Three Octacyanometallate-Based Ln^{III}–M^V (Ln = La, Ce; M = Mo, W) Bimetallic Assemblies with a One-Dimensional Rope-Ladder Chain Structure

Su-Yan Qian,[a] Hu Zhou,[a] Ying Zhang,[a] and Ai-Hua Yuan*[a]

Abstract. Three octacyanometallate-based hetero-bimetallic complexes, $[Ln(H_2O)_4(CH_3CN)_2][M(CN)_8]\cdot CH_3CN$ [Ln = La, M = Mo(**1**), W(**2**); Ln = Ce, M = W(**3**)], were synthesized and characterized structurally. Single-crystal X-ray analysis reveals that **1**–**3** are isomorphous and consist of infinite one-dimensional (1D) 3,3 rope-ladder chains, in which the 12-membered puckered square $Ln_2M_2(CN)_4$ is the basic building unit. The 1D chains are further linked through interchain hydrogen bonds, resulting in a three-dimensional (3D) supramolecular network.

Introduction

In the past few years, octacyanometallates with higher coordination numbers were intensively studied [1]. $[M(CN)_8]^{3-/4-}$ (M = Mo, W) ions, which act as a versatile class of building blocks, can adopt three different spatial configurations, e.g., square antiprismatic (SAPR-8), dodecahedral (DD-8), and bicapped trigonal prismatic (TPRS-8), depending on their surrounding, such as the coordination ligands, and the second metal ions. Numerous octacyano- and transition-metal-based complexes were synthesized and these materials produced various dimensional molecular structures and further displayed exciting magnetism properties such as high Curie temperatures [2], photo-magnetism [3], and single-molecule magnetism [4].

As lanthanide ions often have higher coordination numbers, the combination of $[M(CN)_8]^{3-/4-}$ with the lanthanide ions will afford more complicated topologies and magnetic behaviors than 3d–4d/5d compounds. However, the synthesis of such materials is still challenging owning to the tendency of the rare earth metal ions to adopt high coordination numbers and their ability to easily adapt to a given environment [5]. For instance, *Sieklucka* et al. synthesized a family of two-dimensional (2D) bilayered networks of the general formula $Ln(H_2O)_5M(CN)_8$ (Ln = Eu, Tb, Sm, Gd; M = Mo, W) [5a, 5d] by the reaction of $[M(CN)_8]^{3-}$ and $Ln(NO_3)_3\cdot nH_2O$ in the acetonitrile solution. Among them, $Tb(H_2O)_5W(CN)_8$ presents long-range magnetic ordering and interesting luminescence.

More recently, using the above similar building-block methodology, we have tried to employ $[M(CN)_8]^{3-}$ (M = Mo, W) and $Ln(NO_3)_3\cdot 6H_2O$ (Ln = La, Ce) as precursors to generate $M^V Ln^{III}$ heterometallic layered assemblies. To our surprise,

three one-dimensional (1D) isomorphous complexes with 3,3 rope-ladder chain structure, $[Ln(H_2O)_4(CH_3CN)_2][M(CN)_8]\cdot CH_3CN$ [Ln = La, M = Mo(**1**), W(**2**); Ln = Ce, M = W(**3**)], have been obtained. To the best of our knowledge, octacyanometallate-based complexes with the rope-ladder chain structure are rare [6, 7]. In addition, **1** and **2** present the first examples of bimetallic assemblies involving octacyanometallates and La^{III} atom.

Results and Discussion

Structural Descriptions of 1–3

Single-crystal X-ray diffraction analysis reveals that **1**–**3** are isomorphous and crystallize in the *Pnma* space group. The crystallographic data collection and refinement parameters for **1**–**3** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2, 3, 4. Herein, only the structure of **1** is described in detail. In the structure of **1** (Figure 1), each Mo1 atom has three bridging and five terminal cyano ligands arranged in a slightly distorted square-antiprismatic fashion (Figure 2 a), which is typical for $[Mo(CN)_8]^{3-}$-based complexes [8]. The Mo–C distances range from 2.146(6) to 2.181(4) Å, and the Mo–C–N angles remain almost linear with the maximum deviation from linearity of 4.1°.

The La1 atom exhibits a nine-coordinated environment with three cyano nitrogen atoms, two nitrogen atoms from two coordinated acetonitrile molecules as blocking ligands, and four oxygen atoms from coordinated water molecules. The coordination around lanthanum is slightly distorted tricapped trigonal prismatic with the capping position occupied by N3^{iii}, N6, and N7 (Figure 2b). The mean La–N and La–O bond lengths are 2.679 Å and 2.539 Å, respectively. Due to the large ionic radii of the lanthanide(III) atoms, the cyanide bridges are exceptionally long and the La–N–C bonds are strongly bent with the angles ranging from 157.3(3)° to 164.7(4)°, opposition to the

* Prof. Dr. A.-H. Yuan
 E-Mail: aihuayuan@163.com
[a] School of Material Science and Engineering
 Jiangsu University of Science and Technology
 Zhenjiang 212003, P. R. China

Table 1. Crystal data and structure refinement of X-ray data collection for **1**–**3**.

Complex	**1**	**2**	**3**
Formula	$C_{14}H_{17}LaN_{11}O_4Mo$	$C_{14}H_{17}LaN_{11}O_4W$	$C_{14}H_{17}CeN_{11}O_4W$
M_r	638.20	726.10	727.31
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$Pnma$	$Pnma$	$Pnma$
a /Å	25.342(4)	25.052(10)	25.021(5)
b /Å	9.3626(13)	9.315(4)	9.287(2)
c /Å	10.0711(14)	9.959(4)	9.943(2)
α /°	90.00	90.00	90.00
V /Å^3	2389.5(6)	2324.2(17)	2310.5(9)
Z	4	4	4
D_c /g·cm^{-3}	1.766	2.067	2.082
μ /mm^{-1}	2.329	6.801	6.962
GOF on F^2	1.179	1.048	1.080
R_1, ωR_2 [$I > 2\sigma(I)$]	0.0331, 0.0821	0.0306, 0.0680	0.0224, 0.0496
R_1, ωR_2 (all data)	0.0343, 0.0827	0.0413, 0.0713	0.0271, 0.0511

Table 2. Selected bond lengths /Å and angles /° for **1**.

Mo1–C1	2.181(4)	La1–N3^{iii}	2.628(4)
Mo1–C2	2.146(6)	La1–N6	2.654(5)
Mo1–C3	2.176(5)	La1–N7	2.685(6)
Mo1–C4	2.165(4)	C1–N1	1.153(5)
Mo1–C5	2.160(4)	C2–N2	1.137(9)
La1–O1	2.529(3)	C3–N3	1.135(7)
La1–O2	2.549(3)	C4–N4	1.144(5)
La1–N1	2.714(3)	C5–N5	1.146(5)
Mo1–C1–N1	175.9(3)	Mo1–C5–N5	176.7(4)
Mo1–C2–N2	179.7(8)	La1–N1–C1	157.3(3)
Mo1–C3–N3	176.8(4)	La1–N3^{iii}–C3^{iii}	164.7(4)
Mo1–C4–N4	178.6(4)		
Symmetry code: (iii) $-x$, $-y$, $-z$			

Table 4. Selected bond lengths /Å and angles /° for **3**.

W1–C1	2.164(5)	Ce1–N3^{ii}	2.677(3)
W1–C2	2.165(4)	Ce1–N6	2.651(5)
W1–C3	2.174(4)	Ce1–N7	2.614(4)
W1–C4	2.139(6)	C1–N1	1.140(6)
W1–C5	2.157(4)	C2–N2	1.147(5)
Ce1–O1	2.495(2)	C3–N3	1.144(5)
Ce1–O2	2.525(3)	C4–N4	1.148(8)
Ce1–N1	2.596(4)	C5–N5	1.143(5)
W1–C1–N1	174.9(4)	W1–C5–N5	177.2(3)
W1–C2–N2	176.7(3)	Ce1–N1–C1	162.0(4)
W1–C3–N3	176.9(3)	Ce1–N3^{ii}–C3^{ii}	157.9(3)
W1–C4–N4	177.3(7)		
Symmetry code: (ii) $-x$, $-y$, $-z$.			

Table 3. Selected bond lengths /Å and angles /° for **2**.

W1–C1	2.174(5)	La1–N3^{iii}	2.608(6)
W1–C2	2.160(7)	La1–N6	2.626(7)
W1–C3	2.157(7)	La1–N7	2.672(7)
W1–C4	2.166(5)	C1–N1	1.144(6)
W1–C5	2.155(5)	C2–N2	1.150(9)
La1–O1	2.516(3)	C3–N3	1.147(9)
La1–O2	2.548(4)	C4–N4	1/146(7)
La1–N1	2.698(4)	C5–N5	1.147(7)
W1–C1–N1	177.6(4)	W1–C5–N5	176.8(5)
W1–C2–N2	179.1(6)	La1–N1–C1	157.1(4)
W1–C3–N3	174.4(6)	La1–N3^{iii}–C3^{iii}	162.3(5)
W1–C4–N4	176.4(5)		
Symmetry code: (iii) $-x$, $-y$, $-z$.			
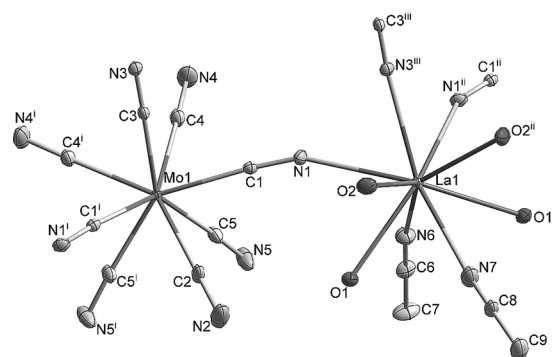
Figure 1. ORTEP diagram of **1**, showing the 30 % probability thermal motion ellipsoid. Hydrogen atoms and disorder solvent acetonitrile molecules were omitted for clarity. Symmetry codes: (i) x, $-y + 1/2$, z; (ii) x, $-y - 1/2$, z; (iii) $-x$, $-y$, $-z$.

linear Mo–C–N unit. The metric parameters of the *Ln* atom are in agreement to those observed in other octacyanomolybdate(V)- and lanthanide(III)-based complexes [5a, 5d].

As a result, the lanthanum and molybdenum atoms are linked in an alternating fashion to form a neutral 1D infinite 3,3 rope-ladder chain running parallel to the *b* axis (Figure 3), in which 12-membered puckered square with the *Ln* and tungsten atoms in the corners and the –CN– linkages on the edges, $La_2Mo_2(CN)_4$, is the basic building unit. Each unit cell has two equivalent chains and the nearest interchain distances for

Mo···Mo and Mo···La are about 9.409 Å and 6.988 Å, respectively. This rope-ladder chain structure was also observed in the hexacyanometallate-based bimetallic system $[Ni(en)_2]_3[M(CN)_6]_2 \cdot nH_2O$ (M = Cr, Mn, Fe, Co) [9]. It should be mentioned here that there are only three examples of this structural type were found in octacyanometallate-based complexes, $[Cu(cyclam)]_3[M(CN)_8]_2 \cdot 5H_2O$ (M = Mo, W) [6] and $\{Cs[Sm(MeOH)_3(DMF)(H_2O)Mo(CN)_8]H_2O\}_n$ [7].
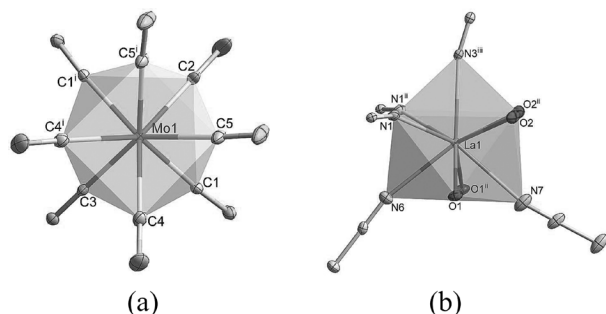
Figure 2. Coordination environments of (a) molybdenum, and (b) lanthanum atoms in the structure of **1**. Symmetry codes: (i) x, $-y+1/2$, z; (ii) x, $-y-1/2$, z; (iii) $-x$, $-y$, $-z$.
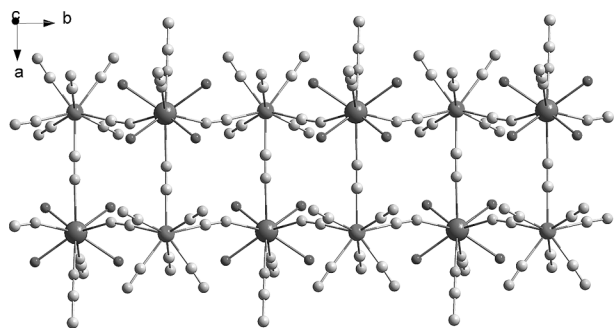

Figure 3. Projection of the 1D 3,3 rope-ladder chain structure for **1** running along the b axis. Hydrogen atoms and disorder solvent acetonitrile molecules were omitted for clarity.

Five terminal cyano ligands coordinated to the molybdenum atom and four water molecules coordinated to the lanthanum atom are involved in hydrogen bonding. Each $\{La^{III}Mo^V\}$ chain strongly interacts through hydrogen-bonding interactions [O1–H1A···N5^{iv} = 2.814(5) Å, O1–H1B···N2 = 2.946(5) Å,

O2–H2A···N4^v = 2.901(5) Å; symmetry codes: (iv): $-x+1/2$, $-y$, $z-1/2$; (v): x, y, $z-1$.] with six other surrounding chains to form a 3D supramolecular network (Figure 4).

Conclusions

Three isomorphous octacyanometallate-based complexes $[Ln(H_2O)_4(CH_3CN)_2][M(CN)_8]\cdot CH_3CN$ (Ln = La, M = Mo(**1**), W(**2**); Ln = Ce, M = W(**3**)) were synthesized and structurally characterized. Single-crystal X-ray diffraction analysis revealed that **1**–**3** consist of 1D 3,3 rope-ladder chains, which are further linked through interchain hydrogen bonds, resulting in a 3D supramolecular network.

Experimental Section

Materials and General Methods: All chemicals were of analytical grade and were used without further purification. The precursors $[HN(n-C_4H_9)_3]_3[M(CN)_8]\cdot 4H_2O$ (M = Mo, W) were prepared according to the published procedure [10]. *Caution!* The reactions must be carried out under low light conditions because $[M(CN)_8]^{3-}$ precursors are readily photo-reduced to $[M(CN)_8]^{4-}$.

$[Ln(H_2O)_4(CH_3CN)_2][M(CN)_8]\cdot CH_3CN$: [$Ln$ = La, M = Mo(**1**), W(**2**); Ln = Ce, M = W(**3**)]. Single crystals of **1**–**3** were prepared at room temperature in the dark by slow diffusion of an acetonitrile solution (3 mL) containing both $Ln(NO_3)_3\cdot 6H_2O$ (Ln = La, Ce) (0.05 mmol) into an acetonitrile solution (15 mL) of $[HN(n-C_4H_9)_3]_3[M(CN)_8]\cdot 4H_2O$ (M = Mo, W) (0.05 mmol). After two weeks, block-shaped yellow crystals were obtained. The crystallized samples of the title complexes (**1**–**3**) were very easy to pulverize to powder, with a color change from yellow to orange after they were removed from the mother liquor and exposed in air. The powder X-ray diffraction patterns (Figure 5) of the powder samples for **2** and **3** corresponded closely with that simulated from the structure of the two-dimensional layered complex $Sm(H_2O)_5W(CN)_8$ reported previously [5l], indicating that the these complexes were isostructural with closely similar framework geometries, and the phase transformation occurred after **1**–**3** were removed from the mother liquor. Based on above reasons, the samples of the title complexes used to other experiments (for example, IR and magnetic measurements) are very difficult to obtain. We have taken the following method when the single-crystal X-ray diffraction was performed: as soon as the well-shaped single crystals of **1**–**3** were removed from acetonitrile, it was immediately introduced into a glass capillary having an open end and fixed. Afterwards, the
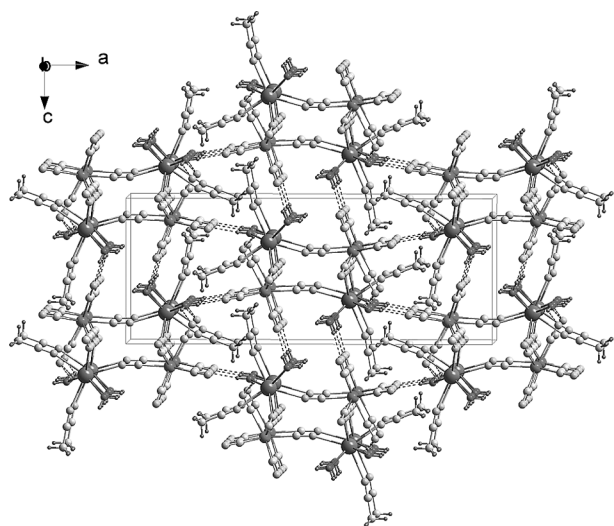

Figure 4. The 3D supramolecular network constructed from interchain hydrogen bonds of **1**. Disorder solvent acetonitrile molecules were omitted for clarity.
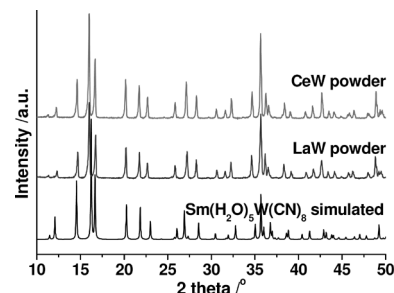

Figure 5. The powder X-ray diffraction patterns of LaW powder and CeW powder samples, compared to that simulated from the single crystal data of $Sm(H_2O)_5W(CN)_8$.

capillary was soon filled with the mother liquor, and sealed for single-crystal X-ray structure determination at 295(2) K.

X-ray Crystallographic Analysis: Single crystal X-ray diffraction measurements for **1**–**3** were carried out with a Bruker APEX II diffractometer equipped with Mo-K_α (λ = 0.71073 Å) radiation. Diffraction data analysis and reduction were performed within SMART, SAINT, and XPREP [11]. Correction for Lorentz, polarization, and absorption effects were performed within SADABS [12]. Structures were solved using Patterson method within SHELXS-97 [13] and refined using SHELXL-97 [14]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of coordinated acetonitrile ligands were calculated at idealized positions with C–H = 0.96 Å and included in the refinement in a riding mode with U_{iso} for H assigned as 1.5 times U_{eq} of the attached atoms. The hydrogen atoms bound to coordinated water molecules were located from difference maps and refining (O–H = 0.85 Å), with U_{iso}(H) = 1.5U_{eq}(O). All atoms of solvent acetonitrile molecules are disorder over two crystallographic positions with the occupancies of 25 % and 75 %, respectively. The hydrogen atoms of these disordered acetonitrile molecules are not found. CCDC-760629 (**1**), CCDC-760630 (**2**), and CCDC-760631 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

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