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Combination between [B- α -SiW₉O₃₄] unit and triangular inorganic Ni₆ core under hydrothermal conditions: from monomer to rare dimer with malposed dodeca-nickel center†Cite this: *Dalton Trans.*, 2013, **42**, 364

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The hydrothermal reactions of α -K₄SiW₁₂O₄₀ with NiCl₂·6H₂O yielded two unprecedented silicotungstates containing a triangular inorganic Ni₆ core. Furthermore, Na₂[Ni₆(μ ₃-OH)₃(H₂O)₉-SiW₉O₃₄]₂·17H₂O (**1**) presents a rare dimer, in which two SiW₉ units sandwich double Ni₆ cores by W–O–Ni linking instead of conventional Ni–O–Ni.

Polyoxometalates (POMs) have attracted considerable interest because of their potential and realized applications in catalysis, photochemistry, medicine, electrical conductivity, magnetism and nanotechnology.¹ Recently, much attention has been focused on the incorporation of transition metal (TM) ions in lacunary polyoxoanion fragments forming high-nuclear transition-metal-substituted POMs (TMSPs) with unique magnetic properties.² So far, most investigations have focused on the syntheses of TMSPs by a conventional aqueous solution method using lacunary polyoxoanions as precursor.³ Most TMSPs present classic sandwich structural types containing no more than five paramagnetic TM clusters^{4–8} (mono-,⁴ di-,⁵ tri-,⁶ tetra-⁷ and penta-nuclear⁸). Thus, interest in their magnetic properties has driven the search for new approaches to make novel structural TMSPs with a higher number of TM clusters.

To date, the chemistry of Ni-substituted TMSPs⁹ has been extensively studied, however, the number of Ni ions in a single lacunary Keggin fragment is seldom more than four. High-nuclear Ni clusters may possess a large spin ground state and a negative axial anisotropy and may exhibit single-molecule magnetism.¹⁰ Therefore, many groups have devoted great efforts to explore synthetic strategies for making TMSPs with novel high-nuclear Ni clusters. Especially, Yang group isolated

the first triangular inorganic–organic hybrid {Ni₆} in 2007.¹¹ Then, a series of isolated hybrid {Ni₆}-containing Ni₆O₇-(μ ₃-OH)₃(L)_{2–3}(H₂O)_xXW₉ (X = Si, P) were synthesized by changing the organic ligand (denoted as L).¹² Further, the terminal water ligands and three μ ₃-OH groups in the {Ni₆} core can be replaced not only by inorganic ligands, but also by rigid carboxylate ligands, forming a suite of fascinating frameworks with 1-, 2-, and 3-D structures.¹³ Besides, the combinations between the Ni₆XW₉ unit and other units generated high-nuclear Ni-substituted polyoxometalates:¹⁴ such as 11 nickel centers^{14a} and 20–22 nickel centers.^{14b,c} As mentioned previously, more terminal water ligands in the Ni₆ core may indicate increased potential to form novel cluster-organic frameworks with organic ligands. Therefore, the Yang group has tried to obtain the Ni₆-encapsulated compounds by removal of en ligands and replacement with water molecules, however, such a pure inorganic Ni₆-cluster has not been isolated.¹²

We were inspired by the above-mentioned work of Yang and took into consideration that whether the pure inorganic Ni₆-cluster could be isolated by changing the [SiW₉O₃₄]^{10–} precursor and controlling the pH value. We chose saturated K₄SiW₁₂O₄₀ as the precursor boiling in the HAc–NaAc buffer solution at an appropriate pH value. Herein, we report the hydrothermal synthesis and structure of two unprecedented silicotungstates containing an inorganic triangular Ni₆ core: Na₂[Ni₆(μ ₃-OH)₃(H₂O)₉ SiW₉O₃₄]₂·17H₂O (**1**) and HNi₆(μ ₃-OH)₃-(H₂O)₁₂SiW₉O₃₄·7H₂O (**2**). As far as we know, **1** and **2** are the first examples of triangular inorganic {Ni₆}-containing silicotungstates. Notably, the polyoxoanion [Ni₆(μ ₃-OH)₃(H₂O)₉-SiW₉O₃₄]₂^{2–} of **1** presents a rare dimer, in which two malposed {Ni₆SiW₉} units sandwich double inorganic {Ni₆} units by Ni–O–W junctions.

Crystals of **1** and **2** were only obtained by hydrothermal reactions and not obtained by solution syntheses at atmospheric pressure. **1** was separated by the reaction of [α -K₄SiW₁₂O₄₀] precursor and NiCl₂·6H₂O in sodium acetate buffer at 160 °C for 7 days.† It is noteworthy that pretreatment

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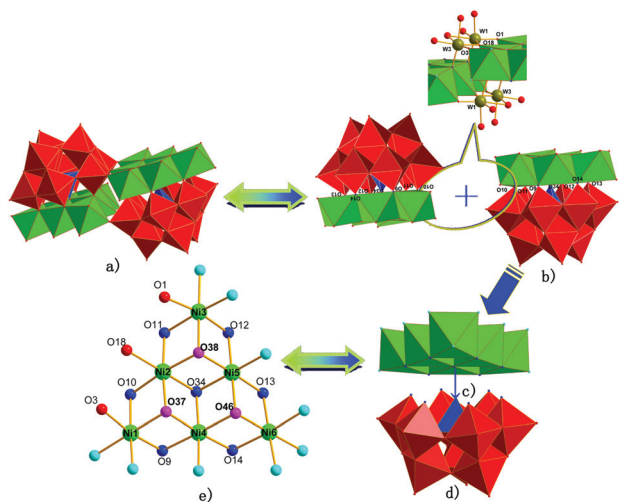


Fig. 1 (a) Side view of **1**, sodium ions and water molecules are omitted for clarity. (b) View of $[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_9\text{SiW}_9\text{O}_{34}]^{2-}$ (Ni_6SiW_9) unit. (c) Polyhedral representation of $\{\text{Ni}_6\}$. (d) View of $\text{B-}\alpha\text{-}[\text{SiW}_9\text{O}_{34}]^{10-}$ unit. (e) Ball-and-stick representation of $\{\text{Ni}_6\}$. The distances for W–O and Ni–O: 1.705(8)–2.404(7) and 1.982(7)–2.244(8) Å, respectively. (Color code: WO_6 , red; SiO_4 , blue; NiO_6 , green; O atoms from SiW_9A , blue; O atoms from SiW_9B , red; O atoms from terminal water, sky blue; O atoms from hydroxyls, purple).

of $\alpha\text{-K}_4\text{SiW}_{12}\text{O}_{40}$ is integral to the purpose of attaining some active fragment of the polyoxoanion. To explore the pH influence on the synthesis system, parallel experiments have been carried out by systematically changing the pH value and monomer **2** was isolated at a higher pH.

X-Ray analyses reveal that **1** and **2** contain a similar hexanuclear $[\text{Ni}_6(\mu_3\text{-OH})_3]^{9+}$ core and trivalent $\text{SiW}_9\text{O}_{34}$ units. Therefore, only the structure of **1** is described in detail. **1** consists of one anion $[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_9\text{SiW}_9\text{O}_{34}]^{2-}$, two Na^+ cations and seventeen water molecules. The structure of the polyanion $[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_9\text{SiW}_9\text{O}_{34}]^{2-}$ in **1** (Fig. 1a) can be viewed as two $[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_9\text{SiW}_9\text{O}_{34}]^-$ (Ni_6SiW_9) units (Fig. 1b) in opposite directions linked by six $\mu_3\text{-O}$ bridge (O18, O10, O11) and four $\mu_2\text{-O}$ bridge (O1, O3) *via* NiO_6 (Ni1-Ni3) octahedra sharing corner O atoms with WO_6 (W1, W3) octahedra. Ni_6SiW_9 can be described as a $\text{B-}\alpha\text{-}[\text{SiW}_9\text{O}_{34}]^{10-}$ unit (Fig. 1d) capped by a triangular Ni_6 core (Fig. 1c), in which a $[\text{Ni}_6(\mu_3\text{-OH})_3]^{9+}$ triangle comprising six Ni^{2+} ions and three hydroxyls (O37, O38, O46) is stabilized by nine terminal water ligands, seven O (O9–O14 and O34) atoms from the $\text{B-}\alpha\text{-}[\text{SiW}_9\text{O}_{34}]^{10-}$ unit (SiW_9A) and three O (O1, O3, O18) atoms from another $\text{B-}\alpha\text{-}[\text{SiW}_9\text{O}_{34}]^{10-}$ unit (SiW_9B).

In the $\{\text{Ni}_6\}$ unit, the Ni^{2+} ions can be divided into two groups according to the located positions: middle of the edge (Ni2/Ni4/Ni5) and vertex of the triangle (Ni1/Ni3/Ni6). The three middle NiO_6 octahedra are located at the trivalent sites of $\text{B-}\alpha\text{-}[\text{SiW}_9\text{O}_{34}]^{10-}$, while the three vertex NiO_6 octahedra are further attached to the middle Ni3 triad unit by edge-sharing to form a novel Ni_6 aggregate. It is also described as the Ni_6 core is linked by three truncated cubanes of $\{\text{Ni}_3\text{O}_4\}$ *via* sharing one edge with each other, and all sharing a common vertex ($\mu_4\text{-O34}$). Albeit all the six crystallographically

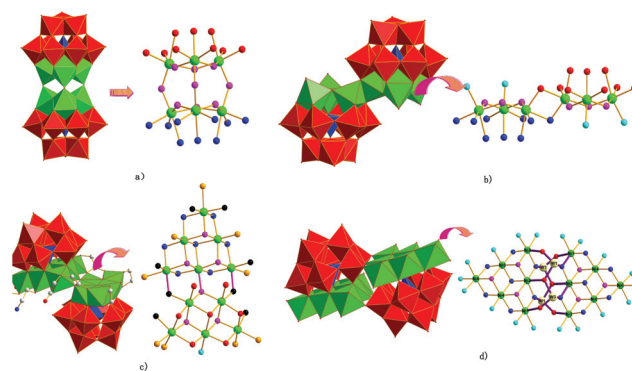


Fig. 2 Structural diversity between **1** and reported TM-substituted Keggin dimers: (a) classical sandwich-type dimer $[(\alpha\text{-SiFe}_3\text{W}_9(\text{OH})_3\text{O}_{34})_2(\text{OH})_3]^{11-15}$ (b) dimer $[(\alpha\text{-Si}(\text{FeOH}_2)_2\text{FeW}_9(\text{OH})_3\text{O}_{34})_2]^{8-15}$ (c) dimer $[\text{Ni}_{11}(\text{PW}_9)_2(\text{IDA})_3(\text{en})_2(\text{Hen})_2(\text{OH})_6]^{6-14a}$ (d) dimer **1** (Color code: MO_6 , green; WO_6 , red; $\text{Si}(\text{P})\text{O}_4$, blue; W, yellow; O atoms from hydroxy, purple; O atoms from XW_9A , blue; O from XW_9B , red; O atoms from terminal water, sky blue; O atoms from organic ligands, black; N, orange).

independent Ni^{II} ions reside in the octahedral geometries, they display four kinds of octahedral environments in **1** (Fig. S1a[†]). Structurally, the Ni_6 core is similar to the reported Ni_6 core,^{11–14} however, the Ni_6 core in **1** and **2** presents three remarkable points of novelty: 1. The Ni_6 core is an inorganic cluster, while the Ni_6 core in the reported compounds is a hybrid cluster; 2. There are eighteen terminal water ligands in **1** and twelve terminal water ligands in **2**, while the highest number of terminal water ligands in the reported Ni_6 core is eight (Fig. S1b[†]); 3. The environments of Ni ions are different (Fig. S1[†]). Additionally, BVS calculations (Tables S2–S3[†]) reveal that the range of bond valences for the nine terminal O atoms is 0.31–0.34, strongly suggesting diprotonation; while the bond valences of the three $\mu_3\text{-O}$ (O37, O38, O46) are 1.16, 1.13 and 1.10, respectively, indicating monoprotonation. This is also consistent with the overall charge balance of **1**.

It is noted that **1** presents a novel dimer different from the reported TM-substituted Keggin dimers (Fig. 2). $[(\alpha\text{-SiFe}_3\text{W}_9(\text{OH})_3\text{O}_{34})_2(\text{OH})_3]^{11-15}$ (Fig. 2a) is the classical dimer in which two directly facing Fe_3SiW_9 units are connected by three $\text{Fe-}\mu_2\text{-OH-Fe}$ bonds. Moreover, two especial dimer polyoxotungstates: $[(\alpha\text{-Si}(\text{FeOH}_2)_2\text{FeW}_9(\text{OH})_3\text{O}_{34})_2]^{8-15}$ and $[\text{Ni}_{11}(\text{PW}_9)_2(\text{IDA})_3(\text{en})_2(\text{Hen})_2(\text{OH})_6]^{6-14a}$ have been reported. In $[(\alpha\text{-Si}(\text{FeOH}_2)_2\text{FeW}_9(\text{OH})_3\text{O}_{34})_2]^{8-}$ (Fig. 2b), two malposed $[\alpha\text{-Si}(\text{FeOH}_2)_2\text{FeW}_9(\text{OH})_3\text{O}_{34}]^{4-}$ units are linked by a single edge *via* two Fe-O-Fe bonds, and in $[\text{Ni}_{11}(\text{PW}_9)_2(\text{IDA})_3(\text{en})_2(\text{Hen})_2(\text{OH})_6]^{6-}$, Ni_6PW_9 and Ni_5PW_9 units are linked by three $\text{Ni-}\mu_3\text{-O-Ni}$ bonds (Fig. 2c). Whereas herein, two malposed Ni_6SiW_9 units are linked by six $\mu_3\text{-O}$ bridge and four $\mu_2\text{-O}$ bridge *via* Ni-O-W bonds instead of M-O(OH)-M bonds (Fig. 2d). Ni-O-W junctions in Keggin dimers are rare, as a majority of complexes structurally characterized to date have exclusively M-O(OH)-M junctions. Additionally, **1** is the fourth example of nickel substituted POMs with the number of the nickel ions higher than 10 reported so far, the other three are $[\text{Ni}_{11}(\text{PW}_9)_2(\text{IDA})_3(\text{en})_2(\text{Hen})_2(\text{OH})_6]^{6-14a}$

$[\text{Ni}(\text{enMe})_2]_3[\text{H}_6\text{Ni}_{20}\text{P}_4\text{W}_{34}(\text{OH})_4 \text{O}_{136}(\text{enMe})_8(\text{H}_2\text{O})_6] \cdot 12\text{H}_2\text{O}$,^{14b} and $[\text{Ni}_{12}(\text{OH})_9\text{WO}_4(\text{W}_7\text{O}_{26}(\text{OH}))(\text{PW}_9\text{O}_{34})_3]^{25-}$,¹⁶ respectively.

2 consists of one anion $[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_{12}\text{SiW}_9\text{O}_{34}]^-$, one proton and seven water molecules (Fig. S2†).

As shown in Fig. S3a,† the two $\{\text{Ni}_6\}$ units are separated by four nonmagnetic WO_6 octahedra and the magnetic coupling among two $\{\text{Ni}_6\}$ units is so weak as to be negligible, and therefore the magnetic behavior of **1** can be viewed as the addition of the magnetic behavior of two isolated $\{\text{Ni}_6\}$ units. The exchange coupling between adjacent Ni^{2+} ions is mainly transmitted through the $\mu_2\text{-O}$, $\mu_3\text{-O}$, $\mu_3\text{-OH}$ and $\mu_4\text{-O}$ bridges. The Ni–O–Ni angles, Ni–O bond distances and Ni...Ni distances in the $\{\text{Ni}_6\}$ lie in the range of $92.3(3)\text{--}100.9(3)^\circ$, $1.982(7)\text{--}2.244(8)$ Å and $3.013\text{--}3.112$ Å in **1** and $93.0(4)\text{--}101.0(3)^\circ$, $1.993(8)\text{--}2.122(8)$ Å and $3.045\text{--}3.090$ Å in **2** (Fig. S3b†). Such a distribution motif of the six octahedral Ni^{2+} ions has been observed in previous studies,^{11–14} in which experimental and theoretical investigations of the magnetic behaviors of the $\{\text{Ni}_6\}$ unit showed that they exhibit ferromagnetic coupling interactions. The bond lengths and angles of **1** and **2** are comparable to those in the nickel substituted Ni_6XW_9 (Fig. S3†), therefore, the presence of ferromagnetic exchange interactions is also expected in **1** and **2**. To further affirm our expectation, **1** was selected as an example for magnetic characterization. Temperature-dependent magnetic susceptibility measurements for **1** were performed in the temperature range of 2–300 K under an external magnetic field of 0.2 T. The temperature dependence of χ_M and $\chi_M T$ is shown in Fig. 3. The χ_M value of **1** slowly increases from $0.05951 \text{ emu mol}^{-1}$ at 300 K to $1.054 \text{ emu mol}^{-1}$ at 32 K, and then rapidly reaches $2.438 \text{ emu mol}^{-1}$ at 2 K. The experimental $\chi_M T$ values of **1** at room temperature are $17.85223 \text{ emu K mol}^{-1}$ at 300 K, which are expected for twelve uncoupled high-spin Ni^{2+} ion with $S = 1$, $g > 2$. Upon cooling, the $\chi_M T$ values of **1** increase to a maximum of $33.74599 \text{ emu K mol}^{-1}$ at 32 K, then decrease sharply, which might be mainly attributed to the presence of zero-field splitting (ZFS). The behavior suggests that there exist overall ferromagnetic interactions with the presence of ZFS for Ni^{2+} ions. The temperature dependence of the reciprocal

susceptibilities ($1/\chi_M$) obeys the Curie–Weiss law above 50 K for **1** with $\theta = 27.771$ K, which further supports the presence of ferromagnetic coupling in **1** (Fig. S4†).

In summary, two unprecedented silicotungstates containing inorganic $\{\text{Ni}_6\}$: $\text{Na}_2[\text{Ni}_6(\text{OH})_3(\text{H}_2\text{O})_9\text{SiW}_9\text{O}_{34}] \cdot 17\text{H}_2\text{O}$ (**1**) and $\text{HNi}_6(\text{OH})_3(\text{H}_2\text{O})_{12}\text{SiW}_9\text{O}_{34} \cdot 7\text{H}_2\text{O}$ (**2**) have been successfully hydrothermally synthesized, characterized by IR spectra, X-ray diffraction, magnetic properties. Notably, **1** and **2** possess a large number of highly active oxygen atoms (terminal oxygen atoms from WO_6 octahedra and terminal water), which provides us with the possibility of forming novel multi-dimensional POMs by introducing heterometallic cations or organic ligands. **1** and **2** promisingly work as readily available precursors in the preparation chemistry of POM-based lanthanide/organometal derivatives with novel magnetic properties. We believe that some interesting results will be obtained in due time.

Acknowledgements

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Notes and references

† Synthesis of **1** and **2**: $\text{K}_4\text{SiW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (0.5 g) was dissolved in the 13 ml HAc–NaAc buffer solution (pH 5.5) boiling for 0.5 h and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2 mmol) and pyridine-2,5-carboxylic acid (0.2 mmol) were added. Stirred for 2 h at room temperature, the resulting mixture was transferred to a Teflon-lined steel autoclave and kept at 160°C for seven days. After slowly cooling to room temperature, the green block single crystals were filtered. **2** was prepared using a method similar to that employed for the synthesis of **1**, except the pH value was adjusted to 8 with NaOH. Anal. Calc. (found %) for $\text{H}_7\text{Na}_2\text{Ni}_{12}\text{O}_{109}\text{Si}_2\text{W}_{18}$ **1**: (Yield: ca. 13% based on $\text{K}_4\text{SiW}_{12}\text{O}_{40}$) Na, 0.77(0.75); H, 1.28(1.26); Ni, 11.86(11.95); Si, 0.95 (0.91); W, 55.74(55.82); for $\text{H}_{42}\text{Ni}_6\text{O}_{58}\text{SiW}_9$ **2**: (Yield: ca. 11% based on $\text{K}_4\text{SiW}_{12}\text{O}_{40}$) H, 1.41(1.43); Ni, 11.84(11.76); Si, 0.94(0.98); W, 55.64(55.54).

§ Crystal data: For **1**, $M_r = 5936.59$, monoclinic, space group $P2_1/c$, $a = 16.7174(17)$, $b = 18.2134(19)$, $c = 15.0644(16)$ Å, $\beta = 96.022(2)^\circ$, $V = 4561.5(8)$ Å³, $Z = 2$, $\mu = 25.170 \text{ mm}^{-1}$, $F(000) = 5332$, $GOF = 1.047$. Of 23614 total reflections collected, 8017 were unique ($R_{\text{int}} = 0.0585$). $R_1(wR_2) = 0.0349$ (0.0786) for 668 parameters and 8017 reflections [$I > 2\sigma(I)$]. For **2**, $M_r = 2973.34$, orthorhombic, space group $Pnma$, $a = 18.8278(15)$, $b = 20.7853(16)$, $c = 12.2101(10)$ Å, $\beta = 90^\circ$, $V = 4778.3(7)$ Å³, $Z = 4$, $\mu = 24.023 \text{ mm}^{-1}$, $F(000) = 5352$, $GOF = 1.026$. Of 30 182 total reflections collected, 6061 were unique ($R_{\text{int}} = 0.0884$). $R_1(wR_2) = 0.0424$ (0.1106) for 355 parameters and 6061 reflections [$I > 2\sigma(I)$].

Data were collected at 296 K on a Bruker Smart APEXII CCD diffractometer for **1** and **2** using graphite-monochromated Mo–K α radiation ($\lambda = 0.71073$ Å), respectively. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program. Direct methods were used to solve the structure and refined by full-matrix least-squares on F^2 using the SHELXTL-97 program package. No H atoms associated with the water molecules were located in the difference Fourier map. Further details on the crystal structure investigations may be obtained from the e-mail: crysdata@fiz-karlsruhe.de, on quoting the depository numbers CSD 424904 (**1**) and 424905 (**2**).

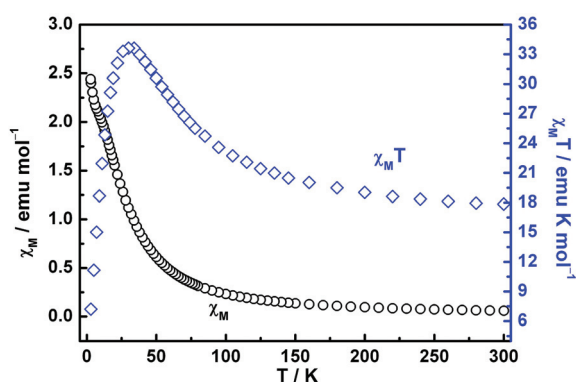


Fig. 3 Thermal dependence of the magnetic susceptibility χ_M (bottom) and the product of the magnetic susceptibility times temperature $\chi_M T$ (top) for **1**, recorded on a powder sample at an applied field of 0.2 T.

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