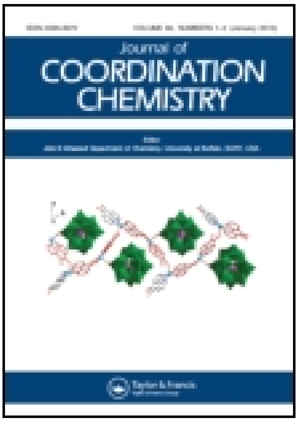

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Three organic–inorganic hybrid B-Anderson polyoxoanions as building blocks: syntheses, structures, and characterization of $[(C_6H_5NO_2)_2Ln(H_2O)_6](CrMo_6O_{24}H_6)\cdot2C_6H_5NO_2\cdot6H_2O$ (Ln = Sm, Dy, Er)

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Three new B-Anderson type polyoxometalates, $[(C_6H_5NO_2)_2Ln(H_2O)_6](CrMo_6O_{24}H_6)\cdot2C_6H_5NO_2\cdot6H_2O$ (Ln = Sm **1**, Dy **2** and Er **3**), have been synthesized in aqueous solution and structurally characterized by single-crystal X-ray diffraction, IR spectra, UV spectroscopy, and fluorescence spectroscopy. Crystal structure analysis reveals that these three compounds have the same composition and are isostructural, assembled by B-Anderson type polyoxoanion $[CrMo_6O_{24}H_6]^{3-}$, rare-earth ions, and ligands. UV spectroscopy shows that **1** is stable when pH is 4.50–5.83. The fluorescence spectra of **2** indicate that both rare-earth ions Dy^{3+} and pyridine-4-carboxylic acid ligands function in the charge transition of the compound.

Keywords: Polyoxometalates; B-Anderson type; Syntheses; Crystal structure

1. Introduction

Polyoxometalates (POMs) play a role in catalysis, material science, optics, and medicine [1–9] because of structural versatility and interesting properties. Many structures based on well-defined POMs, Keggin [10, 11], and Wells–Dawson [12] type, for instance, have been reported. In contrast, structures of Anderson-type polyoxoanions that act as benign inorganic building blocks draw much attention because of their high reactivity [13], but still remain less explored. Investigating this kind of POM to obtain new complexes modified by metal ions, especially rare-earth ions, and organic ligands will be of interest.

Many researchers have synthesized various structures based on Anderson polyoxoanions. In 2003, Das' group reported a compound formulated as $[Cu^{II}(2,2'\ bipy)(H_2O)_2Al(OH)_6Mo_6O_{18}]_n^{n-}$, which represented the first example of a 1-D chain-like compound based on $[Al(OH)_6Mo_6O_{18}]^{3-}$ [14a]. Two years later, Yagasaki *et al.* synthesized $[IMo_9O_{32}(OH)(OH_2)_3]^{4-}$ by using $[IMo_6O_{22}(OMe)_2]^{3-}$ as starting material [14b]. In the same year, Wang and coworkers obtained the first 2-D extended framework constructed

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from $[Cr(OH)_6Mo_6O_{18}]^{3-}$, counterions Na^+ and Cu^{2+} [14c]. In addition, an organic–inorganic hybrid $(H_3O)[(3\text{-}C_5H_7N_2)_2Cr(OH)_6Mo_6O_{18})]\cdot 3H_2O$ was isolated, built up of A-Anderson polyoxoanion and 3-amino-pyridine and extended by $\pi\cdots\pi$ interactions and hydrogen bonds [14d]. Chen Yaguang *et al.* have communicated four POM compounds based on Anderson-type polyoxoanions containing Y^{3+} and Yb^{3+} cations. The single $[M(OH)_6Mo_6O_{18}]^{3-}$ (M = Cr, Al) anions are linked to the coordination complexes via hydrogen-bonding interactions [14e]. A B-Anderson type heteropolyoxometalate $[Cu_2(phen)_2(CH_3COO)_2(H_2O)_2][HAl\text{-}(OH)_6(Mo_6O_{18})]\cdot 2.5H_2O$ containing binuclear metal coordination cations bridged by two acetates was reported by our group in 2005 and the structure was confirmed by IR and thermal analysis [14f]. In 2010, we communicated a 3-D compound $[Na_4(H_2O)_{14}Cu(PDA)_2]H[Al(OH)_6Mo_6O_{18}]\cdot 5H_2O$ (H_2PDA = pyrazine-2,3-dicarboxylic acid), in which, H_2PDA is first employed [14g]. Examples of POMs based on B-type Anderson polyanion and containing rare-earth ions, especially heavy lanthanides, as well as organic ligands are few. Most are coordinated with transition metal ions. Therefore, as a part of our ongoing study, we have explored reaction of $[CrMo_6O_{24}H_6]^{3-}$ as precursor and pyridine-4-carboxylic acid as the protecting ligand in the presence of rare-earth ions in solution by changing reaction conditions, such as pH, temperature, the sequence of adding reactants, etc. Three compounds were separated and formulated as $[(C_6H_5NO_2)_2Ln(H_2O)_6](CrMo_6O_{24}H_6)\cdot 2C_6H_5NO_2\cdot 6H_2O$ (Ln = Sm **1**, Dy **2**, Er **3**). Anderson type polyanions can be divided into two types according to the different chemical valence of the central atoms and the distinctions of combined groups for the central atoms [14f]: (1) $[X^{n+}M_6O_{24}]^{(12-n)-}$ (X = Te^{VI}, I^{VII}, etc. M = Mo^{VI}, W^{VI}), defined as A-Anderson type; (2) $[X^{n+}M_6O_{24}H_6]^{(6-n)-}$ (X = Cr^{III}, Co^{III}, etc. M = Mo^{VI}, W^{VI}) with each oxygen surrounding the central atom are connected by hydrogen and thus classified as B-Anderson type [14f, 15].

We report here the syntheses, structures, and fluorescence of $[(C_6H_5NO_2)_2Ln(H_2O)_6](CrMo_6O_{24}H_6)\cdot 2C_6H_5NO_2\cdot 6H_2O$ (Ln = Sm **1**, Dy **2**, Er **3**) which belong to the B-Anderson type polyoxoanion, $[CrMo_6O_{24}H_6]^{3-}$, together with rare-earth ion and pyridine-4-carboxylic acid ligands.

2. Experimental

2.1. *Instruments and materials*

$Na_3[CrMo_6O_{24}H_6]\cdot nH_2O$ was prepared according to the literature [16] and identified by IR spectrum. $LnCl_3\cdot nH_2O$ (Ln = Sm, Dy, Er) were obtained from Ln_2O_3 (99.9%) by adding concentrated hydrochloric acid. The remaining chemicals were used as purchased without purification. IR spectra (using KBr in pellets) were recorded on a Nicolet Avatar-360 IR spectrometer (4000–400 cm^{-1}). Elemental analyses (C, H, and N) were conducted on a Perkin-Elmer 2400-II CHNS/O Analyzer. UV spectra were obtained on a U–4100 spectrometer (400–190 nm with water as solvent). Emission/excitation spectra were recorded on an F–7000 fluorescence spectrophotometer.

2.2. *Syntheses*

2.2.1. $[(C_6H_5NO_2)_2Sm(H_2O)_6](CrMo_6O_{24}H_6)\cdot 2C_6H_5NO_2\cdot 6H_2O$ (1). A mixture of $SmCl_3\cdot nH_2O$ (0.32 g), pyridine-4-carboxylic acid (0.16 g), and H_2O (30 mL) was stirred for

60 min, then, $Na_3[CrMo_6O_{24}H_6]\cdot nH_2O$ (0.25 g) aqueous solution (20 mL) was added. The mixture was heated at 80 °C for 30 min, after adjustment of pH to 2.6 by addition of HCl. Then the solution was left to evaporate at room temperature slowly. Pink block crystals were collected by filtration after a few days. Yield: 32% based on $Na_3[CrMo_6O_{24}H_6]\cdot nH_2O$, Anal. Found: (Calcd) C, (15.68) 15.50; H, (2.64) 2.58; N, (3.12) 3.01.

2.2.2. $[(C_6H_5NO_2)_2Dy(H_2O)_6](CrMo_6O_{24}H_6)\cdot 2C_6H_5NO_2\cdot 6H_2O$ (2). Compound **2** was synthesized by using a similar experimental procedure as that of **1** except that $DyCl_3\cdot nH_2O$ (0.31 g) was used instead of $SmCl_3\cdot nH_2O$ (0.32 g) and the pH was adjusted to 3.0. Pink block crystals were collected by filtration after a few days. Yield: 29% based on $Na_3[CrMo_6O_{24}H_6]\cdot nH_2O$. Anal. Found (Calcd): C, (15.48) 15.42; H, (2.52) 2.46; N, (2.97) 3.13.

2.2.3. $[(C_6H_5NO_2)_2Er(H_2O)_6](CrMo_6O_{24}H_6)\cdot 2C_6H_5NO_2\cdot 6H_2O$ (3). Compound **3** was synthesized by using a similar experimental procedure as that of **1** except that $ErCl_3\cdot nH_2O$ (0.29 g) was used instead of $SmCl_3\cdot nH_2O$ (0.32 g) and the pH was adjusted to 2.9. Pink block crystals were collected by filtration after a few days. Yield: 32% based on $Na_3[CrMo_6O_{24}H_6]\cdot nH_2O$. Anal. Found (Calcd): C, 15.35 (15.23); H, (2.42) 2.64; N, (3.00) 2.86.

2.3. *Crystal structure analysis*

Intensity data collections for the three compounds were carried out with the Bruker APEX-II diffractometer equipped with a CCD 2-D detector using the monochromated wavelength $\lambda(\text{Mo-}K\alpha) = 0.71073$ Å at 293(2) K. The structures were solved by direct methods and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. All calculations were performed using the SHELXL-97 program [17]. Hydrogen positions were initially determined by geometry and refined by a riding model. Non-H atoms were refined with anisotropic displacement parameters. Crystallographic data and details of data collection together with the refinement procedure for **1**–**3** are given in table 1. Selected bond lengths and angles are listed in tables 2–4, respectively. Selected hydrogen-bonding parameters for **1** are listed in table 5.

3. Results and discussion

Single-crystal X-ray diffraction analysis reveals that **1**–**3** are made up of $[CrMo_6O_{24}H_6]^{3-}$, lanthanum-pyridine-4-carboxylic acid complexes as cations, discrete pyridine-4-carboxylic acid molecules and lattice water (figure 1). Compounds **2** and **3** are isostructured with **1**. Single-crystal X-ray diffraction analyses reveal that the unit cell dimensions, volumes, relative bond distances, and angles are just slightly changed because of lanthanide shrinking, so we take **1** to illustrate. The structure of **1** consists of a B-Anderson type polyanion $[CrMo_6O_{24}H_6]^{3-}$, $[(C_6H_5NO_2)_2Sm(H_2O)_6]^{3+}$, two discrete pyridine-4-carboxylic acid molecules and seven free waters. As depicted in figure 1, $[CrMo_6O_{24}H_6]^{3-}$ exhibits the typical B-Anderson structure in which the heteroatom Cr forms an octahedron of six OH groups

Table 1. The crystal data and structure refinement parameters for **1**, **2** and **3**.

	1	**2**	**3**
Empirical formula	$C_{24}H_{49}N_4O_{44}SmCrMo_6$	$C_{24}H_{49}N_4O_{44}DyCrMo_6$	$C_{24}H_{49}N_4O_{44}ErCrMo_6$
Formula weight	1875.6	1887.8	1892.5
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P-1(2)*	*P-1(2)*	*P-1(2)*
Unit cell dimensions	$a = 12.7893(4)$ Å, $b = 12.9166(4)$ Å, $c = 18.1585(5)$ Å, $\alpha = 93.46(3)°$, $\beta = 105.61(3)°$, $\gamma = 113.06(3)°$	$a = 12.7867(4)$ Å, $b = 12.8920(4)$ Å, $c = 18.1606(3)$ Å, $\alpha = 93.4270(3)°$, $\beta = 105.60°$, $\gamma = 112.76°$	$a = 12.7974(5)$ Å, $b = 12.9271(5)$ Å, $c = 18.1908(7)$ Å, $\alpha = 93.43(0)°$, $\beta = 105.63(0)°$, $\gamma = 113.06(0)°$
Volume (Å^3), Z	2611.45, 2	2613.32, 2	2619.69 (173), 2
Density (calculated) (Mg/m^3)	2.356	2.370	2.370
Absorption coefficient (mm^{-1})	2.815	3.119	3.287
$F(000)$	1792	1800	1804
Crystal size (mm^3)	0.23 × 0.18 × 0.15	0.23 × 0.18 × 0.14	0.19 × 0.15 × 0.13
θ range for data collection (°)	1.83–25.00	1.82–25.00	1.82–25.00
Limiting indices	$-14 \leqslant h \leqslant 15$, $-15 \leqslant k \leqslant 14$, $-21 \leqslant l \leqslant 18$	$-15 \leqslant h \leqslant 15$, $-10 \leqslant k \leqslant 15$, $-18 \leqslant l \leqslant 21$	$-15 \leqslant h \leqslant 14$, $-8 \leqslant k \leqslant 15$, $-21 \leqslant l \leqslant 21$
Reflections collected	13,447	13,530	13,597
Independent reflections	9120($R_{int} = 0.0174$)	9134($R_{int} = 0.0189$)	9155($R_{int} = 0.0181$)
Data/restraints/parameters	9120/0/721	9134/0/721	9155/6/721
Goodness-of-fit on F^2	1.051	1.031	1.065
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0347$, $wR_2 = 0.0995$	$R_1 = 0.0287$, $wR_2 = 0.0784$	$R_1 = 0.0298$, $wR_2 = 0.0784$
R (all data)	$R_1 = 0.0388$, $wR_2 = 0.1022$	$R_1 = 0.0326$, $wR_2 = 0.0806$	$R_1 = 0.0375$, $wR_2 = 0.0822$
Largest diffraction peak and hole (e.Å^{-3})	1.589 and −1.392	1.048 and −0.698	1.028 and −0.683

Note: $^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^bwR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]^{1/2}$.

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

Sm(1)–O(27)	2.255(3)	O(27)–Sm(1)–O(3 W)	89.05(12)
Sm(1)–O(25)	2.268(4)	O(25)–Sm(1)–O(3 W)	103.81(14)
Sm(1)–O(2 W)	2.326(4)	O(2 W)–Sm(1)–O(3 W)	144.57(12)
Sm(1)–O(5 W)	2.369(4)	O(5 W)–Sm(1)–O(3 W)	75.15(13)
Sm(1)–O(1 W)	2.372(3)	O(1 W)–Sm(1)–O(3 W)	144.34(12)
Sm(1)–O(3 W)	2.397(3)	O(27)–Sm(1)–O(6 W)	73.42(12)
Sm(1)–O(6 W)	2.403(3)	O(25)–Sm(1)–O(6 W)	146.70(14)
Sm(1)–O(4 W)	2.421(4)	O(2 W)–Sm(1)–O(6 W)	74.73(13)
O(27)–Sm(1)–O(25)	139.53(13)	O(5 W)–Sm(1)–O(6 W)	72.63(15)
O(27)–Sm(1)–O(2 W)	101.07(14)	O(1 W)–Sm(1)–O(6 W)	125.61(12)
O(25)–Sm(1)–O(2 W)	90.35(15)	O(3 W)–Sm(1)–O(6 W)	75.90(13)
O(27)–Sm(1)–O(5 W)	145.11(14)	O(27)–Sm(1)–O(4 W)	75.77(13)
O(25)–Sm(1)–O(5 W)	75.16(15)	O(25)–Sm(1)–O(4 W)	73.02(14)
O(2 W)–Sm(1)–O(5 W)	77.49(15)	O(2 W)–Sm(1)–O(4 W)	145.00(11)
O(27)–Sm(1)–O(1 W)	73.70(11)	O(5 W)–Sm(1)–O(4 W)	124.84(15)
O(25)–Sm(1)–O(1 W)	73.89(12)	O(1 W)–Sm(1)–O(4 W)	75.17(11)
O(2 W)–Sm(1)–O(1 W)	70.62(12)	O(3 W)–Sm(1)–O(4 W)	70.36(12)
O(5 W)–Sm(1)–O(1 W)	134.80(13)	O(6 W)–Sm(1)–O(4 W)	134.09(12)

and is close to D_{3h} symmetry [18, 19]. The $[CrMo_6O_{24}H_6]^{3-}$ building block has a B-type Anderson structure, in which the central Cr is coordinated with six oxygens forming an edge-sharing octahedron and six {MoO_6} octahedra hexagonally arranged by composing a

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

Mo(1)–O(1)	1.698(3)	Cr(1)–O(20)	1.958(3)
Mo(1)–O(23)	2.312(3)	Cr(1)–O(22)	1.980(4)
Mo(2)–O(2)	1.703(3)	O(28)–Dy(1)–O(26)	139.71(13)
Mo(2)–O(22)	2.310(4)	O(28)–Dy(1)–O(4 W)	145.24(14)
Mo(3)–O(3)	1.697(3)	O(26)–Dy(1)–O(4 W)	74.89(15)
Mo(3)–O(24)	2.279(3)	O(28)–Dy(1)–O(1 W)	73.34(11)
Mo(4)–O(10)	1.696(3)	O(26)–Dy(1)–O(1 W)	74.02(13)
Mo(4)–O(19)	2.310(3)	O(28)–Dy(1)–O(5 W)	89.54(12)
Mo(5)–O(11)	1.698(3)	O(26)–Dy(1)–O(5 W)	103.92(14)
Mo(5)–O(19)	2.343(3)	O(26)–Dy(1)–O(2 W)	146.75(13)
Mo(6)–O(6)	1.696(3)	O(28)–Dy(1)–O(3 W)	75.92(12)
Mo(6)–O(23)	2.324(3)	O(26)–Dy(1)–O(3 W)	73.28(14)

Table 4. Selected bond distances (Å) and angles (°) for **3**.

Er(1)–O(27)	2.252(3)	Cr(1)–O(22)	1.961(3)
Er(1)–O(4 W)	2.421(4)	Cr(1)–O(18)	1.995(2)
Mo(1)–O(1)	1.691(3)	O(27)–Er(1)–O(25)	139.50(12)
Mo(1)–O(21)	2.342(3)	O(27)–Er(1)–O(6 W)	100.86(13)
Mo(2)–O(2)	1.693(3)	O(25)–Er(1)–O(6 W)	90.41(14)
Mo(2)–O(21)	2.310(3)	O(27)–Er(1)–O(5 W)	145.47(13)
Mo(3)–O(9)	1.697(3)	O(25)–Er(1)–O(5 W)	74.76(14)
Mo(3)–O(24)	2.284(3)	O(27)–Er(1)–O(1 W)	73.61(10)
Mo(4)–O(4)	1.701(3)	O(27)–Er(1)–O(2 W)	88.95(12)
Mo(4)–O(18)	2.327(3)	O(25)–Er(1)–O(2 W)	104.07(13)
Mo(5)–O(5)	1.695(3)	O(27)–Er(1)–O(3 W)	73.45(11)
Mo(5)–O(23)	2.316(2)	O(25)–Er(1)–O(3 W)	146.68(13)
Mo(6)–O(6)	1.691(4)	O(27)–Er(1)–O(4 W)	75.75(12)
Mo(6)–O(23)	2.341(3)	O(25)–Er(1)–O(4 W)	73.07(13)

Table 5. Selected hydrogen-bond lengths (Å) and angles (°) for **1**.

D−H···A	d(H···A)	∠DHA	d(D···A)	Symmetry transformation for A
N(1)−H(1B)···O(11 W)	1.82	160	2.646	1−*x*,1−*y*,1−*z*
N(2)−H(2B)···O(7 W)	2.22	136	2.906	*x*,*y*,−1+*z*
N(2)−H(2B)···O(7)	2.32	133	2.979	1−*x*,−*y*,−*z*
N(3)−H(3A)···O(15)	1.92	171	2.768	
N(4)−H(4B)···O(18)	1.77	172	2.623	*x*,1+*y*,*z*
C(2)−H(2A)···O(11)	2.41	145	3.212	−*x*,−*y*,1−*z*
C(4)−H(4A)···O(16)	2.56	137	3.300	
C(11)−H(11A)···O(9)	2.43	136	3.162	
C(13)−H(13A)···O(3)	2.46	135	3.187	
C(13)−H(13A)···O(2)	2.55	138	3.300	1−*x*,1−*y*,−*z*
C(19)−H(19A)···O(7 W)	2.52	136	3.249	1−*x*,1−*y*,1−*z*

closed ring around the central $\{CrO_6\}$. Four different kinds of oxygens can be found in **1** according to the modality of O coordination, central oxygen O_c, double-bridging oxygen O_b, terminal oxygen $O_{t.}$ and terminal oxygen linked to rare-earth ions $O_t{}'$. Therefore, Mo–O bond lengths can be divided into three classes: Mo–O_t 1.691(2)–1.710(5), Mo–O_b 1.900(3)–1.963(3), Mo–O_c 2.284(3)–2.327(7) Å, respectively [20]. The Cr–O distances are

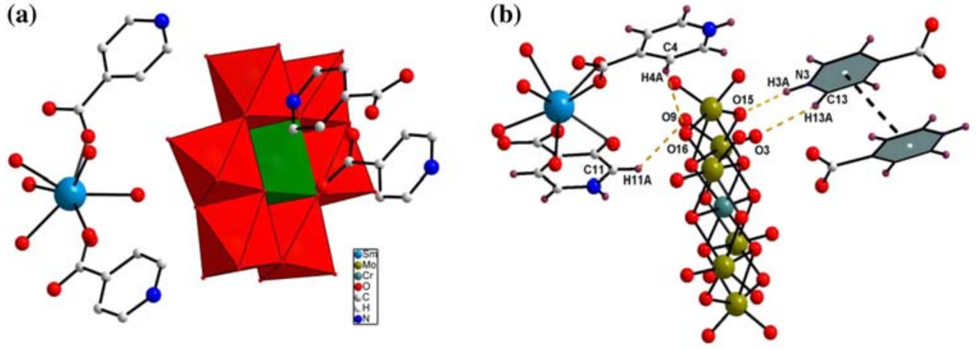

Figure 1. (a) Polyhedral and ball-stick representation of **1**. (b) The representation of the selected hydrogen bonds and π· · ·π interactions in **1**. Lattice waters are omitted for clarity.

1.961(6)–1.995(7) Å in **1**, close to the Cr(III)–O bond lengths of typical octahedra (1.98 ± 0.008 Å). The bond valence sum calculations [21] of **1** show that oxidation states of Cr, Mo, and Ln are +3, +6, and +3, respectively, and the oxidation state of O connected with the central atom Cr of the three compounds is 0.96 ± 0.13, close to 1, indicating that all these oxygens are mono-protonated. It proves that the polyanion of these three compounds belong to the typical B-Anderson structure.

In $[(C_6H_5NO_2)_2Sm(H_2O)_6]^{3+}$, Sm is eight-coordinate, square antiprism, as shown in figure 2, bonding to two oxygens from pyridine-4-carboxylic acids and six from water. Sm is not bonded directly to the building blocks, but acts as counterions coordinated with two pyridine-4-carboxylic acids, together with two discrete pyridine-4-carboxylic acid molecules to balance the negative charges. The Sm–O bond distances are 2.253(3)–2.421(4), 2.350 Å in average. The $[(C_6H_5NO_2)_2Sm(H_2O)_6]^{3+}$ and $[CrMo_6O_{24}H_6]^{3-}$ are connected via N···H–O and C···H–O hydrogen bonds forming a 2-D supramolecular network (figure 3, table 5). Two lattice pyridine-4-carboxylic acid molecules have π· · ·π interactions at 3.568 Å, within the range of the reported POMs [22]. The other compounds are both assembled by a $[CrMo_6O_{24}H_6]^{3-}$, a $[(C_6H_5NO_2)_2Ln(H_2O)_6]^{3+}$ (Ln = Dy, Er), two lattice isonicotinic acid molecules and six waters (figure 4). Hydrogen bonds and π· · ·π interactions are also present in **2** and **3**. This type of structure which contains hydrogen bonds and π· · ·π interactions simultaneously in Ln–Anderson (B-type) POM chemistry is rare.

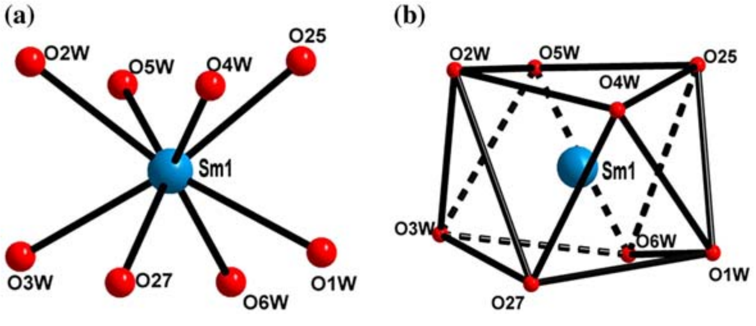

Figure 2. The coordination geometric framework of Sm for **1**.

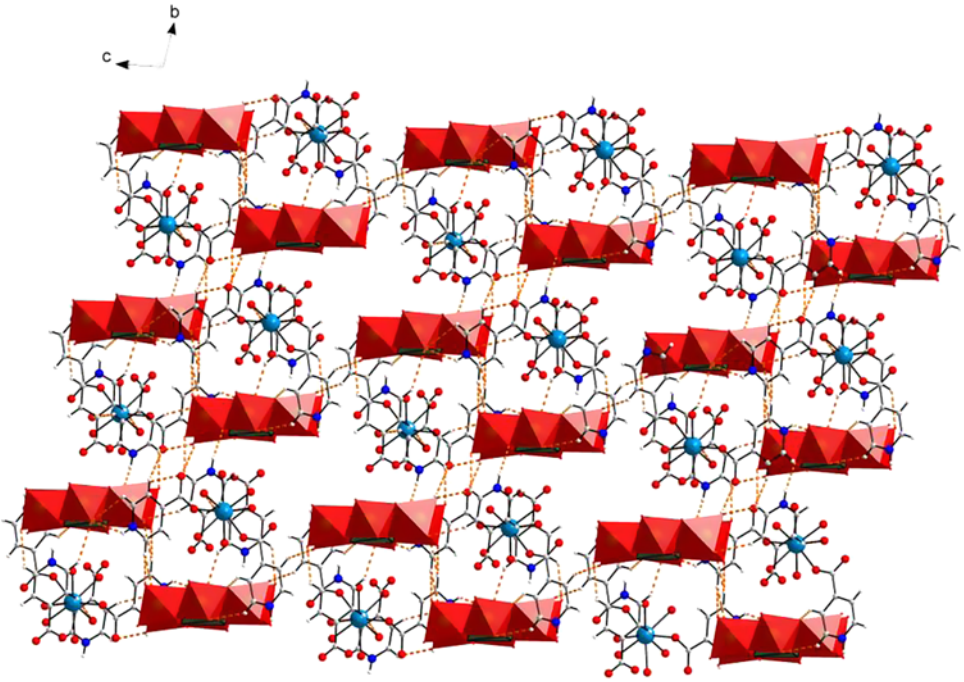

Figure 3. Polyhedral and ball-stick representation of the 2-D chain via hydrogen bond interactions in **1**.

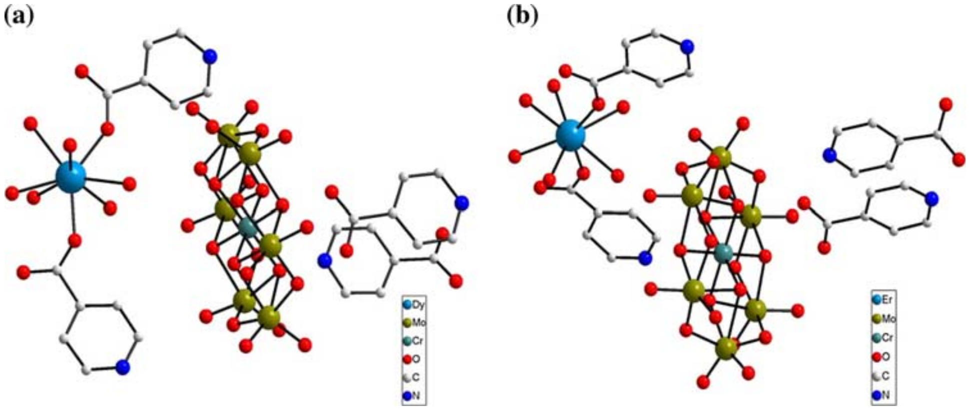

Figure 4. Ball-and-stick representation of **2**(a) and **3**(b); hydrogens are omitted for clarity.

3.1. *IR spectra*

IR spectra of **1**–**3** are shown in Supplementary Material. The four characteristic peaks of $Na_3[CrMo_6O_{24}H_6]\cdot nH_2O$ are at 944, 908, 830, and 657 cm^{-1} [23]. The compounds show similar vibration patterns, with typical peaks of B-Anderson type polyanions. The ν(Mo–O_b–Mo) in **2** split into two components, while the precursor $Na_3[CrMo_6O_{24}H_6]\cdot nH_2O$ has only one peak, indicating that the cation has influence in the anion so that its symmetrical structure has been changed; all peaks have some shift. In comparison with the IR spectrum of free pyridine-4-carboxylic acid, the characteristic peaks of pyridine-4-carboxylic acid of the three compounds shift due to coordination between rare-earth and O donors from the carboxyl of pyridine-4-carboxylic acid.

3.2. *UV spectroscopy*

The UV spectra for **1**–**3** are shown in Supplementary Material from 190 to 400 nm. The plots contain two characteristic bands for **1**–**3**, similar to $Na_3[CrMo_6O_{24}H_6]\cdot 8H_2O$. Bands corresponding to $O_t\rightarrow Mo$ transition are centered at 210 nm (for **1** and **2**) and 206 nm (for **3**). The shoulder bands at 245 nm (for **1**), 244 nm (for **2**), and 241 nm (for **3**) are assigned to $O_b(\pi)\rightarrow Mo(\pi)$ charge transfer transition [24].

Since the three compounds are isostructural, **1** is selected to measure UV properties. **1** is stable when pH is 4.50–5.83. The UV spectra of different pH value of **1** indicate that the peak near 245 nm becomes more inconspicuous when pH is increased from 4.50 (adjusted by diluted NaOH aqueous solution). When pH is 5.83, the peaks almost vanished, indicating the structure framework of **1** has been destroyed, as shown in figure 5.

3.3. *Fluorescence*

The fluorescence of rare-earth complexes containing aromatic ring ligands with extended conjugation has been explored [25]. Solid-state fluorescence properties of **2** are investigated at room temperature intersecting with incidence at an angle of 45. Under excitation wavelength at 365 nm, **2** exhibits two strong emission bands, as shown in figure 6(a). Emission bands centered at 476 and 570 nm correspond to the $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition, respectively, consistent with previous reported emission of Dy^{3+} [26]. The band at 469 nm may be attributed to the split of $^4F_{9/2}\rightarrow{}^6H_{15/2}$ transition. We also measured fluorescence emission of free pyridine-4-carboxylic acid to further explore the reason and influence of the ligand under the same conditions (figure 6(b)). Comparing with **2**, the two emissions

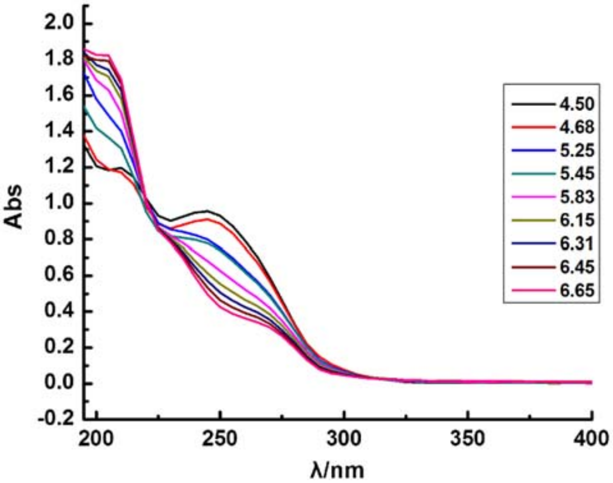

Figure 5. Influence of pH on stability of 1 in aqueous solution.

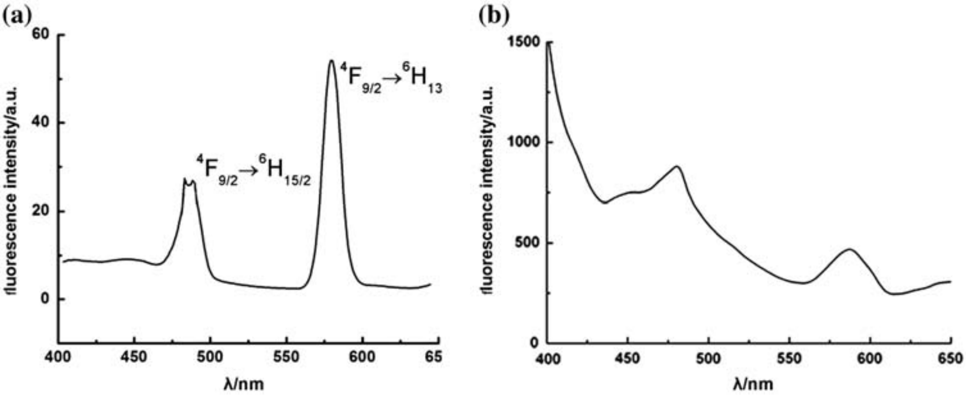

Figure 6. (a) Fluorescence of **2** (excitation wavelengths = 365 nm); (b) The emission spectrum for pyridine-4-carboxylic acid measured under the same condition.

at 478 and 583 nm are close to the bands at 476 and 570 nm of **2** and the intensity is stronger than **2**, which can be attributed to coordination of ligands and Dy^{3+} [27]. The fluorescence behaviors of **2** and pyridine-4-carboxylic acid illustrate that both rare-earth ion and ligand function in the charge transition of **2**.

4. Conclusions

Three organic–inorganic hybrid compounds constructed from B-Anderson polyoxoanion, rare-earth ions, and organic ligands have been synthesized and structurally characterized. All are isostructural and hydrogen bonds involved with heteropolyanions, pyridine-4-carboxylic acid molecules, and water result in a 2-D supramolecular network. The $\pi\cdots\pi$ stacking interactions are also observed between the two lattice pyridine-4-carboxylic acid molecules. There were some examples reported with structures based on B-Anderson type polyoxoanion, organic ligands, and transition metal/rare-earth cations [14e, 22, 28]. However, hydrogen bonds and $\pi\cdots\pi$ stacking interactions simultaneously contained in the structure in Ln–Anderson (B-type) POM chemistry is rarely reported. Furthermore, the studies of UV spectra show that the compounds are stable from pH of 4.50–5.83. Extended research remains to explore their synthetic rules and potential properties.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC) reference numbers 861582 for **1**, 861583 for **2** and 861581 for **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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