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First Structurally Characterized Palladium(II)-Substituted Polyoxoanion: $[Cs_2Na(H_2O)_{10}Pd_3(\alpha\text{-}Sb^{III}W_9O_{33})_2]^{9-}$

Li-Hua Bi,[†] Markus Reicke,[†] Ulrich Kortz,[*,†] Bineta Keita,[‡] Louis Nadjo,[‡] and Ronald J. Clark[§]

School of Engineering and Science, International University Bremen, P.O. Box 750 561,
28725 Bremen, Germany, Laboratoire de Chimie Physique, UMR 8000, CNRS,
Equipe d'Electrochimie et Photoélectrochimie, Université Paris-Sud, Bâtiment 420,
91405 Orsay Cedex, France, and Department of Chemistry and Biochemistry,
Florida State University, Tallahassee, Florida 32306-4390

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The palladium-substituted tungstoantimonate(III) $[Cs_2Na(H_2O)_{10}Pd_3(\alpha\text{-}SbW_9O_{33})_2]^{9-}$ (**1**) has been synthesized and characterized by IR, elemental analysis, and electrochemistry. Single-crystal X-ray analysis was carried out on $Cs_3KNa_5[Cs_2Na(H_2O)_{10}Pd_3(SbW_9O_{33})_2]\cdot16.5H_2O$, which crystallizes in the monoclinic system, space group $P2_1/m$, with $a = 13.3963(13)$ Å, $b = 19.5970(19)$ Å, $c = 18.1723(17)$ Å, $\beta = 100.416(2)°$, and $Z = 2$. Polyanion **1** represents the first structurally characterized palladium(II)-substituted polyoxometalate. The title polyoxoanion consists of two $(\alpha\text{-}Sb^{III}W_9O_{33})$ Keggin moieties linked via three Pd^{2+} ions leading to a sandwich-type structure. The palladium centers are equivalent, and they are coordinated in a square-planar fashion. The central belt of **1** contains also one sodium and two cesium ions which reduces the symmetry of the polyanion to C_{2v}. Polyanion **1** was synthesized in good yield by reaction of $Pd(CH_3COO)_2$ with $Na_9[SbW_9O_{33}]$ in aqueous acidic medium (pH 4.8). A cyclic voltammetry study of polyanion **1** in a pH 5 medium gives essentially the same characteristics as those observed for the deposition of Pd^0 on the glassy carbon electrode surface from Pd^{2+} solutions. The film thickness increases with the number of potential cycles or the duration of potentiostatic electrolysis. The particularly sharp hydrogen sorption/desorption pattern indicates the excellent quality of the Pd^0 deposit from polyanion **1**.

Introduction

The existence of polyoxometalates (POMs for convenience) has been known for almost 200 years, and 1 century later the first structural details were revealed.[1] POMs constitute a rapidly growing class of molecular metal−oxygen clusters with an enormous diversity of structures.[2−8] The significant contemporary interest in POM chemistry is driven by perceived and realized applications in many areas such as catalysis, analysis, medicine, biochemistry, material science, and so on.[4−8]

Among all known transition metal substituted polyoxometalates (TMSPs), the sandwich-type species are probably the largest subfamily.[9] Since the discovery of the first sandwich-type polyoxoanion, $[Co_4(H_2O)_2(B\text{-}\alpha\text{-}PW_9O_{34})_2]^{10-}$, by Weakley et al. in 1973 several other sandwich-type species have been identified over the last 30 years of research activity.[10a]

The class of Weakley-type sandwich species consists of the Keggin derivatives $[M_4(H_2O)_2(B\text{-}\alpha\text{-}XW_9O_{34})_2]^{n-}$ (n =12, X = Ge^{IV}, Si^{IV}, M = Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}; n = 10, X =

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[*] Author to whom correspondence should be addressed. E-mail: u.kortz@iu-bremen.de. Fax: +49-421-200 3229.

[†] International University Bremen.

[‡] Université Paris-Sud.

[§] Florida State University.

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P^V, As^V, M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}; n = 6, X = P^V, As^V, M = Fe^{3+}) and the Wells−Dawson derivatives $[M_4(X_2W_{15}O_{56})_2]^{n-}$ (X = P^V, As^V, n = 16, M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, n = 12, M = Fe^{3+}).[10]

The class of Hervé-type sandwich POMs is based on two lone pair-containing, α-Keggin fragments, e.g. $[\alpha\text{-}As^{III}W_9O_{33}]^{9-}$. The first member of this class ($[Cu_3(H_2O)_2(\alpha\text{-}AsW_9O_{33})_2]^{12-}$) was reported by Hervé et al. in 1982.[11a] Since then a number of isostructural derivatives have been characterized: $[M_3(H_2O)_3(\alpha\text{-}XW_9O_{33})_2]^{n-}$ (n = 12, X = As^{III}, Sb^{III}, M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; n = 10, X = Se^{IV}, Te^{IV}, M = Cu^{2+}) and $[(VO)_3(\alpha\text{-}XW_9O_{33})_2]^{n-}$ (n = 12, X = As^{III}, Sb^{III}, Bi^{III}; n = 11, X = As^{III}).[11,12f]

The class of Krebs-type sandwich POMs is based on two lone pair-containing, β-Keggin fragments, e.g. $[\beta\text{-}Sb^{III}W_9O_{33}]^{9-}$. The first members of this class, ($[M_2(H_2O)_6(WO_2)_2(\beta\text{-}SbW_9O_{33})_2]^{(14-2n)-}$ (M^{n+} = Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}), were reported by Krebs et al. in 1997.[12a] Since then some more isostructural derivatives have been characterized: ($[M_2(H_2O)_6(WO_2)_2(\beta\text{-}BiW_9O_{33})_2]^{(14-2n)-}$ (M^{n+} = Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), $[(VO(H_2O)_2)_2(WO_2)_2(\beta\text{-}BiW_9O_{33})_2]^{10-}$, $[Sn_{1.5}(WO_2(OH))_{0.5}(WO_2)_2(\beta\text{-}XW_9O_{33})_2]^{10.5-}$ (X = Sb^{III}, Bi^{III}), $[M_3(H_2O)_8(WO_2)(\beta\text{-}TeW_9O_{33})_2]^{8-}$ (M = Ni^{2+}, Co^{2+}), $[(Zn(H_2O)_3)_2(WO_2)_{1.5}(Zn(H_2O)_2)_{0.5}(\beta\text{-}TeW_9O_{33})_2]^{8-}$, $[(VO(H_2O)_2)_{1.5}(WO(H_2O)_2)_{0.5}(WO_2)_{0.5}(VO(H_2O))_{1.5}(\beta\text{-}TeW_9O_{33})_2]^{7-}$, and $[M_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{n-}$ (n = 6, X = As^{III} and Sb^{III} , M = Fe^{III} and Cr^{III}; n = 4, X = Se^{IV}, Te^{IV}, M = Fe^{III} and Cr^{III}; n = 8, X = Se^{IV}, Te^{IV}, M = Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, and Hg^{II}).[12]

The class of Knoth-type sandwich POMs is based on two A-α-Keggin fragments, e.g. $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$. The first member of this class, $[Co_3(H_2O)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{12-}$, was reported by Knoth et al. in 1985.[13a] Since then the following isostructural derivatives have been identified: $[M_3(A\text{-}XW_9O_{34})_2]^{n-}$ (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+}), $[(CeO)_3(H_2O)_2(A\text{-}PW_9O_{34})_2]^{12-}$, and $[(ZrOH)_3(A\text{-}SiW_9O_{34})_2]$.[11−13]

It can be noticed that in almost all of the above examples the incorporated transition metal ions are from the first row. There are very few reports on sandwich-type polyoxotungstates substituted by 4d or 5d metals in general and by Pd and Pt in particular. In 1986, Knoth et al. reported on the synthesis of the sandwich-type polyoxoanion $[Pd_3(A\text{-}PW_9O_{34})]^{12-}$ (see above) on the basis of elemental analysis.[13b] In 1991, Tourné et al. described the sandwich-type heteropolyanion $[WZnPd_2(H_2O)_2(B\text{-}\alpha\text{-}ZnW_9O_{34})_2]^{12-}$, which was also characterized by elemental analysis.[14] In 1995, Neumann et al. resynthesized the same species and characterized it by elemental analysis, electrochemistry, IR, UV−vis, and ^{183}W NMR spectroscopy.[15] They also investigated the catalytic activity of this polyanion in the oxidation of alkanes and alkenes by peroxides. More recently the same and also other authors showed that palladium(II)-substituted polyoxotungstates have excellent catalytic properties for the selective and efficient transformation of organic substrates.[16] The palladium congener, platinum, is known to incorporate in the Pt(IV) state into Anderson-type structures.[17]

The above results show that the rational synthesis and structural characterization of noble-metal-substituted POMs is a challenge. Nevertheless, the potentially attractive catalytic properties of such species are a strong motivation to undergo this kind of research. Therefore, we initiated a systematic study on the interaction of Ru^{3+} and Pd^{2+} ions with the entire arsenal of lacunary polyoxotungstates.

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Table 1. Crystal and Structure Refinement Data for $Cs_3KNa_5[Cs_2Na(H_2O)_{10}Pd_3(SbW_9O_{33})_2]\cdot16.5H_2O$ (**1a**)

emp formula	$Cs_5H_{59}KNa_6O_{92.5}Pd_3Sb_2W_{18}$
fw	6253.2
space group (No.)	$P2_1/m$ (11)
a (Å)	13.3963(13)
b (Å)	19.5970(19)
c (Å)	18.1723(17)
β (deg)	100.416(2)
V (Å^3)	4692.1(8)
Z	2
temp (°C)	−100
wavelength (Å)	0.710 73
d_{calc} (Mg m^{-3})	4.369
abs coeff (mm^{-1})	25.171
R [$I > 2\sigma(I)$]^a	0.058
R_w (all data)^b	0.122

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

Here we report for the first time on the structural characterization of a palladium(II)-substituted polyoxoanion.

Experimental Section

Synthesis. The precursor polyanion $[\alpha\text{-}SbW_9O_{33}]^{9-}$ was synthesized according to the published procedure.[12a] The identity of the product was confirmed by infrared spectroscopy. All other reagents were used as purchased without further purification.

$Cs_3KNa_5[Cs_2Na(H_2O)_{10}Pd_3(SbW_9O_{33})_2]\cdot16.5H_2O$ (1a). A 0.14 g (0.62 mmol) sample of $Pd(CH_3COO)_2$ was dissolved with stirring in 20 mL of 0.5 M $Na(CH_3COO)$ buffer (pH 4.8). Then 0.50 g (0.20 mmol) of $Na_9[\alpha\text{-}SbW_9O_{33}]$ was added in small portions. The solution was heated to 80 °C for about 1 h and filtered after it had cooled, and then 0.5 mL of 1.0 M CsCl and KCl solutions, respectively, were added to the red filtrate. Slow evaporation at room temperature led to 0.39 g (yield 63%) of a reddish crystalline product after about 1 month. IR: 937 (m), 884 (m), 851 (m), 765 (s), 672 (m), 518 (w), 472 (w), 444 (w) cm^{-1}. Anal. Calcd (found) for $Cs_3KNa_5[Cs_2Na(H_2O)_{10}Pd_3(SbW_9O_{33})_2]\cdot16.5H_2O$: Cs, 10.6 (9.9); K, 0.6 (0.7); Na, 2.2 (2.1); W, 52.9 (52.3); Pd, 5.1 (4.8); Sb, 3.9 (3.7).

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 173 K on a Bruker D8 SMART APEX CCD single-crystal diffractometer using Mo Kα radiation ($\lambda = 0.710\ 73$ 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).

Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program.[18] 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 $Na(CH_3COO) + CH_3COOH$ (pH 5), and the polyanion concentration was 2×10^{-4} M. All cyclic voltammograms were recorded at a scan rate of 2 mV 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 glassy carbon (GC, Tokai, Japan) electrodes has been described.[19] The glassy carbon samples had a diameter of 3 mm. 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 platinum gauze of large surface area. All experiments were performed at room temperature.

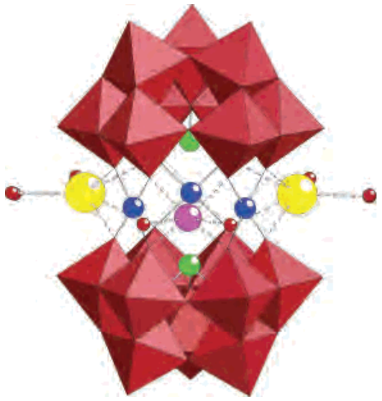

Figure 1. Combined polyhedral/ball-and-stick representation of $[Cs_2Na(H_2O)_{10}Pd_3(SbW_9O_{33})_2]^{9-}$ (**1**). The WO_6 octahedra are shown in red, and the balls represent palladium (blue), antimony (green), cesium (yellow), sodium (purple), and water molecules (red).

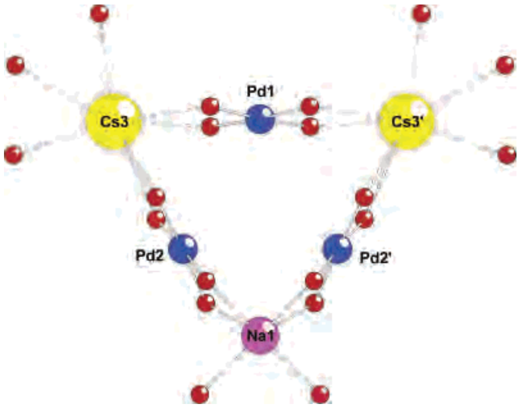

Figure 2. Ball-and-stick representation of the central belt in **1**. The color code is the same as in Figure 1.

Results and Discussion

Synthesis and Structure. The dimeric polyoxoanion $[Cs_2Na(H_2O)_{10}Pd_3(\alpha\text{-}SbW_9O_{33})_2]^{9-}$ (**1**) consists of two (α-SbW_9O_{33}) moieties linked by three square-planar Pd^{2+} ions resulting in a sandwich-type structure (see Figure 1). The central belt of **1** is completed by two Cs^+ and a Na^+ ion which occupy the vacancies between the adjacent palladium centers, resulting in a polyanion with idealized C_{2v} symmetry (see Figure 2). The structure of the title polyoxoanion is closely related to the copper(II)-substituted tungstoantimonate(III) $[Na_3(H_2O)_6Cu_3(\alpha\text{-}SbW_9O_{33})_2]^{9-}$ and the isostructural tungstoarsenate(III) $[Na_3(H_2O)_6Cu_3(\alpha\text{-}AsW_9O_{33})_2]$.[9–11c] The only differences are (a) the copper(II) ions have a square-pyramidal coordination geometry (terminal H_2O ligand) and (b) the space between the copper(II) ions is occupied by three sodium ions. The synthetic procedures of the copper(II) and palladium(II) derivatives are also very similar. Polyanion **1**

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was synthesized in good yield in a simple one-pot procedure by interaction of Pd^{2+} ions with $[\alpha\text{-}SbW_9O_{33}]^{9-}$ in aqueous acidic medium (pH 4.8).

Polyanion **1** represents the first structurally characterized palladium(II)-substituted polyoxoanion. There are very few reports in the literature on palladium(II)-substituted polyanions, but for none of these species the molecular structure could be determined by single-crystal X-ray diffraction.[13b,14,15] Most likely the lack of single crystals suitable for X-ray diffraction prevented such studies. This is somewhat surprising as (a) there are several pure Pd^{2+} salts commercially available which can be reacted directly with lacunary polyoxoanions and (b) in our hands the formation and crystallization of **1** did not prove to be extremely difficult. Nevertheless we have not been able to synthesize the hypothetical arsenic(III) derivative of **1**, $[Cs_2Na(H_2O)_{10}Pd_3(\alpha\text{-}AsW_9O_{33})_2]^{9-}$. By reacting Pd^{2+} ions with $[\alpha\text{-}AsW_9O_{33}]^{9-}$ using an analogous synthetic procedure, we obtained a different product, which will be described elsewhere. Interestingly, Pope et al. also observed formation of different products in their study on lone-pair-containing, monoorganotin-substituted polyanions.[20] This is different from reaction of Cu^{2+} and Zn^{2+} ions with $[\alpha\text{-}SbW_9O_{33}]^{9-}$ and $[\alpha\text{-}AsW_9O_{33}]^{9-}$ in neutral, aqueous medium, which resulted in the isostructural polyanions $[Na_3(H_2O)_6M_3(H_2O)_3(\alpha\text{-}XW_9O_{33})_2]^{9-}$ ($X = As^{III}$, Sb^{III}, $M = Cu^{2+}$, Zn^{2+}).[11c]

The bond lengths and angles of the two $(\alpha\text{-}SbW_9O_{33})$ caps in **1** are not unusual, but it is of interest to investigate all bond lengths and angles within the central section of the polyanion (see Figure 2). The observed square-planar coordination geometry of the palladium(II) centers in **1** is expected for this d^8 metal ion. The Pd−O bond lengths (1.974−1.990(10) Å) are very regular and in the expected range, and the O−Pd−O angles (88.3−91.5(5), 175.8−176.6(4)°) are very close to the ideal values. These results indicate that the square-planar (PdO_4) groups exhibit essentially no strain, which probably explains why polyanion **1** is formed easily. For **1** the Pd···Pd distances are 4.39 Å and the Sb···Sb separation is 4.97 Å, which compares to the isostructural $[Na_3(H_2O)_6Cu_3(H_2O)_3(\alpha\text{-}SbW_9O_{33})_2]^{9-}$ as follows: Cu···Cu, 4.77−4.87 Å, Sb···Sb, 4.85 Å.[11c] The longer Sb···Sb separation in **1** can be explained with the slightly longer Pd−O bond lengths compared to Cu−O (1.919−1.948(6) Å), which leads to a larger separation of the two $(\alpha\text{-}SbW_9O_{33})$ caps in **1**. On the other hand, the shorter Pd···Pd distances can be explained by the larger ionic radius of Pd^{2+} vs Cu^{2+} (0.78 vs 0.71 Å) as well as the fact that the square-pyramidal Cu^{2+} ions are displaced toward the terminal water ligand (i.e. the exterior of the polyanion).

In addition to the three palladium(II) ions polyanion **1** also incorporates two Cs^+ and a Na^+ ion within the central belt (see Figures 1 and 2). This is in complete agreement with the other known sandwich polyanions of the Hervé-type, which all have three alkali metal cations occupying the three vacancies in the central belt.[11] Interestingly, **1** exhibits for the first time cesium ions in these positions, which otherwise had been filled by sodium or potassium ions. Furthermore, **1** is the first example with two different kinds of alkali metal cations in the central belt of one and the same polyanion. The sodium ion (Na1) in **1** is six-coordinated in the usual fashion by four μ_2-oxo groups (Pd−O−W) of **1** and two terminal water ligands (see Figures 1 and 2). The two cesium ions (Cs3, Cs3′) on the other hand are seven-coordinated by the same type of μ_2-oxo groups and three terminal water ligands (see Figure 2). The Na1···O (2.42−2.45(1) Å) and Cs3···O (3.03−3.30(1) Å) distances are in the expected ranges.

Electrochemistry. To date Tourné's polyanion $[WZnPd_2(H_2O)_2(B\text{-}\alpha\text{-}ZnW_9O_{34})_2]^{12-}$ remains the only sandwich-type, Pd-containing heteropolyanion which has been investigated by electrochemistry.[14,15] Neumann et al. studied this species by cyclic voltammetry in 0.5 M NaCl; the main observation consisted in an irreversible peak attributed to the oxidation of Pd^{2+} to Pd^{4+}, followed by "one or possibly two one electron reduction" waves due to "the palladium-mediated reduction of the tungsten ligand".[15]

In the present case, the title compound **1a** was studied by cyclic voltammetry in 0.4 M ($CH_3COO^- + CH_3COOH$) pH 5 buffer corresponding essentially to its synthesis medium (see Experimental Section). The scan rate was 2 mV s^{-1}. Figure 3A sketches the pattern observed for a 2×10^{-4} M solution of **1a**. Provided the first scan was started from −0.1 V vs SCE in the negative potential direction, this pattern was reproducibly obtained in all subsequent runs. In any case, it was necessary to go, at least once, to a potential close to that of the sharp cathodic peak to establish the film characterized in the following. Actually, this program ensures the deposition of Pd^0 on the electrode surface followed by subsequent study of the film. The sharp cathodic peak is narrow, with also a sharp and narrow anodic counterpart. It features the hydrogen sorption/desorption processes. Provisionally, the pronounced symmetry of this hydrogen wave is worth pointing out. The anodic to cathodic peak potentials difference is 17 mV in Figure 3A and remains small (12 mV) for the 5-fold thinner film in Figure 3B. In short, we found that this cyclic voltammogram in Figure 3A features essentially the same characteristics as the deposition behavior of Pd^0 on the glassy carbon electrode surface from Pd^{2+} solutions, as suggested by comparison with results gathered from the pertinent literature.[21]

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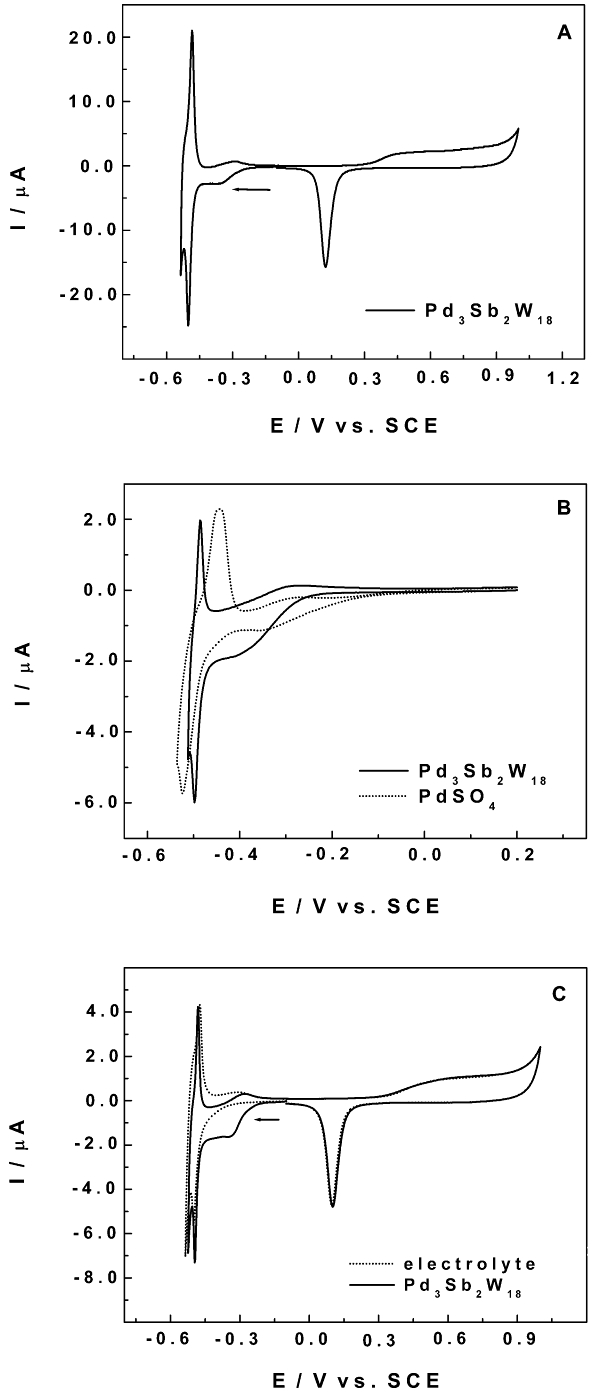

Figure 3. Cyclic voltammetry (CV) characterization of 2×10^{-4} M $Cs_3KNa_5[Cs_2Na(H_2O)_{10}Pd_3(SbW_9O_{33})_2]\cdot 16.5H_2O$ (**1a**) solution in 0.4 M ($CH_3COO^- + CH_3COOH$) pH = 5 buffer: working electrode, glassy carbon; reference electrode, SCE; scan rate, 2 mV s^{-1}. (A) Representative CV of the pattern observed upon cycling continuously the electrode potential between −0.536 and +1.0 V. The arrow indicates the direction of the first scan, which starts at −0.1 V. (B) Comparison of the deposition and hydrogen domains for two thin films built respectively from 2×10^{-4} M **1a** solution and 6×10^{-4} M $PdSO_4$ solution, strictly using the same cycling conditions. (C) Characterization of a thin film, taken out of the deposition solution, thoroughly rinsed with Millipore water and studied successively in the pure pH 5 supporting electrolyte (dotted line) and after addition of 2×10^{-4} M **1a** to the electrolyte (full line). For further details, see the text.

The voltammogram in Figure 3A can be divided in two potential domains to be analyzed 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 the oxidation of the deposited Pd surface followed by the reduction of the oxide. For clarity, the domain from −0.1 to −0.536 V and back was studied in more detail in Figure 3B on a thin film prepared on purpose. The pattern is compared, in superposition with the cyclic voltammogram obtained from a solution of $PdSO_4$ containing the same Pd^{2+} ion concentration as **1a**. Several details linked with the different environments of the Pd^{2+} centers distinguish the two patterns. In Figure 3B, the larger current intensity and the negative potential shift of the broad ”first” cathodic wave of **1a** compared with the corresponding one for uncomplexed Pd^{2+} must be pointed out. A rough evaluation of the difference in half-peak potentials gives 90 mV. Actually, this broad wave exists always from the very first voltammetric run of a solution of **1a**, while it is hardly visible in the first run of free Pd^{2+} ions alone. We found that the film deposition can be performed in a large potential domain; however, the film thickness increases faster and faster when more and more negative values are selected either for the cathodic end of the cyclic potential scan, or, alternatively, for controlled potential electrolysis. As expected, the thickness increases also with the number of cycles or the duration of potentiostatic electrolysis. These observations parallel the literature results for deposition from uncomplexed Pd^{2+} cations.[21] Typically, the potential was cycled in our experiments between −0.1 and −0.536 V for deposition. Also, the perfect symmetry of the hydrogen sorption/desorption wave following the Pd^0 deposition wave from the complex stands in contrast with the relative asymmetry of the same process in the case of uncomplexed Pd^{2+}, for which an anodic to cathodic peak potentials difference of 75 mV was measured in Figure 3B. Tentatively, this difference in shape might be related to the better quality of the Pd^0 deposit from a solution of **1a**.

Finally, Figure 3C sketches the following series of experiments. After deposition of a thin 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 dotted line curve in Figure 3C shows that the pattern obtained in Figure 3A is exactly reproduced, except for the broad “first” deposition wave which is missing. Incidentally, this experiment demonstrates the perfect stability of the film. Upon addition of **1a** to the supporting electrolyte, the full line curve in Figure 3C was obtained with restoration of the usually observed deposition wave. Upon increase of the potential scan rate from 2 to 100 mV s^{-1}, the deposition wave shows a clear tendency for reversibility. Tentatively, this observation might be associated with one or both of the following processes: reoxidation of the reduced heteropolyanion and oxidation or desorption of the two forms of hydrogen. It is worth noting the absence of any clearly defined W-wave in the whole voltammetric pattern. Assistance of such a process by the deposited Pd and its merging with the deposition wave cannot be excluded. Other W-waves might be expected beyond the hydrogen wave, in loose analogy with the previous study of $[Fe_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]$.[6−12d] However, observation of these eventually more negative W-waves is precluded by the large intensity of the hydrogen evolution process (not shown).

The remarkable electrochemical properties of the deposited film call, indeed, for complementary studies. In particular, it is planned to observe the morphology of the film by near-field microscopy. A study of the conductivity can also help to explain its behavior. Finally, EQCM (electrochemical quartz crystal microbalance) will be used to follow the thickness of the film as a function of the charge consumed for its deposition or its oxidation. However, with the present results, only a rough estimate of the film thickness can be given. Typically, the reoxidation of the film shown in Figure 3A necessitates 835×10^{-6} C, which corresponds to about 2.6×10^{15} Pd atoms. With an atomic radius of 1.40 Å for Pd,[22] a monolayer of these atoms would cover an area of 1.6×10^{-4} m^2. With an electrode of 7.07×10^{-6} m^2 surface area, the deposited film corresponds to about 20 monolayers.

Conclusions

We have synthesized the novel tripalladium(II)-substituted heteropolyanion $[Cs_2Na(H_2O)_{10}Pd_3(\alpha\text{-}SbW_9O_{33})_2]^{9-}$ (**1**). The title polyanion **1** represents the first structurally characterized palladium-substituted polyoxometalate. Polyanion **1** contains three equivalent, square planar Pd^{2+} centers linking two (α-SbW_9O_{33}) fragments. The dimeric, sandwich-type structure of **1** has been observed previously for a number of 3d metal ion derivatives, but in all of them the incorporated transition metal ions were five-coordinated resulting in a square pyramidal geometry. Here we reported on the first example of a 4d metal ion derivative of the Hervé-type sandwich structure.

Cyclic voltammetry of the title polyanion **1** in a pH 5 medium resulted in the deposition of a Pd^0 film on the glassy carbon electrode surface. This film is remarkable in that it gives a particularly sharp hydrogen sorption/desorption pattern, thus indicating the excellent quality of the Pd^0 deposit from polyanion **1**.

Currently we investigate if the arsenic(III), selenium(IV), and tellurium(IV) derivatives of **1** can also be synthesized. We are also interested if it is possible to incorporate more than three palladium(II) ions in this structural type. In future work we plan to perform catalytic studies on the title polyanion **1**.

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Note Added after ASAP: A decimal point was missing from the range of Pd−O bond lengths for **1** in the Results and Discussion section of the version of this paper posted ASAP on May 27, 2004. The decimal point is present in the version posted on May 28, 2004.

Supporting Information Available: 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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