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Synthesis, Characterization, and Crystal Structures of Two Novel High-Nuclear Nickel-Substituted Dimeric Polyoxometalates

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Two novel high-nuclear Ni-substituted polyoxometalates $Na_9K[Ni_7(OH)_4(H_2O)(CO_3)_2(HCO_3)(A\text{-}\alpha\text{-}SiW_9O_{34})(\beta\text{-}SiW_{10}O_{37})]\cdot 5H_3O\cdot 18H_2O$ (**1**) and $K_6Na_4[\{Ni_6(H_2O)_4(\mu_2\text{-}H_2O)_4(\mu_3\text{-}OH)_2\}(x\text{-}SiW_9O_{34})_2]\cdot 17.5H_2O$ (**2**) have been obtained by reaction of $K_8[\gamma\text{-}SiW_{10}O_{36}]$ with $NiCl_2\cdot 2H_2O$ in basic conditions. Compounds **1** and **2** all represent the first polyoxometalates substituted by seven and six Ni centers, respectively. Also, compound **1** exhibits a novel asymmetric dimeric structure, composed of $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ and $[\beta\text{-}SiW_{10}O_{37}]^{10-}$ units linked by a Ni_7 cluster and three carbonates, which exhibit tri- and bidentate coordination modes in **1**.

Polyoxometalates (POMs), as early-transition-metal oxide clusters, have been attracting extensive interest in fields such as catalysis, ion exchange, electrochemistry, electrochromism, magnetism, and medicine for their enormous variety of structures and unique properties.[1−3] Recently, much work has been done on the synthesis of the novel POMs possessing unique structures and properties. In the vast amount of reported work, the rapid progress in the synthesis and characterization of new transition-metal-substituted POMs (TMSPs)[4] is driven by interest in their structural diversity and fascinating properties with applications to catalysis, magnetism, and electrochemistry, though the reactive mechanism has not been clear.

Within the class of TMSP, the sandwich-type polyoxoanions, accommodating lots of paramagnetic transition-metal cations between the two lacunary polyoxoanions, are an important subclass, in which the $[M_4(XW_9)_2]^{n-}/[M_4(X_2W_{15})_2]^{n-}$ type[5] with two lacunary polyoxoanions connected by a tetrametal set and the $[M_3(XW_9)_2]^{n-}/[M_3(X_2W_{15})_2]^{n-}$ type[6] with a trimetal set between the two lacunary polyoxoanions are usually reported. Recently, the dinuclear sandwich complexes $[M_2(XW_9)_2]/[M_2(X_2W_{15})_2]$ have been documented.[7] Transition-metal Ni is the most commonly used; up to now, a large number of Ni-substituted complexes have been reported. However, as far as we know, the number of substitutions among the reported examples is less than five.[8] So, it is also highly interesting in the fields to synthesize such polyoxoanions with a larger number of Ni^{2+} ions. Inspired by the aforementioned considerations, we have

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attempted to study the systematic synthesis of multi-Ni-substituted POMs. In this paper, we report two novel high-nuclear Ni-substituted POM compounds: $Na_9K[Ni_7(OH)_4(H_2O)(CO_3)_2(HCO_3)(A\text{-}\alpha\text{-}SiW_9O_{34})(\beta\text{-}SiW_{10}O_{37})]\cdot 5H_3O\cdot 18H_2O$ (**1**) and $K_6Na_4[\{Ni_6(H_2O)_4(\mu_2\text{-}H_2O)_4(\mu_3\text{-}OH)_2\}(x\text{-}SiW_9O_{34})_2]\cdot 17.5H_2O$ (**2**).

Reaction of $K_8[\gamma\text{-}SiW_{10}O_{36}]$ with Ni^{2+} at 95 °C in the pH = 8.2 aqueous solution produced light-green single crystals of **1**, but reaction at 80 °C produced **2**.[9] We also tried to synthesize the analogues of the two compounds in different pH aqueous solutions with various temperatures by using the same synthetic procedure. When pH = 6, we obtained the Ni_4-substituted $K_{12}[\{\beta\text{-}SiNi_2W_{10}O_{36}(OH)_2(H_2O)\}_2]$ (**3**), which has been synthesized by Kortz et al. in a different way.[10] Accordingly, the temperature and pH value play important roles in the formation of such compounds.

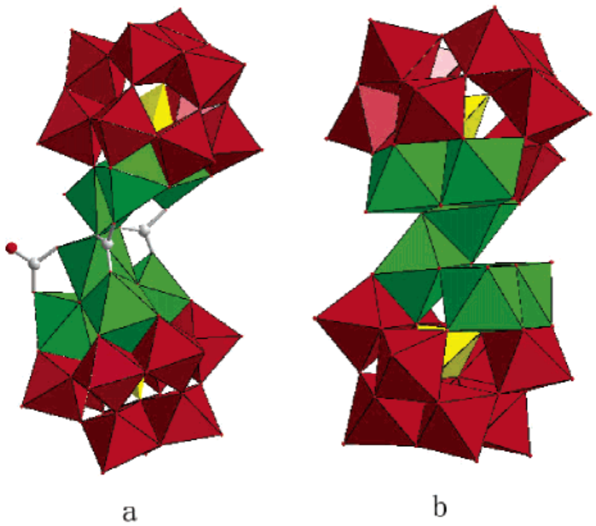

Figure 1. (a) Combined polyhedral/ball-and-stick representation of polyoxoanion **1**. (b) Polyhedral representation of polyoxoanion **2**. The color codes are as follows: WO_6 octahedra, red; central SiO_4 tetrahedra, yellow; NiO_6 octahedra, green; C, light-gray spheres; O, red spheres.

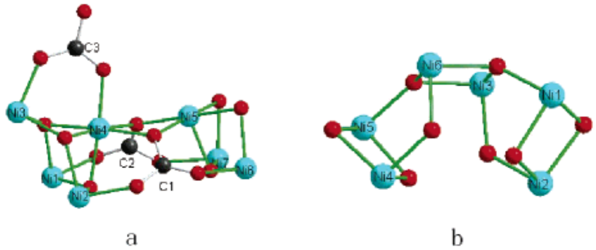

Figure 2. (a) Ball-and-stick representation of the central $\{Ni_7O(OH)_4(H_2O)(CO_3)_2(HCO_3)\}$ cluster of **1**. (b) Ball-and-stick representation of the central $\{Ni_6O_2(\mu_2\text{-}H_2O)_4(\mu_3\text{-}OH)_2\}$cluster of **2**.

Single-crystal X-ray diffraction analysis[11] shows that compound **1** exhibits an asymmetric dimeric structure, composed of $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ and $[\beta\text{-}SiW_{10}O_{37}]^{10-}$ units, which are linked by a Ni_7 cluster and three carbonates (Figure 1a). The $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ and $[\beta\text{-}SiW_{10}O_{37}]^{10-}$ moieties in **1** coordinate to the central Ni7 cluster to form the dimeric structure in different ways. $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ provides nine O donor atoms (three from the central SiO_4 group and one each from the six W atoms) that are capable of coordinating the three Ni^{2+} ions of the central heptameric cluster. Meanwhile, $[\beta\text{-}SiW_{10}O_{37}]^{10-}$ provides eight O donor atoms (two from the central SiO_4 group and one each from the six W atoms) that coordinate to the central heptameric cluster. Also, the central cluster of **1** is constituted by seven octahedral-coordination Ni^{2+} ions, and the arrangement of the seven Ni^{2+} centers is completely unprecedented (Figure 2a). According to the positions at which the Ni^{2+} ions are located, we can divide them into three groups, each assuming their own duties, as described below. $Ni1O_6$, $Ni2O_6$, and $Ni3O_6$ octahedra located at the trivacant sites of $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ are used to complete the α-Keggin structure $[\alpha\text{-}SiNi_3W_9O_{40}]$; the $Ni6O_6$ and $Ni7O_6$ octahedra replace two corner-sharing WO_6 octahedra from $[\beta\text{-}SiW_{12}O_{40}]^{4-}$, resulting in the well-defined β-Keggin structure $[\beta\text{-}SiNi_2W_{10}O_{40}]$, while the remaining two $[Ni4O_6$ and $Ni5O_6]$ are edge-sharing to connect the two Keggin isomers ($[\alpha\text{-}SiNi_3W_9O_{40}]$ and $[\beta\text{-}SiNi_2W_{10}O_{40}]$). Bond-valence-sum calculations[12] reveal that only one terminal O associated with the Ni_7 cluster is diprotonated; the three μ_3-oxo-linked Ni ions are monoprotonated. To the best of our knowledge, there are a few POMs with asymmetric dimeric structures that have been reported, such as the mixed-valence heteropoly and isopoly brown species $[H_4BW^{IV}{}_3W^{VI}{}_{17}O_{66}]^{11-}$ and $[H_6W^{IV}{}_3W^{VI}{}_{17}O_{66}]^{11-}$ [13] and the 6-Co-substituted dimeric $[(Co_3(B\text{-}\alpha\text{-}SiW_9O_{33}(OH))(B\text{-}\alpha\text{-}SiW_8O_{29}(OH)_2))_2]^{22-}$ (**4**).[14] The former two are only constructed from the $[B\text{-}\alpha\text{-}XW_9O_{34}]^{10-}$ and $[\beta\text{-}W_8O_{30}]^{12-}$

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(9) Synthesis of **1**: $K_8[\gamma\text{-}SiW_{10}O_{36}]$ (0.5 g) was dissolved in 10 mL of distilled water with stirring. The insoluble substance was removed by filtration. Next, 1 mL of a $NiCl_2$ solution (1 M) was added dropwise with vigorous stirring. Then, 3 g of KCl was added to the green solution. At this point, 2 M Na_2CO_3 was used to adjust the pH to 8.2, and the resulting solution was heated for 1 h at 95 °C. For a moment, the mixture was cooled to room temperature and then filtered. The filtrate was kept at ambient conditions, and then slow evaporation at room temperature for a few weeks resulted in a light-green crystalline product (yield 19%). **2** was obtained by using the same synthetic procedure, except the temperature was set to 80 °C (yield 28%). IR (cm^{-1}) for **1**: 1502, 1904, 1422, 1371, 985, 937, 885, 800, 678. IR (cm^{-1}) for **2**: 980, 944, 879, 798. Anal. Calcd for **1** (%): C, 0.60; K, 0.65; Na, 3.4; Ni, 6.82; Si, 0.93; W, 57.9. Found: C, 0.59; K, 0.63; Na, 3.5; Ni, 6.84; Si, 0.92; W, 57.6. Anal. Calcd for **2**: K, 4.17; Na, 1.63; Ni, 6.26; Si, 1.00; W, 58.8. Found: K, 4.15; Na, 1.65; Ni, 6.27; Si, 0.98; W, 58.5.

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(11) Single-crystal X-ray data for **1** and **2** were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo KR monochromated radiation ($\lambda = 0.710\,73$ Å) at 293 K in the ranges of $3.00 < \theta < 25°$ (**1**) and $2.99 < \theta < 25°$ (**2**). The dimensions of the two light-green crystals are as follows: **1**, $0.30 \times 0.28 \times 0.25$ mm^3; **2**, $0.35 \times 0.29 \times 0.26$ mm^3. Crystal data for **1**: _$C_3H_{58}KNa_9Ni_7O_{108}Si_2W_{19}$, MW = 6028.80, triclinic, space group $P\bar{1}$, $a = 12.462(3)$ Å, $b = 20.616(4)$ Å, $c = 23.966(5)$ Å, $\alpha = 113.35(3)°$, $\beta = 94.50(3)°$, $\gamma = 92.09(3)°$, $V = 5620.4(19)$ $Å^3$, $Z = 2$, R1 = 0.0738, wR2 = 0.2159. Crystal data for **2**: $H_{53}K_6Na_4Ni_6O_{95.5}Si_2W_{18}$, MW = 5625.72 $Å^3$, monoclinic, space group $P2(1)/c$, $a = 19.580(4)$ Å, $b = 22.550(5)$ Å, $c = 22.521(5)$ Å, $\alpha = 90.00°$, $\beta = 101.22(3)°$, $\gamma = 90.00°$, $V = 9753(3)°$, $Z = 1$, R1 = 0.0610, wR2 = 0.1643.

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units, and the latter, though belonging to the sandwich-type POMs, the polyanion fragments [B-α-$SiW_9O_{33}(OH)$ and B-α-$SiW_8O_{29}(OH)_2$] and the combination fashion between them are different from that of **1**. Therefore, the polyoxoanion of **1** is unprecedented in POM chemistry.

It is also noteworthy that there are three dianions encapsulated in the asymmetric dimeric POMs. The dianion-containing TMSPs, especially for the divalent first-row TMSPs, are comparatively unexplored. The TMSPs containing univalent anions, such as NO_3^-,[15] CH_3COO^-,[16] and Cl^-,[17] are usually reported. The only example of an A-type sandwich complex containing one dianion was the yttium polyoxometalates [$(YOH_2)_3(CO_3)$(A-α-$PW_9O_{34})_2$] (**5**),[18] reported recently by Fang et al. The carbonato ligand in **5** is in a six-coordinate tridentate environment. However, in **1**, two carbonato ligands act as tridentate ligands, and the third one acts as the bidentate ligand (see Figure 1a). Bond-valence-sum calculations[12] show that the terminal O of the third carbonato ligand was monoprotonated; that is, there is a bicarbonate ion encapsulated in the polyoxoanion. In the IR spectrum of **1**, the peaks around 1502, 1494, and 1371 cm^{-1} are ascribed to the vibrations of CO_3^{2-}.[18,19] Also, at 1422 cm^{-1}, the characteristic peaks can be regarded as a feature of the bicarbonate. In the Raman spectrum of compound **1**, the characteristic peak of CO_3^{2-} located at 1087 cm^{-1} is also observed.[20,21]

Compound **2** was composed of two $[SiW_9O_{34}]^{10-}$ units linked by a Ni_6 cluster (Figure 1b). Two $[SiW_9O_{34}]^{10-}$ units each share eight O atoms, including two O atoms on Si, with the central cluster composed of six NiO_6 octahedra. Alternatively, the structure of **2** can also be regarded as a dimer consisting of two well-defined Ni_3-substituted β-Keggin-type polyoxoanions [β-$Ni_3SiW_9O_{40}$]. In each [β-$Ni_3SiW_9O_{40}$] unit, three Ni ions are distributed to two M_3O_{13} triplets. The $Ni3^{2+}$ ion is in the triplet Ni3−W8−W9, and $Ni1^{2+}$ and $Ni2^{2+}$ are in the adjacent triplet (Ni1−Ni2−W7), corner-sharing with $Ni3^{2+}$ ions. This fashion of the Ni_3-substituted polyoxoanion is observed for the first time in TMSP chemistry. The two Ni_3O_{13} segments are linked by two μ_3-OH groups to form a Ni_6 cluster. Figure 2b is the ball-and-stick representation of the central Ni_6 cluster. The coordination geometry of Ni^{2+} ions in **2** is octahedral, and the Ni−O distances fall into the range of 1.991(14)−2.166(16) Å. Bond-valence-sum calculations[12] confirm that the terminal O atoms and the bridged O atoms combining two adjacent Ni ions are all diprotonated and the μ_3-oxo linking three Ni ions are monoprotonated. To the best of our knowledge, no analogous compound containing six Ni atoms between two polyoxoanion units has been reported in the literature.

The cyclic voltammogram of compound **2** (Figure S8 in the Supporting Information) in a pH = 5 buffer solution (0.4 M $CH_3COONa + CH_3COOH$) at a scan rate of 10 $mV \cdot s^{-1}$ shows two reduction peaks located at −663 and −164 mV, respectively. The two reduction peaks correspond to the reduction of the W^{VI} centers,[14,22] although the reduction peak at −164 mV of the unknown *x*-SiW_9O_{34} units is a little more positive than that of substituted tungstosilicate.[4g] Controlled potential electrolysis for **2** in the pH = 5 buffer solution (0.4 M $CH_3COONa + CH_3COOH$) was carried out at −680 and −180 mV, respectively; the solutions turned the characteristic blue color of the W centers.

In summary, we have successfully synthesized two novel multi-Ni-substituted POMs, **1** and **2**. Compound **1** represents a novel class of asymmetric dimeric structures with a Ni_7 core and contains three CO_3^{2-} in the dimeric structure. Compound **2** is constructed from two $[SiW_9O_{34}]^{10-}$ units linked by a Ni_6 cluster. The multi-Ni-substituted polyoxoanions usually exhibit excellent magnetic and catalysis properties. Future research will focus on attempts to study such properties of the two compounds, and the results will be reported after a period of time.

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Supporting Information Available: X-ray crystallographic files for compounds **1** and **2** in CIF format and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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