A Series of Arsenotungstates Based on the $[\text{HAs}_2\text{W}_8\text{O}_{31}]^{7-}$ Building Block: Syntheses by Control of the Reaction Process

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Supporting Information

ABSTRACT: A series of arsenotungstates formulated as $(\text{H}_2\text{en})_3.5[\text{HAs}_2\text{W}_8\text{O}_{31}]^{-7}$ has been synthesized in an aqueous medium by the reaction of NiCl$_2$ and Na$\text{AsO}_2$ with Na$\text{2WO}_4$, then colorless crystals of 1 transformed to yellow-green crystals of 2 for the further development of slow solvent evaporation, and, finally, yellow crystals of 3 generated over a sufficiently long time of solvent evaporation. 3 can also be hydrothermally synthesized in three different routes. Notably, 1 presents a $\text{[HAs}_2\text{W}_8\text{O}_{31}]^{-7}$ building block, 2 exhibits an asymmetric sandwich-type arsenotungstate encapsulating two nonequivalent Keggin fragments $[\text{B}-\text{AsW}_9\text{O}_{34}]^{-9}$ and $[\text{B}-\text{AsW}_8\text{O}_{31}]^{-10}$, and 3 is composed of two $[\text{B}-\text{AsW}_8\text{O}_{31}]^{-9}$ units sandwiching a tetranickel cluster. Their structural difference indicates that controlling the reaction process plays a key role in the structures and topologies of these complexes.

INTRODUCTION

Polyoxometalates (POMs) are a fascinating class of metal–oxygen clusters, which have attracted a widespread interest due to their structural versatility as well as their potential applications in materials science, analytic chemistry, medicine, and catalysis. The vast range of applications has led to many deliberate assembly strategies for the designs and syntheses of novel POM-based materials. One of the most effective and useful assembly strategies in POM synthesis is the incorporation of transition metals, organometallic entities, or any other functional units into lacunary polyoxoanion precursors, resulting in numerous novel transition-metal-substituted POMs (TMSPs) with diverse metal nuclearities, various structural topologies, and unique properties. Therefore, large numbers of TMSPs have been developed since the first sandwich-type $[\text{Co}_2(\text{H}_2\text{O})_4(\text{B}-\text{AsW}_9\text{O}_{34})]^{+6}$ was found in 1973. Hitherto, most investigations of sandwich-type TMSPs are mainly focused on silicotungstates, phosphotungstates, and germanotungstates. In contrast, the reports on arsenotungstates (ATs) are limited, although ATs are an important subfamily of transition-metal-substituted POM chemistry. To date, most of the ATs are usually prepared bearing an enormous diversity of properties and structures in reaction of NiCl$_2$ and Na$\text{AsO}_2$ with Na$\text{2WO}_4$, then colorless crystals of 1 transformed to yellow-green crystals of 2 for the further development of slow solvent evaporation, and, finally, yellow crystals of 3 generated over a sufficiently long time of solvent evaporation. 3 can also be hydrothermally synthesized in three different routes. Notably, 1 presents a $\text{[HAs}_2\text{W}_8\text{O}_{31}]^{-7}$ building block, 2 exhibits an asymmetric sandwich-type arsenotungstate encapsulating two nonequivalent Keggin fragments $[\text{B}-\text{AsW}_9\text{O}_{34}]^{-9}$ and $[\text{B}-\text{AsW}_8\text{O}_{31}]^{-10}$, and 3 is composed of two $[\text{B}-\text{AsW}_8\text{O}_{31}]^{-9}$ units sandwiching a tetranickel cluster. Their structural difference indicates that controlling the reaction process plays a key role in the structures and topologies of these complexes.

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Table 1. Crystallographic Data and Structural Reﬁnements for 1–3

<table>
<thead>
<tr>
<th>compounds</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<tbody>
<tr>
<td>empirical formula</td>
<td>C11H10As2Ni2O16W8</td>
<td>C19H100As2Cl2.5Ni3Na0.5NiO4.5W17</td>
<td>C21H10As2Ni2O16W18</td>
</tr>
<tr>
<td>formula weight</td>
<td>970.20</td>
<td>3532.75</td>
<td>3532.75</td>
</tr>
<tr>
<td>T/K</td>
<td>298(2)</td>
<td>298(2)</td>
<td>298(2)</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P2(1)/c</td>
<td>P21/c</td>
<td>P21/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>10.986(7)</td>
<td>13.2557(14)</td>
<td>16.9333(6)</td>
</tr>
<tr>
<td>b/Å</td>
<td>14.734(9)</td>
<td>17.1985(19)</td>
<td>14.7245(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>26.658(16)</td>
<td>22.291(2)</td>
<td>18.359(5)</td>
</tr>
<tr>
<td>α/deg</td>
<td>90</td>
<td>73.312(2)</td>
<td>90</td>
</tr>
<tr>
<td>β/deg</td>
<td>98.132(10)</td>
<td>74.903(2)</td>
<td>90</td>
</tr>
<tr>
<td>γ/deg</td>
<td>90</td>
<td>80.820(2)</td>
<td>2</td>
</tr>
<tr>
<td>V/Å³</td>
<td>4271.4(4)</td>
<td>4680.0(8)</td>
<td>3950(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>1</td>
<td>2</td>
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<tr>
<td>D_{calc}/Mg m⁻³</td>
<td>3.784</td>
<td>3.645</td>
<td>4.595</td>
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<td>μ/mm⁻¹</td>
<td>23.101</td>
<td>22.235</td>
<td>28.765</td>
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<tr>
<td>F(000)</td>
<td>4332</td>
<td>4596</td>
<td>4848</td>
</tr>
<tr>
<td>R_{int}</td>
<td>0.0531</td>
<td>0.0770</td>
<td>0.0434</td>
</tr>
<tr>
<td>GOF</td>
<td>0.992</td>
<td>1.052</td>
<td>1.002</td>
</tr>
<tr>
<td>R₁</td>
<td>0.0345, 0.0606</td>
<td>0.0512, 0.1219</td>
<td>0.0308, 0.0620</td>
</tr>
<tr>
<td>R₁,w</td>
<td>0.0351, 0.0643</td>
<td>0.0770, 0.1312</td>
<td>0.0434, 0.0656</td>
</tr>
</tbody>
</table>

*aR₁ = \sqrt{\sum |F_{i}^\text{obs} - F_{i}^\text{calc}|/\sum F_{i}^\text{calc} .

*bR₁ = \sqrt{\sum (w(F_{i}^\text{obs} - F_{i}^\text{calc})^2)/\sum (w(F_{i}^\text{calc})^2)}^{1/2} .

oxo unit (\{β-SiW₉O₃₆\}) to gradually generate all three Keggin fragments in solution.18 Cronin’s work demonstrates that the subtly controlling reaction process plays a key role in structural transformation of the starting lacunary K₄[γ-SiW₉O₃₆] precursor to the targeted product under slow solvent evaporation conditions. We were inspired by the above-mentioned work and took into consideration that whether some novel fragments of polyoxycoacns could be isolated by using pretreatment inorganic salts as precursor instead of the classical [AsW₈O₃₄]³⁻-fragment.

Herein, we report the aqueous solution syntheses and structures of a series of ATs formulated as (H₂en)₃.₅[H₂As₂W₈O₃₇·6H₂O (1), NaN₄(H₇en)₄.₅[N₅As(H₇en)][β-α-As₂W₈O₃₇·6H₂O (2), and [H₂en]₃.₅[N₅As(H₇en)][γ-α-As₂W₈O₃₇ ·SH₂O (3). It is interesting that the formations of compounds 1–3 are in a successive process with the absolutely same reaction condition under the slow solvent evaporation condition. Notably, 1 presents the [H₂As₂W₈O₃₇]⁻⁻ building block, 2 represents asymmetric sandwich-type ATs encapsulating two nonequivalent Keggin fragments, and 3 is composed of two [β-α-As₂W₈O₃₄]⁻⁻ units sandwiching a tetraniocluster. Their structural diﬁerences indicate that the reaction process plays a key role on the structures and topologies of these complexes.

**EXPERIMENTAL SECTION**

**General Methods and Materials.** All chemicals and solvents were used as purchased without further puriﬁcation. C, H, and N elemental analyses were performed by using a PerkinElmer 2400-II CHNS/O analyzer. Inductively coupled plasma (ICP) spectra were obtained on a PerkinElmer Optima 2000 ICP-OES spectrometer. The Infrared spectra (using KBr in pellets) were recorded on a Bruker VERTEX 70 IR spectrometer (4000–400 cm⁻¹). The TG analyses were measured under the nitrogen gas atmosphere on a Mettler-Toledo TGA/SDTA851e instrument with a heating rate of 10 °C/min from 25 to 1000 °C. Powder X-ray diﬁraction (PXRD) measurements were obtained by using a Quantum Design MPMS-XL7 SQUID magnetometer at a temperature ranging from 2.69 to 300 K.

**Synthesis of (H₂en)₃.₅[H₂As₂W₈O₃₇·6H₂O (1).** NaN₄W₉O₃₂H₂O (1.4 g, 4.2 mmol) and NaAsO₂ (0.55 g, 4.2 mmol) were dissolved in 50 mL of distilled water; then, the aqueous solution containing NaN₄W₉O₃₂H₂O (0.83 g, 3.5 mmol), 20 mL of H₂O, and 7 mL of en was slowly added, resulting in a purple transparent solution. The solution was stirred at room temperature for 1 h, and the pH value of the mixture was successively adjusted with 6 M HCl to intense stirring. The early stages of the process could be fast, before the pH value of the solution decreased from 11.8 to 7.8 along with the formation of a white precipitate. Following, the 6 M HCl began to be added dropwise with the next addition only when the pH value starts to rise, until the pH value of the mixture reached 6. The total amount of hydrochloric acid (6 M) used was about 20 mL. The 0.3 M HCl was then used to give a more accurate control of the pH value. The pH value was adjusted to 5.5 and kept for 30 min, and the solution turned to yellow. The solution was stirred at 85 °C for 1 h, left to cool to room temperature, and ﬁltered. The resulting saphe solution was decanted into a 100 mL beaker and sealed with porous plastic wrap. After 7 days, colorless rod crystals were collected (Yield: ca. 15% based on NaAsO₂). Elemental analysis calcd (%) for C₂₆H₁₈₂As₂N₇O₃₇W₈: C, 3.04; H, 1.79; N, 3.55; Cl, 1.04; Na, 0.22; As, 3.43; As, 3.43; H, 1.98; Na, 4.01; As, 6.13; W, 60.20. Found: C, 3.59; H, 2.18; N, 4.06; As, 6.08; W, 61.15. [MW = 2443.16 g/mol].

**Synthesis of Na₃[H₇en]₄.₅[N₅As(H₇en)][β-α-As₂W₈O₃₇·Cl₃·5H₂O (2).** After the crystals of 1 emerged, the beaker was covered by preservative ﬁlm instead of porous plastic wrap to prevent the solvent from volatilizing quickly. Two months later, about 30% of the solution had been volatilized, and colorless crystals of 1 all transformed to greenish yellow rhombic crystals of 2 for the further development of slow solvent evaporation. Elemental analysis calcd (%) for C₁₉H₁₀₀As₂Cl₂.₅Na₀.₅NiO₄.₅W₁₇: C, 3.04; H, 1.79; N, 3.55; Cl, 1.04; Na, 0.22; As, 3.43; As, 3.43; As, 2.92; W, 60.92. Found: C, 3.18; H, 1.87; N, 3.59; Cl, 0.92; Na, 0.19; As, 3.48; As, 2.84; W, 61.75. [MW = 10260.16 g/mol].

**Synthesis of Na₃[H₇en]₄.₅[N₅As(H₇en)][β-α-As₂W₈O₃₇·Cl₃·5H₂O (3).** After the crystal 2 formed, the beaker was kept sealed by using preservative ﬁlm. Eventually, the greenish yellow rhombic crystals of 2 completely transformed to yellow block crystals of 3 over a suﬃciently long time of solvent evaporation with more than 30% reduction in the solution volume. 3 can also be hydrothermally synthesized in diﬀerent routes. Mode A: A mixture of 0.2 g of NaN₄W₉O₃₂H₂O, 0.08 g of NaAsO₂, 0.12...
RESULTS AND DISCUSSION

Syntheses. Owing to complicated and largely unpredictable mechanisms of self-assembly in POMs, it is quite difficult to design a rational synthetic route to obtain novel organic–inorganic hybrid POMs. In the process of synthesis, it is well-known that even tiny changes of reaction conditions, such as pH value, initial reactant, starting concentration, reaction temperature, synthesis method, or reactant stoichiometry, can greatly influence the outcome of the reaction in the construction of POM-based organic–inorganic hybrid materials.22−25 For example, Peng’s group has reported two high-dimensional silver complexes of POMs in situ at different pH values.22 Long’s group has studied the influences of the pH values on the structures of complexes based on presynthesized Keggin POMs.23 Cao’s group has synthesized a series of silver complexes of POMs in situ at different pH values.24 Especially, Liu’s group has studied the inorganic hybrid POMs.25 For example, Peng’s group has revealed a different pH 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Scheme 1. Synthesis of 1−3 and the Conversions between Them (the Six Reaction Routes Are Labeled as Letters A–F)"
generate two nonequivalent Keggin fragments $[\text{B-} \beta- \text{AsW}_8\text{O}_{31}]^{9-}$ and $[\text{B-} \alpha- \text{AsW}_9\text{O}_{34}]^{9-}$ in solution. Further, 3 is produced by ulteriorly gaining one tungsten oxo unit and one Ni-en complex, leading to a sandwich-type dimer, in which two $[\text{B-} \alpha- \text{AsW}_9\text{O}_{34}]^{9-}$ units sandwich a tetranickel cluster.

Notably, 1–3 were prepared by Na$_2$WO$_4$·2H$_2$O, NaAsO$_2$, NiCl$_2$, and en in acidic aqueous solution; however, due to the presence of the $[\text{HAs}_2\text{W}_{11}\text{O}_{35}]^{7-}$, $[\text{B-} \beta- \text{AsW}_8\text{O}_{31}]^{9-}$, and $[\text{B-} \alpha- \text{AsW}_9\text{O}_{34}]^{9-}$ fragments, we utilized the Na$_8$H[AsW$_9$O$_{34}$]$\cdot$11H$_2$O precursor to substitute for Na$_2$WO$_4$·2H$_2$O and NaAsO$_2$. We failed to get target products. In addition, the pH value of original resulting sapphire solution is another essential factor in the synthetic process. When the pH value was adjusted to lower than 5.2 (resulting in green solution) or higher than 6.2 (resulting in purple solution), only a white amorphous state powder can be obtained.

**Structure Description.** The powder X-ray diffraction patterns (PXRD) of 1–3 are consistent with those from the single-crystal structure analyses (Figure S1, Supporting Information), indicating the phase purity. On account of the variation in the preferred orientation of the powder sample in the experimental PXRD, the intensities of the experimental and
simulated PXRD patterns have some differences to some degree.

1 consists of one \([\text{HAs}_2\text{W}_8\text{O}_{31}]^{7-}\) anion, three and a half \([\text{H}_2\text{en}]^{2+}\) cations, and six water molecules. The structure of the \([\text{HAs}_2\text{W}_8\text{O}_{31}]^{7-}\) polyoxoanion in 1 (Figure 1a,b) can be viewed as that one As atom is linked to the \([\text{AsW}_8\text{O}_{31}]^{9-}\) unit by two \(O_d\) atoms (O29 and O30); then, the tricoordination of As is completed by a hydroxyl oxygen atom (O31). The \([\text{AsW}_8\text{O}_{31}]^{9-}\) unit consists of two edge-shared \(\text{W}_{3}\text{O}_{13}\) triads to which two edge-shared \(\text{WO}_6\) octahedra are connected via corners; this assembly is stabilized by the central \(\text{AsO}_3\) group via one \(O_\mu^3\) atom (O26) and two \(O_\mu^4\) atoms (O27 and O28).

Albeit both of the two crystallographically independent AsIII atoms reside in the pyramidal geometries, they display two kinds of environments: As1 is combined with three oxygen atoms from the \([\text{AsW}_8\text{O}_{31}]^{9-}\) fragment, \(\text{As}1-O: 1.766(6) - 1.805(8)\) Å and O−As1−O: 96.5(3)−99.3(3); As2 is bonded to two oxygen atoms from the \([\text{AsW}_8\text{O}_{31}]^{9-}\) fragment and an oxygen atom from hydroxyl \(\text{As}2-O: 1.776(7)-1.788(7)\) Å, As2−OH: 1.788(8) Å, and O−As2−O: 96.0(4)−98.6(4)°. The various ATs known up to now always contained \([\text{B}-\beta-\text{AsW}_8\text{O}_{31}]^{12-}\) subunits, whereas the \([\text{HAs}_2\text{W}_8\text{O}_{31}]^{7-}\) block has seldom been reported. As far as we know, \((\text{H}_2\text{en})_{1,5}\text{[HAs}_2\text{W}_8\text{O}_{31}]\cdot6\text{H}_2\text{O}\) 1 is the second example of the \(\beta\)-type \([\text{HAs}_2\text{W}_8\text{O}_{31}]^{7-}\) structure in the AsIII-W family; the other one is \(\text{K}_7(\text{AsW}_8\text{O}_{30}\text{AsOH})\cdot12\text{H}_2\text{O}\). Bond-valence sum calculations25 for 1 (Table S4, Supporting Information) indicate that all the W and As atoms are in +6 and +3 oxidation states, respectively, and confirm a monoprotonated O atom (the bond valence is −1 for O31). From the viewpoint of supramolecular chemistry, taking into account strong hydrogen-bonding interactions between nitrogen atoms of en ligands and surface oxygen atoms of POM units or water molecules, the 3-D supramolecular structure of 1 (Figure 1c) is generated through \(\text{N}−\text{H}···\text{O}\) hydrogen bonds with \(\text{N}···\text{O}\) distances of 2.76−3.408 Å and \(\text{N}−\text{H}···\text{O}\) angles of 111.10−164.10°.

2 is formed by one \(\{\text{Ni}_3(\text{en})\}([\text{B}-\alpha-\text{AsW}_9\text{O}_{34}][\text{B}-\beta-\text{AsW}_8\text{O}_{31}]^{12-}\) polyoxoanion, six and a half \([\text{H}_2\text{en}]^{2+}\) cations, half \(\text{Na}^+\), one and a half \(\text{Cl}^−\), and nine water molecules. The polyoxoanion \(\{\text{Ni}_3(\text{en})\}([\text{B}-\alpha-\text{AsW}_9\text{O}_{34}][\text{B}-\beta-\text{AsW}_8\text{O}_{31}]^{12-}\) (Figure 2a) is composed of two nonequivalent \([\text{B}-\beta-\text{AsW}_8\text{O}_{31}]^{9-}\) (Figure 2b), \([\text{B}-\alpha-\text{AsW}_9\text{O}_{34}]^{9-}\) (Figure 2d), and a triangular \(\text{Ni}_3\) core (Figure 2c). The two nonequivalent Keggin units are held together by the \(\text{Ni}_3\) core in such a way that there is a plane of symmetry passing through both As atoms and the unique Ni atom, resulting in a sandwich-type structure with \(\text{Cs}\) symmetry. The \([\text{B}-\beta-\text{AsW}_8\text{O}_{31}]^{9-}\) fragment has been reported very recently by our group;28 subsequently, the class of Keggin-type polytungstates with the formula \([\text{XW}_8\text{O}_{31}]^{9-}\) (\(X = \text{P, As, Si, Ge}; n = 9, 10\) have been...
represented as lacunary species to accommodate transition metals to form substituted POMs.29

The triangular \{Ni{en}O_{2}\} unit (NiI) comprising three Ni\(^{2+}\) ions is stabilized by seven O atoms (O10–O15 and O34) from the [B-\(\alpha\)-AsW\(_{8}\)O\(_{31}\)]\(^{9-}\) unit (AsW9), five O atoms (O36, O39, O42, O44, O65) from the [B-\(\beta\)-AsW\(_{8}\)O\(_{31}\)]\(^{9-}\) unit (AsW8), and one en ligand. The three crystallographically independent Ni\(^{II}\) ions display two kinds of octahedral environments. The two structurally equivalent Ni ions (Ni2 and Ni3) are linked to each of the lacunary units via four Ni–O–W and two Ni–O–As bonds. The unique Ni1 complements its octahedral coordination sphere by four Ni–O–W linkings, an oxygen atom of the AsO\(_{4}\) hetero group from the [B-\(\beta\)-AsW\(_{8}\)O\(_{31}\)]\(^{9-}\) fragment, and a nitrogen atom from one en ligand. Structurally, the anion \{Ni\(_{3}\)(en)[B-\(\alpha\)-AsW\(_{8}\)O\(_{31}\)]\}\(^{1-}\) is similar to the reported \[Cu\(_{2}\)(H\(_{2}\)O)\] {B-\(\beta\)-GeW\(_{8}\)O\(_{26}\) (OH)}\(^{9-}\) (Figure S2, Supporting Information); however, three remarkable differences are observed between them: (a) Building blocks [B-\(\alpha\)-AsW\(_{8}\)O\(_{31}\)]\(^{9-}\} and [B-\(\beta\)-AsW\(_{8}\)O\(_{31}\)]\(^{9-}\} other than [B-\(\beta\)-GeW\(_{8}\)O\(_{26}\) (OH)]\(^{9-}\} and [B-\(\beta\)-GeW\(_{8}\)O\(_{30}\) (OH)]\(^{9-}\} build the asymmetric sandwich-type arsenotungstate. (b) 2 was prepared by the further development of slow solvent evaporation of 1, whereas \[Cu\(_{2}\)(H\(_{2}\)O)\] {B-\(\beta\)-GeW\(_{8}\)O\(_{26}\) (OH)}\(^{9-}\} was made by the decomposition of the \{\(\gamma\)-GeW\(_{10}\)O\(_{36}\)\} precursor. (c) Ni\(_{3}\)(en)[B-\(\alpha\)-AsW\(_{8}\)O\(_{31}\)]\(^{1-}\} is an organic–inorganic hybrid unit compared to the inorganic \[Cu\(_{2}\)(H\(_{2}\)O)\] {B-\(\beta\)-GeW\(_{8}\)O\(_{26}\) (OH)}\(^{9-}\} \{B-\(\beta\)-GeW\(_{8}\)O\(_{30}\) (OH)]\(^{9-}\} which can be described as that a terminal water group in the Cu\(_{2}\) cluster (Figure S2b, Supporting Information) is replaced by one en ligand in the end-on coordination fashion. To the best of our knowledge, the en ligand often displays a strong chelating mode to the TM ion. Such an end-on coordination fashion of en is rare in the POM family and has states, respectively, and no protonated O atom exists in 3. In addition, abundant N–H···O hydrogen bonds with the N···O distances in the range of 2.765–3.251 Å contribute to the 3-D supramolecular architecture of 3 (Figure 3d).

**Figure 3.** (a) Ball-and-stick and polyhedral representation of 3. (b) Ball-and-stick representation of [B-\(\beta\)-AsW\(_{8}\)O\(_{31}\)]\(^{1-}\} unit. (c) Ball-and-stick representation of the NiI core. (d) The 3-D framework structure of 3 generated through hydrogen bonds.
of 30–104 °C is assigned to the release of five crystal water molecules. The second weight loss of 6.22% in the range of 105–440 °C (calcd 6.76%) corresponds to the loss of en molecules. The last weight loss of 6.37% (calcd 6.04%) from 440 to 825 °C could be assigned to the decomposition of the {As−O−W} framework according to the reaction H10{(NiL(en))2[B−α−As-WO4]13} → As2O3↑ + 18WO3 + 5H2O↑ + O2↑ + 4NiO + 2en↑.

**IR Spectra.** The IR spectra of 1–3 (Figure S4, Supporting Information) show the characteristic vibration patterns resulting from the Keggin POM framework in the range of 1100–700 cm⁻¹. Four groups of characteristic vibration absorption bands are observed at 1053, 951, 873, and 755–705 cm⁻¹ in 2; and 1044, 953, 837–842, and 772–698 cm⁻¹ in 3, which are attributed to the stretching vibration of ν(As=O), ν(W=O), and ν(W−Oc), respectively. The peaks centered at 1510–1630 cm⁻¹ are attributed to the bending vibration of δ(N−H), which confirm the presence of the en ligand in 1–3. The occurrence of the vibration band at 3410–3441 cm⁻¹ suggests the presence of the lattice water molecules in 1–3.

**Magnetic Properties of 3.** Temperature-dependent magnetic susceptibility measurements for 3 were performed in the temperature range of 2.69–300 K under an external magnetic field of 0.2 T. The temperature dependence of χM and χMT is shown in Figure 4. The χM value of 3 slowly increases from 0.01674 emu mol⁻¹ at 300 K to 0.26713 emu mol⁻¹ at 26 K, and then rapidly reaches to 4.96469 emu mol⁻¹ at 2.69 K. The experimental χMT values of 3 at room temperature are 5.02342 emu K mol⁻¹ at 300 K, which are expected for four uncoupled high-spin Ni²⁺ ions with S = 1, g > 2. Upon cooling, the χMT values of 3 increase to a maximum of 13.35501 emu K mol⁻¹ at 2.69 K, which might be mainly attributed to the presence of zero-field splitting (ZFS). The behavior suggests that there exist overall ferromagnetic interactions with the presence of ZFS for Ni²⁺ ions. The temperature dependence of the reciprocal susceptibilities (1/χM) obeys the Curie–Weiss law for 3 with θ = 5.35 K, which further supports the presence of ferromagnetic coupling in 3 (Figure S5, Supporting Information).

**CONCLUSION**

In conclusion, a series of arsenotungstates formulated as (H2en)3.5{HAs2W8O31}·6H2O (1), Na0.5(H2en)6{Ni(III)}[B−α−As-WO4]13·3Cl3·9H2O (2), and [H2en]4−{[Ni(II)]en}{B−α−As-WO4]32}·5H2O (3) have been systematically synthesized under slow solvent evaporation conditions. The successful isolations of 1–3 show us a perspective of extending the POM family through reasonably controlling the reaction process. In the future, we will expand to other reaction systems besides the {As−O−W} system, such as {As−O−Mo}, {P−O−W/Mo}, and {S−O−W/Mo} systems. Therefore, the systematic exploration of the POM system is in progress.

**ASSOCIATED CONTENT**

3 Supporting Information

X-ray crystallographic details (CIF), atomic labeling scheme, and bond valence summations for compounds 1, 2, and 3; PXRD; IR spectra; thermogravimetric (TG) analysis; and some additional structural figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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