

Poly(polyoxotungstate)s with 20 Nickel Centers: From Nanoclusters to One-Dimensional Chains**

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The design and synthesis of transition-metal (TM) substituted polyoxotungstates (POTs) is of contemporary interest, owing to their putative and realized applications in catalysis, photochemistry, and magnetochemistry.^[1–3] In particular, TM-substituted POTs are ideal models for the study of exchange interactions in magnetic TM clusters, as they represent a class of well-insulated clusters of controlled nuclearity and topology. Among the numerous TM-substituted POTs, most possess classic sandwich structures and contain no more than five paramagnetic TM centers. Thus, the synthesis of novel POTs with a higher number of TM centers is predominantly driven by interest not only in their structural diversity but also in their rich electronic and magnetic properties. To date, many research groups have devoted great efforts to exploring synthetic strategies for making POTs with large numbers of TM centers. One effective approach is to use high-lacunary fragments as precursors to react with TM centers for making high-nuclearity TM-substituted POTs by conventional solution-based methods. Resulting species include the Fe₂₈[–], Cu₂₀[–], Nb₁₆[–], and Ti₁₆-substituted poly(POT)s [H₅₆Fe₂₈P₈W₄₈O₂₄₈]^{28–},^[2a] [Cu₂₀Cl(OH)₂₄(H₂O)₁₂(P₈W₄₈O₁₈₄)]^{25–},^[2b] [Nb₄O₆(Nb₃SiW₉O₄₀)₄]^{20–},^[2c] and [(P₂W₁₅Ti₃O₆₂)₄–{Ti(OH)₃Cl}]^{45–}.^[2d] Recently [Ce₂₀Ge₁₀W₁₀₀O₃₇₆(OH)₄–(H₂O)₃₀]^{56–},^[2e] substituted with 20 Ce centers, has also been made.

Compared with the above TM-substituted POTs, the chemistry of Ni-substituted POTs has been extensively studied,^[4] but the largest number of Ni atoms in a molecular POT is only nine.^[4d] High-nuclearity Ni clusters may possess a large spin ground state and a negative axial anisotropy and may exhibit single-molecule magnetism.^[5] Therefore, the synthesis of POTs with larger numbers of Ni atoms has become an attractive but challenging goal. Lately, we have shown that such solids can be made under hydrothermal conditions using trivacant {XW₉O₃₄} (X = Si, P, Ge) fragments as precursors and structure-directing agents (SDAs) to react with Ni ions.^[6] As part of our continuous work, we have successfully made two unprecedented poly(POT)s substituted with 20 Ni centers: nanocluster [Ni(enMe)₂]₃–[H₆Ni₂₀P₄W₃₄(OH)₄O₁₃₆(enMe)₈(H₂O)₆]₃·12 H₂O (**1**) and 1D [Ni(en)₂(H₂O)]₂[H₈Ni₂₀P₄W₃₄(OH)₄O₁₃₆(en)₉(H₂O)₄]₂·16 H₂O (**2**) (enMe = 1,2-diaminopropane; en = ethylenediamine), which not only constitute the largest Ni-substituted POTs to date but also contain the highest number of Ni ions in known POTs.

Green crystals of **1** and **2** were made by hydrothermal reactions of [A-α-PW₉O₃₄]^{9–}, enMe or en, NiCl₂·6H₂O, CH₃COOH, and K₂CO₃ in water at 170 °C for five days. X-ray analyses reveal that **1** is a novel organic–inorganic hybrid poly(POT) containing a 20-Ni-substituted [H₆Ni₂₀P₄W₃₄(OH)₄O₁₃₆(enMe)₈(H₂O)₆]^{6–} ion (**1a**, Figure 1a) with three [Ni(enMe)₂]²⁺ complexes as counteranions (Supporting Information, Figure S1). As shown in Figure 1, **1a** consists of two {Ni₆O₃(OH)₂(H₂O)(enMe)₂(PW₆O₂₆)(PW₉O₃₄)} moieties ({Ni₆P₂W₁₅}, Figure 1b) linked by a central symmetric belt-like {Ni₈W₄O₂₆(H₂O)₄(enMe)₄} segment ({Ni₈W₄}, Figure 1c) through Ni–O–W and Ni–O–P linkages, leading to a structure with idealized C_i symmetry.

The {Ni₆P₂W₁₅} moiety is constructed from a known trilacunary {B-α-PW₉O₃₄} unit and a rare {PW₆O₂₆} unit on either side of the hexanickel cluster {Ni₆O₁₅(OH)₂(H₂O)(enMe)₂} (Figure 1b and Supporting Information, Figure S2), resulting in a previously unobserved sandwich-type structure. The {B-α-PW₉O₃₄} unit is formed from the isomerization of the [A-α-PW₉O₃₄]^{9–} ion to the [B-α-PW₉O₃₄]^{9–} ion during the course of reaction,^[6] while the {PW₆O₂₆} unit can be seen as a hexalacunary Keggin unit derived from removing one edge-shared W₃O₁₃ triad of a trilacunary {B-α-PW₉O₃₄} unit. The triangular skeleton of {Ni₆O₁₅(OH)₂(H₂O)(enMe)₂} is built by three truncated Ni₃O₄ cubanes that share one edge with each other and which all share a common vertex (O11; Supporting Information, Figure S2). The triangular Ni₆O₁₀ core differs from reported Ni₆O₁₀ cores, which are ligated by three organoamines and six terminal H₂O ligands.^[6] The Ni₆O₁₀

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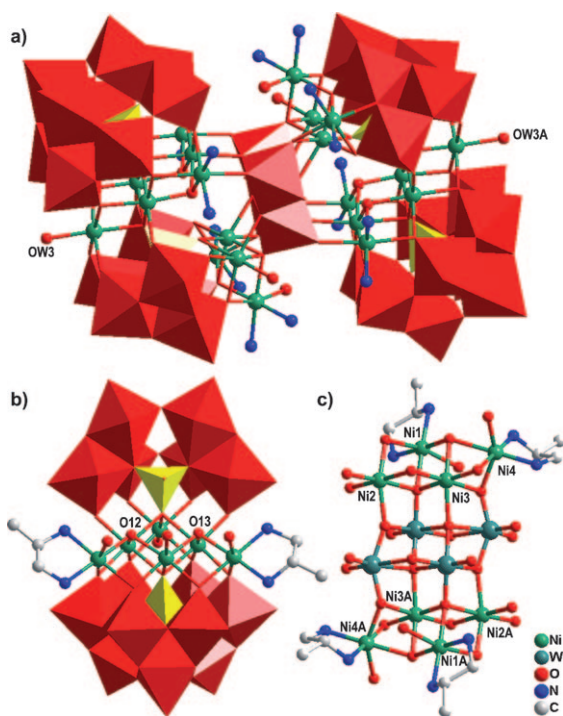


Figure 1. Structures of a) **1a**, b) $\{Ni_6P_2W_{13}\}$, and c) $\{Ni_8W_4\}$. The carbon atoms in (a) and all hydrogen atoms are omitted for clarity. Red WO_6 , yellow PO_4 .

core in **1a** is coordinated by only one terminal H_2O ligand and two enMe ligands, and its remaining coordination sites are all occupied by bridging oxygen atoms from adjacent WO_6 octahedra. Bond valence sum (BVS) calculations^[7] reveal that the bond valences for the μ_3 -O12 and μ_3 -O13 atoms in the Ni_6O_{10} core are -1.13 and -1.12 , respectively, indicating monoprotonation.

The novel belt-like $\{Ni_8W_4\}$ segment is composed of two irregular inorganic–organic hybrid $\{Ni_4O_{10}(H_2O)_2(enMe)_2\}$ units positioned on either side of a rhombohedral W_4O_{16} unit (Figure 1c and Supporting Information, Figure S3). Each $\{Ni_4O_{10}(H_2O)_2(enMe)_2\}$ fragment contains four Ni-based octahedra (two NiO_6 and two NiO_4N_2). Three Ni ions ($Ni1$ – $Ni3$) are joined together by four bridging oxygen atoms to form a truncated Ni_3O_4 cubane. The fourth Ni ion ($Ni4$) attaches to $Ni3$ in an unexpected facial tridentate fashion via three μ -O atoms, forming a unique asymmetric Ni_4O_6 core. A search of the Cambridge Crystallographic Database shows that the linking modes in this Ni_4O_6 core differ from those of known Ni_4 cores. Finally, the Ni_4O_6 core is ligated by two enMe ligands, two terminal water ligands, and four μ -O atoms from adjacent WO_6 and PO_4 polyhedra to form the $\{Ni_4O_{10}(H_2O)_2(enMe)_2\}$ unit. It is noteworthy that the face-shared arrangement of the $Ni3$ and $Ni4$ octahedra leads to significantly shorter $Ni3\cdots Ni4$ separations ($2.647(3)$ Å) and smaller $Ni3$ –O– $Ni4$ angles ($75.9(4)$ – $79.9(5)^\circ$) than other $Ni\cdots Ni$ separations ($3.050(1)$ – $3.224(1)$ Å)

and Ni–O–Ni angles ($92.2(7)$ – $129.5(7)^\circ$) in **1a**. The W_4O_{16} unit is made up of four edge-sharing WO_6 octahedra. Rhombohedral tetranuclear first-row-TM cores have been found in lots of familiar sandwich M_4 -substituted POTs ($M = Mn, Fe, Co, Ni, Cu, Zn$),^[8] but the rhombohedral tetranuclear W_4O_{16} core is rare.

In **1a**, a noteworthy feature is that the two terminal water ligands (OW3 and OW3A) on the $\{Ni_6O_{15}(OH)_2(H_2O)-(enMe)_2\}$ units point out of poly(POT) structure (Figure 1a). Our previous studies confirmed that such terminal water ligands were good centers for further structural derivation, for example, for intramolecular decoration or intermolecular linkage by replacing the terminal water ligand with various bridging organic ligands.^[6] Therefore, **1a** would be an effective precursor for making extended cluster–organic structures. With these considerations in mind, continuous efforts were devoted to making such structures. However, we did not obtain such a complex by changing the conditions of the reaction to form **1**, perhaps owing to steric hindrance of the methyl group of enMe. To reduce the steric hindrance, we replace enMe with en. As expected, an extended cluster–organic chain **2** was successfully isolated (Figure 2), in which the $\{Ni_{20}P_4W_{34}(OH)_4O_{136}(en)_9(H_2O)_4\}$ unit was decorated with two $\{Ni(en)_2(H_2O)\}^{2+}$ groups (Supporting Information, Figure S4). With the exception of the different organic amine ligands, **2** can be derived from **1a** by substituting its terminal

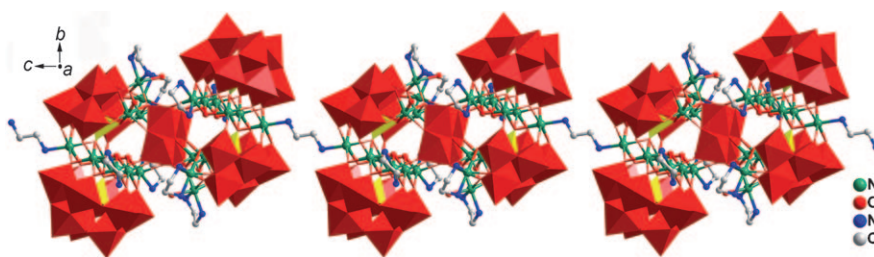


Figure 2. View of the 1D hybrid structure **2**. The nickel complex counteranions are omitted for clarity. Red WO_6 , yellow PO_4 .

water ligands (OW3 and OW3A) with en ligands that act as bridges to link adjacent **1a** units in an end-to-end fashion.

In **1** and **2**, the Ni–O, Ni–N, W=O, W–O, and P–O bond lengths fall in the ranges $1.972(9)$ – $2.240(14)$, $2.000(20)$ – $2.112(13)$, $1.692(18)$ – $1.744(15)$, $1.749(8)$ – $2.526(8)$, and $1.528(8)$ – $1.558(9)$ Å, respectively. BVS calculations show the oxidation states of all P, Ni, and W atoms are $+5$ ($\Sigma_s = 4.79$ – 4.87), $+2$ ($\Sigma_s = 1.89$ – 2.16), and $+6$ ($\Sigma_s = 5.95$ – 6.26), respectively. To balance the charges of **1** and **2**, six and eight protons should be added, respectively. These protons cannot be located crystallographically and are assumed to be delocalized over the entire structures, which is common in polyoxometalates.^[9]

Variable-temperature magnetic susceptibilities for **1** and **2** were measured in the temperature range 2–300 K with an applied magnetic field of 5 kOe (Supporting Information, Figure S5). The experimental $\chi_m T$ values (χ_m is the molar magnetic susceptibility, T is the temperature) of **1** and **2** at 300 K are 28.1 and 27.3 cm³ mol^{−1} K, respectively, which are

expected for 23 and 22 uncoupled high-spin Ni^{2+} ions with $S = 1$ and $g = 2.20$. Upon cooling, the $\chi_m T$ values of **1** and **2** increase to a maximum of $54.61 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 17.1 K and $44.70 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 15.1 K, respectively, then decrease sharply to reach 18.97 and $13.98 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2.0 K, where the sudden decrease might be mainly attributed to the presence of zero-field splitting and intercluster magnetic interactions. The above behaviors suggest that overall ferromagnetic interactions exist in both cases. The temperature dependence of the reciprocal susceptibilities ($1/\chi_m$) obeys the Curie–Weiss law above 50 K for **1** and above 45 K for **2** with positive $\theta = 19.3$ and 12.2 K, respectively (Supporting Information, Figures S6 and S7), which support the presence of overall ferromagnetic coupling between the Ni^{2+} ions in both cases. The Curie constants $C = 27.83$ (**1**) and $26.62 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ (**2**) are also reasonable for 23 and 22 Ni^{2+} ions per formula unit. AC magnetic susceptibilities for **1** and **2** with frequencies between 111 and 3511 Hz were measured under $H_{AC} = 3 \text{ Oe}$, and no frequency dependence is observed.

In summary, two unprecedented 20-Ni-substituted poly(POTs), one a nanocluster and the other a 1D chain, have been successfully made under hydrothermal conditions. The poly(POT) unit in these species, which contains five different metal oxygen fragments, is rare in polyoxometalates. The isolation of the two poly(POT)s not only provides exciting examples of chemical topology but also demonstrates that the combination of hydrothermal techniques and lacunary POT SDAs affords an effective strategy for making large TM-substituted poly(POT)s. Further work is in progress to make novel functional poly(POT)s from other types of multilacunary POT precursors ($[\text{XW}_{10}\text{O}_{36}]^{n-}$, $\text{X} = \text{Si, Ge, P}$; $[\text{X}_2\text{W}_{15}\text{O}_{56}]^{n-}$, $\text{X} = \text{P, As}$; and $[\text{P}_2\text{W}_{12}\text{O}_{48}]^{14-}$) or mixed multilacunary POT precursors under hydrothermal conditions.

Experimental Section

Synthesis of 1: $\text{Na}_9[\text{A}-\alpha\text{-PW}_9\text{O}_{34}]\cdot n\text{H}_2\text{O}$ ($[\text{PW}_9]$) was prepared by the literature method.^[10] $[\text{PW}_9]$ (2.50 g) was stirred in distilled water (20 mL), and then acetic acid (0.125 mL) was added. After stirring for 5 min, $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.80 g) was added to the reaction solution, which was continuously stirred. Further, to this solution K_2CO_3 (0.20 g) and enMe (0.20 mL) were in turn added, and the solution was stirred for 1 h. The resulting solution (pH_s 6.83) was sealed in a 35 mL stainless steel reactor with a Teflon liner and heated at 170 °C for five days and then cooled to room temperature (pH_c 6.62). Green block crystals of **1** were obtained (30.1% yield based on Ni). Elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{186}\text{N}_{28}\text{Ni}_{23}\text{O}_{158}\text{P}_4\text{W}_{34}$: C 4.45, H 1.65, N 3.46, P 1.09, Ni 11.91, W 55.12, found: C 4.34, H 1.82, N 3.37, P 1.04, Ni 12.13, W 54.37. IR (KBr): $\tilde{\nu} = 3437\text{s}, 3281\text{s}, 2943\text{w}, 1593\text{s}, 1453\text{w}, 1387\text{w}, 1345\text{w}, 1041\text{s}, 934\text{s}, 868\text{m}, 786\text{s}, 703\text{s}, 489\text{w cm}^{-1}$.

Synthesis of 2: Solid **2** was obtained using the same procedure as for **1** but substituting en (0.15 mL) for enMe (0.20 mL). 42.3% yield based on Ni. The pH_s and pH_c are 6.73 and 6.58, respectively. Elemental analysis calcd (%) for $\text{C}_{26}\text{H}_{160}\text{N}_{26}\text{Ni}_{22}\text{O}_{162}\text{P}_4\text{W}_{34}$: C 2.81, H 1.45, N 3.28, P 1.12, Ni 11.64, W 56.32; found: C 2.75, H 1.63, N 3.19, P 1.08, Ni 12.01, W 55.99. IR (KBr): $\tilde{\nu} = 3437\text{s}, 2951\text{w}, 1634\text{s}, 1461\text{w}, 1387\text{w}, 1345\text{w}, 1024\text{s}, 942\text{s}, 868\text{m}, 778\text{s}, 712\text{s}, 613\text{m}, 505\text{m cm}^{-1}$.

Crystal data: **1:** $M_r = 11337.3$, monoclinic, space group $P2_1/n$, $a = 14.719(4)$, $b = 33.857(7)$, $c = 22.300(5) \text{ \AA}$, $\beta = 109.09(4)^\circ$, $V = 10502(4) \text{ \AA}^3$, $Z = 2$, $\rho = 3.585 \text{ g cm}^{-3}$, $\mu = 20.671 \text{ mm}^{-1}$, $F(000) = 10236$, GOF = 1.058. A total of 60404 reflections were collected in the range $2.28 \leq \theta \leq 27.50^\circ$, 23877 of which were unique ($R_{\text{int}} =$

0.0479). $R_1(wR_2) = 0.0872(0.1868)$ for 1278 parameters and 17445 reflections ($I > 2\sigma(I)$). **2:** $M_r = 11096.2$, triclinic, space group $P\bar{1}$, $a = 14.848(3)$, $b = 16.819(3)$, $c = 20.934(4) \text{ \AA}$, $\alpha = 89.236(7)$, $\beta = 9.906(5)$, $\gamma = 72.723(5)^\circ$, $V = 4910.7(16) \text{ \AA}^3$, $Z = 1$, $\rho = 3.752 \text{ g cm}^{-3}$, $\mu = 22.008 \text{ mm}^{-1}$, $F(000) = 4986$, GOF = 1.065. A total of 37408 reflections were collected in the range $2.52 \leq \theta \leq 27.48^\circ$, 22307 of which were unique ($R_{\text{int}} = 0.0455$). $R_1(wR_2) = 0.0617(0.1588)$ for 1234 parameters and 19303 reflections ($I > 2\sigma(I)$). CCDC 697696 and 697697 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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