

Chiral Framework | Hot Paper |

The First 3-Connected SrSi₂-Type 3D Chiral Framework Constructed from {Ni₆PW₉} Building UnitsXin-Xiong Li,^[a] Wei-Hui Fang,^[a] Jun-Wei Zhao,^{*,[b]} and Guo-Yu Yang^{*,[a, c]}

Abstract: A novel 3-connected SrSi₂-type 3D chiral framework constructed from hexa-Ni^{II}-cluster-substituted polyoxometalate (POM) units [Ni(enMe)₂]₃[WO₄]₃⁻[Ni₆(enMe)₃(OH)₃PW₉O₃₄]₂·9H₂O (**1**) (enMe = 1,2-diaminopropane) has been made from a hydrothermal synthetic method. This POM represents the first 3D framework based on {Ni₆PW₉} units and {WO₄} connectors.

Polyoxometalates (POMs) as anionic oxide clusters have been attracting extensive interest owing to their enormous structural variety and potential applications in multiple areas, such as catalysis,^[1] magnetism,^[2] and material science.^[3] The POM clusters with diverse shapes, nanosizes, and compositions provide a huge library of readily available and controllable second building units (SBUs) that are prime candidates for the design and construction of interesting and functional architectures by various linkers. To date, many research groups have devoted great efforts to exploring rational synthetic strategies for constructing novel POM-based materials. For example, Müller et al. reported a supramolecular POM-based cage {(M)M₅1₂Fe^{III}₃₀ (M = Mo^{VI}, W^{VI}) based on {M₆O₂₁} SBUs and Fe²⁺ bridges.^[4] Similarly, Cronin et al. created a series of porous frameworks by linking cyclic [P₈W₄₈O₁₈₄]⁴⁰⁻ SBUs with electrophilic Mn²⁺ linkers.^[5] Saturated Keggin/Dawson/Anderson polyanions have often been used as SBUs in the construction of massive inorganic-organic hybrid materials.^[6] Moreover, transition-metal-substituted POMs (TMSPs) can be also utilized as SBUs to build interesting structures from limited aggregates to infinite 3D

frameworks. Typical examples include dimeric/tetrameric aggregates constructed from [V₃P₂W₁₅O₆₂]⁹⁻ and tripodal ligands,^[7] the 1D chain built by [Ni₂₀P₄W₃₄(OH)₄O₁₃₆(en)₆(H₂O)₄]¹²⁻ nanoclusters and en bridges,^[8] the 2D layer consisting of double-Dawson-type [CuP₂W₁₇O₆₀(OH)]₂¹⁴⁻ clusters and [Cu(en)₂]²⁺ linkers,^[9a] the 2D sheet made up of sandwich-type [Zn₄(PW₉O₃₄)₂]¹⁰⁻ units and [Zn(enMe)₂]²⁺ and enMe linkers,^[9b] and the 3D framework assembled from [Cu₆(en)₄(H₂O)₂(SiW₉O₃₄)₂]⁴⁻ clusters and [Cu(H₂O)₂]²⁺ linkers.^[9c] Our group also obtained a class of fascinating 1-, 2- and 3D cluster-organic frameworks based on hexa-Ni^{II}-substituted POM units [Ni₆(μ₃-OH)₃(H₂O)₆(L)₃(B-α-PW₉O₃₄)] (Ni₆PW₉, Ni₆ = [Ni₆(μ₃-OH)₃(H₂O)₆ (L)₃]⁹⁺, PW₉ = [B-α-PW₉O₃₄]⁹⁻, L = en/enMe) connected by multicarboxylate units.^[10a] More interestingly, a hybrid cubic POM molecular cage based on Ni₆PW₉ SBUs and 1,3,5-benzenetricarboxylic acid has also been made by us recently.^[10b]

As shown above, although various kinds of linkers, such as transition-metal cations, multicarboxylates, and organoamine molecules, have been extensively used in the construction of POM-based materials,^[4-10] linking TMSP SBUs by means of oxometal anionic groups generating extended POM-based materials remains largely unexplored, mainly because TMSP SBUs are usually highly negatively charged and have oxygen-rich compositions, which leads to the preferential bonding of metal cations rather than metaloxo anions. Recently, the hydrothermal technique has been proved to be an extraordinarily powerful synthetic strategy for preparing many uncommon structures that cannot be obtained through the conventional solution method.^[11] Thus, we decided to introduce oxometal anionic groups to connect TMSP SBUs for novel POM materials under hydrothermal conditions. In this work, we chose the WO₄²⁻ anion as the bridge and Ni₆PW₉ as the SBU based on the following facts: 1) Ni₆PW₉ units have been proved by us to be highly active SBUs in the construction of extended POM frameworks, as six accessible coordinated water ligands on the top can be easily substituted by other groups,^[10a] and 2) we have observed the substitution of coordinated water ligands on Ni₆ cluster, in a discrete Ni₄₀-based poly(polyoxotungstate) octamer, by in-situ generated WO₄²⁻ anions.^[12]

In this work, we report on the introduction of Na₂WO₄, and successfully realized the replacement of six coordinated water ligands of Ni₆PW₉ by three WO₄²⁻ ions (Figure 1 a,b), affording an unprecedented 3D POM framework [Ni(enMe)₂]₃[WO₄]₃[Ni₆(enMe)₃(OH)₃PW₉O₃₄]₂·9H₂O (**1**), in which Ni₆PW₉ units act as SBUs and tetrahedral WO₄²⁻ groups function as bridges. So far, reports on POM structures containing tetrahedral WO₄²⁻

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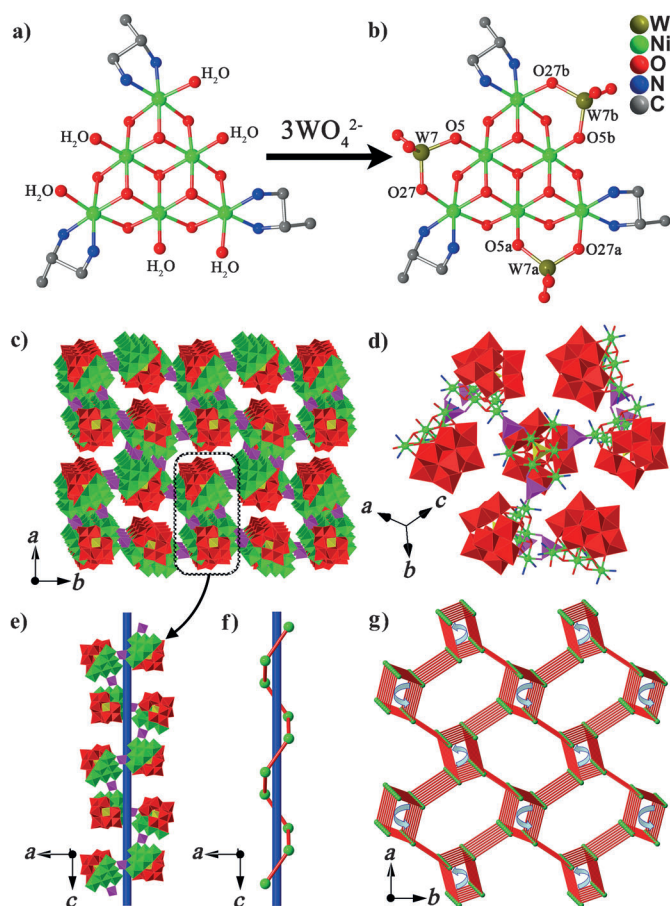


Figure 1. a) Ball and stick representation of Ni_6 cluster. b) Ball and stick representation of WO_4^{2-} ligands substituted Ni_6 cluster. Symmetry codes: a $(-1+y, 1+z, x)$, b $(z, 1+x, -1+y)$. c) View of the 3D framework of **1** along the c axis. d) View of the connectivity of a Ni_6PW_9 SBU with three neighbouring ones along (111) direction. e) View of the right-handed helical chain constructed by Ni_6PW_9 SBUs and WO_4 linkers. f) View of the simplified right-handed helical chain. g) The 3D topology of **1** along the c axis. For d)–e), Ni_6PW_9 node: green. Color code: WO_6 : red; PO_4 : yellow; WO_4 : purple; $\text{NiO}_6/\text{NiO}_4\text{N}_2$: green.

groups are very rare.^[12,13] To our knowledge, **1** is the first 3D POM framework based on Ni_6PW_9 SBUs and tetrahedral $\{\text{WO}_4\}$ linkers.

Crystals of **1** were obtained by the hydrothermal reaction of $[\text{A}-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, enMe, and Na_2WO_4 at 170°C for 3 days, and the consistency of the experimental powder X-ray diffraction pattern with the simulated one indicates the good phase purity of **1** (Figure S1 in the Supporting Information). Single-crystal X-ray structural analysis reveals that **1** crystallizes in the cubic $P2_13$ chiral space group and the structural unit consists of two Ni_6PW_9 clusters, three tetrahedral WO_4^{2-} groups, and three $[\text{Ni}(\text{enMe})_2]^{2+}$ cations. Compound **1** exhibits a 3D extended structure based on Ni_6PW_9 SBUs and WO_4^{2-} bridges (Figure 1 c). The structure of Ni_6PW_9 can be described as a well-known trivalent Keggin $[\text{B}-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ unit capped by a Ni_6 cluster (Figure S2 in the Supporting Information). The Ni_6 cluster is made up of six nearly coplanar Ni^{2+} ions in a triangle motif linked together by three $\mu_3\text{-OH}$ groups, six $\mu_3\text{-O}$ atoms from six WO_6 groups, one $\mu_4\text{-O}$ atom from the central

PO_4 group and further stabilized by six H_2O and three enMe ligands. The most striking structural feature in **1** is that the six coordinated water ligands on Ni_6PW_9 unit are replaced by three WO_4^{2-} groups to form a $\{\text{W}_3\text{O}_6(\text{Ni}_6\text{PW}_9)\}$ unit with C_{3v} symmetry (Figure 1 a,b and Figure S3 in the Supporting Information). Each WO_4^{2-} group coordinates to Ni_6PW_9 by replacing two terminal water ligands and each WO_4^{2-} group adopts the $\eta^1:\eta^1:\mu_2$ coordination mode. Thus, each Ni_6PW_9 unit acts as a triangular three-connected SBU (Figure 1 d, Figure S3 in the Supporting Information). The W–O distances in the WO_4^{2-} groups are in the range of 1.754(6)–1.781(6) Å, and the $\angle\text{O-W-O}$ bond angles vary from 107.3(3) to 110.0(2)°, which is quite close to that of the standard XO_4 group, indicating that WO_4^{2-} groups retain the ideal geometrical configuration without any evidence of distortion after replacing the terminal water ligands. Generally, the distances between two neighboring water ligands in similar Ni_6 clusters are 2.871–3.253 Å,^[10] whereas the O–O distances in the WO_4^{2-} groups in **1** vary between 2.892(4)–2.903(5) Å, which demonstrates that the WO_4^{2-} groups are well matched with Ni_6 cluster with respect to steric considerations, thus WO_4^{2-} groups can substitute the terminal water ligands. So far, the substitution of water ligands on Ni_6 cluster by various organic or inorganic ligands has been observed;^[10,11] however, substitution of all six water ligands by WO_4^{2-} has not been reported. It should be noted that SBUs can further expand to the extended framework by the bridging role of WO_4^{2-} groups, which is another striking structural feature of **1**. Each Ni_6PW_9 unit connects to three neighboring Ni_6PW_9 units through three WO_4^{2-} groups (Figure 1 d), resulting in an unprecedented 3D POM framework (Figure 1 c, Figure S4 in the Supporting Information). In **1**, the alignment of Ni_6PW_9 units and WO_4^{2-} bridges along 2_1 screw axis forms a right-handed helical chain along the c axis (Figure 1 e,f). All the right-handed helical chains are further linked together by WO_4^{2-} along both the a and b axes to yield a 3D chiral framework with 1D irregular channels (dimensions of $1.78 \times 1.06 \text{ nm}^2$, measured between the opposite polyhedra) in which the $[\text{Ni}(\text{enMe})_2]^{2+}$ cations and water molecules are located (Figure S5 in the Supporting Information). In addition, a clockwise orientation arrangement of the Ni_6PW_9 units can be also observed along (111) direction (Figure S6 in the Supporting Information), which further testifies the chiral framework of **1**. From the topological point of view, the 3D framework of **1** is a 3-connected network, in which each Ni_6PW_9 acts as a 3-connected node. A topological analysis of this net was performed with TOPOS 4.0 and the long topological (O’Keeffe) vertex symbol is $10_5 \cdot 10_5 \cdot 10_5$ for Ni_6PW_9 node, which gives the short vertex (Schläfli) symbol of (10^3) , indicating that **1** possesses a chiral SrSi_2 -type topology (Figure 1 g). Although chiral 10^3 networks based on metal ions and organic ligands in metal–organic frameworks have been investigated,^[14] there is no example based on POM units. To our knowledge, **1** represents the first 3D 3-connected SrSi_2 -type POM framework based on Ni_6PW_9 SBUs and WO_4^{2-} bridges.

Variable-temperature magnetic susceptibility of **1** was measured in the temperature range of 2–300 K with an applied magnetic field of 1 KOe (Figure 2). The experimental $\chi_m T$ value

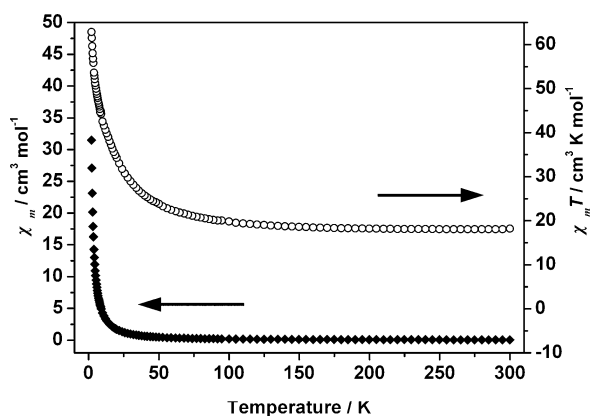


Figure 2. The plots of temperature dependence of χ_m (\blacklozenge) and $\chi_m T$ (\circ) values for **1** between 2 and 300 K.

(χ_m is the molar magnetic susceptibility, T is the temperature) of **1** at 300 K is $18.19 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ per formula unit, being consistent with the theoretical value ($18.15 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) expected for fifteen uncoupled high-spin Ni^{2+} ions with $S=1$ and $g=2.20$. Upon cooling, the $\chi_m T$ value slowly increases to $21.39 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 70 K, and then rapidly reaches the maximum of $62.86 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. This magnetic behaviour suggests that overall ferromagnetic interactions exist between the Ni^{2+} ions in **1**.^[15] The temperature dependence of the reciprocal susceptibility ($1/\chi_m$) obeys the Curie–Weiss law above 25 K (Figure S7 in the Supporting Information) with a positive Weiss constant $\theta = 13.07 \text{ K}$ and Curie constant $C = 17.14 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which further supports the existence of overall ferromagnetic coupling between the Ni^{2+} ions. In **1**, the magnetic interactions within Ni^{2+} ions are chiefly transmitted through the $\mu_3\text{-O}$, $\mu_3\text{-OH}$, and $\mu_4\text{-O}$ bridges. Previous research suggests that the magnetic coupling is highly sensitive to the values of the $\angle\text{Ni-O-Ni}$ bridging angles: the coupling is ferromagnetic for angles in the range of $90 \pm 14^\circ$, while it is antiferromagnetic for larger angles.^[16] The $\angle\text{Ni-O-Ni}$ angles in **1** vary between $91.9(2)$ and $102.4(2)^\circ$, and are thus in the expected range for ferromagnetic coupling. Actually, such distribution motif of six octahedral Ni^{2+} ions was observed in the previous studies.^[10–12] In these studies, the magnetic behavior of the Ni_6 clusters was investigated and the experimental and theoretical results showed that such nickel clusters exhibit ferromagnetic coupling interactions.

In summary, an unprecedented SrSi_2 -type 3D framework based on Ni_6PW_9 SBUs and tetrahedral WO_4^{2-} linkers was synthesized by hydrothermal methods. The experimental result testifies that the inorganic oxometal anionic WO_4^{2-} group is an excellent linker to bridge TMSP clusters together giving rise to novel extended POM-based materials. The successful synthesis of **1** not only enriches the structural diversity of TMSPs, but also provides an effective and feasible strategy to design and create more interesting POM structures. Investigations are underway to use other inorganic anionic linkers, such as MoO_4^{2-} , MnO_4^- , AsO_4^{3-} , SiO_4^{2-} , to replace WO_4^{2-} groups to make the novel extended frameworks under hydrothermal conditions. It is reasonable to believe that the present work will be impor-

tant in expanding the study of the construction of POM-based materials.

Experimental Section

Preparation of 1: $\text{Na}_9[\text{A-}\alpha\text{-PW}_9\text{O}_{34}] \cdot n\text{H}_2\text{O}$ (PW_9) was prepared by the literature method.^[17] $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.300 g, 1.21 mmol) and PW_9 (0.400 g, 0.16 mmol) were stirred in distilled water (15 mL, 833 mmol) for 5 min, forming a light yellow-green solution. enMe (0.20 mL, 2.356 mmol) was added dropwise with continuous stirring. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.300 g, 0.91 mmol) was added and the resulting mixture was stirred for 120 min. The resulting solution ($\text{pH}_s = 8.1$) was sealed in a 35 mL stainless steel reactor with a teflon liner steel autoclave, was heated at 170°C for 3 days, and then cooled to room temperature. Green prismatic crystals of **1** were obtained ($\text{pH}_e = 7.9$). Elemental analysis calcd (%) for $\text{H}_{144}\text{C}_{36}\text{N}_{24}\text{O}_{95}\text{P}_2\text{Ni}_{15}\text{W}_{21}$: C 5.98, H 2.00, N 4.65; found: C 6.06, H 2.07, N 4.62.

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