y, z - 1/2$
O(4)–H(4A)...O(1)	0.850	2.393	2.909	119.70	
O(4)–H(4A)...N(5)	0.850	2.635	3.460	163.83	$x, -y, z - 1/2$
O(4)–H(4B)...N(2)	0.850	2.145	2.823	136.61	$-x + 1/2, -y + 1/2, -z + 1$
O(4)–H(4B)...O(9)	0.850	2.473	2.920	113.67	$-x + 1/2, -y + 1/2, -z + 1$
O(5)–H(5A)...N(3)	0.850	2.011	2.780	149.98	$-x + 1/2, -y - 1/2, -z + 1$
O(5)–H(5B)...N(4)	0.850	1.965	2.795	165.05	
O(6)–H(6A)...O(7)	0.850	2.316	2.762	113.04	$-x + 1/2, -y + 1/2, -z + 1$
O(6)–H(6A)...N(4)	0.850	2.378	2.869	117.34	
O(7)–H(7A)...O(6)	0.930	2.125	2.762	124.58	$-x + 1/2, -y + 1/2, -z + 1$
O(7)–H(7A)...N(2)	0.930	2.696	3.148	110.73	

**Figure 1.** ORTEP view of the basic unit of **1** showing the atom-labelling scheme and ellipsoids at 30% probability. Hydrogen atoms and $[\text{Sm}(\text{H}_2\text{O})_9]^{3+}$ ion have been omitted for the sake of clarity.

from $172.6(7)^\circ$ to $178.8(7)^\circ$, in which two μ -CNs are $172.6(7)^\circ$ [N(1)–C(1)–Mo(1)] and $175.3(7)^\circ$ [N(6)–C(6)–Mo(1)#2 (#2 $-x + 1/2, -y - 1/2, -z + 1$)]. As shown in figure 2, the four cyanide groups of $[\text{Mo}(\text{CN})_8]^{3-}$ bridging Sm^{III} ions give rise to the square-grid pattern of the single layer. The intra-layer distances of Mo...Mo, Mo...Sm, and Sm...Sm are $7.099(4)$, $5.6083(5)$, and $6.97984(4)$ Å, respectively. In addition, the bpy ligands standing the two sides of the layer are involved in the extensive net-

work of π - π stacks linking parallel neighbouring layers through the aryl rings of bpy ligands (see figure 3). As shown in figure 4, the $[\text{Sm}(\text{H}_2\text{O})_9]^{3+}$ as guest molecules is buried in the holes which are made by π - π stacks between adjacent layers. The oxygen atoms coming from Sm(2) $[\text{Sm}(\text{H}_2\text{O})_9]^{3+}$ ions and Sm(1) atoms, respectively, connected with the nitrogen atoms of cyanide groups of the $[\text{Mo}(\text{CN})_8]^{3-}$ by hydrogen-bonds. The relevant details are shown in table 3. These weak interactions are undoubtedly significant in construction of the system. Therefore, these 2D sheets owing to the π - π stacks and hydrogen bonds interaction further give a 3D network.

3.3 Magnetic properties

Variable-temperature (300–2 K) magnetic susceptibilities of **1** have been measured on a crystalline sample in a field of 2000 Oe. Plots of χ_M and $\chi_M T$ vs T are shown in figure 5, where χ_M is the molar magnetic susceptibility for the $\text{Sm}^{\text{III}}_3\text{Mo}^{\text{V}}_2$ unit. As shown in figure 5, the $\chi_M T$ value is $0.525 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at room temperature, which is lower than $1.020 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ expected for isolated three Sm(III) ($J = 5/2$, $g_J = 2/7$) and two Mo(V) $S = 1/2$ ions, the $\chi_M T$ value deviate from at room temperature probably attributed the intrinsic characteristic of the Sm^{III} ion owing to the first- and second-order Zeeman effect contributions of the ground ($^6\text{H}_{5/2}$) and first excited

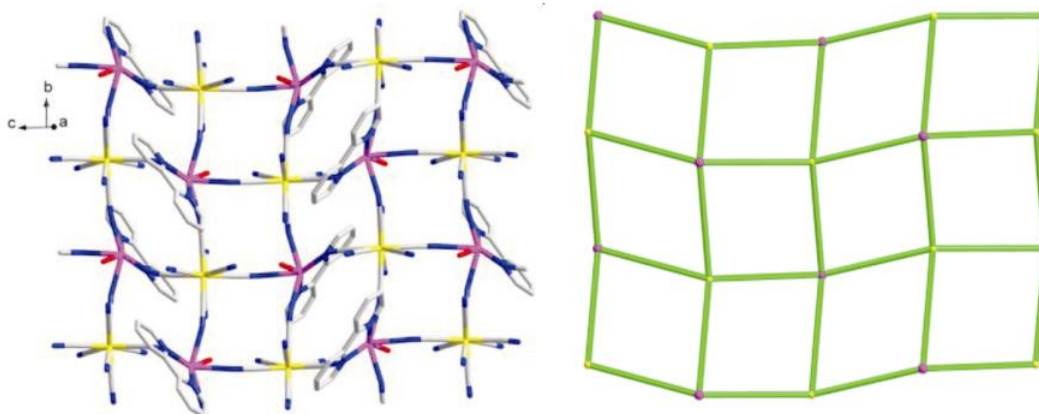


Figure 2. View of the square-grid pattern of the single layer for **1** (left). The topology of **1** belong to 4,4-net (right), the total Schläfli symbol is $\{4^4, 6^2\}\{4^4, 6^2\}$.

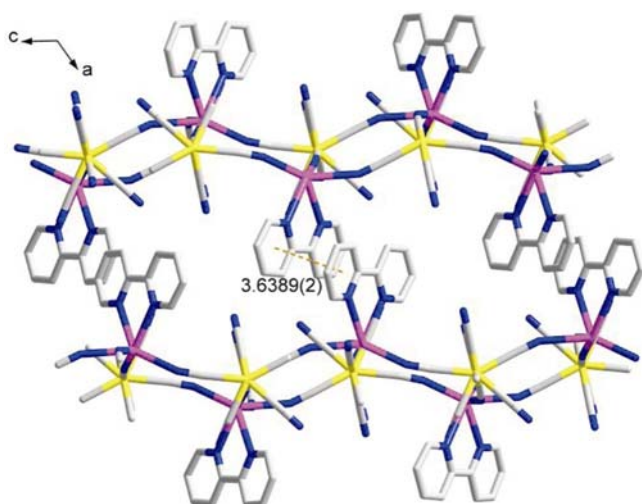


Figure 3. The interactions of π - π stacks for two layers, and hydrogen atoms are omitted for clarity.

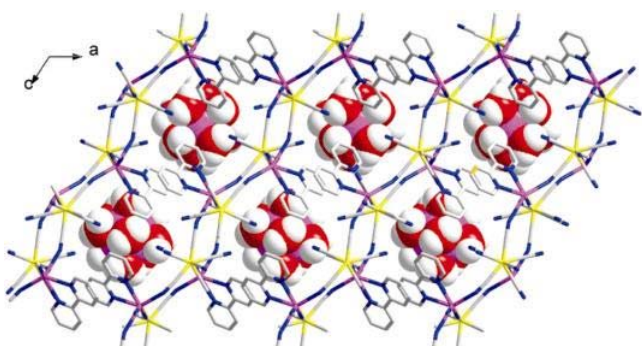


Figure 4. The guest molecules are buried in the holes which are filled with $[Sm(H_2O)_9]^{3+}$ ions (space-filling spheres).

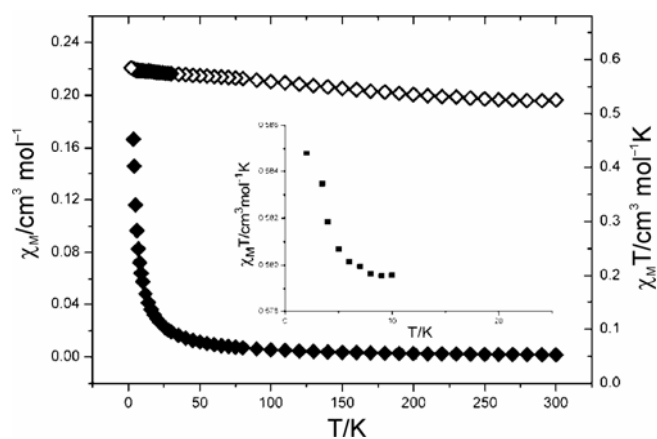


Figure 5. Plots of χ_M (\blacklozenge) and $\chi_M T$ (\square) vs T for **1**. The inset shows that the temperature dependence of $\chi_M T$ for **1** at low temperature range (2–10 K).

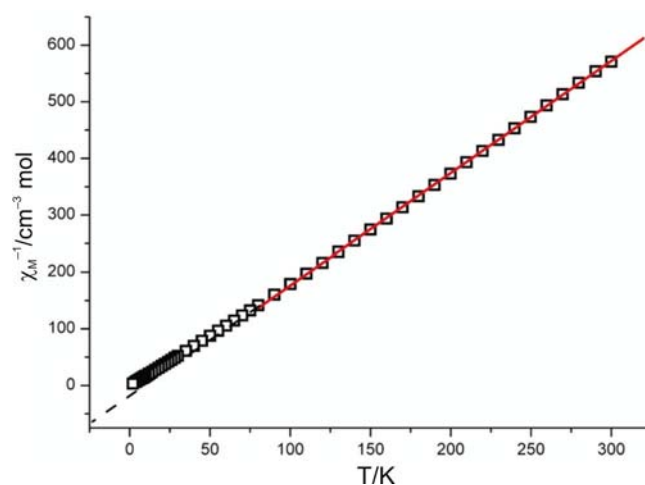


Figure 6. Plot of χ_M^{-1} vs T for **1**. The solid line denotes the theoretical fit at 300–75 K.

(${}^6\text{H}_{7/2}$) states of Sm^{III} ion, while the thermal depopulation of Stark levels, which are close in energy, and thermally populated at room temperature due to the relatively low spin-orbit coupling effect. Therefore, the nature of the magnetic coupling between the $\text{Sm}^{\text{III}}\text{--Mo}^{\text{V}}$ ions cannot simply be determined from the low value of $\chi_{\text{M}}T$ at room temperature (relative $1.020\text{ cm}^3\text{ mol}^{-1}\text{ K}$ expected for isolated ions), which should be due to the superposition of thermal depopulation of the low-lying excited states of Sm^{III} ions magnetic interaction. As shown in figure 5, the $\chi_{\text{M}}T$ product continuously increases with temperature decrease, implying a ferromagnetic coupling is observed in this system. Upon further cooling, a sharp increase is provided about 8 K (see inset figure 5), suggesting the onset of three-dimensional magnetic ordering, and the maximum value of $0.858\text{ cm}^3\text{ mol}^{-1}\text{ K}$ is reached at 2 K. As shown in figure 6, χ_{M}^{-1} vs T obeys the Curie–Weiss law above 75 K with a positive Weiss constant $\theta = +11.02\text{ K}$, confirming further a ferromagnetic coupling between the paramagnetic ions through the magnetic $[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$ passage.

4. Conclusion

In summary, reaction of $(n\text{-Bu}_4\text{N})_3[\text{Mo}^{\text{V}}(\text{CN})_8]$ with $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in the presence of bpy affords a sheet-like bimetallic $\text{Sm}^{\text{III}}\text{--Mo}^{\text{V}}$ assembly. Magnetic results of the complex reveal that **1** obeys the Curie–Weiss law with a positive Weiss constant $\theta = +11.02\text{ K}$, confirming a ferromagnetic interaction between the Sm^{III} and Mo^{V} ions.

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Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 690603. Copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

References

1. Kahn O 1993 *Molecular magnetism* (New York: VCH)
2. Miller J S and Epstein A J 1994 *Angew. Chem., Int. Ed. Engl.* **33** 385
3. Miller J S 2000 *Inorg. Chem.* **39** 4392
4. Gütlich P, Garcia Y and Woike T 2001 *Coord. Chem. Rev.* **219–221** 839
5. Mallah T, Thiébaud S, Verdaguer M and Veillet P 1993 *Science* **262** 1554
6. Pejaković D A, Manson J L, Miller J S and Epstein A J 2001 *Synth. Met.* **122** 529
7. Ohba M, Okawa H 2000 *Coord. Chem. Rev.* **198** 313
8. Ferlay S, Mallah T, Quahès R, Veillet P and Verdaguer M 1995 *Nature* **378** 701
9. Ohba M, Usuki N, Fukita N and Okawa H 1999 *Angew. Chem., Int. Ed.* **38** 1795
10. Inoue K, Imai H, Ghalsasi P S, Kikuchi K, Ohba M, Okawa H and Yakhmi J V 2001 *Angew. Chem., Int. Ed.* **40** 4242
11. Kou H Z, Gao S, Zhang J, Wen G H, Su G, Zheng R K and Zhang X X 2001 *J. Am. Chem. Soc.* **123** 11809
12. Larionova J, Clérac R, Sanchiz J, Kahn O, Golhen S and Ouahab L 1998 *J. Am. Chem. Soc.* **120** 13088
13. Larionova J, Kahn O, Golhen S, Ouahab L and Clérac R 1999 *J. Am. Chem. Soc.* **121** 3349
14. Kaur Sra A, Andruh M, Kahn O, Golhen S, Ouahab L and Yakhmi J V 1999 *Angew. Chem., Int. Ed.* **38** 2606
15. Li D F, Gao S, Zheng L M and Tang W X 2002 *J. Chem. Soc., Dalton Trans.* **2805**
16. Withers J R, Li D F, Triplet J, Ruschman C, Parkin S, Wang G B, Yee G T and Holmes S M 2006 *Inorg. Chem.* **45** 4307
17. Arimoto Y, Ohkoshi S, Zhong Z J, Seino H, Mizobe Y and Hashimoto K 2002 *Chem. Lett.* 832
18. Li D F, Zheng L M, Zhang Y Z, Huang J, Gao S and Tang W X 2003 *Inorg. Chem.* **42** 6123
19. Podgajny R, Desplanches C, Sieklucka B, Sessoli R, Villar V, Paulsen C, Wernsdorfer W, Dromzée Y and Verdaguer M 2002 *Inorg. Chem.* **41** 1323
20. Song Y, Ohkoshi S, Arimoto Y, Seino H, Mizobe Y and Hashimoto K 2003 *Inorg. Chem.* **42** 1848
21. Kashiwagi T, Ohkoshi S, Seino H, Mizobe Y and Hashimoto K 2004 *J. Am. Chem. Soc.* **126** 5024
22. Zhao H H, Shatruck M, Prosvirin A V and Dunbar K R 2007 *Chem. Eur. J.* **13** 6573
23. Yoon J H, Kim H C and Hong C S 2005 *Inorg. Chem.* **44** 7714
24. Li D F, Zheng L M, Wang X Y, Huang J, Gao S and Tang W X 2003 *Chem. Mater.* **15** 2094
25. Korzeniak T, Podgajny R, Alcock N W, Lewiński K, Balanda M, Wasiutyński T and Sieklucka B 2003 *Polyhedron* **22** 2183
26. Ohkoshi S, Arimoto Y, Hozumi T, Seino H, Mizobe Y and Hashimoto K 2003 *Chem. Commun.* 2772
27. Podgajny R, Korzeniak T, Balanda M, Wasiutyński T, Errington W, Kemp T J, Alcock N W and Sieklucka B 2002 *Chem. Commun.* 1138

28. Li D F, Gao S, Zheng L M, Yu K B and Tang W X 2002 *New J. Chem.* **26** 1190
29. Korzeniak T, Stadnicka K, Rams M and Sieklucka B 2004 *Inorg. Chem.* **43** 4811
30. Podgajny R, Chmel N P, Balanda M, Tracz P, Gawel B, Zajac D, Sikora M, Kapusta C, Łasocha W, Wasityński T and Sieklucka B 2007 *J. Mater. Chem.* **17** 3308
31. Korzeniak T, Stadnicka K, Pelka R, Balanda M, Tomala K, Kowalski K and Sieklucka B 2005 *Chem. Commun.* 2939
32. Herrera J M, Marvaud V, Verdaguer M, Marrot J, Kalisz M and Mathonière C 2004 *Angew. Chem., Int. Ed. Engl.* **43** 5468
33. Lim J H, Kang J S, Kim H C, Koh E K, Hong C S 2006 *Inorg. Chem.* **45** 7821
34. You Y S, Yoon J H, Lim J H, Kim H C, Hong C S 2005 *Inorg. Chem.* **44** 7063
35. Ohkoshi S, Ikeda S, Hozumi T, Kashiwagi T and Hashimoto K 2006 *J. Am. Chem. Soc.* **128** 5320
36. Song Y, Zhan P, Ren X M, Shen X F, Li Y Z and You X Z 2005 *J. Am. Chem. Soc.* **127** 3708
37. Herrera J M, Bleuzen A, Dromzée Y, Julve M, Lloret F and Verdaguer M 2003 *Inorg. Chem.* **42** 7052
38. Ohkoshi S, Hamada Y, Matsuda T, Tsunobuchi Y and Tokoro H 2008 *Chem. Mater.* **20** 3048
39. Visinescu D, Desplanches C, Imaz I, Bahers V, Pradhan R, Villamena F A, Guionneau P and Sutter J P 2006 *J. Am. Chem. Soc.* **128** 10202
40. Bonadio F, Gross M, Stoeckli-Evans H and Decurtins S 2002 *Inorg. Chem.* **41** 5891
41. Lim J H, Yoon J H, Kim H C and Hong C S 2006 *Angew. Chem., Int. Ed. Engl.* **45** 7424
42. Freedman D E, Bennett M V and Long J R 2006 *Discussion of Faraday Soc.* 2829
43. Larionova J, Gross M, Pilkington M, Andres H, Stoeckli-Evans H, Güdel H U and Decurtins S 2000 *Angew. Chem., Int. Ed. Engl.* **39** 1605
44. Zhong Z J, Seino H, Mizobe Y, Hidai M, Fujishima A, Ohkoshi S and Hashimoto K 2000 *J. Am. Chem. Soc.* **122** 2952
45. Lim J H, Yoo H S, Yoon J H, Koh E K, Kim H C and Hong C S 2008 *Polyhedron* **27** 299
46. Prins F, Pasca E, Jongh L J D, Kooijman H, Spek A L and Tanase S 2007 *Angew. Chem. Int. Ed.* **46** 6081
47. Ikeda S, Hozumi T, Hashimoto K and Ohkoshi S 2005 *Dalton Trans.* 2120
48. Przychodzeń P, Pelka R, Lewiński K, Supe J, Rams M, Tomala K and Sieklucka B 2007 *Inorg. Chem.* **46** 8924
49. Kosaka W, Hashimoto K and Ohkoshi S 2007 *Bull. Chem. Soc. Jpn.* **80** 2350
50. Przychodzeń P, Lewiński K, Pelka R, Balanda M, Tomala K and Sieklucka B 2006 *Dalton Trans.* 625
51. Ma S L, Ma Y, Liao D Z, Yan S P, Jiang Z H and Wang G L 2008 *Chinese J. Inorg. Chem.* **24** 1290
52. Hozumi T, Ohkoshi S, Arimoto Y, Seino H, Mizobe Y and Hashimoto K 2003 *J. Phys. Chem.* **B107** 11571
53. Chelebaeva E, Larionova J, Guari Y, Sá Ferreira R A, Carlos L D, Almeida Paz F A, Trifonov A and Guérin C 2008 *Inorg. Chem.* **47** 775
54. Bok L D C, Leipoldt J G and Basson S S 1975 *Z. Anorg. Allg. Chem.* **415** 81
55. Sheldrick G M 1997 SHELXS-97 and SHELXL-97 (Germany: University of Göttingen)
56. Willemin S, Larionova J, Clérac R, Donnadiou B, Henner B, Le Goff X F and Guérin C 2003 *Eur. J. Inorg. Chem.* 1866