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Two Octacyanomolybdate(IV)-M(II) (M = Mn, Co) Bimetallic Assemblies: Crystal Structures and Magnetic Properties[1]

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Abstract—Two cyano-bridged bimetallic complexes $\{[M_2(H_2O)_4Mo(CN)_8] \cdot 4H_2O\}_n$ [M = Mn (I) and Co (II)] have been synthesized and structurally characterized. The single-crystal X-ray analyses reveal that these two compounds have three-dimensional structures, and cell parameters are similar in a tetragonal system with space group $I\bar{4}$. In the both complexes, each $[Mo(CN)_8]^{4-}$ building block is linked with M^{2+} [M = Mn and Co] ions through its eight CN ligands. Each M^{2+} center is connected to four Mo units forming a three-dimensional framework. In addition, magnetic studies of these complexes have been presented.

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INTRODUCTION

Recently bimetallic octacyanometalates have attracted much attention because of their interesting structure and magnetic properties [1–6]. The $[M(CN)_8]^{3-,4-}$ (M = Mo, W, Nb) units exhibit various geometrical structures such as square antiprism, dodecahedron, bicapped trigonal prism, and cyanide group, being a kind of good bridging building block for transition metals complexes. These characteristics enable them to be the potential building blocks to construct various architectures. For example, a few bimetallic octacyanometalates with Mn^{2+} ion compounds, $Mn_9^{II}M_6^{V}$ (M = Mo and W) [7–10] and $[Mn(Bipy)_2]_4[Mo(CN)_8]_2 \cdot xH_2O$ (x = 14 or 8) [11], have been isolated as polynuclear clusters. The complex $\{[Mn(Bipy)(DMF)_2]_2[Mo(CN)_8]_2[Mn(DMF)_4]\}_n$ [12] with the 1D structure and $\{[Mn(DMF)_4]_3[Mo(CN)_8]_2\}_n$ [13] with the 2D network structure have also been reported. Nevertheless, structurally characterized coordination polymers based on $[Mo(CN)_8]^{3-,4-}$ are still relatively rare [14].

In this paper, we report two 3D bimetallic complexes of $\{[M_2(H_2O)_4Mo(CN)_8] \cdot 4H_2O\}_n$ [M = Mn (**I**) and Co (**II**)] with the 3D supramolecular network. Their preparation, crystal structure, and magnetic properties of **I** are discussed as well.

EXPERIMENTAL

Materials and methods. $K_4[Mo(CN)_8] \cdot 2H_2O$ was synthesized as described previously [15, 16]. All other chemicals are reagent grade and used without further purification. Elemental analysis 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} regions, using KBr pellets. Variable temperature magnetic susceptibilities were measured on a SQUID magnetometer in a magnetic field of 5000 Oe at temperature in the range of 1.8–300 K. The diamagnetic corrections were applied by using Pascal's constants.

Synthesis of I. The yellow block crystals of complex **I** is obtained by adding 8 ml of an aqueous solution of $K_4[Mo(CN)_8] \cdot H_2O$ (0.1 mmol, 49.7 mg) into one arm of an H-shaped tube and 8 ml of an aqueous solution of $MnCl_2 \cdot 4H_2O$ (0.2 mmol, 39.6 mg) into an other. The two shoulders of an H-shaped tube are filled with MeOH solvent.

For $C_8H_{16}Mn_2MoN_8O_8$ (M_c = 558.1)

anal. calcd, %:	C, 17.2;	H, 2.9;	N, 20.1.
Found, %:	C, 17.3;	H, 2.7;	N, 19.8%.

IR spectrum (KBr; ν, cm^{-1}): 3559, 3385, 2129, 1610, 626.

Synthesis of II. The orange block crystals of complex **II** is obtained by the same procedure as above, but using $CoCl_2 \cdot 6H_2O$ (0.2 mmol, 47.6 mg) instead of $MnCl_2 \cdot 4H_2O$.

For $C_8H_{16}Co_2MoN_8O_8$ (M_c = 566.1)

anal. calcd, %:	C, 17.0;	H, 2.8;	N, 19.8.
Found, %:	C, 17.1;	H, 2.7;	N, 19.6%.

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IR spectrum (KBr; ν, cm^{-1}): 3554, 3408, 2138, 1616, 626.

X-ray structure determination. All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated MoK_α radiation (λ = 0.71073 Å). A summary of crystallographic data are given in Table 1. The empirical absorption corrections by semiempirical equivalents were carried out. The structures were solved by direct methods using the SHELXS-97 program and refined with SHELXL-97 [17] by the 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.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (nos. 716924 for **I** and 716923 for **II**, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The IR spectra of the two complexes exhibit one typical C≡N band at 2129 for **I** and 2138 cm^{-1} for **II**, respectively. The shift of ν(C≡N) to higher frequencies compared to those of $K_4[Mo(CN)_8]$ (2125 s, 2102 s cm^{-1}) clearly show coordination of all the CN groups to M^{2+}, which is in agreement with the formation of one type of ν(C≡N) bridges [18]. Two broad peaks at 3559, 3385 for **I** and 3554, 3408 cm^{-1} for **II**, respectively, are due to O–H stretching vibration modes and support the presence of both coordinated and non-coordinated water molecules.

The single-crystal X-ray structural determination reveals that compounds **I** and **II** (Fig. 1) have three-dimensional structures. The cell parameters of these two compounds are similar. Selected bond lengths and angles are listed in Tables 2 and 3. In these two complexes, the axial-coordinated water molecules point directly into the channels of the network, which are involved in hydrogen–bonding interactions with H_2O solvated molecules located in the void of the framework, namely, this coordination scaffold is framing square-shaped apertures forming channels, where both the coordinated H_2O and non-coordinated H_2O molecules are located. These water molecules further interacted with each other to give rise to a tetrameric cluster of water as shown in Fig. 2. Selected hydrogen-bonding lengths are presented in Table 4. The M^{2+} ion is six-coordinated with four cyanide nitrogen and two oxygen atoms of H_2O (solvated molecules) forming a distorted octahedral environment in which four N–C–Mo linkages and two water molecules in the *trans* configuration surround the M^{2+} (M = Mn and Co) sites. The M–N bond lengths are equal to 2.204(3) and 2.246(3) Å for **I** and 2.1243(17) and 2.1630(16) Å for **II**. The M–O(1) and M–O(2) bond lengths are equal to 2.157(6) and 2.195(5) Å for **I** and 2.085(2) and 2.121(2) Å for **II**,

Table 1. Crystallographic data and details of the experiment and refinement of structures **I** and **II**

Parameter	Value	
	I	**II**
Temperature, K	293(2)	293(2)
Crystal system	Tetragonal	Tetragonal
Space group	$I\bar{4}$	$I\bar{4}$
a, Å	11.9150 (9)	11.8132 (10)
c, Å	13.2632 (18)	13.136 (2)
V, $Å^3$	1882.9 (3)	1833.2 (4)
Z	4	4
ρ_{calcd}, g/cm^3	1.969	2.051
μ(MoK_α), mm^{-1}	2.031	2.518
F(000)	1104	1120
Crystal size	0.24 × 0.20 × 0.16	0.26 × 0.20 × 0.14
θ range for data collection, deg	2.30 to 26.37	2.32 to 26.37
Limiting indices	$-13 \le h \le 14$ $-13 \le k \le 14$ $-10 \le l \le 16$	$-14 \le h \le 13$ $-14 \le k \le 14$ $-10 \le l \le 16$
Reflections collected/unique	4757/1012 (R_{int} = 0.0408)	5190/986 (R_{int} = 0.0370)
Data/restraints/parameters	1012/3/68	986/6/67
Final *R* indices ($I > 2\sigma(I)$)	R_1 = 0.0316, wR_2 = 0.0919	R_1 = 0.0172, wR_2 = 0.0462
R indices (all data)	R_1 = 0.0330, wR_2 = 0.0928	R_1 = 0.0196, wR_2 = 0.0472
Largest diff. peak and hole, *e* $Å^{-3}$	0.783 and –0.409	0.368 and –0.462

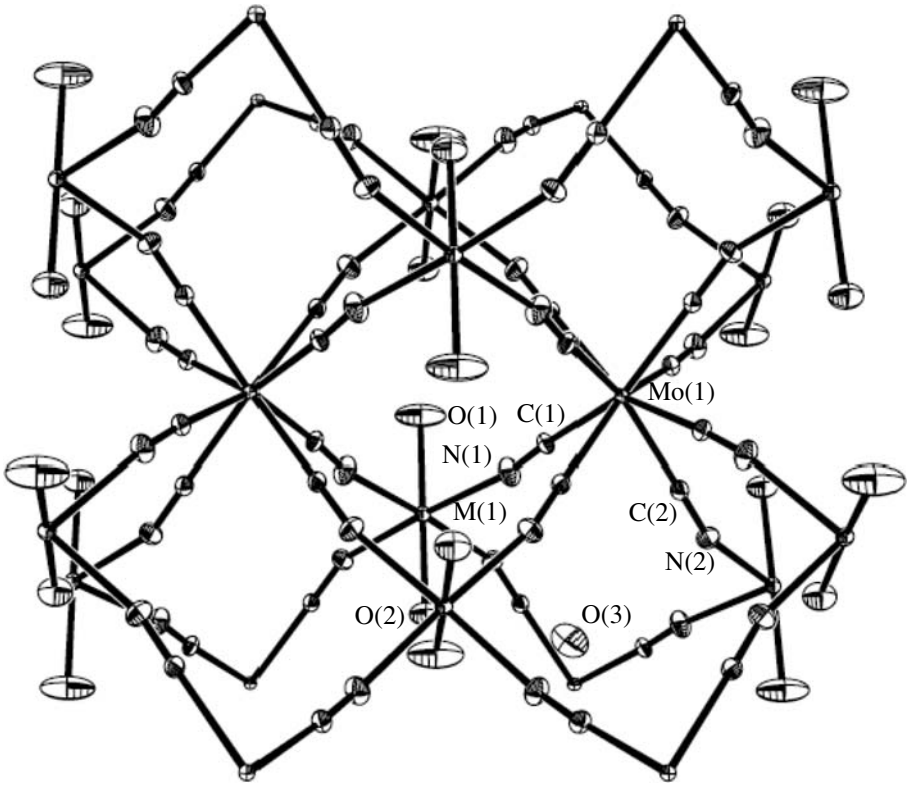

Fig. 1. Molecular structures of **I** and **II**, and atomic labeling scheme. Hydrogen atoms are omitted for clarity.

respectively. The Mo–C–N bonded angles are close to 180° (MoC(1)N(1) 176.3(4)°; MoC(2)N(2) 175.8(3)° for **I**, 174.74(16) and 174.74(16)° for **II**), while the MNC bonded angles deviate significantly from 180° (166.1(3), 154.3(3)° for **I**, 155.86(16) and 166.84(16))° for **II**). Each $[Mo(CN)_8]^{4-}$ building block is linked to M^{2+} ions through its eight CN ligands and each M^{2+} center is connected to four Mo units forming a three-dimensional framework. The Mo–C bond lengths are equal to 2.154(4) and 2.158(4) Å for **I** and 2.1753(19) and 2.1798(19) Å for **II**. The C–N bond lengths are equal to 1.145(5) and 1.161(5) Å for **I** and 1.155(2) and 1.150(2) Å for **II**. For the complexes **I** and **II**, the organization is highly symmetrical and may be described as a grid-like 3D arrangement of Mn–NC–Mo–CN–Mn (M = Mn and Co) linkages. The arrangement is reminiscent to that found in related $[Mo(CN)_8]^{4-}/M^{2+}$ 3D coordination polymers [19–22].

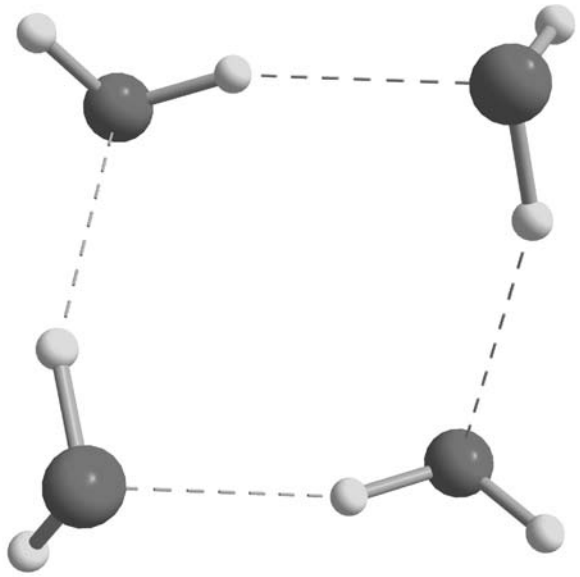

Fig. 2. Tetrameric cluster of the water molecule of **I**.

As shown in Fig. 3, for the topology structures of both the complexes, all the complexes have the same topology, which belongs to a 3D {4, 8} network with stoichiometry $(4\text{-}c)_2(8\text{-}c)$; 2-nodal network, in which Schläfli symbol of Mn (or Co) atom is $\{4^4, 6^2\}$, Mo atom is $\{4^{16}, 6^{12}\}$, total Schläfli symbol of the type complexes is $\{4^{16}, 6^{12}\}\{4^4, 6^2\}_2$.

For complex **I**, at room temperature, the μ_{eff} value is 5.88 μ_B (Fig. 4), and this value is close to the expected spin-only value (5.92 μ_B per Mn^{2+} ion). On lowering the temperature, the μ_{eff} values keep almost constant until 30 K and then decreases sharply reaching a minimum value of 4.27 μ_B at 1.8 K. Such kind of magnetic behavior is characteristic of zero-filed splitting of Mn^{2+} ion. To take this effect into account, the theoretical expres-

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

Bond	*d*, Å	Bond	*d*, Å
Mn(1)–O(1)	2.157(6)	Mo(1)–C(2)	2.154(4)
Mn(1)–N(1)	2.204(3)	Mo(1)–C(1)	2.158(4)
Mn(1)–N(2)$^{\#4}$	2.246(3)	Mn(1)–O(2)	2.195(5)
N(1)–C(1)	1.145(5)	N(2)–C(2)	1.161(5)
Angle	**ω, deg**	**Angle**	**ω, deg**
C(2)$^{\#1}$Mo(1)C(2)	72.67(9)	C(2)$^{\#2}$Mo(1)C(1)	146.17(14)
C(2)Mo(1)C(1)$^{\#1}$	138.99(14)	C(2)Mo(1)C(1)	76.31(14)
C(2)$^{\#1}$Mo(1)C(1)	80.76(14)	C(1)$^{\#1}$Mo(1)C(1)	72.77(9)
C(1)$^{\#2}$Mo(1)C(1)	114.05(19)	O(1)Mn(1)O(2)	176.4(2)
O(1)Mn(1)N(1)	85.83(16)	O(2)Mn(1)N(1)	91.61(15)
N(1)Mn(1)N(1)$^{\#3}$	90.6(2)	O(1)Mn(1)N(2)$^{\#4}$	96.20(16)
O(2)Mn(1)N(2)$^{\#4}$	86.50(14)	N(1)Mn(1)N(2)$^{\#4}$	92.55(14)
C(1)N(1)Mn(1)	166.1(3)	C(2)N(2)Mn(1)$^{\#4}$	154.3(3)
N(1)C(1)Mo(1)	176.3(4)	N(2)C(2)Mo(1)	175.8(3)

* Symmetry operators: $^{\#1}$ $-y, x, z$; $^{\#2}$ $-x, -y, z$; $^{\#3}$ $x, y, -z$; $^{\#4}$ $-x + 1/2, -y + 1/2, -z + 1/2$.

Table 3. Selected bond lengths (Å) and angles (deg) for complex **II***

Bond	*d*, Å	Bond	*d*, Å
Mo(1)–C(1)	2.1753(19)	Co(1)–N(1)	1.1630(16)
Mo(1)–C(2)$^{\#2}$	2.1798(19)	N(1)–C(1)	1.155(2)
Co(1)–O(1)	2.085(2)	Co(1)–O(2)	2.121(2)
Co(1)–N(2)	2.1243(17)	N(2)–C(2)	1.150(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
C(1)Mo(1)C(1)$^{\#1}$	113.67(10)	N(2)C(2)Mo(1)$^{\#3}$	175.97(17)
C(1)Mo(1)C(2)$^{\#3}$	75.83(7)	C(1)Mo(1)C(2)$^{\#2}$	81.52(7)
C(1)Mo(1)C(2)$^{\#5}$	138.01(7)	C(1)Mo(1)C(2)$^{\#4}$	147.21(7)
O(1)Co(1)N(2)	87.10(7)	O(1)Co(1)O(2)	177.50(9)
N(2)Co(1)N(2)	89.42(10)	O(2)Co(1)N(2)	91.13(6)
O(2)Co(1)N(1)	87.09(6)	O(1)Co(1)N(1)	94.74(7)
N(2)Co(1)N(1)	177.44(7)	N(2)Co(1)N(1)	92.44(7)
N(1)Co(1)N(1)	85.65(9)	C(1)N(1)Co(1)	155.86(16)
C(2)N(2)Co(1)	166.84(16)	N(1)C(1)Mo(1)	174.74(16)

* Symmetry operators: $^{\#1}$ $-x + 1, -y + 1, z$; $^{\#2}$ $-y + 1/2, x + 1/2, -z + + 1/2$; $^{\#3}$ $-x + 1/2, -y + 1/2, -z + 1/2$; $^{\#4}$ $x + 1/2, y + 1/2, -z + 1/2$; $^{\#5}$ $y + 1/2, -x + 1/2, -z + 1/2$.

sion of magnetic susceptibility for the complex is as follow [23]:

$$\chi_{\parallel} = \frac{Ng_z^2\beta^2}{4kT} \times \left[\frac{1 + 9\exp(-2D/kT) + 25\exp(-6D/kT)}{1 + \exp(-2D/kT) + \exp(-6D/kT)}\right],$$

$$\chi_{\perp} = \frac{Ng_x^2\beta^2}{4kT} \times \left[\frac{9 + 8/X - 11\exp(-2X)/2X - 5\exp(-6X)/2X}{1 + \exp(-2X) + \exp(-6X)}\right]. \quad (1)$$

$$X = D/kT,$$

$$\chi = \frac{2\chi_{\perp} + \chi_{\parallel}}{3},$$

where, an additional coupling parameter, zJ' was added in Eq. (2) to take the molecular field approximation into account for the magnetic behavior at low temperature [24]. The total magnetic susceptibility is

$$\chi_M = \frac{\chi}{1 - (2zJ'/Ng^2\beta^2)\chi}, \quad (2)$$

where D is the axial zero-field splitting parameter for the Mn^{2+} ion, χ_M is the corrected molar magnetic susceptibility per Mn atom and $g_x = g_z = g$. A least-squares fitting of the experimental data led to $|D| = 0.998$ cm^{-1}, $zJ' = -0.330$ cm^{-1}, $g = 2.0$ and $R = 1.66 \times 10^{-3}$ for **I**. Fitting result ($|D| = 0.998$ cm^{-1}) further confirms the occurrence of significant zero-field splitting in the Mn^{2+} ion at low temperature.

Thus, it should be noted that structurally characterized polynuclear compounds based on the use of $[Mo(CN)_8]^{4-}$ as a building block are still rare. In the paper, two cyanide-bridged complexes based on $[Mo(CN)_8]^{4-}$ anion and M^{2+} [M = Mn and Co] ions have been crystallized structurally characterized. For complex **I**, magnetic properties have been investigated utilizing a model containing zero-field splitting of Mn^{2+}

Table 4. Selected hydrogen-bond lengths (Å) for both complexes **I** and **II**

Contact D–H···A	Distance, Å				Symmetry code of A and B
	D–H	H···A	A···D	Angle D–H···A, deg	
			I		
O(1)–H(1*A*)···O(2)	0.85	2.21	2.966	149	–*y*, *x*, *z*
O(1)–H(1*B*)···O(1)	0.85	1.94	2.728	155	–*x*, –*y* + 1, –*z*
O(2)–H(2*A*)···O(3)	0.85	2.20	2.943	147	
O(2)–H(2*A*)···O(1)	0.85	2.36	2.966	130	*y*, –*x*, –*z*
O(2)–H(2*B*)···N(2)	0.85	2.40	3.233	166	*y* + 1/2, –*x* + 1/2, *z* – 1/2
O(3)–H(3*A*)···N(2)	0.85	2.47	3.202	144	
O(3)–H(3*B*)···O(3)	0.85	2.35	2.921	124	*y* + 1/2, –*x* + 1/2, –*z* + 1/2
O(3)–H(3*B*)···N(2)	0.85	2.65	3.412	150	*y* + 1/2, –*x* + 1/2, –*z* + 1/2
			II		
O(1)–H(1*A*)···O(3)	0.85	2.25	3.009	148	–*y*, *x*, –*z*
O(1)–H(1*A*)···O(2)	0.85	2.61	3.070	115	–*y*, *x*, *z*
O(1)–H(1*B*)···O(1)	0.85	2.03	2.752	143	–*x*, –*y* + 1, –*z*
O(2)–H(2*A*)···N(1)	0.85	2.55	3.252	140	–*y* + 1, *x*, *z*
O(2)–H(2*B*)···O(3)	0.85	2.08	2.891	157	
O(3)–H(3*A*)···N(1)	0.84	2.57	3.225	136	–*x* + 1/2, –*y* + 1/2, –*z* + 1/2
O(3)–H(3*B*)···O(3)	0.84	2.12	2.926	159	*y* + 1/2, –*x* + 1/2, –*z* + 1/2

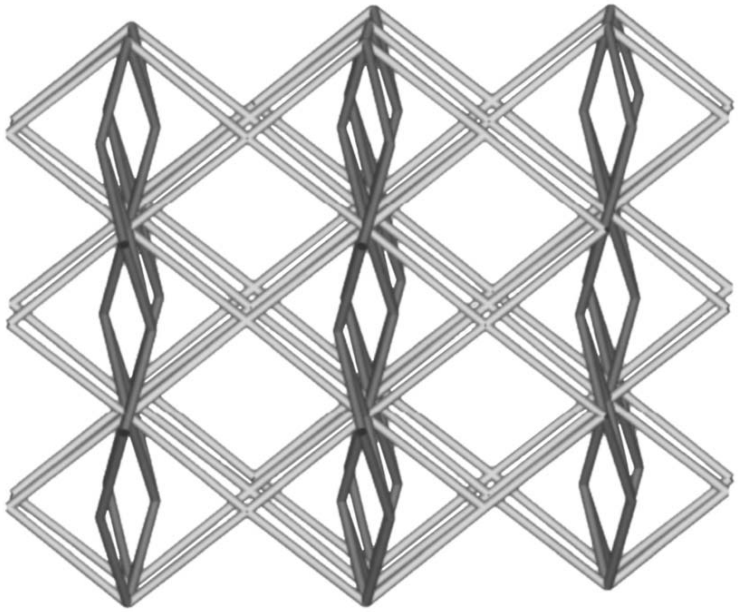

Fig. 3. Topological representation of the 3D {4, 8} net of **I** and **II**.

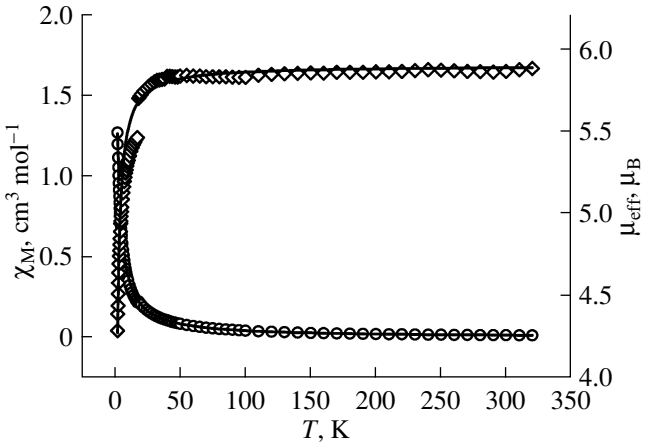

Fig. 4. Temperature dependence of χ_M and μ_B of **I**.

ion. Fitting result ($|D| = 0.998$ cm^{-1}) further confirms the occurrence of significant zero-field splitting in the Mn^{2+} ion at low temperature.

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