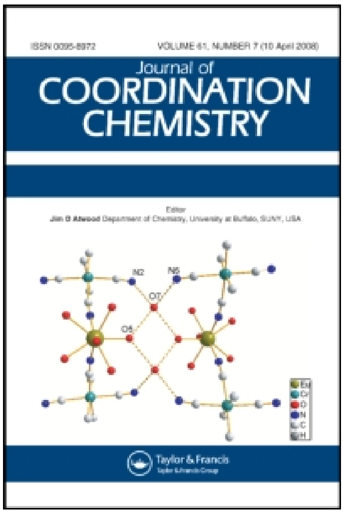

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Synthesis, crystal structure and magnetic properties of a three-dimensional cyano-bridged heterometallic complex of manganese(II) and molybdenum(IV)

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Synthesis, crystal structure and magnetic properties of a three-dimensional cyano-bridged heterometallic complex of manganese(II) and molybdenum(IV)

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A bimetallic cyano-bridged complex $\{[Mn(ImH)(H_2O)_2]_2[Mo(CN)_8]\cdot 4H_2O\}_n$ (ImH = imidazole) has been prepared and characterized. Single-crystal X-ray analysis reveals that the complex crystallizes in space group $C2/c$ with $a = 15.665(2)$, $b = 14.616(2)$, $c = 12.307(2)$ Å, $\alpha = 90$, $\beta = 108.31(1)$, $\gamma = 90°$. The structure of the complex demonstrates a three-dimensional network through cyano-bridges. Each Mo(IV) atom has six –CN–Mn linkages and two terminal cyano ligands arranged in a square antiprismatic arrangement. The Mn(II) atom is in a distorted octahedral environment formed by three $MoCN \rightarrow Mn$ linkages along with one imidazole and two water molecules in cis configuration. Variable temperature magnetic susceptibility shows an antiferromagnetic coupling between Mn^{2+} ions through the NC–Mo^{IV}–CN diamagnetic bridges within the three-dimensional network. The IR spectra have also been investigated.

Keywords: Manganese(II); Molybdate(IV); Cyano-bridge; Crystal structure; Magnetic properties

1. Introduction

Much attention is currently being devoted to the design and construction of molecular-based magnets exhibiting spontaneous magnetization [1, 2]. The main synthetic strategy is to connect two paramagnetic centers through a bridging ligand to generate polynuclear or extended arrays. Extended arrays of higher dimensionalities may exhibit higher ordering with temperature due to increased interacting neighbors. A cyano-bridge, with effective coupling of d-metal centers via σ-donor and π^*-acceptor bonding, plays an important role in the design of polynuclear or extended networks with specific magnetic properties. Furthermore, an enhanced exchange interaction may be expected due to increased overlap between more spatially extended orbitals of 4d or 5d metal ions and those of 3d metal ions and, consequently, magnetic ordering at higher temperature. Thus cyano-bridged systems based upon octacyanomolybdate

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or octacyanotungstate building blocks attract considerable interest and a few bimetallic complexes based on $[M(CN)_8]^{n-}$ (M: Mo or W) and high spin Mn^{2+} have been structurally and magnetically characterized. These Mo–Mn or W–Mn complexes form various crystal structures, e.g., zero-dimensional (0D) [3–6], 1D [7, 8], 2D [9] and 3D [10, 11]. Among them, two three-dimensional complexes $[Mn^{II}_2(H_2O)_2(CH_3COO)][W^V(CN)_8]\cdot 2H_2O$ and $\{[Mn^{II}_6(H_2O)_9][W^V(CN)_8]_4\cdot 13H_2O\}_n$, are ferrimagnets with magnetic ordering temperatures of 45 and 54 K, respectively, and one-dimensional complex $[Mn^{II}_2(L)_2(H_2O)][Mo^{IV}(CN)_8]\cdot H_2O$ (L = macrocycle) exhibits interesting photomagnetic propreties when irradiated in the near-UV range. Herein we report the synthesis, crystal structure and magnetic properties of a new bimetallic (Mo^{IV} and Mn^{II}) polymeric network with cyanide bridges.

2. Experimental

2.1. *Preparation*

The starting material, $K_4[Mo(CN)_8]\cdot 2H_2O$, was prepared according to the literature [12]. A 10 mL aqueous solution of $K_4[Mo(CN)_8]\cdot 2H_2O$ (124 mg, 0.25 mmol) was added to a 10 mL aqueous solution of $MnSO_4\cdot H_2O$ (85 mg, 0.5 mmol) and $C_3H_4N_2$(ImH) (34 mg, 0.5 mmol). The resulting yellow solution was left to stand in a brown bottle after stirring for an hour at room temperature. One week later bright yellow crystals suitable for single-crystal X-ray determination were formed. C, H and N, analyzed with an Erba 1160 instrument, supported the product as $\{[Mn(ImH)(H_2O)_2]_2[Mo(CN)_8]\cdot 4H_2O\}_n$. Anal. Calcd for: $C_{14}H_{24}N_{12}O_8Mn_2Mo$ (%): C, 24.20; H, 3.46; N, 24.20. Found: C, 24.12; H, 3.17; N, 24.35. Infrared spectra were recorded using a TENSOR27(Bruker) Spectrophotometer (4000–400 cm^{-1}) with a crystalline sample spread on KBr pellets. Variable-temperature magnetic susceptibility data on the crystalline sample were collected with a Quantum Design MPMS-5SP SQUID magnetometer in the temperature range of 5–300 K on 10,000 Oe field.

2.2. *Crystal structure determination*

A single crystal with dimension $0.30 \times 0.24 \times 0.24\,mm^3$ was mounted on a glass fiber and used for structure determination. Diffraction intensity data were collected at 296(2) K on a Siemens P4 diffractometer up to $(2\theta)_{max}$ of 51.0° with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω scan technique. A total of 2489 independent reflections were collected, among which 2164 reflections were considered as observed $[I > 2\sigma(I)]$ and used for the structure refinement. Usual Lp and empirical absorption corrections were applied.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL software [13]. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms of coordinated-water were located in a difference Fourier map and other hydrogen atoms were treated as riding atoms. Three carbon atoms, C1–C3, and two oxygen atoms of crystalline water, O3 and O4, were disordered with two orientations. Anisotropic refinement including all non-H atoms converged to agreement factors $R = 0.0236$ and $R_w = 0.0622$, where $w = 1/[\sigma^2(F_o^2) + (0.03798P)^2]$. The highest peak in the final difference Fourier map was 0.383 e Å^{-3}. Atomic scattering factors used were taken from International Tables for X-ray crystallography [14].

3. Results and discussion

3.1. *Crystal structure*

Crystal data: $C_{14}H_{24}N_{12}O_8Mn_2Mo$, $M = 694.27$, monoclinic, space group $C2/c$, $a = 15.665(2)$, $b = 14.616(2)$, $c = 12.307(2)$ Å, $\alpha = 90$, $\beta = 108.31(1)$, $\gamma = 90°$, $V = 2675.1(7)$ Å^3, $Z = 4$, $Dc = 1.724$ g cm^{-3}, $F(000) = 1392$, μ (Mo-Kα) = 1.452 mm^{-1}.

Fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in table 1. Selected bond distances and angles are listed in table 2.

The molecular structure of the title complex is presented in figure 1 as an ORTEP view of the molecule, together with the atomic labeling scheme. Each Mo(IV) atom has six –CN–Mn linkages and two terminal cyano ligands arranged in a square antiprismatic arrangement. The Mo–C bond lengths are between 2.146(3) and 2.172(3) Å, typical for octacyanomolybdates(IV) with metal or nonmetal cations [3, 15]. The mean Mo–C and C–N distances are 2.161(3) and 1.146(3) Å, respectively. The Mo–C–N bond angles, as expected, are almost linear with angles ranging from 176.9 to 179.2°. The Mn(II) atom is in a distorted octahedral environment formed by three MoCN → Mn linkages along with one imidazole and two water molecules cis. The Mn ← NC bond lengths range from 2.206(2) to 2.286(2) Å, which are slightly longer than those found in $[Mn(bpy)_2]_4[Mo(CN)_8]_2 \cdot 8H_2O$ [3] and $[Mn_2(tea)Mo(CN)_7] \cdot H_2O$ (tea = triethanolamine) [16]. The Mn–O distance values of 2.198(3) and 2.223(3) Å are comparable with those reported for $Mn_2(H_2O)_5Mo(CN)_7 \cdot 4H_2O$ [17], and slightly longer than those found in $[Mn(mal)(2,2'\text{-bpy})(H_2O)_2]$ (mal = malonate) [18].

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x/a	y/b	z/c	U_{eq}
Mo	5000	7059(1)	2500	14(1)
Mn	2981(1)	4193(1)	3249(1)	25(1)
O(1)	1863(2)	4711(2)	1772(2)	64(1)
O(2)	2304(2)	4963(2)	4277(2)	66(1)
O(3)	1803(3)	6352(3)	815(4)	56(2)
O(4)	4483(7)	9618(5)	6398(11)	91(3)
N(1)	3505(2)	3460(2)	2029(3)	50(1)
N(2)	4083(3)	3238(3)	637(4)	94(1)
N(3)	2023(2)	3005(2)	3210(2)	34(1)
N(4)	3910(2)	3723(2)	4911(2)	32(1)
N(5)	3758(2)	5412(2)	3074(2)	34(1)
N(6)	4871(2)	8673(2)	4311(2)	48(1)
C(1)	4049(17)	3714(18)	1515(19)	57(5)
C(2)	3335(7)	2727(8)	281(8)	96(4)
C(3)	2962(6)	2836(6)	1129(7)	75(3)
C(4)	1334(2)	2652(2)	2976(2)	23(1)
C(5)	4285(2)	3471(2)	5810(2)	22(1)
C(6)	4187(2)	5988(2)	2881(2)	23(1)
C(7)	4922(2)	8113(2)	3679(2)	27(1)

Table 2. Selected bond distances (Å) and angles (°).

Mo–C(6)	2.160(3)	Mo–C(5E)	2.172(3)
Mo–C(7)	2.146(3)	Mn–O(1)	2.223(2)
Mo–(C6A)	2.160(3)	Mn–O(2)	2.198(3)
Mo–C(7A)	2.146(3)	Mn–N(1)	2.202(3)
Mo–C(4B)	2.166(3)	Mn–N(3)	2.286(2)
Mo–C(4C)	2.166(3)	Mn–N(4)	2.214(2)
Mo–C(5D)	2.172(3)	Mn–N(5)	2.206(2)
C(7A)–Mo–C(5D)	74.35(9)	C(7A)–Mo–C(4B)	68.92(9)
C(6)–Mo–C(5D)	77.76(9)	C(6)–Mo–C(4B)	144.67(9)
C(6A)–Mo–C(5D)	72.27(9)	C(6A)–Mo–C(4B)	76.38(9)
C(4B)–Mo–C(5D)	124.40(9)	C(7)–Mo–C(4C)	68.92(9)
C(4C)–Mo–C(5D)	73.78(9)	C(7A)–Mo–C(4C)	77.55(10)
C(7)–Mo–C(5E)	74.35(9)	C(6)–Mo–C(4C)	76.38(9)
C(7A)–Mo–C(5E)	141.42(9)	C(6A)–Mo–C(4C)	144.67(9)
C(6)–Mo–C(5E)	72.27(9)	C(4B)–Mo–C(4C)	132.78(13)
C(6A)–Mo–C(5E)	77.76(9)	C(7)–Mo–C(5D)	141.42(9)
C(4B)–Mo–C(5E)	73.78(9)	O(2)–Mn–N(1)	172.62(11)
C(4C)–Mo–C(5E)	124.40(9)	N(4)–Mn–O(1)	168.86(11)
C(5D)–Mo–C(5E)	138.23(13)	N(3)–Mn–N(5)	172.00(8)
C(7)–Mo–C(7A)	88.20(14)	N(3)–C(4)–Mo(F)	176.9(2)
C(7)–Mo–C(6)	102.19(10)	N(4)–C(5)–Mo(E)	178.0(2)
C(7A)–Mo–C(6)	146.06(9)	N(5)–C(6)–Mo	179.2(2)
C(7)–Mo–C(6A)	146.06(9)	N(6)–C(7)–Mo	179.2(3)
C(7A)–Mo–C(6A)	102.19(10)	C(4)–N(1)–Mn	154.9(2)
C(6)–Mo–C(6A)	87.13(14)	C(5)–N(4)–Mn	170.6(2)
C(7)–Mo–C(4B)	77.55(10)	C(6)–N(5)–Mn	171.7(2)

Symmetry code. (A) $-x+1$, y, $-z+1/2$; (B): $x+1/2$, $y+1/2$, z; (C): $-x+1$, $y+1/2$, $-z+1/2$; (D): x, $-y+1$, $z-1/2$; (E): $-x+1$, $-y+1$, $-z+1$; (F): $x-1/2$, $y-1/2$, z.

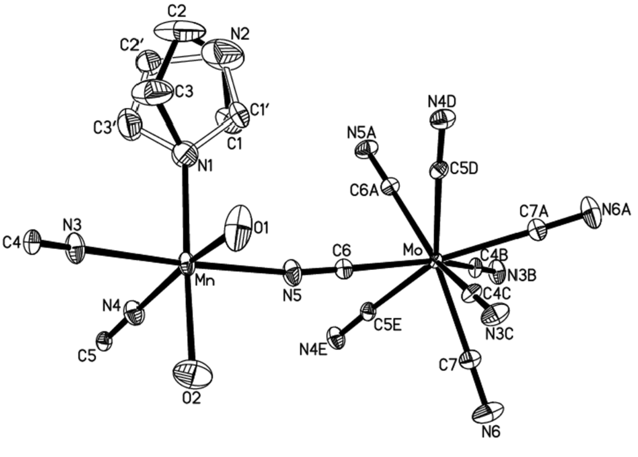

Figure 1. An ORTEP view of the title complex with atom labels, showing 35% probability displacement ellipsoids. H atoms are omitted for clarity.

The Mn–N (Imidazole) bond distance is 2.202(3) Å. Bond angles around Mn range from 84.16(9) to 101.60(10)° and from 168.86(11) to 172.62(11)°, instead of 90 and 180° for an ideal octahedron. The Mn–N–C(cyanide) bond angles significantly deviate from 180° ranging from 154.9(2) to 171.7(2)°.

As shown in figure 2, the title complex has a polymeric structure based on a network of $Mo(CN)_8$ units and Mn(II) ions with solvate water molecules. Each $Mo(CN)_8$

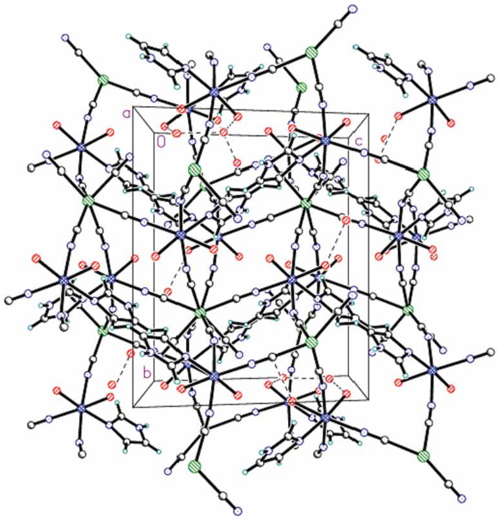

Figure 2. View of the three-dimensional network of the title complex.

building block is linked to Mn(II) ions through its six CN ligands, forming a three-dimensional framework. The shortest distances of adjacent Mo–Mn bridged by cyanide is 5.448 Å. Noncoordinated water molecules are located in the voids of the three-dimensional network. Hydrogen bonds exist between noncoordinated water molecules and coordinated water molecules (O1–H1A–O3 0.819(10), 1.867(15), 2.661(4), 163(4); O2–H2A–O4 0.819(10), 1.98(3), 2.729(11), 152(5), 7(566)). Nonbridging CN groups are also hydrogen-bonded with coordinated water molecules (O1–H1B–N6 0.817(10), 2.215(11), 3.031(4), 176(4), 4(545)).

3.2. *Infrared spectrum*

The two characteristic bands of the CN groups in the region between 2100 and 2200 $\mathrm{cm^{-1}}$ indicate both their bridging and terminal functions, and this is in agreement with the IR spectra of $[(\mathrm{Me_3Sn})_4\mathrm{Mo(CN)_8}]$ with a three-dimensional network structure, where $\nu_{(\mathrm{C{\equiv}N})}$ bands at 2143 and 2105 $\mathrm{cm^{-1}}$ were observed [19]. The band located at 2104 $\mathrm{cm^{-1}}$ can be attributed to the terminal cyanide groups. It is well-known that a shift of $\nu_{(\mathrm{C{\equiv}N})}$ to high frequency is observed in most cases for octacyanomolybdate(IV)–M(II) polymers [20]. Therefore, the band of 2145 $\mathrm{cm^{-1}}$ at higher frequency is assigned to the bridging cyanide groups. The higher frequency band is stronger than the lower one, suggesting that most of the CN groups are bridging [11]. This is in accord with the X-ray structure.

3.3. *Magnetic properties*

Variable temperature magnetic susceptibility measurements (5–300 K) for the title complex were carried out at a magnetic field of 10000 Oe on a crystalline sample taken from the same uniform batch used for the structural determination. The magnetic behavior is shown in figure 3, in the form of $\chi_\mathrm{M}T$ versus T. At 300 K, $\chi_\mathrm{M}T$ has a value of 8.73 $\mathrm{emu\,K\,mol^{-1}}$, corresponding to the value of 8.75 $\mathrm{emu\,K\,mol^{-1}}$ expected

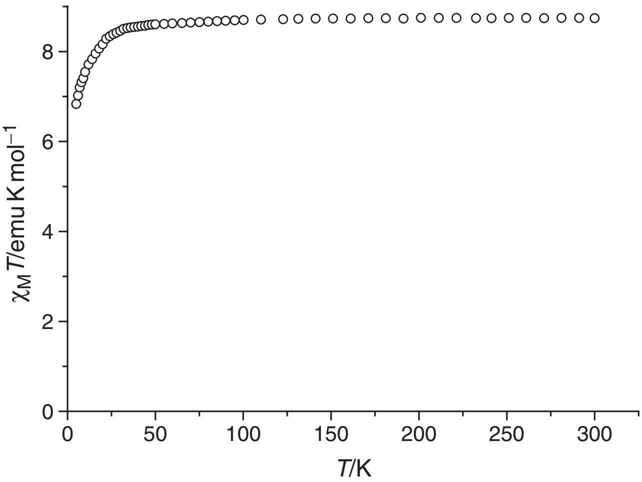

Figure 3. Magnetic data for the $[Mn(ImH)(H_2O)_2]_2[Mo(CN)_8] \cdot 4H_2O\}_n$ crystalline sample at 5–300 K.

for two high-spin isolated $Mn^{II}(S = 5/2)$ ions. On cooling, $\chi_M T$ is almost constant and slowly decreased at low temperature. A decrease in the low temperature $\chi_M T$ data may have two main origins: the presence of an antiferromagnetic coupling between Mn^{2+} ions through the NC–Mo^{IV}–CN diamagnetic bridges within the three-dimensional network and zero-field splitting of the $^6A_{1g}$ ground state imposed by a distortion of the Mn^{2+} octahedron [21]. This behaviour is similar to what has been observed in the one-dimensional complex $[Mn_2^{II}(L)_2(H_2O)][Mo^{IV}(CN)_8] \cdot H_2O$ (L = macrocycle) [8].

Supplementary material

Full lists of crystallographic data are available from the author upon request.

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