

Ni^{II}₃₆-Containing 54-Tungsto-6-Silicate: Synthesis, Structure, Magnetic and Electrochemical Studies

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Abstract: The 36-Ni^{II}-containing 54-tungsto-6-silicate, [Ni₃₆(OH)₁₈(H₂O)₃₆(SiW₉O₃₄)₆]⁶⁻ (Ni₃₆) was synthesized by a simple one-pot reaction of the Ni₂-pivalate complex [Ni₂(μ-OH₂)(O₂CCMe₃)₄(HO₂CCMe₃)₄] with the trilacunary [SiW₉O₃₄]¹⁰⁻ polyanion precursor in water and structurally characterized by a multitude of physicochemical techniques including single-crystal XRD, FTIR, TGA, elemental analysis, magnetic and electrochemical studies. Polyanion Ni₃₆ comprises six equivalent {Ni₆SiW₉} units which are linked by Ni–O–W bridges forming a macrocyclic assembly. Magnetic studies demonstrate that the {Ni₆} building blocks in Ni₃₆ remain magnetically intact while forming a hexagonal ring with antiferromagnetic exchange interactions between adjacent {Ni₆} units. Electrochemical studies indicate that the first reduction is reversible and associated with the W^{VI/V} couple, whereas the second reduction is irreversible attributed to the Ni^{II/0} couple.

Polyoxometalates (POMs) are discrete, anionic metal-oxo clusters with a large variety of structures, compositions and physicochemical properties. While plenary POMs such as [XW₁₂O₄₀]ⁿ⁻ (X = P, Si, Ge) are not reactive, lacunary derivatives such as the monolacunary [XW₁₁O₃₉]ⁿ⁻ or trilacunary [XW₉O₃₄]ⁿ⁻ (prepared by controlled base hydrolysis of the plenary precursor) are highly reactive towards oxophilic electrophiles such as *d* and *f* block metal ions.^[1] For decades the synthesis of high-nuclearity transition metal ion-containing POMs has received much attention, mainly aiming at novel structures with associated interesting magnetic, electrochemical, catalytic and biomedical properties.^[2] From a magnetism point of view, high-nuclearity magnetic POMs may possess large uniaxial anisotropy (*D*) and high-spin ground states (*S*), possibly resulting in single-molecule magnetic behaviour and relevance for high-density magnetic data storage and nanotechnology.^[3] Some selected examples of high-nuclearity, magnetic *d*-metal ion-containing POMs^[4] are [Mn₄₀P₃₂W₂₂₄O₈₈₈]¹⁴⁴⁻,^[4c] [Mn₁₉(OH)₁₂(SiW₁₀O₃₇)₆]³⁴⁻,^[4e] [Fe₄₈(OH)₇₆(H₂O)₁₆(H₂P₂W₁₂O₄₈)₈]²⁸⁻,^[4a] [Fe₂₈P₈W₄₈O₂₄₈H₅₆]²⁸⁻,^[4g]

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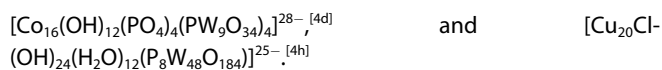
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With respect to the synthesis of Ni^{II}-containing POMs, several species with different nickel-nuclearities ranging from 2 to 40 have been reported.^[5,6] Most of these species have a sandwich-type structure, with a recent member being the heptanuclear tungstosilicate $[\text{Ni}_7(\text{OH})_6(\text{H}_2\text{O})_4(\text{SiW}_9\text{O}_{31})_2]^{12-}$, which showed ferromagnetic coupling between the hydroxo-bridged Ni^{II} centres.^[5a] In 2013 the 14-nickel-containing $[\text{Ni}_{14}(\text{OH})_6(\text{H}_2\text{O})_{10}(\text{HPO}_4)_4(\text{P}_2\text{W}_{15}\text{O}_{56})_4]^{34-}$ was reported,^[5d] and in 2015 the 25-nickel-containing $[\text{Ni}_{25}(\text{OH})_{18}(\text{H}_2\text{O})_2(\text{CO}_3)_2(\text{PO}_4)_6(\text{SiW}_9\text{O}_{34})_6]^{50-}$.^[5b] Most of the known examples involve bridging secondary ligands such as HPO_4^{2-} , PO_4^{3-} , BO_3^{3-} or CO_3^{2-} .^[5] Some POMs contain $\{\text{Ni}_6\text{XW}_9\}$ (X = P, Si, Ge) units, which are connected to adjacent units via Ni–O–W bonds, resulting in different topologies.^[6a–e] The hydroxo-bridged $\{\text{Ni}_6\}$ subunit represents a key fragment of the brucite-type sheet structure, which has also been observed in $[\text{Mn}_{19}(\text{OH})_{12}(\text{SiW}_{10}\text{O}_{37})_6]^{34-}$ ($\{\text{Mn}_{19}\}$).^[4e] Interestingly, Long et al. used a $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpydc})_6$ “lacunary” MOF to capture $\{\text{M}_{19}\}$ brucite-type sheet structures, very similar to the $\{\text{Mn}_{19}\}$ sheets, but with halide bridges rather than OH. This resembles the situation in MX_2 solid-state structures in general for X = Cl, Br, I, and OH. In general, the occupancy is around 13–17, out of the maximum calculated 19. This suggests that using lacunary POMs as capping groups is a more robust strategy than trying to fill “holes” in MOF structures, as there are no defects in the former.^[6b]

Here we report on the synthesis of a 36 Ni^{II}-containing POM comprising exclusively trilacunary 9-tungstosilicate ions and hydroxo ligands. Reaction of the dinuclear coordination complex $[\text{Ni}_2(\mu\text{-OH})_2(\text{O}_2\text{CCMe}_3)_4(\text{HO}_2\text{CCMe}_3)_4]$ (**Ni₂-Piv**) (Piv = HO_2CCMe_3)^[7] with the trilacunary 9-tungstosilicate $[\text{SiW}_9\text{O}_{34}]^{10-}$ in water under hydrothermal conditions resulted in the formation of $[\text{Ni}_{36}(\text{OH})_{18}(\text{H}_2\text{O})_{36}(\text{SiW}_9\text{O}_{34})_6]^{6-}$ (**Ni₃₆**), which was isolated as a hydrated sodium salt, $\text{Na}_6[\text{Ni}_{36}(\text{OH})_{18}(\text{H}_2\text{O})_{36}(\text{SiW}_9\text{O}_{34})_6] \cdot 105\text{H}_2\text{O}$ (**Na-Ni₃₆**). The title compound was characterized by a multitude of physicochemical techniques including single-crystal XRD, IR, TGA, elemental analysis, magnetic and electrochemical studies. Single-crystal XRD revealed that **Na-Ni₃₆** crystallized in the triclinic system with space group $P\bar{1}$. The crystallographic parameters are shown in the Supporting Information (Table S1). The polyanion **Ni₃₆** consists of six $\{\text{Ni}_6\text{SiW}_9\}$ subunits, each comprising a trilacunary $\{B\text{-}\alpha\text{-SiW}_9\}$ Keggin unit with six incorporated Ni^{II} ions coordinated octahedrally and bridged to each other by hydroxo ligands, and arranged in a coplanar fashion (Figure 1). The six $\{\text{Ni}_6\text{SiW}_9\}$ subunits are connected to each other via Ni–O–W bonds, leading to a cyclic assembly with the $\{\text{Ni}_6\text{SiW}_9\}$ subunits alternatingly pointing up and down, resulting in polyanion **Ni₃₆** with S_6 point group symmetry. Interestingly, a side view of **Ni₃₆** reveals six, planar $\{\text{Ni}_6\}$ assemblies arranged in a coplanar cyclic fashion and sandwiched by three $\{B\text{-}\alpha\text{-SiW}_9\}$ units from above and below, respectively. Bond valence sum (BVS) calculations confirm that all the 36 nickel ions in **Ni₃₆** have a +2 oxidation state (Table S2), and that the bridging oxygens are monoprotonated and hence hydroxo groups (Table S3).^[8] A close inspec-

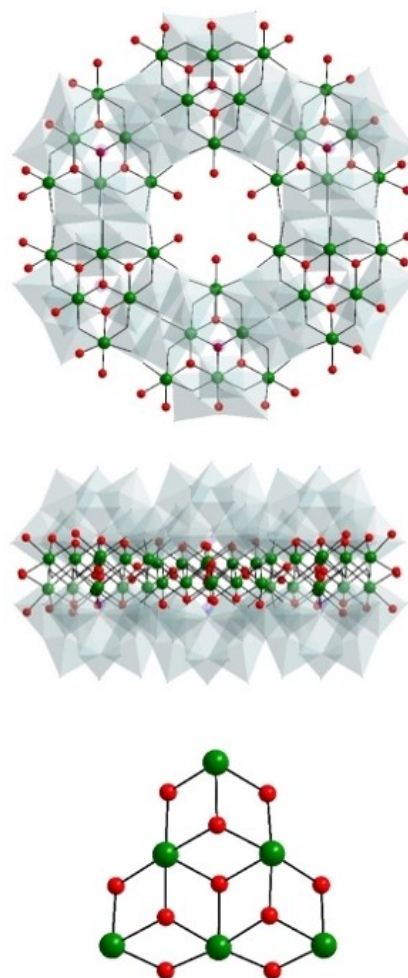


Figure 1. Structural representation of **Ni₃₆** in top view (top), side view (middle), and one of the six hydroxo-bridged $\{\text{Ni}_6\}$ subunits (bottom). Color code: nickel (green), oxygen (red). The WO_6 octahedra and Si heteroatoms are shown as transparent octahedra and balls, respectively, to highlight the six $\{\text{Ni}_6\}$ subunits within **Ni₃₆**.

tion of the $\{\text{Ni}_6\text{SiW}_9\}$ subunits in **Ni₃₆** indicates that each planar Ni_6 -hydroxo cluster comprises four interconnected Ni_3O_4 cubane units. Such Ni_3O_4 or Ni_4O_4 motifs are known in POM chemistry as well as in coordination complexes.^[9]

The magnetic properties of **Na-Ni₃₆** have been measured in powdered sample employing a SQUID magnetometer, in the temperature range of 2 to 300 K and fields ranging from 0 to 7 T. The χT at room temperature is $53.1 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is in the expected range for six uncoupled Ni_6 units.^[10] Upon cooling, the χT profile increases, reaching a maximum χT value of 81.1 cm^3 at ca. 40 K, before decreasing to $13.2 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. The upsurge indicates the existence of ferromagnetic interactions, as observed within the composing Ni_6 units. The $M(B)$ plot shows no saturation of the magnetization, with an almost linear profile with increasing field. Expectations were that the magnetism of **Ni₃₆** is equal to that of its six uncoupled independent Ni_6 subunits. Both, χT versus T as well as M versus B , see Figure 2, suggest that there is a small exchange interaction through O–W–O bridges that couple adjacent Ni_6

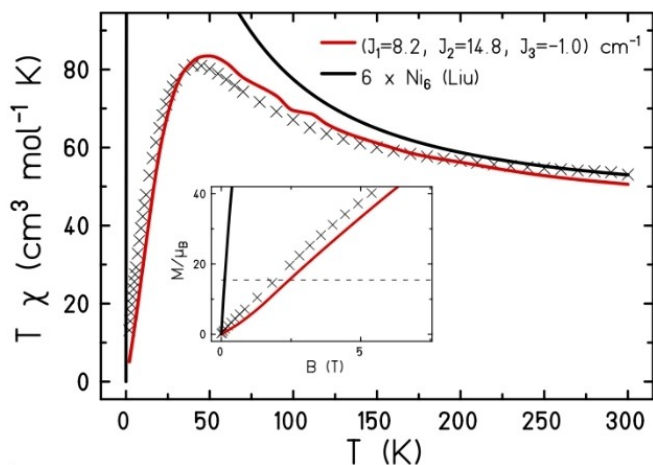


Figure 2. Magnetic susceptibility at $B=0.1$ T and magnetization at $T=2.0$ K (inset) – experimental data (symbols), ALPS QMC simulation (red curves), simulations of 6 independent Ni_6 subunits (black curves).

triangles. We model this interaction by a single exchange integral J_3 (blue in Figure 3), while leaving J_1 and J_2 as previously derived from the magnetism of the Ni_6 subunits.^[11]

The magnetism of discrete molecular objects as large as Ni_{36} cannot be modelled by exact diagonalization due to a prohibitive size of the related Hilbert space.^[12] However, the magnetic interactions of Ni_{36} are non-frustrating since J_1 and J_2 are ferromagnetic and only J_3 is antiferromagnetic; therefore, quantum Monte Carlo (QMC) calculations can be used. We simulated the magnetic observables using the program *dirloop_sse* of the ALPS package.^[13] As a result, we found that a weak antiferromagnetic exchange $J_3 = -1 \text{ cm}^{-1}$ connects neighboring subunits. The agreement with the experimental data is very good. Small deviations may result from not considered Ni anisotropies, possible modifications of J_1 or J_2 , or an exchange pattern that differs from Figure 3. The tiny wiggles of the red curves are due to the fact that the QMC calculations are not yet fully converged, even after several days of simulation.

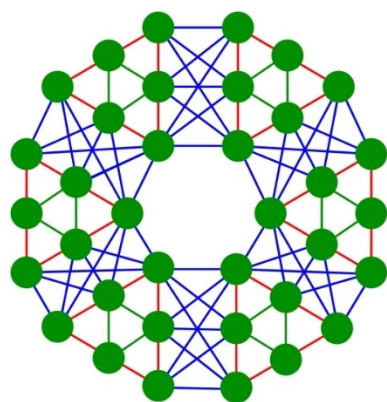


Figure 3. Schematic representation of exchange interactions in Ni_{36} : J_1 (red) and J_2 (green) as in Liu,^[10] J_3 (blue) denotes the exchange between adjacent $\{\text{Ni}_6\}$ triangles. A “ $-2J$ ”-Hamiltonian was employed in the calculations.

The electrochemistry of Na-Ni_{36} was carried out in aqueous solutions in a pH 7.8 acetate medium, which is close to the pH used for the synthesis. For this purpose, the stability of polyanion Ni_{36}^{4-} was assessed by cyclic voltammetry (CV). Only the tungsten centers are expected to give rise to an electrochemical response, with the Ni^{II} ions being silent at our experimental conditions.^[14] The solid Na-Ni_{36} was first immobilized on the surface of the basal plane of the pyrolytic graphite disk (PGB) and the electrochemical responses studied in pH 7.8 acetate medium. Figure 4A and B features the CVs of Ni_{36} obtained at 20 mV.s^{-1} , at two different reverse potentials in a pH 7.8 acetate medium. The CV of Ni_{36} exhibits a quasi-reversible reduction wave at -0.980 V versus SCE (step I), followed by the second irreversible wave at -1.232 versus SCE (step II), which is very close to the solvent discharge. As shown in Figure 4B (dark-blue and dark-red curves), nearly the same cyclic voltammograms were measured after the first and the second scan without polishing the electrode showing the chemically reversible W-reduction at -0.980 V versus SCE for the first step. In contrast, the second reduction (step II) corresponds to an irreversible multielectron transfer (Figure S3, blue curve). It must be noted that at the reverse sweep, one additional anodic peak at -0.502 V versus SCE appeared (peak *). It corresponds to the anodic dissolution peak of Ni^0 and indicates that during the second irreversible reduction at

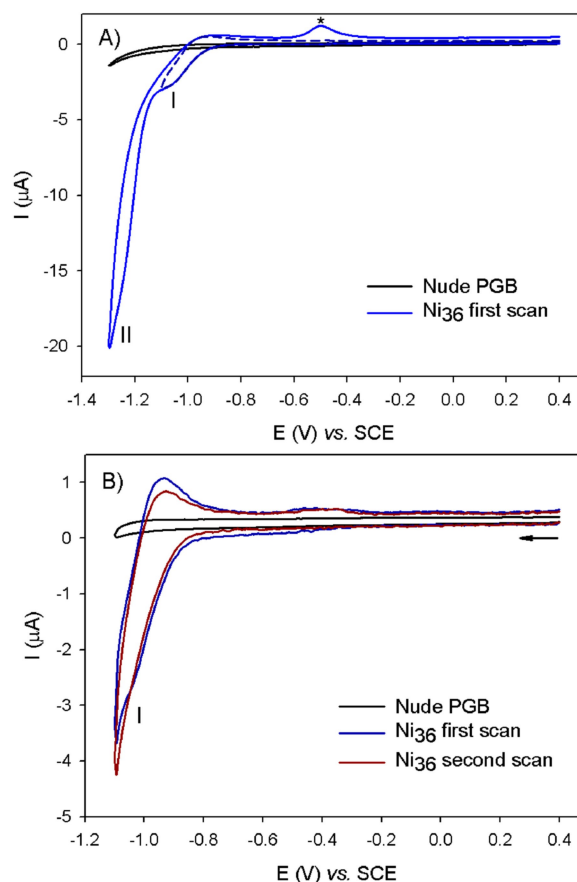


Figure 4. Cyclic voltammograms of Na-Ni_{36} immobilized at a PGB electrode ($d=2$ mm) in a 1 M pH 7.8 LiOAc-HAcO solution. Scan rate: 20 mV.s^{-1} .

–1.232 versus SCE, reduction of Ni^{II} to Ni⁰ occurred, leading to decomposition of Ni₃₆, but only during the second reduction.

Comparable measurements on a 0.50 mM solution of Ni₃₆ were obtained using a glassy carbon electrode (GC) in acetate medium at pH 7.8, as shown in Figure S4 (see Supporting Information). After polishing the GC electrode, similar CV curves were always obtained, even after 1 day. Moreover, no change of the UV-visible spectrum was observed (Figure S6). These results indicate that Ni₃₆ is stable in acetate medium at pH 7.8.

In summary, we have synthesized and structurally characterized the 36 Ni^{II}-containing discrete, cyclic polyanion Ni₃₆, which not only contains a record number of Ni^{II} ions, but the magnetic core is constructed without the need for any secondary bridging capping groups such as phosphate, borate or carbonate. The title polyanion Ni₃₆ is prepared by reaction of the dinuclear coordination complex Ni₂-Piv with the trilacunary {SiW₉} Keggin polyanion precursor in water, and heating in a stainless-steel autoclave under autogenous pressure at 140 °C for three days. The structure of Ni₃₆ can be rationalized as a cyclic assembly of six identical {Ni₆SiW₉} units, which are oriented in alternating up/down orientations, resulting in a structure with S₆ symmetry. The magnetic properties of Ni₃₆ result from the combined action of ferromagnetic exchange interactions within the {Ni₆} units, as well as antiferromagnetic exchange interactions between neighboring {Ni₆} units. For low temperatures and fields this qualitatively corresponds to a hexagonal ring of weakly antiferromagnetically interacting {Ni₆} units, each {Ni₆} unit possessing an effective spin S = 6. The electrochemical properties indicate a good stability of Ni₃₆ toward the first reduction step, which is almost reversible, whereas the polyanion decomposes at the second reduction step, due to the reduction of Ni^{II} to Ni⁰.

Experimental Section

Synthesis of Na₆[Ni₃₆(H₂O)₃₆(OH)₁₈(SiW₉O₃₄)₆] · 105H₂O (Na-Ni₃₆): The coordination complex [Ni₂(μ-OH₂)(O₂CMe₃)₄(HO₂CMe₃)₄] (Ni₂-Piv) (Piv = HO₂CMe₃)^[7] (0.255 g, 0.272 mmol) was dissolved in H₂O (40 mL) and then Na₁₀[A-α-SiW₉O₃₄] · 24H₂O (0.200 g, 0.068 mmol)^[15] was added with constant stirring for 10 min at room temperature. The resultant reaction mixture was transferred into a Teflon-lined stainless-steel autoclave and was heated under autogenous pressure at 140 °C for three days. After overnight cooling a precipitate had formed at the bottom of the Teflon container, which was removed by centrifugation and/or filtration. The solution was kept in an open vial at room temperature to allow for slow evaporation. After about one month a green, crystalline product started to appear. Evaporation was allowed to continue until most of the solvent had disappeared. Then the solid product was collected by filtration and air dried. Yield 15 mg (7%, based on W). IR (2% KBr pellet): $\tilde{\nu}$ = 3412(br), 1619(s), 1379(sh), 947(s), 878(s), 833(sh), 790(s), 687(s), 541(w), 513(w), 478(sh). Elemental analysis (%) for Na₆[Ni₃₆(H₂O)₃₆(OH)₁₈(SiW₉O₃₄)₆] · 105H₂O (Na-Ni₃₆), calcd: W 53.79, Ni 11.45, Na 0.75, Si 0.91; found W 51.35, Ni 12.02, Na 0.78, Si 0.77. Elemental analysis was performed at CREALINS (Villeurbanne, France), except for Na, which was determined by atomic absorption at Jacobs University.

Deposition Number 2001196 (Na-Ni₃₆) contains the supplementary crystallographic data for this paper. These data are provided free of

charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Electrochemistry · magnetic properties · nickel · polyoxometalates · structure elucidation

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