

# 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.<sup>1,2</sup> 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)<sup>3</sup> to long-range ordered magnets.<sup>4-6</sup> 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.<sup>7</sup> 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.<sup>8,9</sup> 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<sup>10,11</sup> and there are a few of coordination complexes containing octacyanometalates and lanthanide ions.<sup>12-14</sup> 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.<sup>15,16</sup> 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.<sup>17</sup> All other reagents were commercial available and used as received. Infrared spectra were obtained within the 4000-400  $cm^{-1}$  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.<sup>18</sup>

**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.<sup>19</sup> Structures were solved by direct methods using the program SHELXL-97.<sup>20</sup> 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	<b>1</b>	<b>2</b>
Empirical formula	C <sub>46</sub> H <sub>46</sub> N <sub>14</sub> O <sub>2</sub> MoTb	C <sub>46</sub> H <sub>46</sub> N <sub>14</sub> O <sub>2</sub> 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)
$\alpha$ / °	90.00	90.00
$\beta$ / °	90.00	90.00
$\gamma$ / °	90.00	90.00
<i>V</i> / Å <sup>3</sup>	9189(1)	9085(1)
<i>Z</i>	8	8
<i>D</i> <sub>calc</sub> / g·cm <sup>-3</sup>	1.564	1.587
<i>F</i> (000)	4344	4352
Limits of data collection <sup>o</sup>	1.74 ≤ θ ≤ 26.00	1.60 ≤ θ ≤ 25.00
Reflections collected	47344	46657
Independent reflections ( <i>R</i> <sub>int</sub> )	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> <sub>1</sub> = 0.0519, <i>wR</i> <sub>2</sub> = 0.1220	<i>R</i> <sub>1</sub> = 0.0453, <i>wR</i> <sub>2</sub> = 0.1163
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0627, <i>wR</i> <sub>2</sub> = 0.1276	<i>R</i> <sub>1</sub> = 0.0764, <i>wR</i> <sub>2</sub> = 0.1359

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \omega R_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]^{1/2}}$$

**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.

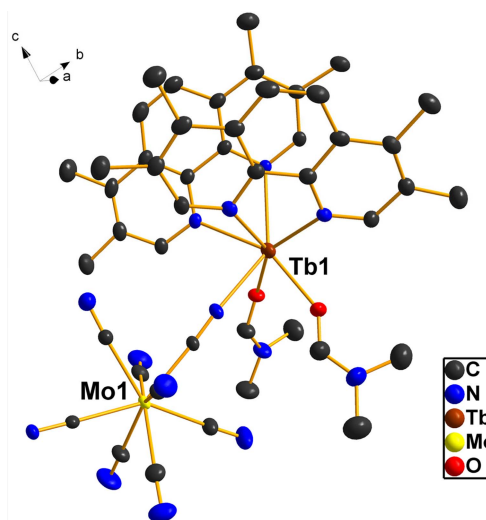
## Results and Discussions

**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)<sub>2</sub>(DMF)<sub>2</sub>]<sup>3+</sup> and a [Mo(CN)<sub>8</sub>]<sup>3-</sup>. 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**

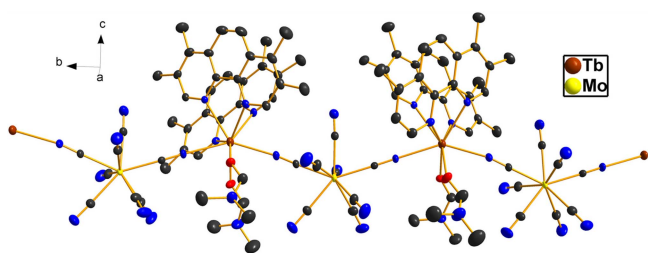
Mo(1)-C(1)	2.165(7)	Mo(1)-C(2)	2.165(7)
Mo(1)-C(3)	2.145(8)	Mo(1)-C(4)	2.162(8)
Mo(1)-C(5)	2.164(7)	Mo(1)-C(6)	2.162(7)
Mo(1)-C(7)	2.142(8)	Mo(1)-C(8)	2.155(8)
Dy(1)-O(1)	2.277(5)	Dy(1)-O(2)	2.311(5)
Dy(1)-N(1)	2.464(5)	Dy(1)-N(5)#1	2.459(6)
Dy(1)-N(9)	2.520(5)	Dy(1)-N(10)	2.507(5)
Dy(1)-N(11)	2.538(5)	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  $\pi$ - $\pi$  stacking effect. The Tb-N<sub>tmphen</sub> bond lengths range from 2.546(4) to 2.559(4) Å, the Tb-N<sub>CN</sub> from 2.476(4) to 2.478(4) Å, and the Tb-O<sub>DMF</sub> distances are slightly shorter in the range of 2.313(4)-2.329(4) Å. The Tb-N≡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.<sup>15b</sup> Mo<sup>V</sup>(CN)<sub>8</sub> takes a slightly distorted square anti-prism geometry, in which two cyanides (C1N1 and C4N4) connect to the two neighboring [Tb(tmphen)<sub>2</sub>(DMF)<sub>2</sub>]<sup>3+</sup> 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≡N from 1.132(8) to 1.151(8) Å, and the Mo-C≡N linkages are almost linear from 176.0(5)° to 179.3(7)°. For complex **2**, the Mo-CN bond lengths range



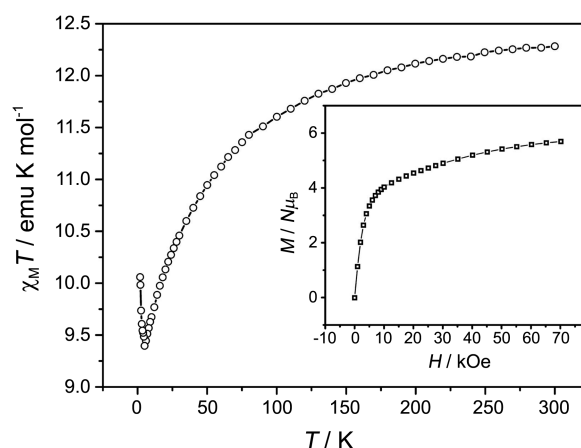
**Figure 2.** The 1D infinite structure of **1** along *bc* plane. Hydrogen atoms have been omitted for clarity.

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)<sub>8</sub> in complexes **1–2** are comparable with those in reported literatures.<sup>3–6</sup>

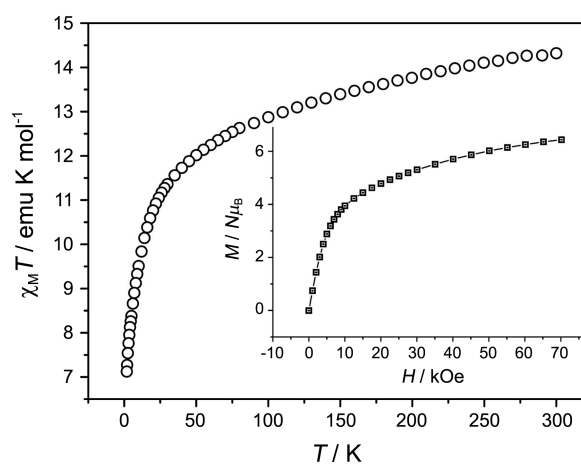
In complex **1**, [Tb(tmphen)<sub>2</sub>(DMF)<sub>2</sub>]<sup>3+</sup> and [Mo(CN)<sub>8</sub>]<sup>3–</sup> ions are linked in an alternating fashion to form a 1D cyano-bridged chain as shown in Figure 2. In a unit cell, four equivalent chains separate from each other with a minimum intermetallic 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<sup>III</sup>Mo<sup>V</sup>}<sub>n</sub> 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 4f<sup>n</sup> configuration splitting into <sup>2S+1</sup>L<sub>J</sub> 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<sup>III</sup> ions (with the exception of Gd<sup>III</sup>). 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 cm<sup>3</sup> K mol<sup>–1</sup> at 300 K (spin-only values of 11.815 cm<sup>3</sup> K mol<sup>–1</sup> for isolated Tb<sup>III</sup> (*J* = 6, *g* = 3/2) and 0.375 cm<sup>3</sup> K mol<sup>–1</sup> for Mo<sup>V</sup> (*S* = 1/2, *g* = 2)) to a minimum of 9.40 cm<sup>3</sup> K mol<sup>–1</sup> at 5 K, which is mainly ascribed to the depopulation of the Stark levels of the terbium <sup>7</sup>F<sub>6</sub> ground state. Upon cooling, the value increases to a maximum of 10.06 cm<sup>3</sup> K mol<sup>–1</sup> 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<sub>B</sub> mol<sup>–1</sup> 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<sup>V</sup> 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*<sub>||</sub> = 10 and *g*<sub>⊥</sub> = 0 for Tb<sup>III</sup> ion.<sup>6,12–14</sup> So, it is suggested that the cyano-bridge mediates the ferromagnetic interaction between Mo<sup>V</sup> and Tb<sup>III</sup> ions.

For **2**, the  $\chi_M T$  value is 14.32 cm<sup>3</sup> K mol<sup>–1</sup> at the room temperature, slightly lower than the sum of the spin-only values of 14.145 cm<sup>3</sup> K mol<sup>–1</sup> expected for isolated Dy<sup>III</sup> and 0.375 cm<sup>3</sup> K mol<sup>–1</sup> for Mo<sup>V</sup>. Upon cooling,  $\chi_M T$  value invariably decreases and reaches 7.12 cm<sup>3</sup> K mol<sup>–1</sup> 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<sub>B</sub> mol<sup>–1</sup> at 7 T, indicating that the cyano-bridge also mediates the ferromagnetic interaction between Mo<sup>V</sup> and Dy<sup>III</sup> ions (1 + 5.23) *N*μ<sub>B</sub>.<sup>21</sup> 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<sup>III</sup> ion.

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

Mo(CN)<sub>8</sub>]<sub>∞</sub> (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](mailto:deposit@ccdc.cam.ac.uk)].

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