

# Two one-dimensional mono-substituted heteropolytungstates based on Keggin anion units

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## Abstract

Two kinds of complexes  $[\text{Ni}(\text{DETA})_2]_3[\text{SiNiW}_{11}\text{O}_{39}] \cdot 2.5\text{H}_2\text{O}$  (DETA = diethylenetriamine) (**1**) and  $[\text{H}_2\text{en}]_2[\text{Ba}_{0.15}(\text{H}_2\text{O})_2(\text{Hen}_2)]\text{H}_{1.7}[\text{SiNaW}_{11}\text{O}_{39}] \cdot 2\text{H}_2\text{O}$  (**2**) were obtained from the hydrothermal reaction and characterized by single crystal X-ray diffraction analysis and IR spectra. Crystal data:  $\text{C}_{24}\text{H}_{83}\text{N}_{18}\text{Ni}_4\text{O}_{41.5}\text{SiW}_{11}$  (**1**), monoclinic,  $Pn$ ,  $a = 10.926(2) \text{ \AA}$ ,  $b = 23.022(5) \text{ \AA}$ ,  $c = 13.221(3) \text{ \AA}$ ,  $\beta = 94.27(3)^\circ$ ,  $V = 3316.4(11) \text{ \AA}^3$ ,  $Z = 2$ ;  $\text{C}_8\text{H}_{46.7}\text{N}_8\text{Ba}_{0.15}\text{NaO}_{43}\text{SiW}_{11}$  (**2**), monoclinic,  $P2_1$ ,  $a = 12.840(3) \text{ \AA}$ ,  $b = 11.174(2) \text{ \AA}$ ,  $c = 16.693(3) \text{ \AA}$ ,  $\beta = 91.14(3)^\circ$ ,  $V = 2394.4(8) \text{ \AA}^3$ ,  $Z = 2$ . Both of them consists of one mono-substituted Keggin unit  $[\text{SiMW}_{11}\text{O}_{39}]^{(8-n)-}$  ( $M = \text{Ni}, \text{Na}$ ,  $n = 2, 1$ ) obtained by metal atom substituting for a W atom from the plenary anion  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ . This unit then connects with other adjacent units via  $M\text{--O--W}$  bridges constructing an infinitely one-dimensional chain-like structure in which the metal cation and polyanion alternate. Moreover, both of Ni or Na atoms are in a distorted octahedral environment with six oxygen atoms and occupy one position in the oxometalate shell of the Keggin structure.

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**Keywords:** Polyoxometalates; Keggin; Hydrothermal synthesis; Crystal structure; Tungstate; Ni; Na

## 1. Introduction

There is significant interest in crystal engineering of organic–inorganic solid-state materials reflecting their diverse properties, with applications to catalysis, sorption, calthration, electrical conductivity, magnetism, and photochemistry [1]. Such materials were usually synthesized through the following two strategies [2]. One strategy is to exploit appropriate metal centers that are linked through suitable polydentate ligands for the self-assembly of extended networks. Another strategy is that exploiting molecular building blocks in the synthesis of solid-state materials, relies on linking molecular cluster subunits from the vast family of chemically robust polyoxoanions, either through direct condensation to form oxo-bridged arrays of clusters or through transition metal coordination compounds acting as inorganic bridging ligand. In recent years, the hydrothermal techniques have been thought as an important way to

synthesize hybrid materials containing novel structure and especial properties under mechanism not being fully understood. Through the two strategies a number of complex structures, as one-, two-, and three-dimensional framework, were synthesized successfully [2–11].

Transition metal substituted polyoxotungstates based on Keggin or Dawson frameworks have received considerable attention and have been synthesized and studied widely in aqueous solution for their catalytic properties in organic oxidations [12–16] since Baker and his co-workers [17] first described the heteropolyanions of the type  $[\text{X}^{x+}\text{Z}^{z+}\text{W}_{11}\text{O}_{40}\text{H}_n]^{(14-x-z-n)-}$ , in which one tungsten atom of the Keggin [18] anion  $[\text{X}^{x+}\text{W}_{12}\text{O}_{40}]^{(8-x)-}$  has been replaced by a Z atom (usually of the first transition series). However, extended structures based on vacant Keggin anions have been observed rarely. Furthermore the transition metal atoms in these anions were always disordered and we could not determine the location of the transition metal atoms, as previously reported transition metal substituted discrete units [19] or one-dimensional [8,20,21] polyoxometalates. Herein we report the hydrothermal synthesis and

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single crystal structure of two one-dimensional chain-like compounds:  $[\text{Ni}(\text{DETA})_2]_3[\text{SiNiW}_{11}\text{O}_{39}] \cdot 2.5\text{H}_2\text{O}$  (DETA = diethylenetriamine) **1** and  $[\text{H}_2\text{en}]_2[\text{Ba}_{0.15}(\text{H}_2\text{O})_2(\text{Hen}_2)]\text{H}_{1.7}[\text{SiNaW}_{11}\text{O}_{39}] \cdot 2\text{H}_2\text{O}$  **2**, in which the two substituted metal atoms are fully ordered.

## 2. Experimental

### 2.1. General considerations

All reagents were purchased from commercial sources and used without further purification. All syntheses were carried out in 23 mL Teflon-lined acid digestion bomb inside a programmable electric furnace. The starting pH values of the reaction mixture were adjusted with hydrochloric acid (2 M). The mixture was stirred several hours before heated. C, H and N elements were analyzed on a Perkin–Elmer 240C elemental analyzer. Other elements were analyzed on a Jarrell–Ash 1100+2000 ICP quantometer for **1**. IR spectra were recorded from KBr pellets on a Nicolet 170 SXFT-IR instrument.

### 2.2. Synthesis of $[\text{Ni}(\text{DETA})_2]_3[\text{SiNiW}_{11}\text{O}_{39}] \cdot 2.5\text{H}_2\text{O}$ **1**

A mixture of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{C}_4\text{H}_{13}\text{N}_3$ , and  $\text{H}_2\text{O}$  in the mole ratio 1:1:0.1:11:550 was acidified to pH = 7. The mixture was sealed in the acid digestion bomb and heated at 160°C for 4 days. After the mixture was slowly cooled to room temperature for 2 days black crystals were isolated from the black solid, washed with water and dried at ambient temperature in 31% yield based on W. Anal. Calc. for  $\text{C}_{24}\text{H}_{83}\text{N}_{18}\text{Ni}_4\text{O}_{41.5}\text{SiW}_{11}$  (3573.37): C, 8.06; H, 2.32; N, 7.05. Found: C, 7.81; H, 2.33; N, 6.97%.

### 2.3. Synthesis of $[\text{H}_2\text{en}]_2[\text{Ba}_{0.15}(\text{H}_2\text{O})_2(\text{Hen}_2)]\text{H}_{1.7}[\text{SiNaW}_{11}\text{O}_{39}] \cdot 2\text{H}_2\text{O}$ **2**

A mixture of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , en, and  $\text{H}_2\text{O}$  in the mole ratio 1:0.45:0.1:9:310 was acidified to pH = 2.5. The mixture was sealed in the acid digestion bomb and heated at 160°C for 4 days. After the mixture was slowly cooled to room temperature for 2 days, brown yellow crystals were separated from white solid, washed with water and dried at ambient temperature in 38% yield based on W. Anal. Calc. for  $\text{C}_8\text{H}_{46.7}\text{N}_8\text{Ba}_{0.15}\text{NaO}_{43}\text{SiW}_{11}$  (3037.26): C, 3.16; H, 1.54; N, 3.69; Ba, 0.68; Na, 0.76; Si, 0.92; W, 66.58. Found: C, 3.09; H, 1.79; N, 3.37; Ba, 0.47; Na, 0.69; Si, 0.80, W, 65.80%.

### 2.4. X-ray crystallographic analysis

Crystals with dimensions  $0.16 \times 0.12 \times 0.10 \text{ mm}^3$  for **1** and  $0.26 \times 0.11 \times 0.09 \text{ mm}^3$  for **2** were selected and

intensity data collections at 293(2) K on a Rigaku RAXIS-IV image plate area detector using graphite monochromated  $\text{MoK}\alpha$  diffraction ( $\lambda = 0.71073 \text{ \AA}$ ). A total of 15,856 independent reflections were measured in the range of  $1.76^\circ \leq 2\theta \leq 50.00^\circ$  with  $-12 \leq h \leq +12$ ,  $-27 \leq k \leq +27$ ,  $-15 \leq l \leq +15$ , 9424 of which ( $R_{\text{int}} = 0.0593$ ) were used in the refinement for **1**. A total of 4651 independent reflections were measured in the range of  $2.44^\circ \leq 2\theta \leq 51.50^\circ$  ( $0 \leq h \leq 15$ ,  $0 \leq k \leq 13$ ,  $-20 \leq l \leq 20$ ), all of which were refinement for **2**. The intensities were corrected by Lorentz-polarization factors and empirical absorption. The structures were solved by direct methods and refined by a full-matrix least-squares technique based on  $F^2$  using the SHELXTL-97 program [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical models. The maximum and minimum peaks on the final difference Fourier map are corresponding to  $3.787$  and  $-1.892 \text{ e}\text{\AA}^{-3}$  for **1** and  $3.801$  and  $-3.891 \text{ e}\text{\AA}^{-3}$  for **2**, respectively. The crystallographic data and structure determination parameters for complexes **1** and **2** are summarized in Table 1. Selected bond distances and angles are given in Tables 2 and 3, respectively.

CCDC reference numbers 206688 (**1**) and 206687 (**2**).

## 3. Results and discussion

### 3.1. Synthesis

The hydrothermal method has been exploited widely as a routine for the synthesis of a large numbers of novel organic–inorganic solid-state materials. Under hydrothermal conditions new phases are accessed with often previously unseen compositions and topologies, such as the chain or layer hybrid organic–inorganic phases. Inspired by the recently successful synthesis of organic–inorganic hybrid materials  $[\text{Co}(\text{dpa})_2(\text{OH}_2)_2]_2[\text{Hdpa}][\text{PCoW}_{11}\text{O}_{39}]$  [8] by the hydrothermal reaction of NaF, dpa,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$ , we have successfully prepared two isostructural one-dimensional heteropolytungstates. However, the hydrothermal process is relatively complex affected by many factors as the type of initial reactants, starting concentration, pH, crystallization temperature and pressure. During the course of preparing the two title compounds, we found that final products are sensitive to acidity of the starting reaction solution. The pH values of the reaction system were controlled at 6–8 for **1** and 2–4 for **2** to obtain a pure crystallized product, whereas beyond this pH range no crystals could be obtained. While changing the amounts of templates, temperature (within 160–180°C range), and reactions times (4–6 days) have little influence over the final product.

Table 1  
Summary of crystallographic data for **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	C <sub>24</sub> H <sub>83</sub> N <sub>18</sub> Ni <sub>4</sub> O <sub>41.5</sub> SiW <sub>11</sub>	C <sub>8</sub> H <sub>46.7</sub> N <sub>8</sub> Ba <sub>0.15</sub> NaO <sub>43</sub> SiW <sub>11</sub>
Formula weight	3573.37	3037.26
Crystal system	<i>Pn</i>	<i>P2</i> <sub>1</sub>
<i>a</i> (Å)	10.926(2)	12.840(3)
<i>b</i> (Å)	23.022(5)	11.174(2)
<i>c</i> (Å)	13.221(3)	16.693(3)
$\beta$ (deg)	94.27(3)	91.14(3)
<i>Z</i>	2	2
<i>V</i> (Å <sup>3</sup> )	3316.4(11)	2394.4(8)
<i>T</i> (°C)	20	20
$\lambda$ (MoK $\alpha$ ) (Å)	0.71073	0.71073
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	3.576	4.213
$\mu$ (mm <sup>-1</sup> )	20.216	26.574
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0515, 0.1141	0.0584, 0.1394
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0640, 0.1185	0.0658, 0.1449

$w^{-1} = [\sigma^2(F_o^2) + (aP)^2]$ ,  $P = (F_o^2 + 2F_c^2)/3$ , where  $a = 0.0753$  and  $0.0963$  for **1** and **2**, respectively.

Table 2  
Selected bond distances (Å) and angles (deg) for **1**

Si(1)–O(39)	1.593(18)	Si(1)–O(36)	1.631(16)
Si(1)–O(38)	1.641(17)	Si(1)–O(37)	1.664(17)
Ni(1)–O(27)	2.030(17)	Ni(1)–O(26)	2.02(2)
Ni(1)–O(12)	2.00(2)	Ni(1)–O(35)	2.10(2)
Ni(1)–O(11)#1	2.26(2)	Ni(1)–O(39)	2.306(16)
W(1)–O(1)	1.71(2)	W(2)–O(2)	1.74(2)
W(3)–O(3)	1.721(18)	W(4)–O(4)	1.689(17)
W(5)–O(5)	1.75(2)	W(6)–O(6)	1.70(2)
W(7)–O(7)	1.689(17)	W(8)–O(8)	1.70(2)
W(9)–O(9)	1.721(18)	W(10)–O(10)	1.706(19)
W(11)–O(11)	1.71(2)	Ni(2)–N(5)	2.062(17)
Ni(2)–N(3)	2.08(3)	Ni(2)–N(1)	2.12(3)
Ni(2)–N(4)	2.14(3)	Ni(2)–N(6)	2.08(2)
Ni(2)–N(2)	2.13(3)	W(11)#2–O(11)–Ni(1)	168.5(14)
O(39)–Si(1)–O(38)	111.4(10)	O(39)–Si(1)–O(37)	111.4(8)
O(39)–Si(1)–O(36)	109.2(9)	O(38)–Si(1)–O(37)	108.3(8)
O(38)–Si(1)–O(36)	108.6(8)	O(36)–Si(1)–O(37)	107.7(9)
O(27)–Ni(1)–O(26)	87.9(7)	O(27)–Ni(1)–O(12)	88.6(8)
O(12)–Ni(1)–O(26)	166.1(8)	O(11)–Ni(1)–O(39)	153.7(7)
O(26)–Ni(1)–O(35)	89.0(8)	O(12)–Ni(1)–O(35)	91.0(8)

Symmetry transformations used to generate equivalent atoms: #1 $x-1$ ,  $y$ ,  $z$ ; #2 $x+1$ ,  $y$ ,  $z$ .

### 3.2. Structure description

As shown in Fig. 1, the molecule structure of **1** consists of three discrete cations [Ni(DETA)<sub>2</sub>]<sup>2+</sup>, one heteropolyanion [SiNiW<sub>11</sub>O<sub>39</sub>]<sup>6-</sup> and two point five non-coordinating water. In the [Ni(2)(DETA)<sub>2</sub>]<sup>2+</sup> ion, the Ni(2) atom is octahedrally coordinated with six N atoms coming from two diethylenetriamine molecules (Fig. 2). The Ni(2)–N distances range from 2.062(17) to 2.14(3) Å with mean length 2.102 Å and average value of 89.2° for N–Ni(2)–N angle, which shown the octahedron is distorted severely. Besides, the three groups of N atoms N1, N3, N4, N6; N2, N3, N5, N6; N1, N2, N4, N5 construct three planes,  $\alpha$ ,  $\gamma$  and  $\beta$  whose mean

Table 3  
Selected bond distances (Å) and angles (deg) for **2**

Si(1)–O(38)	1.63(2)	Si(1)–O(37)	1.61(2)
Si(1)–O(39)	1.64(2)	Si(1)–O(36)	1.67(2)
Ba(1)–N(1)	3.13(4)	Ba(1)–N(2)	3.17(3)
Ba(1)–N(3)	3.16(3)	Ba(1)–O(1W)	3.14(4)
Ba(1)–O(2W)	3.27(4)	Na(1)–O(13)	2.17(3)
Na(1)–O(7)#1	2.43(3)	Na(1)–O(12)	2.24(3)
Na(1)–O(37)	2.46(2)	W(1)–O(1)	1.69(2)
W(2)–O(2)	1.71(2)	W(3)–O(3)	1.69(3)
W(4)–O(4)	1.77(3)	W(5)–O(5)	1.68(3)
W(6)–O(6)	1.66(3)	W(7)–O(7)	1.77(3)
W(8)–O(8)	1.72(3)	W(9)–O(9)	1.74(3)
W(10)–O(10)	1.70(3)	W(11)–O(11)	1.69(3)
O(38)–Si(1)–O(39)	109.0(13)	O(38)–Si(1)–O(36)	108.6(13)
O(38)–Si(1)–O(37)	109.9(10)	O(39)–Si(1)–O(36)	107.7(10)
O(39)–Si(1)–O(37)	110.5(13)	O(37)–Si(1)–O(36)	110.9(12)
O(30)–Na(1)–O(13)	85.8(11)	O(30)–Na(1)–O(16)	90.5(11)
O(30)–Na(1)–O(12)	160.4(13)	O(13)–Na(1)–O(16)	162.6(12)
O(7)#1–Na(1)–O(37)	163.4(9)	W(7)–O(7)–Na(1)#2	154.4(13)

Symmetry transformations used to generate equivalent atoms: #1 $x$ ,  $y-1$ ,  $z$ ; #2 $x$ ,  $y+1$ ,  $z$ .

deviations are 0.0109, 0.0377 and 0.0112 Å and the Ni(2) atom deviates 0.0143, 0.0135 and 0.0077 Å from the ideal planes,  $\alpha$ ,  $\gamma$  and  $\beta$ , respectively. It is evident that the Ni(2) atom is nearly in the plane  $\beta$ . The dihedral angles for  $\gamma$  and  $\alpha$ ,  $\gamma$  and  $\beta$ ,  $\alpha$  and  $\beta$  are 99.0°, 97.8° and 88.1°, respectively, so they are not vertical to each other. Fig. 3 shows anionic structure of [SiNi(1)W<sub>11</sub>O<sub>39</sub>]<sup>6-</sup>, the Ni(1) atom substitutes for a W atom of its parent anion [SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup>. The Ni(1) atom is coordinated to six oxygen atoms, one O<sub>t</sub>,<sup>1</sup> one O<sub>a</sub>, (see footnote 1) two O<sub>b</sub>, (see footnote 1) and two O<sub>c</sub> (see footnote 1). The

<sup>1</sup>O<sub>a</sub> refers to oxygen atoms connecting the Si (Ge, P) and W(Mo) atoms; O<sub>b</sub> refers to atoms located in the share corners between two W<sub>3</sub>O<sub>13</sub> unit; O<sub>c</sub> refers to oxygen atoms connecting edge-sharing WO<sub>6</sub> octahedra in the W<sub>3</sub>O<sub>13</sub> units; O<sub>t</sub> are the terminal oxygen atoms.

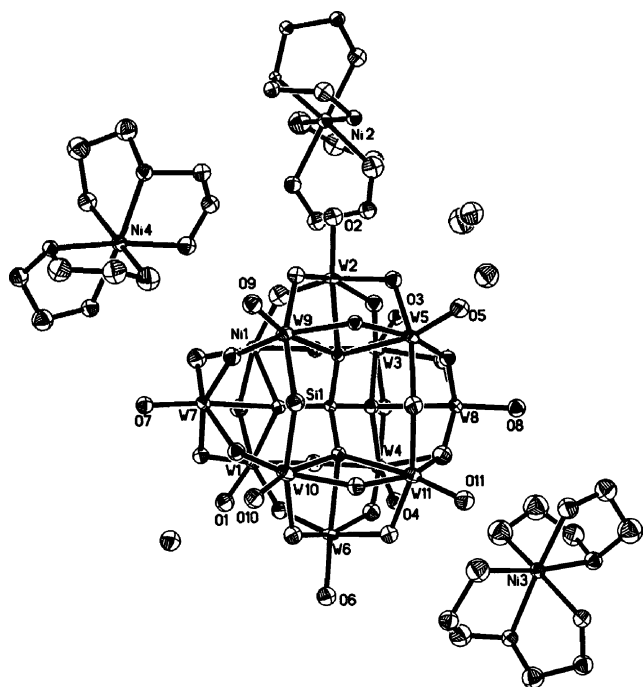


Fig. 1. Molecular structure of  $[\text{Ni}(\text{DETA})_2]_3[\text{SiNiW}_{11}\text{O}_{39}] \cdot 2.5\text{H}_2\text{O}$  with partial atom labeling scheme. All the hydrogen atoms are omitted for clarity.

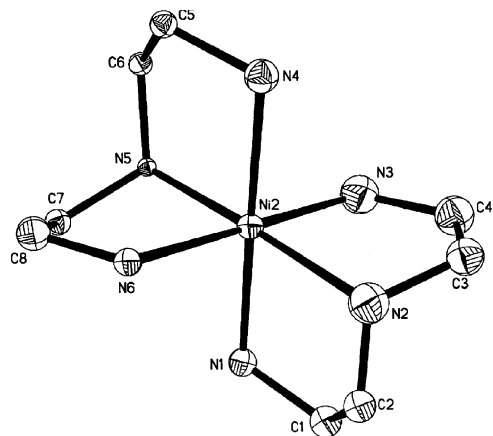


Fig. 2. Cationic structure of  $[\text{Ni}(\text{DETA})_2]^{2+}$ . The hydrogen atoms are not shown for clarity.

$\text{Ni}(1)\text{--O}$  distances are in the range of 2.00(2)–2.306(16) Å with average length 2.119 Å. It should be noted that the  $\text{Ni}(1)\text{--O}(11)\#1$  2.26(2) Å and  $\text{Ni}(1)\text{--O}(39)$  2.306(16) Å are longest in the six sets of  $\text{Ni}(1)\text{--O}$  bonds, which are 0.142 and 0.187 Å longer than the mean value, respectively. Thus the  $\text{Ni}(1)\text{O}_6$  octahedron is elongated along the  $\text{O}(39)\cdots\text{Ni}(1)\cdots\text{O}(11)$  axis and distorted greatly. The  $\text{W}\text{--O}_t$ ,  $\text{W}\text{--O}_{b,c}$  and  $\text{W}\text{--O}_a$  distances are 1.689(17)–1.75(2) Å 1.78(2)–2.100(19) Å and 2.303(16)–2.414(16) Å, in which the shortest  $\text{W}\text{--O}$  distance is,  $\text{W}(4)\text{--O}(4)$ , 1.689(17) Å and the longest,  $\text{W}(8)\text{--O}(36)$ , is 2.414(16) Å. The  $\text{W}(11)\text{--O}(11)$  distance, 1.71(2) Å, is consistent with the average  $\text{W}\text{--O}_t$  lengths. The bond

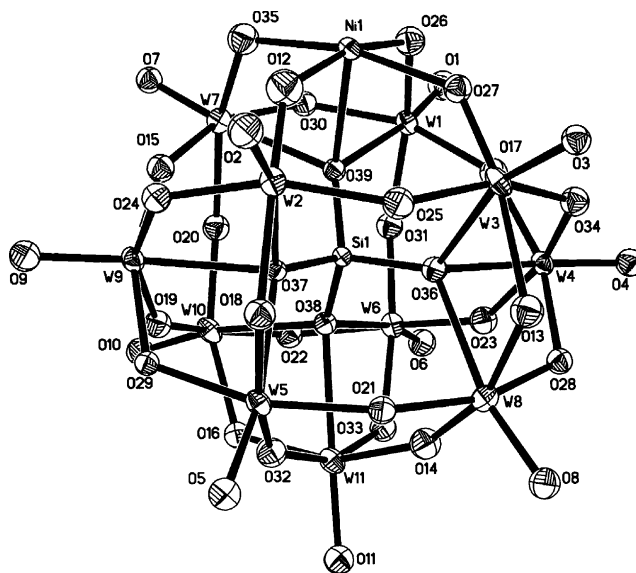


Fig. 3. Anion structure of  $[\text{SiNiW}_{11}\text{O}_{39}]^{6-}$ .

valences [23]  $S_{\text{W}(11)\text{--O}(11)}$  and  $S_{\text{Ni}(1)\text{--O}(11)}$  are 1.75 and 0.19, respectively. The results indicate that although after the  $\text{O}(11)$  atom is coordinated to Ni atom and the primary  $\text{W}(11)\text{--O}(11)$  bond become weak,  $\text{W}(11)\text{--O}(11)$  bond lengths doesn't elongate obviously. For the  $\text{SiO}_4$  tetrahedron, the  $\text{Si}\text{--O}$  distances vary from 1.593(18) to 1.664(17) Å with the average value 1.632 Å, which is 0.002 Å longer than that of previous report [24]. The average  $\text{O}\text{--Si}\text{--O}$  angle  $109.43^\circ$  is  $0.20^\circ$  larger than that in  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  [24]. These results show that the  $\text{WO}_6$  octahedrons and  $\text{SiO}_4$  tetrahedron of the polyanion are distorted severely due to the strong interactions between the transitional metal  $\text{Ni}^{2+}$  (1) cation and  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  anion. It is interesting that the anionic units  $[\text{SiNi}(1)\text{W}_{11}\text{O}_{39}]^{6-}$  are connected into a one-dimensional chain through  $\text{Ni}\text{--O}\text{--W}$  links, as seen in Fig. 4. This is similar to these compounds  $[\text{Cu}(\text{en})_2(\text{OH}_2)]_2[\text{H}_2\text{en}][\{\text{Cu}(\text{en})_2\}_2\text{P}_2\text{CuW}_{17}\text{O}_{61}] \cdot 5\text{H}_2\text{O}$ , [8]  $[\text{Cu}(\text{en})_2(\text{OH}_2)]_2[\text{Cu}(\text{en})_{2,0.5}[\text{H}_2\text{en}]_{0.5}\{\{\text{Cu}(\text{en})_2\}_2\text{P}_2\text{CuW}_{17}\text{O}_{61}\}] \cdot 5\text{H}_2\text{O}$ , [8] and  $[\text{Co}(\text{dpa})_2(\text{OH}_2)_2][\text{Hdpa}][\text{PCoW}_{11}\text{O}_{39}]$ , [8] in which the heteropolyanions are linked through  $\text{M}\text{--O}\text{--W}$  (M: usually the first transition series) bridges to form one-dimensional chain-like structure. However, the Ni(1) atom in the title compound can be determined, which is different from  $\text{Cu}(\alpha)$  and  $\text{W}(\epsilon)$  with an occupancy of one half in  $[\text{Cu}(\text{en})_2(\text{OH}_2)]_2[\text{H}_2\text{en}][\{\text{Cu}(\text{en})_2\}_2\text{P}_2\text{CuW}_{17}\text{O}_{61}] \cdot 5\text{H}_2\text{O}$  [8] and  $[\text{Cu}(\text{en})_2(\text{OH}_2)]_2[\text{Cu}(\text{en})_{2,0.5}[\text{H}_2\text{en}]_{0.5}\{\{\text{Cu}(\text{en})_2\}_2\text{P}_2\text{CuW}_{17}\text{O}_{61}\}] \cdot 5\text{H}_2\text{O}$  [8]. The bond angle in  $\text{O}(11)$   $168.5^\circ$  is larger than the  $\text{Co}\text{--O}(11)\text{--W}$  ( $160.4^\circ$ ) in  $[\text{Co}(\text{dpa})_2(\text{OH}_2)_2][\text{Hdpa}][\text{PCoW}_{11}\text{O}_{39}]$  [8], which indicates that the links of the chains are distorted.

The structure of 2, as shown in Fig. 5, is essentially similar to that of 1. It also contains a Keggin unit  $[\text{SiNaW}_{11}\text{O}_{39}]^{7-}$ . Besides, it consists of isolated en molecule, one alkali earth metal coordination cation



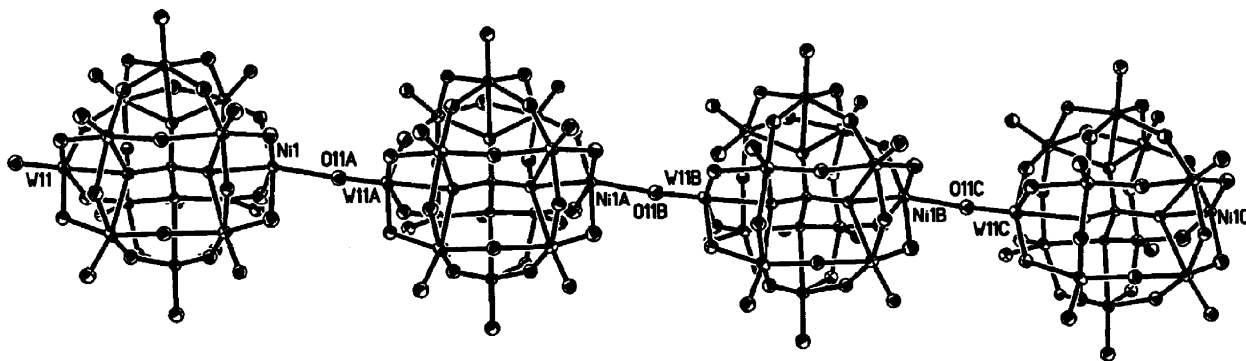


Fig. 4. View of the one-dimensional chain-like structure in **1** with partial atom labeling scheme.

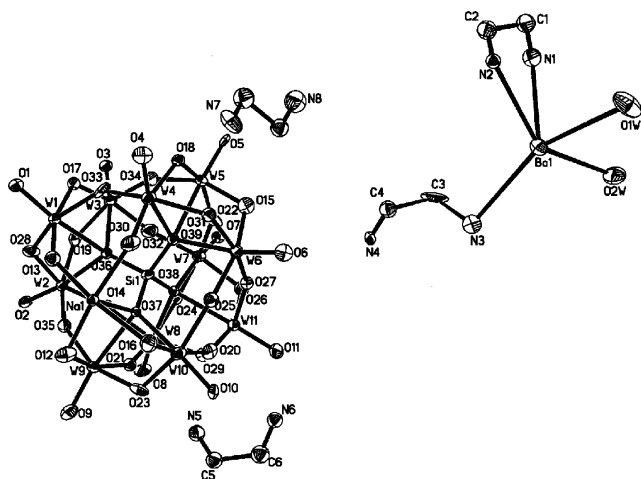


Fig. 5. Molecular structure of  $[\text{H}_2\text{en}]_2[\text{Ba}_{0.15}(\text{H}_2\text{O})_2(\text{Hen}_2)]\text{H}_{1.7}[\text{SiNaW}_{11}\text{O}_{39}] \cdot 2\text{H}_2\text{O}$ . The hydrogen atoms are deleted for clarity.

$[\text{Ba}_{0.15}(\text{H}_2\text{O})_2(\text{Hen}_2)]^{1.3+}$ , two non-coordinating  $\text{H}_2\text{O}$ . The alkali metal Na(1) atom in  $[\text{SiNa}(1)\text{W}_{11}\text{O}_{39}]^{7-}$  anion substitutes for a W atom from the parent anion  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  and forms a  $\text{Na}(1)\text{O}_6$  octahedron with  $\text{Na}(1)\text{--O}$  distances ranging from 2.17(3) to 2.46(2) Å.  $\text{Na}(1)\text{--O}(7)\#1$  [2.43(3) Å],  $\text{Na}(1)\text{--O}(37)$  [2.46(2) Å] are longest in the six sets of  $\text{Na--O}$  bonds, which are 0.14 and 0.17 Å longer than the average value 2.29 Å, whereas the average  $\text{O--Na}(1)\text{--O}$  angle is  $89.58^\circ$ . So the  $\text{Na}(1)\text{O}_6$  octahedron is also distorted by elongation of the  $\text{O}(37)\cdots\text{Na}\cdots\text{O}(7)\#1$  axis, which is similar to that of  $\text{Ni}(1)\text{O}_6$  octahedron in **1**. It is interesting that the anion unit  $[\text{SiNa}(1)\text{W}_{11}\text{O}_{39}]^{7-}$  then connects with other adjacent units also constructing one-dimensional chain similarly to compound **1**. Moreover, the location of Na(1) atom in the unit can be determined, too. The bond angle at  $\text{O}(7)$   $154.4^\circ$  is  $14.1^\circ$  smaller than that bond angle at  $\text{O}(11)$  in **1**. This proves that the links of the chains in **2** are also distorted severely. The  $\text{W--O}_t$ ,  $\text{W--O}_{b,c}$ , and  $\text{W--O}_a$  bond distances range are 1.66(3)–1.77(3) Å, 1.71(3)–2.14(2) Å, and 2.266(19)–2.43(2) Å, respectively. The bonds for  $\text{W}(6)\text{--O}(6)$  [1.66(3) Å] and  $\text{W}(5)\text{--O}(39)$  [2.43(2) Å] are the shortest and longest in

the anion, respectively. The  $\text{W}(7)\text{--O}(7)$  distance, 1.77(3) Å, is longer than other  $\text{W--O}_t$  bonds because after the  $\text{O}(7)$  atom is bound to Na atom, the primary  $\text{W=O}$  double bond become weaker so that the bond lengths to become longer obviously, which is quite different from  $\text{W}(11)\text{--O}(11)$  distance in **1**. The results can be proved by the bond valence [23] for  $S_{\text{W}(7)\text{--O}(7)} = 1.53$  and  $S_{\text{Na}(1)\text{--O}(7)\#1} = 0.19$ . For  $\text{SiO}_4$ , the  $\text{Si--O}$  distances are 1.61(2)–1.67(2) Å with average length 1.64 Å. The average bond angle for  $\text{O--Si--O}$ ,  $109.43^\circ$ , is  $0.20^\circ$  larger than that in  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  [24]. These results show that the  $\text{WO}_6$  octahedrons and  $\text{SiO}_4$  tetrahedron are also distorted in the polyanion due to the strong interactions between Na(1) ion and  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  anion. It is noteworthy that in the counterion  $[\text{Ba}_{0.15}(\text{H}_2\text{O})_2(\text{Hen}_2)]^{1.3+}$  the alkali earth metal Ba site is defined by two water molecules and three nitrogen atoms from two en ligands and formed a distorted square pyramid with  $\text{Ba--N}$  distances ranging from 3.13(4)–3.17(3) Å and with  $\text{Ba--O}$  lengths varying from 3.14(4)–3.27(4). Moreover, there is an unusual characterization that not the alkali earth metal Ba but alkali metal Na occupies the place of a tungsten atom in **2** in that the radius of  $\text{Ba}^{2+}$  ion is too big to fill the place of the lacunary W atom. According to our knowledge, it is observed for the first time. It is noteworthy that the structures **1** and **2** exhibit extensive hydrogen bonding interactions between the amine nitrogen atoms and the terminal and bridging oxygen of the mono-vacant Keggin anions with  $\text{N--H}\cdots\text{O}$  distances 2.868–2.997 Å in **1** and  $\text{N--H}\cdots\text{O}$  lengths 2.759–2.964 Å in **2**.

Comparing **2** with **1**, both of them contain a similarly one-dimensional anionic chain, in which the common bridging oxygen atom connects two opposite positions of the Keggin unit occupied by  $M$  (Ni or Na) and W. Furthermore, their places for substituted metal Ni and Na are fully ordered. It is well known that although the mono-substituted Keggin polytungstates are reported much, no discrete crystal structure analysis has been made up to now that allow detail description of the bonding environments of the mono-substituted  $M$  atom like the two title complexes, which occupies one position

in the oxometalate shell of the Keggin unit. In many crystalline salts of the mono-substituted Keggin anion, the metal atom is randomly distributed over all 12 heavy atom positions as a consequence of the cubic crystal structure [8, 19–21]. Whether  $[\text{Ni}(\text{DETA})_2]^{2+}$  cation in **1**, or  $[\text{Ba}_{0.15}(\text{H}_2\text{O})_2(\text{Hen}_2)]^{1.3+}$  and  $\text{H}_2\text{en}^{2+}$  cations in **2**, all of them are not covalently bound to the anion  $[\text{Si}M\text{W}_{11}\text{O}_{39}]^{(8-n)-}$  ( $M = \text{Ni}, \text{Na}$ ) and only interact with Keggin anion through hydrogen bonds or the van der Waals forces. The successful synthesis of the two one-dimensional chain-like structures, on one hand reflects that appropriate combination of organic ligands, acidity and hydrothermal synthetic conditions can obtain novel organic–inorganic composites based on chain-like heteropolytungstates, on the other hand may serve as a useful model to study the mono-substituted Keggin complexes and their relevant properties in Si–O– $M$  ( $M = \text{W}, \text{Mo}, \text{V}$ ) system.

### 3.3. IR spectra

Besides cation bands three characteristic asymmetric vibrations from the polyanion of  $[\text{Si}M\text{W}_{11}\text{O}_{39}]^{(8-n)-}$  ( $M = \text{Ni}, \text{Na}$ ) in **1** and **2**, namely,  $\nu_{\text{as}}(\text{Si}-\text{O}_a)$ ,  $\nu_{\text{as}}(\text{W}=\text{O}_t)$ , and  $\nu_{\text{as}}(\text{W}-\text{O}_c)$ . The peaks appear at 898, 970, and 804 (shoulder peak 704)  $\text{cm}^{-1}$  in **1** and 883, 967, and 785 (shoulder peak 710)  $\text{cm}^{-1}$  in **2**, respectively. Comparing the IR spectra of **1** and **2** with that of  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  [24], The vibration bands of Si– $\text{O}_a$  bonds have a red shift from 926 to 898  $\text{cm}^{-1}$  in **1** and from 926 to 883  $\text{cm}^{-1}$  in **2**, respectively. The vibrational bands of  $\text{W}=\text{O}_t$  bonds also have a red shift from 980 to 970  $\text{cm}^{-1}$  in **1** and from 980 to 967  $\text{cm}^{-1}$  in **2** due to the coordination effect and increasing of negative charge density in the anionic surface. These results show that the Si– $\text{O}_a$  and  $\text{W}=\text{O}_t$  bonds are weakened in the two complexes. The  $\text{W}-\text{O}_c$  bond has a splitting of 785  $\text{cm}^{-1}$  to 804 and 704  $\text{cm}^{-1}$  in **1** and of 785  $\text{cm}^{-1}$  to 784 and 710  $\text{cm}^{-1}$  in **2** due to the appearing of un-equivalent  $\text{W}-\text{O}_c$  bonds after the metal Ni or Na atom substitutes for a tungsten atom from the plenary  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  anion. However, because the absorption bands of anti-stretching vibration for Si– $\text{O}_a$  bond turn to broad, so that the vibrational bands of the  $\text{W}-\text{O}_b$  bonds are covered. Though after the tungsten atom of the Keggin anion  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  is substituted by the Ni or Na atom and the symmetry of  $[\text{Si}M\text{W}_{11}\text{O}_{39}]^{(8-n)-}$  ( $M = \text{Ni}, \text{Na}$ ) anion reduces, the  $[\text{Si}M\text{W}_{11}\text{O}_{39}]^{(8-n)-}$  anion still retains the Keggin structure. This is agreement with the results of the single crystal X-ray diffraction analysis.

## 4. Conclusions

Two novel hybrid materials based on one-dimensional anionic chain constructing from alternative mono-

vacant Keggin units  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  and  $M$  ( $M = \text{Ni}, \text{Na}$ ) metal were synthesized by hydrothermal techniques and elucidated by single crystal X-ray diffraction for the first time. It is interesting that two mono-substituted metal atoms are fully ordered in their polyanions. Successful synthesis of the two title compounds can act as a good model to prepare infinite chains of heteropolytungstates in which the heteroatoms are Si under the appropriately hydrothermal conditions.

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