Syntheses, characterization and electrocatalytical comparison of two cadmium-containing mono-lacunary Wells–Dawson polyoxometalates, $\alpha_1$- and $\alpha_2$-[P$_2$W$_{17}$Cd(H$_2$O)O$_{61}$]$^{8-}$

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Abstract: Two new cadmium-containing Wells–Dawson polyoxometalates K$_8$($\alpha_1$-[P$_2$W$_{17}$Cd(H$_2$O)O$_{61}$]$^{14\text{H}_2\text{O}}$ ($\alpha_1$-[P$_2$W$_{17}$Cd]) and K$_8$($\alpha_2$-[P$_2$W$_{17}$Cd(H$_2$O)O$_{61}$]$^{16\text{H}_2\text{O}}$ ($\alpha_2$-[P$_2$W$_{17}$Cd]) were synthesized as water-soluble potassium salts. The cadmium-substituted complexes were characterized by IR, $^{31}$P-NMR, $^{113}$Cd-NMR spectroscopy and cyclic voltammetry (CV). Redox activities for the tungsten and cadmium centers were observed by cyclic voltammetry. It was found that the presence of cadmium decreased the electrocatalytic activity of the $[\alpha_1$-LiP$_2$W$_{18}$O$_{62}]^{9-}$ and $\alpha_2$-[P$_2$W$_{17}$O$_{61}$]$^{10-}$ heteropolyanions.

Keywords: polyoxometalates; Wells–Dawson; electrocatalytic; cadmium; cyclic voltammetry.

INTRODUCTION

Polyoxometalates (POMs), as a rich class of inorganic metal oxide cluster compounds, have different applications in molecular materials, medicine, biology and catalysis due to their molecular, structural, and electronic versatility. The Dawson-type heteropolyanions with highly symmetric structures are famous as one kind of POMs. Their formula is [$X_2W_{18}O_{62}]^{9-}$, where X is a heteroatom such as phosphorus. Removal of a WO unit from a cap WO$_6$ polyhedron of the ($\alpha$-[P$_2$W$_{18}$O$_{62}$]$^{9-}$ (Wells–Dawson structure) results in the lacunary ($\alpha_2$-[P$_2$W$_{17}$O$_{61}$]$^{10-}$ isomer that has $C_8$ symmetry, and removal of a WO unit from a belt WO$_6$ polyhedron results in the lacunary ($\alpha_1$-[P$_2$W$_{17}$O$_{61}$]$^{10-}$ isomer, that has $C_1$ symmetry (Fig. 1). An important structural characteristic of Dawson-type heteropolyanions is the possibility of replacing one of the tungsten atoms by a...
transition metal cation, which possesses five bridging oxygens and a sixth oxo-group, which is occupied by a water molecule. For instance, transition metal mono-substituted Dawson anions with the general formula $K_8[\alpha_2-P_2W_{17}M-(H_2O)O_6]_1$ (M= Zr(IV), Hf(IV), Mn(II), Zn(II), Fe(II), Co(II), Cu(II) or Ni(II)) were investigated. Furthermore, these compounds have also been used as heterogeneous catalysts.

Fig. 1. A) The monovacant $\alpha_1-[LiP_2W_{17}O_{61}]^{9-}$ unit obtained by removing a WO$_6$ octahedron in the equatorial site of the parent Wells–Dawson structure, B) The monovacant $\alpha_2-[P_2W_{17}O_{61}]^{10-}$ unit obtained by removing a WO$_6$ octahedron in the capping region of the parent Wells–Dawson structure.

Until now, only a few cadmium-containing polyoxometalates have been reported. The first cadmium-containing heteropolyanions, related to the mono-lacunary anion of the Keggin structure (XW11) were presented by Contant. In 1995, Kirby and Baker reported the first sandwich-type heteropolyanions including Cd$^{2+}$ based on the $[P_2W_{15}O_{56}]^{12-}$ defect structure, and later Bi et al. prepared a series of dimeric polytungstates by reacting $[As_2W_{15}O_{56}]^{12-}$ with M$^{2+}$ (M = Cu(II), Mn(II), Co(II), Ni(II), Zn(II) or Cd(II)). Subsequently, Alizadeh et al. synthesized and structurally characterized $[Cd_4(H_2O)_2(PW_{9}O_{34})_2]^{10-}$. In 2005, Kortz et al. reported another cadmium containing polyoxometalate, $[Cd_4Cl_2(B-\alpha-AsW_{9}O_{34})_2]^{12-}$. Finally, Zhao et al. prepared and characterized $[Cd_4(H_2O)_2(B-\alpha-SiW_{9}O_{34})_2]^{12-}$.

Over past years, electrochemical methods were shown to be an inexpensive and effective method for the determination of some inorganic and organic substrates. In particular, POMs exhibited multi-electron reversible redox characteristics, which enables them to be redox electrocatalysts for some irreversible electrochemical processes. In electrochemistry, the main processes include the reduction of protons or the oxidation of hydrogen, the reduction of dioxygen, and the electrochemical processes of nitrogen oxides NO$_x$ and carbon oxides CO$_x$, complemented by the electrocatalysis of bromate, iodate and so forth. All of these reactions have important implications in environmental problems and/or are potentially considered to be abundant, inexpensive sources for the production of useful chemicals.

In this paper, the syntheses of two new cadmium-containing...
α1- and α2-mono-lacunary Dawson-type polyoxometalates, $K_8[\alpha_1-P_2W_{17}Cd-\{(H_2O)O_6\}]\cdot14H_2O$ ($\alpha_1-P_2W_{17}Cd$) and $K_8[\alpha_2-P_2W_{17}Cd(H_2O)O_6]\cdot16H_2O$ ($\alpha_2-\quad-P_2W_{17}Cd$), are described. Several attempts to prepare single crystals of $\alpha_1-P_2W_{17}Cd$ and $\alpha_2-P_2W_{17}Cd$ failed. Therefore, these compounds were characterized by elemental analysis, and FT-IR, $^{31}P$-NMR and $^{113}Cd$-NMR spectroscopic methods. The electrochemical properties of these compounds and the electrocatalytic reductions of nitrite were investigated in detail by cyclic voltammetry.

EXPERIMENTAL

All reagents were of analytical grade and were used as received from commercial sources without further purification. The mono-lacunary POMs $K_{10}[\alpha_2\cdot P_2W_{17}O_{61}]\cdot20H_2O$ and $K_9[\alpha_1\cdot LiP_{2W_{17}O_{61}}]\cdot20H_2O$ were prepared according to the literature and characterized accordingly. FT-IR spectra were recorded in the range 400–4000 cm$^{-1}$ on an Alpha Centaurt FT-IR spectrophotometer using the KBr pellet technique. The NMR spectrum was recorded on a Bruker BRX-300 Avance spectrometer. The resonance frequencies for the $^{31}P$ and $^{113}Cd$ nuclei are at 202.46 and 110.92 MHz, respectively. The chemical shifts for the $^{31}P$- and $^{113}Cd$-NMR spectra were externally referenced relative to 85 % H$_3$PO$_4$ and 0.1 M cadmium perchlorate, respectively. Elemental analyses were realized using an Integra XL inductively coupled plasma spectrometer. The water used for all electrochemical measurements was obtained by passing through a Millipore Q water purification set. The solutions were deaerated thoroughly for at least 30 min by bubbling with pure N$_2$ and kept under N$_2$ atmosphere during the whole experiment. The electrochemical set-up was a Metrohm 797VA computrace polarographic analyzer. A conventional three-electrode system was used. The working electrode was a glassy carbon electrode. A platinum electrode was used as the counter electrode and an Ag/AgCl (3 M KCl) electrode was employed as the reference electrode. All potentials were measured and reported vs. the Ag/AgCl electrode. All voltammetric experiments were performed at room temperature.

Synthesis of $K_8[\alpha_1\cdot P_2W_{17}Cd(H_2O)O_6]\cdot14H_2O$

Cd(NO$_3$)$_2\cdot4H_2O$ (0.72 g, 2.33 mmol) was dissolved in 40 mL of sodium acetate buffer (0.25 M, pH 4.7). The solution was heated to 80 °C and then, 10 g (2.08 mmol) of $K_9[\alpha_1\cdot LiP_{2W_{17}O_{61}}]\cdot20H_2O$ was added gradually. After 2 h, the solution was cooled to room temperature, and precipitate was removed by filtration. This solid was recrystallized from boiling water and dried under vacuum. Yield: 41.58 %; Anal. Calcd. for CdH$_{30}$K$_8$O$_{76}$P$_2$W$_{17}$: Cd, 2.31; K, 6.43; P, 1.27; W, 64.32; H$_2$O, 5.18 %. Found: Cd, 2.28; K, 6.30; P, 1.23; W, 64.35; H$_2$O, 5.24 %. IR (KBr, cm$^{-1}$): 1084, 1060, 1014 (P–O stretching bonds), 948 (W–O term stretching bonds), 898 (W–Ob stretching bonds), 784, 738 (W–Oc stretching bonds).

Synthesis of $K_8[\alpha_2\cdot P_2W_{17}Cd(H_2O)O_6]\cdot16H_2O$

A 0.72 g (2.33 mmol) of Cd(NO$_3$)$_2\cdot4H_2O$ was dissolved in 40 mL of sodium acetate buffer (0.25 M, pH 4.7). The solution was heated to 90 °C and then 10 g (2.03 mmol) of $K_9[\alpha_2\cdot (P_2W_{17}O_{61})]\cdot20H_2O$ was added gradually. After 2 h, the solution was cooled to room temperature and precipitate was removed by filtration. This solid was recrystallized from boiling water and dried under vacuum. Yield: 61.4 %; Anal. Calcd. for CdH$_{34}$K$_8$O$_{78}$P$_2$W$_{17}$: Cd, 2.29; K, 6.39; P, 1.26; W, 63.85; H$_2$O, 5.88 %. Found: Cd, 2.24; K, 5.45; P, 1.16; W, 64.38.
RESULTS AND DISCUSSION

IR spectra

The compounds $\alpha_1$-$P_{2}W_{17}Cd$ and $\alpha_2$-$P_{2}W_{17}Cd$, synthesized in this work, showed typical bands of transition metal-substituted Wells–Dawson heteropolyanion in the range of 700–1200 cm$^{-1}$. The solid-state FT-IR measurements of $K_6[\alpha_1$-$P_{2}W_{18}O_{62}]$, $K_9[\alpha_1$-$LiP_{2}W_{17}O_{61}]$, $\alpha_1$-$P_{2}W_{17} Cd$, $K_{10}[\alpha_2$-$P_{2}W_{17}O_{61}]$, and $\alpha_2$-$P_{2}W_{17} Cd$ (Fig. 2, curves a–e, respectively) show the spectral patterns characteristic of the Dawson POM framework.

![IR spectra](image)

As seen in Fig. 2, it is remarkable that only two bands of (P–O) stretching vibration were observed within the range of 1000–1200 cm$^{-1}$ in the $[\alpha_2$-$P_{2}W_{18}O_{62}]^6$-heteropolyanion, whereas three bands were observed within the range of 1000–
–1200 cm⁻¹ in the [α₁-LiP₂W₁₇O₆₁]⁹⁻ heteropolyanion. In α₁-P₂W₁₇Cd, by replacing Cd²⁺ in the mono-lacunary [α₁-LiP₂W₁₇O₆₁]⁹⁻ polyoxometalate, significant changes were observed in the (P–O) stretching region. As seen in Fig. 2, curve c, the 1122 cm⁻¹ band was observed as a shoulder and therefore, the pattern of the spectrum of α₁-P₂W₁₇Cd was approximately similar to that of [α₁-P₂W₁₈O₆₂]⁶⁻. It was surmised that removal of the bands was due to the increase in the symmetry of PO₄ unit caused by transition metal substitution. 31 Moreover, the FT-IR spectra of α₁-P₂W₁₇Cd in the (M–O) region are very similar to that of K₀[α₁-LiP₂W₁₇O₆₁], especially with regards to the (M–Oₚ) oxygen atoms (948 cm⁻¹ for α₁-P₂W₁₇Cd and 945 cm⁻¹ for K₀[α₁-LiP₂W₁₇O₆₁]), the bands assignable to corner-sharing (M–Oₚ–M) oxygen atoms (898 cm⁻¹ for α₁-P₂W₁₇Cd and 912 cm⁻¹ for K₀[α₁-LiP₂W₁₇O₆₁]) and the bands assignable to edge-sharing (M–Oₚ–M) oxygen atoms (784 and 732 cm⁻¹ for K₀[α₁-LiP₂W₁₇O₆₁]). The FT-IR spectra of α₂-P₂W₁₇Cd in the polyoxometalate region were very similar to that of K₁₀[α₂-P₂W₁₇O₆₁], especially with regards to the multiple (P–O) bands (1085, 1053 and 1016 cm⁻¹ for α₂-P₂W₁₇Cd; 1083, 1047, and 1016 cm⁻¹ for K₁₀[α₂-P₂W₁₇O₆₁]), the bands assignable to (M–Oₚ) oxygen atoms (943 cm⁻¹ for α₂-P₂W₁₇Cd and 939 cm⁻¹ for K₁₀[α₂-P₂W₁₇O₆₁]), the bands assignable to corner-sharing (M–Oₚ–M) oxygen atoms (889 cm⁻¹ for α₂-P₂W₁₇Cd and 885 cm⁻¹ for K₁₀[α₂-P₂W₁₇O₆₁]) and the bands assignable to edge-sharing (M–Oₚ–M) oxygen atoms (800 and 730 cm⁻¹ for α₂-P₂W₁₇Cd; 868 and 736 cm⁻¹ for K₁₀[α₂-P₂W₁₇O₆₁]).

31P-NMR spectroscopy is a very sensitive technique to characterize polyoxometalates and evaluate the purity of these compounds. The 31P-NMR data obtained in this study work and the data for some transition-metal substituted Dawson-type polyoxometalates are given in Table I. In this table, P (1) refers to

<table>
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<th>Compound</th>
<th>P (1)</th>
<th>P (2)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₆[α-P₂W₁₈O₆₂]</td>
<td>–12.50</td>
<td>–12.5</td>
<td>28</td>
</tr>
<tr>
<td>K₆[α₁-LiP₂W₁₇O₆₁]</td>
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<td>–13.1</td>
<td>28</td>
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<tr>
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<td>32</td>
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<tr>
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<td>–13.45</td>
<td>33</td>
</tr>
<tr>
<td>K₆[α₂-P₂W₁₇Zn(H₂O)O₆₁]</td>
<td>–8.65</td>
<td>–14.15</td>
<td>33</td>
</tr>
<tr>
<td>K₇[α₁-P₂W₁₇La(H₂O)O₆₁]</td>
<td>–10.58</td>
<td>–13.64</td>
<td>34</td>
</tr>
<tr>
<td>K₇[α₁-P₂W₁₇La(H₂O)O₆₁]</td>
<td>–10.57</td>
<td>–13.55</td>
<td>34</td>
</tr>
<tr>
<td>K₇[α₁-P₂W₁₇La(H₂O)O₆₁]</td>
<td>–10.58</td>
<td>–13.61</td>
<td>34</td>
</tr>
<tr>
<td>K₈[α₁-P₂W₁₇Cd(H₂O)O₆₁]</td>
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<td>–14.19</td>
<td>This work</td>
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<tr>
<td>K₈[α₂-P₂W₁₇Cd(H₂O)O₆₁]</td>
<td>–6.72</td>
<td>–13.00</td>
<td>This work</td>
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</tbody>
</table>
the resonance attributed to the P atom nearer to the site of substitution (or defect) and P (2) refers to the P atom far away from the site of substitution (or defect). In addition, $^{31}$P-NMR spectra of $\alpha_1$-P$_2$W$_{17}$Cd and $\alpha_2$-P$_2$W$_{17}$Cd are shown in Fig. 3. The two-line $^{31}$P-NMR spectra strongly suggest the presence of a single species in solution, thereby precluding the presence of even minor, phosphorus-containing impurities in $\alpha_1$-P$_2$W$_{17}$Cd or $\alpha_2$-P$_2$W$_{17}$Cd. Finally, the integrated intensity of P (1) appears smaller than that of P (2) because of a slow relaxation rate (large $T_1$).

Fig. 3. $^{31}$P-NMR spectra of A) $\alpha_1$-P$_2$W$_{17}$Cd and B) $\alpha_2$-P$_2$W$_{17}$Cd.

$^{113}$Cd-NMR

The $^{113}$Cd-NMR spectra in D$_2$O show clean, single spectra with a resonance at $\delta = 63.34$ ppm for $\alpha_1$-P$_2$W$_{17}$Cd (Fig. 4A) and at $\delta = -22.86$ ppm for $\alpha_2$-P$_2$W$_{17}$Cd (Fig. 4B). As shown in Fig. 4, a considerable difference was observed between the chemical shifts in the $^{113}$Cd-NMR spectra of $\alpha_1$-P$_2$W$_{17}$Cd and $\alpha_2$-P$_2$W$_{17}$Cd. Francesconi et al.$^{35}$ reported that the basic oxygen of the $\alpha_1$ structure is bound to one tungsten atom, while the corresponding oxygen of the $\alpha_2$ structure is bound to two tungsten atoms. This observation is ascribed mainly to

Fig. 4. $^{113}$Cd-NMR spectra of A) $\alpha_1$-P$_2$W$_{17}$Cd and B) $\alpha_2$-P$_2$W$_{17}$Cd.
the large framework distortion induced by the vacancy in the \( \alpha_1 \) site, and to the nature of the cadmium substituent, which could be considered as not filling the vacancy completely and hence, its resonance moves to an upfield value. On the other hand, for the \( \alpha_2 \) site, the cadmium substituent fills the vacancy perfectly and therefore its resonance is downfield shifted.

**Electrochemical behavior of \( \alpha_1\)P2W17Cd and \( \alpha_2\)P2W17Cd**

Electrochemical behavior of \( \alpha_1\)P2W17Cd. The electrochemical behavior of \( \alpha_1\)P2W17Cd was studied in 0.5 M acetate buffer solution by cyclic voltammetry (CV), and the obtained results are compared in Fig. 5 with those for \([\alpha_1\text{-LiP2W17O61}]^{9–}\). As can be clearly seen in Fig. 5, four quasi-reversible redox peaks appeared in the potential range \(-1.1 \) to \(-0.3 \) V at a scan rate of 75 mV s\(^{-1}\). The cathodic peak potentials were at \(-0.97 \) V (tungsten center), \(-0.84 \) V (tungsten center), \(-0.61 \) V (tungsten and cadmium centers) and \(-0.46 \) V (tungsten center) for \( \alpha_1\)P2W17Cd while the corresponding peaks were found at \(-0.97\), \(-0.7\), \(-0.6 \) and \(-0.43 \) V, respectively, for \([\alpha_1\text{-LiP2W17O61}]^{9–}\). On considering these data, when cadmium replaced in polyoxometalate vacancy, the cadmium potential would be shifted toward negative potential and the current intensity at \(-0.6 \) V would be increased considerably, however the oxidation and reduction of Cd\(^{2+}/\text{Cd}\), in the free ion state, occurs at \(-0.4 \) V.\(^{36}\)

![Cyclic voltammograms of \( \alpha_1\)P2W17Cd (solid line) and \( \text{K}_9[\alpha_1\text{-LiP2W17O61}] \) (dashed line).](image)

The cyclic voltammograms of \( \alpha_1\)P2W17Cd in 0.5 M acetate buffer solution at different scan rates are shown in Fig. 6. When the scan rate was varied from 25 to 750 mV s\(^{-1}\), the cathodic peak potentials shifted in the negative direction and the corresponding anodic peak potentials shifted in the positive direction with increasing scan rate. The plots of peak (III) current vs. scan rate are shown in the inset of Fig. 6. At scan rates slower than 100 mV s\(^{-1}\), the anodic currents were proportional to the square root of the scan rate, which indicates that the redox
process was diffusion-controlled; however, at scan rates higher than 100 mV/s, the anodic currents were proportional to the scan rate, suggesting that the redox process was surface-confined.

![Fig. 6. Cyclic voltammograms of α₁-P₂W₁₇Cd in 0.5 M acetate buffer solutions at different scan rates of a) 25, b) 50, c) 75, d) 100, e) 200, f) 300, g) 400, h) 500 and i) 750 mV s⁻¹. The inset shows plots of the anodic peak current of III against scan rate.](image)

**Electrochemical behavior of α₂-P₂W₁₇Cd.** The electrochemical behavior of α₂-P₂W₁₇Cd was studied in 0.5 M acetate buffer solution by cyclic voltammetry (CV). The obtained results are compared with the corresponding results for [α₂-P₂W₁₇O₆₁]¹₀⁻ in Fig. 7, from which it can be clearly seen that in the potential range –1.1 to –0.3 V, three quasi-reversible redox peaks appeared and the cathodic peak potentials for a scan rate of 75 mV s⁻¹ were at –0.87 (tungsten center), –0.61 (tungsten and cadmium centers) and –0.47 V (tungsten center) for α₂-P₂W₁₇Cd and at –0.95, –0.67 and –0.54 V, respectively, for [α₂-P₂W₁₇O₆₁]¹₀⁻.

![Fig. 7. Cyclic voltammograms of α₂-P₂W₁₇Cd (solid line) and K₁₀[α₂-P₂W₁₇O₆₁] (dashed line).](image)
ancy, the cadmium potential was shifted toward negative potentials and the current intensity at –0.6 V increased considerably, although the oxidation and reduction of Cd\(^{2+}/\text{Cd}\) in the free ion state occurs at –0.4 V.\(^{36}\)

On comparison of cathodic potential data between \(\alpha_1\)-P\(_2\)W\(_{17}\)Cd and \([\alpha_1-\text{LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}\), and between \(\alpha_2\)-P\(_2\)W\(_{17}\)Cd and \([\alpha_2-\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}\), it is obvious that when cadmium replaced the vacancy in \([\alpha_1-\text{LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}\), no significant changes in the cathodic potentials for \(\alpha_1\)-P\(_2\)W\(_{17}\)Cd were observed. However, when cadmium replaced the vacancy in \([\alpha_2-\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}\), considerable changes in these potentials were observed for \(\alpha_2\)-P\(_2\)W\(_{17}\)Cd. These results indicate that cadmium, which substituted completely in the \([\alpha_2-\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}\) vacancy affects the redox potentials of the tungsten centers of the polyoxometalate, while cadmium in \(\alpha_1\)-P\(_2\)W\(_{17}\)Cd does not fill the vacancy of \([\alpha_1-\text{LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}\) completely.

Figure 8 shows the cyclic voltammograms of \(\alpha_2\)-P\(_2\)W\(_{17}\)Cd at different scan rates in the 0.5 M acetate buffer solution. When the scan rate was varied from 10 to 750 mV s\(^{-1}\), the cathodic peak potentials were shifted in the negative direction and the corresponding anodic peak potentials shifted in the positive direction with increasing scan rate. The plots of peak (III) current vs. scan rate are shown in the inset of Fig. 8. At scan rates lower than 75 mV s\(^{-1}\), the anodic currents were proportional to the square root of the scan rate, which indicates that the redox process was diffusion-controlled; however, at scan rates faster than 75 mV s\(^{-1}\), the anodic currents were proportional to the scan rate, suggesting that the redox process is surface-confined.

![Fig. 8. Cyclic voltammograms of \(\alpha_1\)-P\(_2\)W\(_{17}\)Cd in 0.5 M acetate buffer solutions at different scan rates of a) 10, b) 25, c) 50, d) 75, e) 100, f) 200, g) 300, h) 400, i) 500 and j) 750 mV s\(^{-1}\). The inset shows plots of the anodic peak current of III against scan rate.](Available on line at www.shd.org.rs/JSCS/)

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Electrocatalysis of NO$_2^-$ reduction

As is known, POMs have been exploited extensively in electrocatalytic reductions.\textsuperscript{37} For example, Keita et al. reported the first examples of efficient participation of selected metal-ion-substituted heteropolyanions in the electrocatalytic reduction of nitrate and that vanadium-substituted Dawson-types are versatile electrocatalysts.\textsuperscript{38,39}

Electrocatalysis of NO$_2^-$ reduction by $\alpha_1$-$P_2W_{17}Cd$

The polyoxometalates $[\alpha_1$-$LiP_2W_{17}O_{61}]^{9-}$ and $\alpha_1$-$P_2W_{17}Cd$ were tested at pH 4.7 for their activity in the reduction of nitrite ion. The CVs for the electrocatalytic reduction of NO$_2^-$ by glassy carbon electrode in the 0.5 M acetate buffer solution are shown in Fig. 9.

Fig. 9. A) Cyclic voltammograms (scan rate: 75 mV s$^{-1}$) for the electrocatalytic reduction of NO$_2^-$ with a 5×10$^{-4}$ M solution of $\alpha_1$-$P_2W_{17}Cd$ in a 0.5 M acetate buffer solution (from top to bottom $\gamma = 0, 1, 2, 3$ and 4). B) Cyclic voltammograms (scan rate: 75 mV s$^{-1}$) for the electrocatalytic reduction of NO$_2^-$ with a 5×10$^{-4}$ M solution of K$_9[\alpha_1$-$LiP_2W_{17}O_{61}]$ in a 0.5 M acetate buffer solution (from top to bottom $\gamma = 0, 1, 2, 3$ and 4). The excess parameter defined as $\gamma = c^0(NO_2^-)/c^0(POM)$ Inset: the relationship between catalytic current and the NO$_2^-$ concentration.
Clearly, with the addition of NaNO₂ to the solution, even for small values of the excess parameter, \( \gamma \), which is defined here as:

\[
\gamma = \frac{c^{0}(\text{NO}_2)}{c^{0}(\text{POM})}
\]

the cathodic current of all waves increased and the corresponding anodic current decreased. The catalytic efficiency \( CAT \) for waves I and II of \([\alpha_1-\text{LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}\) varied from 53.20 to 274.02 % and 4.53 to 19.84 %, respectively (Table II), when \( \gamma \) increase from 1 to 4, while the \( CAT \) for \( \alpha_1-\text{P}_2\text{W}_{17}\text{Cd} \) varied from 34.74 to 127.9 % (wave I) and 9.26 to 43.6 % (wave II), Table III. \( CAT \) is defined as:

\[
CAT = 100\times \left[ \frac{I_p(\text{POM},\text{NaNO}_2) - I_p(\text{POM})}{I_p(\text{POM})} \right]
\]

where \( I_p(\text{POM}) \) and \( I_p(\text{POM},\text{NaNO}_2) \) are the cathodic peak currents in the absence and in the presence of NaNO₂, respectively.

**TABLE II.** Catalytic efficiency for \([\alpha_1-\text{LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}\); \( CAT \)w, refers to catalytic efficiency for the \( x^{th} \) wave

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>( CAT\text{w}_1 / % )</th>
<th>( CAT\text{w}_2 / % )</th>
<th>( CAT\text{w}_3 / % )</th>
<th>( CAT\text{w}_4 / % )</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>53.20</td>
<td>4.53</td>
<td>2.80</td>
<td>3.52</td>
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<tr>
<td>2</td>
<td>123.78</td>
<td>10.39</td>
<td>6.84</td>
<td>8.01</td>
</tr>
<tr>
<td>3</td>
<td>191.07</td>
<td>11.34</td>
<td>5.78</td>
<td>6.73</td>
</tr>
<tr>
<td>4</td>
<td>274.02</td>
<td>19.84</td>
<td>10.87</td>
<td>1.21</td>
</tr>
</tbody>
</table>

**TABLE III.** Catalytic efficiency for \( \alpha_1-\text{P}_2\text{W}_{17}\text{Cd} \); \( CAT\text{w}, \) refers to catalytic efficiency for the \( x^{th} \) wave

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>( CAT\text{w}_1 / % )</th>
<th>( CAT\text{w}_2 / % )</th>
<th>( CAT\text{w}_3 / % )</th>
<th>( CAT\text{w}_4 / % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34.74</td>
<td>9.26</td>
<td>3.57</td>
<td>4.51</td>
</tr>
<tr>
<td>2</td>
<td>61.01</td>
<td>19.66</td>
<td>0.71</td>
<td>1.61</td>
</tr>
<tr>
<td>3</td>
<td>99.15</td>
<td>35.27</td>
<td>5.00</td>
<td>6.29</td>
</tr>
<tr>
<td>4</td>
<td>127.90</td>
<td>43.60</td>
<td>2.10</td>
<td>4.03</td>
</tr>
</tbody>
</table>

It is noticeable from Tables II and III that the electrocatalytic activity of \([\alpha_1-\text{LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}\) was greater than that of \( \alpha_1-\text{P}_2\text{W}_{17}\text{Cd} \) in wave I, while this behavior was vice versa for wave II. This trend may be attributed to the presence of Cd\(^{2+}\). However, the electrocatalytic activity of \([\alpha_1-\text{LiP}_2\text{W}_{17}\text{O}_{61}]^{9-}\) decreased on cadmium ion substitution.

The inset of Fig. 9 presents four straight lines over a wide range of concentrations with different slopes, indicating that wave I had a higher catalytic activity than the other waves.
Electrocatalysis of $\text{NO}_2^-$ reduction by $\alpha_2$-$\text{P}_2\text{W}_17\text{Cd}$

The polyoxometalates $[\alpha_2$-$\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ and $\alpha_2$-$\text{P}_2\text{W}_{17}\text{Cd}$ were tested at pH 4.7 for their activity in the reduction of nitrite ion. The CVs for the electrocatalytic reduction of $\text{NO}_2^-$ by GC in 0.5 M acetate buffer solution are shown in Fig. 10.

Clearly, with the addition of NaNO$_2$ to the solution, even for small values of the excess parameter $\gamma$, cathodic current of all waves increased and the corresponding anodic current decreased. The catalytic efficiency $\text{CAT}$ for wave I of $[\alpha_2$-$\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ varied from 8.34 to 28.17 % (Table IV) when $\gamma = 1$, 5 and 20, while the $\text{CAT}$ variations for $\alpha_2$-$\text{P}_2\text{W}_{17}\text{Cd}$ were from 0.65 to 10.46 % when $\gamma = 1$, 5, 10 and 20 (Table V).
TABLE IV. Catalytic efficiency for \( \alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61} \)\(^{10-}\); \( CAT_{w\gamma} \) refers to catalytic efficiency for the \( \gamma \)th wave

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>( CAT_{w1} / % )</th>
<th>( CAT_{w2} / % )</th>
<th>( CAT_{w3} / % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.34</td>
<td>1.27</td>
<td>1.45</td>
</tr>
<tr>
<td>5</td>
<td>11.60</td>
<td>1.74</td>
<td>1.94</td>
</tr>
<tr>
<td>20</td>
<td>28.17</td>
<td>0.69</td>
<td>0.97</td>
</tr>
</tbody>
</table>

TABLE V. Catalytic efficiency for \( \alpha_2\text{-P}_2\text{W}_{17}\text{Cd} \); \( CAT_{w\gamma} \) refers to catalytic efficiency for the \( \gamma \)th wave

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>( CAT_{w1} / % )</th>
<th>( CAT_{w2} / % )</th>
<th>( CAT_{w3} / % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.65</td>
<td>0.00</td>
<td>0.22</td>
</tr>
<tr>
<td>5</td>
<td>2.61</td>
<td>0.00</td>
<td>0.55</td>
</tr>
<tr>
<td>10</td>
<td>6.53</td>
<td>0.49</td>
<td>1.00</td>
</tr>
<tr>
<td>20</td>
<td>10.46</td>
<td>0.49</td>
<td>0.33</td>
</tr>
</tbody>
</table>

It is noticeable from Tables IV and V that the electrocatalytic activity of \( \alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61} \)\(^{10-}\) was greater than that of \( \alpha_2\text{-P}_2\text{W}_{17}\text{Cd} \) in wave I, due to the presence of \( \text{Cd}^{2+} \) ion.

The inset of Fig. 10 presents four straight lines over a wide range of concentrations with different slopes, indicating that wave I had a higher catalytic activity than the other waves.

CONCLUSIONS

Two new cadmium-containing Wells–Dawson polyoxometalates were synthesized as water-soluble potassium salts. \(^{113}\text{Cd-NMR} \) indicated that cadmium was substituted completely in the \( \alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61} \)\(^{10-}\) vacancy, whereas cadmium in \( \alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61} \)\(^{9-}\) did not fill completely the vacancy. Moreover, electrochemical investigations were in good agreement with this result because remarkable differences in the redox peaks were not observed between the \( \alpha_1\text{-P}_2\text{W}_{17}\text{Cd} \) and \( \alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61} \)\(^{9-}\) compounds.

The electrochemistry of \( \alpha_1\text{-P}_2\text{W}_{17}\text{Cd} \) and \( \alpha_2\text{-P}_2\text{W}_{17}\text{Cd} \) was studied. First, these polyoxoanions exhibited four- and three-step redox waves attributed to the tungsten–oxo and cadmium–oxo redox processes in pH 4.7 solutions. The best electrocatalytic activity for \( \alpha_1\text{-P}_2\text{W}_{17}\text{Cd} \) and \( \alpha_2\text{-P}_2\text{W}_{17}\text{Cd} \) was observed in wave I, which is related to tungsten–oxo redox centers. In addition, decreases in the electrocatalytic activity of mono-lacunary Dawson-type (\( \alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61} \)\(^9-\) and \( \alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61} \)\(^{10-}\) ) follows from the presence of cadmium metal ion in these compounds. The presence of cadmium metal ion in the mono-lacunary Dawson-type (\( \alpha_1\text{-LiP}_2\text{W}_{17}\text{O}_{61} \)\(^9-\) and \( \alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61} \)\(^{10-}\) ) caused decreases in electrocatalytic activity of these compounds.

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ИЗВОД

У овом раду су синтетизоване калијумове соли два Wells–Dawson полиоксометалата који садрже кадмијум, $\text{K}_8[\alpha_1-P_2W_{17}Cd(H_2O)O_{61}]\cdot14\text{H}_2\text{O} (\alpha_1-P_2W_{17}Cd)$ и $\text{K}_8[\alpha_2-P_2W_{17}Cd-(H_2O)O_{61}]\cdot16\text{H}_2\text{O} (\alpha_2-P_2W_{17}Cd)$. Синтетизовани комплекси суokaрактерисани применом IR, $^{31}\text{P}$- и $^{113}\text{Cd}$-NMR спектроскопије, док су редокс потенцијали волфрама и кадмијума у овим јединињама одређени применом цикличне волтаметрије (CV). Добијени резултати су показали да присуство јона кадмијума утиче на смањење електрокаталитичке активности $[\alpha_1-\text{LiP}_2W_{17}O_{61}]^{9-}$ и $[\alpha_2-[P_2W_{17}O_{61}]^{10-}$ хетерополианјона.

(Примљено 18. јануара, ревидирано 18. маја, прихваћено 28. маја 2014)

REFERENCES