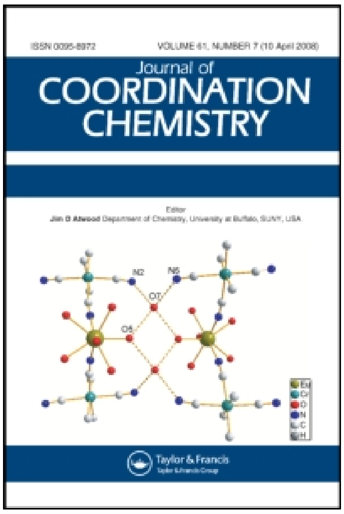

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A new dimeric polyoxotungstate based on the monovacant anion $[SiW_{11}O_{39}]$ connected by a hexa-metal cluster $Ce^{III}Cs_5$

Hongli Chen[ab]; Enbo Wang[a]; Yan Ding[ac]; Zhiming Zhang[a]; Xinxin Xu[a]; Xinlong Wang[a]
[a] Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun 130024, P.R. China [b] Department of Chemistry, Chengde Normal College, Chengde 067000, China [c] Jilin Business and Technology College, Changchun 130062, China

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A new dimeric polyoxotungstate based on the monovacant anion $[SiW_{11}O_{39}]$ connected by a hexa-metal cluster $Ce^{III}Cs_5$¶

HONGLI CHEN†‡, ENBO WANG*†, YAN DING†§, ZHIMING ZHANG†,
XINXIN XU† and XINLONG WANG†

†Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun 130024, P.R. China
‡Department of Chemistry, Chengde Normal College, Chengde 067000, China
§Jilin Business and Technology College, Changchun 130062, China

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A new dimeric polyoxotungstate, based on the monovacant anion $[SiW_{11}O_{39}]$ connected by a hexa-metal cluster $Ce^{III}Cs_5$, is synthesized and characterized by single-crystal X-ray diffraction, IR, TG and electrochemistry. The polyoxoanions are connected to 3D structures by additional alkali metal ions.

Keywords: Monovacant; Keggin-type polyoxotungstates; Three-dimensional; Thermal stability

1. Introduction

Polyoxometalates (POMs) are molecular metal oxide clusters of interest as soluble metal oxides and for their application in catalysis, medicine, and materials science [1–6]. POMs are versatile inorganic building blocks for construction of molecular-based materials [7–9]. By means of their multiple coordination requirements and oxophilicity, transition metal and lanthanide cations are suitable to link POM building blocks to form new classes of materials with potentially useful magnetic and luminescent properties [10–13]. The incorporation of lanthanide or transition metal cations into POMs may provide an entry to new classes of materials that combine the intrinsic properties of both constituents [14, 15]. Lanthanides can impart useful functionality such as luminescent, magnetic, or Lewis acid catalytic centers to POMs, thus extending their range of physical and chemical properties and gaining access to an array of new potential applications of the resulting complexes [16–19]. In 2000, Pope *et al.* investigated the structural characterization of the one-dimensional 1 : 1 $[Ln(SiW_{11}O_{39})(H_2O)_3]^{5-}$ ($Ln = La^{III}$, Ce^{III}) compounds, showing that these anions are

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*Corresponding author. Tel./Fax: +86-431-85098787. Email: wangenbo@public.cc.jl.cn; wangeb889@nenu.edu.cn

¶We dedicate this article to the retirement of Professor Peter Williams from the Journal of Coordination Chemistry.

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polymeric in the solid state. In 2003, Mialane *et al.* reported the solid-state structures of the Ln/$[SiW_{11}O_{39}]^{8-}$ (Ln = Yb^{III}, Nd^{III} Eu^{III}, Gd^{III}). In 2004, Mialane *et al.* reported the dimeric $K_{12}[(SiW_{11}O_{39}Ln)_2(CH_3COO)_2]$ (Ln = Gd^{III}, Yb^{III}) complexes. The studies mentioned indicate interest in the lanthanide cation and monovacant Keggin-type polyanion system [20–24].

Alkali metal ions such as Li, Na, K, Rb, Cs exhibit appealing structural features, and also possess applications in catalysis, separations, ion exchange, imaging, sorption, medicine, functional materials, and molecular electronics. Especially the Cs ion, possessing a larger range of bond length (<3.7 Å) [25], could be used as a versatile linker to link POMs into extended frameworks.

Based on the aforementioned points, we have focused on studying the reaction of monovacant Keggin-type silicotungstates with lanthanide cations in the presence of Cs^I. In this paper, we report a new dimeric complex $Cs_{10}Na_3[Ce(SiW_{11}O_{39})_2] \cdot 14H_2O$, which is constructed by the monovacant anions $[SiW_{11}O_{39}]$ connected by a hexa-metal cluster $Ce^{III}Cs_5$.

2. Experimental section

2.1. *Materials and methods*

All chemicals purchased were of reagent grade and used without further purification. The Si, W, Na, Cs and Ce contents were determined by a Leaman inductively coupled plasma (ICP) spectrometer. FT/IR spectra were recorded in the range 4000–400 cm^{-1} on an Alpha Centaut FT/IR spectrophotometer using KBr pellets. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10°C min^{-1}. The electrochemical analyses were performed on a CHI 600 electrochemical workstation with a digital-586 personal computer. All measurements were performed at room temperature.

2.2. *Syntheses of 1*

A sample, 0.694 g (0.25 mmol) of $Na_9H[SiW_9O_{34}] \cdot 19H_2O$ [26], was dissolved in 20 mL of sodium acetate buffer solution (0.5 M, pH = 5.2) followed by dropwise addition of 0.054 g (0.125 mmol) of $Ce(NO_3)_3 \cdot 6H_2O$ in 10 mL of DMF (DMF = *N*,*N*-dimethylformamide) at 60°C for 4 h. Cooling to room temperature, insoluble material was removed by centrifugation. Solid CsCl (0.34 g, 2 mmol) was added to the solution slowly and the mixture was cooled in an ice-water bath. After several hours, the brown oil-like precipitate separated was washed with EtOH, and dried with Et_2O. The resulting powder was dissolved in hot water and allowed to crystallize at room temperature. After several days crystals of **1**, suitable for X-ray diffraction, were collected. Yield: 0.372 g (51% based on W). Anal. Calcd for $Cs_{10}Na_3[Ce(SiW_{11}O_{39})_2] \cdot 14H_2O$: Cs, 18.62; Na, 0.97; Ce, 1.96; Si, 0.79; W, 56.65. Found: Cs, 18.70; Na, 0.99; Ce, 1.88; Si, 0.76; W, 56.18. IR (KBr pellets, cm^{-1}): 3411 (s), 948 (s), 883 (s), 827 (s), 720 (s), 523 (m).

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

Empirical formula	$H_{28}CeCs_{10}Na_3O_{92}Si_2W_{22}$
Formula weight	7139.29
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensionsb (Å, °)	
a	15.510(3)
b	17.982(4)
c	19.561(4)
α	104.31(3)
β	104.69(3)
γ	90.23(3)
Volume (Å^3)	5100.4
Z	2
Calculated density	4.649
F (000)	6122
θ range for data collection	3.03–25.00
Limiting indices	$-18 \leq h \leq 18$, $-21 \leq k \leq 21$, $-23 \leq l \leq 23$
Reflections collected	38,795
Reflections unique	17,561
R (int)	0.1206
Goodness-of-fit on F^2	1.006
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0785$, $wR_2 = 0.1807$
R indices (all data)	$R_1 = 0.1151$, $wR_2 = 0.2043$

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

2.3. *X-ray crystallography*

Single crystal of the title complexes was glued on a glass fiber. Data were collected on a Rigaku R–AXIS RAPID IP diffractometer at 293 K using graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) and IP technique. Empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL 97 crystallographic software package [27, 28]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. Further details of the X-ray structural analysis are given in Table 1. Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters are available in the supplementary crystallographic data.

3. Results and discussion

3.1. *Structure descriptions*

The single crystal structural analysis shows that the structure of **1** is a unique 2D framework. The 2D structure can be considered through three steps. First, two $SiW_{11}O_{39}$ polyanions are connected by one Ce^{III} and five Cs^{I} ions, the Ce^{III} metal ion connects with eight oxygen atoms, the Ce–O bond distances range from 2.420 to 2.550 Å and the bond angles are in the range of 69.5 to 148.0°. The Cs–O bond distances

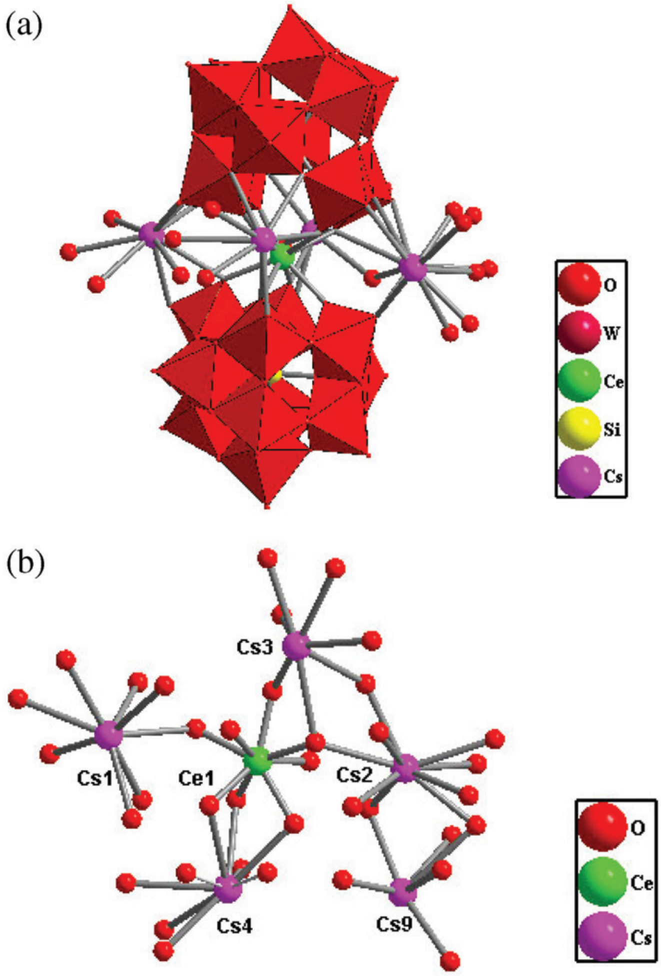

Figure 1. (a) The fundamental unit of **1**. (b) The Ce(III) and Cs(I) metal ions between the $SiW_{11}O_{39}$.

range from 3.18 to 3.58 Å and fall in the feasible range [25]. The five Cs(I) ions are connected by one Ce^{III} metal ion through oxygen atoms to form a six metal cluster as shown in Figure 1(b), obtained for the first time in lanthanide-containing dimeric polyoxoanions. Second, adjacent $[Ce^{III}Cs_5(SiW_{11}O_{39})_2]$ building units are connected by Cs^{I} metal ions to form a one-dimensional chain like structure as shown in Figure 2(a). Such chains are linked by metal ions to form an interesting two-dimensional layer structure as shown in Figure 2(b). The isolated $[Ce^{III}(XW_{11}O_{39})_2]$ anion and the 1D structure linked by the Na ions have been reported previously [29].

3.2. *IR spectroscopy*

In the low-wavenumber region of the IR spectra, compound **1**, displays characteristic vibration patterns of Keggin-type structure. Four sharp characteristic vibration peaks resulting from Keggin-type polyanions, namely, $\nu_{as}(W\text{–}O_d)$, $\nu_{as}(Si\text{–}O_a)$, $\nu_{as}(W\text{–}O_b)$, and

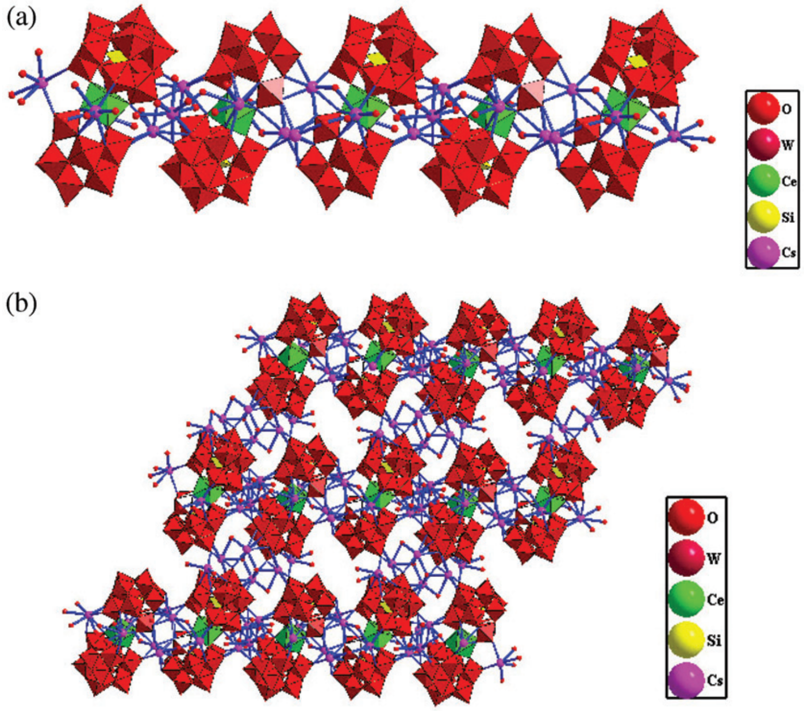

Figure 2. (a) The one-dimensional chain like structure of **1**. (b) The two-dimensional layer structure of **1**.

ν_{as}(W–O$_c$), appear at 948, 883, 827, and 720 cm^{-1}. The IR spectral studies also indicate strong interactions between the monovacant polyanions and rare earth cations in the solid state [30].

3.3. *Thermogravimetric analyses*

The thermal stability of **1** has been determined on single crystal samples in a nitrogen atmosphere by thermogravimetric analysis (TG). The curve of TG exhibits one-step weight loss, which has been observed in the other Ce-containing dimeric polyoxoanions [31]; weight loss of 3.41% from 80–150°C represents loss of water (Calcd: 3.53%).

3.4. *Electrochemistry*

Figure 3 shows the typical cyclic voltammetric behavior of **1** in the pH = 3 (0.1 M $Na_2SO_4 + H_2SO_4$) buffer solution at a scan rate of 50 mv s^{-1}. In the potential range −0.4 to −1.0 V, three quasireversible redox peaks appear with mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ are −0.5900 V (I–I′), −0.7606 V (II–II′) and −1.0224 V (III–III′) (*vs.* Ag/AgCl), respectively. The three peaks I–I′, II–II′ and III–III′ correspond to redox of the W^{VI} in the polyoxoanion framework. The peaks II–II′ and III–III′ are also observed in Ce-containing polyoxoanions [29b] and the domain where the three waves are located was also observed in other heteropolyoxotungstates [32].

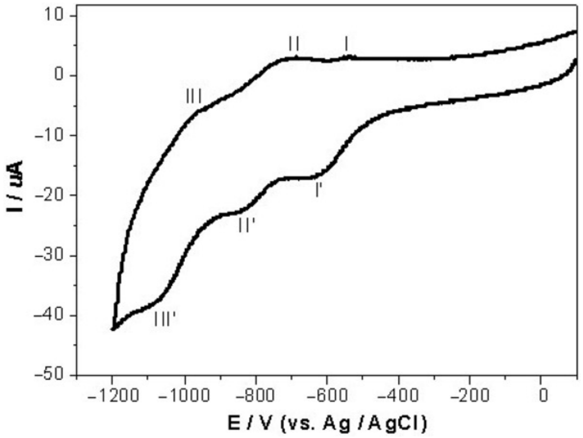

Figure 3. Cyclic voltammograms of **1** at pH = 3 (0.1 M $Na_2SO_4 + H_2SO_4$) at the scan rate of $50\,mv\,s^{-1}$. The working electrode was glassy carbon; the reference electrode was Ag/AgCl.

4. Conclusions

We synthesized a new dimeric polyoxotungstate, $Cs_{10}Na_3[Ce(SiW_{11}O_{39})_2] \cdot 14H_2O$, by the standard reaction. Furthermore, the electrochemical and the thermal stability of **1** are studied.

Supplementary materials

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; Email: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD- 418087 for **1**.

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