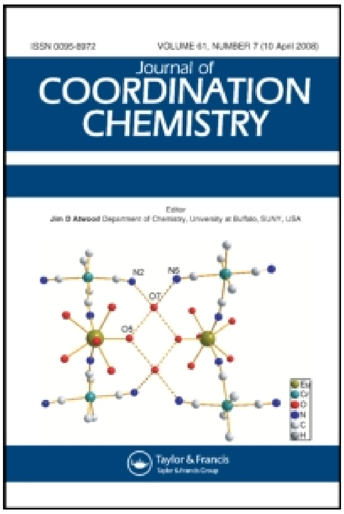

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Structural characterization of two lanthanide compounds based on polyoxometalate building units

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Structural characterization of two lanthanide compounds based on polyoxometalate building units

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Two new compounds $[Hbpy]_2[Ce(Hbpy)(DMF)_5(H_2O)_2][H_2W_{12}O_{40}] \cdot 0.5H_2O$ (**1**) and $[La(DMF)_7(H_2O)][PMo_{12}O_{40}] \cdot DMF \cdot (CH_3)_2NH$ (**2**) (DMF = N,N-dimethylformamide, bpy=4,4′-bipyridine) have been synthesized and characterized by single-crystal X-ray diffraction, IR spectra, TG analysis and electrochemical analysis. In **1**, the $[Ce(Hbpy)(DMF)_5(H_2O)_2]^{4+}$ unit is supported on the α-Keggin polyoxoanion $[H_2W_{12}O_{40}]^{6-}$ via bridging oxygen atoms, and further extended into 2-D supramolecular networks by hydrogen-bonding and π–π interactions. There exist one-dimensional channels surrounded by supramolecular interactions, in which 4,4′-bipy ligands reside. Compounds constructed from Ln(III) and $[H_2W_{12}O_{40}]^{6-}$ polyoxoanions are rare. For **2**, the $[La(DMF)_7(H_2O)]^{3+}$ is supported by $[PMo_{12}O_{40}]^{3-}$ units via the surface bridging oxygens, and further extended into 2-D supramolecular networks through hydrogen bonds. As for **1**, a one-dimensional channel exists in **2**, in which DMF resides. To our surprise, $(CH_3)_2NH$ molecules exist in the structure of **2**, from hydrolysis of DMF under catalysis of 12-molybophosphate. The electrochemistry of **1** is investigated.

Keywords: Polyoxometalate; Lanthanide cations; Supramolecular networks; Hydrogen bond; Electrochemical property

1. Introduction

Polyoxometalates (POMs) have received attention for their potential applications in catalysis, electric conductivity, magnetism, and photochemistry [1–3]. Furthermore, POMs are versatile inorganic building blocks for construction of molecular-based materials by extension and decoration [4]. Transition metal and lanthanide cations are suitable linkers to connect POM building blocks to form new classes of materials with potential applications in many fields [5–7]. The introduction of lanthanide or transition

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metal cations into POMs may provide an entry to new classes of materials that combine the intrinsic properties of both constituents [8, 9]. Lanthanides can impart useful functionality such as luminescent, magnetic, or Lewis acid catalytic centers to POMs, thus extending their range of physical and chemical properties and gaining access to an array of complexes [10]. In comparison to the large number of hybrid polyoxoanion-based solid materials modified by transition metal complexes, lanthanide coordination compound decorated POMs has been less explored [11, 12]. However, integration of lanthanide complexes and POMs need to solve certain problems [13]: (a) the variable and large coordination numbers of 4f metals allow less rational design of lanthanide complexes or polymers to construct target products; (b) the variety of POM building blocks may lead to different physical properties and structures of the final products.

To synthesize new compounds built from Ln(III) metal ions and POM building units, we chose $[PMo_{12}O_{40}]^{3-}$ and $[H_2W_{12}O_{40}]^{6-}$ as building units for the following reasons: (a) the high symmetry of POM building units may simplify the prediction of products, (b) catalysis by $[PMo_{12}O_{40}]^{3-}$ may introduce *in situ* reaction in the synthesis [14], (c) $[H_2W_{12}O_{40}]^{6-}$ has high charge density and value-adding properties [15] resulting in compounds with interesting physical properties.

Two compounds, $[Hbpy]_2[Ce(Hbpy)(DMF)_5(H_2O)_2][H_2W_{12}O_{40}] \cdot 0.5H_2O$ (**1**) and $[La(DMF)_7(H_2O)][PMo_{12}O_{40}] \cdot DMF \cdot (CH_3)_2NH$ (**2**) (DMF = *N*,*N*-dimethylformamide, bpy = 4,4′-bipyridine), have been synthesized under about the same synthetic conditions using different polyoxoanions. The electrochemistry of **1** has been studied via bulk-modified carbon paste electrodes.

2. Experimental

2.1. *Materials and methods*

Reagent grade chemicals were purchased and used without further purification. Elemental analyses (C, N, and H) were performed on a Perkin–Elmer 2400 CHN elemental analyzer. The W and Ln contents were determined using a Leaman inductively-coupled plasma (ICP) spectrometer. FT/IR spectra were recorded in the range 4000–400 cm^{-1} on an Alpha Centauri FT/IR spectrophotometer using KBr pellets. All measurements were performed at room temperature. A CHI 660 Electrochemical Workstation connected to a Digital-586 personal computer was used to control the electrochemical measurements and for data collection. A conventional three-electrode system was used, glassy carbon electrode as the working electrode, platinum wire as the counter electrode, and Ag/AgCl/KCl (3M) as reference electrode.

2.2. *Synthesis*

2.2.1. Synthesis of (1). Compound **1** was synthesized by a conventional solution method. $Na_2WO_4 \cdot 2H_2O$ (3.30 g, 10 mmol) was dissolved in water (20 mL). Hydrochloric acid (6M) was added with stirring to adjust the pH to 5. The solution was kept at room temperature for one week, forming $[H_2W_{12}O_{40}]^{6-}$ [16]. A mixture of $Ce(NO_3)_3 \cdot 6H_2O$ (0.22 g, 0.5 mmol) and 4,4′-bpy (0.16 g, 1 mmol) in 5 mL DMF was added to the above solution at 50°C. After 20 h, the solution was cooled to room temperature and a precipitate formed which was removed by filtration. After one week, brown hexagonal columnar crystals of **1** suitable for X-ray diffraction were collected (Yield: 0.71 g, 36% based on Ce). Anal. Calcd for $C_{45}H_{69}CeN_{11}O_{47.5}W_{12}$ (3870.65): C, 13.97; H, 1.80; N, 3.98; W, 57.00; Ce, 3.62%. Found (Experimental): C, 14.59; H, 1.87; N, 4.27; W, 56.30; Ce, 3.42%.

2.2.2. Synthesis of 2. $LaCl_3 \cdot 7H_2O$ (0.19 g, 0.5 mmol) was dissolved in 10 mL of DMF at 60°C for 1 h followed by a dropwise addition of α-$H_3PMo_{12}O_{40} \cdot nH_2O$ [17] (0.95 g, 0.5 mmol) in 5 mL of water at 80°C. After 4 h, the solution was cooled to room temperature and the precipitate removed by filtration. The filtrate was kept at ambient conditions, and then slow evaporation at room temperature for a few weeks resulted in yellow crystals of **2** suitable for X-ray diffraction (Yield: 0.39 g, 29% based on La). Anal. Calcd for $C_{26}H_{65}LaMo_{12}N_9O_{49}P$ (2608.98): C, 11.97; H, 2.51; N, 4.83; P, 1.19; Mo, 44.13; La, 5.32%. Found (Experimental): C, 12.48; H, 2.58; N, 5.04; P, 1.14; Mo, 43.02; La, 5.20%.

2.3. *X-ray crystallography*

Single crystals of **1** and **2** were glued on a glass fiber. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and IP technique. Numerical absorption correction was applied [18]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97 crystallographic software [19, 20]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms except the water molecules. Details of structure solution are shown in table 1 and distances and angles in tables 2 and 3.

3. Results and discussion

3.1. *Structure description*

Single crystal X-ray analysis showed that **1** is constructed from $[Ce(Hbpy)(DMF)_5(H_2O)_2]^{4+}$, $[H_2W_{12}O_{40}]^{6-}$, two protonated 4,4′-bipy cations, and 0.5 water (shown in figure 1). The polyoxoanion of **1** is the α-metatungstate, $[H_2W_{12}O_{40}]^{6-}$, which has the α-Keggin structure. The oxygens in the Keggin unit can be divided into three groups: 12 terminal O atoms each bonded to one W atom with W–O bond distances ranging from 1.681(17) to 1.750(14) Å, 24 doubly bridging oxygens coordinated to two tungstens with W–O distances in the range 1.873(16)–2.014(15) Å and four triply-bridging oxygens each shared with three W atoms with W–O distances between 2.023(14) and 2.314(16) Å (table 2). Different from the usual structural pattern observed in Keggin type anions, the central oxygen here, common to three tungsten octahedra, is not bonded to a heteroelement in tetrahedral environment but the central cavity contains two protons [21, 22].

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{45}H_{69}CeN_{11}O_{47.50}W_{12}$	$C_{26}H_{65}LaMo_{12}N_9O_{49}P$
Formula weight	3870.43	2609.03
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/n$	$P\bar{1}$
Unit cell dimensions (Å,°)		
a	18.384(4)	13.105(3)
b	20.825(4)	14.085(3)
c	21.592(4)	20.117(4)
α	90	98.51(3)
β	100.90(3)	92.59(3)
γ	90	106.42(3)
Volume (V)	8117(3)	3507.9(12)
Z	4	2
Calculated density (g cm^3)	3.167	2.470
Θ range for data collection (°)	3.14 – 25.00	3.00 – 25.00
Limiting indices	$-21 \leq h \leq 21$, $-24 \leq k \leq 24$, $-25 \leq l \leq 25$	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-23 \leq l \leq 23$
Completeness (%)	99.0	97.3
Goodness-of-fit on F^2	0.926	1.049
Final R indices [$I > 2\sigma$(I)]	$R_1 = 0.0697$, $wR_2 = 0.1417$	$R_1 = 0.0501$, $wR_2 = 0.1450$
R indices (all data)	$R_1 = 0.1326$, $wR_2 = 0.1680$	$R_1 = 0.0731$, $wR_2 = 0.1620$

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

Table 2. Selected bond lengths (Å) for **1**.

W(1)–O(35)	1.697(16)	W(2)–O(38)	1.698(15)	W(3)–O(41)	1.710(17)
W(1)–O(21)	1.884(14)	W(2)–O(28)	1.891(16)	W(3)–O(1)	1.873(16)
W(1)–O(2)	1.985(16)	W(2)–O(12)	1.979(16)	W(3)–O(29)	2.007(16)
W(1)–O(24)	2.314(16)	W(2)–O(31)	2.213(16)	W(3)–O(31)	2.280(15)
W(4)–O(22)	1.721(14)	W(5)–O(14)	1.701(18)	W(6)–O(10)	1.726(16)
W(4)–O(13)	1.851(15)	W(5)–O(26)	1.881(17)	W(6)–O(29)	1.876(16)
W(4)–O(15)	1.979(15)	W(5)–O(34)	1.954(14)	W(6)–O(13)	1.982(16)
W(4)–O(37)	2.174(16)	W(5)–O(24)	2.265(18)	W(6)–O(31)	2.263(16)
W(7)–O(33)	1.707(17)	W(8)–O(8)	1.750(14)	W(9)–O(40)	1.699(16)
W(7)–O(17)	1.886(14)	W(8)–O(5)	1.896(17)	W(9)–O(32)	1.910(14)
W(7)–O(21)	1.952(15)	W(8)–O(17)	2.014(15)	W(9)–O(27)	1.996(15)
W(7)–O(18)	2.224(15)	W(8)–O(18)	2.023(14)	W(9)–O(37)	2.193(17)
W(10)–O(16)	1.729(17)	W(11)–O(36)	1.681(17)	W(12)–O(39)	1.702(16)
W(10)–O(11)	1.899(15)	W(11)–O(4)	1.884(15)	W(12)–O(20)	1.876(18)
W(10)–O(20)	1.976(18)	W(11)–O(7)	1.932(16)	W(12)–O(32)	1.988(16)
W(10)–O(18)	2.154(15)	W(11)–O(24)	2.287(16)	W(12)–O(37)	2.212(17)
Ce(1)–O(45)	2.44(2)	Ce(1)–O(8)	2.526(14)	Ce(1)–O(47)	2.515(17)
Ce(1)–O(23)	2.444(16)	Ce(1)–O(42)	2.53(3)	Ce(1)–O(1W)	2.524(19)
Ce(1)–O(46)	2.494(19)	Ce(1)–O(3W)	2.60(2)	Ce(1)–N(7)	2.86(2)

The Keggin anion in **1** is decorated by a $[Ce(Hbpy)(DMF)_5(H_2O)_2]^{4+}$ building unit *via* a terminal oxygen. The Ce(III) atom coordinates to two oxygens from water [Ce–Ow 2.524(19), 2.60(2) Å], five oxygens from DMF [Ce–O 2.44(2)–0.253(3) Å], one oxygen from $[H_2W_{12}O_{40}]^{6-}$ [Ce–Od 2.526(14) Å] and one nitrogen from 4,4′-bpy ligand with Ce–N bond length of 2.86(2) Å. The uncoordinated nitrogen of 4,4′-bpy from $[Ce(Hbpy)(DMF)_5(H_2O)_2]^{4+}$ connects with the oxygen of the $[H_2W_{12}O_{40}]^{6-}$

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

La(1)–O(49)	2.485(7)	La(1)–O(45)	2.521(8)
La(1)–O(46)	2.503(6)	La(1)–O(48)	2.513(7)
La(1)–O(44)	2.480(7)	La(1)–O(35)	2.535(6)
La(1)–O(47)	2.516(6)	La(1)–O(7)	2.602(7)
La(1)–O(42)	2.669(5)		
Mo(1)–O(32)	1.680(6)	Mo(2)–O(40)	1.652(6)
Mo(1)–O(18)	1.873(7)	Mo(2)–O(8)	1.866(6)
Mo(1)–O(12)	1.972(6)	Mo(2)–O(18)	1.950(6)
Mo(1)–O(14)	2.436(5)	Mo(2)–O(14)	2.441(6)
Mo(3)–O(39)	1.669(6)	Mo(4)–O(31)	1.675(7)
Mo(3)–O(30)	1.872(6)	Mo(4)–O(34)	1.876(6)
Mo(3)–O(34)	1.950(6)	Mo(4)–O(13)	1.956(6)
Mo(3)–O(29)	2.413(5)	Mo(4)–O(29)	2.457(6)
Mo(5)–O(42)	1.677(5)	Mo(6)–O(36)	1.658(6)
Mo(5)–O(10)	1.867(6)	Mo(6)–O(23)	1.892(5)
Mo(5)–O(8)	1.946(6)	Mo(6)–O(17)	1.930(6)
Mo(5)–O(14)	2.382(5)	Mo(6)–O(29)	2.416(5)
Mo(7)–O(38)	1.668(6)	Mo(8)–O(41)	1.665(7)
Mo(7)–O(1)	1.879(6)	Mo(8)–O(12)	1.846(6)
Mo(7)–O(24)	1.944(6)	Mo(8)–O(26)	1.984(6)
Mo(7)–O(5)	2.413(5)	Mo(8)–O(5)	2.413(5)
Mo(9)–O(33)	1.667(6)	Mo(10)–O(37)	1.684(6)
Mo(9)–O(24)	1.870(6)	Mo(10)–O(2)	1.857(6)
Mo(9)–O(4)	1.949(6)	Mo(10)–O(1)	1.940(6)
Mo(9)–O(5)	2.438(5)	Mo(10)–O(9)	2.409(5)
Mo(11)–O(27)	1.686(7)	Mo(12)–O(28)	1.668(6)
Mo(11)–O(16)	1.872(6)	Mo(12)–O(20)	1.888(7)
Mo(11)–O(11)	1.965(6)	Mo(12)–O(21)	1.951(6)
Mo(11)–O(9)	2.434(6)	Mo(12)–O(9)	2.425(5)
P(1)–O(5)	1.523(6)	P(1)–O(14)	1.534(5)
P(1)–O(9)	1.527(5)	P(1)–O(29)	1.535(5)
O(5)–P(1)–O(9)	109.3(3)	O(5)–P(1)–O(29)	109.6(3)
O(5)–P(1)–O(14)	110.0(3)	O(9)–P(1)–O(29)	109.7(3)
O(9)–P(1)–O(14)	109.1(3)	O(14)–P(1)–O(29)	109.1(3)

cluster *via* a N–H $\cdots$ O hydrogen bond (N(8)–H $\cdots$ O(1) hydrogen bond distance is 2.992 Å). The oxygen from water of $[\mathrm{Ce(Hbpy)(DMF)_5(H_2O)_2}]^{4+}$ links with an oxygen of $[\mathrm{H_2W_{12}O_{40}}]^{6-}$ *via* a hydrogen bond, O(1w)–H $\cdots$ O(16) hydrogen bond distance is 2.705 Å. This weak interaction leads to one-dimensional double chains (figure 2).

Such one-dimensional double chains are connected to form a two-dimensional supramolecular layer structure by π–π interactions (center distance = 3.433 Å) from free 4,4′-bpy ligands isolated between the double chains and hydrogen bonds between the polyoxoanions and 4,4′-bpy molecules [N(2)–H $\cdots$ O(25) 2.795 Å] (figure 3).

We applied elemental analysis and X-ray diffraction to obtain information about **2**, which proved the existence of free molecules of $\mathrm{(CH_3)_2NH}$. Analysis of the experiment process and references [23, 24] indicate this may originate from hydrolysis of DMF under catalysis by 12-molybophosphate. Compound **2** is constructed from $[\mathrm{La(DMF)_7(H_2O)}]^{3+}$ decorated $[\mathrm{PMo_{12}O_{40}}]^{3-}$ anions, DMF and $\mathrm{(CH_3)_2NH}$. In the Keggin-type $[\mathrm{PMo_{12}O_{40}}]^{3-}$, the Mo centers exhibit distorted $[\mathrm{MoO_6}]$ octahedral environments and Mo–O distances can be divided into several different groups according to the type of oxygen. The Mo–Od distances range from 1.652(6) to 1.686(7) Å, mean 1.671 Å; Mo–Oa distances range from 2.382(5) to 2.457(6) Å, mean 2.423 Å; Mo–Ob, c distances range from 1.846(6) to 1.984(6) Å, mean 1.912 Å.

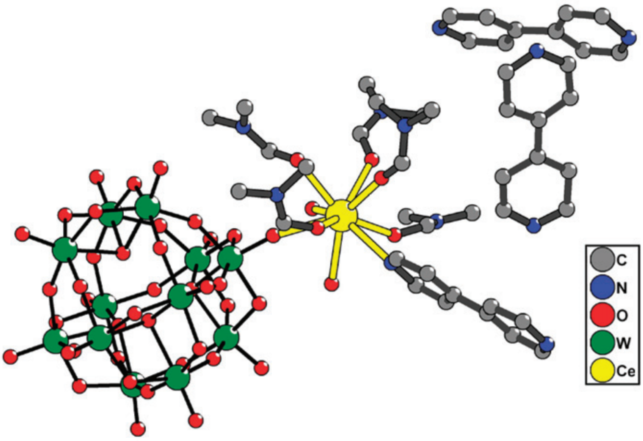

Figure 1. The fundamental unit of **1**.

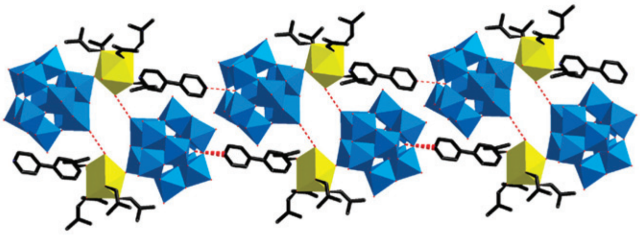

Figure 2. The one-dimensional double chain-like supramolecular structure of **1**.

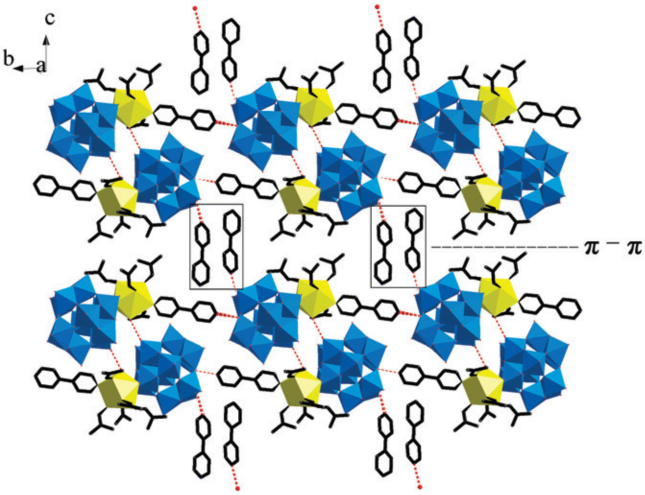

Figure 3. The two-dimensional layer structure of **1**.

The P–O bond distances range from 1.523(6) to 1.535(5) Å, mean 1.530 Å for **2**, and the O–P–O bond angles range from 109.1(3)° to 110.0(3)°. These results show that the MoO_6 octahedra of the polyanions in the title compounds are slightly distorted from influence of the outer coordination cations. The assignments of oxidation state for molybdenums are consistent with their coordination geometries and confirmed by valence sum calculations [25]; all molybdenums of polyoxoanions are in the +6 oxidation state (calculated average value 6.10).

The Keggin anion in **2** is decorated by a $[La(DMF)_7(H_2O)]^{3+}$ building unit *via* a terminal oxygen atom (figure 4). La(III) ions are coordinated with nine oxygens in a distorted monocapped square antiprism, seven oxygens from DMF molecules with La–O distances ranging from 2.480(7) to 2.535(6) Å, one oxygen from water with La–Ow = 2.602(7) Å, and one oxygen from $[PMo_{12}O_{40}]^{3-}$, La–Od = 2.669(5) Å. That the mean La–O_{DMF} bond distance is shorter than La–O(w) and the La–Od, indicates that the La–O_{DMF} bonds are stronger than La–O(w) and La–Od bonds.

The oxygen from water of $[La(DMF)_7(H_2O)]^{3+}$ links with oxygen of the $[PMo_{12}O_{40}]^{3-}$ cluster *via* a hydrogen bond with O(7w)–H···O(37) hydrogen bond distance of 2.837 Å. The uncoordinated nitrogen from $(CH_3)_2NH$ links with an oxygen of the $[PMo_{12}O_{40}]^{3-}$ cluster, N(9)–H···O(26) hydrogen bond distance of 2.911 Å, and N(9)–H···O(1) hydrogen bond distance of 3.026 Å. These weak interactions result in a one-dimensional double chain-like supramolecular structure (figure 5). The adjacent one-dimensional double chains are further extended to a two-dimensional layer

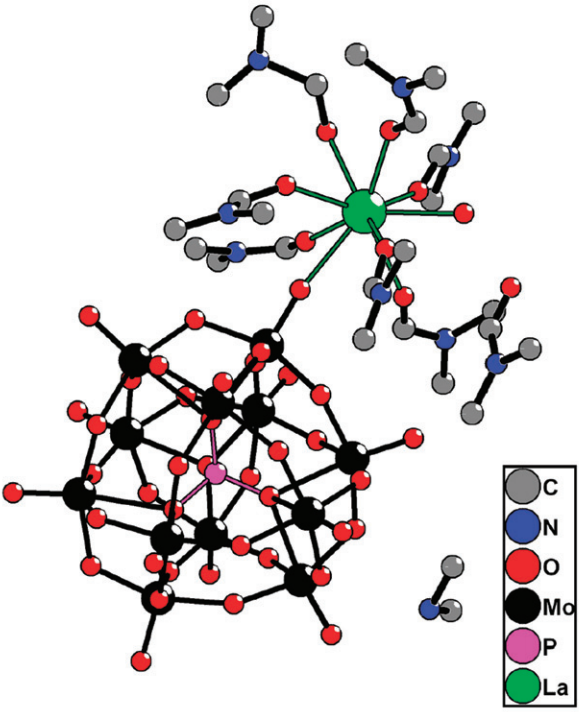

Figure 4. The fundamental unit of **2**.

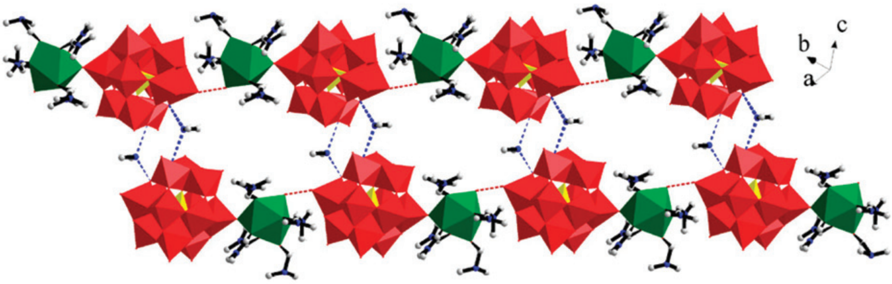

Figure 5. The one-dimensional double chain-like supramolecular structure of **2**.

structure *via* hydrogen bonds among DMF ligands (figure 6) with bond distances of 3.113 Å for C(20)–H(20C) $\cdots$ O(45), and 2.627 Å for H(20C) $\cdots$ O(45), consistent with a report [26].

3.2. *IR spectroscopy*

For **1**, ν(W = O) and ν(W–O–W) are observed at 940, 888, 772, 670, 630 and 616 cm^{-1}; the shape of peaks in the range 600–1000 cm^{-1} is nearly identical to that of $[H_2W_{12}O_{40}]^{6-}$ except for slight shifts of some peaks due to coordination, indicating that the polyoxoanion in **1** retains the basic $[H_2W_{12}O_{40}]^{6-}$ structure. For **2**, the P–O$_a$ bond vibrations are red-shifted from 1064 to 1057 cm^{-1}, the Mo–O$_d$ vibration red-shifted from 981 to 950 cm^{-1}; the peak due to the Mo–O$_c$ vibration is blue-shifted from 784 to 794 cm^{-1}; and the Mo–O$_b$ vibration blue-shifts from 870 to 875 cm^{-1} [17]. These results indicate that the polyanions in **2** retain the basic Keggin structure, in agreement with the result of single-crystal X-ray diffraction analysis.

3.3. *Thermogravimetric analyses*

For **1** and **2**, thermogravimetric analyses were carried out in flowing N_2 with a heating rate of 10°C min^{-1}. For **1**, TGA exhibits two-step weight loss: the first weight loss of 1.32% from 60–150°C is attributed to loss of water. The second weight loss of *ca.* 22.17% from 200–480°C is ascribed to loss of free 4,4′-bpy, DMF and 4,4′-bpy coordinated to Ce(III). The weight loss (23.49%) is in agreement with the calculated value (22.86%). TGA of **2** exhibits four-step weight loss: the first two weight losses of 5.42% from 40–160°C are due to loss of water, free $(CH_3)_2NH$ and DMF molecules. The continuous third and fourth weight loss of 20.56% from 160–430°C is attributed to loss of DMF coordinated to La(III). The whole weight loss of 25.98% is consistent with the calculated value (24.83%).

3.4. *Electrochemical properties*

The electrochemistry of **1** is shown in figure 7 as the voltammetric behavior of the working electrode in (0.1 M $Na_2SO_4 + H_2SO_4$) mixed aqueous solution. In the potential

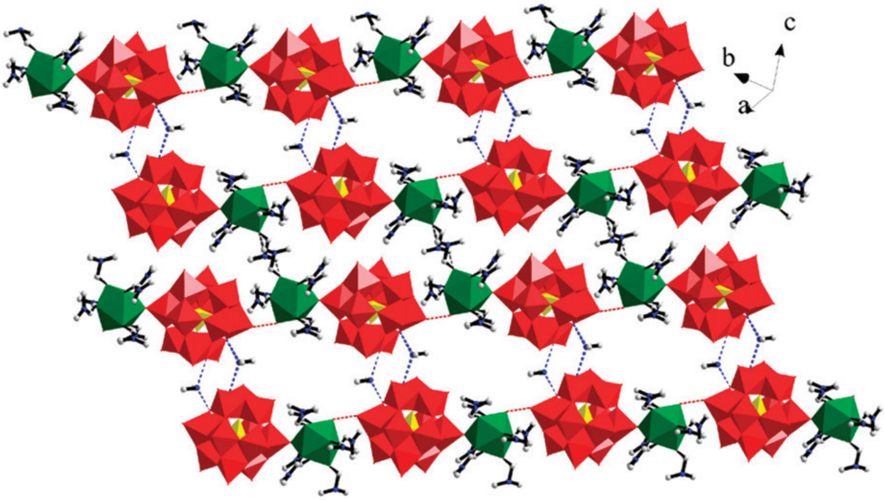

Figure 6. The two-dimensional layer structure of **2**.

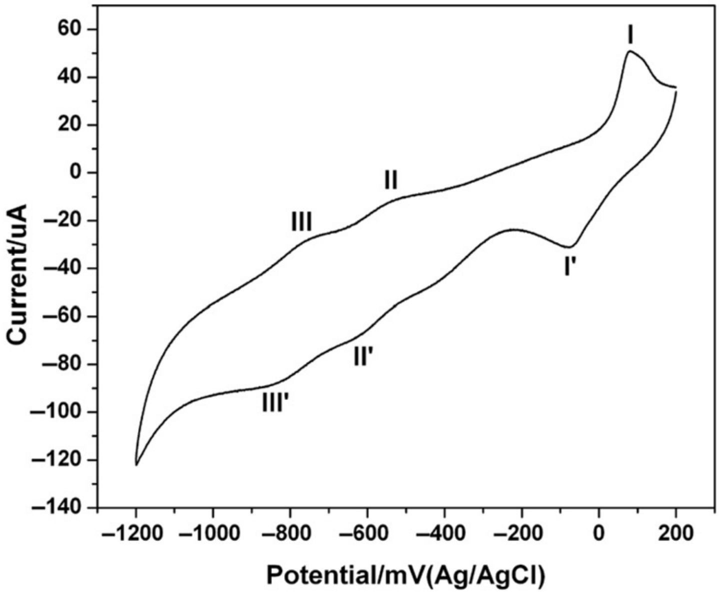

Figure 7. Cyclic voltammograms of **1** in the pH = 2.6 (0.1M $Na_2SO_4 + H_2SO_4$) mixed aqueous solution at the scan rate of $50\,mV\,s^{-1}$. Glassy carbon electrode as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode.

range 200 to −1200 mV at scan rate of $50\,mV\,s^{-1}$, three redox peaks appear and the mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ are 10(I), −571 (II) and −781 (III) mV in **1**. The peak-to-peak separations between the corresponding anodic and cathodic peaks (ΔE_p) at the **1**-CPE for peaks I–I′, II–II′, III–III′ are 147, 97 and 90 mV, respectively. The first peak (I–I′) can be attributed to redox of Ce^{IV}/Ce^{III}. The second and third peaks (II–II′, III–III′) can be ascribed to two single-electron processes of tungstate [27]:

$$\left[H_2W_{12}^{VI}O_{40}\right]^{6-}+e^- = \left[H_2W_{11}^{VI}W^{V}O_{40}\right]^{7-}$$
$$\left[H_2W_{11}^{VI}W^{V}O_{40}\right]^{7-}+e^- = \left[H_2W_{10}^{VI}W_2^{V}O_{40}\right]^{8-}$$

The shifts of W or Ce can be ascribed to different coordination environments in **1** [28].

4. Conclusion

Two interesting supramolecular compounds based on polyoxoanions decorated by Ln(III) metal-organic moieties have been synthesized and characterized by single-crystal X-ray diffraction, IR spectra, TG analysis and electrochemistry for **1**.

Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 648724 and 653065. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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