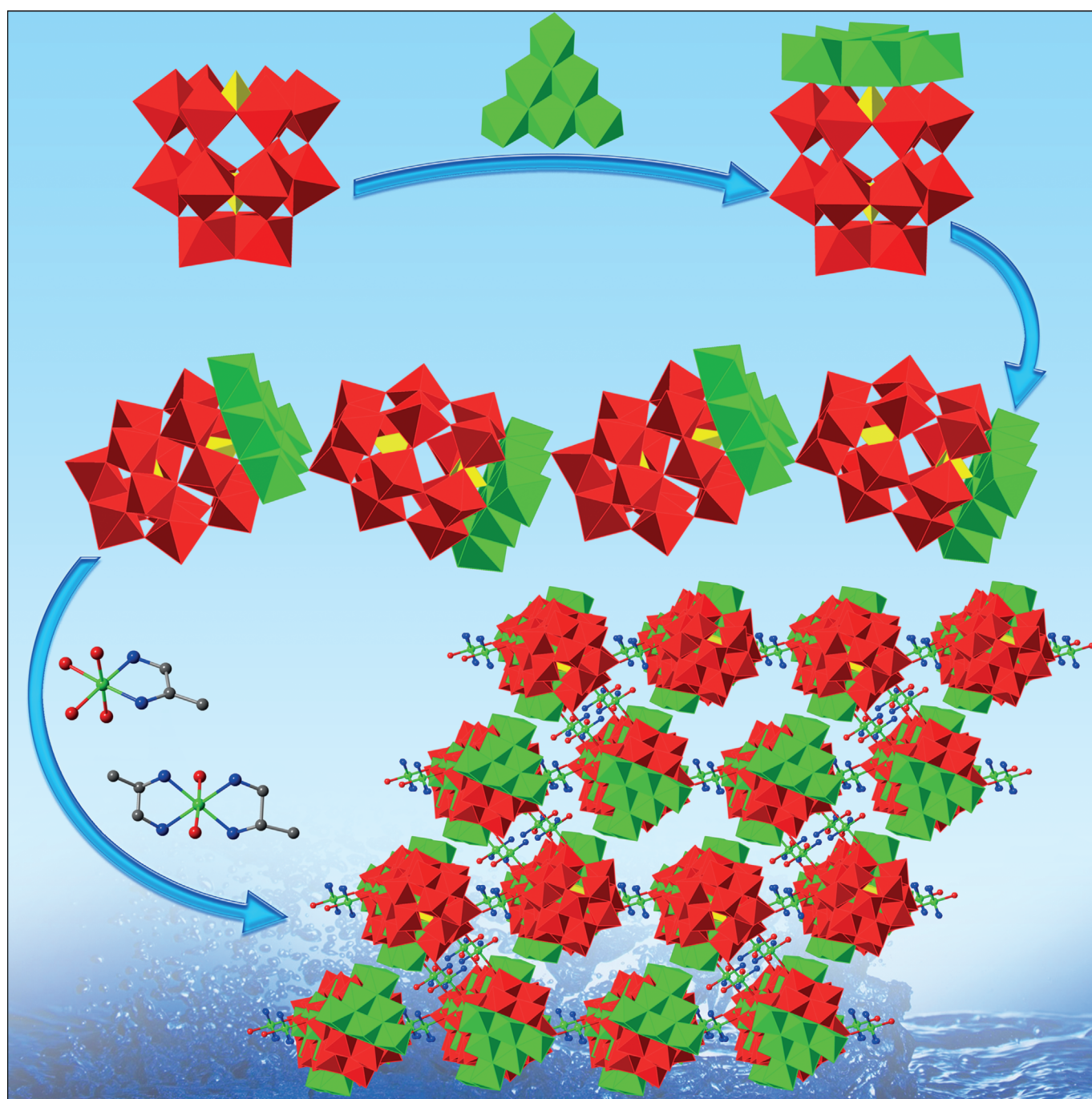


Polyoxometalates

Hydrothermal Combination of Trilacunary Dawson Phosphotungstates and Hexanickel Clusters: From an Isolated Cluster to a 3D Framework

Xin-Xiong Li,^[a] Wei-Hui Fang,^[a] Jun-Wei Zhao,^{*,[b]} and Guo-Yu Yang^{*,[a, c]}

Abstract: Three novel hexa-Ni-substituted Dawson phosphotungstates $[\text{Ni}_6(\text{en})_3(\text{H}_2\text{O})_6(\mu_3\text{-OH})_3(\text{H}_3\text{P}_2\text{W}_{15}\text{O}_{56})] \cdot 14 \text{H}_2\text{O}$ (**1**), $[\text{Ni}(\text{enMe})_2(\text{H}_2\text{O})][\text{Ni}_6(\text{enMe})_3(\mu_3\text{-OH})_3(\text{H}_2\text{O})_6(\text{HP}_2\text{W}_{15}\text{O}_{56})] \cdot 10 \text{H}_2\text{O}$ (**2**), and $[\text{Ni}(\text{enMe})_2]_3[\text{Ni}(\text{enMe})_2(\text{H}_2\text{O})][\text{Ni}(\text{enMe})(\text{H}_2\text{O})_2] \cdot [\text{Ni}_6(\text{enMe})_3(\mu_3\text{-OH})_3(\text{Ac})_2(\text{H}_2\text{O})(\text{P}_2\text{W}_{15}\text{O}_{56})]_2 \cdot 6 \text{H}_2\text{O}$ (**3**) (en = ethylenediamine, enMe = 1, 2-diaminopropane, Ac = CH_3COO^-) have been made under hydrothermal conditions and were characterized by IR spectroscopy, elemental analysis, diffuse reflectance spectroscopy, thermogravimetric analysis, powder X-ray diffraction, and single-crystal X-ray diffraction. The common structural features of compounds **1–3** contain the similar hexa-Ni-substituted Dawson polyoxometalate (POM) units that can be viewed as a $[\text{Ni}_6(\mu_3\text{-OH})_3]^{9+}$ cluster capping on a $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ fragment. Compounds **1** and **2**

are two isolated clusters, whereas compound **3** is the first 3D POM framework constructed from hexa-Ni-substituted Dawson POM units and Ni(enMe) complex bridges. The preparations of compounds **1–3** not only indicate that triangle coplanar Ni_6 clusters are very stable fragments in both trivacant Keggin and trivacant Dawson POM systems, but also offer that the hydrothermal technique can act as an effective strategy for making novel Dawson-type high-nuclear transition-metal cluster substituted POMs by combination of lacunary Dawson precursors with transition-metal cations in the tunable role of organic ligands. In addition, magnetic measurements illustrate that there exist overall ferromagnetic interactions in compound **3**.

Introduction

The design and synthesis of novel transition-metal-substituted polyoxometalate (TMSP) clusters based on the classical lacunary Keggin or Dawson fragments have raised extreme interest due to their structural varieties and unexpected properties,^[1] which gives rise to potential applications in magnetism,^[2] material sciences,^[3] catalysis,^[4] and biomedicine.^[5] A rather effective approach commonly used for TMSPs is to utilize multilacunary polyoxometalate (POM) precursors (such as lacunary Keggin $[\text{A}-\alpha\text{-XW}_9\text{O}_{34}]^{9/10-}$ ($\text{X} = \text{P}^{\text{IV}}/\text{Si}^{\text{IV}}/\text{Ge}^{\text{IV}}$)) to react with transition-metal (TM) ions by the conventional aqueous solution or the hydrothermal technique. So far, many groups have devoted great efforts to synthetically implement this strategy for making novel TMSPs with a large variable range of the number of TM cations.^[6,7] Like the lacunary $[\alpha\text{-XW}_9\text{O}_{34}]^{9/10-}$ (XW_9) fragments, the trilacunary Dawson fragment $[(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})]^{12-}$ (P_2W_{15}) unit is also an important precursor and has been used to make some neotype TMSPs,^[8–10] such as tri-V-/Nb-/Sn-substituted P_2W_{15} -based POMs,^[8] tetra-/hexa-TM sandwiched $[\text{P}_4\text{W}_{30}\text{M}_4\text{O}_{112}]^{16-}$ ($\text{M} = \text{Mn}/\text{Fe}/\text{Co}/\text{Ni}/\text{Cu}/\text{Zn}$),^[9a–d] and $[\text{P}_4\text{V}_6\text{W}_{30}\text{O}_{120}]^{10-, [9e]}$ lanthanide-encapsulated $[\{\text{Y}_4(\mu_3\text{-OH})_4(\text{H}_2\text{O})_8\}(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{16-}$ and $[\{\text{Yb}_6(\mu_6\text{-O})(\mu_3\text{-OH})_6(\text{H}_2\text{O})_6\}(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{14-, [9f]}$

U-substituted $[(\text{UO}_2)_{12}(\mu_3\text{-O})_4(\mu_2\text{-H}_2\text{O})_{12}(\text{P}_2\text{W}_{15}\text{O}_{56})_4]^{32-, [10a]}$ Ti-based $[\{\text{Ti}_3\text{P}_2\text{W}_{15}\text{O}_{57.5}(\text{OH})_3\}_4]^{24-, [10b]}$ $[(\text{P}_2\text{W}_{15}\text{Ti}_3\text{O}_{62})_4(\mu_3\text{Ti}(\text{OH})_3)_4\text{Cl}]^{45-, [10c]}$ and $[(\text{P}_2\text{W}_{15}\text{Ti}_3\text{O}_{60.5})_4(\text{NH}_4)_3]^{35-, [10d]}$ Mo-based polyoxothiometalates $[(\text{H}_2\text{P}_2\text{W}_{15}\text{O}_{56})_4(\text{Mo}_2\text{O}_2\text{S}_2(\text{H}_2\text{O})_2)_4(\text{Mo}_4\text{S}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O}))_2]^{28-, [10e]}$ Fe-/V-/Co-/Ni-/Ta-substituted $[\text{KFe}_{12}(\text{OH})_{18}(\text{P}_2\text{W}_{15}\text{O}_{56})_4]^{29-, [10f]}$ $[(\text{C}_{16}\text{H}_{36}\text{N})_{19}(\text{H}_2\text{NC}(\text{CH}_2\text{O})_3\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59})_4]^{5-, [10g]}$ $[\text{Co}_{14}\text{P}_{10}\text{W}_{60}\text{O}_{232}(\text{OH})_9(\text{H}_2\text{O})_6]^{35-}/[\text{Co}_9\text{P}_8\text{W}_{45}\text{O}_{176}(\text{OH})_3(\text{H}_2\text{O})_6]^{27-, [10h]}$ $[\text{Ni}_{14}(\text{OH})_6(\text{H}_2\text{O})_{10}(\text{HPO}_4)_4(\text{P}_2\text{W}_{15}\text{O}_{56})_4]^{34-, [10i]}$ and $[\text{P}_8\text{W}_{60}\text{Ta}_{12}(\text{H}_2\text{O})_4(\text{OH})_8\text{O}_{236}]^{20-, [10j]}$ It is noteworthy that the above-illustrated TMSPs were made under conventional aqueous solution techniques. On the contrary, the design and synthesis of novel TMSPs based on trilacunary P_2W_{15} remain largely unexplored under hydrothermal conditions,^[11] albeit the hydrothermal technique has been proven to be a particularly powerful synthetic method in making Keggin TMSPs.^[6,7]

Under the guidance of the synthetic strategy of lacunary POM precursors combined with the hydrothermal technique, a series of intriguing high-nuclear TMSPs based on lacunary Keggin XW_9 precursors have been obtained by our lab.^[7] Inspired by these results, we decided to utilize this strategy for a lacunary Dawson P_2W_{15} system. Firstly, three Dawson-type TMSPs $[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_3(\text{dien})_3(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})] \cdot 4.5 \text{H}_2\text{O}$ (0D, dien = diethylenetriamine), $[\text{Ni}(2,2'\text{-bpy})(\text{H}_2\text{O})_2]_2[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_{11}\text{H}(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})]_2 \cdot 26 \text{H}_2\text{O}$ (1D, 2,2'-bpy = 2,2'-bipyridine), and $[\text{Ni}(\text{en})_2][\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_6(\text{en})_3\text{H}(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})] \cdot 5.5 \text{H}_2\text{O}$ (1D) were discovered,^[11] which consist of the highest number of Ni atoms on a single Dawson trivacant P_2W_{15} among reported TMSPs. These results demonstrate the great potential of this synthetic strategy extension from lacunary Keggin XW_9 to Dawson P_2W_{15} for making new TMSPs, which will encourage us to continuously explore this domain. Fortunately, another three Dawson-based TMSPs $[\text{Ni}_6(\text{en})_3(\text{H}_2\text{O})_6(\mu_3\text{-OH})_3(\text{H}_3\text{P}_2\text{W}_{15}\text{O}_{56})] \cdot 14 \text{H}_2\text{O}$ (**1**), $[\text{Ni}(\text{enMe})_2(\text{H}_2\text{O})][\text{Ni}_6(\text{enMe})_3(\mu_3\text{-OH})_3(\text{H}_2\text{O})_6(\text{HP}_2\text{W}_{15}\text{O}_{56})] \cdot 10 \text{H}_2\text{O}$ (**2**), and $[\text{Ni}(\text{enMe})_2]_3[\text{Ni}(\text{enMe})_2(\text{H}_2\text{O})][\text{Ni}(\text{enMe})(\text{H}_2\text{O})_2][\text{Ni}_6(\text{enMe})_3(\mu_3\text{-OH})_3(\text{Ac})_2(\text{H}_2\text{O})(\text{P}_2\text{W}_{15}\text{O}_{56})]_2 \cdot 6 \text{H}_2\text{O}$ (**3**) have been made (en = ethylenediamine, enMe = 1,2-diaminopropane, Ac = CH_3COO^-). Though some lacunary Dawson TMSPs have been reported,^[8–10,12] the number of metal ions in a monomeric trivacant Dawson fragment is

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not more than four, except for the hepta-nuclear heterometal-substituted monomeric lacunary Dawson POM [$[\alpha\text{-P}_2\text{W}_{16}\text{O}_{57}(\text{OH})_2\{\text{Ce}^{\text{IV}}\text{Mn}^{\text{IV}}\text{O}_3(\text{O}_2\text{CCH}_3)_8\}]^{8-}$,^[12b] and our recent work,^[11] however, the number of Ni ions located in the vacant positions in compounds 1–3 is six. In compounds 1–3, the hexa-Ni unit $[\text{Ni}_6(\mu_3\text{-OH})_3]^{9+}$ (Ni_6) caps on the top of P_2W_{15} to form hexa-Ni-substituted TMSPs. Compounds 1 and 2 are isolated structures and compound 3 displays a 3D framework. To the best of our knowledge, compound 3 is the first 3D TMSP framework built from hexa-Ni-substituted Dawson units and nickel-organoamine bridges.

Results and Discussion

Synthesis and spectroscopic characterization

Many novel Dawson TMSPs have been obtained by reaction of Dawson lacunary POM precursors with TM ions at atmospheric pressure and room temperature.^[8–10,12] Although the conventional solution strategies for making Dawson-type TMSPs have been well developed, the application of the hydrothermal technique used for preparations of lacunary Dawson-type TMSPs is still in its infancy. Because the pressure and temperature are increased under hydrothermal conditions, the original physical and chemical equilibria conducted under conventional solution conditions will be broken and the reaction was shifted from the thermodynamic to the kinetic directions. Moreover, the solubility of different phases can be increased and various organic components can be easily introduced. Finally, some structurally complicated metastable or intermediate phases can be created, which may result in novel products that cannot be obtained in the conventional aqueous solution.^[7] Therefore, we decide to extend the hydrothermal reaction system from trilacunary Keggin XW_9 to trilacunary Dawson P_2W_{15} to explore novel TMSPs.

As is well known, in a specific hydrothermal process, many factors such as the reactant concentration, the pH value, the temperature, the reaction time, additional additives, and so on can affect the reaction mechanism, the crystal growth, and the resulting products. In our case, crystals of compounds 1–3 were only obtained by hydrothermal reactions of $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$, en/enMe and $\text{NiAc}_2\cdot 4\text{H}_2\text{O}$ in NaCl solution at 120 °C for eight days. We found that some synthetic parameters are of great importance for the formations of compounds 1–3: 1) the amines are absolutely indispensable during the reaction process. Our attempts without amines to make analogues of compounds 1–3 failed. 2) The reaction must be proceeded in NaCl solution, mainly because sodium chloride may reduce the transformation rate of $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-} \rightarrow [\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ and is also good for the crystallization of products.^[13] Our experiments without sodium chloride were fruitless. 3) Crystallization of compounds 1–3 was found to be sensitive to the pH value of the reaction mixture. The optimal pH value for the crystal growth is in the range of pH 6–7. With a pH value below six, the P_2W_{15} precursor can easily transform to PW_9 during the reaction process, giving rise to hexa-Ni-substituted Keggin species,^[7c] and no crystalline products were obtained

when the pH value was adjusted to higher than seven. 4) The reaction temperature plays a vital role in the formation of compounds 1–3. When the reaction temperature was adjusted to 150 °C, hexa-Ni-substituted Keggin-type products were usually obtained, whereas when the reaction temperature was set at 100 °C, the yield decreased quickly and the sizes of the crystals were not enough for single-crystal X-ray analysis. The results indicate that the PXRD patterns of these yellow-green powders can match with the XRD patterns for compounds 1–3 calculated from single-crystal structures, respectively. Their IR spectra were in agreement with those of compounds 1–3. Therefore, these yellow-green powders should be the same for compounds 1–3, respectively. Evidently, the decrease in temperature leads to the low yield of products. 5) In the preparation of compounds 2 and 3, only the volume of H_2O solvent was changed, but their structures were greatly affected. Thus, the concentration of the starting reactants may have a significant impact on the structures of compounds 2 and 3. Moreover, we also found that the crystal growth of compounds 1–3 is not sensitive to the cooling rate of the reaction system.

For compounds 1–3, the good accordance between the experimental and simulated powder XRD patterns indicates the good phase purity of the samples (Figure S1 in the Supporting Information). The IR spectra of compounds 1–3 were recorded between $\tilde{\nu}=4000\text{--}400\text{ cm}^{-1}$ (Figure S2 in the Supporting Information), which display the characteristic vibration patterns derived from the Dawson polyanions in the range of $\tilde{\nu}=700\text{--}1100\text{ cm}^{-1}$. The adsorption bands at $\tilde{\nu}=1090\text{--}1080$, $943\text{--}930$, $906\text{--}877$, and $729\text{--}717\text{ cm}^{-1}$ were attributed to the $\nu(\text{P}\text{--}\text{O}_a)$, $\nu(\text{W}\text{--}\text{O}_i)$, $\nu(\text{W}\text{--}\text{O}_b)$, and $\nu(\text{W}\text{--}\text{O}_c)$ vibration, respectively. The stretching bands of the --OH , --NH_2 , and --CH_2 groups were observed at $\tilde{\nu}=3460\text{--}3400$, $3380\text{--}3150$, and $3010\text{--}2920\text{ cm}^{-1}$, respectively, whereas the bending vibration bands of the --NH_2 and --CH_2 groups appear at $\tilde{\nu}=1630\text{--}1560$ and $1463\text{--}1368\text{ cm}^{-1}$, respectively. In comparison with the spectra containing PW_9 fragments,^[7] the strong adsorption bands of the $\nu(\text{P}\text{--}\text{O}_a)$ vibration in compounds 1–3 were shifted from about $\tilde{\nu}=1040\text{ cm}^{-1}$ to $\tilde{\nu}=1090\text{--}1080\text{ cm}^{-1}$, which can be used as a convenient prediction of the polyanion type through IR spectra.^[14] The occurrence of these resonance signals confirms the compositions of compounds 1–3, which is consistent with the single-crystal structural analyses.

To evaluate the optical properties of compounds 1–3, the measurements of diffuse reflectance spectra for powdered crystal samples were performed to obtain their band gaps (E_g). The band gap was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a plot of the Kubelka–Munk function against the energy E (Figures S3–S5 in the Supporting Information).^[15a,b] Their band gaps E_g are 2.15, 2.53, and 2.01 eV for compounds 1–3, respectively. These band gaps are related to the energy-level difference between the oxygen p-type HOMO and the tungsten p-type LUMO.^[15c] Similar behaviors have been observed in several reported TMSPs, such as $[\{\text{Ni}_6(\mu_3\text{-OH})_3(\text{en})_2(\text{H}_2\text{O})_8\}(\text{B}\text{--}\alpha\text{-PW}_9\text{O}_{34})\}\cdot 7\text{H}_2\text{O}]$ ($E_g=2.89\text{ eV}$),^[7c] $[\text{Co}_2(\text{bpy})_6(\text{W}_6\text{O}_{19})_2]$ ($\text{bpy}=4,4\text{'-bipyridine}$, $E_g=2.2\text{ eV}$),^[15d] and $[\text{Ag}_2(3\text{atrz})_2][\text{HPMo}_{10}^{\text{VI}}\text{Mo}_2^{\text{V}}\text{O}_{40}]$ ($E_g=2.15\text{ eV}$)

(3atrz = 3-amino-1,2,4-triazole).^[15e] The band gaps of the compounds decrease with increasing dimensionality or complexity of the structures, as pointed out by Kanatzidis et al.^[16] and Papavassiliou.^[17] The band gap of compound **3** is smaller than those of compounds **1** and **2** and those of isolated or low-dimensional Ni₆-substituted structures previously reported by us,^[7a] which is consistent with their structural dimensionality.

Structures of [Ni₆(en)₃(H₂O)₆(μ₃-OH)₃(H₃P₂W₁₅O₅₆)]·14H₂O (1**) and [Ni(enMe)₂(H₂O)]₂[Ni₆(enMe)₃(μ₃-OH)₃(H₂O)₆(HP₂W₁₅O₅₆)]·10H₂O (**2**)**

Both compounds **1** and **2** crystallize in the monoclinic space group *P2₁/c*. The structure consists of a Ni₆-substituted polyanion [Ni₆(en)₃(H₂O)₆P₂W₁₅]³⁻ for compound **1** (Figure 1A) and

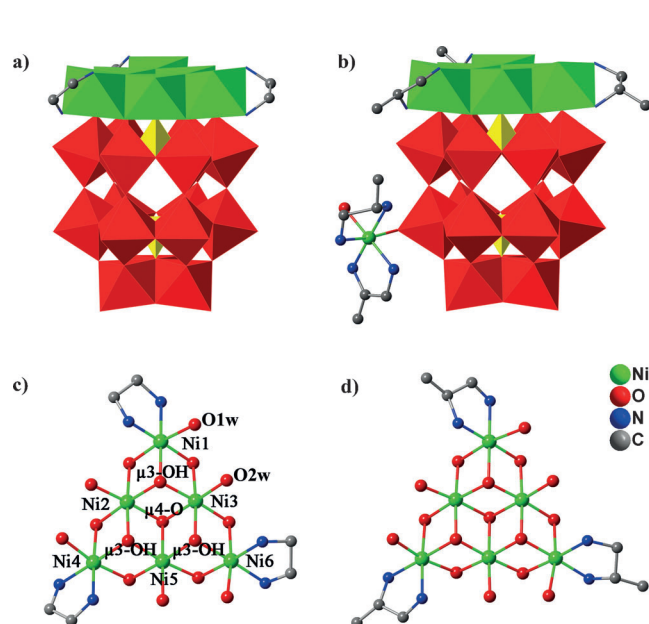


Figure 1. A) The [Ni₆(en)₃(H₂O)₆P₂W₁₅]³⁻ cluster in compound **1**. B) The {Ni(enMe)₂(H₂O)}₂[Ni₆(enMe)₃(H₂O)₆P₂W₁₅]³⁻ cluster in compound **2**. C) The coordination environment of the Ni₆ unit in compound **1**. D) The coordination environment of the Ni₆ unit in compound **2**. Color codes: WO₆ = red, PO₄ = yellow, NiO₆/NiO₃N₂(H₂O)₂ = green.

{Ni(enMe)₂(H₂O)}₂[Ni₆(enMe)₃(H₂O)₆P₂W₁₅]³⁻ for compound **2** (Figure 1B). The structures of the Ni₆P₂W₁₅ polyanions in compounds **1** and **2** can be described as a P₂W₁₅ unit capped by a triangular Ni₆ cluster with different exterior ligands. The Ni₆ cluster is made up of six nearly coplanar Ni²⁺ ions in a triangle motif linked together by three μ₃-OH bridges (Ni–μ₃-OH: 2.015(9)–2.026(9) Å for compound **1** and 2.006(9)–2.055(10) Å for compound **2**, and stabilized by six μ₃-O bridges from six WO₆ octahedra (Ni–μ₃-O: 2.063(10)–2.162(9) Å for compound **1** and 2.062(9)–2.168(11) Å for compound **2** and one μ₄-O from the central PO₄ tetrahedron (Ni–μ₄-O: 2.123(9)–2.128(9) Å for compound **1** and 2.111(10)–2.112(9) Å for compound **2**). Moreover, the Ni₆ cluster is surrounded by six H₂O ligands and three en ligands to form the Ni₆(H₂O)₆(en)₃ unit in compound **1** (Figure 1C) [Ni–N: 2.047(13)–2.077(11) Å and Ni–Ow: 2.055(4)–

2.137(4) Å]; six H₂O ligands and three enMe ligands to form the Ni₆(H₂O)₆(enMe)₃ unit in compound **2** (Figure 1D) (Ni–N: 2.050(13)–2.094(13) Å and Ni–Ow: 2.046(11)–2.157(9) Å). The Ni₆(H₂O)₆(en)₃ and Ni₆(H₂O)₆(enMe)₃, respectively, caps on a α-P₂W₁₅ fragment through seven exposed oxygen atoms from six WO₆ octahedra and one PO₄ tetrahedron, forming a hexa-Ni-substituted cluster [Ni₆(en)₃(H₂O)₆(μ₃-OH)₃(P₂W₁₅O₅₆)]³⁻ in compound **1** and [Ni₆(enMe)₃(μ₃-OH)₃(H₂O)₆(P₂W₁₅O₅₆)]³⁻ in compound **2**. The further stacking of these hexa-Ni-substituted clusters in compounds **1** and **2** are shown in Figure S6 in the Supporting Information. It is noteworthy that three interior Ni^{II} ions in the Ni₆ cluster adopt a β-junction mode and incorporate to the trivacant sites of the P₂W₁₅ unit to form a {β-Ni₃P₂W₁₅} unit (Figure 2A), which is different from reported [α-

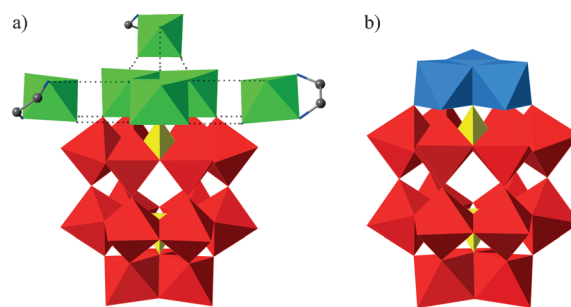


Figure 2. A) Polyhedral view of the β-junction fashion of the polyanion in {β-Ni₃P₂W₁₅}; B) Polyhedral view of the α-junction fashion of the polyanion in {α-M₃P₂W₁₅}.

M₃O₆P₂W₁₅O₅₆]ⁿ⁻ (M = V, Nb, n = 9) isomers (Figure 2B).^[18] Previous studies have demonstrated that the β isomer is more unstable than the α isomer.^[19] The main reason why the {β-Ni₃P₂W₁₅} units are stable in compounds **1** and **2** may be that the further coordination and aggregation of three exterior NiO₄N₂ octahedra in the presence of organoamine ligands are the main driving force under hydrothermal conditions. This observation also testifies the superiority of the hydrothermal technique in creating uncommon metastable or intermediate phases.

Structure of [Ni(enMe)₂]₃[Ni(enMe)₂(H₂O)][Ni(enMe)(H₂O)₂][Ni₆(enMe)₃(μ₃-OH)₃(Ac)₂(H₂O)(P₂W₁₅O₅₆)]₂·6H₂O (3**)**

Single-crystal X-ray diffraction reveals that compound **3** crystallizes in the monoclinic space group *P2₁/c* and its structural unit consists of two independent hexa-Ni-substituted Dawson polyanions [Ni₆(enMe)₃(Ac)₂(H₂O)P₂W₁₅]⁵⁻ (Figure 3A), two isolated [Ni(enMe)₂]²⁺ ions, one [Ni(enMe)₂(H₂O)]²⁺ ion, one bridging [Ni(enMe)₂]²⁺ ion, and one linking [Ni(enMe)(H₂O)₂] group (Figure S7 in the Supporting Information). Different from compounds **1** and **2**, compound **3** is a novel 3D framework constructed from [Ni₆(enMe)₃(Ac)₂(H₂O)P₂W₁₅]⁵⁻ fragments and [Ni(enMe)₂]²⁺ bridges. The structure of the hexa-Ni-substituted Dawson polyanion in compound **3** is similar to those in compounds **1** and **2** except for the coordination environments of the Ni₆ clusters. In compounds **1** and **2**, the Ni₆ clusters are sta-

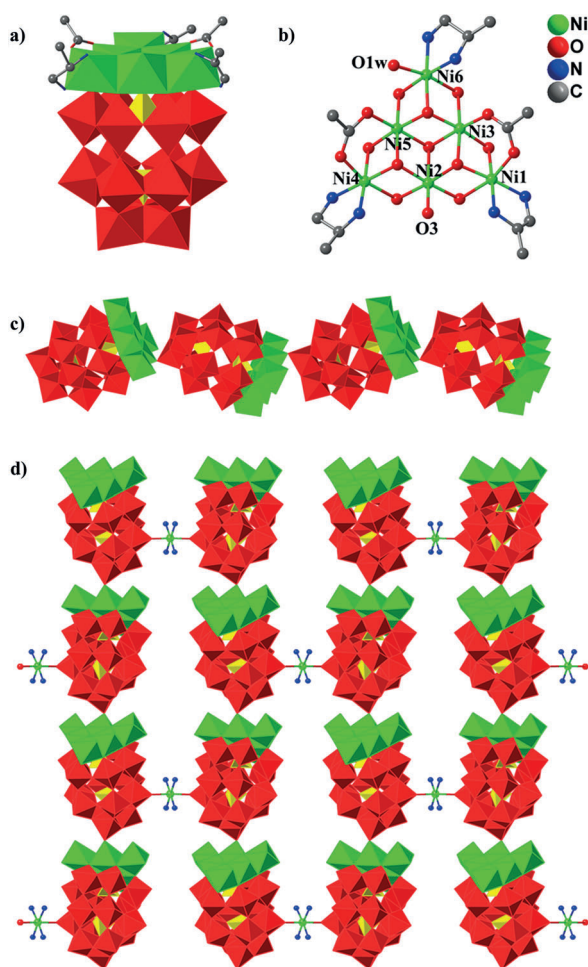


Figure 3. A) The $[\text{Ni}_6(\text{enMe})_3(\text{Ac})_2(\text{H}_2\text{O})\text{P}_2\text{W}_{15}]^{5-}$ cluster in compound **3**. B) The coordination environment of the Ni_6 unit in compound **3**. C) View of the 1D cluster-chain in compound **3**. D) View of the 2D layer along the c axis in compound **3**. Color codes: $\text{WO}_6 = \text{red}$, NiO_6 and $\text{NiO}_4\text{N}_2 = \text{green}$, $\text{PO}_4 = \text{yellow}$.

bilized by three amine and six H_2O ligands (Figures 1 C and D), whereas the Ni_6 cluster in compound **3** is surrounded by one H_2O ligands, three enMe ligands, two acetate group, and one terminal oxygen atom of WO_6 from another polyanion. The substitution of coordinated water ligands by bidentate acetate groups has been observed in Keggin systems,^[7a] however, it has not been reported in Dawson systems. Besides, the water ligand on the exterior Ni_2 ion of the Ni_6 core is replaced by one terminal oxygen atom (O3) of one WO_6 group from an adjacent polyanion (Figure 3B), which leads to the formation of the extended 1D zigzag cluster-chain, which is made up of $[\text{Ni}_6(\text{enMe})_3(\text{Ac})_2(\text{H}_2\text{O})\text{P}_2\text{W}_{15}]^{5-}$ units through vertex-sharing between NiO_6 and WO_6 octahedra (Figure 3C). Compared with a similar 1D zigzag cluster-chain made of Ni_6 clusters and PW_9 fragments previously reported by our group,^[7a] the angle between adjacent polyanions and the distance between the Ni_6 cores in compound **3** are larger than those in a PW_9 system due to the bigger size of the P_2W_{15} fragment. Worthy of mention is that these zigzag cluster-chains can be further interconnected in compound **3**. The neighboring chains were inter-

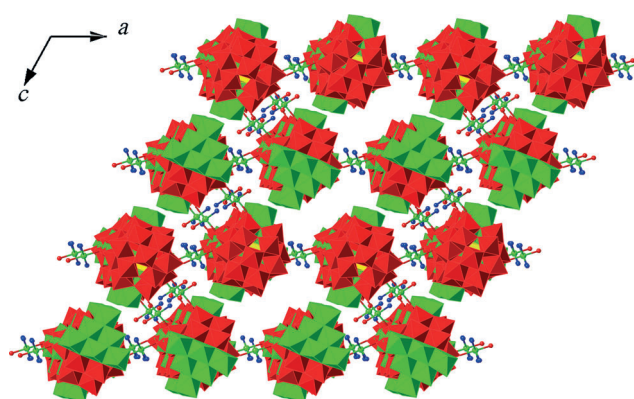


Figure 4. View of the 3D extended architecture of compound **3** down the b axis. Color codes: $\text{WO}_6 = \text{red}$, NiO_6 and $\text{NiO}_4\text{N}_2 = \text{green}$, $\text{PO}_4 = \text{yellow}$.

linked by $[\text{Ni}(\text{enMe})_2]^{2+}$ bridges to form a 2D layer (Figure 3D), which is further connected by $[\text{Ni}(\text{enMe})(\text{H}_2\text{O})_2]^{2+}$ ions, forming an infinite 3D framework (Figure 4). To the best of our knowledge, compound **3** is the first example of a 3D-extended architecture constructed from hexa-Ni-substituted Dawson-type TMSPs and TM complexes. From the topological point of view, the 3D framework of compound **3** is a four-connected 3D network, where each hexa-Ni-substituted polyanion acts as a four-connected node. A topological analysis of this net was performed with TOPOS 4.0 professional.^[20] The overall 3D network of compound **3** can be rationalized as a four-connected $(4^2\cdot 6^3\cdot 8)$ topology (Figure 5). Comparing the topology of com-

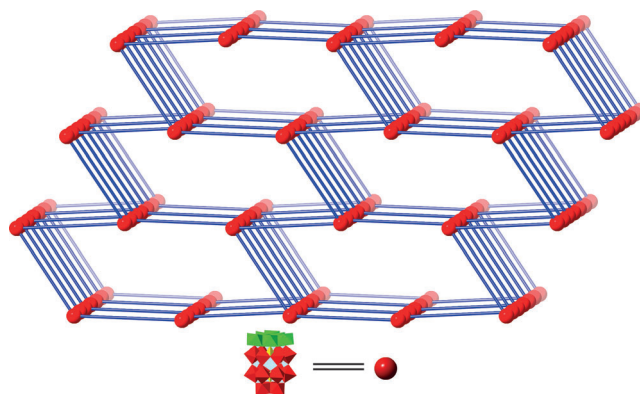


Figure 5. View of the 3D SrAl_2 topology of compound **3** along the b axis.

compound **3** with those of known minerals, compound **3** possesses the $(4^2\cdot 6^3\cdot 8)$ SrAl_2 topology,^[21] being obviously different from other four-connected topologies of minerals, that is, diamond $(6_2\cdot 6_2\cdot 6_2\cdot 6_2\cdot 6_2\cdot 6_2)$, NbO $(6_2\cdot 6_2\cdot 6_2\cdot 6_2\cdot 8_2\cdot 8_2)$, PtS $(4\cdot 4\cdot 8_2\cdot 8_2\cdot 8_2\cdot 8_2)$, and CrB_4 $(4\cdot 6_2\cdot 6\cdot 6\cdot 6\cdot 6)$.^[22]

Magnetic properties

Because compounds **1–3** contain a similar Ni_6 core, only the magnetic properties of compound **3** were investigated. The magnetic susceptibility of compound **3** was measured in the

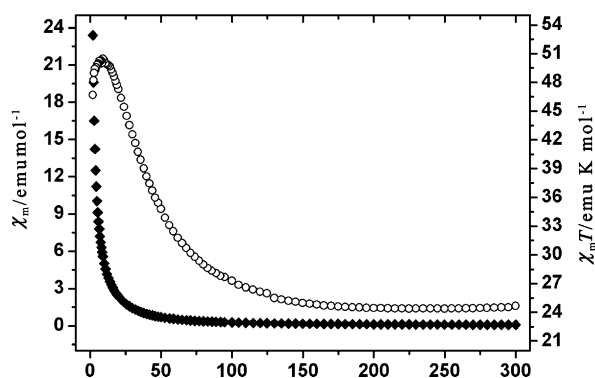


Figure 6. Temperature dependence of the molar magnetic susceptibility χ_m (\blacklozenge) and the product of the molar magnetic susceptibility and the temperature $\chi_m T$ (\circ) for compound **3** between 2.0 and 300 K.

region 2–300 K with an applied magnetic field of 1 kOe. The plot of $\chi_m T$ versus T of compound **3** is shown in Figure 6. The experimental value of $\chi_m T$ at room temperature is 24.48 emu K mol⁻¹ per formula unit, being consistent with the theoretical value (i.e., 20.57 emu K mol⁻¹) expected for seventeen uncoupled high-spin Ni²⁺ ions with $S=1$ and $g=2.20$.^[23] Upon cooling, the $\chi_m T$ value increases to a maximum of 50.67 emu K mol⁻¹ at 9.0 K. This magnetic behavior testifies to the ferromagnetic coupling interactions between adjacent Ni²⁺ centers. A sudden decrease of the $\chi_m T$ value below 9 K might be mainly attributed to the presence of the significant zero-field-splitting (ZFS) effects in the ground state and/or antiferromagnetic intercluster interactions.^[7a,c] The magnetic data for compound **3** can be fitted to the Curie–Weiss law in the range of 300–25 K (Figure S8 in the Supporting Information) with a Curie constant of 23.05 emu K mol⁻¹ and a positive Weiss constant of $\theta=13.90$ K. The positive Weiss constant further confirms the ferromagnetic behavior of compound **3**. The magnetic exchange interactions within the Ni²⁺ cations in compound **3** are chiefly transmitted through μ_3 -O, μ_3 -OH, and μ_4 -O bridges. As we know, the magnetic coupling is highly sensitive to the values of the \angle Ni-O-Ni bridging angles: the coupling is ferromagnetic for angles in the range of $(90 \pm 14)^\circ$, whereas it is antiferromagnetic for larger angles.^[24] The case that \angle Ni-O-Ni varies between 90.8 and 104.7° in compound **3** shows that the ferromagnetic coupling is not unexpected. Theoretical analyses of such hexa-Ni cluster performed in our previous study^[7,11] also testify the existence of ferromagnetic coupling among the Ni²⁺ centers.

Conclusion

In summary, three novel organic–inorganic hybrids Ni₆-substituted trivacant Dawson-type TMSPs have been successfully obtained under hydrothermal conditions and characterized by elemental analysis, IR spectroscopy, TG analysis, and single-crystal X-ray crystallography. Compounds **1** and **2** are two isolated clusters, whereas compound **3** is the first extended architecture based on Ni₆-substituted Dawson segments and [Ni(enMe)₂]²⁺ bridges. The key points of the synthetic proce-

dures have been discussed. Like trivacant Keggin fragments, trivacant Dawson fragments can also be used to the structure-directing agents to induce the formation of Ni₆ clusters with the help of amines under appropriate conditions. Furthermore, the successful syntheses of compounds **1–3** not only indicate that triangle coplanar Ni₆ clusters are very stable fragments in both trivacant Keggin and trivacant Dawson POM systems, but also offer that the hydrothermal technique can function as an effective route for making novel Dawson-type TMSPs by means of combination of lacunary Dawson POM precursors with high-nuclear TM clusters. Further work based on the following aspects is in progress: 1) replacing six terminal H₂O ligands and three μ_3 -OH groups of the [Ni₆(H₂O)₆P₂W₁₅] by rigid carboxylic ligands and tripodal alcohol ligands to make cluster-organic cages/chains/networks/frameworks^[7f,j] and 2) introducing other multilacunary POM precursors such as [α-H₂P₂W₁₂O₄₈]¹²⁻,^[14c] [P₆W₁₈O₇₉]²⁰⁻,^[25a] [As₂W₁₉O₆₇(H₂O)]¹⁴⁻,^[25b] [As₄W₄₀O₁₄₀]²⁸⁻,^[25c] [As₆W₆₅O₂₁₇(H₂O)₇]²⁶⁻,^[25b] [Sb₂W₂₂O₇₄(OH)₂]¹²⁻,^[25d] [Na₂Sb₈W₃₆O₁₃₂(H₂O)₄]²²⁻,^[25d] [NaSb₃W₂₁O₈₆]¹⁸⁻^[25e] to react with TMs or lanthanides to explore novel metal-substituted POMs.

Experimental Section

Na₁₂[α-P₂W₁₅O₅₆]-24H₂O(P₂W₁₅) was prepared by following the literature-known method.^[14c] All other chemicals were used as purchased without further purification.

Synthesis of compound 1: NiAc₂·4H₂O (0.75 g, 3.0 mmol) was dissolved in distilled H₂O (10 mL, 556 mmol) and then NaCl (0.50 g, 8.6 mmol) was added. After stirring for 5 min, en (0.025 mL, 0.370 mmol) was dropwise added to the reaction solution, which was continuously stirred for 10 min and then P₂W₁₅ (0.45 g, 0.10 mmol) was added. The mixture was stirred for 2 h (pH_s 6.80) and was sealed in a 35 mL stainless steel reactor with a Teflon liner and heated at 120 °C for seven days and then cooled to room temperature (pH_e 6.50). Yellow-green block crystals of compound **1** were obtained (31% yield based on P₂W₁₅). IR (KBr): $\tilde{\nu}=3447$ (s), 1626 (s), 1457 (w), 1400 (s), 1285 (w), 1090 (vs), 1052 (m), 1036 (m), 939 (s), 900 (m), 793 (s), 717 (m), 518 (m), 447 cm⁻¹ (w); elemental analysis calcd (%) for H₇₀C₆N₆O₇₉P₂Ni₆W₁₅: C 1.55, H 1.51, N 1.80; found: C 1.46, H 1.50, N 1.72.

Synthesis of compound 2: NiAc₂·4H₂O (0.747 g, 3.0 mmol) was dissolved in distilled H₂O (15 mL, 833 mmol) and then NaCl (0.5 g, 8.6 mmol) was added. After stirring for 5 min, enMe (0.20 mL, 2.36 mmol) was added to the reaction solution drop by drop, which was continuously stirred for 10 min and then P₂W₁₅ (0.45 g, 0.10 mmol) was added. The mixture was stirred for 2 h (pH_s 6.76) and was sealed in a 35 mL stainless steel reactor with a Teflon liner and heated at 120 °C for seven days and then cooled to room temperature (pH_e 6.03). Yellow-green block crystals of compound **2** were obtained (15% yield based on P₂W₁₅). IR (KBr): $\tilde{\nu}=3421$ (s), 2964 (w), 2877 (w), 1629 (m), 1594 (m), 1458 (w), 1412 (m), 1303 (w), 1199 (w), 1084 (vs), 1049 (m), 943 (s), 931 (s), 906 (m), 790 (s), 729 (w), 523 (w), 474 cm⁻¹ (w); elemental analysis calcd (%) for H₈₈C₁₅N₁₀O₇₆P₂Ni₇W₁₅: C 3.71, H 1.83, N 2.88; found: C 3.75, H 1.90, N 2.95.

Synthesis of compound 3: Compound **3** was obtained by using the same procedure as described for compound **2**, but the amount of H₂O was decreased to 8 mL (444 mmol). Yellow-green block crystals of compound **3** were obtained (yield 52% based on P₂W₁₅). The pH_s and pH_e values were 6.61 and 5.98, respectively. IR (KBr):

$\bar{\nu}$ = 3452 (s), 3331 (s), 3270 (s), 2964 (w), 1583 (s), 1559 (s), 1459 (w), 1411 (m), 1302 (w), 1197 (w), 1083 (vs), 1042 (s), 930 (vs), 903 (m), 877 (w), 797 (s), 717 (s), 563 (w), 520 (w), 443 cm^{-1} (w); elemental analysis calcd (%) for $\text{H}_{190}\text{C}_{53}\text{N}_{30}\text{O}_{137}\text{P}_4\text{Ni}_{17}\text{W}_{30}$: C 6.31, H 1.90, N 4.17; found: C 5.95, H 2.04, N 4.12.

Physical measurements: Elemental analyses of C, H, and N were carried out with a Vario EL III elemental analyzer. IR spectra (KBr pellets) were recorded on an ABB Bomem MB 102 spectrometer. The optical diffuse reflectance spectra of powdered compounds **1–3** were measured at room temperature by using a PerkinElmer Lambda 900 UV/Vis spectrophotometer equipped with an integrating sphere attachment and BaSO_4 as reference. Thermal analyses were performed in a dynamic air atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$ by using a METTLER TGA/SDTA851^e thermal analyzer. Powder XRD patterns were obtained by using a Philips X'Pert-MPD diffractometer with $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.54056 \text{ \AA}$). Variable-temperature susceptibility measurements were carried out in the temperature range 2–300 K at a magnetic field of 1 T for compound **3** on polycrystalline samples with a Quantum Design PPMS-9T magnetometer. The experimental susceptibilities were corrected for the Pascal's constants.

X-ray crystallography: Good-quality single crystals for compounds **1–3** were mounted on a glass fiber for indexing and intensity data were collected at 293 K on a Rigaku SCX mini CCD diffractometer with graphite-monochromatized $\text{Mo}_{\text{K}\alpha}$ radiation ($\lambda = 0.71073 \text{ \AA}$). Direct methods were used to solve the structures and to locate the heavy atoms by using the SHELXTL-97 program package.^[26] The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. Routine Lorentz polarization corrections and empirical absorption correction were applied to the intensity data. No hydrogen atoms associated with H_2O molecules were located from the difference Fourier map. Hydrogen atoms attached to carbon and nitrogen atoms were geometrically placed. All hydrogen atoms were refined isotropically as a riding mode by using the default SHELXTL parameters. For compound **1**, four carbon atoms (C3–C6) and five discrete H_2O molecules were refined isotropically and the remaining atoms were refined anisotropically. For compound **2**, one carbon atom (C3) and all isolated H_2O molecules were refined isotropically and the remaining atoms were refined anisotropically. For compound **3**, all non-hydrogen atoms were refined anisotropically except for four free H_2O molecules (O7W–O11W), three nitrogen atoms (N21, N29, and N30), and sixteen carbon atoms (C39–C55). To balance the charge of compounds **1** and **2**, three protons and one proton should be added, respectively. These protons cannot be located crystallographically and are assumed to be delocalized over the entire structure, which is common in POMs.^[27] Crystallographic

Table 1. X-ray crystallographic data for compounds **1–3**.

	1	2	3
formula	$\text{C}_6\text{H}_{30}\text{N}_6\text{Ni}_6\text{O}_{70}\text{P}_2\text{W}_{15}$	$\text{C}_{15}\text{H}_{88}\text{N}_{10}\text{Ni}_7\text{O}_{76}\text{P}_2\text{W}_{15}$	$\text{C}_{53}\text{H}_{190}\text{N}_{30}\text{Ni}_{17}\text{O}_{137}\text{P}_4\text{W}_{30}$
M_r	4478.31	4855.32	10077.80
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	14.566(4)	16.944(5)	28.908(8)
b [Å]	17.926(5)	23.840(7)	27.871(6)
c [Å]	28.894(7)	28.871(6)	28.100(8)
α [°]	90	90	90
β [°]	94.798(4)	125.067(12)	118.816(4)
γ [°]	90	90	90
V [Å ³]	7518(3)	9545(4)	19836(9)
Z	4	4	4
ρ_{calcd} [g cm ⁻³]	3.956	3.379	3.375
μ [mm ⁻¹]	24.459	19.473	19.018
T [K]	293(2)	293(2)	293(2)
limiting indices	$-18 \leq h \leq 18$ $-23 \leq k \leq 23$ $-37 \leq l \leq 37$	$-21 \leq h \leq 21$ $-26 \leq k \leq 30$ $-36 \leq l \leq 37$	$-37 \leq h \leq 37$ $-36 \leq k \leq 25$ $-36 \leq l \leq 36$
reflins collected	55896	72763	152788
independent reflins	17164	21527	44833
data/restraints/parameters	17164/3/863	21527/1/1096	44833/45/2323
goodness-of-fit on F^2	1.080	1.057	1.065
final R indices [$I > 2\sigma(I)$] ^[a]	$R_1 = 0.0500$ $wR_2 = 0.1334$	$R_1 = 0.0597$ $wR_2 = 0.1404$	$R_1 = 0.0707$ $wR_2 = 0.1332$
R indices (all data)	$R_1 = 0.0659$ $wR_2 = 0.1441$	$R_1 = 0.0831$ $wR_2 = 0.1557$	$R_1 = 0.1230$ $wR_2 = 0.1539$

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_c^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$, in which $x = 0.066300$, $y = 88.7204$ for compound **1**, $x = 0.0661$, $y = 22.9287$ for compound **2**, and $x = 0.0372$, $y = 0$ for compound **3**.

data and structure refinements for compounds **1–3** are summarized in Table 1. CCDC 821476 (**1**), 821477 (**2**), and 821478 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: Dawson • hydrothermal synthesis • nickel • polyoxometalates • tungsten

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