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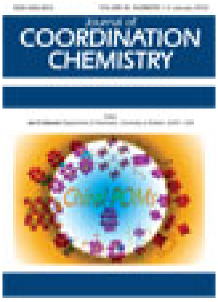

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Assembly of a new circle connecting circle chain through exerting the template role of a Keggin polyoxometalate

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By using the flexible bis(triazole) ligand 1,2-bis(1,2,4-triazol-1-yl)ethane (bte), a polyoxometalate-templated compound, $[Zn_2(bte)_4(SiW_{12}O_{40})]\cdot 2H_2O$ (**1**), was synthesized under hydrothermal conditions. The compound was characterized by single-crystal X-ray diffraction, elemental analyses, IR spectroscopy, photoluminescence spectroscopy, and cyclic voltammetry. Compound **1** is constructed from two motifs: the $[SiW_{12}O_{40}]^{4-}$ polyanion and a bi-nuclear metal-organic circle $[Zn_2(bte)_2]^{4+}$. The polyanion exerts a template role, inducing the formation of the bi-nuclear circle. The circles build a 1-D circle connecting circle chain through sharing the same Zn ions. Adjacent circles in the chain are vertical with each other. The template polyanion is surrounded by four circles from four different 1-D chains, forming a 3-D supramolecular structure.

Keywords: Keggin polyanion; Template; Hydrothermal synthesis; Flexible ligand

1. Introduction

Polyoxometalates (POMs), as a rich family of metal–oxygen clusters, have attracted attention owing to their various structures [1–3] and versatile physical and chemical properties [4–6], such as magnetism, catalytic activity, ion exchange, photochemical, and electrochemical activity. A branch of the field is to design and synthesize new POM-based compounds combining different transition-metal complexes (TMCs) [7, 8]. The polyanions in these compounds usually exert two roles. First, the polyanions offer bridging/terminal oxygen atoms to link TMC subunits. A series of these compounds have been obtained with 1-D, 2-D, and 3-D frameworks [9–11] such as a reported 1-D compound $[Cu^{I}(4,4'\text{-bpy})]_2[H_2SiW_{12}O_{40}]\cdot 2H_2O$ [12]. Second, the polyanions maintain discrete structures as templates, inducing diverse frameworks of TMCs [13–17]. In zeolites and zeolite-like compounds, organic amines are often templates [18]. However, in this series POMs are selected as inorganic templates, with versatile structural topologies and abundant chemical combinations with controllable shapes and sizes,

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such as Keggin (10.45 × 10.45 Å), Wells–Dawson (13.45 × 10.36 Å), and Anderson (9.07 × 9.07 Å). Polyanions also possess high negative charge that is conducive to assemble cationic metal-organic subunits. Compounds templated by POMs are relatively rare compared with POM-linking compounds. Thus, it is still a challenge to design and synthesize POM-templated compounds.

Reported POM-templated compounds are based on rigid organic ligands, such as 4,4′-bipyridine [19] and triazole [20]. Flexible organic ligands are seldom used [21]. Such ligands possess flexibility and conformational freedom, which can allow them to conform to the coordination environments of TM ions and POMs and induce interpenetrating structures [22–24]. Thus, using flexible organic ligands to construct POM-templated compounds becomes an attractive and challenging field. In this work, we chose Keggin polyanions as templates to induce a new Zn-flexible bis(triazole) ligand framework.

Herein, we report $[Zn_2(bte)_4(SiW_{12}O_{40})] \cdot 2H_2O$ (**1**) by utilizing the flexible bis(triazole) ligand 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) as shown in scheme 1. Compound **1** contains bi-nuclear metal-organic circles $[Zn_2(bte)_2]^{4+}$, which connect with each other through sharing the same Zn ions to build a 1-D circle connecting circle chain. The polyanions have template roles.

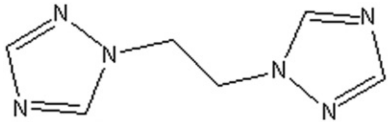
2. Experimental

2.1. *Materials and methods*

All reagents were of reagent grade and used as received from commercial sources. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Si, W, and Zn were determined by a Leaman inductively coupled plasma spectrometer. IR spectrum was obtained on an Alpha Centaurt FT/IR spectrometer as a KBr pellet from 400 to 4000 cm^{-1}. Fluorescence spectra were carried out on an F-4500 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source. A CHI 440 Electrochemical Quartz Crystal Microbalance was used for the electrochemical experiments. A conventional three-electrode cell was used at room temperature. Chemically bulk-modified carbon-paste electrode (CPE) was used as the working electrode. An SCE and a platinum wire were used as reference and auxiliary electrodes, respectively.

2.2. *Synthesis $[Zn_2(bte)_4(SiW_{12}O_{40})] \cdot 2H_2O$ (1)*

A mixture of $H_4[SiW_{12}O_{40}] \cdot 14H_2O$ (0.47 g, 0.15 mmol), $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.23 g, 1 mmol), and bte (0.1 g, 0.6 mmol) was dissolved in 10 mL of distilled water at



Scheme 1. The 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) molecule used in **1**.

room temperature. The pH was adjusted to 4.5 with 1.0 mol L^{-1} HCl and the suspension was placed into a Teflon-lined autoclave and kept under autogenous pressure at 160°C for 4 days. After slow cooling to room temperature (final pH = 3.2), colorless block crystals were filtered and washed with distilled water (30% yield based on W). Anal. Calcd for $C_{24}H_{36}N_{24}O_{42}Zn_2SiW_{12}$ (3698): C, 7.80; H, 0.98; N, 9.09; Si, 0.76; W, 59.66; Zn, 3.54. Found: C, 7.84; H, 0.95; N, 9.14; Si, 0.69; W, 59.81; Zn, 3.61.

2.3. *X-ray crystallography*

X-ray diffraction analysis data for **1** were collected on a Bruker Smart Apex CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software package [25]. All hydrogen atoms attached to carbons were generated geometrically. The crystal and structure refinement data for **1** are summarized in table 1. Selected bond lengths (Å), angles (°), and symmetry codes of **1** are listed in table 2.

2.4. *Preparation of 1 bulk-modified CPE*

Compound **1** bulk-modified CPE was used as the working electrode, prepared by the following process: 90 mg of graphite powder and 8 mg of **1** were mixed and ground together by an agate mortar and pestle to achieve a uniform mixture, and then 0.1 mL of Nujol was added with stirring. The homogenized mixture was packed into a glass tube with a 1.5 mm inner diameter, and the tube surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode.

3. Results and discussion

3.1. *Structure description*

Single-crystal X-ray structural analysis reveals that **1** is constructed from two discrete subunits, a Keggin cluster $[SiW_{12}O_{40}]^{4-}$ (abbreviated to SiW_{12}) (**A**) and a bi-nuclear circle $[Zn_2(bte)_2]^{4+}$ (**B**), as shown in figure 1.

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

Empirical Formula	$C_{24}H_{36}N_{24}O_{42}Zn_2SiW_{12}$
Formula weight	3698
Crystal system	Tetragonal
Space group	P4/mnc
Unit cell dimension (Å)	
a	14.4569(10)
c	15.1276(14)
Volume (Å^3), *Z*	3161.7(4), 2
Calculated density (g·cm^{-3})	3.880
Absorption coefficient (mm^{-1})	22.606
F(000)	3284
Final R_1[a], wR_2[b] $[I > 2\sigma(I)]$	0.0341, 0.0857
Final R_1[a], wR_2[b] (all data)	0.0364, 0.0868
Goodness-of-fit on F^2	1.074
Largest difference peak and holes (eÅ^{-3})	1.770 and −1.562

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

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

W(1)–O(4)	1.677(8)	W(1)–O(2)	1.889(8)
W(1)–O(6)	1.899(10)	W(1)–O(3)	1.898(9)
W(1)–O(1)#1	2.390(11)	W(1)–O(1)	2.405(11)
W(2)–O(5)	1.658(11)	W(2)–O(3)	1.893(9)
W(2)–O(6)#2	1.885(9)	W(2)–O(1)	2.378(11)
W(2)–O(1)#3	2.378(11)	Zn(1)–N(1)	1.999(8)
N(1)–Zn(1)–N(1)#3	114.0(5)	N(1)–Zn(1)–N(1)#4	107.6(5)
N(1) –Zn(1)–N(1)#4	114.0(5)	N(1)#5–Zn(1)–N(1)#4	106.9(5)

Symmetry codes: #1: $-y+1$, $x+1$, z; #2: $y-1$, $-x+1$, $-z$; #3: x, y, $-z$; #4: $-y+1/2$, $-x+1/2$, $-z+1/2$; #5: $-x$, $-y+1$,z.

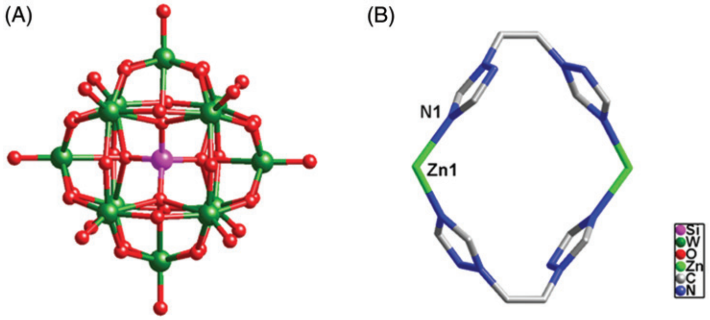


Figure 1. Two subunits in **1**: (A), the Keggin cluster SiW_{12}; (B), the bi-nuclear circle $[Zn_2(bte)_2]^{4+}$.

The **A** subunit shows a classical α-Keggin type anion (figure 1A). The central Si is surrounded by a cube of eight oxygen atoms, with each oxygen site half-occupied with Si–O distance of 1.636(11) Å. The W–O distances vary from 1.658(11)–2.405(11) Å and can be divided into three groups: (i) the Mo–O_d (O_d=terminal oxygen) bonds are 1.658(11) and 1.677(8) Å; (ii) Mo–$O_{b/c}$ ($O_{b/c}$=bridging oxygen) distances vary from 1.877(8) to 1.899(10) Å; (iii) the longest Mo–O_a (O_a=oxygen coordinated with Si) bonds are in the range 2.378(11)–2.405(11) Å. The Si–O and W–O lengths are in the normal ranges [26]. In **1**, the SiW_{12} polyanion retains the discrete structure and plays a template role.

In **B** subunit, two bte ligands are fused by two Zn ions to construct a bi-nuclear circle (figure 1B). In the circle, the dimensions are 7.6 × 8.8 Å, exhibiting a hexagon configuration (figure S1). The Zn is four-coordinate with four nitrogen atoms from four bte ligands with Zn–N distance of 1.999(8) Å, while the N–Zn–N angles are 106.9(5)–114.0(5)°. These bond distances and angles are comparable to those of similar four-coordinate Zn^{II} compounds [27]. The bte adopts a U-like conformation, offering two apical N donors to link two Zn ions. The formation of the circle is related to the flexible $–(CH_2)_2–$ spacer of bte, which can bend and rotate freely. Furthermore, through sharing the same Zn ions, the bi-nuclear circles link with each other to construct a 1-D circle connecting circle chain, as shown in figure 2(a). Adjacent circles in the 1-D chain are perpendicular to each other (figure 2b and c). This linking mode may decrease repulsions between circles.

Subunit **A** acting as a template induces the 1-D circle connecting circle chain. The dimensions of SiW_{12} polyanion (10.45 × 10.45 Å) are larger than the bi-nuclear circle

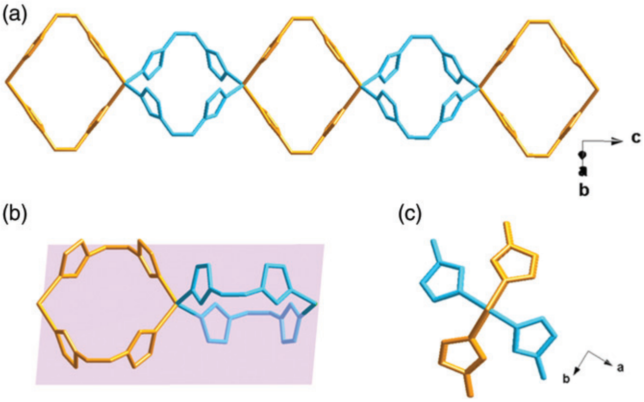


Figure 2. (a) The 1-D circle connecting circle chain in **1**. (b)–(c) The adjacent circles in the 1-D chain are perpendicular to each other.

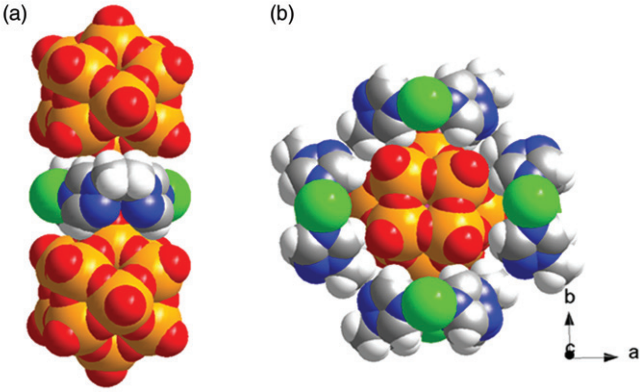


Figure 3. (a) Each bi-nuclear circle is covered with two SiW_{12} polyanions. (b) Each SiW_{12} polyanion is surrounded by four bi-nuclear circles.

(7.6 × 8.8 Å) in this 1-D chain. Thus, each bi-nuclear circle is covered with two SiW_{12} polyanions, a bi-nuclear circle supports two polyanions (figure 3a). Furthermore, each SiW_{12} polyanion is surrounded by four bi-nuclear circles, as shown in figure 3(b), such that four sets of 1-D circle connecting circle chains enwrap the polyanions viewed from the *c*-axis (figure 4). Thus, through hydrogen bonds a 3-D supramolecular structure of **1** is formed.

3.2. *FT-IR spectrum*

The IR spectrum of **1** is shown in figure S2. Characteristic bands at 976, 922, 878, and 791 cm^{-1} are attributed to $\nu(W–O_d)$, $\nu(Si–O)$, and $\nu(W–O_c–W)$ bands, respectively. Bands at 1627–1142 cm^{-1} are attributed to the bte ligands.

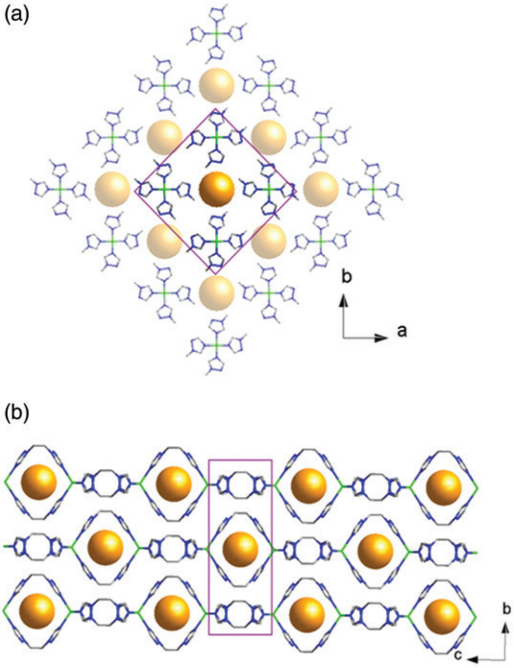


Figure 4. Four sets of 1-D circle connecting circle chains enwrap polyanions to form a 3-D supramolecular structure of **1** viewed from the *c*-axis (a) and the *a*-axis (b).

3.3. *Photoluminescence property*

Photoluminescence spectrum of powder sample of **1** at room temperature is shown in figure S3. Compound **1** exhibits photoluminescence with an emission maximum at 467 nm upon excitation at 254 nm. The emission peak would be assigned to ligand-to-metal charge transfer [28].

3.4. *Cyclic voltammetry*

As **1** is insoluble in water and common organic solvents, the bulk-modified CPE becomes the optimal choice to study electrochemical properties, which is inexpensive, easy to prepare and handle [29]. Redox properties of **1**–CPE were studied in 1 mol L^{-1} H_2SO_4 aqueous solution. The cyclic voltammograms for **1**–CPE at different scan rates are presented in figure 5 in the potential range 0 to −700 mV. There exist three reversible redox peaks I–I′, II–II′, and III–III′ with the half-wave potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ at −330 (I–I′), −450 (II–II′), and −605 (IV–IV′) mV (scan rate: 100 $mV \cdot s^{-1}$), respectively. Redox peaks I–I′ and II–II′ correspond to two consecutive one-electron processes of W centers, while III–III′ corresponds to a two-electron process [30]. Furthermore, when the scan rates were varied from 100 to 500 $mV \cdot s^{-1}$ for **1**−CPE, the peak potentials gradually change, cathodic peak potentials shift negative, and the corresponding anodic peak potentials positive with increasing scan rates.

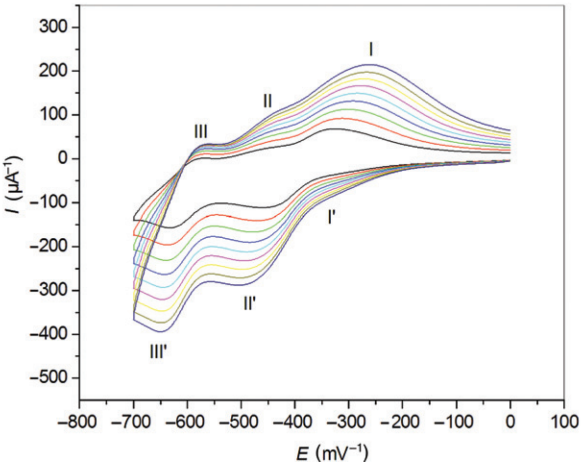


Figure 5. The cyclic voltammograms of the **1**–CPE in 1 molL^{-1} H_2SO_4 at different scan rates (from inner to outer: 100, 150, 200, 250, 300, 350, 400, 450, and 500 mV · s^{-1}).

The results verify that the redox ability of the parent α-Keggin polyanions can be maintained in the hybrid solids, which promises an application of this kind of inorganic–organic hybrid materials in electrochemistry.

4. Conclusion

In this article, **1** has been synthesized under hydrothermal conditions through exerting the template role of Keggin polyanions. In **1**, SiW_{12} polyanion retains its discrete structure but induces a bi-nuclear metal-organic circle $[Zn_2(bte)_2]^{4+}$. Furthermore, through sharing the same Zn ions, these circles connect to build a 1-D circle connecting circle chain. Adjacent circles in the chain are perpendicular. The SiW_{12} polyanions are surrounded by four sets of these 1-D chains. This work enriches examples of POM-templated compounds, especially using flexible organic ligands. Further study on other flexible organic ligands and transition metal ions is underway for construction of POM-templated compounds.

Supplementary material

CCDC 832461 for **1** contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Centre *via* www.ccdc.cam.ac.uk/data-request/cif

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