Double-Keggin-type Anion-templated Synthesis of a 3D Porous Coordination Polymer of Eu(III) Ions and dpdo Ligands

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A porous coordination polymer, $\{[Eu(dpdo)_4(H_2O)_3]H(SiMo_{12}O_{40})(dpdo)_{0.5}(CH_3CN)_{0.5}(H_2O)_4\}_n$ (**1**), (where dpdo is 4,4′-bipyridine-*N*,*N*′-dioxide) templated by double-Keggin-type polyanions has been synthesized through the self-assembly of Eu(III) ions and dpdo in acetonitrile/water solution and structurally characterized by elemental analysis, IR spectra and single crystal X-ray diffraction. The X-ray structure analysis reveals that compound **1** exhibits a 3D non-interwoven framework with large cavities housing centro-symmetrically related shoulder-by-shoulder double-Keggin anions as guests. The result of a thermogravimetric analysis suggests that the metal-organic framework has high thermal stability.

Key words: Coordination Polymer, Polyoxometalate, 4,4′-Bipyridine-*N*,*N*′-dioxide, Europium Complex

Introduction

Molecular and materials science have provided solid systems with a wide range of topologies and connectivities. Recent studies on inorganic/organic hybrid materials, especially in the area of metal-ligand coordination polymers, have enriched this area substantially [1, 2]. Meanwhile, polyoxometalates (POMs) with unique properties and a diverse compositional range represent an outstanding class of inorganic templates for the construction of cationic coordination polymer hosts [3 – 12]. Despite a number of coordination polymer hosts templated by Keggin-type and Lindqvist-type POMs have already been reported [8 – 11], there are few reports about assembling 3D open metal-organic frameworks with larger channels or cavities based on the templates of double-Keggin anions [8c, 12]. 4,4-Bipyridine-*N*,*N*-dioxide plays an important role in both lanthanide and transition metal coordination polymers, resulting in a family of extended assemblies with different topologies based on different connection modes of this ligand [13 – 15]. To better understand the correlation of the influence of double-Keggin anions on the resultant structure, herein, Eu^{3+} ions that generally adopt coordination numbers higher than six and have an excellent hard acid/hard base complementarity with dpdo, as well as Keggin-type $[SiMo_{12}O_{40}]^{4-}$ polyanions were chosen to construct a 3D open framework with a novel topology and channels templated by double-Keggin-type polyanions. Based on coordination, hydrogen bonding and π-π stacking interactions, the title compound forms a porous supramolecular network with each pore being *ca.* 10.4×21.1 Å^2 based on the sizes of the Keggin anions and large enough to accommodate a centrosymmetrical shoulder-by-shoulder double-Keggin anion.

Results and Discussion

Structure description

Reaction of europium silicomolybdates and dpdo ligands with a Eu:dpdo:$[SiMo_{12}O_{40}]^{4-}$ stoichiometry of 1 : 4 : 1 in acetonitrile/water solution by the layering method gave compound **1**, which exhibits a 3D non-interwoven framework with large cavities occupied by the double-Keggin-type polyanions. As shown in Fig. 1, a molecular unit consists of one coordinated cation $[Eu(dpdo)_4(H_2O)_3]^{3+}$, one polyanion $[SiMo_{12}O_{40}]^{4-}$, a half of a free dpdo molecule, four crystal water molecules and a half of an acetonitrile molecule. The Eu^{3+} ion is coordinated by eight oxygen atoms from three water molecules [mean Eu–O (water) 2.412(6) Å] and from four independent dpdo ligands and a symmetry-related dpdo ligand [mean Eu–

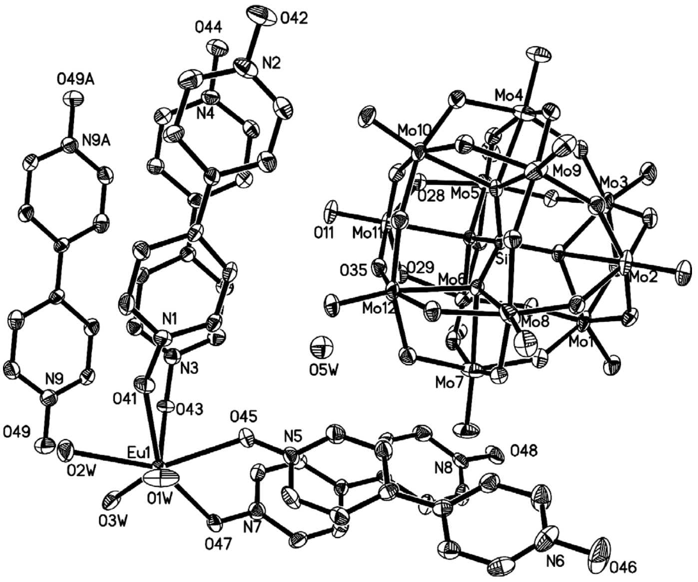

Fig. 1. Molecular structure of **1** showing the labeling of atoms with displacement ellipsoids at the 30 % probability level. Hydrogen atoms are omitted for clarity.

O(dpdo) 2.385(6) Å]. Dpdo ligands in **1** fall into three groups: a bridging one, three terminal ones and a half of a free one. The dihedral angle between the N(3) ring (*i. e.* the N(3)-containing pyridine ring) and the N(4) ring of the bridging dpdo ligand is 24.3°, the one between the N(1) ring and the N(2) ring of the terminal one is 23.1°, another one between the N(5) ring and the N(6) ring of the terminal one is 5.8°, and the last one between the N(7) ring and the N(8) ring of the terminal one is 3.5°.

Compound **1** consists of 1D chain polymers along the *a* axis with the Eu···Eu separation bridged by a single dpdo ligand of 13.3 Å length (Fig. 2a). Hydrogen bonds between a coordinated water molecule O(1W) and an oxygen atom O(42) from a neighboring parallel terminal ligand are found to stabilize the chains as cooperative interactions. Two adjacent 1D chains construct a one-dimensional ribbon through centro-symmetrically related two-fold hydrogen bonds formed by one of the other two terminal dpdo ligands containing oxygen atoms O(47) and O(48) and contacting a coordinated water molecule O(3W) from the centro-symmetrically related lanthanide ion (Fig. 2a).

Face-to-face π-π stacking interactions within these bridging pairs are also found to stabilize the ribbons. Partially overlapping arrangements between neighboring dpdo ligands are observed in the crystal. The centroid distances of 3.545 Å between the N(1) ring and the N(3) ring, 3.738 Å between the N(2) ring and the N(4) ring, 3.811 Å between the N(7) ring and the

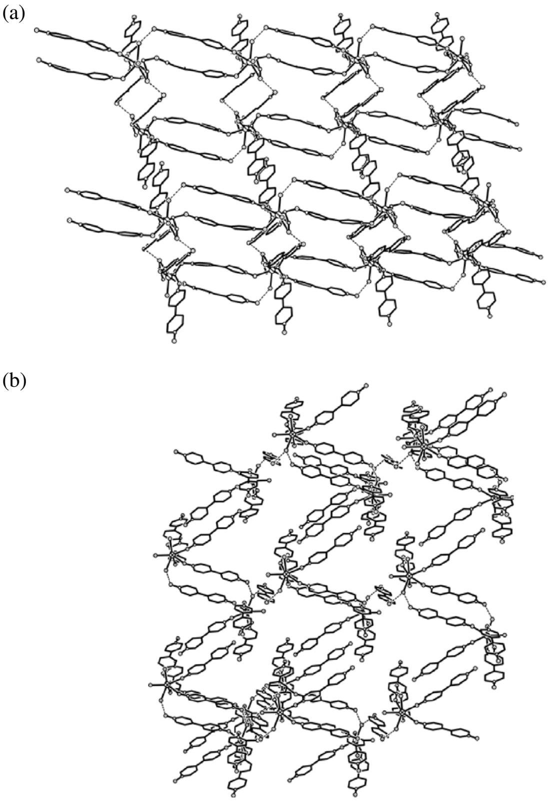

Fig. 2. (a) View of the 1D chain, 1D ribbon and 2D sheet consisting of $[Eu(dpdo)_4(H_2O)_3]^{3+}$ units along the *ac* plane. (b) Packing diagram of the porous 3D structure along the *bc* plane with the uncoordinated dpdo molecules as hydrogen bonding bridges. Hydrogen atoms are omitted for clarity.

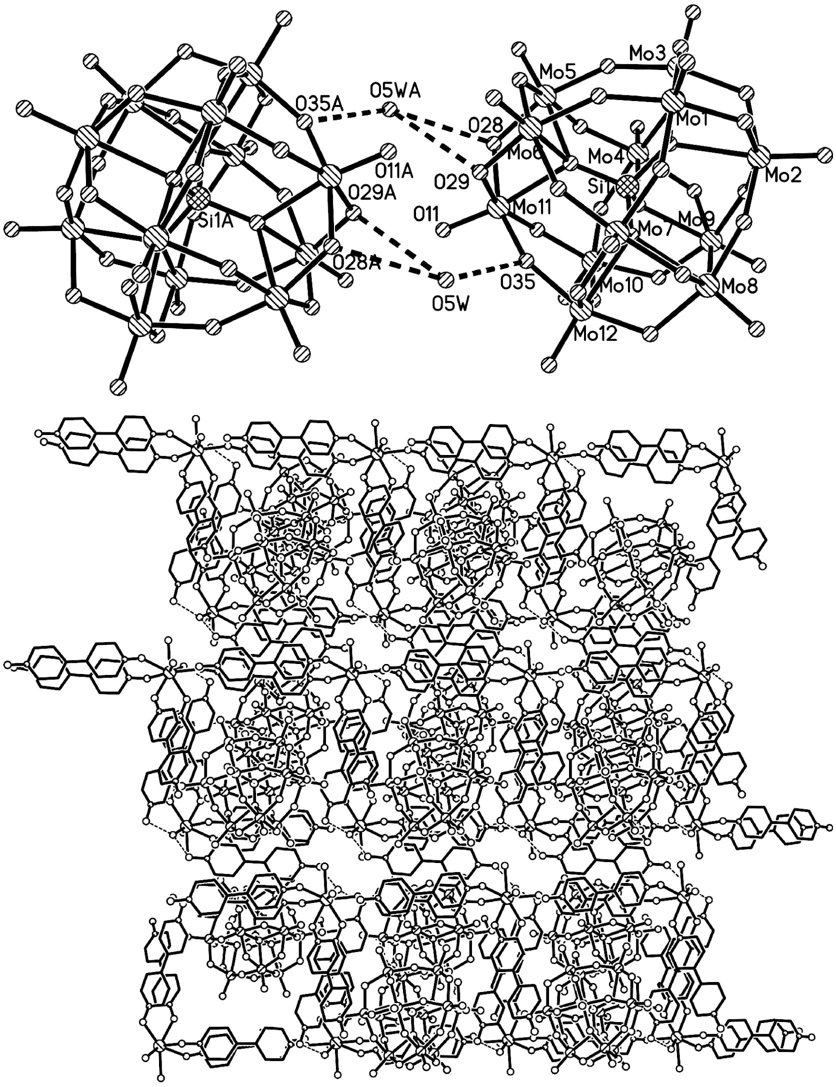

Fig. 3. The double-Keggin anion (top) and packing diagram of the 3D framework along the *ab* plane with each void occupied by a shoulder-by-shouder double-Keggin anion (bottom). Hydrogen atoms and solvent molecules of crystallization are omitted for clarity.

symmetry-related N(8) ring ($-x+2$, $-y+1$, $-z+1$), and 3.811 Å between the N(8) ring and the symmetry-related N(7) ring ($-x+2$, $-y+1$, $-z+1$) clearly suggest the existence of aromatic π-π stacking interactions. Adjacent ribbons are linked together through π-π stacking interactions between the N(5) ring and the symmetry-related N(6) ring ($-x+2$, $-y+1$, −z) (centroid distances of 3.798 Å), as well as between the N(6) ring and the symmetry-related N(5) ring ($-x+2$, $-y+1$, −z) (centroid distances of 3.798 Å) to form a 2D layer (Fig. 2a).

Further, adjacent layers are linked through hydrogen bonds between the oxygen atom O(49) of the free dpdo ligand and the coordinated water molecule O(3W) to form a 3D network (Fig. 2b), which is stabilized by intermolecular π-π stacking interactions between the free and the coordinated dpdo ligands with a centroid distance of 3.936 Å between the N(3) ring and the N(9) ring, as well as by hydrogen bonds among one crystal water molecule O(4W), one coordinated water molecule O(2W) and the oxygen atom O(49) of a free ligand. These stacked aromatic rings divide the framework into voids with a centro-symmetrically related shoulder-by-shoulder dimeric polyanion embedded in each of these voids (Fig. 3). Interestingly, compound **1** forms a supramolecular network with 3D tunnels, and the section size of the tunnels is *ca.* 10.4×21.1 Å^2 based on the sizes of the Keggin anions. Each pore is large enough to accommodate two centro-symmetrical Keggin ions in a shoulder-by-shoulder mode.

Though the basic structure of the POMs-based polymer **1** could be determined easily based on the X-ray structure analysis, it is not clear whether its protons sit near one of the oxygen atoms of the polyanion, near one of the oxygen atoms of the free dpdo ligand or around the water molecules. It was reported that based on high-resolution solid-state ^{1}H and ^{31}P NMR, there are at least three different types of protons in $H_3PW_{12}O_{40} \cdot n\ H_2O$, (i) protons present in highly hydrated samples, (ii) protonated water which is hydrogen-bonded to terminal oxygen atoms, $W{=}O\cdots H^+ (H_2O)_2$ (n = 6), and (iii) a proton which is directly bonded to a bridging oxygen atom, W–OH–W (n = 0) [16]. More recently, it was reported that based on REDOR experiments acidic protons are localized on both bridging (Oc) and terminal (Od) oxygen atoms of the Keggin unit in the anhydrous form of $H_3PW_{12}O_{40}$ [17]. In compound **1**, there are four crystal water molecules, and the separations between them are too long to stabilize the excess proton. Therefore, we think that the excess proton is not localized on the surface of the polyanion and not able to form such oligomers as $H_5O_2{}^+$ or $H_7O_3{}^+$. Dpdo ligands with N-oxide groups having formal partial negative and positive charges on the oxygen and nitrogen atoms, respectively, may be protonated at the oxygen atoms, but to our knowledge, no examples of such a protonation have been reported as yet. Since the O(5W) centers are located closely to the polyanions with the two shoulder-by-shoulder polyanions closed to form a double-Keggin anion (Fig. 3), the most likely position of the excess proton is at the O(5W) center, where the presence of positively charged species could draw the anions together [13]. In each of these anions, there are some short atom-atom separations: O(5W)···O(28A) 3.20(2), O(5W)···O(29A) 3.18(4), O(5W)···O(29) 3.28(4), O(5W)···O(35) 3.05(2), O(11)···O(6A) 2.97(3) and O(11)···O(29A) 3.34(4) Å (symmetry code A: $-x+1$, $-y+1$, $-z+1$).

In compound **1**, the bond lengths Si–O and Mo–O are 1.618(5)–1.638(6) and 1.660(6)–2.357(5) Å, respectively, comparable to those of 1.607(5)–1.624(5) and 1.655(6)–2.357(5) Å, respectively, in the complex $\{Gd(dpdo)_4(H_2O)_3\ H(SiMo_{12}O_{40})(dpdo)_{0.5}(CH_3CN)_{0.5}(H_2O)_4\}_n$ [8c]. In addition, the O–Si–O angles are in the range of 108.9(3)–109.9(3)°. All these results indicate that the $[SiMo_{12}O_{40}]^{4-}$ units have a normal Keggin structure in the dimeric anions. It is supposed that these double-Keggin anions may serve as templates during the assembly so that the cationic framework is aggregated around them, leading to the large-pore supramolecular network [8–12]. In other words, the non-coordinating double-Keggin-type anions play not only a charge-compensating role, but they can dramatically influence the overall solid-state architecture through their templating function. Thus, this strategy provides a new synthetic approach to access novel topologies and to develop a better understanding of the formation of double-Keggin anions within the resultant structure.

Thermogravimetric analysis

Thermogravimetric analysis of the powder of the crystalline sample of compound **1** in an atmosphere of N_2 shows a weight loss of 4.67 % in the temperature range of 25–200 °C, corresponding to four solvate water molecules, three coordinated water molecules and an acetonitrile molecule (calcd. 4.94 %). There is no weight loss in the temperature range of 200–350 °C, and the anhydrous product begins to rapidly decompose at 350 °C. The weight loss in the temperature range of 350–700 °C corresponds to the loss of dpdo ligands and the disrupting of the structural skeletons of the $[SiMo_{12}O_{40}]^{4-}$ anion.

Conclusion

In summary, we have successfully obtained a metal coordination polymer with 3D tunnels from dpdo ligands and Eu(III) ions in acetonitrile/water solution templated by centro-symmetrically shoulder-by-shoulder double-Keggin-type anions.

Experimental Section

General

All organic solvents and materials used for synthesis were of reagent grade and used without further purification. $EuCl_3 \cdot 6H_2O$ was prepared by dissolving Eu_2O_3 (99.9 %) in hydrochloric acid followed by drying and crystallization. α-$H_4SiMo_{12}O_{40} \cdot 14H_2O$ was prepared according to a literature method [18] and characterized by an IR spectrum and TG analysis. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C analyzer. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. Thermogravimetric analyses were carried out on a Perkin-Elmer thermal analyzer in

Table 1. Crystal structure data for **1**.

Formula	$C_{46}H_{52.5}EuMo_{12}N_{9.5}O_{56}Si$
M_r	2965.81
Cryst. size, mm^3	$0.40 \times 0.30 \times 0.30$
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	13.250 (3)
b, Å	16.539(4)
c, Å	18.526(5)
α, deg	88.519(5)
β, deg	81.887(4)
γ, deg	83.185(4)
V, Å^3	3990.6(17)
Z	2
D_{calcd}, g cm^{-3}	2.47
$\mu(MoK_\alpha)$, cm^{-1}	0.3
θ range for data collection, deg	2.04 – 25
$F(000)$, e	2848
hkl range	$-15 \le h \le +15$, $-19 \le k \le +18$, $-22 \le l \le +16$
Refl. measured	19638
Refl. unique	11538
R_{int}	0.094
Param. refined	1117
$R1/wR2$ [$I \ge 2\sigma(I)$]	0.062/0.167
$R(F)/wR(F^2)$[a] (all reflections)	0.072/0.174
GoF	1.051
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	1.87/−2.10

[a] $w = 1/[\sigma^2(F_o^2) + (0.1083P)^2 + 6.5588P]$, where $P = (F_o^2 + 2F_c^2)/3)$.

an atmosphere of N_2 with a heating rate of 10 °C/min between ambient temperature and 700 °C.

Synthesis

The metal:ligand ratio chosen is based on the possible maximum of the coordination number of metal centers and dpdo ligands all acting as bridging ligands. Compound **1** was prepared by neutralization of the acid α-$H_4SiMo_{12}O_{40} \cdot 14H_2O$ (40 mg, 0.02 mmol) and adding $EuCl_3 \cdot 6H_2O$ (8 mg, 0.02 mmol) dissolved in water (2 mL). The solution was heated to 80 °C in a water bath. Yellow crystals were formed after cooling the saturated solution and slow evaporation at r. t., and characterized by the IR spectrum. A buffer layer of a solution (10 mL) of acetonitrile/water (3 : 2, v/v) was carefully layered over 4 mL of an aqueous solution of 4,4′-bipyridine-*N*,*N*′-dioxide hydrate (0.1 mmol, 22 mg). Then an acetonitrile/water (3 : 1, v/v) solution (4 mL) of the resultant heteropolyacid europium salts was carefully layered over the buffer layer. Orange crystals appeared after 4 – 5 weeks and were collected and dried in air after being quickly washed with water. Yield: 80 % based on α-$H_4SiMo_{12}O_{40} \cdot 14H_2O$. $C_{46}H_{52.5}EuMo_{12}N_{9.5}O_{56}Si$ (2965.81): calcd. C 18.63, H 1.78, N 4.49; found C 18.36, H 1.63, N 4.26. – IR (KBr): four characteristic vibrations resulting from heteropolyanions with the Keggin structure: ν(Mo=Ot) = 951, ν(Mo–Ob) = 865, ν(Mo–Oc) = 793, ν(Si–Oa) = 905 cm^{-1}; four characteristic vibrations resulting from dpdo molecules: ν(N–O) = 1228, ν(ring) = 1470, δ(C–H, in plane) = 1181, δ(N–O) = 838 cm^{-1}.

Table 2. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses[a].

Distances		Distances	
Si1–O38	1.618(5)	Mo1–O40	2.332(5)
Si1–O40	1.625(5)	Eu1–O44	2.346(6)$^{\#1}$
Si1–O37	1.625(5)	Eu1–O43	2.354(6)
Si1–O39	1.638(6)	Eu1–O45	2.383(6)
Mo1–O1	1.696(6)	Eu1–O47	2.406(6)
Mo1–O13	1.917(6)	Eu1–O1W	2.409(7)
Mo1–O15	1.957(6)	Eu1–O3W	2.414(6)
Mo1–O17	1.889(6)	Eu1–O2W	2.414(6)
Mo1–O16	1.880(5)	Eu1–O41	2.436(6)
Angles		Angles	
O37–Si1–O39	108.9(3)	O16–Mo1–O40	85.0(2)
O40–Si1–O39	109.6(3)	O17–Mo1–O40	85.9(2)
O38–Si1–O39	109.9(3)	O13–Mo1–O40	73.5(2)
O40–Si1–O37	109.7(3)	O15–Mo1–O40	74.1(2)
O38–Si1–O37	108.9(3)	O43–Eu1–O45	79.9(2)
O38–Si1–O40	109.8(3)	O44$^{\#1}$–Eu1–O47	70.7(2)
O16–Mo1–O17	86.8(2)	O45–Eu1–O47	72.7(2)
O17–Mo1–O11	88.7(3)	O44$^{\#1}$–Eu1–O1W	67.2(2)
O16–Mo1–O15	88.9(2)	O45–Eu1–O1W	81.6(3)
O13–Mo1–O15	87.6(3)	O44$^{\#1}$–Eu1–O3W	79.5(2)
O3W–Eu1–O2W	69.1(2)	O43–Eu1–O3W	74.2(2)
O43–Eu1–O41	76.9(2)	O47–Eu1–O3W	72.6(2)
O45–Eu1–O41	78.1(2)	O44$^{\#1}$–Eu1–O2W	89.7(2)
O1W–Eu1–O41	66.3(2)	O1W–Eu1–O2W	86.4(3)
O2W–Eu1–O41	69.0(2)		

[a] Symmetry code: $^{\#1}$ $x+1, y, z$.

X-Ray structure determination

The crystal structure of the title complex was determined from single crystal X-ray diffraction data. Intensity data were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) using the programs SMART and SAINT [19]. The structure was solved by Direct Methods and refined on F^2 by full-matrix least-squares methods with SHELXTL (version 5.1) [20]. All non-hydrogen atoms except the oxygen atoms of the solvate water molecules and the nitrogen and carbon atoms of the solvate acetontrile molecule were refined anisotropically. Hydrogen atoms of the organic molecules were placed in calculated positions and refined using a riding model. Hydrogen atoms of coordinated water molecules were localized by difference Fourier maps and refined by fixing the isotropic displacement factors being 1.2 times that of the mother oxygen atoms attached. Hydrogen atoms of the acetontrile molecule were localized by difference Fourier maps and refined by fixing the isotropic displacement factors at 1.2 times that of the mother carbon atoms. Crystal parameters, data collection and refinement results for compound **1** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

CCDC 667020 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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