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Syntheses, characterization and electrocatalytical comparison of two cadmium-containing mono-lacunary Wells–Dawson polyoxometalates, α_1- and α_2-$[P_2W_{17}Cd(H_2O)O_{61}]^{8-}$

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Abstract: Two new cadmium-containing Wells–Dawson polyoxometalates $K_8[\alpha_1\text{-}P_2W_{17}Cd(H_2O)O_{61}]\cdot 14H_2O$ (α_1-$P_2W_{17}Cd$) and $K_8[\alpha_2\text{-}P_2W_{17}Cd(H_2O)\text{-}O_{61}]\cdot 16H_2O$ (α_2-$P_2W_{17}Cd$) 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 $[\alpha_1\text{-}LiP_2W_{17}O_{61}]^{9-}$ and α_2-$[P_2W_{17}O_{61}]^{10-}$ 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,[1] medicine, biology[2,3] and catalysis[4,5] 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 $[X_2W_{18}O_{62}]^{n-}$, where X is a heteroatom such as phosphorus.[6] Removal of a WO unit from a cap WO_6 polyhedron of the (α-$P_2W_{18}O_{62}$)$^{6-}$ (Wells–Dawson structure) results in the lacunary (α_2-$P_2W_{17}O_{61}$)$^{10-}$ isomer that has C_s symmetry, and removal of a WO unit from a belt WO_6 polyhedron results in the lacunary (α_1-$P_2W_{17}O_{61}$)$^{10-}$ isomer, that has C_1 symmetry (Fig. 1).[7,8] An important structural characteristic of Dawson-type heteropolyanions is the possibility of replacing one of the tungsten atoms by a

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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 $K_8[\alpha_2\text{-}P_2W_{17}M\text{-}(H_2O)O_{61}]$ (M= Zr(IV), Hf(IV), Mn(II), Zn(II), Fe(II), Co(II), Cu(II) or Ni(II)) were investigated.[9,10] Furthermore, these compounds have also been used as heterogeneous catalysts.[11–13]

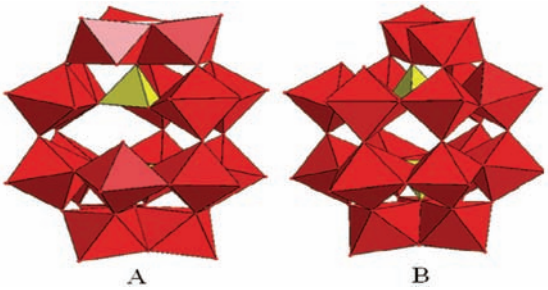

Fig. 1. A) The monovacant α_1-$[LiP_2W_{17}O_{61}]^{9-}$ unit obtained by removing a WO_6 octahedron in the equatorial site of the parent Wells–Dawson structure, B) The monovacant α_2-$[P_2W_{17}O_{61}]^{10-}$ unit obtained by removing a WO_6 octahedron in the capping region of the parent Wells–Dawson 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.[14] In 1995, Kirby and Baker[15] 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.*[16] 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.*[17] synthesized and structurally characterized $[Cd_4(H_2O)_2(PW_9O_{34})_2]^{10-}$. In 2005, Kortz *et al.*[18] reported another cadmium containing polyxoxometalate, $[Cd_4Cl_2(B\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$. Finally, Zhao *et al.*[19] prepared and characterized $[Cd_4(H_2O)_2(B\text{-}\alpha\text{-}SiW_9O_{34})_2]^{12-}$.

Over past years, electrochemical methods were shown to be an inexpensive and effective method for the determination of some inorganic and organic substrates.[20–23] In particular, POMs exhibited multi-electron reversible redox characteristics, which enables them to be redox electrocatalysts for some irreversible electrochemical processes.[24–26] 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.[27] In this paper, the syntheses of two new cadmium-containing

α_1- and α_2-mono-lacunary Dawson-type polyoxometalates, $K_8[\alpha_1\text{-}P_2W_{17}Cd(H_2O)O_{61}]\cdot 14H_2O$ (α_1-$P_2W_{17}Cd$) and $K_8[\alpha_2\text{-}P_2W_{17}Cd(H_2O)O_{61}]\cdot 16H_2O$ (α_2-$P_2W_{17}Cd$), are described. Several attempts to prepare single crystals of α_1-$P_2W_{17}Cd$ and α_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 $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20H_2O$ and $K_9[\alpha_1\text{-}LiP_2W_{17}O_{61}]\cdot 20H_2O$ were prepared according to the literature and characterized accordingly.[28] 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_3PO_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 $K_8[\alpha_1\text{-}P_2W_{17}Cd(H_2O)O_{61}]\cdot 14H_2O$

$Cd(NO_3)_2\cdot 4H_2O$ (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 $K_9[\alpha_1\text{-}LiP_2W_{17}O_{61}]\cdot 20H_2O$ 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 $CdH_{30}K_8O_{76}P_2W_{17}$: Cd, 2.31; K, 6.43; P, 1.27; W, 64.32; H_2O, 5.18 %. Found: Cd, 2.28; K, 6.30; P, 1.23; W, 64.35; H_2O, 5.24 %; IR (KBr, cm^{-1}): 1084, 1060, 1014 (P–O stretching bonds), 948 (W–O_{term} stretching bonds), 898 (W–O_b stretching bonds), 784, 738 (W–O_c stretching bonds).

Synthesis of $K_8[\alpha_2\text{-}P_2W_{17}Cd(H_2O)O_{61}]\cdot 16H_2O$

A 0.72 g (2.33 mmol) of $Cd(NO_3)_2\cdot 4H_2O$ 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 $K_{10}[\alpha_2\text{-}(P_2W_{17}O_{61})]\cdot 20H_2O$ 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 $CdH_{34}K_8O_{78}P_2W_{17}$: Cd, 2.29; K, 6.39; P, 1.26; W, 63.85; H_2O, 5.88 %. Found: Cd, 2.24; K, 5.45; P, 1.16; W,

64.81; H_2O, 5.82 %. IR (KBr, cm^{-1}): 1085, 1053, 1016 (P–O stretching bonds), 945 ($W–O_{term}$ stretching bonds), 889 ($W–O_b$ stretching bonds), 800, 730 ($W–O_c$ stretching bonds).

RESULTS AND DISCUSSION

IR spectra

The compounds α_1-$P_2W_{17}Cd$ and α_2-$P_2W_{17}Cd$, synthesized in this work, showed typical bands of transition metal-substituted Wells–Dawson heteropolyanion in the range of 700–1200 cm^{-1}.[29] The solid-state FT-IR measurements of $K_6[\alpha\text{-}P_2W_{18}O_{62}]$, $K_9[\alpha_1\text{-}LiP_2W_{17}O_{61}]$, α_1-$P_2W_{17}Cd$, $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ and α_2-$P_2W_{17}Cd$ (Fig. 2, curves a–e, respectively) show the spectral patterns characteristic of the Dawson POM framework.

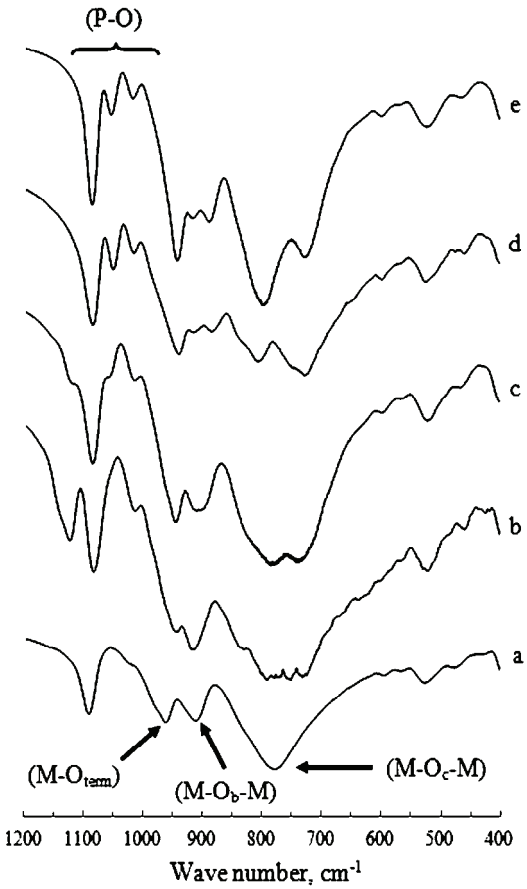

Fig. 2. IR spectra of: a) $K_6[\alpha\text{-}P_2W_{18}O_{62}]$; b) $K_9[\alpha_1\text{-}LiP_2W_{17}O_{61}]$; c) α_1-$P_2W_{17}Cd$, d) $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$; e) α_2-$P_2W_{17}Cd$.

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 $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ heteropolyanion,[30] whereas three bands were observed within the range of 1000–

–1200 cm^{-1} in the [α_1-LiP$_2$W$_{17}$O$_{61}$]$^{9-}$ heteropolyanion. In α_1-P$_2$W$_{17}$Cd, by replacing Cd^{2+} in the mono-lacunary [α_1-LiP$_2$W$_{17}$O$_{61}$]$^{9-}$ 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 α_1-P$_2$W$_{17}$Cd was approximately similar to that of [α-P$_2$W$_{18}$O$_{62}$]$^{6-}$. It was surmised that removal of the bands was due to the increase in the symmetry of PO$_4$ unit caused by transition metal substitution.[31] Moreover, the FT-IR spectra of α_1-P$_2$W$_{17}$Cd in the (M–O) region are very similar to that of K$_9$[α_1-LiP$_2$W$_{17}$O$_{61}$], especially with regards to the (M–O$_{term}$) oxygen atoms (948 cm^{-1} for α_1-P$_2$W$_{17}$Cd and 945 cm^{-1} for K$_9$[α_1-LiP$_2$W$_{17}$O$_{61}$]), the bands assignable to corner-sharing (M–O$_b$–M) oxygen atoms (898 cm^{-1} for α_1-P$_2$W$_{17}$Cd and 912 cm^{-1} for K$_9$[α_1-LiP$_2$W$_{17}$O$_{61}$]) and the bands assignable to edge-sharing (M–O$_c$–M) oxygen atoms (784 and 738 cm^{-1} for α_1-P$_2$W$_{17}$Cd; 790 and 732 cm^{-1} for K$_9$[α_1-LiP$_2$W$_{17}$O$_{61}$]). The FT-IR spectra of α_2-P$_2$W$_{17}$Cd in the polyoxometalate region were very similar to that of K$_{10}$[α_2-P$_2$W$_{17}$O$_{61}$], especially with regards to the multiple (P–O) bands (1085, 1053 and 1016 cm^{-1} for α_2-P$_2$W$_{17}$Cd; 1083, 1047, and 1016 cm^{-1} for K$_{10}$[α_2-P$_2$W$_{17}$O$_{61}$]), the bands assignable to (M–O$_{term}$) oxygen atoms (943 cm^{-1} for α_2-P$_2$W$_{17}$Cd and 939 cm^{-1} for K$_{10}$[α_2-P$_2$W$_{17}$O$_{61}$]), the bands assignable to corner-sharing (M–O$_b$–M) oxygen atoms (889 cm^{-1} for α_2-P$_2$W$_{17}$Cd and 885 cm^{-1} for K$_{10}$[α_2-P$_2$W$_{17}$O$_{61}$]) and the bands assignable to edge-sharing (M–O$_c$–M) oxygen atoms (800 and 730 cm^{-1} for α_2-P$_2$W$_{17}$Cd; 868 and 736 cm^{-1} for K$_{10}$[α_2-P$_2$W$_{17}$O$_{61}$]).

^{31}P-NMR

^{31}P-NMR spectroscopy is a very sensitive technique to characterize polyoxometalates and evaluate the purity of these compounds. The ^{31}P-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 I. ^{31}P-NMR chemical shift patterns (δ / ppm) for some phosphotungstate Dawson-type polyoxometalates; P (1) refers to the resonance attributed to the phosphorus atom nearer to the site of substitution (or defect); P (2) refers to the P atom far away from the site of substitution (or defect)

Compond	P (1)	P (2)	Ref.
K$_6$[α-P$_2$W$_{18}$O$_{62}$]	–12.50	–12.5	28
K$_9$[α_1-LiP$_2$W$_{17}$O$_{61}$]	–9.00	–13.1	28
K$_{10}$[α_2-P$_2$W$_{17}$O$_{61}$]	–6.90	–13.70	32
K$_8$[α_1-P$_2$W$_{17}$Zn(H$_2$O)O$_{61}$]	–8.56	–13.45	33
K$_8$[α_2-P$_2$W$_{17}$Zn(H$_2$O)O$_{61}$]	–8.65	–14.15	33
K$_7$[α_1-P$_2$W$_{17}$La(H$_2$O)$_4$O$_{61}$]	–10.58	–13.64	34
K$_7$[α_1-P$_2$W$_{17}$Lu(H$_2$O)$_4$O$_{61}$]	–10.57	–13.55	34
K$_7$[α_2-P$_2$W$_{17}$Lu(H$_2$O)$_4$O$_{61}$]	–10.58	–13.61	34
K$_8$[α_1-P$_2$W$_{17}$Cd(H$_2$O)O$_{61}$]	–7.99	–14.19	This work
K$_8$[α_2-P$_2$W$_{17}$Cd(H$_2$O)O$_{61}$]	–6.72	–13.00	This work

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 α_1-$P_2W_{17}Cd$ and α_2-$P_2W_{17}Cd$ 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 α_1-$P_2W_{17}Cd$ or α_2-$P_2W_{17}Cd$. Finally, the integrated intensity of P (1) appears smaller than that of P (2) because of a slow relaxation rate (large T_1).

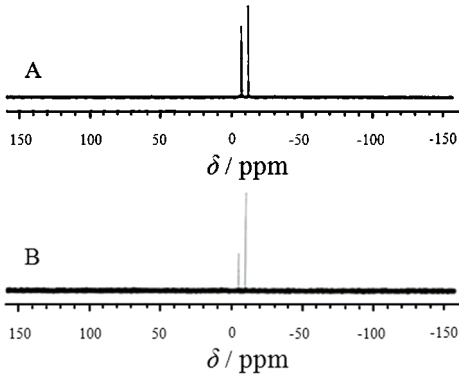

Fig. 3. ^{31}P-NMR spectra of A) α_1-$P_2W_{17}Cd$ and B) α_2-$P_2W_{17}Cd$.

^{113}Cd-NMR

The ^{113}Cd-NMR spectra in D_2O show clean, single spectra with a resonance at δ = 63.34 ppm for α_1-$P_2W_{17}Cd$ (Fig. 4A) and at δ = –22.86 ppm for α_2-$P_2W_{17}Cd$ (Fig. 4B). As shown in Fig. 4, a considerable difference was observed between the chemical shifts in the ^{113}Cd-NMR spectra of α_1-$P_2W_{17}Cd$ and α_2-$P_2W_{17}Cd$. Francesconi *et al.*[35] reported that the basic oxygen of the α_1 structure is bound to one tungsten atom, while the corresponding oxygen of the α_2 structure is bound to two tungsten atoms. This observation is ascribed mainly to

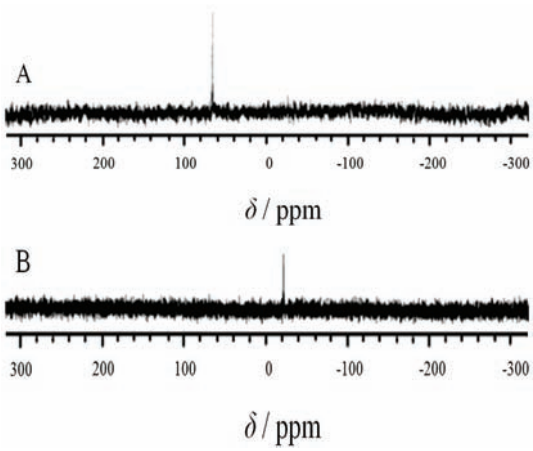

Fig. 4. ^{113}Cd-NMR spectra of A) α_1-$P_2W_{17}Cd$ and B) α_2-$P_2W_{17}Cd$.

the large framework distortion induced by the vacancy in the α_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 α_2 site, the cadmium substituent fills the vacancy perfectly and therefore its resonance is downfield shifted.

Electrochemical behavior of α_1*-*$P_2W_{17}Cd$ *and* α_2*-*$P_2W_{17}Cd$

Electrochemical behavior of α_1*-*$P_2W_{17}Cd$*.* The electrochemical behavior of α_1-$P_2W_{17}Cd$ 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 [α_1--$LiP_2W_{17}O_{61}$]$^{9-}$. 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 α_1-$P_2W_{17}Cd$ while the corresponding peaks were found at –0.97, –0.7, –0.6 and –0.43 V, respectively, for [α_1-$LiP_2W_{17}O_{61}$]$^{9-}$. 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+}/Cd, in the free ion state, occurs at –0.4 V.[36]

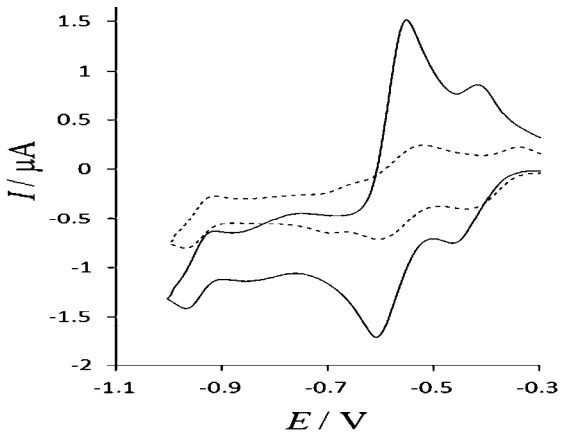

Fig. 5. Cyclic voltammograms of α_1-$P_2W_{17}Cd$ (solid line) and K_9[α_1--$LiP_2W_{17}O_{61}$] (dashed line).

The cyclic voltammograms of α_1-$P_2W_{17}Cd$ 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.

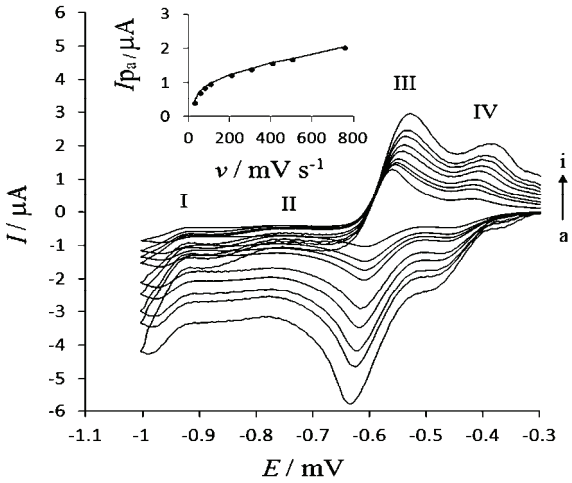

Fig. 6. Cyclic voltammograms of α_1-$P_2W_{17}Cd$ in 0.5 M acetate buffer solutions at different scan rates of a) 25, b) 50, c) 75, d) 100, e) 200, f) 300, g) 400, h) 500 and i) 750 mV s^{-1}. The inset shows plots of the anodic peak current of III against scan rate.

Electrochemical behavior of α_2-*$P_2W_{17}Cd$.* The electrochemical behavior of α_2-$P_2W_{17}Cd$ was studied in 0.5 M acetate buffer solution by cyclic voltammetry (CV). The obtained results are compared with the corresponding results for $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ 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 α_2-$P_2W_{17}Cd$ and at –0.95, –0.67 and –0.54 V, respectively, for $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$. Similar to α_1-$P_2W_{17}Cd$, on substituting cadmium in the polyoxometalate vac-

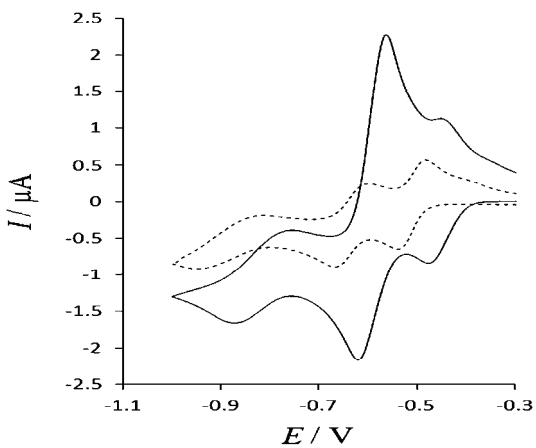

Fig. 7. Cyclic voltammograms of α_2-$P_2W_{17}Cd$ (solid line) and $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ (dashed line).

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+}/Cd in the free ion state occurs at –0.4 V.[36]

On comparison of cathodic potential data between α_1-$P_2W_{17}Cd$ and [α_1-$LiP_2W_{17}O_{61}]^{9-}$, and between α_2-$P_2W_{17}Cd$ and [α_2-$P_2W_{17}O_{61}]^{10-}$, it is obvious that when cadmium replaced the vacancy in [α_1-$LiP_2W_{17}O_{61}]^{9-}$, no significant changes in the cathodic potentials for α_1-$P_2W_{17}Cd$ were observed. However, when cadmium replaced the vacancy in [α_2-$P_2W_{17}O_{61}]^{10-}$, considerable changes in these potentials were observed for α_2-$P_2W_{17}Cd$. These results indicate that cadmium, which substituted completely in the [α_2-$P_2W_{17}O_{61}]^{10-}$ vacancy affects the redox potentials of the tungsten centers of the polyoxometalate, while cadmium in α_1-$P_2W_{17}Cd$ does not fill the vacancy of [α_1-$LiP_2W_{17}O_{61}]^{9-}$ completely.

Figure 8 shows the cyclic voltammograms of α_2-$P_2W_{17}Cd$ 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.

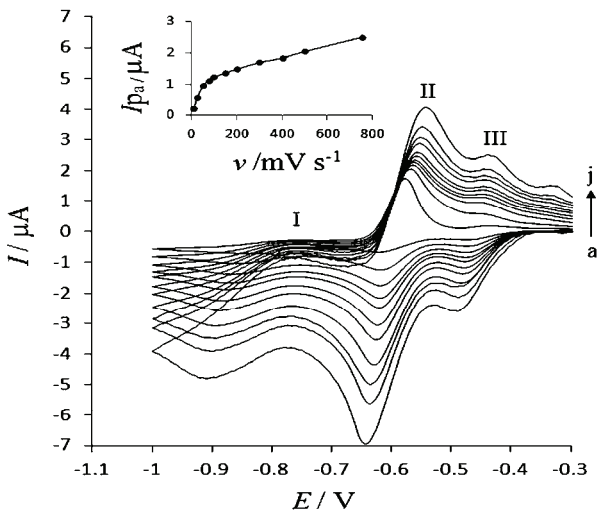

Fig. 8. Cyclic voltammograms of α_1-$P_2W_{17}Cd$ in 0.5 M acetate buffer solutions at different scan rates of a) 10, b) 25, c) 50, d) 75, e) 100, f) 200, g) 300, h) 400, i) 500 and j) 750 mV s^{-1}. The inset shows plots of the anodic peak current of III against scan rate.

Electrocatalysis of NO_2^- reduction

As is known, POMs have been exploited extensively in electrocatalytic reductions.[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.[38,39]

Electrocatalysis of NO_2^- reduction by α_1-$P_2W_{17}Cd$

The polyoxometalates $[\alpha_1\text{-}LiP_2W_{17}O_{61}]^{9-}$ and α_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.

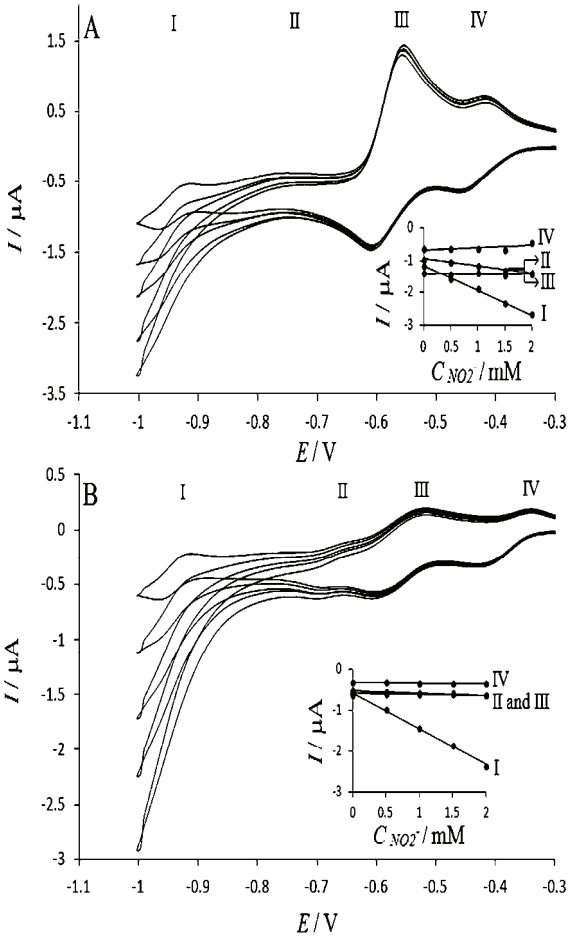

Fig. 9. A) Cyclic voltammograms (scan rate: 75 mV s^{-1}) for the electrocatalytic reduction of NO_2^- with a 5×10^{-4} M solution of α_1-$P_2W_{17}Cd$ in a 0.5 M acetate buffer solution (from top to bottom γ = 0, 1, 2, 3 and 4). B) Cyclic voltammograms (scan rate: 75 mV s^{-1}) for the electrocatalytic reduction of NO_2^- with a 5×10^{-4} M solution of $K_9[\alpha_1\text{-}LiP_2W_{17}O_{61}]$ in a 0.5 M acetate buffer solution (from top to bottom γ = 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 $NaNO_2$ to the solution, even for small values of the excess parameter, γ, which is defined here as:

$$\gamma = \frac{c^0_{(NO_x)}}{c^0_{(POM)}}$$

the cathodic current of all waves increased and the corresponding anodic current decreased. The catalytic efficiency *CAT* for waves I and II of $[\alpha_1\text{-}LiP_2W_{17}O_{61}]^{9-}$ varied from 53.20 to 274.02 % and 4.53 to 19.84 %, respectively (Table II), when γ increase from 1 to 4, while the *CAT* for $\alpha_1\text{-}P_2W_{17}Cd$ varied from 34.74 to 127.9 % (wave I) and 9.26 to 43.6 % (wave II), Table III. *CAT* is defined as:

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

where I_p(POM) and I_p(POM,$NaNO_2$) are the cathodic peak currents in the absence and in the presence of $NaNO_2$, respectively.

TABLE II. Catalytic efficiency for $[\alpha_1\text{-}LiP_2W_{17}O_{61}]^{9-}$; $CATw_x$ refers to catalytic efficiency for the xth wave

γ	$CATw_1$ / %	$CATw_2$ / %	$CATw_3$ / %	$CATw_4$ / %
1	53.20	4.53	2.80	3.52
2	123.78	10.39	6.84	8.01
3	191.07	11.34	5.78	6.73
4	274.02	19.84	10.87	1.21

TABLE III. Catalytic efficiency for $\alpha_1\text{-}P_2W_{17}Cd$; $CATw_x$ refers to catalytic efficiency for the xth wave

γ	$CATw_1$ / %	$CATw_2$ / %	$CATw_3$ / %	$CATw_4$ / %
1	34.74	9.26	3.57	4.51
2	61.01	19.66	0.71	1.61
3	99.15	35.27	5.00	6.29
4	127.90	43.60	2.10	4.03

It is noticeable from Tables II and III that the electrocatalytic activity of $[\alpha_1\text{-}LiP_2W_{17}O_{61}]^{9-}$ was greater than that of $\alpha_1\text{-}P_2W_{17}Cd$ 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 $[\alpha_1\text{-}LiP_2W_{17}O_{61}]^{9-}$ 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 NO_2^- reduction by α_2-$P_2W_{17}Cd$

The polyoxometalates $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ and α_2-$P_2W_{17}Cd$ 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 GC in 0.5 M acetate buffer solution are shown in Fig. 10.

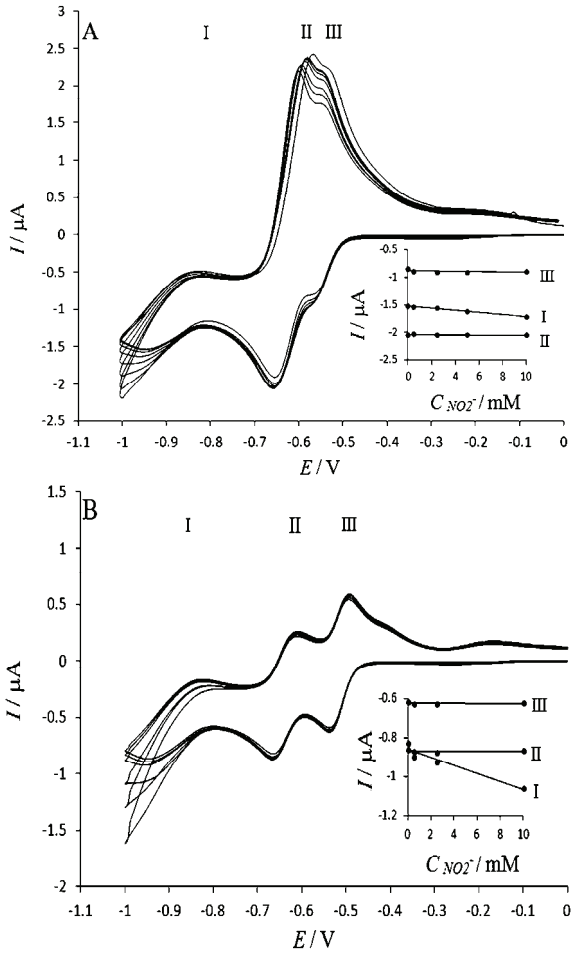

Fig. 10. A) Cyclic voltammograms (scan rate: 75 mV s^{-1}) for the electrocatalytic reduction of NO_2^- with a 5×10^{-4} M solution of α_2-$P_2W_{17}Cd$ in a 0.5 M acetate buffer solution (from top to bottom γ = 0, 1, 5, 10 and 20). B) Cyclic voltammograms (scan rate: 75 mV s^{-1}) for the electrocatalytic reduction of NO_2^- with a 5×10^{-4} M solution of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ in a 0.5 M acetate buffer solution (from top to bottom γ = = 0, 1, 5 and 20). The excess parameter defined as $\gamma = c^0_{(NO_2^-)}/c^0_{(POM)}$. Inset: the relationship between catalytic current and NO_2^-concentration.

Clearly, with the addition of $NaNO_2$ to the solution, even for small values of the excess parameter γ, cathodic current of all waves increased and the corresponding anodic current decreased. The catalytic efficiency *CAT* for wave I of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ varied from 8.34 to 28.17 % (Table IV) when γ = 1, 5 and 20, while the *CAT* variations for α_2-$P_2W_{17}Cd$ were from 0.65 to 10.46 % when γ = 1, 5, 10 and 20 (Table V).

TABLE IV. Catalytic efficiency for $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$; $CATw_x$ refers to catalytic efficiency for the xth wave

γ	$CATw_1$ / %	$CATw_2$ / %	$CATw_3$ / %
1	8.34	1.27	1.45
5	11.60	1.74	1.94
20	28.17	0.69	0.97

TABLE V. Catalytic efficiency for $\alpha_2\text{-}P_2W_{17}Cd$; $CATw_x$ refers to catalytic efficiency for the xth wave

γ	$CATw_1$ / %	$CATw_2$ / %	$CATw_3$ / %
1	0.65	0.00	0.22
5	2.61	0.00	0.55
10	6.53	0.49	1.00
20	10.46	0.49	0.33

It is noticeable from Tables IV and V that the electrocatalytic activity of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ was greater than that of $\alpha_2\text{-}P_2W_{17}Cd$ in wave I, due to the presence of 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}Cd-NMR indicated that cadmium was substituted completely in the $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ vacancy, whereas cadmium in $[\alpha_1\text{-}LiP_2W_{17}O_{61}]^{9-}$ 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 $\alpha_1\text{-}P_2W_{17}Cd$ and $[\alpha_1\text{-}LiP_2W_{17}O_{61}]^{9-}$ compounds.

The electrochemistry of $\alpha_1\text{-}P_2W_{17}Cd$ and $\alpha_2\text{-}P_2W_{17}Cd$ 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 $\alpha_1\text{-}P_2W_{17}Cd$ and $\alpha_2\text{-}P_2W_{17}Cd$ 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 ($[\alpha_1\text{-}LiP_2W_{17}O_{61}]^{9-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$) follows from the presence of cadmium metal ion in these compounds. The presence of cadmium metal ion in the mono-lacunary Dawson--type ($[\alpha_1\text{-}LiP_2W_{17}O_{61}]^{9-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$) caused decreases in electrocatalytic activity of these compounds.

ИЗВОД

СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И УПОРЕЂИВАЊЕ ЕЛЕКТРОКАТАЛИТИЧКЕ АКТИВНОСТИ ДВА МОНОЛАКУНАРНА WELLS–DAWSON ПОЛИОКСОМЕТАЛАТА КОЈИ САДРЖЕ КАДМИЈУМ, α_1- И α_2-$[P_2W_{17}Cd(H_2O)O_{61}]^{8-}$

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У овом раду су синтетизоване калијумове соли два Wells–Dawson полиоксометалата који садрже кадмијум, $K_8[\alpha_1\text{-}P_2W_{17}Cd(H_2O)O_{61}]\cdot 14H_2O$ (α_1-$P_2W_{17}Cd$) и $K_8[\alpha_2\text{-}P_2W_{17}Cd\text{-}(H_2O)O_{61}]\cdot 16H_2O$ (α_2-$P_2W_{17}Cd$). Синтетизовани комплекси су окарактерисани применом IR, ^{31}P- и ^{113}Cd-NMR спектроскопије, док су редокс потенцијали волфрама и кадмијума у овим једињењима 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 α_2-$[P_2W_{17}O_{61}]^{10-}$ хетерополианјона.

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