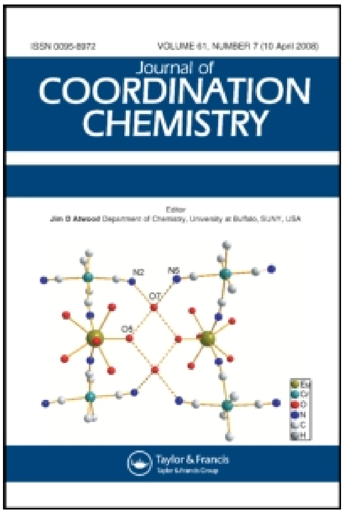

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A water chain with trimeric/hexameric clusters trapped in a POM/Ln compound

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A new 3-D supramolecular compound based on a Keggin polyoxometalate and lanthanide (Ln) coordination cations $[Ce(H_2O)_3L_3]_2[HSiMo_{12}O_{40}]_2[L]\cdot 7H_2O$ (**1**) (L = isonicotinic acid) has been synthesized and characterized by routine methods. Compound **1** has a water chain with trimeric and hexameric water clusters trapped in the network. The isonicotinic acid plays a key role in forming the 1-D water chains. Compound **1** shows intense photoluminescence at room temperature.

Keywords: Polyoxometalate; Water chain; Lanthanide; Luminescence properties

1. Introduction

Water plays a crucial role in many biological and chemical processes, and water clusters have attracted increasing attention as they can provide new insight into the structures of bulk water and/or ice [1]. While these studies have significantly advanced understanding of "discrete" water clusters involving hexamers [2, 3], octamers [4, 5], decamers [6], dodecamers [7], and even hexadecamers [8], very little is known about how these clusters link to form infinite 1-D or 2-D water morphologies. Many fundamental biological processes [9, 10] and properties of materials [11, 12] depend on the unique properties of 1-D water morphologies. Recent studies have shown that 1-D water morphologies as "proton wires" exist in gramicid in a membrane channel [13], bacteriorhodopsin [14], and *a*-amylase [15] for rapid transport of protons. Only a few 1-D water morphologies have been reported [16–20] and the formation of 1-D water morphologies remains challenging.

Polyoxometalates (POMs) have attracted long-lasting interest in photochemistry, catalysis, medicine, electrical conductivity, materials science, and magnetism [21–23]. A new advance is the design and construction of compounds containing POMs and lanthanide cations because such compounds are good candidates for electronic, magnetic, and photosensitive materials [24–33]. Keggin heteropolyanions are very

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important in the family of POMs and have been employed as building blocks to synthesize lanthanide compounds by many groups. Thanks to the work of Pope [25], Mialane [26], Niu [28], Hill [30], and others that many compounds containing POMs and lanthanide cations have been synthesized. Most of the reported work is on unsaturated Keggin hetero-POMs. In contrast, only a few composed of lanthanide cations and saturated Keggin hetero-POMs have been reported. Notable examples include 1-D chains [34], 2-D [29], and 3-D [35] supramolecular networks. Therefore, it will be useful to study the saturated Keggin POM/lanthanide field.

Recently, remarkable 1-D/2-D water morphologies have been synthesized by Chen *et al.* [19], in which metal–organic complexes serve as effective building blocks for the stabilization of 1-D/2-D water morphologies. Here we introduce isonicotinic acid ligands to construct a new saturated Keggin POM/lanthanide compound containing 1-D or 2-D water morphologies. Isonicotinic acid can use its O-donors to bridge lanthanide cations and the proton of the O-donor may be transferred to nitrogen in isonicotinic acid. The protonated isonicotinic acid can act as hydrogen-bond donors and/or acceptors, which may induce free water molecules or discrete water clusters to extend themselves to 1-D/2-D water morphologies. The highly oxophilic rare earth ions easily form precipitates instead of crystals. So the introduction of protecting ligands coordinated with rare earth ions can decrease the oxophilic properties of rare earth ions and should be effective to inhibit precipitation [36]. Fortunately, we obtained such a compound, $[Ce(H_2O)_3L_3]_2[HSiMo_{12}O_{40}]_2[L] \cdot 7H_2O$ (**1**) (L = isonicotinic acid), which contains a water chain with trimeric and hexameric water clusters.

2. Experimental

2.1. *Materials and general procedures*

All reagents were purchased commercially and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Mo and Ce were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were obtained on an Alpha Centaurt FT/IR spectrometer with KBr pellets from 400 to 4000 cm^{-1}. XPS analysis was performed on a VGESCALABMKII spectrometer with a Mg-Kα (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10°C min^{-1}. Luminescence measurements were carried out on a Hitachi F-4500 fluorescence spectrophotometer.

2.2. *Synthesis of $[Ce(H_2O)_3L_3]_2[HSiMo_{12}O_{40}]_2[L] \cdot 7H_2O$ (1)*

$H_4SiMo_{12}O_{40} \cdot 13H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and isonicotinic acid in the ratio of 1 : 2 : 4 were dissolved in water and the pH was carefully adjusted with a dilute NaOH solution (1 mol L^{-1}) to 3.2. After stirring for 30 min at 80°C and cooling to room temperature, the resulting solution was filtered and the filtrate was kept at room temperature. Yellow block crystals of **1** were isolated after 1 week (yield 46% based on Ce). Elemental Anal. Found (%): Mo, 45.96; Ce, 5.42; C, 10.87; N, 2.18. Calcd (%): Mo, 43.80; Ce, 5.33;

C, 10.96; N, 2.13. FT/IR data (cm^{-1}): 3443.79(s), 3376.26(s), 1727.65(s), 1644.75(s), 1599.41(s), 1396.28(s), 1245.29(m), 944.55(vs), 906.98(vs), 755.13(vs), 657.19(m), 410.42(m).

2.3. *X-ray crystallography*

X-ray diffraction data were collected on a SMART CCD diffractometer with graphite monochromated Mo-Kα radiation at room temperature. An empirical absorption correction was applied and the structure was solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELXL-97 program package. Organic hydrogens were generated geometrically [37]; hydrogen atoms on water were positioned from difference Fourier maps and fixed in the refinement. Crystal data for $Ce_2Si_2Mo_{24}O_{116}N_8C_{48}H_{72}$ (**1**): $M_r = 5252.09$, triclinic, space group *P-1*, $a = 11.4274(3)$ Å, $b = 14.4570(4)$ Å, $c = 19.0060(5)$ Å, $\alpha = 90.4280(10)^\circ$, $\beta = 92.3460(10)^\circ$, $\gamma = 96.6200(10)^\circ$, $V = 3116.12(14)$ Å^3, $Z = 1$, $D_c = 2.799\ g\,cm^{-3}$, $1.77 \leq \theta \leq 28.29^\circ$, $F(000) = 2492.0$, $T = 293(2)$ K, and $R_{int} = 0.019$. Structure solution and refinement based on 14,295 independent reflections with $[I > 2\sigma(I)]$ and 940 parameters gave R_1 and wR_2 as 0.0663 and 0.1563, respectively, and $S = 1.193$.

3. Results and discussion

3.1. *Crystal structures*

Compound **1** was synthesized from aqueous media and isolated as yellow block crystals. Single-crystal X-ray diffraction analysis reveals that **1** is constructed from two $[SiMo_{12}O_{40}]^{4-}$ ($SiMo_{12}$) clusters, two Ce^{3+} ions, seven L ligands, and 13 water molecules (figure S1). The valence sum calculations [38] show that all Mo and Ce atoms are in the +VI and +III oxidation states, respectively. As **1** was isolated from acidic aqueous solution, one proton was attached to $SiMo_{12}$ to compensate for charge balance, similar to

Table 1. Hydrogen-bonding lengths and angles in **1**.

Kinds of hydrogen-bonding interactions	D–H···A[a]	D–H (Å)	H···A (Å)	D···A (Å)	∠DHA	Symmetry operation for A
Water···water	O-1W–H-1WA···O-3W	0.84	2.38	3.20(3)	163	$-x+1, -y+1, -z$
	O-2W–H-2WA···O-7W	0.84	1.99	2.831(18)	176	x, y, z
	O-3W–H-3WA···O-4W	0.82	2.09	2.92(2)	177	x, y, z
	O-4W–H-4WA···O-1W	0.86	2.59	3.45(2)	173	$-x+1, -y+1, -z$
	O-5W–H-5WA···O-7W	0.85	2.01	2.875(16)	174	x, y, z
	O-7W–H-7WB···O-4W	0.84	2.00	2.842(18)	174	$-x, -y+1, -z$
	O-7W–H-7WA···O-2W	0.85	1.97	2.831(18)	175	x, y, z
Water···L	O-5W–H-5WB···N-1	0.85	2.03	2.888(15)	173	$-x, -y, -z+1$
	N-3–H-3B···O-4W	0.86	1.92	2.771(14)	169	$x-1, y-1, z$
Water···POM	O-1W–H-1WB···O-42	0.83	2.16	2.982(16)	164	$-x+1, -y, -z$
	O-3W–H-3WB···O-43	0.84	2.28	3.13(2)	178	$-x+1, -y+1, -z$

[a] D = donor atom, A = acceptor atom.

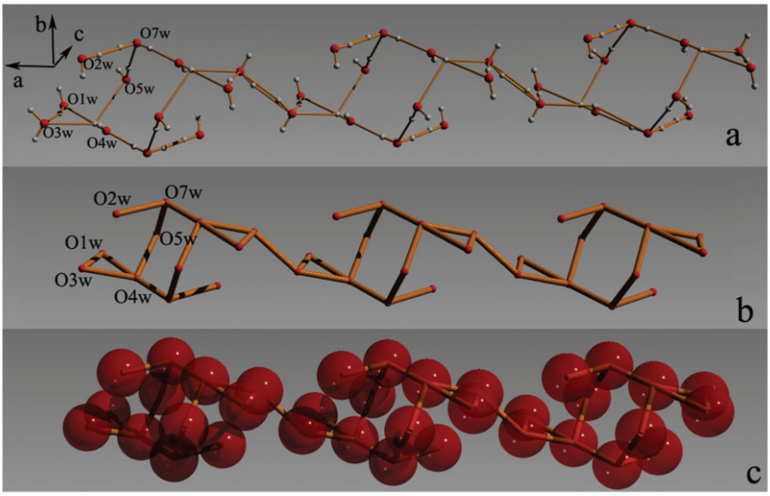

Figure 1. (a) Combined ball/stick representation of the water chain in **1**. (b) and (c) Combined ball/stick representation of the O···O interactions in water chain.

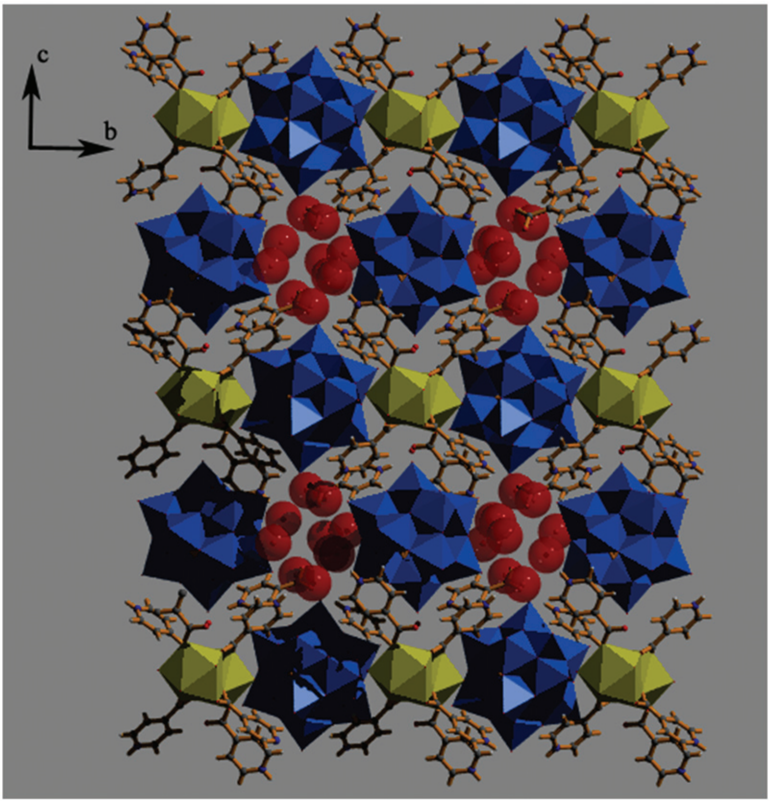

Figure 2. Combined polyhedral/ball/stick representation of the 3-D supramolecular networks.

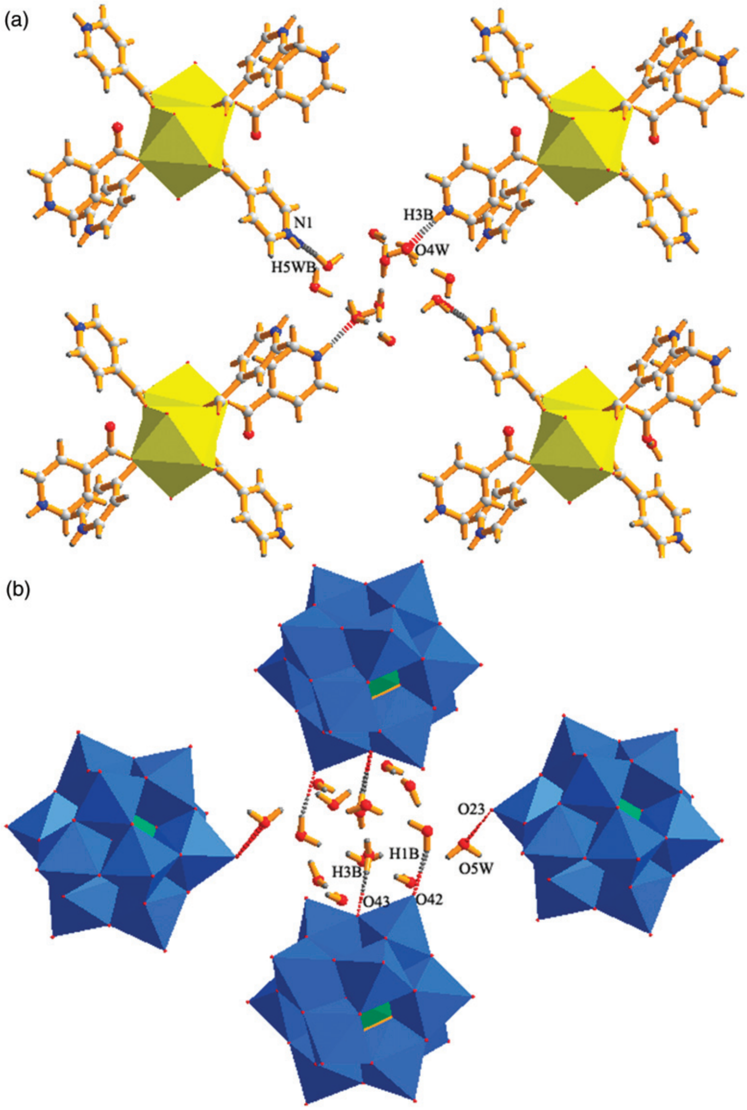

Figure 3. Combined polyhedral/ball/stick representation of the interactions between water clusters and dinuclear units (a); combined polyhedral/ball/stick representation of the interactions between water clusters and SiW_{12} units (b).

$[Ag_2(3atrz)_2]_2[(HPMo^{VI}_{10}Mo^{V}_2O_{40})]$ [39] and $\{[Cu(4,4'\text{-bipy})]_3[HSiMo_{12}O_{40}]\} \cdot 1.5H_2O$ [40]. Compound **1** is formulated as $[Ce(H_2O)_3L_3]_2[HSiMo_{12}O_{40}]_2[L] \cdot 7H_2O$.

The $SiMo_{12}$ anion possesses the well-known α-Keggin structure and central SiO_4 is disordered with a half occupation of oxygens. This disorder often appears in $[XM_{12}O_{40}]^{n-}$ Keggin clusters, explained by Evans and Pope [41]. In **1** there is a crystallographically unique Ce, which is coordinated by nine oxygens in a distorted monocapped square antiprism with six carboxyl oxygens from four L and three waters. Ce–O bond distances are between 2.396(8) and 2.854(7) Å and the bond angles

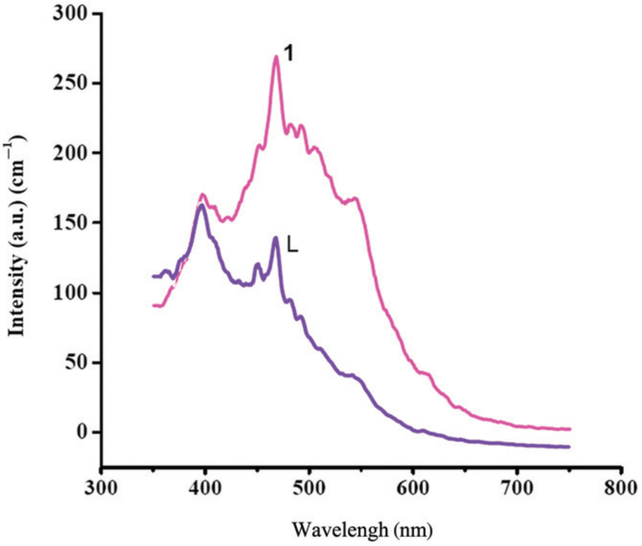

Figure 4. Solid-state emission spectra of L (blue) and **1** (pink) at room temperature.

of O–Ce–O are 67.9(3)°–146.4(3)°. The four L ligands adopt three coordination modes (scheme S1): the μ_1 (η^1)-carboxylato, the μ_2 (η^1,η^1)-carboxylato bridge, and the μ_3 (η^1,η^2)-carboxylato bridge mode. A dinuclear unit $\{[Ce(H_2O)_3L_3]_2\}$ is formed with Ce $\cdots$ Ce distance of 4.1477(11) Å (figure S2).

Seven crystallographically unique free water molecules are observed in the unit cell of **1**; six waters (O-1W, O-2W, O-3W, O-4W, O-5W, and O-7W) and their equivalents are associated by O–H $\cdots$ O hydrogen bonds to a $(H_2O)_{12}$ cluster. The geometric parameters of the cluster are summarized in table 1. As shown in figure 1(a), the $(H_2O)_{12}$ cluster consists of one $(H_2O)_6$ subunit and two $(H_2O)_3$ subunits. O-4W, O-5W, and O-7W are linked by hydrogen bonds to their equivalents derived by crystallographic inversion centers to form a $(H_2O)_6$ cluster. O1W, O3W, and O-4W form a $(H_2O)_3$ cluster and atoms equivalent to O-1W, O-3W, and O-4W form another $(H_2O)_3$ cluster. Adjacent $(H_2O)_{12}$ clusters are self-assembled by O-3W–H-3WA $\cdots$ O3W hydrogen bonds into a zigzag water chain along the *a* axis. To the best of our knowledge, such water chain represents the first characterized example in which trimeric and hexameric water clusters coexist (figure 1b and c).

A 3-D supramolecular network is formed in **1**, as shown in figure 2. In the network, the $SiMo_{12}$ anions, dinuclear $\{[Ce(H_2O)_3L_3]_2\}$, and water chains are linked *via* complicated hydrogen-bonding interactions shown in table 1, figure 3(a and b), where L are hydrogen-bond donors and acceptors while the $SiMo_{12}$ anions serve as hydrophilic units, perhaps inducing free water to form 1-D water chains.

3.2. *Thermal analysis*

The TG curve of **1** exhibits two weight-loss steps from 49°C to 490°C attributed to the loss of free and coordinated water molecules and decomposition of L (figure S4). The total weight loss (25.1%) is consistent with the calculated value (24.7%).

3.3. *Luminescence properties*

The luminescence properties of free ligand and **1** were investigated in the solid state at room temperature (figure 4). Free L displays three emission bands at 396, 468, and 539 nm when excited at 254 nm. A blue-fluorescent emission maximum at 467 nm and two other emission bands at 402 and 540 nm were observed for **1** upon excitation at 254 nm. The contrast between the emission spectra of **1** and L leads us to draw the conclusion that the luminescence of **1** is attributable to ligand-centered emission, and the obvious enhancement is attributed to an internal heavy metal effect [42].

4. Conclusions

We have obtained a 3-D supramolecular network constructed by $SiMo_{12}$ ions and lanthanide complexes, which embed water chains with trimeric and hexameric water clusters. Isonicotinic acid is a linker between two Ce^{3+} and serves as a structure directing agent to form 1-D water chains. The present findings further confirm that the proper metal–organic complexes can act as effective building blocks for the stabilization of extended water morphologies.

Supplementary material

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Center with a CCDC number 684763. Supplementary data associated with this article: IR, TG, scheme S1, and structural figures of **1**.

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