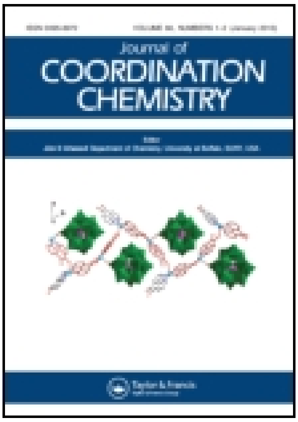
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:53
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

pH-dependent assembly of saturated to dilacunary Keggin-based silicotungstate: $[Cu(en)_2(H_2O)][H_2en]\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}\cdot 7.5H_2O$

Lei Yang [a] [b] , Lili Hou [c] , Pengtao Ma [a] & Jingyang Niu [a]
[a] Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University , Kaifeng , P.R. China
[b] The Department of Physics-Chemistry , Henan Polytechnic University , Jiaozuo , P.R. China
[c] Pharmaceutical College, Henan University , Kaifeng , P.R. China
Accepted author version posted online: 28 Feb 2013.Published online: 09 Apr 2013.

To cite this article: Lei Yang , Lili Hou , Pengtao Ma & Jingyang Niu (2013) pH-dependent assembly of saturated to dilacunary Keggin-based silicotungstate: $[Cu(en)_2(H_2O)][H_2en]\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}\cdot 7.5H_2O$, Journal of Coordination Chemistry, 66:8, 1330-1339, DOI: 10.1080/00958972.2013.780051

To link to this article: http://dx.doi.org/10.1080/00958972.2013.780051

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

Journal of Coordination Chemistry, 2013
Vol. 66, No. 8, 1330–1339, http://dx.doi.org/10.1080/00958972.2013.780051

pH-dependent assembly of saturated to dilacunary Keggin-based silicotungstate: $[Cu(en)_2(H_2O)][H_2en]\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}\cdot 7.5H_2O$

LEI YANG†,‡, LILI HOU§, PENGTAO MA† and JINGYANG NIU†*

†Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, P.R. China
‡The Department of Physics-Chemistry, Henan Polytechnic University, Jiaozuo, P.R. China
§Pharmaceutical College, Henan University, Kaifeng, P.R. China

(*Received 21 September 2012; in final form 12 December 2012*)

By controlling the pH of the reaction system, a dilacunary γ-Keggin silicotungstate $[Cu(en)_2(H_2O)][H_2en]\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}\cdot 7.5H_2O$ (**1**) (en = ethylenediamine) has been hydrothermally synthesized by the reaction of $CuCl_2$ with $\alpha\text{-}H_4SiW_{12}O_{40}$ and characterized by IR spectra, thermogravimetric analysis, and single-crystal X-ray diffraction. The product is prepared in the pH range 7.9–8.2, which reveals that pH plays a key role in the assembly of saturated $\alpha\text{-}H_4SiW_{12}O_{40}$ to dilacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ polyoxometalate. The polyoxoanion $\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}^{4-}$ of **1** presents a rare $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$-retaining structure, in which two lacunary sites of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ are unoccupied, meanwhile, two $[Cu(en)_2(H_2O)]^{2+}$ groups are grafted on either side of the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ unit by Cu–O–W bond.

Keywords: pH-Dependent; Dilacunary; Hydrothermal synthesis; Silicotungstate

1. Introduction

Polyoxometalates (POMs) have attracted interest for their potential and applications in catalysis, photochemistry, medicine, electrical conductivity, magnetism, and nanotechnology [1–3]. Currently, attention is concentrated on the incorporation of transition metal (TM) ions in lacunary polyoxoanion fragments due to a variety of structures with improved magnetic, catalytic, and electrochemical properties [4–7]; Keggin-based TM-substituted silicotungstates (TMSSTs) represent a large subfamily. Compared with abundant reports of trilacunary $[SiW_9O_{34}]^{10-}$ and monolacunary $[SiW_{11}O_{39}]^{8-}$-based TMSSTs, dilacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$-containing derivatives (abbreviated $\gamma\text{-}\{SiW_{10}\}$) are rare, but particularly interesting in catalysis because of their unique reactivities that depend on compositions and structures of their active sites [8–11]. Since the first γ-Keggin dilacunary silicotungstate $K_8[\gamma\text{-}SiW_{10}O_{36}]$ was reported by Hervé in 1986 [12], some $\gamma\text{-}\{SiW_{10}\}$ derivatives have been synthesized using $K_8[\gamma\text{-}SiW_{10}O_{36}]$ as a precursor [13–23]. In 2011, $Na_{34}[Mn_{19}(OH)_{12}(\alpha\text{-}SiW_{10}O_{37})_6]\cdot 115H_2O$ containing 19 manganese(II) centers and

---

*Corresponding author. Email: jyniu@henu.edu.cn

60-tungsto-6-silicate were reported by Kortz *et al.* [24], which was isolated by the reaction of Mn^{II} with the trilacunary precursor $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{12-}$ controlling the pH at 8. Subsequently, the Cronin group reported a silicotungstate, $K_{18}[Mn^{III}{}_2Mn^{II}{}_4(\mu_3\text{-}O)_2(H_2O)_4(B\text{-}\beta\text{-}SiW_8O_{31})(B\text{-}\beta\text{-}SiW_9O_{34})(\gamma\text{-}SiW_{10}O_{36})]\cdot 40H_2O$, composed of three inequivalent lacunary silicotungstate Keggin fragments, obtained by carefully controlling pH using $K_8[\gamma\text{-}SiW_{10}O_{36}]$ as a precursor [25]. The work of Kortz and Cronin demonstrate that controlling pH plays a key role in structural transformation of lacunary $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{12-}$ or $K_8[\gamma\text{-}SiW_{10}O_{36}]$ precursor to targeted product.

Inspired by this work, we considered whether carefully controlling pH could lead to the structural transformation of starting saturated $\alpha\text{-}H_4SiW_{12}O_{40}$ precursor to targeted $\gamma\text{-}\{SiW_{10}\}$. Controlling pH of decomposition of saturated $H_4SiW_{12}O_{40}$ precursor can result in different lacunary silicotungstate Keggin fragments. Therefore, parallel experiments have been carried out by systematically changing pH. We obtained three lacunary Keggin-based silicotungstates: dilacunary $[Cu(en)_2(H_2O)][H_2en]\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}\cdot 7.5H_2O$ (**1**), monolacunary $\{[Cu(en)_2(H_2O)]_2[Cu(en)_2][\alpha\text{-}SiCuW_{11}O_{39}]\}\cdot 5H_2O$ (**2**), and trilacunary $[H_2en]_{3.5}Na_2H[A\text{-}\alpha\text{-}SiW_9O_{36}]\cdot 10H_2O$ (**3**) at pH 8, 7.2, and 8.9, respectively. The parallel experiments unambiguously demonstrate that saturated $\alpha\text{-}H_4SiW_{12}O_{40}$ precursor has variable stability, undergoing structural transformations at high pH. The polyoxoanion $\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2]\}^{4-}$ of **1** presents a rare $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$-retaining structure with idealized C_{2V} symmetry, in which two lacunary sites of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ are still unoccupied, while two $[Cu(en)_2(H_2O)]^{2+}$ groups are grafted on either side of the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ unit by Cu–O–W bond bridge. Compound **1** is very different from the above-mentioned $\gamma\text{-}\{SiW_{10}\}$ derivatives, in which two lacunary sites are occupied by TM cations to reconstitute the saturated POMs. As far as we know, such $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$-retaining silicotungstate with supporting Cu-en complexes has not been reported.

2. Experimental

2.1. *Materials and methods*

All chemicals are analytical grade and used without purification. Hydrothermal syntheses were carried out in polytetrafluoroethylene-lined stainless steel containers. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C elemental analyzer. Inductively coupled plasma (ICP) spectra were performed on a Perkin-Elmer Optima 2000 ICP-OES spectrometer. IR spectra were obtained from KBr pellets on a Nicolet 170 SXFT-IR spectrometer from 400 to 4000 cm^{-1}. Thermogravimetric analyses were performed in N_2 on a Perkin-Elmer-7 instrument with a heating rate of 10 °C/min. PXRD measurements were performed on a Philips X'Pert-MPD instrument with CuKα radiation ($\lambda = 1.54056A$) at 293 K.

2.2. *Synthesis*

2.2.1. $[Cu(en)_2(H_2O)][H_2en]\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}\cdot 7.5H_2O$ (1). $H_4SiW_{12}O_{40}\cdot xH_2O$ (0.5 g), $CuCl_2$ (0.1 mmol), and HAc (0.5 ml) were dissolved in H_2O (10 ml). The mixture was stirred and its pH adjusted to 8.0 with en. After stirring for 2 h at room temperature, the resulting mixture was transferred to a Teflon-lined steel autoclave and kept at

130 °C for seven days. After slowly cooling to room temperature, purple block single crystals of **1** were filtered (Yield: *ca.* 72% based on $CuCl_2$). Anal. Calcd (%) for $C_{14}H_{79}Cu_3N_{14}O_{46.5}SiW_{10}$: C, 5.18; H, 2.45; N, 6.04; Si, 0.86; Cu, 5.87; W, 56.64. Found (%): C, 5.14; H, 2.59; N, 6.09; Si, 0.79; Cu, 5.83; W, 56.30.

2.2.2. $\{[Cu(en)_2(H_2O)]_2[Cu(en)_2][\alpha\text{-}SiCuW_{11}O_{39}]\}\cdot 5H_2O$ (2). **2** was prepared using a method similar to that employed for **1**, except pH was adjusted to 7.2 with en. Purple strip single crystals of **2** were obtained, which had been synthesized by Zhao *et al.* in a different way [26].

2.2.3. $[H_2en]_{3.5}Na_2H[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 10H_2O$ (3). **3** was prepared by similar method except with pH of 8.9. After slowly cooling to room temperature, the resulting purple solution was retained under slow solvent evaporation. After a month, colorless block crystals were collected (Yield: *ca.* 20% based on $H_4SiW_{12}O_{40}\cdot xH_2O$). Anal. Calcd (%) for $C_7H_{56}N_7Na_2O_{44}SiW_9$: C, 3.15; H, 2.11; N, 3.67; Si, 1.05; W, 61.92. Found (%): C, 3.08; H, 2.19; N, 3.62; Si, 1.16; W, 61.83.

2.3. *Crystallographic data collection and structure determination*

Data were collected on a Bruker APEX-II CCD diffractometer with Mo-Kα radiation at 298 K. Absorption corrections were applied using the multi-scan program SADABS [27]. The structures were solved by direct methods and non-hydrogen atoms were refined anisotropically by the least-squares method on F^2 by full-matrix least-squares using SHELXTL

Table 1. Crystal data and structure refinement parameters for **1** and **3**.

Empirical formula	$C_{14}H_{79}Cu_3N_{14}O_{46.50}SiW_{10}$ (**1**)	$C_7H_{56}N_7Na_2O_{44}SiW_9$ (**3**)
Formula weight	3245.12	2671.31
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, *P21/c*	Monoclinic, *P21/n*
a (Å)	17.015(3)	15.854(11)
b (Å)	17.001(3)	17.306(12)
c (Å)	23.964(4)	17.526(12)
β (°)	106.299(3)	93.405(14)
V (Å^3)	6653.5(18)	4800(6)
Z	4	4
D_c (g cm^{-3})	3.504	3.696
Crystal size	0.26 × 0.17 × 0.14 mm	0.35 × 0.27 × 0.21 mm
Absorption coefficient (mm^{-1})	18.267	21.635
F(000)	5896	4804
Theta range for data collection (°)	1.5–25	1.68–25
Limiting indices	$-20 \leqslant h \leqslant 20$ $-20 \leqslant k \leqslant 11$ $-27 \leqslant l \leqslant 28$	$-18 \leqslant h \leqslant 18$ $-19 \leqslant k \leqslant 20$ $-16 \leqslant l \leqslant 20$
Reflections collected/unique	34,302/11,690 [*R*(int) = 0.0585]	23,869/8442 [*R*(int) = 0.1087]
Data/restraints/parameters	11,690/115/811	8442/342/626
Goodness-of-fit on F^2	1.019	0.978
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0425$, $wR_2 = 0.1019$	$R_1 = 0.0450$, $wR_2 = 0.0797$
R indices (all data)	$R_1 = 0.0647$, $wR_2 = 0.1094$	$R_1 = 0.0639$, $wR_2 = 0.0845$

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

97 [28]. The heaviest atoms could be unambiguously located. C, N, and O atoms were subsequently located in the difference Fourier maps. Hydrogens residing on en were placed geometrically and no hydrogens associated with water were located in the difference Fourier map. Crystal data, as well as details of the data collection and refinement, for **2** and **3** are summarized in table 1.

3. Results and discussion

3.1. *Synthesis*

All reported γ-{SiW_{10}}-containing polyoxotungstates have been obtained by the reaction of a TM with $K_8[\gamma\text{-}SiW_{10}O_{36}]$ under slow solvent evaporation. The metastable precursor $K_8[\gamma\text{-}SiW_{10}O_{36}]$ usually undergoes isomerization dissolved in aqueous solution, leading to α or β isomer derivatives [12]. As a result, the encapsulation and substitution of TM cations into $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with the retention of the γ-Keggin framework have generally been considered to be very difficult. Herein, we chose $H_4SiW_{12}O_{40}$ as the precursor and synthesize by hydrothermal method based on the following considerations: (1) $H_4SiW_{12}O_{40}$ is a stable precursor with high yield compared to $K_8[\gamma\text{-}SiW_{10}O_{36}]$; (2) TMSSTs also can be obtained by the decomposition of saturated $H_4SiW_{12}O_{40}$ precursor through controlling of pH; and (3) The hydrothermal synthetic method has been widely used for POMs to obtain new compounds with desirable structures and properties, not easily obtainable under conventional aqueous solution conditions. In the process of hydrothermal synthesis, critical factors, such as initial reactants, reaction time, concentration, pH, and temperature, can significantly

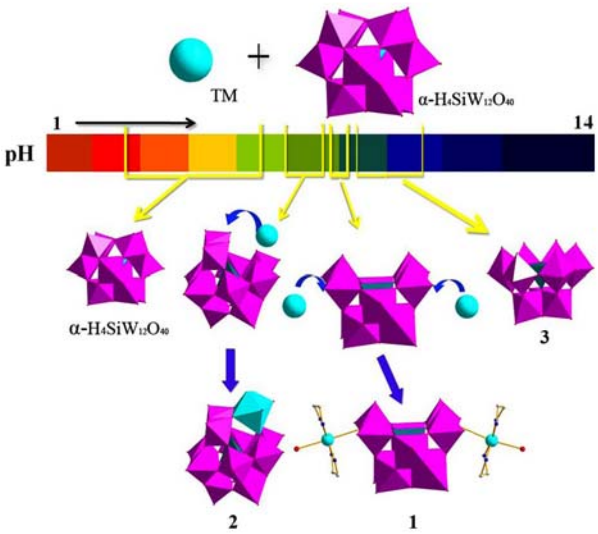


Figure 1. Schematic pH influence on the assembly of saturated to lacunary Keggin-based polyoxosilicotungstates. $H_4SiW_{12}O_{40}$ was separated in the pH range 4.0–6.5, with the pH value increasing, mono, di, and trilacunary silicotungstate (compounds **2**, **1**, **3**) were obtained in the ranges 7.0–7.5, 7.9–8.2, and 8.6–9.5, respectively. (Color code: WO_6, purple; Si, blackish green; Cu, sky blue; O, red; N, mazarine blue, and C gray (see http://dx.doi.org/10.1080/00958972.2013.780051 for color version).)

affect product composition. Herein, pH is the primary factor influencing the assembly of saturated to lacunary Keggin-based silicotungstate, which can be easily seen from figure 1.

To investigate the influence of pH on the structural transformation in the hydrothermal reaction system of $\{\alpha\text{-}H_4SiW_{12}O_{40}\text{–}CuCl_2\text{–en}\}$, we carried out parallel experiments by systematically changing in the pH range 1–14 at an interval of 0.1. $H_4SiW_{12}O_{40}$ was separated in the pH range 4.0–6.5, with the pH value increasing, mono-, di-, and trilacunary silicotungstate (compounds **2**, **1**, **3**) were obtained at 7.0–7.5, 7.9–8.2, and 8.6–9.5, respectively. The structural transformation of saturated $H_4SiW_{12}O_{40}$ to mono, di, and trilacunary silicotungstate from low pH (left) to high pH (right) is symbolically depicted by figure 1. High pH leads to decomposition of $H_4SiW_{12}O_{40}$ and the corresponding lacunary silicotungstate may be obtained by controlling the pH.

When $H_4SiW_{12}O_{40}$ was replaced by $K_4SiW_{12}O_{40}$, we isolated **1**, **2,** and **3** except with different amounts of en. When $H_4SiW_{12}O_{40}$ was replaced by $K_8SiW_{11}O_{39}$ or $K_{10}SiW_9O_{34}$, only **2** can be obtained. During the synthesis of **1**, HAc did not exist in the final structure. However, if HAc was not introduced into the reaction mixture or replaced by other acid (oxalate, boracic acid, or hydrochloric acid), no crystal products were isolated under similar reaction conditions, so it may be presumed that HAc is necessary for obtaining high quality crystals and enhancing the product yields of **1**.

3.2. *Structural description*

Single-crystal X-ray diffraction reveals that **2** displays the same structural framework as reported by Zhao [26] and **3** is constituted of a well-known $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ polyoxoanion, three and a half $[H_2en]^{2+}$, two Na^+ ions, and 10 crystal waters (figure S1). Therefore, only the structure of **1** is described in detail.

The asymmetric unit of **1** (figure 2) is constructed from a $\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}^{4-}$ polyoxoanion, one $[H_2en]^{2+}$, one $[Cu(en)_2(H_2O)]^{2+}$, and seven and a half crystal waters. The $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$-retaining polyoxoanion is different from the previously reported $\gamma\text{-}\{SiW_{10}\}$ derivatives.

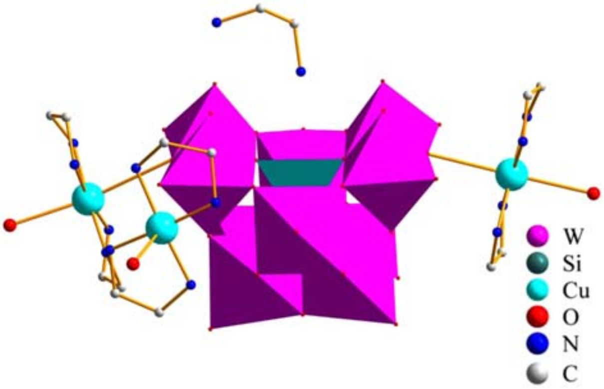


Figure 2. The polyhedral and ball-and-stick representation of the asymmetric unit of **1**. For simplification, crystal waters and hydrogens are omitted. (Color code: WO_6, purple; Si, blackish green; Cu, sky blue; O, red; N, mazarine blue, and C gray (see http://dx.doi.org/10.1080/00958972.2013.780051 for color version).)

Reported γ-{SiW$_{10}$} derivatives can be reduced to four kinds, sketched in figure 3. The two lacunary sites of $K_8[\gamma\text{-}SiW_{10}O_{36}]$ are occupied by TM cations to reconstitute the saturated POMs, resulting in: (1) dimetal-substituted monomer $[\gamma\text{-}SiW_{10}M_2O_{40}]^{n-}$ [13–16, 29] (figure 3(a)); (2) dimer constructed from two equivalent $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ units [17–22] (figure 3(b)); (3) trimer composed of three $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ units [22, 23] (figure 3(c)); and (4) trimer constituted with three inequivalent lacunary silicotungstate Keggin fragments [25] (figure 3(d)). In the polyoxoanion of **1**, two $[Cu(en)_2(H_2O)]^{2+}$ groups are grafted on $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$, meanwhile, the two lacunary sites of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ unit remain unoccupied.

Furthermore, the polyoxoanion $\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}^{4-}$ (figure 4(a)) is compared with the analogous monomer $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$ [29] (figure 4(b)). Two $PhPO_2$ groups are grafted on $[SiW_{10}O_{36}]^{8-}$ unit via terminal oxygens and act as electrophiles occupying two lacunary sites, forming the saturated $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$. While herein, two $[Cu(en)_2(H_2O)]^{2+}$ groups are incorporated into $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ via two μ_3-O instead of occupying lacunary sites to form the polyoxoanion $\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}^{4-}$, in which the skeleton of divacant $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ is still maintained.

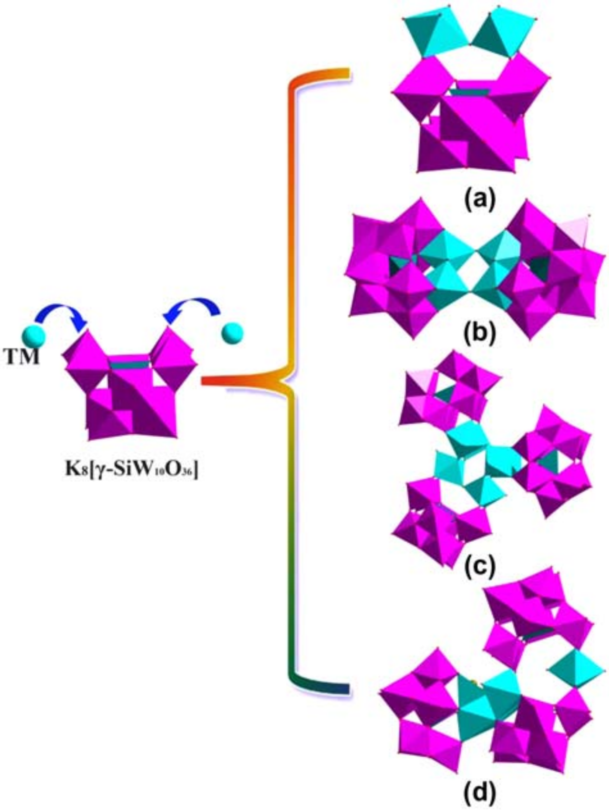


Figure 3. The reported $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ containing derivatives obtained from reactions between $K_8[\gamma\text{-}SiW_{10}O_{36}]$ precursor and TM under slow solvent evaporation. The two lacunary sites in $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ are occupied by TM forming (a) dimetal-substituted monomer $[\gamma\text{-}SiW_{10}M_2O_{40}]^{n-}$ [13–16, 29], (b) dimer constructed from two equivalent $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ units [17–22], (c) trimer composed of three $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ units [22, 23], (d) trimer constituted with three inequivalent lacunary silicotungstate Keggin fragments [25]. (Color code: WO_6, purple; Si, blackish green; TM, sky blue; O, red (see http://dx.doi.org/10.1080/00958972.2013.780051 for color version).)

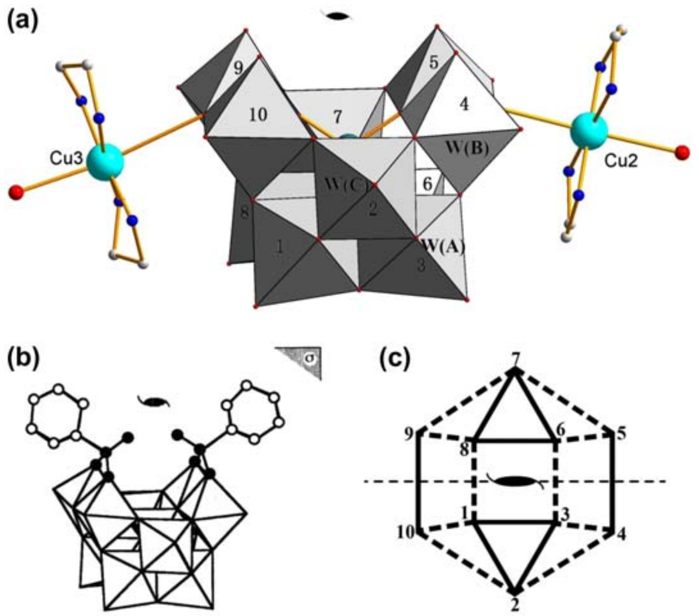


Figure 4. (a) Schematic representation of $\{[Cu(en)_2(H_2O)]_2[\gamma\text{-}SiW_{10}O_{36}]\}^{4-}$. For simplification the tungstens W(i) which become equivalent in the idealized C_{2v} symmetry will be given the following symbolism: W(A) for $i=1$, 3, 6, 8; W(B) for $i=4$, 5, 9, 10; W(C) for $i=2$ and 7. (b) Schematic representation of $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$ [27]. (c) Schematic plane representation of the polytungstate framework in **1**. Edge and corner junctions are symbolized by solid and dotted lines, respectively.

$\{\gamma\text{-}SiW_{10}O_{36}[Cu(en)_2(H_2O)]_2\}^{4-}$ adopts a geometry consistent with C_{2v} symmetry of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$. Actually the two $[Cu(en)_2(H_2O)]^{2+}$ groups are contained in a pseudo-mirror plane, orthogonal to the lacunary plane (figure 4(a)). Schematic plane representation of the polyoxotungstate framework is shown in figure 4(c), in which edge and corner junctions are symbolized by solid and dotted lines, respectively. For simplification, the tungstens W(i) which become equivalent in the idealized C_{2v} symmetry will be given the following symbolism [12]: W(A) for $i=1$, 3, 6, 8; W(B) for $i=4$, 5, 9, 10; W(C) for $i=2$ and 7.

The W–O bond lengths and the W(A)–O–W(B)–O junction are shown in table 2 and figure 5, respectively. There is an increase in W(A)–O(AB) and W(B)–O(P) bond lengths and a decrease in W(B)–O(AB) bond lengths compared with the dilacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ (figure 5(c)) in $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$ (figure 5(b)), in which the terminal

Table 2. Comparison of W–O distances among **1**, $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$ and $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ polyoxoanion. O(Cu): μ_3-oxo bridging between W(B) and Cu in **1** and bridge atom in $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$. O(P): μ-oxo bridging between W(B) and P in polyoxoanion $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$ and terminal atom in $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ anion.

Compound	Bond length	W(B)–O(Cu)	W(B)–O(P)	W(B)–O_t	W(B)–O(AB)	W(A)–O(AB)
1	Range	1.920–1.949		1.717–1.764	2.129–2.159	1.793–1.824
	Mean	1.935		1.744	2.142	1.815
$[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$	Range		1.99–2.03	/	1.80–1.85	1.98–2.01
	Mean		2.02		1.83	2.00
$[\gamma\text{-}SiW_{10}O_{36}]^{8-}$	Range			1.70–1.79	2.11–2.25	1.73–1.89
	Mean			1.74	2.19	1.82

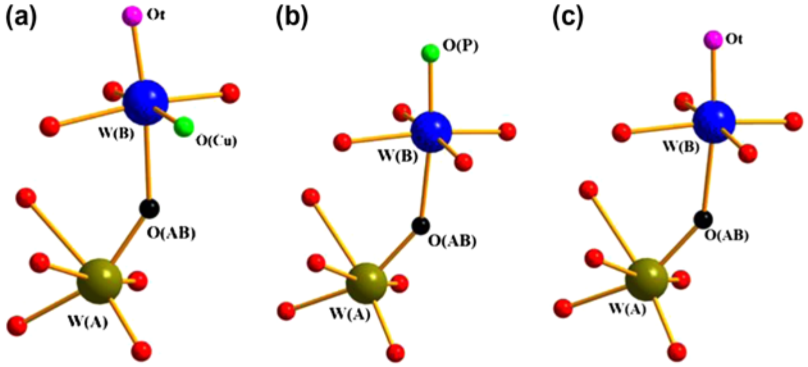


Figure 5. Focus on the W(A)–O–W(B)–O junction in: (a) **1**; (b) polyoxoanion $[\gamma\text{-SiW}_{10}O_{36}(PhPO)_2]^{4-}$; and (c) $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ anion.

oxygen (O_t) becomes bridging (O_P) resulting in variations of corresponding W–O bonds. The original μ_2-O becomes μ_3-O (O_{Cu}) bridging between W(B) and Cu in **1** (figure 5(a)); W(B)–O(AB), W(B)–O_t, and W(A)–O(AB) bond lengths have little variation with corresponding bond lengths in $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$. The above descriptions unambiguously demonstrate that coordination of Cu^{2+} on μ_3-O site has little influence on the skeleton of $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$. Si displays tetrahedron, which has been somewhat deformed resulting from the removal of two W octahedra compared with the saturated Keggin structure. The Si–O bond distances vary from 1.623(8) to 1.647(8) Å, the O–Si–O bond angles are 108.1 (4)–111.2(4)°. Cu1 is five-coordinate, coordinating with two en and one water. Cu2 and Cu3 are six-coordinate with distorted octahedral geometry, both defined by four nitrogens from two en in the plane and two oxygens on apical site, one from a water and the other from the skeleton of $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$. Bond valence sum (BVS) calculations [30] indicate that the oxidation states of all W and Cu in **1** are + 6 and + 2, respectively.

One diprotonated en and one $[Cu(en)_2(H_2O)]^{2+}$ are counterions stabilizing the polyoxoanion skeleton. N–H···O hydrogen bonds, including inter-molecular hydrogen bonds, exist between en and polyoxoanions or lattice waters with N···O distances 2.824–3.383 Å, which contribute to the chemical stability of **1**.

3.3. *TG curve of 1*

The TG curve of **1** (figure S2) shows two weight losses from 30 to 800 °C. The first weight loss of 6.00% (Calcd 5.82%) from 30 to 243 °C is assigned to the release of seven and a half crystal waters and three coordinated waters, followed by loss of 13.10% (Calcd 13.47%) from 244 to 680 °C corresponding to the decomposition of the {Si–O–W} framework according to the reaction $H_2[Cu(en)_2][en]\{\gamma\text{-SiW}_{10}O_{36}[Cu(en)_2]_2\} \rightarrow 10\ WO_3 + SiO_2 + H_2O\uparrow + 3CuO + 7en\uparrow$.

3.4. *IR spectrum*

The IR spectrum of **1** (figure S3) shows the characteristic vibrations resulting from Keggin POM framework at 1000–700 cm^{-1} [30]. Four groups of characteristic absorptions resulting from the dilacunary Keggin-type silicotungstate framework [29] are observed at 1042, 985, 937–811, and 737 cm^{-1}, attributed to the stretching vibrations of ν(Si–O), ν(W=O$_t$), ν(W–O$_b$), and ν(W–O$_c$), respectively. In comparison with those of $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ [12], the stretching vibrational bands ν(W–O$_b$–W) and ν(W=O$_t$) shift to higher frequency, attributed to the impact of the polyoxometallic moiety through fixation of the $[Cu(en)_2(H_2O)]$ units. The ν(N–H) is observed at 3244 cm^{-1} and ν(C–N) is at 1323 cm^{-1}. Peaks centered at 1587 and 1395 cm^{-1} are attributed to δ(N–H) and δ(C–H) [31], which confirms the presence of en in **1**. The occurrence of the vibration at 3434 cm^{-1} suggests the presence of lattice water in **1**. The IR spectrum is consistent with X-ray diffraction structural analysis.

4. Conclusions

By controlling pH, mono, di, and trilacunary silicotungstates ($\{[Cu(en)_2(H_2O)]_2[Cu(en)_2][\alpha\text{-SiCuW}_{11}O_{39}]\}\cdot 5H_2O$ **2**, $[Cu(en)_2(H_2O)][H_2en]\{\gamma\text{-SiW}_{10}O_{36}[Cu(en)_2(H_2O)]_2\}\cdot 7.5H_2O$ **1,** and $[H_2en]_{3.5}Na_2H[A\text{-}\alpha\text{-SiW}_9O_{34}]\cdot 10H_2O$ **3**) have been hydrothermally synthesized by the reaction of $CuCl_2$ with $\alpha\text{-H}_4SiW_{12}O_{40}$ in the presence of en. *The isolation of **1** shows an approach to extending the* γ-{SiW$_{10}$} *through reasonable controlling of the* pH. *We will expand to* other transition-metal cations (such as Zn, Fe, Ni, Mn, Cr) or other organic amines for more multidimensional γ-{SiW$_{10}$} derivatives. *Furthermore, the* lacunary sites of $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ unit in **1** are still unoccupied, which provides possibility to introduce TM heterometallic cations into the lacunary sites *forming* multidimensional TM heterometallic silicotungstates. Therefore, the systematic exploration of the POM system is in progress.

Supplementary material

CCDC 843866 for **1** and 861927 for **3** contain the Supplemental material crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version.

Acknowledgments

This work was supported by the Natural Science Foundation of China, Special Research Fund for the Doctoral Program of Higher Education, Innovation Scientists and Technicians Troop Construction Projects of Henan Province, the National Science Fund for Young Scholars of China (no. 21101059) and the Open Research Fund of State Key Laboratory of Inorganic Synthesis and Preparative Chemistry (grant no. 2011-26).

References

[1] D.L. Long, E. Burkholder, L. Cronin. *Chem. Soc. Rev.*, **36**, 105 (2007).
[2] L. Cronin, P. Kögerler, A. Müller. *J. Solid State Chem.*, **152**, 57 (2000).
[3] M.A. Aldamen, S.F. Haddad. *J. Coord. Chem.*, **64**, 4244 (2011).
[4] B.S. Bassil, S.S. Mal, M.H. Dickman, U. Kortz, H. Oelrich, L. Walder. *J. Am. Chem. Soc.*, **130**, 6696 (2008).
[5] Y. Kikukawa, S. Yamaguchi, Y. Nakagawa, K. Uehara, S. Uchida, K. Yamaguchi, N. Mizuno. *J. Am. Chem. Soc.*, **130**, 15872 (2008).

[6] R. Khoshnavazi, S. Tayamon. *J. Coord. Chem.*, **63**, 3356 (2010).

[7] (a) P.T. Ma, Y. Wang, H. Chen, J.P. Wang, J.Y. Niu. *J. Coord. Chem.*, **64**, 2497 (2011); (b) A.X. Tian, X.L. Lin, Y.J. Liu, G.Y. Liu, J. Ying, X.L. Wang, H.Y. Lin. *J. Coord. Chem.*, **65**, 2147 (2012); (c) X.F. Wang, X.Y. Ma, Y.Q. Xu, C.W. Hu. *J. Coord. Chem.*, **65**, 1043 (2012); (d) R. Yang, S.X. Liu, Q. Tang, S.J. Li, D. D. Liang. *J. Coord. Chem.*, **65**, 891 (2012).

[8] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno. *Science*, **300**, 964 (2003).

[9] P. Mialane, C. Duboc, J. Marrot, E. Riviére, A. Dolbecq, F. Sécheresse. *Chem. Eur. J.*, **12**, 1950 (2006).

[10] A. Yoshida, M. Yoshimura, K. Uehara, S. Hikichi, N. Mizuno. *Angew. Chem. Int. Ed.*, **45**, 1956 (2006).

[11] Y. Kikukawa, K. Yamaguchi, N. Mizuno. *Angew. Chem. Int. Ed.*, **49**, 6096 (2010).

[12] J. Canny, A. Tézé, R. Thouvenot, G. Hervé. *Inorg. Chem.*, **25**, 2114 (1986).

[13] X.Y. Zhang, C.J. Connor, G.B. Jameson, M.T. Pope. *Inorg. Chem.*, **35**, 30 (1996).

[14] J. Canny, R. Thowenot, A. Tézé, G. Hervé, M.L. Loftus, M.T. Pope. *Inorg. Chem.*, **30**, 976 (1991).

[15] Y. Nakagawa, K. Uehara, N. Mizuno. *Inorg. Chem.*, **44**, 9068 (2005).

[16] K. Wassermann, H.J. Lunk, R. Palm, J. Fuchs, N. Steinfeldt, R. Stosser, M.T. Pope. *Inorg. Chem.*, **35**, 3273 (1996).

[17] Y. Goto, K. Kamata, K. Yamaguchi, K. Uehara, S. Hikichi, N. Mizuno. *Inorg. Chem.*, **45**, 2347 (2006).

[18] F. Xin, M.T. Pope. *Inorg. Chem.*, **35**, 5693 (1996).

[19] P. Mialane, A. Dolbecq, J. Marrot, E. Riviére, F. Sécheresse. *Chem. Eur. J.*, **11**, 1771 (2005).

[20] Y. Kikukawa, K. Yamaguchi, N. Mizuno. *Inorg. Chem.*, **49**, 8194 (2010).

[21] Z.M. Zhang, Y.G. Li, E.B. Wang, Y.F. Qi, X.L. Wang, C. Qin, H.Q. Tan. *J. Mol. Struct.*, **831**, 69 (2007).

[22] B. Bogdan, K. Paul, L.H. Craig. *Inorg. Chem.*, **48**, 5398 (2007).

[23] B. Botar, Y.V. Geletii, P. Kögerler, D.G. Musaev, K. Morokuma, I.A. Weinstock, C.L. Hill. *J. Am. Chem. Soc.*, **128**, 11268 (2006).

[24] B.S. Bassil, M. Ibrahim, R.A. Oweini, M. Asano, Z.X. Wang, J. Tol, N.S. Dalal, K.Y. Choi, R.N. Biboum, B. Keita, L. Nadjo, U. Kortz. *Angew. Chem. Int. Ed.*, **50**, 5961 (2011).

[25] S.G. Mitchell, P.I. Molina, S. Khanra, H.N. Miras, A. Prescimone, G.J.T. Cooper, R.S. Winter, E.K. Brechin, D.L. Long, R.J. Cogdell, L. Cronin. *Angew. Chem. Int. Ed.*, **50**, 9154 (2011).

[26] J.W. Zhao, S.T. Zheng, G.Y. Yang. *J. Solid State Chem.*, **181**, 2205 (2008).

[27] SAINT, version 6.36A, Bruker AXS Inc., Madison, Wisconsin, USA (2002).

[28] G.M. Sheldrick. SHELXL 97, Version 5.1, *Program for Crystal Structure Solution and Refinement,* University of Göttingen, Göttingen, Germany (1997).

[29] C.R. Mayer, P. Herson, R. Thouvenot. *Inorg. Chem.*, **38**, 6152 (1999).

[30] I.D. Brown, D. Altermatt. *Acta Crystallogr., Sect. B*, **41**, 244 (1985).

[31] P.T. Ma, L.J. Chen, J.W. Zhao, W. Wang, J.P. Wang, J.Y. Niu. *Inorg. Chem. Commun.*, **14**, 415 (2011).