

Rapid communication

# Two unprecedented inorganic–organic boxlike and chainlike hybrids based on arsenic–vanadium clusters linked by nickel complexes

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## Abstract

Two novel organic–inorganic hybrid arsenic–vanadates,  $[\{\text{Ni}(\text{en})_2\}_4(4,4'\text{-bipy})_4\{\text{Ni}(\text{H}_2\text{O})_2\}]_2[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]_4 \cdot 16\text{H}_2\text{O}$  **1** and  $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]_2[\{\text{Ni}(\text{en})_2(\text{H}_2\text{O})\}_2\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]\{\{\text{Ni}(\text{en})_2\}\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)\} \cdot 6\text{H}_2\text{O}$  **2** are reported in this study. Crystal data for compound **1**: Tetragonal,  $I4/m$ ,  $a = 27.507(4) \text{ \AA}$ ,  $b = 27.507(4) \text{ \AA}$ ,  $c = 22.101(4) \text{ \AA}$ ;  $V = 16722(5) \text{ \AA}^3$ ,  $Z = 2$ ,  $R(\text{final}) = 0.0508$ . Crystal data for compound **2**: Triclinic,  $P-1$ ,  $a = 11.530(2) \text{ \AA}$ ,  $b = 14.883(3) \text{ \AA}$ ,  $c = 21.330(4) \text{ \AA}$ ,  $\alpha = 76.94(3)^\circ$ ,  $\beta = 76.58(3)^\circ$ ,  $\gamma = 69.54(3)^\circ$ ,  $V = 3293.4(1) \text{ \AA}^3$ ,  $Z = 1$ ,  $R(\text{final}) = 0.0559$ . The boxlike structure of compound **1** is designed from  $[\{\text{Ni}(\text{en})_2\}_4(4,4'\text{-bipy})_4\{\text{Ni}(\text{H}_2\text{O})_2\}]$  sheets pillared by  $[\alpha\text{-As}_8\text{V}_{14}\text{O}_{42}]$  clusters, which represents the first mixed-organic ligand-decorated tetrameric As–V–O cluster. Compound **2** is constructed from the rarely  $[\beta\text{-As}_8\text{V}_{14}\text{O}_{42}]$  clusters and Ni coordination complex fragments. The electrochemical property and magnetic property of compound **1** have been studied.

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**Keywords:** Polyoxometalates; Arsenic–vanadium; Mixed ligands; Electrochemical property; Magnetic properties

## 1. Introduction

The interest in organic–inorganic hybrid materials reflects their enormous variety of structure topologies and potential applications in catalysis, electron conductivity, magnetism and material science [1,2]. The evolution of organic–inorganic hybrid materials is dependent upon the synthesis of novel solids possessing unique structures and properties. One successful approach is employing various well-characterized polyoxometalates as molecular building blocks to bridge or support transition metal complexes to producing new families of organic–inorganic hybrids [3]. Consequently, a series of novel organic–inorganic hybrids belonging to the  $\{MxLy/V/O\}$ ,  $\{MxLy/V/P/O\}$ ,  $\{MxLy/Mo/O\}$  and  $\{MxLy/Mo/P/O\}$  systems ( $M$  = transition metal,  $L$  = organic ligand) have been prepared [4–9]. However, the arsenic–vanadium clusters, as a member of

the large POMs family, combining with the organic or metal–organic complexes have not far been explored. Among the field of arsenic–vanadium clusters, the  $[\text{As}_8\text{V}_{14}\text{O}_{42}]$  cluster [10,11] is chosen in this study because (a) the  $[\text{As}_8\text{V}_{14}\text{O}_{42}]$  building block has been synthesis and structurally characterized identically in a number of compounds, such as  $\text{Rb}_5[\text{As}_8\text{V}_{14}\text{O}_{42}\text{Cl}] \cdot 2\text{H}_2\text{O}$  [12] and  $[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{SO}_4)][\text{Ni}(\text{en})_2]_3 \cdot 4.5\text{H}_2\text{O}$  [13]. (b) The steric orientation of the coordination sites is considerably flexible, which will cause the  $\text{V} = \text{O}$  groups to connect metal ions in different directions. (c) The As(III) atoms with the electron lone pairs capping on  $[\text{As}_8\text{V}_{14}\text{O}_{42}]$  cluster can block the coordination sites that are not required and thus leave specific sites free for transition-metal connectors. The selection of such POMs may be beneficial to guarantee limited growth, reduce the problems occurred in the one-pot reactions that the compositions and structures of the products could not be predicted.

In recent years, Yang's group has performed a few interesting studies in the organic–inorganic hybrid As–V–O field [14] and utilized the  $[\text{As}_8\text{V}_{14}\text{O}_{42}]$  cluster to prepare

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some novel polymers with charming compositions, such as, the 1D chain  $[\text{Zn}(2,2'\text{-bpy})_2]_2[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$  [15] and the 2D framework  $[\text{Ni}(\text{en})_2]_3[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{HPO}_3)] \cdot 4\text{H}_2\text{O}$  [15] or  $[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{CO}_3)] \cdot [\text{Cu}(\text{en})_2]_3 \cdot 10\text{H}_2\text{O}$  [16]. A further step is to construct 3D architecture based on As–V–O cluster [17]. 4, 4'-bipyridine has been proved for the construction of extended structures due to its two-connected bridging features, however, the organic ligands used in the As–V–O system are mainly restricted within the N-containing chelating bidentate ligands, such as ethylenediamine or 2,2'-bipyridine, no such compound based on As–V–O clusters linked by 4, 4'-bipyridine has been reported so far. In addition, introducing more than one type of organic molecule with distinctive linking manners and coordination preferences into the inorganic substructures is a promising goal to the design and synthesis of organic–inorganic hybrid materials with remarkable structural features and attractive properties [18,19].

Based on the aforementioned points, the aim of this study is to synthesize higher dimensional organic–inorganic hybrid materials basing on As–V–O building blocks. This will be of interest for the magnetic material and the crystal engineering of porous framework and provide information about the surface restriction of the  $[\text{As}_8\text{V}_{14}\text{O}_{42}]$  cluster at the basic structural level. We reported herein a novel boxlike tetrameric As–V–O cluster compound with cavity, prepared by introducing Ni hybrid metal and mixed organic components:  $[\{\text{Ni}(\text{en})_2\}_4(4,4'\text{-bipy})_4\{\text{Ni}(\text{H}_2\text{O})_2\}]_2[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]_4 \cdot 16\text{H}_2\text{O}$  **1**, and an unprecedented compound based on the rarely  $[\beta\text{-As}_8\text{V}_{14}\text{O}_{42}]$  cluster and Ni complexes fragments, in which the chain and bisupporting motifs coexist:  $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]_2[\{\text{Ni}(\text{en})_2(\text{H}_2\text{O})\}_2\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]\{\text{Ni}(\text{en})_2\}\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3) \cdot 6\text{H}_2\text{O}$  **2**. The electrochemical property and magnetic property of compound **1** have also been studied.

## 2. Experimental

### 2.1. General procedures

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. Ni, As and V were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range  $400\text{--}4000\text{ cm}^{-1}$  on an Alpha Centaur FT/IR Spectrophotometer using KBr pellets. TG analyses were performed on a Perkin–Elmer TGA7 instrument in flowing  $\text{N}_2$  with a heating rate of  $10^\circ\text{C min}^{-1}$ . A CHI 660 Electrochemical Workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used. The working electrode was  $[\{\text{Ni}(\text{en})_2\}_4(4,4'\text{-bipy})_4\{\text{Ni}(\text{H}_2\text{O})_2\}]_2\text{-}[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]_4 \cdot 16\text{H}_2\text{O}$  bulk-modified carbon paste electrode (**1-CPE**). An SCE was used as a reference electrode and Pt gauze as a counter electrode.

### 2.2. Synthesis of $[\{\text{Ni}(\text{en})_2\}_4(4,4'\text{-bipy})_4\{\text{Ni}(\text{H}_2\text{O})_2\}]_2[\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]_4 \cdot 16\text{H}_2\text{O}$ **1**

A mixture of  $\text{NH}_4\text{VO}_3$  (0.5 mmol),  $\text{As}_2\text{O}_3$  (0.5 mmol),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol), 4,4'-bipy (0.35 mmol),  $\text{HNO}_3$  (0.1 mL, 16 M), en (0.2 mL) was dissolved in deionized water (5 mL) and stirred for 30 min in air. Then the solution was sealed in a 15 mL Teflon-lined bomb at  $170^\circ\text{C}$  for 5 days resulted in black block crystals of **1** (yield: ca. 69.6% based on V). Anal. Calc.  $\text{C}_{112}\text{H}_{168}\text{As}_{32}\text{N}_{52}\text{Ni}_{10}\text{O}_{200}\text{V}_{56}$ : C, 11.93; H, 1.50; N, 6.46; As, 21.25; Ni, 5.20; V, 25.29%. Found: C, 12.11; H, 1.38; N, 6.37; As, 21.38; Ni, 5.34; V, 25.38%.

Compound **1** can also be prepared in good crystal quality by replacing  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.5 mmol), en (0.12 mL);  $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$  (0.5 mmol), en (0.25 mL) or  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol), en (0.25 mL) at  $170^\circ\text{C}$  for 5 days.

### 2.3. Synthesis of

### $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]_2[\{\text{Ni}(\text{en})_2(\text{H}_2\text{O})\}_2\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]\text{-}[\{\text{Ni}(\text{en})_2\}\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)] \cdot 6\text{H}_2\text{O}$ **2**

The same procedure for preparing compound **1** was used, except that 1,3-bis(4-pyridyl)propane was used instead of 4, 4'-bipy (10% yield based on V). After slow cooling the bomb to room temperature, the resulting crystals of **2** were collected as a minor phase from the black slurry and amorphous solid. The crystals were manually selected, washed with distilled water, and dried at ambient temperature. Anal. Calc.  $\text{C}_{20}\text{H}_{64}\text{As}_{16}\text{N}_{22}\text{Ni}_5\text{O}_{102}\text{V}_{28}$ : C, 4.65; H, 1.25; N, 5.97; Ni, 5.68; As, 23.22; V, 27.62%. Found: C, 4.55; H, 1.28; N, 5.86; Ni, 5.73; As, 23.37; V, 27.54%. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3450(m), 1631(s), 1460(w), 1385(m), 1358(m), 1279(w), 1022(m), 983(vs), 902(w), 836(m), 726(s), 684(s), 592(s), 456(s).

### 2.4. X-ray crystallography

The structures of compounds **1** and **2** were determined by single crystal X-ray diffraction. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with  $\text{MoK}\alpha$  ( $\lambda = 0.71073\text{ \AA}$ ) at 293 K. Empirical absorption corrections ( $\psi$  scan) were applied for compounds **1** and **2**. The structures were solved by the direct method and refined by the full-matrix least squares on  $F^2$  using the SHELXL-97 software [20]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were fixed in ideal positions. The hydrogen atoms attached to water were not located.

A summary of crystal data and structure refinements for compounds **1** and **2** is provided in Table 1. Selected bond lengths and angles are listed in Table 2.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 613,899 for **1** and 615,437 for **2**.

Table 1  
Crystal data and structure refinements for **1** and **2**

	1	2
Empirical formula	C <sub>112</sub> H <sub>168</sub> As <sub>32</sub> N <sub>52</sub> Ni <sub>10</sub> O <sub>200</sub> V <sub>56</sub>	C <sub>20</sub> H <sub>64</sub> As <sub>16</sub> N <sub>22</sub> Ni <sub>5</sub> O <sub>102</sub> V <sub>28</sub>
Formula weight	11296.16	5131.52
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Tetragonal, <i>I4/m</i>	Triclinic, <i>P</i> -1
<i>a</i> (Å)	27.507(4)	11.530(2)
<i>b</i> (Å)	27.507(4)	14.883(3)
<i>c</i> (Å)	22.101(4)	21.330(4)
$\alpha$	90	76.94(3)
$\beta$	90	76.58(3)
$\gamma$	90	69.54(3)
Volume (Å <sup>3</sup> )	16722(5)	3293.4(1)
<i>Z</i> , D <sub>c</sub> (mg m <sup>-3</sup> )	2, 2.240	1, 2.587
<i>M</i> (mm <sup>-1</sup> )	5.273	6.678
<i>F</i> (000)	10856	2450
Crystal size (mm)	0.28 × 0.25 × 0.20	0.39 × 0.25 × 0.21
$\theta$ range for data collection (deg)	2.98–27.46	3.11–27.48
Limiting indices	–35 ≤ <i>h</i> ≤ 35 –35 ≤ <i>k</i> ≤ 33 –25 ≤ <i>l</i> ≤ 28	–14 ≤ <i>h</i> ≤ 14 –18 ≤ <i>k</i> ≤ 19 –27 ≤ <i>l</i> ≤ 27
Reflections collected/unique	76545/9765 [ <i>R</i> <sub>(int)</sub> = 0.1032]	30967/14605 [ <i>R</i> <sub>(int)</sub> = 0.0721]
Completeness to theta = 27.46	99.5%	96.7%
Absorption correction	Empirical	Empirical
Data/restraints/parameters	9765/72/604	14605/630/910
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.025	1.046
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0508	0.0559
w <i>R</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	0.1220	0.1261
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0788, w <i>R</i> <sub>2</sub> = 0.1337	<i>R</i> <sub>1</sub> = 0.0950, w <i>R</i> <sub>2</sub> = 0.1471
Largest diff. peak and hole	1.031 and –1.324 e Å <sup>-3</sup>	1.498 and –1.287 e Å <sup>-3</sup>

$$^a R_1 = \frac{\sum ||F_0| - |F_C||}{\sum |F_0|}$$

$$^b wR_2 = \frac{\sum [w(F_0^2 - F_C^2)]^2}{\sum [w(F_0^2)]^2}^{1/2}$$

### 3. Results and discussion

The boxlike structure of compound **1** is constructed from two  $[\{\text{Ni}(\text{en})_2\}_4(4,4'\text{-bipy})_4\{\text{Ni}(\text{H}_2\text{O})_2\}]^{10+}$  fragments, pillared by four anionic clusters  $[\text{As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^{5-}$  clusters. These clusters were converted into a novel tetrameric As–V–O cluster containing “guest” water molecules, as shown in Scheme 1. The basic unit of compound **1**,  $[\text{As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^{5-}$ , (Fig. S1) consists of 14 VO<sub>5</sub> square pyramids and 8 AsO<sub>3</sub> trigonal pyramids, with a NO<sub>3</sub><sup>-</sup> anion in the center. The  $[\text{As}_8\text{V}_{14}\text{O}_{42}]$  cluster are well known as a molecular container to encapsulate molecules (0.5H<sub>2</sub>O) and ions (SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, etc.) of varying sizes and shapes [21]. The N–O bond lengths of the anion NO<sub>3</sub><sup>-</sup> vary from 1.147(8) to 1.319(1) Å. There are ten crystallographically independent V atoms and four As atoms in an asymmetric unit. Each square-pyramidal V atom is defined by a terminal oxygen atom and four bridging oxygen atoms with the V–O bond lengths in the range of 1.594(6)–2.022(4) Å and O–V–O angles 75.1(2)–150.0(1)°. The As–O distances are from 1.761(4) to 1.792(4) Å and O–As–O angles are between 98.4(2)° and 100.4(2)°. Two AsO<sub>3</sub> groups are joined together by an oxygen bridge to form an As<sub>2</sub>O<sub>5</sub> moiety. Eight VO<sub>5</sub> square

pyramids are held together to form a 8-membered ring by edge-sharing oxygen atoms. In addition, other six vanadium oxygen square pyramids are divided into two groups, each group of VO<sub>5</sub> square pyramids share their edges to form a trimer. The two trimers are on the opposites of the ring and connected across the ring by sharing the edges with two VO<sub>5</sub> square pyramids, respectively. The remaining four faces are capped by the As<sub>2</sub>O<sub>5</sub> units to give a ball-like structure.

The remarkable tetrameric structure of compound **1** is formed by two  $[\{\text{Ni}(\text{en})_2\}_4(4,4'\text{-bipy})_4\{\text{Ni}(\text{H}_2\text{O})_2\}]^{10-}$  fragments linked to four  $[\text{As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^{5-}$ , shown in Fig. 1. Each  $[\text{As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^{5-}$  in compound **1** acts as a didentate ligand supporting to two  $\{\text{Ni}(\text{I})(\text{en})_2\}$ , to give a new  $[\{\text{Ni}(\text{en})_2\}_2\text{As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^-$  anion. Then four  $[\{\text{Ni}(\text{en})_2\}_2\text{As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^-$  anions are further joined together through two  $[\text{Ni}(2)(4,4'\text{-bpy})_2]^{2+}$  complexes in the linkage of –V = O–Ni(1)–Ni(2)–Ni(1)–O = V– to form a neutral tetramer. It is notable that this kind of connection mode results in the formation of a fascinating cavity of about 607.4 Å<sup>3</sup> (calculate by PLATON) which is occupied by the lattice water molecules. There are two different coordination environments Ni atoms in the asymmetric unit (Fig. 2). The Ni(1) atom is coordinated by four

Table 2  
Select important bond lengths (Å)

Compound 1			
As(1)–O(21)	1.762(4)	As(2)–O(23)	1.761(4)
As(1)–O(10)	1.777(3)	As(2)–O(20)	1.774(4)
As(1)–O(22)	1.777(4)	As(2)–O(12)	1.775(2)
As(3)–O(14)	1.764(4)	As(4)–O(19)	1.771(4)
As(3)–O(4)	1.773(4)	As(4)–O(5)	1.772(4)
As(3)–O(16)	1.784(4)	As(4)–O(16)	1.792(4)
Ni(1)–N(4)	2.091(5)	Ni(2)–N(2)#1	2.093(5)
Ni(1)–O(1)	2.119(4)	Ni(2)–N(2)	2.093(5)
Ni(1)–N(5)	2.123(5)	Ni(2)–N(2)#2	2.093(5)
Ni(1)–N(6)	2.131(5)	Ni(2)–N(2)#3	2.093(5)
Ni(1)–N(1)	2.143(5)	Ni(2)–O(1W)	2.102(11)
Ni(1)–N(3)	2.154(5)	Ni(2)–O(2W)	2.188(12)
V(1)–O(1)	1.621(4)	V(2)–O(25)#4	1.920(4)
V(1)–O(3)	1.921(4)	V(2)–O(2)	1.937(4)
V(1)–O(2)	1.941(4)	V(2)–O(5)	2.005(4)
V(1)–O(5)	1.973(4)	V(2)–O(21)#4	2.011(4)
V(1)–O(4)	1.985(4)	V(2)–O(7)	1.596(5)
V(3)–O(9)	1.599(6)	V(4)–O(8)	1.609(6)
V(3)–O(25)	1.932(4)	V(4)–O(24)#4	1.929(4)
V(3)–O(25)#4	1.932(4)	V(4)–O(24)	1.929(4)
V(3)–O(21)#4	2.005(4)	V(4)–O(23)#4	1.999(4)
V(3)–O(21)	2.005(4)	V(4)–O(23)	1.999(4)
V(5)–O(6)	1.598(4)	V(6)–O(13)	1.608(6)
V(5)–O(3)	1.940(4)	V(6)–O(25)#4	1.926(4)
V(5)–O(24)	1.942(4)	V(6)–O(25)	1.926(4)
V(5)–O(23)#4	2.000(4)	V(6)–O(19)#4	2.022(4)
V(5)–O(4)	2.005(4)	V(6)–O(19)	2.022(4)
V(7)–O(18)	1.594(6)	V(8)–O(17)	1.604(6)
V(7)–O(14)#4	1.974(4)	V(8)–O(24)	1.932(4)
V(7)–O(14)	1.974(4)	V(8)–O(24)#4	1.932(4)
V(7)–O(19)	1.984(4)	V(8)–O(14)	2.021(4)
V(7)–O(19)#4	1.984(5)	V(8)–O(14)#4	2.021(4)
V(9)–O(15)	1.608(4)	V(10)–O(11)	1.604(6)
V(9)–O(2)	1.928(4)	V(10)–O(20)#4	1.966(4)
V(9)–O(3)	1.947(4)	V(10)–O(20)	1.966(4)
V(9)–O(20)#4	1.988(4)	V(10)–O(22)	1.978(4)
V(9)–O(22)#4	2.013(4)	V(10)–O(22)#4	1.978(4)
Compound 2			
As(1)–O(17)	1.769(6)	As(2)–O(27)	1.758(6)
As(1)–O(31)	1.784(6)	As(2)–O(41)	1.765(6)
As(1)–O(24)	1.785(6)	As(2)–O(31)#1	1.777(6)
As(3)–O(16)	1.768(6)	As(4)–O(36)	1.754(6)
As(3)–O(42)	1.771(6)	As(4)–O(20)	1.763(6)
As(3)–O(23)	1.778(6)	As(4)–O(42)	1.779(6)
As(5)–O(19)	1.774(5)	As(7)–O(22)	1.765(6)
As(5)–O(14)	1.778(6)	As(7)–O(18)	1.767(6)
As(5)–O(10)	1.782(5)	As(7)–O(19)#2	1.777(5)
As(6)–O(8)	1.763(6)	As(8)–O(5)	1.764(6)
As(6)–O(12)	1.778(6)	As(8)–O(4)	1.769(5)
As(6)–O(7)#2	1.794(6)	As(8)–O(7)	1.772(5)
V(1)–O(38)	1.643(6)	V(8)–O(32)	1.621(6)
V(1)–O(9)	1.927(6)	V(8)–O(13)	1.930(6)
V(1)–O(3)	1.934(5)	V(8)–O(11)	1.948(6)
V(1)–O(2)	1.942(6)	V(8)–O(15)	1.954(6)
V(1)–O(1)	1.953(6)	V(8)–O(6)	1.956(6)
V(2)–O(40)	1.596(5)	V(9)–O(34)	1.581(6)
V(2)–O(1)	1.942(6)	V(9)–O(11)	1.931(6)
V(2)–O(2)	1.944(6)	V(9)–O(13)	1.934(6)
V(2)–O(8)	1.995(6)	V(9)–O(27)	2.009(6)
V(2)–O(22)	2.013(6)	V(9)–O(20)	2.016(6)
V(3)–O(26)	1.600(7)	V(10)–O(33)	1.610(6)
V(3)–O(3)	1.932(6)	V(10)–O(6)	1.918(6)

Table 2 (continued)

Compound 2			
V(3)–O(1)	1.936(5)	V(10)–O(13)	1.932(6)
V(3)–O(4)	1.998(5)	V(10)–O(41)	1.995(6)
V(3)–O(18)	1.999(6)	V(10)–O(16)#1	2.004(6)
V(4)–O(28)	1.600(6)	V(11)–O(37)	1.615(7)
V(4)–O(9)	1.930(5)	V(11)–O(15)	1.896(6)
V(4)–O(3)	1.933(6)	V(11)–O(6)	1.927(5)
V(4)–O(14)	1.999(6)	V(11)–O(24)	1.988(6)
V(4)–O(5)	2.006(5)	V(11)–O(23)#1	2.002(6)
V(5)–O(25)	1.600(6)	V(12)–O(35)	1.599(6)
V(5)–O(2)	1.942(6)	V(12)–O(11)	1.917(6)
V(5)–O(9)	1.943(6)	V(12)–O(15)	1.928(6)
V(5)–O(10)	1.981(5)	V(12)–O(17)	2.001(6)
V(5)–O(12)	1.986(6)	V(12)–O(36)	2.024(6)
V(6)–O(21)	1.593(6)	V(13)–O(29)	1.587(6)
V(6)–O(10)#2	1.967(6)	V(13)–O(20)	1.955(6)
V(6)–O(12)#2	1.971(6)	V(13)–O(24)#1	1.974(6)
V(6)–O(18)	1.979(5)	V(13)–O(23)	1.981(6)
V(6)–O(4)	1.981(5)	V(13)–O(27)	1.990(6)
V(7)–O(39)	1.597(6)	V(14)–O(30)	1.586(6)
V(7)–O(14)#2	1.976(5)	V(14)–O(17)	1.963(6)
V(7)–O(5)#2	1.979(6)	V(14)–O(16)	1.974(6)
V(7)–O(22)	1.980(6)	V(14)–O(41)#1	1.983(6)
V(7)–O(8)	1.982(5)	V(14)–O(36)	1.993(6)
Ni(1)–N(2)	2.111(7)	Ni(2A)–N(6)	2.040(9)
Ni(1)–N(2)#3	2.111(7)	Ni(2A)–N(3)	2.085(11)
Ni(1)–N(1)	2.123(8)	Ni(2A)–N(5)	2.105(9)
Ni(1)–N(1)#3	2.123(8)	Ni(2A)–O(32)	2.126(7)
Ni(1)–O(38)#3	2.193(6)	Ni(2A)–O(1W)	2.143(9)
Ni(1)–O(38)	2.193(6)	Ni(2A)–N(4)	2.157(11)
Ni(3)–N(10)	2.102(8)	Ni(2B)–O(1W)	1.447(13)
Ni(3)–N(8)	2.113(8)	Ni(2B)–N(3)	1.816(15)
Ni(3)–N(7)	2.116(8)	Ni(2B)–O(32)	2.055(12)
Ni(3)–N(9)	2.129(8)	Ni(3)–O(3W)	2.155(7)
Ni(3)–O(2W)	2.158(7)		

Symmetry transformations used to generate equivalent atoms: #1  $-x+1$ ,  $-y+1$ ,  $z$ ; #2  $-y+1$ ,  $x$ ,  $z$ ; #3  $y$ ,  $-x+1$ ,  $z$ ; #4  $x$ ,  $y$ ,  $-z+1$ .

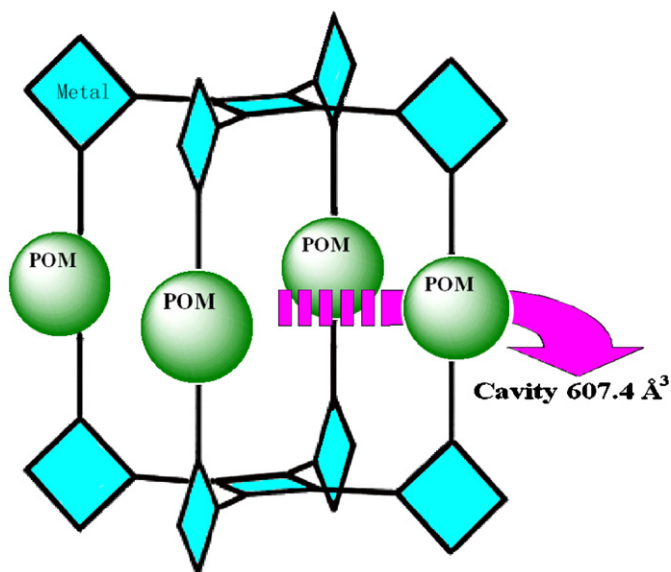
Symmetry transformations used to generate equivalent atoms: #1  $-x+1$ ,  $-y+2$ ,  $-z$ ; #2  $-x+1$ ,  $-y+1$ ,  $-z+1$ ; #3  $-x+1$ ,  $-y+2$ ,  $-z+1$ .

nitrogen atoms from two different en ligands [Ni(1)–N(3), 2.154(5), Ni(1)–N(4), 2.091(5) Å, Ni(1)–N(5), 2.123(5) Å, Ni(1)–N(6), 2.131(5) Å], one oxygen atom from the  $[\text{As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^{5-}$  anion with Ni(1)–O(1) distances of 2.119(4) Å and one nitrogen atom from 4,4'-bipy ligand [Ni(1)–N(1), 2.143(5) Å] in order to achieve its distorted octahedral coordination environment, while the Ni(2) atom is coordinated by four nitrogen atoms from four 4,4'-bipy ligands [Ni(2)–N(2), 2.093(5) Å] and two aqua ligands [Ni(2)–O(1W), 2.102(1) Å; Ni(2)–O(2W), 2.188(1) Å], exhibiting octahedral coordination environment. To the best of our knowledge, no analogous boxlike structure consisting of this kind of POM has been reported in the literature. In addition, compound **1** represents the first tetrameric arsenic–vanadium cluster with cavity constructed from mixed organic ligands and Ni ions.

The average BVS values [22] for vanadium and arsenic are 4.27 and 3.13 in compound **1**. The oxidation states of the V atoms and the As atoms are consistent with the



formula of compound **1**. In the IR spectrum of compound **1** (Fig. S4), vibration modes for  $\nu(\text{V}=\text{O})$ ,  $\nu(\text{V}-\text{O}-\text{M})$  and  $\nu(\text{As}-\text{O})$  ( $M = \text{V}$  or  $\text{As}$ ) are observed at 977, 811, 768, 708, 634, 548 and  $457\text{ cm}^{-1}$ . The characteristic absorption bands of organonitrogen ligands occur from 1031 to  $1600\text{ cm}^{-1}$ .



Scheme 1. Schematic representation of the cavity of **1**.

In order to prepare more unique cavity structures based on compound **1**, we tried to use linear flexible ligand, 1, 3-bis(4-pyridyl)propane, instead of the 4,4'-bipy. However, the 1, 3-bis(4-pyridyl)propane was not involved in the result production. It provided a suitable basic and reductive condition with en and finally deduced to the transformation of the polyoxoanion's framework from  $\alpha\text{-As}_8\text{V}_{14}\text{O}_{42}$  to  $\beta\text{-As}_8\text{V}_{14}\text{O}_{42}$  (Fig. 3). In the crystal structure of compound **2**, the novel  $[\beta\text{-As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^{5-}$  anion cluster is similar to that of the reported  $[\text{H}_2\text{en}]_4[\beta\text{-As}_8\text{V}_{14}\text{O}_{42}(\text{SO}_4)] \cdot 2\text{HSO}_4$  [23] which consists of 14 distorted  $\text{VO}_5$  square pyramids and four  $\text{As}_2\text{O}_5$  units, with a  $\text{NO}_3^-$  anion in its center. On one hand, eight  $\text{VO}_5$  square pyramids share their edges to form an 8-ring. On the other hand,  $\text{VO}_5$  atoms share their edges to form another 8-ring. Sharing two of the 14  $\text{VO}_5$  square pyramids, the two 8-rings are mutually perpendicular to form a cage. The four windows of the cage are each capped by a  $\text{As}_2\text{O}_5$  unit to give a spherical shell of composition  $[\beta\text{-As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}]^{4-}$  (Fig. S2). The structure of  $[\beta\text{-As}_8\text{V}_{14}\text{O}_{42}]^{4-}$  can also be derived from  $[\alpha\text{-As}_8\text{V}_{14}\text{O}_{42}]^{4-}$  by a  $90^\circ$  rotation of one-half of the  $[\alpha\text{-As}_8\text{V}_{14}\text{O}_{42}]^{4-}$  around its  $S_4$  axes (Fig. 3). There are fourteen crystallographically independent V atoms and eight As atoms in the unit. Each square-pyramidal V atoms is defined by a terminal oxygen atom and four bridging oxygen atoms (V–O bond lengths, 1.581(6)–2.024(6) Å; O–V–O angles 76.0(1)–149.2(5) $^\circ$ ; As–O distances,

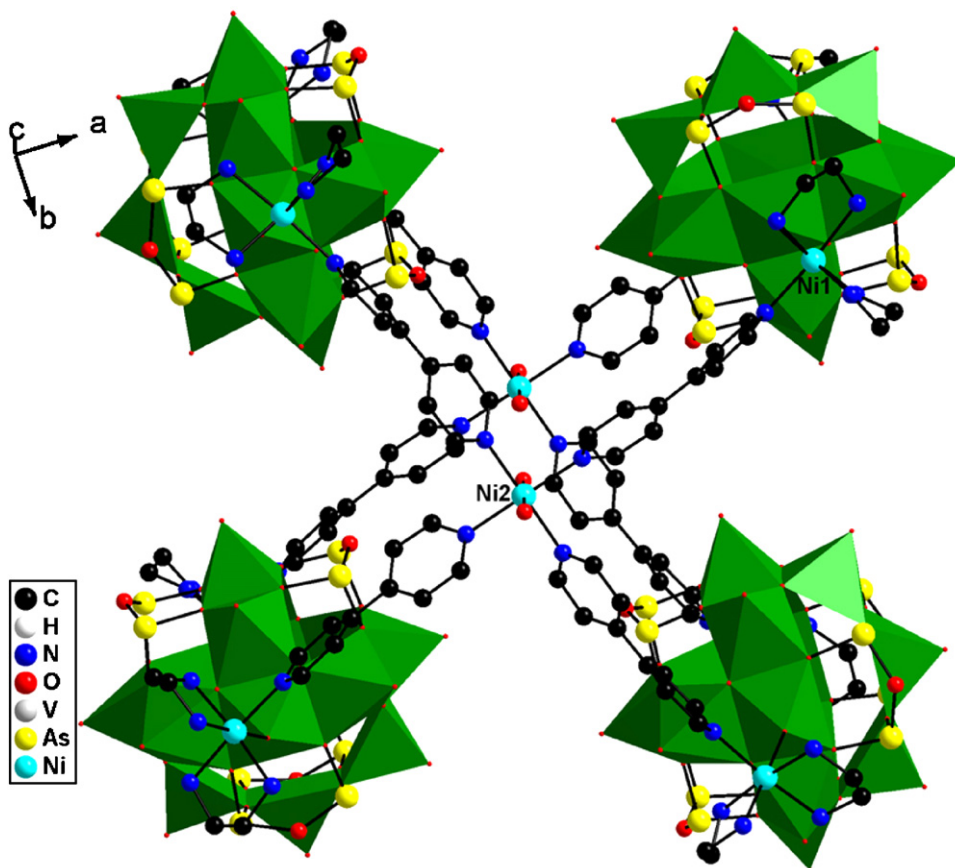


Fig. 1. View of the tetrameric structure of **1**. H atom and uncoordinated water molecules were omitted for clearing.

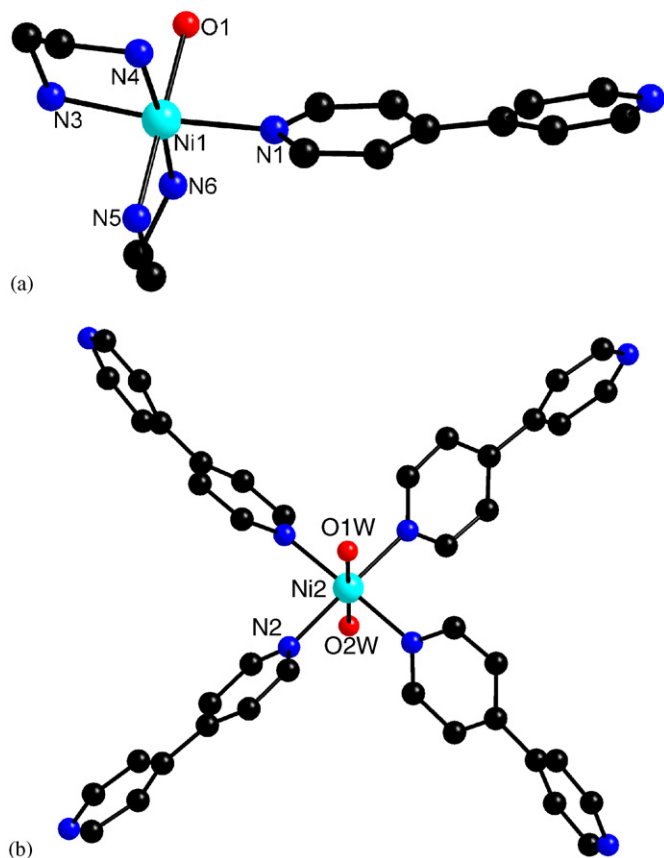


Fig. 2. View the coordination environment around Ni atoms of **1**.

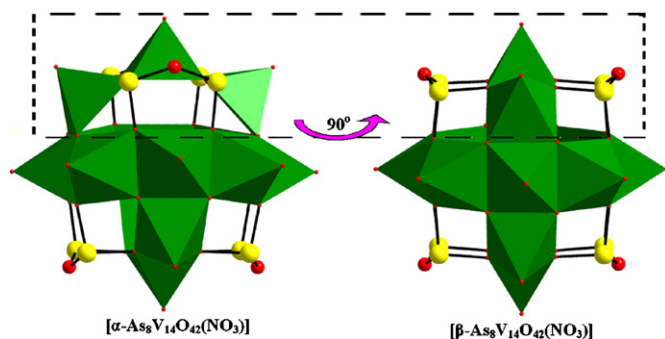


Fig. 3. Rotation one of the trimers by  $90^\circ$  around its  $S_4$  axes transforms  $\alpha$ - $\text{As}_8\text{V}_{14}\text{O}_{42}$  in compound **1** into  $\beta$ - $\text{As}_8\text{V}_{14}\text{O}_{42}$  in compound **2**.

1.754(6)–1.794(6) Å; O–As–O angles,  $97.8(3)$ – $99.5(7)^\circ$ . Bond valence calculations [22] show that the average valence of the V atoms and As atoms are in the +4.30 and +3.14 oxidation state.

The structure determination of compound **2** shows the presence of three crystallographically independent motifs in the same crystal (Fig. 4). One motif is a bisupporting  $[\{\text{Ni}(\text{en})_2(\text{H}_2\text{O})\}_2\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]^-$  anion cluster which consists of full reduced  $[\beta\text{-As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^{5-}$  anion and two Ni (II) complex fragments  $[(\text{H}_2\text{O})\text{Ni}(\text{en})_2]^{2+}$  (Fig. 4a). The Ni(2) atom is coordinated by four nitrogen atoms from two ethylenediamine ligands (Ni(2)–N, 1.816(2)–2.157

(1) Å), one oxygen atom from the  $[\beta\text{-As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^{5-}$  anion (Ni(2)–O32, 2.108(5) Å) and a terminal ligand water molecule (Ni(2)–OW7 2.158(7) Å), exhibiting distorted octahedral coordination environment.

The second motif of compound **2** is a one-dimensional chain anion structure  $[\{\text{Ni}(\text{en})_2\}_2\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]^-$ . The  $[\beta\text{-As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^{5-}$  anion acts as a didentate ligand coordinate to two nickel coordination complexes via the doubly bridging oxygen atoms. Therefore, each  $\{\beta\text{-As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)[\text{Ni}(\text{en})_2]\}^-$  cluster is connected with the neighbor one through the  $[\text{Ni}(1)(\text{en})_2]^{2+}$  bridging group to form a 1-D chain-like anion polymer (Fig. 4b). The nickel site exhibits a octahedron coordination geometry which is defined by four nitrogen coordination from the ethylenediamine ligands (Ni(1)–N(1) = 2.123(8) Å, Ni(1)–N(2) = 2.111(7) Å) and two trans doubly bridging oxygen atoms from two different As–V–O anions (Ni(1)–O38 = 2.193(6) Å).

The third motif and also the cation part of compound **2** is  $[\text{Ni}(3)(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$  (Fig. 4c). The Ni atom links to four nitrogen atoms from ethylenediamine ligands (Ni(3)–N = 2.130(4) Å, 2.101(3) Å, 2.113(3) Å and 2.116(3) Å, respectively) and two terminal ligand water molecules (Ni(3)–O3W, 2.115(7) Å; Ni(3)–O2W, 2.158(7) Å) to form a roughly octahedral geometry. The coexistence of different structural motifs in the same crystal is rather rare. Compound **2**, in which the bisupporting polyoxoanions and 1-D chain-like polyoxoanions coexist, has not been reported in the modified POMs.

The pillared boxlike framework in compound **1** and the multimotifs coexisted organic–inorganic hybrid structure in compound **2** are all synthesized from the similar inorganic materials. The obvious structural difference between compounds **1** and **2** is due to the introduction of different organic molecules. This has further demonstrated that organic molecules may profoundly affect not only the structure of framework but also the structure of polyoxoanions.

The TG curve of compound **1** exhibits two major mass losses (Fig. S6). The first weight loss of 5.69% at 29–371 °C is due to the loss of water molecules and  $\text{NO}_3^-$  ions. The second weight loss of 45.80% at 371–900 °C is caused by the decomposition of organoamine ligands and the sublimation of  $\text{As}_2\text{O}_3$  molecules. The whole weight loss 51.49% is in consistent with the calculated value 52.41%.

To determine the redox property of compound **1**, 1-bulk-modified carbon paste electrode (1-CPE) was fabricated as the working electrode due to its insolubility in most solvents [24,25]. Fig. 5 shows the voltammetric behavior of the working electrode at different scan rates in the 1 M  $\text{H}_2\text{SO}_4$  aqueous solution. It is noticed that in the potential range 1200 to –1000 mV at scan rate  $30 \text{ mV s}^{-1}$ , three redox peaks appear and the mean peak potentials  $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$  are 871 (I), 536 (II) and –479.5(III) mV, respectively, in compound **1**. The redox peaks I–I' and II–II' may attribute to V(V)/V(IV), V(III)/V(IV) and the redox peak III–III' attributes to As (III)/

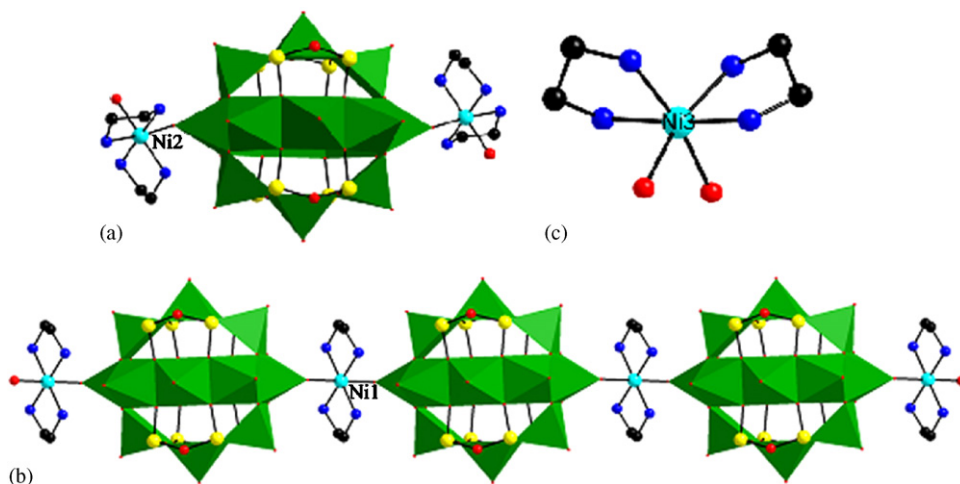


Fig. 4. A view of bisupporting motif  $[\{\text{Ni}(\text{en})_2(\text{H}_2\text{O})\}_2\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]^-$  (a), the chainlike motif  $[\{\text{Ni}(\text{en})_2\}_2\text{As}_8\text{V}_{14}\text{O}_{42}(\text{NO}_3)]^-$  (b) and the  $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})]^{2+}$  cation (c) in **2**.

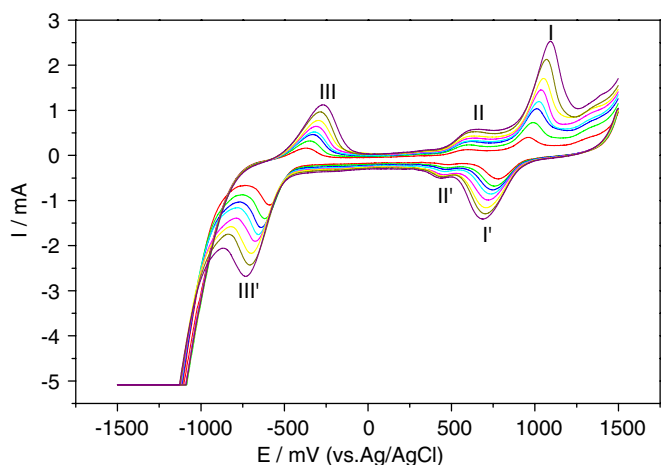


Fig. 5. The cyclic voltammograms of compound **1** in 1 M  $\text{H}_2\text{SO}_4$  at different scan rates (from inner to outer: 30, 40, 50, 60, 70, 80, 90 and  $110 \text{ mV s}^{-1}$ ).

As(IV), respectively. It is consistent with both black crystal and the result of valence sum calculations. When the scan rate varied from 30 to  $110 \text{ mV s}^{-1}$ , the peak potentials changed gradually: the cathodic peak potentials shifted to the negative direction and the corresponding anodic peak potentials shifted to the positive direction with increasing scan rate.

The variable temperature magnetic susceptibility of compound **1** was measured from 2 to 300 K at 1000 Oe and is shown in Fig. 6. As  $T$  reducing, the  $\chi_M T$  value continuously decreases nearly linearly to  $15.59 \text{ cm}^3 \text{ K mol}^{-1}$  at 40 K, and then decreases rapidly from 40 K and reaches a minimum value of  $6.60 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. Such magnetic behavior is characteristic of antiferromagnetic coupling interaction. The  $\chi_M T$  shows a value of  $16.53 \text{ cm}^3 \text{ K mol}^{-1}$  at room temperature, which is much lower than the expected value ( $31 \text{ cm}^3 \text{ K mol}^{-1}$ ) for 56 uncoupled  $S = 1/2$  spins of  $\text{V}^{4+}$  atoms and 10 uncoupled  $S = 1$  spins of  $\text{Ni}^{2+}$  atoms (assuming  $g = 2$  for  $\text{V}^{4+}$  and

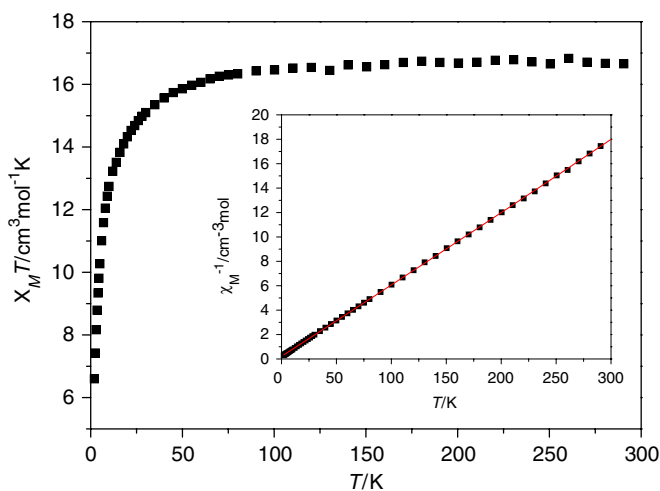


Fig. 6. Plot of  $\chi_M T$  vs. temperature for **1**.

$g = 2.20$  for  $\text{Ni}^{2+}$ ). Similar trends have also been observed in other high-nuclearity spin oxovanadium clusters [26–28]. These antiferromagnetic coupling interactions are related to electron delocalization. Previous studies indicated that electron delocalization can favor spin pairing, suggesting that the  $[\text{As}_8^{\text{III}}\text{V}_{14}^{\text{IV}}\text{O}_{42}(\text{NO}_3)]^{5-}$  polyoxovanadate clusters of compound **1** may be antiferromagnetic coupled. Unfortunately, it is too difficult to fit the experimental magnetic data of this tetramer using a suitable theoretical model. However, the magnetic susceptibility obeys the Curie–Weiss law in the whole range of 40.0–300.0 K giving a Weiss constant  $\theta = -5.11 \text{ K}$  and a Curie constant  $C = 17.54 \text{ cm}^3 \text{ K mol}^{-1}$ , characteristic of an overall antiferromagnetic interaction.

In this paper, we have synthesized and structurally characterized two unique organic–inorganic hybrids based on As–V–O clusters by exploiting hydrothermal syntheses. The successful synthesis of **1** provides an interesting illustration of the use of polyoxometalate clusters and

mixed organic ligands to obtain novel high-dimensional organic–inorganic hybrid polyoxometalates with unique structures and remarkable properties. Meanwhile, compound **2** shows us some new interesting structure information about the rarely [ $\beta$ -As<sub>8</sub>V<sub>14</sub>O<sub>42</sub>] cluster.

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