

Synthesis and Crystal Structure of the Tetra-nickel Substituted $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ Polyoxoanion

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Dedicated to Professor Kurt O. Klepp on the occasion of his 60th birthday

The new polyoxotungstate $(\text{NH}_4)_6\text{Na}_4[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 20 \text{ H}_2\text{O}$ (**1**) was synthesized in aqueous solution and characterized by IR and UV/Vis spectroscopy, energy dispersive X-ray fluorescence and single-crystal X-ray analysis. It contains the tetra-nickel substituted $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ polyoxoanion, in which the four Ni atoms are in a common plane and form a regular rhombus. **1** crystallizes in the monoclinic crystal system, space group $P2_1/n$ with $a = 11.849(2)$, $b = 16.718(3)$, $c = 21.243(4)$ Å, $\beta = 100.48(3)^\circ$, and $Z = 2$. The anions are linked via hydrogen bonds and sodium cations.

Key words: Polyoxometalates, Nickel, Tungsten, Crystal Structure

Introduction

Polyoxometalates constitute a unique class of metal-oxygen clusters with an enormous diversity of structures [1, 2]. They are gaining widespread attention owing to their applications in numerous fields of chemistry such as catalysis, material science, analytical chemistry, magnetochemistry or photochemistry [3, 4]. Polyoxometalates are formed in aqueous acidic solution by condensation reactions and can be described as molecular blocks of metal oxides formed by MO_6 octahedra sharing corners, edges and faces. For the exact description of polyoxometalate structures, single-crystal X-ray structure analysis is the most powerful tool as the standard analytical techniques like IR, UV/vis and elemental analysis are often insufficient.

Within the class of polyoxotungstates, the Keggin anion $[\text{XW}_{12}\text{O}_{40}]^{(8-x)-}$ (where X is the central atom and x its oxidation state) and its defect fragments are the basis for a large number of structurally different polyoxoanions. In our work, we focus on the systematic synthesis of sandwich-type polyoxotungstates containing As, Sb and Bi [5–12]. Most of these tungstates belong to three different structure types: the $\text{M}_3\text{X}_2\text{W}_{18}$ -type consists of two trivacant $\alpha\text{-B}(\text{XW}_9\text{O}_{33})^{n-}$ fragments which are connected via three transition metal atoms M. Two trivacant

$\beta\text{-B}(\text{XW}_9\text{O}_{33})^{n-}$ fragments, connected via two transition metal and two tungsten atoms, form the $\text{M}_2\text{X}_2\text{W}_{20}$ structure type. In both structure types, partial disorder M/W is often observed. Sandwich-type polyoxoanions belonging to the $\text{M}_4\text{X}_2\text{W}_{18}$ -type, constitute a class of well-known compounds in which two trivacant $\alpha\text{-B}(\text{XW}_9\text{O}_{34})^{n-}$ fragments ($\text{X} = \text{P}^{\text{V}}, \text{As}^{\text{V}}, \text{Si}^{\text{IV}}, \text{Ge}^{\text{IV}}$ etc.) are connected via a belt of four transition metal atoms. The first anion of this type, $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$, was reported in 1973 by Weakley *et al.* [13], and the corresponding nickel-substituted anion was published in 1999 [14]. Some analogous structures with As^{V} and $\text{M} = \text{Zn}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Cd}^{\text{II}}, \text{Ni}^{\text{II}}$ were reported [15, 16]. However, only the manganese and copper substituted compounds were characterized in single crystal X-ray structure analyses. Kortz *et al.* were able to synthesize the first examples of sandwich-type silicotungstates, $[\text{M}_4(\text{H}_2\text{O})_2(\text{SiW}_9\text{O}_{34})_2]^{12-}$ ($\text{M} = \text{Mn}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}$) [17] and germanotungstates $[\text{M}_4(\text{H}_2\text{O})_2(\text{GeW}_9\text{O}_{34})_2]^{12-}$ ($\text{M} = \text{Mn}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}$) [18]. Our group reported two novel anions of the $\text{M}_4\text{X}_2\text{W}_{18}$ -type in which the transition metal atoms M can also be found in the center of the $\alpha\text{-B}(\text{XW}_9\text{O}_{34})^{n-}$ fragment ($\text{M} = \text{X} = \text{Cu}^{\text{II}}, \text{Fe}^{\text{III}}$) [19].

Beyond the tetra-substituted anions of this type, there are some examples for tri-substituted anions

Table 1. Crystallographic data for $(\text{NH}_4)_6\text{Na}_4[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 20 \text{H}_2\text{O}$.

	1
Formula	$\text{As}_2 \text{H}_{68} \text{N}_6 \text{Na}_4 \text{Ni}_4 \text{O}_{90} \text{W}_{18}$
Formula weight $[\text{g mol}^{-1}]$	5378.0
Crystal size $[\text{mm}^3]$	$0.4 \times 0.4 \times 0.2$
Crystal color, habit	green plates
Crystal system	monoclinic
Space group	$P2_1/n$
a $[\text{\AA}]$	11.849(2)
b $[\text{\AA}]$	16.718(3)
c $[\text{\AA}]$	21.243(4)
β $^\circ$	100.48(3)
V $[\text{\AA}^3]$	4137.9(13)
Z	2
Index range	$-14 \leq h \leq 14, -20 \leq k \leq 20, -26 \leq l \leq 26$
Density (calcd.) $[\text{g cm}^{-3}]$	4.317
μ $[\text{mm}^{-1}]$	26.73
T $[\text{K}]$	213(2)
2θ Range	$8.60^\circ < 2\theta < 51.94^\circ$
Reflections collected	29548
Independent reflections	8023 $[R(\text{int}) = 0.2327]$
Parameters	323
$R(I > 2\sigma(I))$	$R_1^a = 0.0536$ $wR_2^b = 0.1407$
R (all data)	$R_1^a = 0.0656$ $wR_2^b = 0.1495$
Goodness-of-fit on F^2	1.061 ^c
Largest diff. peak and hole $[\text{e}^- \text{\AA}^{-3}]$	3.901 / -3.211

^a $R_1 = \Sigma ||F_{\text{obs}}| - |F_{\text{calc}}|| / \Sigma |F_{\text{obs}}|$; ^b $wR_2 = \{\Sigma [w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2] / \Sigma [w(F_{\text{obs}}^2)^2]\}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (0.039 P)^2 + 63.95 P]$; with $P = (\text{Max}(F_{\text{obs}}^2, 0) + 2F_{\text{calc}}^2) / 3$; ^c $\text{goof} = [\Sigma (w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2) / (n - p)]^{1/2}$, n = number of reflections, p = parameter used.

in which the position of one transition metal atom is occupied by a sodium atom. Kortz reported on the structures of $[\text{Ni}_3\text{Na}(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{11-}$ and $[\text{Ni}_3\text{Na}(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{11-}$ [20, 21]. Interestingly, he found the trisubstituted species to be more stable than the tetrasubstituted anions. Here we present the crystal structure of $(\text{NH}_4)_6\text{Na}_4[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 20 \text{H}_2\text{O}$ which contains the still missing $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ anion, and compare it with the P^V analogue.

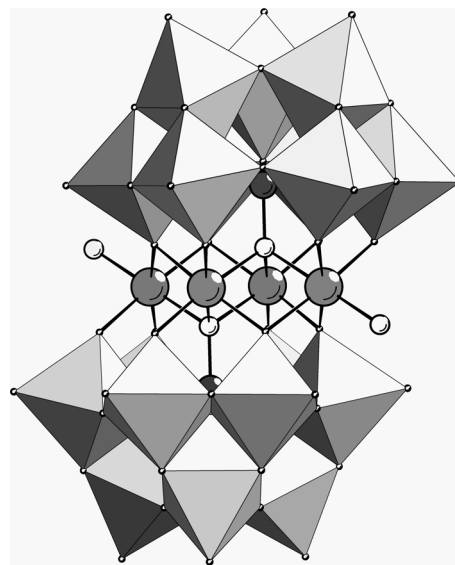
Results and Discussion

The novel polyoxotungstate $(\text{NH}_4)_6\text{Na}_4[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 20 \text{H}_2\text{O}$ (**1**) can be synthesized in aqueous solution by reaction of stoichiometric amounts of $\text{Na}_2\text{WO}_4 \cdot 2 \text{H}_2\text{O}$, $\text{As}_2\text{O}_5 \cdot 5 \text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ at a pH of 6.5. After adding a saturated solution of NH_4Cl , green single crystals suitable for X-ray diffraction can be obtained by slow evaporation of the solvent. Previous attempts to synthesize **1** resulted in

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) of the polyoxometalate **1** (standard deviations in parentheses). The subscripts indicate the atoms bonded to the oxygen atom.

$\text{W}-\text{O}_t^a$	1.70(2)–1.74(2)	$\text{W}-\text{O}_{\text{W}2}$	1.86(2)–2.05(2)
$\text{W}-\text{O}_{\text{W}Ni}$	1.78(2)–1.80(2)	$\text{W}-\text{O}_{\text{W}Ni2}$	1.83(2)
$\text{W}-\text{O}_{\text{AsW}3}$	2.35(1)–2.49(1)	$\text{As}-\text{O}_{\text{AsW}3}$	1.66(1)–1.69(1)
$\text{As}-\text{O}_{\text{AsNi}3}$	1.68(1)	$\text{Ni}-\text{O}_{\text{W}Ni}$	1.97(2)–2.02(2)
$\text{Ni}-\text{O}_{\text{W}Ni2}$	2.07(2)–2.10(2)	$\text{Ni}-\text{O}_{\text{AsNi}3}$	2.11(1)–2.15(1)
$\text{Ni}-\text{OH}_2$	2.05(2)	$\text{Na}-\text{O}$	2.40(2)–2.71(2)
$\text{Na}-\text{OH}_2$	2.16(3)–2.57(4)		
$\text{O}-\text{W}-\text{O}_{cis}$	70.5(4)–106.3(5)	$\text{O}-\text{W}-\text{O}_{trans}$	153.4(5)–172.3(5)
$\text{O}-\text{As}-\text{O}$	106.4(5)–112.9(5)	$\text{O}-\text{Ni}-\text{O}_{cis}$	79.2(4)–99.6(5)
$\text{O}-\text{Ni}-\text{O}_{trans}$	168.6(5)–178.2(5)	$\text{O}-\text{Na}-\text{O}_{cis}$	63.9(12)–113.9(12)
$\text{O}-\text{Na}-\text{O}_{trans}$	150.7(11)–176.4(12)		

^a Terminal.

Fig. 1. Polyhedral representation of the $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ anion. W light gray octahedra, As dark gray, Ni middle gray, O white.

the formation of $\text{Na}_{16.5}\text{Ni}_{0.25}[\text{Ni}_6\text{As}_3\text{W}_{24}\text{O}_{94}(\text{H}_2\text{O})_2] \cdot 54 \text{H}_2\text{O}$ and the tri-nickel substituted $\text{Na}_{11}[\text{NaNi}_3(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 30.5 \text{H}_2\text{O}$ [21]. These polyoxotungstates are formed in 1 M NaCl solution and with a ratio of $(\text{AsW}_9\text{O}_{34})^{9-} : \text{Ni}$ of 2 : 3.6. **1** crystallizes in the monoclinic crystal system, space group $P2_1/n$. The asymmetric unit contains half a formula unit, the unit cell contains two formula units. The details of data collection and refinement are summarized in Table 1.

The crystal structure of **1** shows a double Keggin structure with nickel as a secondary heteroatom. The $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ anion exhibits two α -B- $(\text{AsW}_9\text{O}_{34})^{9-}$ fragments that can be formally derived

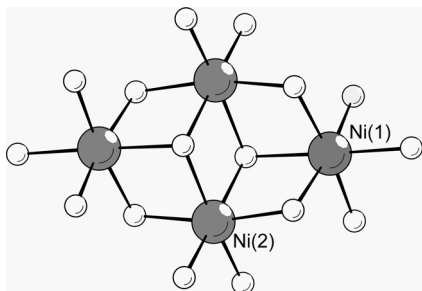


Fig. 2. Ball and stick representation of the central $\text{Ni}_4\text{O}_{14}(\text{H}_2\text{O})_2$ belt.

from the α -Keggin structure by removing one of the W_3O_{13} groups. The W-O bond lengths and O-W-O bond angles summarized in Table 2 show typical values and differ only slightly from known structures of the $\text{M}_4\text{X}_2\text{W}_{18}$ - type. The centered As^{V} atom is surrounded tetrahedrally by four oxygen atoms. Three of these oxygen atoms are situated in the centers of the three W_3O_{13} groups with bonds to three tungsten atoms. The fourth oxygen atom is bonded to three Ni atoms.

The two $(\text{AsW}_9\text{O}_{34})^{9-}$ Keggin fragments are connected *via* a $\text{Ni}_4\text{O}_{14}(\text{H}_2\text{O})_2$ belt. The two crystallographically independent Ni atoms in **1** have both a distorted octahedral coordination sphere. Ni(1) is bonded to one water molecule, two oxygen atoms of one $(\text{AsW}_9\text{O}_{34})^{9-}$ subunit and three oxygen atoms of the second $(\text{AsW}_9\text{O}_{34})^{9-}$ subunit. For Ni(2), each of the subunits provides three oxygen atoms. All Ni-O distances are in the range between 1.97 and 2.15 Å, and the O-Ni-O bond angles summarized in Table 2 show the distortion of the NiO_6 octahedra. Comparing the coordination environment with that of the Cu^{II} analogue [16], the NiO_6 octahedra are only slightly distorted, whereas the $[\text{Cu}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ anion shows Jahn-Teller distortion of the CuO_6 octahedra. The axial Cu-O distances (2.33–2.49 Å) differ significantly from the equatorial ones (1.95–2.03 Å).

A comparison of the Ni...Ni distances in $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ (anion in **1**) and $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ [14] is given in Table 3. In the rhombic M_4O_{16} clusters, the Ni...Ni distances in **1** are elongated when compared to the phosphorus-containing anion. The side lengths of the Ni_4 unit differ by less than 0.05 Å, whereas the shortest diagonal (Ni(2)...Ni(2*)) is almost 0.1 Å longer in **1**. Similar results can be observed in the Cu^{II} and Zn^{II}

Table 3. Ni...Ni distances (Å) and O-Ni-O angles (deg) in $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ (anion in **1**) and $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$.

	$[\text{Ni}_4(\text{H}_2\text{O})_2(\text{XW}_9\text{O}_{34})_2]^{10-}$	
	X = As	X = P
Ni(1)...Ni(1*)	5.384	5.352
Ni(1)...Ni(2)	3.149	3.124
Ni(1)...Ni(2*)	3.156	3.109
Ni(2)...Ni(2*)	3.282	3.196
Ni-O-Ni	96.7–98.6	97.7–99.0

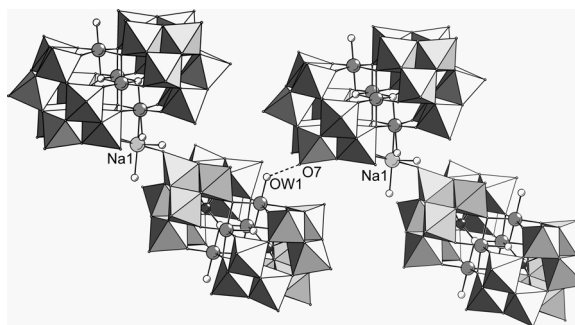


Fig. 3. Linkage of $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ anions *via* Na(1) and $\text{O}^{\text{W}}(1)\cdots\text{O}(7)$.

substituted anions of the $\text{M}_4\text{As}_2\text{W}_{18}$ and $\text{M}_4\text{P}_2\text{W}_{18}$ series [16].

For charge balance, five cations per asymmetric unit are necessary. Two sodium cations could be located during the refinement of the crystal structure. In accordance with the elemental analysis, we assume that three NH_4^+ cations are present in the asymmetric unit. Na(1) is coordinated octahedrally by four crystal water molecules and two oxygen atoms of two $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ anions. Na(2) is surrounded octahedrally by six water molecules and not bonded to the $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ anion. Table 2 summarizes the relevant bond lengths and angles. The shortest intercluster O...O distance is 2.71(2) Å between $\text{O}^{\text{W}}(1)$ and $\text{O}(7)$ (O^{W} = oxygen atom of a water molecule). Although the hydrogen atoms have not been located during the refinement, the O...O distance indicates a linkage of the polyoxoanions *via* hydrogen bonds [22]. Fig. 3 shows the linkage of the polyoxoanions *via* Na(1) and $\text{O}^{\text{W}}(1)\cdots\text{O}(7)$.

The IR spectrum shows the O-H and N-H absorption bands as well as typical frequencies for W-O bonds. The UV/vis spectra of polyoxometalates generally convey no structural information. However, an absorption band around *ca.* 195 nm and a shoulder at *ca.* 250 nm are observed in all $\text{M}_4\text{As}_2\text{W}_{18}$ polyoxo-

tungstates, indicating the similarity of the electronic structures [16]. The UV/vis spectrum of **1** shows a band at 192 nm ($\epsilon \approx 14950 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 245 nm ($\epsilon \approx 4170 \text{ M}^{-1} \text{ cm}^{-1}$), both attributed to charge transfer $\text{O} \rightarrow \text{W}$.

Experimental Section

Syntheses

All starting materials and chemicals were used as received without further purification:

Preparation of $(\text{NH}_4)_6\text{Na}_4[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 20 \text{ H}_2\text{O}$ (1**):** A sample of $\text{Na}_2\text{WO}_4 \cdot 2 \text{ H}_2\text{O}$ (3 g, 9.09 mmol) was dissolved in 30 ml of distilled water. $\text{As}_2\text{O}_5 \cdot 5 \text{ H}_2\text{O}$ (0.129 g, 1 mmol) was dissolved in 2 ml of distilled water and added dropwise. The pH was adjusted to 6.5 and the solution was heated to 70 °C. After half an hour, a solution of $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ (0.47 g, 2 mmol dissolved in 2 ml of distilled water) was added slowly, the pH was again adjusted to 6.5, and the solution was heated for one hour. The solution was allowed to cool, filtered and treated with 1 ml of a saturated solution of NH_4Cl . Green single crystals were obtained on slow evaporation. – Yield: 1.3 g (48%). $\text{As}_2\text{H}_{68}\text{N}_6\text{Na}_4\text{Ni}_4\text{O}_{90}\text{W}_{18}$ (5378.0): calcd. N 1.56, H 1.27; found N 1.68, H 1.44%. EDX: calcd. ratio Ni : As : W = 4.00 : 2.00 : 18.00; found: = 3.72 : 2.18 : 18.00. IR: $\tilde{\nu} (\text{cm}^{-1}) = 3492\text{vs} (\nu (\text{O-H})); 3128\text{s} (\nu (\text{N-H})); 1623\text{s} (\delta (\text{H-O-H})); 1400\text{s} (\delta (\text{H-N-H})); 1255\text{w}; 951\text{vs} (\nu (\text{W-O}_i)); 888\text{s} (\nu (\text{W-O}_c)); 747\text{s} (\nu (\text{W-O}_e)); 519\text{w}, 463\text{w}$. (t terminal, e edge, c corner).

Instrumentation and analytical procedures

The IR spectrum was measured on a Perkin Elmer 683 spectrometer as a KBr pellet. Elemental analysis was carried out on an Elementar Vario EL III analyzer. The atomic ratios of the heavy elements were determined by energy dispersive X-ray fluorescence analysis (EDX). The UV/vis spectrum was measured at 25 °C on a Hewlett-Packard 8453 diode array spectrometer using a quartz cuvette (1 cm). Diffraction experiments were performed on a STOE IPDS imaging plate system using Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods with the SHELXS-97 and refined with the SHELXL-97 program [23]. No hydrogen atoms were included during the refinement. The tungsten, arsenic, nickel and sodium atoms were refined anisotropically by full-matrix least-squares calculations based on F^2 , the oxygen and nitrogen atoms were refined isotropically. The program DECAY was applied for absorption correction [24]. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-414227.

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