

Palladium(II)-Substituted Tungstosilicate [Cs₂K(H₂O)₇Pd₂WO(H₂O)(A-α-SiW₉O₃₄)₂]⁹⁻

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Received August 17, 2004

The palladium(II)-substituted tungstosilicate [Cs₂K(H₂O)₇Pd₂WO(H₂O)(A-α-SiW₉O₃₄)₂]⁹⁻ (**1**) has been synthesized and characterized by IR, elemental analysis, and electrochemistry. Single-crystal X-ray analysis was carried out on Cs₃K₂Na₄[Cs₂K(H₂O)₇Pd₂WO(H₂O)(A-α-SiW₉O₃₄)₂]⁹⁻·5H₂O (**1a**), which crystallizes in the monoclinic system, space group *P*2₁/*n*, with *a* = 16.655(3) Å, *b* = 19.729(4) Å, *c* = 25.995(5) Å, β = 95.46(3)°, and *Z* = 4. Polyanion **1** represents the first structurally characterized palladium(II)-substituted tungstosilicate. The title polyanion consists of two (A-α-SiW₉O₃₄) Keggin moieties linked via a {WO(H₂O)}⁴⁺ group and two equivalent, square-planar Pd²⁺ ions leading to a sandwich-type structure with C_{2v} symmetry. The central belt of **1** contains also one potassium and two cesium ions. Polyanion **1** was synthesized by reaction of Pd(CH₃COO)₂ with K₁₀[A-α-SiW₉O₃₄] in aqueous acidic medium (pH 4.8). A cyclic voltammetry study of polyanion **1** in a pH 5 medium shows a Pd⁰ deposition process on the glassy carbon electrode surface. The corresponding wave and that of tungsten redox processes could be separated clearly during the first few runs before their merging into a broad composite wave. The film thickness increases with the number of potential cycles or the duration of potentiostatic electrolysis. As judged from hydrogen sorption/desorption pattern, the quality of the film deposited from polyanion **1** is better than that of a film deposited directly from Pd²⁺ solutions.

Introduction

Polyoxometalates (POMs) are metal–oxygen cluster species with an enormous structural variety and interesting properties.^{1–4} The class of POMs has been known for almost 200 years since the time of Berzelius.⁵ However, POM chemistry has generated substantial interest in recent years, and numerous novel structural types with fascinating topo-

logical beauty and important electronic, optical, magnetic, and catalytic properties have been developed.^{6–8} Parallel to the rapid progress of POMs, synthesis of and studies on transition metal-substituted POMs (TMSPs) have also exploded. Nowadays, TMSPs can be considered as the largest subclass of polyanions.⁹ Within the class of TMSPs, the sandwich-type compounds represent the largest family. To date, the Hervé-,¹⁰ Weakley-,¹¹ Krebs-,¹² and Knoth-type¹³ sandwich polyanions can be distinguished. The most interesting, but also the most difficult, challenges in POM chemistry

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involve the synthesis of fundamentally novel, discrete polyanions. Transition metal-substituted, sandwich-type polyanions are of particular interest, because of their highly tunable nature, coupled with their chemical robustness. This unique combination of properties is of interest for applications in catalysis, medicine, and material science.¹⁴

The class of Knoth-type sandwich POMs is based on two A - α -Keggin fragments, e.g. $[A-\alpha-PW_9O_{34}]^{9-}$. In 1985, Knoth et al. reported the first member of this class, $[Co_3(H_2O)_3(A-\alpha-PW_9O_{34})_2]^{12-}$.^{13a} Since then the following isostructural derivatives have been identified: $[M_3(A-XW_9O_{34})_2]^{n-}$ ($n = 14$, $X = Si^{IV}$, $M = Sn^{2+}$, Co^{2+} ; $n = 12$, $X = P^V$, $M = Mn^{2+}$, Ni^{2+} , Cu^{2+} , Zn^{2+} , Pd^{2+} , Sn^{2+} ; $n = 9$, $X = P^V$, $M = Fe^{3+}$);^{13b,d,e} $[(CeO_3)(H_2O)_2(A-PW_9O_{34})_2]^{12-}$,^{13b} $[(ZrOH)_3(A-SiW_9O_{34})_2]^{11-}$,^{13c} $[(YOH)_3(CO_3)(A-PW_9O_{34})_2]^{11-}$,¹⁵ $[Na_2(NpO_2)_2(A-PW_9O_{34})_2]^{14-}$,¹⁶ $[Na_2(UO_2)_2(A-PW_9O_{34})_2]^{12-}$.¹⁷

There are very few reports on POMs containing 4d and 5d elements in general and palladium in particular. In 1986, Knoth et al. reported on the synthesis of the palladium-substituted, sandwich-type polyanion $[Pd_3(A-PW_9O_{34})_2]^{12-}$ on the basis of elemental analysis.^{13b} In 1991, Tourné et al. described the sandwich-type species $[WZnPd_2(H_2O)_2(B-\alpha-ZnW_9O_{34})_2]^{12-}$, which was also characterized by elemental analysis.¹⁸ In 1994 Angus-Dunne et al. reported on the synthesis and structure of $[Pd_2W_{10}O_{36}]^{8-}$, which represents the first palladium(II)-substituted isopolytungstate.¹⁹ In 1995, Neumann et al. resynthesized $[WZnPd_2(H_2O)_2(B-\alpha-$

$ZnW_9O_{34})_2]^{12-}$ and characterized it by elemental analysis, electrochemistry, and IR, UV-vis, and ¹⁸³W NMR spectroscopy.²⁰ It was shown that palladium(II)-substituted polyoxotungstates have excellent catalytic properties for the selective and efficient transformation of organic substrates and the oxidation of alkanes and alkenes by peroxides.²¹ Very recently our group reported on the first structurally characterized palladium(II)-substituted tungstoantimonate(III), $[Cs_2-Na(H_2O)_{10}Pd_3(\alpha-Sb^{III}W_9O_{33})_2]^{9-}$.²²

The above indicates that the rational synthesis and structural characterization of palladium-substituted POMs is difficult, but the potentially attractive catalytic properties of such species are a strong motivation to undergo this kind of research.

Tungstosilicates are a well-known class of POMs, and they represent probably the second largest subclass besides tungstophosphates.¹ A number of mono-, di-, and trilacunar tungstosilicates has been known for many years (e.g. α - $[SiW_{11}O_{39}]^{8-}$, $[\gamma-SiW_{10}O_{36}]^{8-}$, $[A-\alpha-SiW_9O_{34}]^{10-}$), and the synthetic procedures for all these species have been developed by the groups of Hervé and Tézé.²³ Lacunar tungstosilicates can be used as precursors for reactions with transition metal ions, and our group has been particularly interested in the dilacunar $[\gamma-SiW_{10}O_{36}]^{8-}$. We have shown that this species is highly reactive, and we discovered that with first-row transition metal ions dimeric,^{24a,b} trimeric,^{24c} and even tetrameric^{24d} products with unexpected structures are formed. Furthermore, we noticed that during reaction the $(\gamma-SiW_{10}O_{36})$ fragment tends to isomerize to β - or α -Keggin fragments, depending on the transition metal.²⁴ This isomerization can even be accompanied by loss of tungsten, e.g. $(\gamma-SiW_{10}O_{36}) \rightarrow (B-\alpha-SiW_9O_{34})$.

The sodium salt of the trilacunar tungstosilicate, $Na_{10}[A-x-SiW_9O_{34}]$ ($x = \alpha, \beta$), has been the common precursor for reactions of this polyanion.^{25,26} However, recently Hervé et al. prepared the potassium salt $K_{10}[A-\alpha-SiW_9O_{34}]$ by controlled hydrolysis of $[\alpha-SiW_{11}O_{39}]^{8-}$.^{13e} Then these authors investigated reaction of $K_{10}[A-\alpha-SiW_9O_{34}]$ with Co^{2+} ions in aqueous solution and they isolated the sandwich-type polyanion $[Co_3(H_2O)_3(A-\alpha-SiW_9O_{34})_2]^{14-}$.^{13e}

Here we report on interaction of $K_{10}[A-\alpha-SiW_9O_{34}]$ with Pd^{2+} ions in aqueous medium.

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Experimental Section

Synthesis. The lacunary tungstosilicate precursor K₁₀[A- α -SiW₉O₃₄] \cdot 24H₂O was synthesized according to the published procedure.^{13c} The identity of the product was confirmed by infrared spectroscopy. All other reagents were used as purchased without further purification.

Cs₃K₂Na₄[Cs₂K(H₂O)₇Pd₂WO(H₂O)(A- α -SiW₉O₃₄)₂] \cdot 5H₂O (1a). A 0.11 g (0.49 mmol) sample of Pd(CH₃COO)₂ was dissolved with stirring in 20 mL of 0.5 M Na(CH₃COO) buffer (pH 4.8). Then 1.0 g (0.33 mmol) of K₁₀[A- α -SiW₉O₃₄] \cdot 24H₂O was added. The solution was heated to 80 °C for about 1 h and filtered after it had cooled. Then 1.5 mL of 1.0 M CsCl solution was added to the red filtrate. Slow evaporation at room temperature led to 0.39 g (yield 40%) of a red crystalline product after about 1 month. IR: 1001 (m), 957 (sh), 939 (m), 892 (s), 777 (vs), 710 (sh), 685 (sh), 587 (sh), 551 (w), 533 (w), 441 (w) cm⁻¹. Anal. Calcd (found) for **1a**: Cs, 11.1 (11.8); K, 2.0 (1.9); Na, 1.5 (1.4); W, 58.5 (57.6); Pd, 3.6 (3.7); Si, 0.9 (1.1).

Elemental analysis was performed by Kanti Labs Ltd. in Mississauga, Canada. Infrared spectra were recorded on KBr pellets using a Nicolet Avatar spectrophotometer.

X-ray Crystallography. A crystal of **1a** was mounted on a glass fiber for indexing and intensity data collection at 293 K on a Rigaku Mercury single-crystal diffractometer using Mo K α radiation (λ = 0.710 73 Å). Direct methods were used to solve the structure and to locate the heavy 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 (all W, Pd, Si, Cs, K, and Na atoms), and isotropic thermal parameters (all O atoms), converged at R = 0.052 and R_w = 0.120 ($I > 2\sigma(I)$). No hydrogens were included in the refinement. In the final difference map the deepest hole was $-4.494 \text{ e} \cdot \text{Å}^{-3}$ and the highest peak $6.092 \text{ e} \cdot \text{Å}^{-3}$. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the MULTISCAN program.²⁷ Crystallographically we could identify 5 Cs⁺, 2.5 K⁺, and 1 Na⁺ counterion, but elemental analysis indicated that indeed 3 K⁺ and 4 Na⁺ were present in **1a**. Therefore, the charge of -9 for **1** (based on bond valence sum analysis)²⁸ is fully balanced in the solid state by 3 cesium, 2 potassium, and 4 sodium counterions. Disorder of alkali metal ions is a common problem in polyanion chemistry, and our results indicate nicely that this problem increases in the sequence Cs, K, Na. Crystallographic data are summarized in Table 1.

Electrochemistry. Pure water was used throughout. It was obtained by passing through a RiOs 8 unit followed by a Millipore-Q Academic purification set. The measurements were performed in 0.4 M Na(CH₃COO) + CH₃COOH (pH 5), and the concentration of **1** was 2×10^{-4} M. All cyclic voltammograms were recorded at a scan rate of 2 mV \cdot s⁻¹, unless otherwise stated. The solutions were deaerated thoroughly for at least 30 min with pure argon and kept under a positive pressure of this gas during the experiments. The source, mounting, and polishing of the 3 mm diameter glassy carbon disk (GC, Tokai, Japan) have been described.²⁹ The electrochemical setup was an EG&G 273 A driven by a PC with the M270 software. Potentials are quoted against a saturated calomel electrode (SCE). The counter electrode was a

Table 1. Crystal and Structure Refinement Data for Cs₃K₂Na₄[Cs₂K(H₂O)₇Pd₂WO(H₂O)(A- α -SiW₉O₃₄)₂] \cdot 5H₂O (**1a**)

emp formula	Cs ₅ H ₂₆ K ₃ Na ₄ O ₈₂ Pd ₂ Si ₂ W ₁₉
fw	5974.2
space group (No.)	P2 ₁ /n (14)
a (Å)	16.655(3)
b (Å)	19.729(4)
c (Å)	25.995(5)
β (deg)	95.46(3)
V (Å ³)	8503(3)
Z	4
temp (°C)	20
wavelength (Å)	0.710 73
d_{calc} (Mg m ⁻³)	4.615
abs coeff (mm ⁻¹)	28.374
R [$I > 2\sigma(I)$] ^a	0.052
R_w (all data) ^b	0.120

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

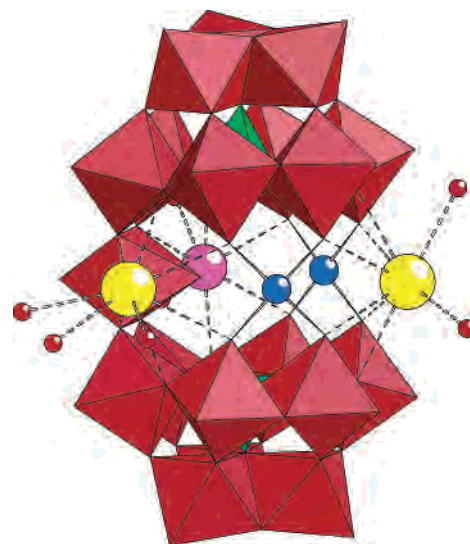


Figure 1. Combined polyhedral/ball-and-stick representation of [Cs₂K(H₂O)₇Pd₂WO(H₂O)(A- α -SiW₉O₃₄)₂]⁹⁻ (**1**). The octahedra represent WO₆ (red) and SiO₄ (green), and the balls are palladium (blue), cesium (yellow), potassium (purple), and oxygen (red).

platinum gauze of large surface area. All experiments were performed at the laboratory temperature.

Results and Discussion

Synthesis and Structure. The novel palladium(II)-substituted, dimeric tungstosilicate [Cs₂K(H₂O)₇Pd₂WO(H₂O)(A- α -SiW₉O₃₄)₂]⁹⁻ (**1**) has been synthesized by reaction of Pd(CH₃COO)₂ with K₁₀[A- α -SiW₉O₃₄] in aqueous, acidic medium and isolated as a mixed cesium–potassium–sodium salt. Polyanion **1** represents only the second structurally characterized palladium-substituted heteropolytungstate.²² The title polyanion **1** consists of two [A- α -SiW₉O₃₄]¹⁰⁻ Keggin fragments linked via two square-planar Pd²⁺ ions and a {WO(H₂O)}⁴⁺ moiety leading to a structure with idealized C_{2v} symmetry (see Figure 1). Alternatively, **1** can be described as a dilacunary [Si₂W₁₉O₆₉(H₂O)]¹⁶⁻ fragment which has taken up two Pd²⁺ ions. The [Si₂W₁₉O₆₉(H₂O)]¹⁶⁻ polyanion is highly interesting because it represents a novel class of lacunary tungstosilicates. Interestingly, [Si₂W₁₉O₆₉(H₂O)]¹⁶⁻ was formed from [A- α -SiW₉O₃₄]¹⁰⁻ in situ during the synthesis of **1** (see below). The jawlike shape of the dimeric, dilacunary [Si₂W₁₉O₆₉(H₂O)]¹⁶⁻ resembles the well-

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known, lone pair containing $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$. The latter species was synthesized for the first time about 30 years ago by Tourné et al.,³⁰ and recently Kortz et al. confirmed the proposed structure by single-crystal X-ray diffraction.³¹ The dilacunary $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ has been used as a precursor for the synthesis of transition metal- and monoorganotin-substituted derivatives as well as a large tungstoarsenate.^{10b,31–33} Both polyanion ligands, $[\text{Si}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]^{16-}$ and $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$, are composed of two trilacunary Keggin fragments linked by a $\{\text{WO}(\text{H}_2\text{O})\}^{4+}$ moiety which acts like a hinge. Therefore, the vacant sites of these lacunary polyanions are flexible and can adjust to the bond lengths requirements of the incorporated transition metal ions. However, it must be noticed that both polyanion ligands support predominantly square-planar or square-pyramidal coordination geometries.

The subtle structural differences between $[\text{Si}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]^{16-}$ and $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ are centered around the trilacunary Keggin fragments and in particular their hetero groups. The title polyanion **1** is composed of two (*A*- α - $\text{SiW}_9\text{O}_{34}$) fragments which contain a tetrahedral (SiO_4) hetero group each. On the other hand, $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ is composed of two (*B*- α - $\text{As}^{\text{III}}\text{W}_9\text{O}_{33}$) fragments which contain a trigonal pyramidal ($\text{As}^{\text{III}}\text{O}_3$) hetero group that has a lone pair of electrons associated with it. We believe that $[\text{Si}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]^{16-}$ can, in analogy to $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$, exist independently and most likely alkali metal ions (e.g. K^+) are needed to stabilize the vacant sites. This would give rise to a novel dilacunary precursor which could then be reacted with a variety of electrophiles (e.g. transition metal ions, organotin species) resulting in novel products with interesting properties.

Polyanion **1** was synthesized in acetate buffer (pH 4.8) by interaction of Pd^{2+} ions with the potassium salt trilacunary Keggin precursor $[\text{A}-\alpha-\text{SiW}_9\text{O}_{34}]^{10-}$. Therefore, the mechanism of formation of **1** involves insertion of Pd^{2+} in the lacunary precursor followed/accompanied by dimerization. The structure of **1** contains a tungsten atom in the central belt in addition to the two palladiums, which indicates that some $[\text{A}-\alpha-\text{SiW}_9\text{O}_{34}]^{10-}$ must have decomposed in the course of the reaction. We also tried to synthesize **1** using the sodium salt of $[\text{A}-\alpha-\text{SiW}_9\text{O}_{34}]^{10-}$ but without success.

It is not unexpected that a small degree of decomposition occurs for $[\text{A}-\alpha-\text{SiW}_9\text{O}_{34}]^{10-}$ in aqueous, acidic (pH 4.8) medium upon heating. It must be remembered that this trilacunary precursor is synthesized at around pH 9 and therefore it is expected at pH 4.8 to slowly transform to di- or monolacunary derivatives (e.g. $[\alpha-\text{SiW}_{11}\text{O}_{39}]^{8-}$). This transformation inevitably involves decomposition of some polyanions to provide the required tungsten atoms. It is also

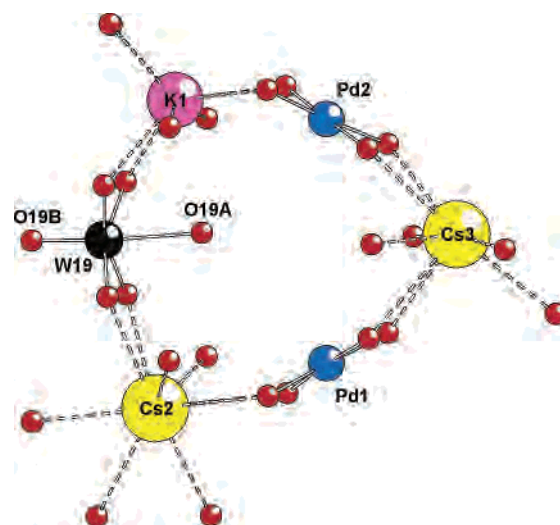


Figure 2. Ball-and-stick representation of the central belt in **1**. The color code is the same as in Figure 1, and O19A is a water molecule.

known that upon heating at pH 4.8 the sodium salt of $[\text{A}-\alpha-\text{SiW}_9\text{O}_{34}]^{10-}$ isomerizes to $[\text{B}-\alpha-\text{SiW}_9\text{O}_{34}]^{10-}$.^{24a} All of the above processes appear to be strongly influenced by the alkali metal cations or cation mixtures present in solution.^{13c} However, to date we only have a superficial understanding of how counterions influence the above transformations and of their role in polyoxoanion solution chemistry in general. Nevertheless, our results suggest that K^+ counterions stabilize the trilacunary $[\text{A}-\alpha-\text{SiW}_9\text{O}_{34}]^{10-}$ and allow one to isolate products containing this fragment. It appears that K^+ ions (and maybe also Cs^+ ions) are crucial for the formation of both, **1** and the dilacunary fragment $[\text{Si}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]^{16-}$. This observation is in complete agreement with $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$, which is stabilized by potassium ions in the lacunary site.^{31,32c}

Bond-valence sum calculations for **1** indicate that the central, hingelike tungsten atom has a terminal water ligand ($\text{W19}-\text{O19A}$, 2.37(1) Å) pointing inside the central cavity of **1** and trans to it a terminal oxo group ($\text{W19}-\text{O19B}$, 1.74(1) Å).²⁸ Interestingly, this is exactly opposite to $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$, in which the central W atom has an internal oxo and an external water ligand.³¹ We believe that this is a result of the lone pair of electrons on the heteroatoms in $[\text{As}^{\text{III}}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ which point at each other and toward the center of the cavity in the polyanion. As there are no other protonation sites on **1** besides the water molecule associated with W19, the charge of the title polyanion must be -9 . This result is fully consistent with elemental analysis, which indicated the presence of 5 cesium, 3 potassium, and 4 sodium ions. Three of the counterions are closely associated with the title polyanion, namely K1, Cs2, and Cs3, which are all present in the central belt of **1** (see Figure 2). Interestingly, the “unsymmetrical” distribution of these 3 counterions within the central belt of **1** results in a reduction of the idealized C_{2v} symmetry to only C_s symmetry.

The potassium ion K1 is eight-coordinated by six μ_2 -oxo groups of **1**, one terminal water molecule (O9W), and a terminal oxo group (O15T) of a neighboring polyanion (see Figure 2). The $\text{K1}\cdots\text{O}$ distances are in the expected ranges

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(2.69–2.90(1) Å). In analogy to K1, the cesium ions Cs2 and Cs3 are bound to the same type of six μ_2 -oxo groups of **1**. In addition, Cs2 has three terminal oxo ligands (O12T, O13T, O123) which belong all to a neighboring polyanion. The Cs3 atom has two terminal ligands of which one is a water molecule (O5W) and the other is an oxo group (O10T) of a neighboring polyanion. The Cs2···O and Cs3···O distances are in the expected ranges (3.06–3.41(1) Å). The above indicates that the solid-state structure of **1a** is a fairly compact 3D network dominated by closely spaced polyanions that are linked to each other via two bonds involving the three alkali metal ions incorporated in the central belt of **1** (e.g. POM–K1···O15T–W15–POM).

In **1**, the Pd–O bond lengths (1.97–1.99(1) Å) are very regular and in the expected range and the O–Pd–O angles (88.9–91.0(4), 175.9–177.5(4)°) are very close to the ideal values. This indicates that the square-planar (PdO₄) groups exhibit essentially no strain. The Pd···Pd distance in **1** is 5.8 Å, which is significantly larger than the Pd···Pd distances (4.39 Å) in $[Cs_2Na(H_2O)_{10}Pd_3(\alpha-Sb^{III}W_9O_{33})_2]^{9-}$.²² The Pd···Pd separation in **1** is somewhat (0.3 Å) smaller than the Pd···W19 distances (6.1 Å). This observation is a result of the fact that W19 is displaced toward its terminal oxo group, which is at the exterior site.

Electrochemistry. Except for $[WZnPd_2(H_2O)_2(B-\alpha-ZnW_9O_{34})_2]^{12-}$, studied by Neumann et al.,²⁰ only one other Pd-containing heteropolyanion, $[Cs_2Na(H_2O)_{10}Pd_3(\alpha-SbW_9O_{33})_2]^{9-}$ (**2**) has been thoroughly characterized by cyclic voltammetry to date.²² In the latter example, the cyclic voltammetry study shows the deposition of Pd⁰ on the glassy carbon electrode surface, giving a film with a particularly well-behaved hydrogen sorption/desorption pattern. In the present case, polyanion **1** was studied by cyclic voltammetry in 0.4 M (CH₃COO⁻ + CH₃COOH) pH 5 buffer corresponding to its synthesis medium. The scan rate was 2 mV·s⁻¹.

Figure 3A shows the pattern observed for a 2×10^{-4} M solution of **1** during the first few voltammetric runs. The first cathodic peak features the Pd⁰ deposition process, well-separated from the reduction of W centers, and this separation persists for several runs. This observation constitutes a remarkable difference with the patterns for PdSO₄ solutions or the more closely related **2**. In the latter case, such a pattern could be observed only during the very first voltammetric run on a clean glassy carbon surface. This difference can probably not be attributed to charge differences of **1** and **2**, which would be the same (–9) in case the three alkali metal ions in the belt (**1**, 2 Cs⁺, K⁺; **2**, 2 Cs⁺, Na⁺) remain closely associated with the polyanions in solution. Most likely structural and/or compositional differences between **1** and **2** (e.g. the number of incorporated palladium atoms) are responsible for the observed behavior. With PdSO₄, a broad drawn-out deposition wave was obtained, in agreement with the usual observation that the deposition can be performed in a large potential domain.³⁴ For all three compounds, the subsequent sharp cathodic peak and the sharp and narrow anodic counterpart feature the hydrogen sorption/desorption processes.

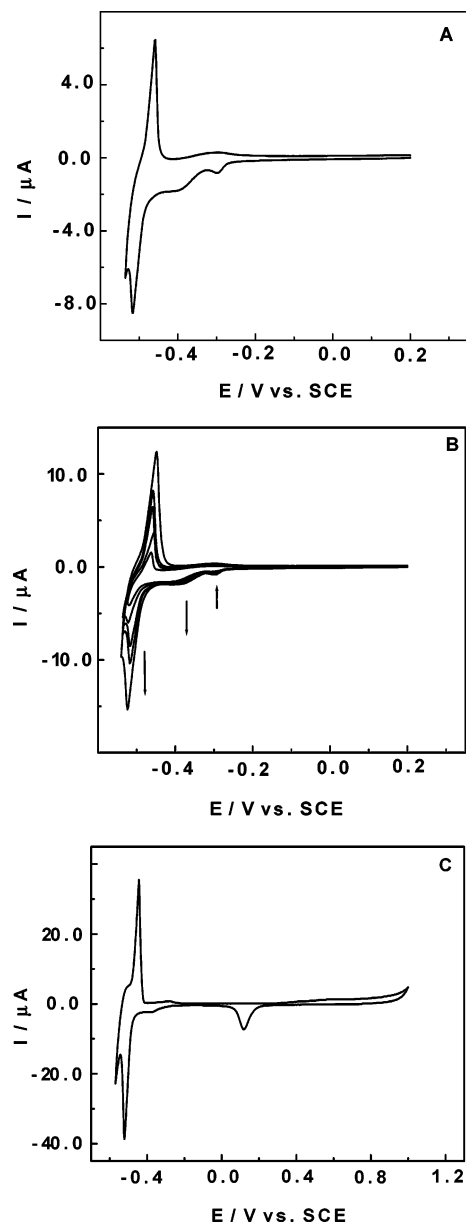


Figure 3. Cyclic voltammetry (CV) characterization of a solution of 2×10^{-4} M **1** in 0.4 M (CH₃COO⁻ + CH₃COOH) pH = 5 buffer: working electrode, glassy carbon; reference electrode, SCE; scan rate, 2 mV·s⁻¹. (A) A representative CV of the pattern observed during the first few runs of the electrode potential from +0.200 to –0.536 V and back. (B) The evolution of cyclic voltammograms during the 2nd, 3rd, 4th, 5th, and 7th runs (the last cathodic peak current increases steadily for every consecutive run). The arrows indicate the evolutions of the current intensities of the waves for every consecutive run. (C) A representative CV of the pattern observed for a film when the electrode potential was scanned from –0.100 to –0.536 V and then to +1.0 V and back to –0.1 V.

In short, results gathered from the pertinent literature³⁴ suggest that Figure 3A features the characteristics of the deposition behavior of Pd⁰ on the glassy carbon electrode surface. The potential cycling program in Figure 3A ensures the deposition of Pd⁰ on the electrode surface. Alternatively, film deposition can be realized by potentiostatic electrolysis. The faster the increase in film thickness, the more negative the potential selected for the cathodic end of the cyclic potential scan or, alternatively, the value chosen for controlled-potential electrolysis. As expected, the thickness increases also with the number of cycles or the duration of potenti-

static electrolysis. These observations parallel the literature results for deposition from uncomplexed Pd^{2+} ions.³⁴ Figure 3B shows the evolution of cyclic voltammograms during the 2nd, 3rd, 4th, 5th, and 7th runs. The film growth is accompanied by the decrease and finally disappearance of the Pd^0 deposition wave which becomes engulfed in a broad composite palladium deposition and W-reduction wave. The observation is rewarding in that it constitutes a direct proof of the main processes active in the drawn-out composite wave. A final comparison concerns the hydrogen sorption/desorption patterns obtained with the films deposited from polyanions **1**, **2**, and Pd^{2+} , respectively. Contrasting with the almost perfect symmetry observed in the case of **2**,²² the patterns are more dissymmetrical with the other two films as can be viewed in Figure 3B for polyanion **1**. Even so, we found that the anodic to cathodic peak potential difference remains roughly 1.5 to twice as large for the film deposited from Pd^{2+} than for the one obtained from polyanion **1**. This result underscores the favorable influence of the polyanion framework on the quality of the deposited film.

Figure 3C features a complete study of the film during its deposition from polyanion **1**. The voltammogram can be divided in two potential domains to be described in sequence. The domain starting from -0.1 to $+1.0$ V in the positive potential direction and back to -0.1 V represents unambiguously oxidation of the deposited Pd surface followed by reduction of the oxide. This part of the pattern is exactly the same as obtained previously with **2**.²² However, the following qualitative difference was observed: the current intensities of both the oxidation wave and the oxide reduction wave indicate a faster film growth for **2** than for **1**.

The domain from -0.1 to -0.536 V and back was studied in detail in Figure 3B. A complementary experiment (not shown) was also carried out. After deposition of a film on the glassy carbon surface, the electrode was taken out of the solution, copiously rinsed with Millipore water, eventually left for some time in the open air, and then soaked in pure supporting electrolyte (pH = 5). The pattern obtained in Figure 3C was exactly reproduced, except for the broad “first” deposition wave which was missing. Incidentally, this experiment demonstrates the perfect stability of the film.

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Upon addition of polyanion **1** to the supporting electrolyte, the curve in Figure 3C was obtained with restoration of the usually observed deposition wave. A rough estimate of the film thickness in Figure 3C can be calculated as follows. Typically, the reoxidation of the film shown in this figure requires 480×10^{-6} C, which corresponds to about 1.5×10^{15} Pd atoms. With an atomic radius of 140 pm for Pd,³⁵ a monolayer of these atoms would cover an area of 1.6×10^{-4} m². With an electrode of surface area 7.07×10^{-6} m², the deposited film corresponds to about 13 monolayers.

Conclusions

We have synthesized the novel palladium(II)-substituted tungstosilicate $[\text{Cs}_2\text{K}(\text{H}_2\text{O})_7\text{Pd}_2\text{WO}(\text{H}_2\text{O})(\text{A}-\alpha\text{-SiW}_9\text{O}_{34})_2]^{9-}$ (**1**). The title polyanion **1** represents the second structurally characterized palladium-substituted heteropolyanion. The tungsten-oxo fragment in **1** is composed of two (A- α - $\text{SiW}_9\text{O}_{34}$) Keggin fragments linked via a $\{\text{WO}(\text{H}_2\text{O})\}^{4+}$ moiety. The dimeric $[\text{Si}_2\text{W}_{19}\text{O}_{69}(\text{H}_2\text{O})]^{16-}$ represents a novel, dilacunary polyoxotungstate precursor. We expect several transition metal substituted as well as hybrid organic-inorganic polyanions to evolve from our work. It is also of interest to find out if one or even both palladium sites in **1** can be substituted by tungsten centers. This would result in analogues of the known tungstoarsenates(III) (e.g. $[\text{As}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})]^{10-}$, $[\text{As}_2\text{W}_{21}\text{O}_{69}(\text{H}_2\text{O})]^{6-}$) or tungstophosphates (e.g. $[\text{P}_2\text{W}_{20}\text{O}_{70}(\text{H}_2\text{O})_2]^{10-}$, $[\text{P}_2\text{W}_{21}\text{O}_{71}(\text{H}_2\text{O})_3]^{6-}$). Furthermore, we will investigate if the germanium analogue of **1** exists. In future work we also plan to investigate the redox catalytic properties of **1**.

Cyclic voltammetry of **1** in a pH 5 medium resulted in deposition of a Pd^0 film on the glassy carbon electrode surface. The voltammetric pattern shows clearly separated Pd-deposition and W-reduction processes during the first few runs. To our knowledge, this observation is unprecedented. This work opens several new perspectives, e.g. the morphology of the deposited film will be observed by near-field microscopies and its conductivity will be evaluated. Comparisons will be made with the film obtained from **2**, which is currently under investigation. Finally, the lacunary tungsten-oxo framework of polyanion **1** suggests that mixed noble metal derivatives can be synthesized. Such compounds could allow for electrochemical codeposition of the two metals for catalytic applications.

Acknowledgment. U.K. thanks the International University Bremen for research support. B.K. and L.N. thank the University Paris Sud XI and the CNRS (UMR 8000) for research support. Figures 1 and 2 were generated by Diamond Version 2.1e (copyright Crystal Impact GbR).

Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC048864Z

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