

Synthesis, Crystal Structures, and Magnetic Properties of One-dimensional Lanthanide(III)-Octacyanomolybdate(V) Assemblies with 3,4,7,8-Tetramethyl-1,10-phenanthroline as a Blocking Ligand

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The study of molecular magnets is a hot topic in the field of material science because of its promising application in the future. Cyanide is usually applied as a bridging ligand between spin carriers, which is due to the fact that cyanide can mediate foreseeable magnetic coupling interaction. Recently, cyano-bridged bimetallic systems based on octacyanometalates $[M^{IV(V)}(CN)_8]^{4-(3-)}$ ($M = Mo, W$ and Nb) have attracted great attention in molecular magnetism because of their interesting and special properties.^{1,2} Comparing to the widely investigated hexacyanometalate, the octacyanometalate building blocks are more versatile due to more spatial configurations (*e.g.*, square antiprism (D_{4d}), dodecahedron (D_{2d}) and bicapped trigonal prism (C_{2v})), so that the octacyanometalate-based complexes show rich magnetic properties from low-dimensional magnets (SMMs and SCMs)³ to long-range ordered magnets.⁴⁻⁶ On the other hand, lanthanide ions have been widely used in the field of molecular magnets because of its considerable single ion anisotropy and high spin numbers.⁷ Furthermore, the lanthanide ions often have high coordination numbers, so the complexes containing lanthanide ions may have a lot of very complicated structures, further show interesting magnetic properties.^{8,9} Therefore, the association of lanthanide with paramagnetic octacyanometalate building blocks seems to be an interesting way in the field of molecular magnets. In fact, the investigation of octacyanometalate-based bimetallic systems has mainly focused on first-row transition-metal ions^{10,11} and there are a few of coordination complexes containing octacyanometalates and lanthanide ions.¹²⁻¹⁴ 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) as a blocking ligand has been used in the construction of hexacyanometalate-based low-dimensional magnets.^{15,16} Similarly, we choose tmphen as the additional ligand to obtain two 1D lanthanide octacyanometalate-based metal assemblies, $[Ln(tmphen)_2(DMF)_2Mo(CN)_8]$ ($Ln = Tb(1)$ and $Dy(2)$, $DMF = N,N$ -dimethylformamide). Herein, the synthesis, structures, and magnetic properties are reported.

Experimental Section

Materials and Physical Measurements. The reagent 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) was pur-

chased from Aldrich and used without further purification. $Cs_3[W(CN)_8] \cdot 2H_2O$ was prepared according to literature.¹⁷ All other reagents were commercial available and used as received. Infrared spectra were obtained within the $4000\text{--}400\text{ cm}^{-1}$ as KBr disks on a VECTOR 22 spectrometer. Elemental analyses were performed on a Perkin Elmer 240C elemental analyzer. Magnetic measurements on microcrystalline sample were carried out on a Quantum Design MPMP-XL7 superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were made for both the sample holder as the background and the compound estimated from Pascal's constants.¹⁸

Synthesis of Complexes 1-2. To a solution of $Tb(NO_3)_3 \cdot 6H_2O$ (0.1 mmol, 45.3 mg) or $Dy(NO_3)_3 \cdot 6H_2O$ (0.1 mmol, 45.6 mg) and $Cs_3[Mo(CN)_8] \cdot 4H_2O$ (15.5 mg, 0.02 mmol) in H_2O (5 mL), a solution of tmphen (4.7 mmol, 0.02 mmol) in CH_3CN (2 mL) was added dropwise with gentle stirring. The yellow precipitate was dissolved using *ca.* 2 mL of DMF. The resulting solution mixture was allowed to stand in the dark without disturbance for several weeks and red prism single crystals suitable for X-ray analysis were obtained.

Complex 1: Yield 8.9 mg (41.1%). Calculated for $C_{46}H_{46}N_{14}O_2MoTb$: C, 51.07%; H, 4.29%; N, 18.13%. Found: C, 51.15%; H, 4.30%; N, 18.32%, IR stretching cyanide (KBr)/ cm^{-1} : 2118, 2160.

Complex 2: Yield 9.1 mg (41.9%). Calculated for $C_{46}H_{46}N_{14}O_2MoDy$: C, 50.90%; H, 4.27%; N, 18.07%. Found: C, 50.84%; H, 4.26%; N, 17.91%, IR stretching cyanide (KBr)/ cm^{-1} : 2121, 2154.

Structural Determination and Refinement. The crystal structures were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated $Mo-K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at room temperature. All absorption corrections were performed by using the SADABS program.¹⁹ Structures were solved by direct methods using the program SHELXL-97.²⁰ All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. A summary of the structural determination and refinement for the title complexes 1-2 is listed in Table 1 and the selected bond distances and angles are shown in Tables

Table 1. Crystal and experimental data of complexes **1-2**

Complex	1	2
Empirical formula	C ₄₆ H ₄₆ N ₁₄ O ₂ MoTb	C ₄₆ H ₄₆ N ₁₄ O ₂ MoDy
Formula weight	1081.84	1085.41
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> / Å	16.643(1)	16.448(1)
<i>b</i> / Å	21.637(2)	21.738(2)
<i>c</i> / Å	25.518(2)	25.410(2)
α / °	90.00	90.00
β / °	90.00	90.00
γ / °	90.00	90.00
<i>V</i> / Å ³	9189(1)	9085(1)
<i>Z</i>	8	8
<i>D</i> _{calc} /g·cm ⁻³	1.564	1.587
<i>F</i> (000)	4344	4352
Limits of data collection/°	1.74 ≤ θ ≤ 26.00	1.60 ≤ θ ≤ 25.00
Reflections collected	47344	46657
Independent reflections (<i>R</i> _{int})	9023 (0.0936)	7988 (0.0901)
Goodness of fit	1.112	1.077
<i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0519, <i>wR</i> ₂ = 0.1220	<i>R</i> ₁ = 0.0453, <i>wR</i> ₂ = 0.1163
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0627, <i>wR</i> ₂ = 0.1276	<i>R</i> ₁ = 0.0764, <i>wR</i> ₂ = 0.1359

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$$

Table 2. Selected bond distances (Å) and angles (°) for **1**

Mo(1)-C(1)	2.150(5)	Mo(1)-C(2)	2.152(6)
Mo(1)-C(3)	2.169(7)	Mo(1)-C(4)#2	2.145(5)
Mo(1)-C(5)	2.162(7)	Mo(1)-C(6)	2.145(7)
Mo(1)-C(7)	2.150(6)	Mo(1)-C(8)	2.166(7)
Tb(1)-O(1)	2.313(4)	Tb(1)-O(2)	2.329(4)
Tb(1)-N(1)	2.476(4)	Tb(1)-N(4)	2.478(4)
Tb(1)-N(9)	2.546(4)	Tb(1)-N(10)	2.550(5)
Tb(1)-N(11)	2.559(4)	Tb(1)-N(12)	2.557(4)
N(1)-C(1)-Mo(1)	176.0(5)	N(2)-C(2)-Mo(1)	176.6(6)
N(3)-C(3)-Mo(1)	178.6(6)	N(4)-C(4)-Mo(1)#1	178.9(5)
N(5)-C(5)-Mo(1)	179.3(7)	N(6)-C(6)-Mo(1)	178.4(6)
N(7)-C(7)-Mo(1)	178.1(6)	N(8)-C(8)-Mo(1)	176.9(7)
C(1)-N(1)-Tb(1)	166.7(4)	C(4)-N(4)-Tb(1)	176.8(5)

Symmetry transformations used to generate equivalent atoms: 1 -x+3/2, y+1/2, z; #2 -x+3/2, y-1/2, z.

2-3.

Results and Discussions

Crystal Structures of Complexes 1-2. Complexes **1-2** have the same structural skeleton with the orthorhombic space group *Pbca*, we only depict the crystal structure of complex **1** in detail. As shown in Figure 1, the asymmetric unit of complex **1** consists of a [Tb(tmphen)₂(DMF)₂]³⁺ and a [Mo(CN)₈]³⁻. The eight coordination environment around Tb ion is composed of two tmphen, two DMF molecules and two bridging cyanide ligands forming a distorted square

Table 3. Selected bond distances (Å) and angles (°) for **2**

Mo(1)-C(1)	2.165(7)	Mo(1)-C(2)	2.165(7)
Mo(1)-C(3)	2.145(8)	Mo(1)-C(4)	2.162(8)
Mo(1)-C(5)	2.164(7)	Mo(1)-C(6)	2.162(7)
Mo(1)-C(7)	2.142(8)	Mo(1)-C(8)	2.155(8)
Dy(1)-O(1)	2.277(5)	Dy(1)-O(2)	2.311(5)
Dy(1)-N(1)	2.464(5)	Dy(1)-N(5)#1	2.459(6)
Dy(1)-N(9)	2.520(5)	Dy(1)-N(10)	2.507(5)
Dy(1)-N(11)	2.538(5)	Dy(1)-N(12)	2.537(5)
N(1)-C(1)-Mo(1)	176.1(6)	N(2)-C(2)-Mo(1)	178.0(7)
N(3)-C(3)-Mo(1)	179.9(8)	N(4)-C(4)-Mo(1)	178.7(7)
N(5)-C(5)-Mo(1)	178.7(6)	N(6)-C(6)-Mo(1)	175.9(6)
N(7)-C(7)-Mo(1)	176.6(7)	N(8)-C(8)-Mo(1)	179.2(6)
C(1)-N(1)-Dy(1)	167.4(5)	C(5)-N(5)-Dy(1)#2	177.3(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2, y+1/2, z; #2 -x+3/2, y-1/2, z.

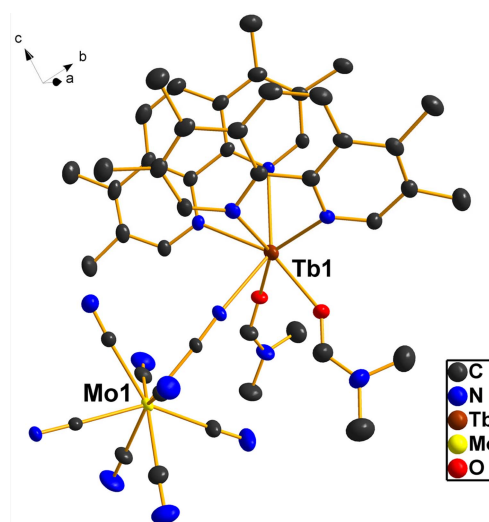


Figure 1. ORTEP drawing of the asymmetrical unit of **1** with atomic labeling for metal ions and donor atoms. Displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms have been omitted for clarity.

anti-prism. Two tmphen and two DMF molecules coordinate to Tb ion on two sides, and the tmphen molecules stabilize the structure by intramolecule π - π stacking effect. The Tb-N_{tmphen} bond lengths range from 2.546(4) to 2.559(4) Å, the Tb-N_{CN} from 2.476(4) to 2.478(4) Å, and the Tb-O_{DMF} distances are slightly shorter in the range of 2.313(4)-2.329(4) Å. The Tb-N \equiv C linkages are poorly linear with the angles of 166.7(4) and 176.8(5) Å. In all complexes **1-2**, the bond lengths and angles related to lanthanide ions are in good agreement with those in the reported literature.^{15b} Mo^V(CN)₈ takes a slightly distorted square anti-prism geometry, in which two cyanides (C1N1 and C4N4) connect to the two neighboring [Tb(tmphen)₂(DMF)₂]³⁺ units by cisoid mode to form a chain structure, while the other cyanides are terminal. The Mo-CN bond lengths range from 2.145(5) to 2.169(7) Å, the C \equiv N from 1.132(8) to 1.151(8) Å, and the Mo-C \equiv N linkages are almost linear from 176.0(5)° to 179.3(7)°. For complex **2**, the Mo-CN bond lengths range

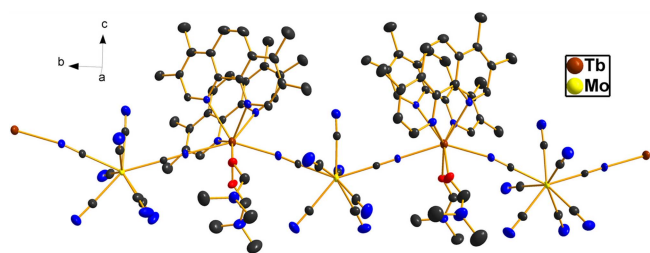


Figure 2. The 1D infinite structure of **1** along *bc* plane. Hydrogen atoms have been omitted for clarity.

from 2.142(8) to 2.165(7) Å, the C≡N from 1.143(9) to 1.162(9) Å, and the Mo–C≡N linkages are from 175.9(6)° to 179.9(8)°. All bond lengths and angles based Mo(CN)₈ in complexes **1–2** are comparable with those in reported literatures.^{3–6}

In complex **1**, [Tb(tmphen)₂(DMF)₂]³⁺ and [Mo(CN)₈]^{3–} ions are linked in an alternating fashion to form a 1D cyano-bridged chain as shown in Figure 2. In a unit cell, four equivalent chains separate from each other with a minimum intermetallic distance between Tb and Mo of 11.348 Å. The intramolecular distances Tb–Mo is 5.719 Å (Tb–C1≡N1–Mo) and 5.758 Å (Tb–C4≡N4–Mo). The Mo1–Tb–Mo1 angle is 140.99° for **1**, which is an indication of the zig-zag chain structure. In the solid state, the neighboring {Tb^{III}Mo^V}_n chains weakly interact through the face-to-face π–π stacking of the tmphen aromatic rings, leading to the 2D supra-molecular folded layer. However, no hydrogen bonding is observed, so the structure of the solid state for complex **1** is stabilized mainly by van der Waals forces.

Magnetic Properties of Complex 1–2. In lanthanide complexes, the spin-orbital coupling leads to the 4fⁿ configuration splitting into ^{2S+1}L_J states, and further into Stark components under the crystal-field perturbation. So, usually, the variable-temperature magnetic behavior of lanthanide-based complexes mainly arises from the significant orbital contributions of Ln^{III} ions (with the exception of Gd^{III}). Above room temperature, all of the Stark levels are populated, but as the temperature decreases, the effective magnetic moment of the lanthanide ion will change as a result of thermal depopulation of the Stark sublevels.

For **1**, $\chi_M T$ slowly decreases from 12.28 cm³ K mol^{–1} at 300 K (spin-only values of 11.815 cm³ K mol^{–1} for isolated Tb^{III} (*J* = 6, *g* = 3/2) and 0.375 cm³ K mol^{–1} for Mo^V (*S* = 1/2, *g* = 2)) to a minimum of 9.40 cm³ K mol^{–1} at 5 K, which is mainly ascribed to the depopulation of the Stark levels of the terbium ⁷F₆ ground state. Upon cooling, the value increases to a maximum of 10.06 cm³ K mol^{–1} at 1.8 K, which indicates that the coupling interaction between metal ions overcomes the depopulation of the ground state leading to a net spin along the field, but cannot draw a conclusion about the magnetic coupling nature. The variable-field magnetic properties show that the magnetization undiversified increases with the external field and goes up to 5.69 *N*μ_B mol^{–1} at 7 T which is consistent with the ferromagnetic ground state spin based on a spin of *S* = 1/2 with *g* = 2 for Mo^V ion and an effective spin

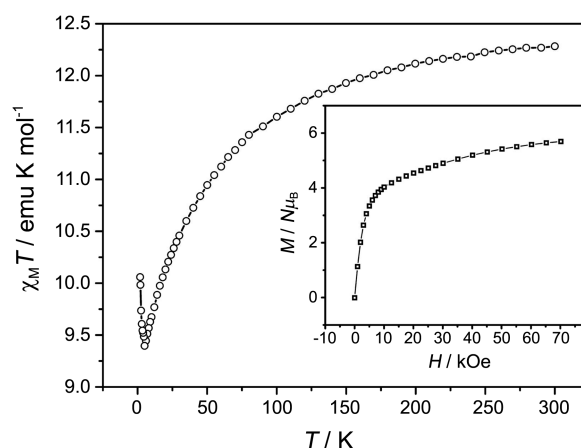


Figure 3. Temperature dependence of the $\chi_M T$ product for **1** at 100 Oe. The inset shows the magnetization versus the applied magnetic field at 1.8 K.

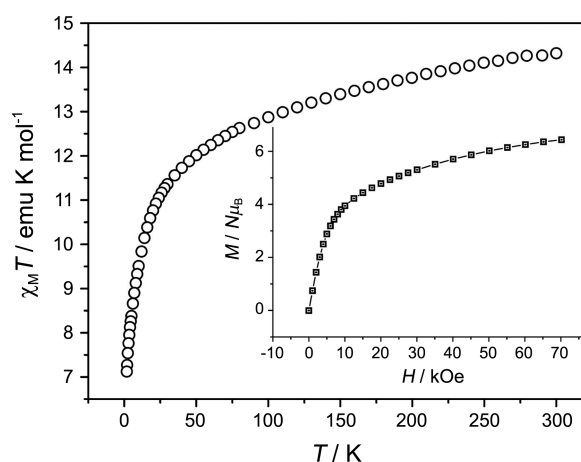


Figure 4. Temperature dependence of the $\chi_M T$ product for **2** at 100 Oe. The inset shows the magnetization versus the applied magnetic field at 1.8 K.

of *S* = 1/2 with *g*_{||} = 10 and *g*_⊥ = 0 for Tb^{III} ion.^{6,12–14} So, it is suggested that the cyano-bridge mediates the ferromagnetic interaction between Mo^V and Tb^{III} ions.

For **2**, the $\chi_M T$ value is 14.32 cm³ K mol^{–1} at the room temperature, slightly lower than the sum of the spin-only values of 14.145 cm³ K mol^{–1} expected for isolated Dy^{III} and 0.375 cm³ K mol^{–1} for Mo^V. Upon cooling, $\chi_M T$ value invariably decreases and reaches 7.12 cm³ K mol^{–1} at 1.8 K (Figure 4). The variable-field magnetic properties show that the magnetization monotonously increases with the external field and goes up to 6.44 *N*μ_B mol^{–1} at 7 T, indicating that the cyano-bridge also mediates the ferromagnetic interaction between Mo^V and Dy^{III} ions (1 + 5.23) *N*μ_B.²¹ No increase of $\chi_M T$ observed at low temperature like that of complex **2** implies that the ferromagnetic interaction is very weak relative to the depopulation of the Stark levels of the Dy^{III} ion.

In conclusion, we report here the synthesis, structures, and magnetic characterization of two new one-dimensional cyano-bridged coordination polymers [Ln(tmphen)₂(DMF)₂–

$\text{Mo}(\text{CN})_8]_\infty$ (Ln = Tb(**1**) and Dy(**2**)). Two complexes are isostructural and crystallize in the orthorhombic space group *Pbca*. Magnetic investigations show that the ferromagnetic interaction exists in complexes **1-2**.

Supplementary Material. CCDC-836416(**1**) and 836411(**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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