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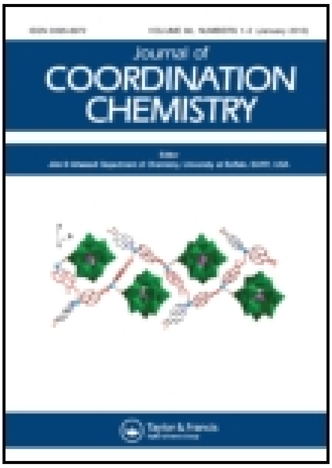

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A new 1-D chain based on the trivacant monocapped Keggin arsenomolybdate and the copper complex linker: synthesis, crystal structure, and ESI-MS analyses

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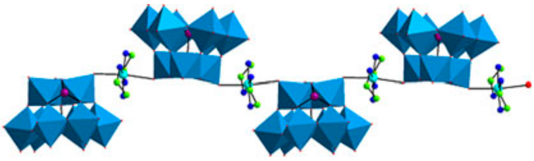

A new organic–inorganic hybrid $(H_2en)_2[[Cu(en)_2]As^{III}As^{V}Mo^{VI}_9O_{34}]\cdot 6H_2O$ (**1**), containing a 1-D helical chain based on the trivacant monocapped Keggin arsenomolybdate and the copper complex linker $\{[Cu(en)_2][As^{III}As^{V}Mo^{VI}_9O_{34}]\}_n^{4n-}$ (en = ethylenediamine), has been synthesized and characterized by IR spectra, TG analyses, single-crystal X-ray diffraction, and high-resolution electrospray ionization mass spectrometry (ESI-MS). Large voids are observed and a 1-D chain containing repeated $(H_2O)_8$ water units from lattice water molecules is formed along the *a* axis in the crystal structure. The high-resolution ESI-MS shows that the intact framework $[Cu(en)_2][As^{III}As^{V}Mo^{VI}_9O_{34}]^{4-}$ exists in solution.

Keywords: Polyoxometalate; Organic–inorganic hybrid; Water cluster; 1-D chain; ESI-MS

1. Introduction

Heteropolyoxometalates, dominated mainly by heteropolytungstate (HPT) and heteropolymolybdate (HPM), are a fascinating class of metal–oxygen clusters, which exhibit compositional diversity and structural versatility, resulting in potential application in materials science, medicine, and catalysis [1–4]. There has been increasing interest in the assembly of HPOM clusters in extended inorganic or hybrid inorganic–organic solids, in which the polyoxoanions serve as inorganic linkages by providing terminal and/or bridging oxygens to coordinate transition metal ions of transition metal complexes [5–9]. These solid materials

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*Corresponding author. Email: glxue@nwu.edu.cn are attractive for their variety of topologies and intriguing frameworks and electric, magnetic, catalytic, and optical properties [10–16]. To date, the classical Keggin-, Dawson-, Strandberg- and Anderson-type fragments used as cluster building blocks have dominated this area. Compared with the large number of classical HPT fragments, HPMs, especially containing unconventional HPM building blocks, are rare. It is especially interesting when new types of polyoxometalates are employed as the building blocks to construct extended solid frameworks. In 2007, Yang *et al.* reported the first example of a pure inorganic 1-D chain based on the sandwich-type arsenomolybdates, $M(H_2O)_5]_{2n}(H_3O)_{2n}\{M(H_2O)_5\}_2(MAs^{V}Mo_9O_{33})_2]_n[M(H_2O)_4(MAs^{V}Mo_9O_{33})_2]^{8n-}$ (M = Mn^{2+}, Co^{2+}) [17]. Later, 1-D inorganic–organic chains based on sandwich-type germanomolybdates, $(Him)_8Na_7H_7[Cu(im)_4(CuGeMo_9O_{33})_2][(CuGeMo_9O_{33})_2]\cdot 41H_2O$ (im = imidazole) [18] and $(H_2en)_2H\{[Na_{2.5}(H_2O)_{12}]_2[Cu(en)_2][Cu_2(\beta\text{-}YGeMo_9O_{33})_2]\}\cdot 8H_2O$ [19], and 2-D framework structure $[Cu(en)_2]_2[Cu(en)_2(H_2O)]_2\{[Cu(en)_2]_2[Cu_2(\beta\text{-}Y\text{-}GeMo_9O_{33})_2]\}\cdot 8H_2O$ [19] were reported by Li *et al.*, respectively. Several extended inorganic–organic hybrids based on $[H_2As^{V}{}_2Mo_6O_{26}]^{4-}$, $[(CuO_6)Mo_6O_{18}(As^{III}{}_3O_3)_2]^{4-}$, and monocapped trivacant $[As^{III}As^{V}Mo_9O_{34}]^{6-}$ fragments, such as 1-D chain structure $[Cu_4(en)_4O_2(H_2O)_2][H_2As^{V}{}_2Mo_6O_{26}]$, $(H_2en)[Cu(en)_2][(CuO_6)Mo_6O_{18}(As^{III}{}_3O_3)_2]\cdot 10H_2O$ [20], $\{[Cu(en)_2][Cu(en)(H_2O)][(Cu(en)_2(H_2O)][As^{III}As^{V}Mo_9O_{34})]\}\cdot 2H_2O$ [21], and $(H_2en)_{1.5}[Cu(en)(Hen)][As^{III}As^{V}Mo_9O_{34}]\cdot 2H_2O$ [22], and the 2-D framework structure $[Cu(dap)_2]_4[Cu(dap)_2(H_2O)][Cu(dap)_2(As^{III}As^{V}Mo_9O_{34})_2]\cdot 2H_2O$ (dap = 1,2-diaminopropane) [10], have been reported. We have synthesized new types of extended hybrid inorganic–organic solids based on unconventional arsenomolybdate building blocks, such as 2-D frameworks based on $[As_6CuMo_6O_{30}]^{4-}$ and $[As_3Mo_3O_{15}]^{3-}$, $(As_6CuMo_6O_{30})\{[Cu(imi)_4]_3[As_6CuMo_6O_{30}]\}_2\cdot 6H_2O$, and $[Cu(enMe)_2]_3[As_3Mo_3O_{15}]_2\cdot 2H_2O$ [23]. Based on the above, there are chances for exploring novel extended inorganic or hybrid inorganic–organic solids. As a continuation of our work, herein we report a new 1-D chain based on the trivacant monocapped Keggin arsenomolybdate fragment $[As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{6-}$ and the copper complex linker $[Cu(en)_2]^{2+}$, $(H_2en)_2[[Cu(en)_2]As^{III}As^{V}Mo^{VI}{}_9O_{34}]\cdot 6H_2O$, which was characterized by IR spectra, single-crystal X-ray diffraction, and high-resolution ESI-MS.

2. Experimental

2.1. *Materials and methods*

All chemicals were commercially purchased and used without purification. Elemental analysis (C, H, and N) was performed on a Perkin-Elmer 2400 CHN elemental analyzer. Cu, Mo, and As were analyzed on an IRIS Advantage ICP atomic emission spectrometer. Infrared spectra were recorded from 400 to 4000 cm^{-1} on an EQUINOX55 FT/IR spectrometer with KBr pellets. Thermogravimetry (TG) analyses were performed on a NETZSCH STA 449C TGA instrument in flowing N_2 at a heating rate of 10 °C min^{-1}. MicroTOF-QII mass spectrometer with an electrospray ionization (ESI) source (Bruker, Germany) was used. The electrospray source was used with a drying nitrogen gas temperature at 180 °C, and the ion polarity for all MS data collections was negative. A capillary voltage of 4.5 kV was used, with a collision energy of −10.0 eV. Time-of-flight mass spectra were acquired at a resolution of ca. 17,500 (full width at half maximum) at *m/z* 2000. The calibration solution used was Agilent ESI tuning mix solution, lot No. LB78436, enabling calibration between

0 and 3000 *m/z*. Samples were introduced into the MS via direct injection at 180 µL h^{-1}. All data were processed using the Bruker Daltonics Data Analysis 4.0 software, while simulated isotope patterns were investigated using Bruker Isotope Pattern software.

2.2. Synthesis of $(H_2en)_2[[Cu(en)_2]As^{III}As^{V}Mo^{VI}{}_9O_{34}]\cdot 6H_2O$ (1)

The synthesis of **1** was accomplished by adding a solution of As_2O_3 (0.146 g, 0.74 mM) dissolved in 4 M nitric acid (5 mL) to a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.78 g, 0.63 mM) dissolved in H_2O (10 mL) with vigorous stirring; the pH was adjusted to 6.5 with aqueous ammonia. Then 0.126 g of $CuCl_2\cdot 2H_2O$ (0.74 mM) dissolved in 1 mL of water was added and heated to 90 °C for 10 min. Followed by the addition of 0.8 mL of en, the mixture was stirred for another 30 min, filtered, and allowed to cool to ambient temperature. After one month, purple block crystals were collected (0.493 g, 35% yield based on Cu). Elemental Anal. Calcd (%) for $C_8H_{48}N_8As_2CuMo_9O_{40}$: N, 5.68; H, 2.45; C, 4.87; Cu, 3.22; As, 7.59; Mo, 43.75. Found (%): N, 5.66; H, 2.35; C, 4.64; Cu, 3.21; As, 7.62; Mo, 43.5.

2.3. Crystallographic structure determination

The selected crystal of **1** was mounted on a glass fiber capillary for indexing and intensity data collection at 296 K on a BRUKER SMART APEX II CCD diffractometer using Mo K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXTL-97) and refined by full-matrix-block least-squares on F^2. All non-hydrogen atoms were refined anisotropically except those of free water and ethylenediamine molecules. No hydrogens associated with water were located from the difference Fourier maps. Positions of the hydrogens attached to carbon and nitrogen were geometrically placed. All hydrogens were

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

Empirical formula	$C_8H_{48}N_8As_2CuMo_9O_{40}$
Formula weight	1973.38
T (K)	296(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.4768(8)
b (Å)	21.5073(17)
c (Å)	20.7633(16)
β (°)	100.4080(10)
V (Å^3)	4601.6(6)
Z	4
d_{Calcd}/g cm^{-3}	2.848
μ (mm^{-1})	4.364
Reflections measured	23,220
Independent reflections	8176
Reflections used	6091
R_{int}	0.0472
GoF on F^2	0.994
$R_1{}^a$ [$I > 2\sigma(I)$], $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0742, 0.2171
$R_1{}^a$ (*all data*), $wR_2{}^b$ (*all data*)	0.0982, 0.2456
$\Delta\rho_{min/max}$ (e/Å^3)	2.661/−4.275

$^aR_1 = [\Sigma|F_o| - |F_c|]/[\Sigma|F_c|]$.
$^bwR_2 = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$.

refined isotropically as a riding mode using the default SHELXTL parameters. A summary of the crystal data and structure refinements for **1** is given in table 1. Crystallographic data for the structural analysis of **1** has been deposited with the Cambridge Crystallographic Data Center, CCDC No.: 998241.

3. Results and discussion

3.1. *Description of the structure*

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the space group $P2_1/c$, its asymmetry consists of one $[As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{6-}$ polyanion, one $[Cu(en)_2]^{2+}$ cation, six lattice water molecules, and two diprotonated en cations (figure 1). The structural feature of **1** is that the $[As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{6-}$ polyoxoanion is a bidentate ligand by utilizing its O_t oxygens linked to $[Cu(en)_2]^{2+}$ cation to form a 1-D chain (figure 2). In this chain, the adjacent $[As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{6-}$ anions open in the opposite direction and en ligands are perpendicular to the extension of the chain to lead to a 2_1 symmetry along the *b* direction. $[As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{6-}$ was first reported by He *et al.* in 1999 [24]; it is derived from the trivacant Keggin $[A\text{-}\alpha\text{-}As^{V}Mo_9O_{34}]^{9-}$ moiety capped by an As^{III} through three bridging oxygens. In the skeleton of the $[As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{6-}$ unit, the tetrahedral $\{AsO_4\}$ is located in the center of the $[A\text{-}\alpha\text{-}As^{V}Mo_9O_{34}]^{9-}$ cluster and shares four oxygens with three $\{Mo_2O_{10}\}$ groups and a $\{Mo_3O_{13}\}$ triad with the As–O bond distances ranging from 1.642(10) to 1.698(9) Å. The $\{AsO_3\}$ group has two short As–O bonds of 1.806(9) Å and one long As–O bond of 1.888(9) Å. All other bond lengths and bond angles are consistent with those reported in the literature [21, 22]. Valence sum (Σs) calculations [25] show the oxidation states of Mo ions are + 6, the As1 associated with $\{AsO_4\}$ tetrahedron is + 5, the As2 associated with the triangular pyramidal $\{AsO_3\}$ group is + 3, and the Cu ions are + 2. Therefore, part of the As_2O_3 must have been oxidized in the reaction. Cu^{2+} adopts {4 + 2} distorted octahedral coordination $\{CuN_4O_2\}$ and is coordinated to four nitrogens from two en ligands building the equatorial plane and two oxygens from $[As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{6-}$ units lying on axial sites of the elongated octahedron. The Cu–O distances are 2.504(15)–2.696(14) Å and the Cu–N distances are 1.974(13)–2.010(14) Å.

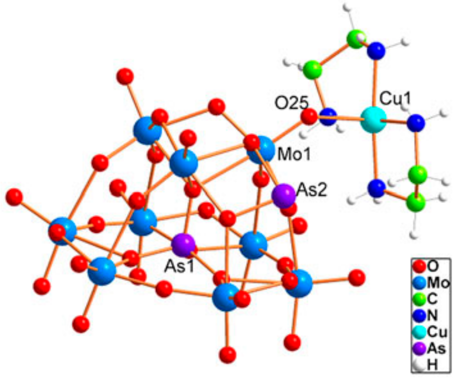


Figure 1. Ball-and-stick representation of the asymmetric unit of **1** with the selected labeling scheme. Lattice waters and en cations are not included.

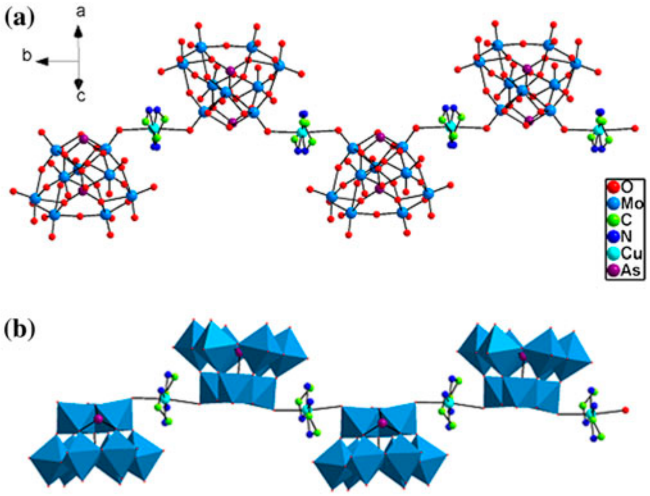


Figure 2. (a) Ball-and-stick and (b) combined polyhedral/ball-and-stick representation of the 1-D chain-like arrangement of **1**. Hydrogens were omitted for clarity.

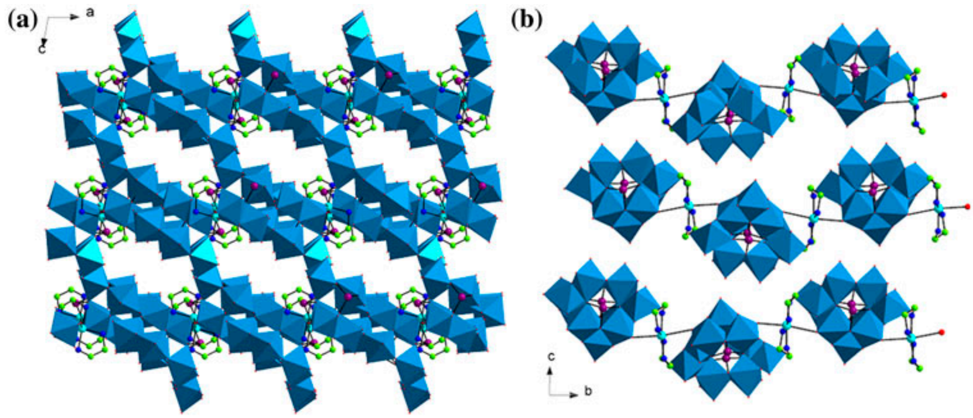


Figure 3. (a) Combined polyhedral/ball-and-stick representation along the *b* direction and (b) along the *a* direction, showing the large voids existing in the crystal structure of **1**. Hydrogens, lattice water molecules, and en cations are omitted for clarity.

The neighboring chains are arranged in parallel to form the 3-D supramolecular framework. Along the *a* direction, there exist large voids occupied by water molecules or en cations (figure 3). A 1-D chain containing repeated $(H_2O)_8$ water units constructed from lattice water molecules was formed along the *a* axis in **1** [figure 4(a)]. Strong hydrogen bond interaction exists among the water clusters and oxygens from adjacent polyanions, such as short $O_W\cdots O$ distances of 2.85–2.99 Å between $O_W(103)\cdots O(9)$, $O_W(103)\cdots O(12)$, $O_W(105\cdots O(6)$, $O_W(105)\cdots O(10)$, and $O_W(105\cdots O(33)$, which expanded **1** [figure 4(b)].

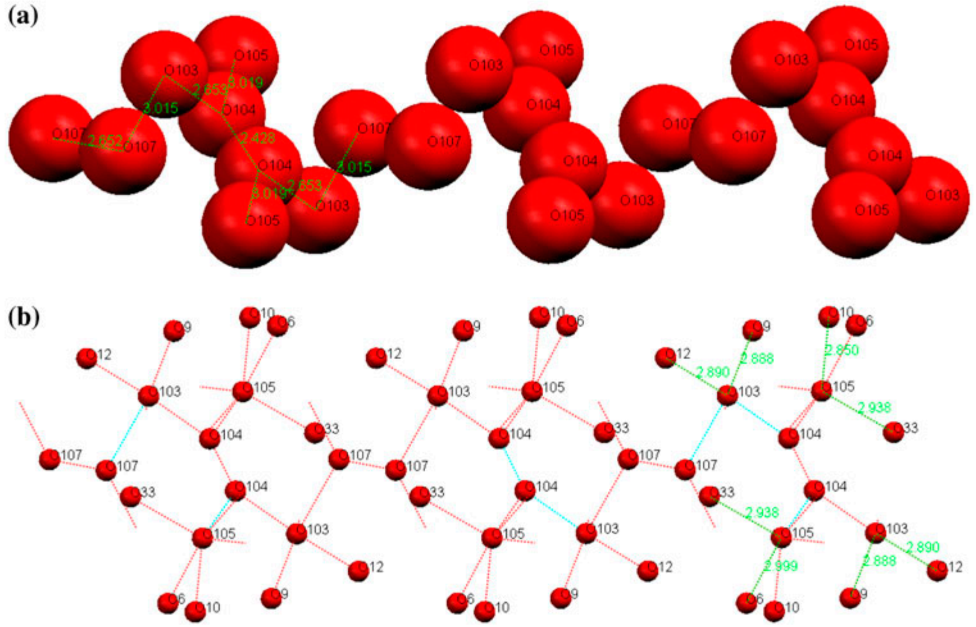


Figure 4. (a) Spacefill representation of 1-D chain containing repeated $(H_2O)_8$ water units constructed from lattice water molecules along the *a* axis. (b) The strong hydrogen bond interaction exists among the water units and oxygen atoms from adjacent polyanions.

3.2. *Synthesis*

The trivacant monocapped Keggin arsenomolybdate fragment $[As^{III}As^{V}Mo^{VI}_9O_{34}]^{6-}$ and the transition metal complexes can form a series of inorganic–organic hybrids (in figure 5), and the species and configurations of final products depend on pH values, reaction temperature, initial reactants, stoichiometric ratio, organic ligands, counter cations, *etc*. Compound **1** was synthesized by treating a suspension of As_2O_3, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $CuCl_2\cdot 2H_2O$, and en at 90 °C at pH 6.5. Compared to the synthesis of **1**, **2** was obtained by the same initial reactants except for adding 1,10′-phen at 130 °C at pH 4.6 [20]. Compounds **3**–**5** [21, 22] were prepared by the mixture of As_2O_3, $Na_2MoO_4\cdot 2H_2O$, $CuCl_2\cdot 2H_2O$, and en with pH values ranging from 4.6 to 5.4 under hydrothermal conditions. Compound **5** was isolated at pH 4.6 and en ligands adopt two coordination modes, one as a bidentate chelate ligand and the other only a terminal N donor coordinating to Cu in $[Cu(en)(Hen)]^{3+}$ bridges. In **3** and **4**, which were obtained at pH 4.8 for **3** and 5.4 for **4**, two en molecules in $[Cu(en)_2]^{2+}$ bridge as a bidentate chelate ligand. Compound **6** was obtained by a mixture of $Na_2MoO_4\cdot 2H_2O$, $NaAsO_2$, $NiCl_2\cdot 2H_2O$, and en with the molar ratio of 2.1 : 2.1 : 1.6 : 0.4 at the reaction temperature of 140 °C at pH 6.0 [26]. The higher pH does not favor the stability of $[As^{III}As^{V}Mo^{VI}_9O_{34}]^{6-}$ fragment and is prone to the formation of the dicapped Anderson-type $[(CuO_6)Mo_6O_{18}(As_3O_3)_2]^{4-}$ polyoxoanion [27]. Therefore, pH plays a crucial role in the construction of different structural configurations in this reaction system. It is possible that the hydrothermal condition is prone to the formation of $[Cu(en)_2]^{2+}$ or $[Cu(en)(H_2O)_2]^{2+}$ grafting to the vacant site of $[As^{III}As^{V}Mo^{VI}_9O_{34}]^{6-}$ through μ–O. The systematic exploration on this system still remains a challenge.

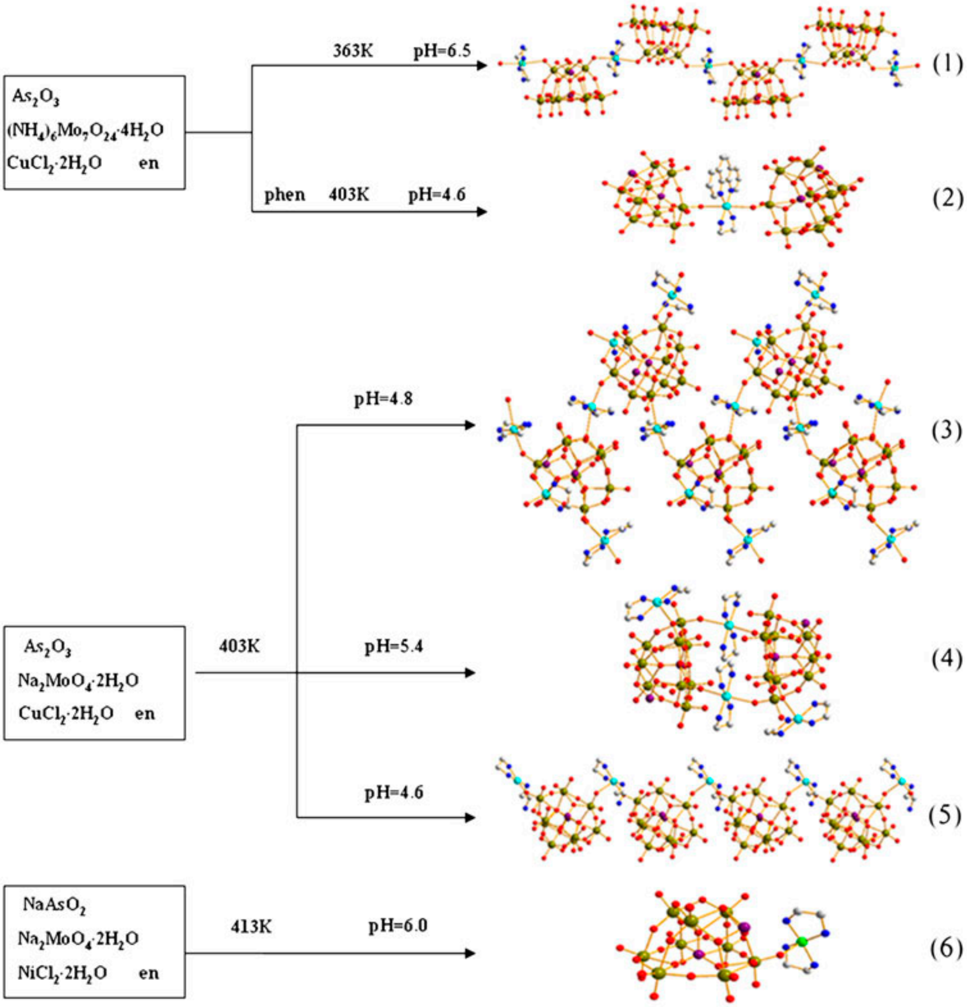


Figure 5. A series of inorganic–organic hybrids based on the fragment $[As^{III}As^{V}Mo^{VI}{}_{9}O_{34}]^{6-}$ and transition metal complex cations.

3.3. *Thermal analyses*

Thermogravimetric analysis of **1** exhibits three weight-loss stages from 30 to 600 °C (figure 6). The first weight loss of 5.98% occurs between 30 and 160 °C due to loss of all water molecules (Calcd 5.48%). The second weight loss of 11.92% from 160 to 402 °C is assigned to the decomposition of four en molecules (Calcd 12.18%). The third stage at 390–585 °C corresponds to the decomposition of the polyanion framework structure with the sublimation of As_2O_3, according to the reaction $H_4As_2CuMo_9O_{34} \rightarrow As_2O_3\uparrow + 2H_2O\uparrow + 0.5\ O_2\uparrow + 9MoO_3 \cdot CuO$. The observed total weight loss of 29.53% compares well with the calculated value of 30.32%.

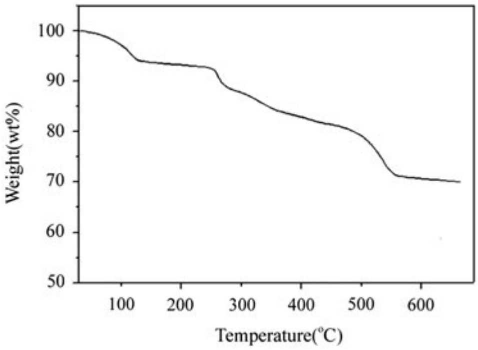


Figure 6. The TG curve of **1**.

3.4. *IR spectra*

IR spectra of **1** display the characteristic vibration patterns derived from the Keggin framework at 1080–689 cm^{-1} (figure S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.947968). Four characteristic vibrations attributable to ν(As–O$_a$), ν(W–O$_t$), ν(W–O$_b$), and ν(W–O$_c$) are at 1080–1043, 918, 857, and 788–689 cm^{-1} [9, 10]. In addition, the stretching bands of –OH and –NH$_2$ are observed at 3430 and 3289–3231 cm^{-1}. The bending of –NH$_2$ and –CH$_2$ groups appear at 1589 and 1443 cm^{-1}, respectively. Weak resonances between 1277 and 1176 cm^{-1} are attributed to C–N stretches. The occurrence of these absorptions confirms the presence of organic amine groups, in agreement with the single-crystal structural analysis.

3.5. *Electrospray mass spectra*

The negative mode electrospray mass spectrum in 50 : 50 MeCN–H$_2$O containing 0.1% formic acid solution of **1** recorded under wide declustering conditions is shown in figure 7. The spectrum shows four dominant bands centered at *m/z* 439.7, 881.4, 910.9, and 933.3. The signals at *m/z* = 910.9 and 933.3 regularly spaced with Δ*m/z* = 0.5 which imply a double charge

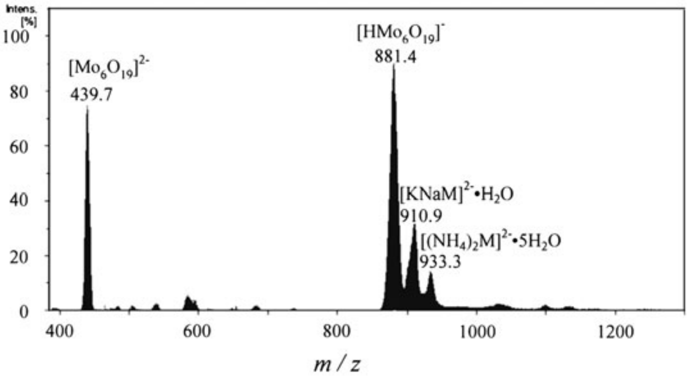
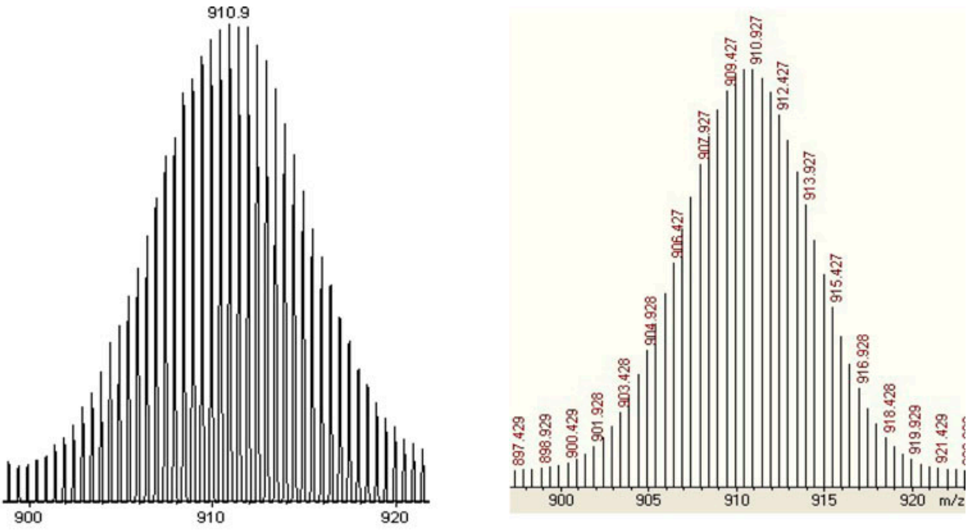
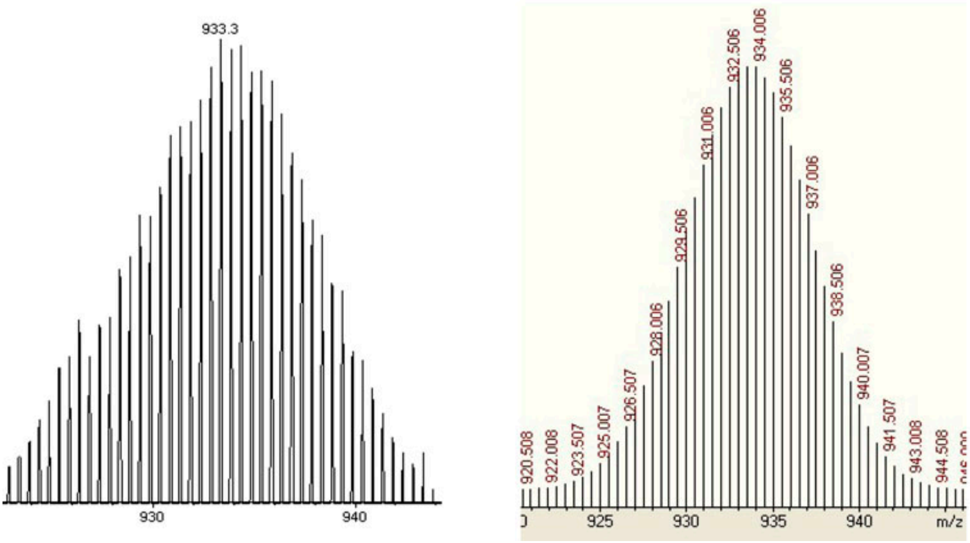


Figure 7. Negative ESI-MS spectrum in 50 : 50 MeCN–H$_2$O with 0.1% formic acid solution of **1** recorded under wide declustering conditions (M = $[Cu(en)_2][As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{4-}$).

are observed and could be assigned to $[KNaM]^{2-}\cdot H_2O$ and $[(NH_4)_2\ M]^{2-}\cdot 5H_2O$ ($M = [Cu(en)_2][As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{4-}$), respectively, corresponding to the main fragment peaks of polyanion **1**. The results show that the intact framework $[Cu(en)_2][As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{4-}$ exists in solution. The signal at *m/z* 439.7 regularly spaced with $\Delta m/z = 1/2$ which implies a two-charge could be attributed to $[Mo_6O_{19}]^{2-}$, and the signal at *m/z* 881.4 spaced with



$[KNaM]^{2-}\cdot H_2O$



$[(NH_4)_2M]^{2-}\cdot 5H_2O$

Figure 8. Comparison of the experimental (left) and simulated isotopic envelope (right) for the peaks of $[KNaM]^{2-}\cdot H_2O$ and $[(NH_4)_2\ M]^{2-}\cdot 5H_2O$ ($M = [Cu(en)_2][As^{III}As^{V}Mo^{VI}{}_9O_{34}]^{4-}$).

$\Delta m/z = 1$ to $[HMo_6O_{19}]^-$ composed of the basic framework $[Mo_6O_{19}]^{2-}$ attached to one proton. The signals related to $[Mo_6O_{19}]^{2-}$ are the most intense peaks, suggesting that the $[Mo_6O_{19}]^{2-}$ polyanion is a very stable fragment ion in electrospray ionization or in solution, which is consistent with its known stability. The observed isotopic pattern of each compound perfectly matches the simulated isotope pattern, which provides further proof for the identification of these species (figures 8 and S2).

4. Conclusion

A new organic–inorganic hybrid arsenomolybdate constructed from monocapped trivacant $[As^{III}As^{V}Mo^{VI}_9O_{34}]^{6-}$ fragments with $[Cu(en)_2]^{2+}$ has been synthesized by a conventional method. Compound **1** exhibits an unusual helical 1-D chain assembled by $[Cu(en)_2]^{2+}$ bridging adjacent trivacant $[HAs^{III}As^{V}Mo^{VI}_9O_{34}]^{5-}$ polyoxoanions opened towards the opposite direction to lead to 2_1 symmetry. Large voids exist in **1** which led to 1-D chain containing repeated $(H_2O)_8$ water units formed. The intact fragment $[Cu(en)_2][As^{III}As^{V}Mo^{VI}_9O_{34}]^{4-}$ was observed in the high-resolution ESI-MS, suggesting that $[As^{III}As^{V}Mo^{VI}_9O_{34}]^{6-}$ polyanion and $[Cu(en)_2]^{2+}$ cation are combined by strong chemical bonds in solution.

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