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Sandwich-Type Phosphotungstates: Structure, Electrochemistry, and Magnetism of the Trinickel-Substituted Polyoxoanion $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$

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The novel nickel-substituted, dimeric phosphotungstate $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ (**1**) has been synthesized and characterized by IR spectroscopy, elemental analysis, and electrochemistry. X-ray single-crystal analysis was carried out on $Na_{11}[Ni_3Na(H_2O)_2(PW_9O_{34})_2]\cdot21.25H_2O$, which crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 12.2467(6)$ Å, $b = 16.6031(7)$ Å, $c = 22.4017(12)$ Å, $\alpha = 73.9870(10)°$, $\beta = 87.6060(10)°$, $\gamma = 79.344(2)°$, and $Z = 2$. The polyanion consists of two lacunary B-α-$[PW_9O_{34}]^{9-}$ Keggin moieties linked via three nickel(II) centers and a sodium ion. The structure of **1** is composed of two fused Keggin fragments that represent different Baker–Figgis isomers (α- vs β-type). Electrochemical studies show that **1** exhibits a stable and reproducible voltammetric pattern, with a first wave featuring a chemically reversible four-electron/four-proton process. An investigation of the magnetic properties indicates that the three nickel centers exhibit ferromagnetic exchange interaction.

Introduction

Polyoxoanions are metal−oxygen clusters with an enormous structural diversity.[1,2] Although the first polyoxometalates were synthesized almost 2 centuries ago, a detailed structural description was accomplished only much later. The reason is that the use of standard analytical techniques (e.g. IR, UV−vis, MS, electrochemistry, elemental analysis) alone is usually insufficient for a detailed structural characterization. Single-crystal X-ray diffraction is the most powerful technique for determining the structure of a novel species. Usually the solid-state structures of polyoxoanions are retained in solution, which can often be demonstrated by multinuclear NMR.

In addition to their esthetic structural features the unique combination of interesting properties renders polyoxometalates a unique class of inorganic compounds.[3−5] Applications of polyoxometalates include catalysis, medicine, materials science, photochemistry, analytical chemistry, and magnetochemistry.

The mechanism of formation of polyoxometalates is not well understood and commonly described as self-assembly. More efforts are needed in order to understand better the mysterious equilibria of formation of polyoxometalates, so that eventually rational syntheses of novel species may be possible.

Sandwich-type polyoxometalates based on two B-α-$[XW_9O_{34}]^{n-}$ ($X = P^V, As^V, Si^{IV}$) or B-α-$[X_2W_{15}O_{56}]^{12-}$ ($X = P^V, As^V$) fragments, and four transition metal centers constitute a well-known class of compounds.[6] The first example of this type, $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, was reported by Weakley et al.[6a] Later Finke et al. reported on an analogous structural type based on two lacunary Wells−

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Dawson ions, $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ (M = Co^{2+}, Cu^{2+}, Zn^{2+}).[6c] Evans et al. were the first to report on a As(V) derivative of the Keggin type, $[Zn_4(H_2O)_2(AsW_9O_{34})_2]^{10-}$.[6d] Recently Bi et al. described the first arsenic(V) analogues of the Wells−Dawson type, ($[M_4(H_2O)_2(As_2W_{15}O_{56})_2]^{16-}$ (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}).[6p] Also recently Kortz et al. reported on the first examples of sandwich-type tungstosilicates, $[M_4(H_2O)_2(SiW_9O_{34})_2]^{12-}$ (M = Mn^{2+}, Cu^{2+}, Zn^{2+}).[6q] These polyanions were synthesized from the dilacunary, metastable precursor $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$.

Recently Hill and co-workers described the first example of a sandwich-type species with less than four transition metals.[7] The diiron(III)-substituted polyanion, $[Fe_2(NaOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$, is based on two Wells−Dawson fragments, and the two equivalent exterior positions are occupied by sodium ions in the solid state. Hill et al. also showed that this polyanion reacts with Cu^{2+} or Co^{2+} ions in aqueous solution, leading to a trisubstituted mixed-metal sandwich-type polyanion.[8] Very recently the same authors described the triiron(III)-substituted polyanion, $[Fe_2(FeOH_2)(NaOH_2)(P_2W_{15}O_{56})_2]^{14-}$.[9] The di- and trisubstituted cobalt(II) analogues of this polyanion are also known.[10]

Here we report on the first example of a trisubstituted sandwich-type polyoxoanion based on the *B*-α-$[PW_9O_{34}]^{9-}$ Keggin fragment.

Experimental Section

Synthesis. All reagents were used as purchased without further purification.

$Na_{11}[Ni_3Na(H_2O)_2(PW_9O_{34})_2]\cdot 21.25H_2O$. A 8.00 g (1.6 mmol) sample of $K_7[H_4PW_{18}O_{62}]\cdot 18H_2O$[11] was added to 20 mL of H_2O upon stirring at room temperature, and then 8.00 g (57 mmol) $NaClO_4\cdot H_2O$ was added. The solution was vigorously stirred for 15 min and then cooled in an ice bath for about 2 h. The solid $KClO_4$ that had formed was isolated by filtration, and then about 5 g of solid NaCl was added to the yellow filtrate. At this point 25 mL of 1 M Na_2CO_3 solution was added, resulting in slow decoloring of the solution. After about 15 min a white precipitate started to appear, but the solution (pH 8.5) was stirred for another 30 min. Then the precipitate was isolated by filtration and washed consecutively with 1 M NaCl, ethanol, and diethyl ether. The solid was air-dried, resulting in 2.30 g of $Na_9[A\text{-}PW_9O_{34}]\cdot 5H_2O$ as based on infrared spectroscopy and electrochemistry, using the product obtained by the method of Domaille[12] as a reference.

A 0.31 g (1.30 mmol) sample of $NiCl_2\cdot 6H_2O$ was added with stirring to 20 mL of a 1 M NaCl solution. Then 2.00 g (0.79 mmol) of $Na_9[A\text{-}PW_9O_{34}]\cdot 5H_2O$ (synthesized as decribed above)[13] was added in small portions over 5 min. The solution was heated to 60 °C for about 30 min in a water bath and then filtered. The green, clear filtrate (pH 6.9) was placed in a refrigerator (4 °C). After several months a mixture of green and yellow crystals (in approximately equal amounts) had formed. We were able to isolate a sufficient amount of each product by manual separation of the respective crystals under a microscope. The green compound (0.12 g) corresponds to Coronado's trimeric $Na_{16}[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]$ as based on FTIR.[14] The yellow crystals (0.14 g, yield 7%) correspond to the title compound. IR for $Na_{11}[Ni_3Na(H_2O)_2(PW_9O_{34})_2]\cdot 14H_2O$: 1062(sh), 1039(s), 1023(s), 963(s), 940(s), 899(s), 788(sh), 739(vs), 585(vw), 486(w), 330(w) cm^{-1}. Anal. Calcd (Found) for $Na_{11}[Ni_3Na(H_2O)_2(PW_9O_{34})_2]\cdot 14H_2O$: Na, 5.3 (5.6); W, 63.7 (63.5); Ni, 3.4 (3.6); P, 1.2 (1.3).

The sample used for elemental analysis and IR was air-dried, and therefore it has a reduced degree of hydration (14 H_2O) compared to the result of single-crystal X-ray diffraction (21.25 H_2O). Elemental analysis was performed by Kanti Labs Ltd. in Missisauga, Canada. The IR spectrum was recorded on a Bio-Rad FTS 165 FTIR spectrophotometer using KBr pellets.

X-ray Crystallography. A yellow block of the sodium salt of **1** with dimensions 0.20 × 0.06 × 0.06 mm^3 was mounted on a glass fiber for indexing and intensity data collection at 293 K on a Bruker D8 SMART APEX CCD single-crystal diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å). Of the 21 241 unique reflections ($2\theta_{max} = 56.64°$), 16 423 reflections ($R_{int} = 0.048$) were considered observed ($I > 2\sigma(I)$). Direct methods were used to solve the structure and to locate the tungsten and nickel atoms (SHELXS97). Then the remaining atoms were found from successive difference maps (SHELXL97). The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (W, Ni, and P atoms) and isotropic thermal parameters (Na and O atoms) converged at $R = 0.052$ and $R_w = 0.119$ ($I > 2\sigma(I)$). In the final difference map the highest peak was 5.255 e $Å^{-3}$ and the deepest hole −2.178 e $Å^{-3}$.

Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program.[15] Crystallographic data are summarized in Table 1. The X-ray crystallographic structure determination of the title compound

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(13) Currently we are attempting to also synthesize the title polyanion $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ (**1**) by interaction of Ni^{2+} ions with $[A\text{-}PW_9O_{34}]^{9-}$, which has been synthesized by the method of Domaille.[12] However, no crystals of **1** have been formed to date.

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Table 1. Crystal Data and Structure Refinement for $Na_{11}[Ni_3Na(H_2O)_2(PW_9O_{34})_2]\cdot 21.25H_2O$

empirical formula	$H_{46.5}Na_{12}Ni_3O_{91.25}P_2W_{18}$	volume, Å^3	4302.6(4)
Fw	5330.2	Z	2
space group	$P\bar{1}$ (No. 2)	temp, °C	20
a, Å	12.2467(6)	wavelength, Å	0.710 73
b, Å	16.6031(7)	density (calcd), g/cm^3	4.02
c, Å	22.4017(12)	abs. coeff, mm^{-1}	24.789
α, deg	73.9870(10)	$R(F_o)^a$	0.052
β, deg	87.6060(10)	$R_w(F_o)^b$	0.119
γ, deg	79.344(2)		

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

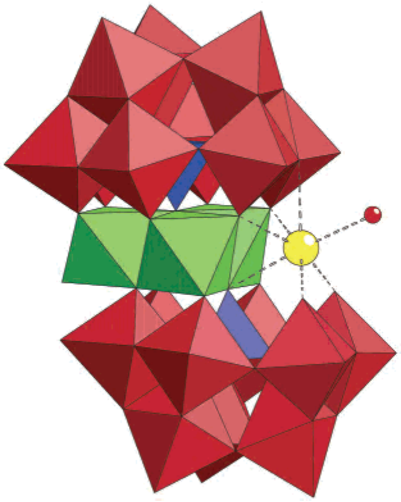

Figure 1. Combined polyhedral/ball-and-stick representation of $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ (**1**). The PO_4, WO_6, and NiO_6 polyhedra are shown in blue, red, and green, respectively. The sodium atom is shown as a yellow ball and its terminal water molecule as a red ball.

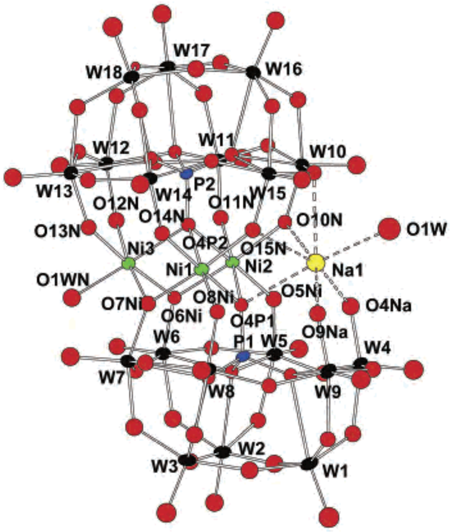

Figure 2. Ball-and-stick representation of $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ (**1**) showing 50% probability ellipsoids and the labeling scheme for all atoms except oxygens of the tungsten−oxo framework (for clarity).

was performed twice. The first was done by Mr. Patrick Herson at the Université Pierre et Marie Curie, Paris, on a Nonius CAD4 diffractometer and the second by U.K. at the Florida State University, Tallahassee, on a Bruker D8 SMART APEX CCD diffractometer. Only the latter is reported here, because it turned out to be of significantly better quality.

Results and Discussion

The novel polyoxoanion $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ (**1**) consists of two lacunary B-α-$[PW_9O_{34}]^{9-}$ Keggin moieties linked via three Ni^{2+} ions and a sodium ion (see Figures 1 and 2). The arrangement of the central, rhomblike Ni_3NaO_{16} group and the two Keggin fragments leads to a sandwich-type structure. The core of **1** is composed of two Ni^{2+} ions located in the two internal positions, and one of the two external positions is occupied by another Ni^{2+} ion, whereas the other is occupied by a sodium ion. Both of the latter are distinct sites without crystallographic disorder, because the entire polyanion is present in the asymmetric unit. All nickel centers are octahedrally coordinated (2.00−2.21(1) Å), whereas the sodium ion has bonding interaction with seven oxygen atoms (2.27−2.70(1) Å) leading to a distorted, monocapped-octahedral coordination environment. As expected, the external nickel center and the sodium ion have a terminal water ligand each. The bond lengths and angles of the tungsten−oxo framework are within the usual ranges.

Bond-valence sum calculations confirm that the terminal oxygens of Ni3 and Na1 are the only protonated sites of **1**.[16] This means that eleven sodium counterions are present in addition to Na1, which was confirmed by elemental analysis. It was not unexpected that only 8.5 out of 11 sodium ions could be identified by X-ray diffraction, because of disorder.

It is of interest to examine the junctions of the two Keggin fragments with the central unit in **1** in order to identify which Baker−Figgis isomers are present. It turns out that two types of cap rotation isomers can be observed, α and β. The junction involving the three Ni^{2+} ions is of the α-type, whereas the junction involving the two central Ni^{2+} ions and the sodium ion is of the β-type. By contrast, the linkages of all known tetrasubstituted sandwich-type Keggin complexes (e.g. $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$) have two junctions of the β-type. However, the observations for **1** are in complete agreement with those of Hill et al. for their family of iron(III)-substituted Wells−Dawson sandwich complexes. The tetrairon-substituted $[Fe_2(FeOH_2)_2(P_2W_{15}O_{56})_2]^{12-}$ has two β-junctions, the diiron-substituted $[Fe_2(NaOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$ has two α-junctions, and the triiron-substituted $[Fe_2(FeOH_2)(NaOH_2)(P_2W_{15}O_{56})_2]^{14-}$ has one β-junction and one α-junction.[7,9,17] In analogy to **1** the α-junction of the triiron-substituted species involves the three iron sites, whereas the β-junction is formed by the two central iron sites and the sodium ion. Using the configuration methodology suggested

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by Hill et al., the complete description of the title polyanion with an indication of the junction connectivity is $\alpha\alpha\beta\alpha$-$[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$.

Interestingly synthesis of **1** is accomplished by interaction of Ni^{2+} ions with the trivacant Keggin isomer of the *A*-type, $[A\text{-}PW_9O_{34}]^{9-}$. However, the Keggin fragments present in **1** are of the *B*-type, which means that during the course of the reaction the following isomerization must have taken place: $[A\text{-}PW_9O_{34}]^{9-} \rightarrow [B\text{-}PW_9O_{34}]^{9-}$. Some time ago Knoth et al.[18] have demonstrated that $[A\text{-}PW_9O_{34}]^{9-}$ can be transformed to $[B\text{-}PW_9O_{34}]^{9-}$ in solution upon heating, and then Domaille[12] showed that the same isomerization can be accomplished in the solid state. When Knoth et al. reacted $[A\text{-}PW_9O_{34}]^{9-}$ with divalent first-row transition metals in a ratio of about 1:2 at room temperature, they obtained dimeric heteropolyanions of the type $[M_3(A\text{-}PW_9O_{34})_2]^{12-}$ (M = Mn, Fe, Co, Ni, Cu, Zn).[18] However, heating of these solutions above 60 °C resulted in a transformation to the well-known family of tetrasubstituted polyoxoanions, $[M_4(H_2O)_2(B\text{-}PW_9O_{34})_2]^{10-}$. The title polyanion **1** belongs to the same class of sandwich compounds, but with the significant difference that only three nickel centers are present. The tetranickel-substituted analogue, $[Ni_4(H_2O)_2(B\text{-}PW_9O_{34})_2]^{10-}$, has been fully characterized by Coronado et al.[14] Interestingly this species was not synthesized from a preformed (PW_9O_{34}) lacunary precursor, but directly from a source of the three composing elements phosphorus(V), tungsten(VI), and nickel(II). Using the same synthetic approach Coronado et al. also synthesized the trinickel-substituted species $[Ni_3(H_2O)_3(B\text{-}PW_9O_{34})WO_5H_2O]^{7-}$ and the nonanickel-substituted species $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(B\text{-}PW_9O_{34})_3]^{16-}$, which occurred also as a byproduct in the synthesis of **1**.[14] Some time ago Kortz et al. reported on $[Ni_4(OH)_3(H_2O)_6(B\text{-}H_2PW_9O_{34})]^{2-}$, which is another member of the family of nickel-substituted polyoxotungstates containing the $(B\text{-}PW_9O_{34})$ fragment.[19] This species was synthesized by interaction of Ni^{2+} ions with the preformed $[B\text{-}PW_9O_{34}]^{9-}$ unit.

During the course of our investigation of Ni-substituted polyoxotungstates we have been able to synthesize Coronado's species, but starting with the $(B\text{-}PW_9O_{34})$ precursor. This clearly indicates that the reaction conditions are more important than the type of precursor used. Furthermore we discovered that all of the above-mentioned species are present in the pH range 5−7, but which of them dominates at a given pH depends on the interplay of factors, including ionic strength, temperature, concentration of reagents, ratio of reagents, and type of spectator ions (cations and anions). Our research has shown that it appears almost impossible to identify conditions where only one product is present in solution. This observation was confirmed by Coronado et al. who isolated their title polyanions by fractional crystallization in order to avoid contamination with side products.[14] It must be realized that the structurally very diverse class of nickel-containing tungstophosphates appears to be extremely sensitive to a modification of any of the factors mentioned above. However, if a set of conditions has been identified at which the equilibrium of formation of any one polyoxotungstate dominates, an excess of Ni^{2+} ions does not seem to have a strong influence on the product composition. We have experimental evidence for this conclusion, and Coronado et al. have made the same observation.[14]

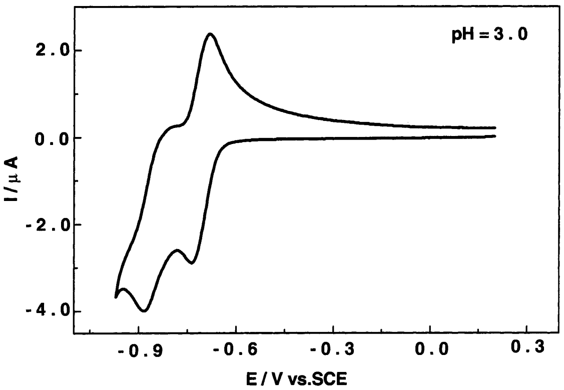

Figure 3. Representative cyclic voltammogram of 2 × 10^{-4} M $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ (**1**) in an aqueous pH 3 solution (0.2 M Na_2SO_4 + H_2SO_4). Working electrode, glassy carbon disk; reference electrode, SCE; scan rate, 10 mV s^{-1}.

The reason **1** is formed rather than $[Ni_4(H_2O)_2(B\text{-}PW_9O_{34})_2]^{10-}$ under our reaction conditions could be due to various reasons: (1) we performed the reaction in 1 M NaCl, because Hill et al. had shown that a high concentration of sodium ions stabilizes lacunary, sandwich-type species;[7a,8,9] (2) the $Ni^{2+}/(PW_9O_{34})$ ratio of 1.65 is too low for formation of the tetranickel-substituted species; (3) the byproduct $Na_{16}[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]$ starts to crystallize before **1**. This means that at the time of crystallization of **1** the ratio of $Ni^{2+}/(PW_9O_{34})$ in solution is reduced even further. This might be an important lead in the search of reaction conditions that result only in **1**, without any byproducts. This work is currently in progress.[20]

It is worth noting that **1** exhibits a perfectly stable and reproducible voltammetric pattern, at least in the pH 3 and pH 5 media studied here. This is in contrast to the lacunary $[A\text{-}PW_9O_{34}]^{9-}$ precursor species used for the synthesis of **1**, which undergoes a wealth of transformations in aqueous solution. The cyclic voltammogram of **1** (see Figure 3) was run in a pH 3 medium (0.2 M Na_2SO_4 + H_2SO_4) with a thoroughly polished glassy carbon electrode.[21] This voltammogram is restricted to its first two waves. The first wave features a four-electron process as confirmed by controlled potential coulometry. It shows complete chemical reversibility at a scan rate of 10 mV s^{-1} used for running the voltammogram. Also, quantitative reoxidation of the reduced product was achieved after the coulometry. At pH 5, the current intensity of the first wave does not change, but in comparison with the value observed in the pH 3 medium, a

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(20) During the review period of this manuscript we discovered that the title compound $Na_{11}[Ni_3Na(H_2O)_2(PW_9O_{34})_2]\cdot 14H_2O$ can also be synthesized starting from $[B\text{-}PW_9O_{34}]^{9-}$ instead of $[A\text{-}PW_9O_{34}]^{9-}$. The identity of the product was demonstrated by electrochemistry and FTIR.

(21) Keita, B.; Belhouari, A.; Nadjo, L.; Contant, R. *J. Electroanal. Chem.* **1998**, *442*, 49.

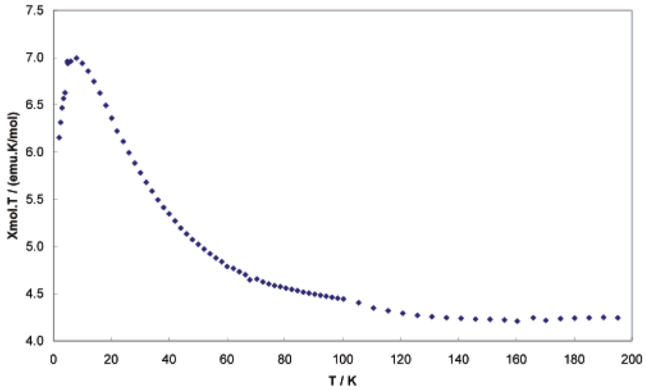

Figure 4. Plot of the product X_mT for $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ (**1**) as a function of T. The data were recorded in a 1000 Oe field.

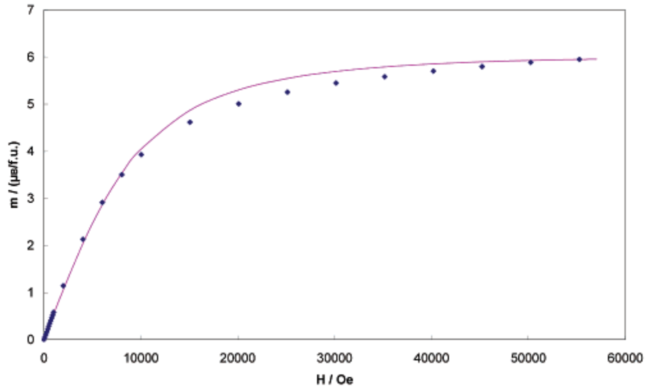

Figure 5. Plot of the magnetization of $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ (**1**) as a function of the applied field, recorded at 2 K. The continuous line represents a Brillouin function for an $S = 3$ state with a Landé factor $g = 2$.

shift of its peak potential by 128 mV in the negative direction was observed. This shift combined with the coulometry results is indicative of an overall four-electron/four-proton process.

Magnetic measurements of the title compound were also carried out on a polycrystalline sample using a SQUID magnetometer (Quantum Design MPMS-5). The temperature dependence of the magnetization was studied in a 1000 Oe field. The product X_mT deduced from it was corrected for diamagnetic contributions and plotted as a function of T as shown in Figure 4. The product X_mT has a maximum value (7.0 emu·K·mol^{-1}) at 8 ± 1 K and becomes practically constant (4.25 ± 0.05 emu·K·mol^{-1}) above 130 K. Such behavior indicates ferromagnetic exchange interactions between the nickel atoms of the cluster transmitted through the oxo bridges and suggests a $S = 3$ ground state. The measurement of the field dependence of the magnetization, carried out at 2 K, leads to a similar conclusion (see Figure 5). The experimental data are very close to a Brillouin function describing an $S = 3$ state with a Landé factor $g = 2.0$. Moreover, this behavior indicates that the Ni_3 intercluster interactions are negligible, which is in agreement with the rather large distances between neighboring polyoxoanions. The above conclusions are in agreement with other tri- and tetranickel-substituted polyoxoanions.[6k,o,19,22]

The title compound is also of interest for redox catalysis and electrocatalysis. It is also expected that reaction of **1** with other transition metals besides nickel can lead to mixed-metal sandwich-type Keggin polyoxoanions. These studies will be performed as soon as the synthesis of **1** has been optimized.

Conclusion

Trisubsituted sandwich-type tungstophosphates constitute a novel class of polyoxoanions that has been discovered very recently. Only very few compounds of this type are known, and all of them are based on the Wells–Dawson fragment $[P_2W_{15}O_{56}]^{12-}$. This work has presented the first species based on the Keggin fragment $[B\text{-}PW_9O_{34}]^{9-}$. In all of these compounds the lacunary site in the central, rhomblike plane of the dimeric structure is occupied by a sodium ion. Therefore it appears that the presence of Na^+ ions is essential for the formation of trisubsituted sandwich-type polyoxoanions. Interestingly the trisubstituted species seem to be more stable than their tetrasubstituted analogues and in addition they exhibit very promising catalytic activity. Substitution of the sodium ion by a variety of transition metal centers should lead to a series of mixed-metal-substituted polyoxoanions with even more interesting properties.

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Supporting Information Available: Cyclic voltammetric data at pH 3 and 5 (Table S1) and one X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] Kortz, U.; Jeannin, Y. P.; Tézé, A.; Hervé, G.; Isber, S. *Inorg. Chem.* **1999**, *38*, 3670.