

# A Series of Arsenotungstates Based on the [HAs<sub>2</sub>W<sub>8</sub>O<sub>31</sub>]<sup>7-</sup> Building Block: Syntheses by Control of the Reaction Process

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Supporting Information

ABSTRACT: A series of arsenotungstates formulated as (H2en)3.5[HAs2W8O31].6H2O (1),  $Na_{0.5}(H_2en)_{6.5}[Ni_3(en)[B-\alpha-AsW_9O_{34}][B-\beta-AsW_8O_{31}]]Cl_{1.5}\cdot9H_2O$  (2), and  $[H_2en]_4[[Ni_4(Hen)_2][B-\alpha-AsW_9O_{34}]_2]\cdot 5H_2O$  (3) have been sequentially synthesized by controlling the reaction process. First, 1 was synthesized in an aqueous medium by the reaction of NiCl<sub>2</sub> and NaAsO<sub>2</sub> with Na<sub>2</sub>WO<sub>4</sub>, 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  $[HAs_2W_8O_{31}]^{7-}$  building block, 2 exhibits an asymmetric sandwich-type arsenotungstate encapsulating two nonequivalent Keggin fragments  $[B-\alpha-AsW_9O_{34}]^{9-}$  and  $[B-\beta-AsW_8O_{31}]^{9-}$ , and 3 is composed of two  $[B-\alpha-AsW_9O_{34}]^{9-}$  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 metaloxygen 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.<sup>1</sup> The vast range of applications has led to many deliberate assembly strategies for the designs and syntheses of novel POM-based materials.<sup>1d</sup> 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.<sup>2</sup> Therefore, large numbers of TMSPs have been developed since the first sandwich-type  $[Co_4(H_2O)_2(B-\alpha-PW_9O_{34})_2]^{10-}$  was found in 1973.<sup>3</sup> 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 bearing an enormous diversity of properties and structures in POM chemistry. To date, most of the ATs are usually prepared in a one-pot reaction of transition-metal ions with lacunary polytungstate precursors under hydrothermal conditions and present classic dimeric sandwich-type complexes constructed by trivacant Keggin building fragments, such as  $[Cu_3(H_2O)_2(\alpha AsW_9O_{33})_2]^{12^{-},4}$   $[As_2W_{18}M_4(H_2O)_2O_{68}]^{10^{-}}$  (M = Cd, Co, Cu, Fe, Mn, Ni or n),<sup>5</sup>  $[M_3(H_2O)_3(\alpha - AsW_9O_{33})_2]^{12^{-}}$  (M = Mn<sup>2+</sup>

 $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ),  ${}^{6}$  [Zn(Hen)]<sub>6</sub>[B-a-AsW<sub>9</sub>O<sub>33</sub>]<sub>2</sub>·6H<sub>2</sub>O,  ${}^{7}$ and  $[Cu(dap)_2]_3[Cu_6(dap)_2(H_2O)_2(B-\alpha-AsW_9O_{34})_2]\cdot 4H_2O.^8$ Compared with the abundant reports of dimeric sandwichtype complexes, a small quantity of ATs encapsulating nonequivalent Keggin fragments have been reported, sketched as follows:  $[enH_2]_2[(\alpha-H_2As^VW_6O_{26})Fe_3(H_2O)(B-\alpha-H_4As^V-$ 
$$\begin{split} & W_9O_{34})]_2[Fe]_{2}\cdot 8H_2O,^9 \ [M_6(H_2O)_2(AsW_9O_{34})_2(AsW_6O_{26})]^{17-} \\ & (M^{II} = Ni^{II}, \ Mn^{II}, \ Co^{II}, \ Zn^{II}),^{10} \ [Ni_6As_3W_{24}O_{94}(H_2O)_2]^{17-},^{11} \end{split}$$
 $[enH_2]_2[Ni(H_2O)_4]_2[Ni(en)_2]_2[Ni(en)]_2\{[(\alpha-AsW_6O_{26})Ni_6 (OH)_{2}(H_{2}O)_{3}(en)(B-\alpha-AsW_{9}O_{34})]_{2}[W_{4}O_{16}][Ni_{3}(H_{2}O)_{2}-(en)]_{2}\cdot16H_{2}O_{1}^{12}$  and  $[Na(H_{2}O)_{3}]_{2}[Ni(H_{2}O)_{6}]_{2}[Ni(H_{2}O)_{5}]$ - $\{[Ni_3(dap)(H_2O)_2]_2(H_2W_4O_{16})\}\{(\alpha - H_2AsW_6O_{26})[Ni_6(OH)_2 - M_2AsW_6O_{26})]\}$  $(H_2O)(dap)_2](B-\alpha-HAsW_9O_{34})_2\cdot7H_2O^{.13}$  Furthermore, some ATs containing giant clusters, such as  $[As_{12}Ce_{16}(H_2O)_{36}]^{76-,14}$  $W_{148}O_{524}]^{76-,14}$   $[As^{III}_{6}W_{65}O_{217}(H_2O)_7]^{26-,15}$  and  $[Cs{Eu-(H_2O)_2(\alpha-AsW_9O_{33})}_4]^{23-,16}$  have been reported.

In 2011, Cronin's group reported a novel silicotungstate,  $\begin{array}{l} K_{18}[Mn^{III}_{2}Mn^{II}_{4}(\mu_{3}\text{-}O)_{2}(H_{2}O)_{4}(B-\beta\text{-}SiW_{8}O_{31})(B-\beta\text{-}SiW_{9}O_{34})\text{-}\\ (\gamma\text{-}SiW_{10}O_{36})]\cdot40H_{2}O,^{17} \text{ composed of three nonequivalent} \end{array}$ lacunary Keggin fragments, which was obtained by carefully controlling a three-step reaction process and using  $K_8[\gamma$ - $SiW_{10}O_{36}$ ] as precursor. The formation of the compound may involve an initial loss of two tungsten oxo units (converting  $\{\gamma$ -SiW<sub>10</sub>} into { $\beta$ -SiW<sub>8</sub>}) and a subsequent gain of one tungsten

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compounds	1	2	3
empirical formula	$C_7H_{48}As_2N_7O_{37}W_8$	$C_{13}H_{91}As_2Cl_{1.50}N_{13}Na_{0.50}Ni_3O_{74}W_{17}$	$C_{12}H_{68}As_2N_{12}Ni_4O_{78}W_{18}\\$
formula weight	2443.16	5130.08	5322.75
T/K	296(2)	296(2)	296(2)
crystal system	monoclinic	triclinic	monoclinic
space group	P2(1)/c	$P\overline{1}$	P21/c
a/Å	10.986(7)	13.2557(14)	16.933(6)
b/Å	14.734(9)	17.1985(19)	14.724(5)
c/Å	26.658(16)	22.291(2)	18.359(5)
$\alpha/\text{deg}$	90	73.312(2)	90
$\beta/\text{deg}$	98.132(10)	74.903(2)	120.21(2)
γ/deg	90	80.820(2)	90
$V/Å^3$	4271(4)	4680.0(8)	3956(2)
Z	4	1	2
$D_{\rm calc}/{ m Mg}~{ m m}^{-3}$	3.784	3.645	4.595
$\mu/\mathrm{mm}^{-1}$	23.101	22.235	28.765
F(000)	4332	4596	4848
R <sub>int</sub>	0.0531	0.0770	0.0434
GOF	0.992	1.052	1.002
$R_1^{a}_{l} w R_2^{b} [I > 2\sigma(I)]$	0.0345, 0.0606	0.0512, 0.1219	0.0308, 0.0620
$R_1^{a}_{, w} R_2^{b}$ [all data]	0.0531, 0.0643	0.0770, 0.1312	0.0434, 0.0656

$${}^{b}wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}.$$

 ${}^{a}R_{1} = \sum ||F_{0}| - |F_{c}|| / \sum |F_{0}|.$ 

oxo unit  $(\{\beta$ -SiW<sub>8</sub> $\}$  to  $\{\beta$ -SiW<sub>9</sub> $\})$  to gradually generate all three Keggin fragments in solution.<sup>18</sup> Cronin's work demonstrates that the subtly controlling reaction process plays a key role in structural transformation of the starting lacunary  $K_8[\gamma$ - $SiW_{10}O_{36}$ ] precursor to the targeted product under slow solvent evaporation conditions. We were inspired by the abovementioned work and took into consideration that whether some novel fragments of polyoxoanions could be isolated by using pretreatment inorganic salts as precursor instead of the classical [AsW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> fragment.

Herein, we report the aqueous solution syntheses and structures of a series of ATs formulated as (H<sub>2</sub>en)<sub>3.5</sub>[HAs<sub>2</sub>- $W_8O_{31}]\cdot 6H_2O$  (1),  $Na_{0.5}(H_2en)_{6.5}\{Ni_3(Hen)[B-\alpha-AsW_9O_{34}] [B-\beta-AsW_8O_{31}]$ Cl<sub>15</sub>·9H<sub>2</sub>O (2), and  $[H_2en]_4[[Ni_4(Hen)_2]]$ B- $\alpha$ -AsW<sub>9</sub>O<sub>34</sub>]<sub>2</sub> $\cdot$ 5H<sub>2</sub>O (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  $[HAs_2W_8O_{31}]^{7-}$  building block, 2 represents asymmetric sandwich-type ATs encapsulating two nonequivalent Keggin fragments, and 3 is composed of two  $[B-\alpha-AsW_9O_{34}]^{9-}$  units sandwiching a tetranickel cluster. Their structural difference indicates that controlling 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<sup>-1</sup>). 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 diffraction (PXRD) measurements were taken by a Philips X'Pert-MPD instrument with Cu K $\alpha$  radiation  $(\lambda = 1.54056 \text{ Å})$  at 293 K. Magnetic susceptibility measurements were

obtained by the use of a Quantum Design MPMS-XL7 SQUID magnetometer at a temperature ranging from 2.69 to 300 K.

Synthesis of  $(H_2 en)_{3.5}^{-1}[HAs_2W_8O_{31}]\cdot 6H_2O$  (1).  $Na_2WO_4\cdot 2H_2O$  (1.4) g, 4.2 mmol) and NaAsO<sub>2</sub> (0.55 g, 4.2 mmol) were dissolved in 50 mL of distilled water; then, the aqueous solution containing NiCl<sub>2</sub>·6H<sub>2</sub>O (0.83 g, 3.5 mmol), 20 mL of H<sub>2</sub>O, 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 with 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 precipitation. 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 sapphire. The solution was then stirred at 85 °C for 1h, left to cool to room temperature, and filtered. The resulting sapphire 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 NaAsO<sub>2</sub>). Elemental analysis calcd (%) for C<sub>7</sub>H<sub>48</sub>As<sub>2</sub>N<sub>7</sub>O<sub>37</sub>W<sub>8</sub>: C, 3.44; H, 1.98; N, 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  $Na_{0.5}(H_2en)_{6.5}\{Ni_3(en)[B-\alpha-AsW_9O_{34}][B-\beta-AsW_8O_{31}]\}$ - $Cl_{1.5}$ ·9H<sub>2</sub>O (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 C<sub>26</sub>H<sub>182</sub>-As<sub>4</sub>Cl<sub>3</sub>N<sub>26</sub>NaNi<sub>6</sub>O<sub>148</sub>W<sub>34</sub>: C, 3.04; H, 1.79; N, 3.55; Cl, 1.04; Na, 0.22; Ni, 3.43; As, 2.92; W, 60.92. Found: C, 3.18; H, 1.87; N, 3.59; Cl, 0.92; Na, 0.19; Ni, 3.48; As, 2.84; W, 61.75. [MW = 10260.16 g/mol].

Synthesis of  $[H_2en]_4 \{ [Ni_4(Hen)_2] [B-\alpha - AsW_9O_{34}]_2 \} \cdot 5H_2O$  (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 Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, 0.08 g of NaAsO<sub>2</sub>, 0.12 g of NiCl<sub>2</sub>, 1 mL of en, and 15 mL of distilled water was stirred for 1 h and the pH adjusted to 5.5 by 6 mol/L HCl solution, sealed in a 25 mL Teflon-lined autoclave, kept at 140 °C for 3 days, and then cooled to room temperature. Mode B: 1 (or 2) was added to the resulting sapphire solution and sealed in a 25 mL Teflon-lined autoclave, kept at 140 °C for 3 days, and then cooled to room temperature. Elemental analysis calcd (%) for  $C_{12}H_{68}As_2N_{12}Ni_4O_{78}W_{18}$ : C, 2.71; H, 1.28; N, 3.16; Ni, 4.41; As, 2.82; W, 62.17. Found: C, 2.66; H, 1.39; N, 2.99; Ni, 4.34; As, 2.77; W, 62.45. [MW = 5322.75 g/mol].

X-ray Crystallographic Analyses. A crystal with dimensions of 0.38  $\times$  0.16  $\times$  0.13 mm<sup>3</sup> for 1, 0.41  $\times$  0.21  $\times$  0.16 mm<sup>3</sup> for 2, and 0.33  $\times$  $0.21 \times 0.12 \text{ mm}^3$  for 3 was stuck on a glass fiber, and intensity data for 1-3 were collected at 296 K using a Bruker APEX-II CCD diffractometer with the graphite-monochromated Mo K $\alpha$  radiation  $(\lambda = 0.71073 \text{ Å})$ . Data integration was performed using SAINT.<sup>19</sup> Routine Lorentz and polarization corrections were applied. Multiscan absorption corrections were performed using SADABS.<sup>20</sup> Direct methods (SHELXS97) successfully located the tungsten atoms, and successive Fourier syntheses (SHELXL97) revealed the remaining atoms. Refinements were full-matrix least-squares against  $F^2$  using all data.<sup>21</sup> Positions of the hydrogen atoms attached to the carbon and nitrogen atoms were geometrically placed, and no H atoms associated with the water molecules were located in the difference Fourier map. All non-hydrogen atoms were refined anisotropically except for some water molecules. These data can be obtained free of charge at the Cambridge Crystallographic Data Centre (CCDC, www.ccdc.cam.ac. uk/conts/retrieving.html). Crystal parameters and other experimental details of the data collection for complexes 1-3 are summarized in Table 1. Selected bond lengths and bond angles are listed in the Supporting Information, Tables S1-S3. The CCDC reference numbers are 910206-910208 for complexes 1-3, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/date\_request/ cif.

# 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 organicinorganic hybrid POMs. In the process of synthesis, it is wellknown 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.<sup>22–25</sup> For example, Peng's group has reported two highdimensional silver complexes of POMs by using the presynthesized Wells-Dawson POM building blocks at different pH values.<sup>22</sup> Long's group has studied the influences of the pH values on the structures of complexes based on presynthesized Keggin POMs.<sup>23</sup> Cao's group has also synthesized a series of silver complexes of POMs in situ at different pH values.<sup>24</sup> Especially, Liu's group has revealed a controllable assembly and disassembly reaction process based on niobium-substituted germanotungstates achieved by controlling the pH and by adding H<sub>2</sub>O<sub>2</sub>, respectively.<sup>25</sup> As mentioned, the research of influencing factors mainly focuses on controlling the pH or adding additional reactant, whereas herein, compounds 1-3 are isolated in a successive process with the same reaction condition.

The syntheses of 1-3 and the transformations between them were achieved by strictly controlling the reaction process, as shown in Scheme 1. The pH value of the reaction system of Na<sub>2</sub>WO<sub>4</sub>-NaAsO<sub>2</sub>-NiCl<sub>2</sub>-H<sub>2</sub>O-en was carefully adjusted to 5.5 by HCl, and it was stirred at 85 °C for 1h and filtrated, resulting in the sapphire transparent solution. The resulting Scheme 1. Synthesis of 1-3 and the Conversions between Them (the Six Reaction Routes Are Labeled as Letters A-F)<sup>*a*</sup>



<sup>*a*</sup>Color code: WO<sub>6</sub>, green; O atoms, red; Ni atoms, sky blue; As atoms, purple; C atoms, grey; N atoms, blue.

sapphire solution was sealed for solvent evaporation. After 7 days, colorless rod crystals of 1 were collected (Route A in Scheme 1). Importantly, one should be careful to adjust the pH value for about 2 h, and the preparation of the resulting sapphire solution was a crucial factor in the syntheses of compounds 1-3. The colorless crystals of 1 transformed to greenish yellow rhombic crystals of 2 for the further development of slow solvent evaporation (Route B in Scheme 1). During the transformation of  $1 \rightarrow 2$ , 1 and 2 could coexist for about 1 month, and 1 transformed into 2 completely in about two and a half months. Finally, greenish yellow crystals of 2 fully transformed to yellow crystals of 3 over 6 months of solvent evaporation (Route C in Scheme 1). When 2 and 3 are suspended in the mother liquor for weeks, they remain stable, indicating that the transformations of  $1 \rightarrow 2$  and  $2 \rightarrow 3$  are irreversible. The resulting sapphire solution (15 mL) was sealed in a 25 mL Teflon-lined autoclave, kept at 140 °C for 3 days, and then cooled to room temperature, which generated 3 as well (Route D in Scheme 1). 3 also could be obtained by 1 and 2 as precursor, respectively (Routes E and F in Scheme 1). In a word, compounds 1-3 are sequentially synthesized through a slow solvent evaporation method in a successive process, which can be obviously distinguished by the different colors. 3 can also be hydrothermally synthesized in two different routes. The results of the experiments illustrate an interesting phenomenon of the transformation from the kinetically favored crystalline phase of 1 and 2, to a thermodynamically stable phase of 3, by crystal dissolution and recrystallization.

The transformation process from 1 to 3 can be proposed as Scheme 2. Since the starting polyoxoanion for the reaction is the  $[HAs_2W_8O_{31}]^{7-}$  unit in 1, it appears that the formation of 2 may involve a loss of one arsenic oxo unit (converting the  $[HAs^{III}_2W_8O_{31}]^{7-}$  unit into the  $[B-\beta-As^VW_8O_{31}]^{9-}$  unit with the oxidation of the  $As^{III}$  atom) and a gain of one tungsten oxo unit (converting  $[B-\beta-AsW_8O_{31}]^{9-}$  into  $[B-\alpha-AsW_9O_{34}]^{9-}$ ) to

Scheme 2. Schematic Illustration of Transformation Process from 1 to 3<sup>a</sup>







Figure 1. (a) Ball-and-stick and polyhedral representation of  $[HAs_2W_8O_{31}]^{7-}$  unit. (b) Ball-and-stick representation of  $[HAs_2W_8O_{31}]^{7-}$  unit. (c) The 3D framework structure of 1 generated through hydrogen bonds.

generate two nonequivalent Keggin fragments  $[B-\beta-As-W_8O_{31}]^{9-}$  and  $[B-\alpha-AsW_9O_{34}]^{9-}$  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  $[B-\alpha-AsW_9O_{34}]^{9-}$  units sandwich a tetranickel cluster.

Notably, 1–3 were prepared by Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, NaAsO<sub>2</sub>, NiCl<sub>2</sub>, and en in acidic aqueous solution; however, due to the presence of the  $[HAs_2W_8O_{31}]^{7-}$ ,  $[B-\beta-AsW_8O_{31}]^{9-}$ , and  $[B-\alpha-AsW_9O_{34}]^{9-}$  fragments, we utilized the Na<sub>8</sub>H[AsW<sub>9</sub>O<sub>34</sub>]. 11H<sub>2</sub>O precursor to substitute for Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and NaAsO<sub>2</sub>. 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



**Figure 2.** (a) Ball-and-stick and polyhedral representation of **2**. (b) Ball-and-stick representation of  $[B-\beta-AsW_8O_{31}]^{9-}$  unit. (c) Ball-and-stick representation of the Ni<sub>3</sub> core. O atoms from  $[B-\beta-AsW_8O_{31}]^{9-}$  unit, light green; O atoms from  $[B-\alpha-AsW_9O_{34}]^{9-}$  unit, red. (d) Ball-and-stick representation of  $[B-\alpha-AsW_9O_{34}]^{9-}$  unit. (e) The 3D framework structure of **2** generated through hydrogen bonds.

simulated PXRD patterns have some differences to some degree.

1 consists of one  $[HAs_2W_8O_{31}]^{7-}$  anion, three and a half  $[H_2en]^{2+}$  cations, and six water molecules. The structure of the  $[HAs_2W_8O_{31}]^{7-}$  polyoxoanion in 1 (Figure 1a,b) can be viewed as that one As atom is linked to the  $[AsW_8O_{31}]^{9-}$  unit by two  $O_d$  atoms (O29 and O30); then, the tricoordination of As is completed by a hydroxyl oxygen atom (O31). The [As-W<sub>8</sub>O<sub>31</sub>]<sup>9-</sup> unit consists of two edge-shared W<sub>3</sub>O<sub>13</sub> triads to which two edge-shared WO<sub>6</sub> octahedra are connected via corners; this assembly is stabilized by the central AsO<sub>3</sub> group via one  $O\mu_3$  atom (O26) and two  $O\mu_4$  atoms (O27 and O28). Albeit both of the two crystallographically independent As<sup>III</sup> atoms reside in the pyramidal geometries, they display two kinds of environments: As1 is combined with three oxygen atoms from the  $[AsW_8O_{31}]^{9-}$  fragment, [As1-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  $[AsW_8O_{31}]^{9-}$  fragment and an oxygen atom from hydroxyl [As2-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  $[B-\beta-$ AsW<sub>8</sub>O<sub>31</sub>]<sup>9-</sup> subunits, whereas the [HAs<sub>2</sub>W<sub>8</sub>O<sub>31</sub>]<sup>7-</sup> block has seldom been reported. As far as we know, (H2en)3.5[HAs2- $W_8O_{31}]\cdot 6H_2O$  1 is the second example of the  $\beta$ -type  $[HAs_2W_8O_{31}]^{7-}$  structure in the As<sup>III</sup>-W family; the other one is  $K_7(AsW_8O_{30}AsOH) \cdot 12H_2O.^{26}$  Bond-valence sum calculations<sup>27</sup> 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 N-H···O hydrogen bonds with N···O distances of 2.76–3.408 Å and N-H···O angles of 111.10–164.10°.

**2** is formed by one {Ni<sub>3</sub>(en)[B- $\alpha$ -AsW<sub>9</sub>O<sub>34</sub>][B- $\beta$ -As-W<sub>8</sub>O<sub>31</sub>]<sup>12-</sup> polyoxoanion, six and a half [H<sub>2</sub>en]<sup>2+</sup> cations, half Na<sup>+</sup>, one and a half Cl<sup>-</sup>, and nine water molecules. The polyoxoanion {Ni<sub>3</sub>(en)[B- $\alpha$ -AsW<sub>9</sub>O<sub>34</sub>][B- $\beta$ -AsW<sub>8</sub>O<sub>31</sub>]<sup>12-</sup> of **2** (Figure 2a) is composed of two nonequivalent [B- $\beta$ -As-W<sub>8</sub>O<sub>31</sub>]<sup>9-</sup> (Figure 2b), [B- $\alpha$ -AsW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> units (Figure 2d), and a triangular Ni<sub>3</sub> core (Figure 2c). The two nonequivalent Keggin units are held together by the Ni<sub>3</sub> 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 *Cs* symmetry. The [B- $\beta$ -AsW<sub>8</sub>O<sub>31</sub>]<sup>9-</sup> fragment has been reported very recently by our group;<sup>28</sup> subsequently, the class of Keggin-type polytungstates with the formula [XW<sub>8</sub>O<sub>31</sub>]<sup>n-</sup> (X = P, As, Si, Ge; n = 9, 10) have been

represented as lacunary species to accommodate transition metals to form substituted POMs.<sup>29</sup>

The triangular  $\{Ni_3enO_{12}\}$  unit  $(Ni_3)$  comprising three  $Ni^{2+}$ ions is stabilized by seven O atoms (O10-O15 and O34) from the  $[B-\alpha-AsW_9O_{34}]^{9-}$  unit (AsW9), five O atoms (O36, O39, O42, O44, O65) from the  $[B-\beta-AsW_8O_{31}]^{9-}$  unit (AsW8), and one en ligand. The three crystallographically independent Ni<sup>II</sup> 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 completes its octahedral coordination sphere by four Ni-O-W linkings, an oxygen atom of the AsO4 hetero group from the  $[B-\beta-AsW_8O_{31}]^{9-}$  fragment, and a nitrogen atom from one en ligand. Structurally, the anion  ${Ni_3(en)[B-\alpha-AsW_9O_{34}][B-\beta-AsW_8O_{31}]^{12-}}$  is similar to the reported  $[Cu_3(H_2O)(B-\beta-GeW_9O_{33}(OH))(B-\beta-GeW_8O_{30}(OH))]^{12-30}$  (Figure S2, Supporting Information); however, three remarkable differences are observed between them: (a) Building blocks  $[B-\alpha-AsW_9O_{34}]^{9-}$  and  $[B-\beta-AsW_8O_{31}]^{9-}$  other than  $[B-\beta-GeW_9O_{33}(OH)]^{9-}$  and  $[B-\beta-GeW_8O_{30}(OH)]^{9-}$ build the asymmetric sandwich-type arsenotungstate. (b) 2 was prepared by the further development of slow solvent evaporation of 1, whereas  $[Cu_3(H_2O)(B-\beta-GeW_9O_{33}(OH)))(B-\beta-GeW_9O_{33}(OH))(B-\beta-GeW_9O_{33}(OH)))(B-\beta-GW_9O_{33}(OH))(B-\beta-GW_9O_{33}(OH)))(B-\beta-GW_9O_{33}(OH)))(B-\beta-GW_9O_{33}(OH)))(B-\beta-GW_9O_{33}(OH)))(B-\beta-GW_9O_{33}(OH)))(B-\beta-GW_9O_{33}(OH)))(B-\beta-GW_9O_{33}(OH)))(B-\beta-GW_9O_{33}(OH)))(B-\beta-GW_9O_{33}(OH)))(B-\beta-GW_9O_{33}(OH)))))$  $\beta$ -GeW<sub>8</sub>O<sub>30</sub>(OH))]<sup>12-</sup> was made by the decomposition of the { $\gamma$ -GeW<sub>10</sub>O<sub>36</sub>} precursor. (c) Ni<sub>3</sub>(en)[B- $\alpha$ -AsW<sub>0</sub>O<sub>34</sub>][B- $\beta$ -As- $W_8O_{31}$ <sup>12-</sup> is an organic-inorganic hybrid unit compared to the inorganic  $[Cu_3(H_2O)(B-\beta-GeW_9O_{33}(OH))(B-\beta-GeW_8O_{30}-B)(B-\beta-GW_8O_{30}-B)($ (OH))]<sup>12-</sup> , which can be described as that a terminal water group in the Cu<sub>3</sub> 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 been observed in  $(NH_4)_2[Ni_4(enMe)_8(H_2O)_2Ni_4(enMe)_2(P-W_9O_{34})_2]\cdot 9H_2O$ ,<sup>31</sup> {Co(Hen)[Co<sub>6</sub>As<sub>3</sub>W<sub>24</sub>O<sub>94</sub>(H<sub>2</sub>O)<sub>2</sub>]}<sub>2</sub>,<sup>32</sup> and [Zn(Hen)]<sub>6</sub>[B-a-AsW<sub>9</sub>O<sub>33</sub>]<sub>2</sub>·6H<sub>2</sub>O.<sup>7</sup> Bond-valence sum calculations for 2 (Table S5, Supporting Information) indicate that all the W, As, and Ni atoms are in +6, +5, and +2 oxidation states, respectively, and no protonated O atom exists in 2. In addition, the 3-D supramolecular framework of 2 (Figure 2e) is generated through abundant N-H…O hydrogen bonds (2.76-3.26 Å) and N–H···Cl hydrogen bonds (3.53 Å).

The asymmetric unit of 3 is constructed from a sandwichtype  ${[Ni_4(Hen)_2][B-\alpha-AsW_9O_{34}]_2}^{4-}$  polyoxoanion, four  $[H_2en]^{2+}$  cations, and five crystal water molecules. The polyoxoanion (Figure 3a) consists of two trivacant  $[B-\alpha AsW_9O_{34}$ <sup>9-</sup> Keggin moieties (Figure 3b) sandwiching a central symmetric rhomblike  $\{Ni_4O_{14}(en)_2\}$  segment (Figure 3c) via the W-O-Ni and As-O-Ni connecting modes. The rhomblike  ${Ni_4O_{14}(en)_2}$  segment is formed by two NiO<sub>6</sub> and two NiO<sub>5</sub>N octahedra by an edge-shared mode, in which the Ni-O bond lengths are between 1.971(7) and 2.194(7) Å, and the equivalent Ni-N distance is 2.053(8) Å. In the  ${Ni_4O_{14}(en)_2}$  segment, two en molecules are used as substitutes for two H<sub>2</sub>O molecules of the regular rhomblike  ${Ni_4O_{14}(H_2O)_2}$  cluster. It is interesting that one N atom of each en molecule coordinates to one Ni2+ ion; thus, two en molecules are supported on either side of the sandwich-type polyoxoanion. The entire W centers exhibit octahedral coordination environments, and the W-O bond lengths are in the range of 1.697(7)-2.471(6) Å. Bond-valence sum calculations for 3 (Table S6, Supporting Information) indicate that all the W, As, and Ni atoms are in +6, +5, and +2 oxidation



**Figure 3.** (a) Ball-and-stick and polyhedral representation of **3**. (b) Ball-and-stick representation of  $[B-\beta-AsW_9O_{31}]^{9-}$  unit. (c) Ball-and-stick representation of the Ni<sub>4</sub> core. (d) The 3D framework structure of **3** generated through hydrogen bonds.

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).

**TG Analyses.** The TG curve of **1** is divided into three stages with a total weight loss of 22.77% (calcd 24.07%) (Figure S3a, Supporting Information). The first stage occurring from 30 to 107 °C can be ascribed to the loss of six crystal water molecules (3.89%), which is in agreement with the calculated value (4.42%). The second weight loss of 8.55% (calcd 8.60%) in the range of 108–485 °C corresponds to the loss of en molecules. The last stage between 485 and 830 °C could be attributed to the decomposition of the {As−O−W} framework, according to the reaction  $H_8As^{III}_2W_8O_{31} \rightarrow As_2O_3\uparrow + 8WO_3 + 4H_2O\uparrow;^{33}$  the observed total weight loss is 10.33% (calculated value 11.05%) in this stage.

The TG curve of **2** displays three weight loss steps with a total weight loss of 17.60% (calcd 18.66%) (Figure S3b, Supporting Information). The first weight loss of 2.52% (cald 3.15%) occurring from 30 to 101 °C can be ascribed to the loss of nine crystal water molecules. The second weight loss of 7.54% in the range of 102–480 °C (calcd 7.60%) corresponds to the loss of en molecules. The last stage between 481 and 820 °C could be attributed to the decomposition of the {As–O–W} framework according to the reaction H<sub>13</sub>{Ni<sub>3</sub>(en)[B- $\alpha$ -AsW<sub>9</sub>O<sub>34</sub>][B- $\beta$ -AsW<sub>8</sub>O<sub>31</sub>]}  $\rightarrow$  As<sub>2</sub>O<sub>3</sub>↑ + 17WO<sub>3</sub> + 6.5H<sub>2</sub>O↑ + 3/4O<sub>2</sub>↑ + 3NiO + en↑. The observed total weight loss in this stage (7.60%) compares well with the calculated value (7.91%).

The TG curves of **3** (Figure S3c, Supporting Information) shows a three-step weight loss process in the range of 30–900 °C with a total weight loss of 14.37% (calcd 14.46%). The first weight loss of 1.78% (calcd 1.69%) that occurred in the range

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  $H_{10}{[Ni_4-(en)_2][B-\alpha-AsW_9O_{34}]_2} \rightarrow As_2O_3\uparrow + 18WO_3 + 5H_2O\uparrow + O_2\uparrow + 4NiO + 2en\uparrow$ .

**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<sup>-1</sup>. Four groups of characteristic vibration absorption bands are observed at 1053, 951–930, 815, and 730–674 cm<sup>-1</sup> in 1; 1035, 949, 874, and 755–705 cm<sup>-1</sup> in 2; and 1044, 953, 873–842, and 772–698 cm<sup>-1</sup> in 3, which are attributed to the stretching vibration of  $\nu$ (As–Oa),  $\nu$ (W=Ot),  $\nu$ (W–Ob), and  $\nu$ (W–Oc), respectively. The peaks centered at 1510–1630 cm<sup>-1</sup> are attributed to the bending vibration of  $\delta$ (N–H), which confirm the presence of the en ligand in 1–3. The occurrence of the vibration band at 3410–3441 cm<sup>-1</sup> 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  $\chi_{\rm M}$  and  $\chi_{\rm M}T$  is shown in Figure 4. The  $\chi_{\rm M}$  value of 3 slowly increases



**Figure 4.** Temperature dependence of the molar magnetic susceptibility  $\chi_{\rm M}$  (bottom) and the  $\chi_{\rm M}T$  (top) product for **3** between 2.69 and 300 K.

from 0.01674 emu mol<sup>-1</sup> at 300 K to 0.26713 emu mol<sup>-1</sup> at 26 K, and then rapidly reaches to 4.96469 emu mol<sup>-1</sup> at 2.69 K. The experimental  $\chi_{\rm M}T$  values of 3 at room temperature are 5.02342 emu K mol<sup>-1</sup> at 300 K, which are expected for four uncoupled high-spin Ni<sup>2+</sup> ions with S = 1, g > 2. Upon cooling, the  $\chi_{\rm M}T$  values of 3 increase to a maximum of 13.35501 emu K mol<sup>-1</sup> at 2.69 K, which might be mainly attributed to the presence of zero-field splitting (ZFS).<sup>34</sup> The behavior suggests that there exist overall ferromagnetic interactions with the presence of ZFS for Ni<sup>2+</sup> ions. The temperature dependence of the reciprocal susceptibilities  $(1/\chi_{\rm M})$  obeys the Curie–Weiss law for 3 with  $\theta = 5.35$  K, which further supports the presence of ferromagnetic coupling in 3 (Figure S5, Supporting Information).

# CONCLUSION

In conclusion, a series of arsenotungstates formulated as  $(H_2en)_{3.5}[HAs_2W_8O_{31}]\cdot 6H_2O$  (1),  $Na_{0.5}(H_2en)_{6.5}\{Ni_3(en)[B-\alpha-AsW_9O_{34}][B-\beta-AsW_8O_{31}]\}Cl_{1.5}\cdot 9H_2O$  (2), and  $[H_2en]_4-\{[Ni_4(Hen)_2][B-\alpha-AsW_9O_{34}]_2\}\cdot 5H_2O$  (3) have been sequentially 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

#### 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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