#### Inorganica Chimica Acta 444 (2016) 87-94



Contents lists available at ScienceDirect

# Inorganica Chimica Acta

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A new sandwich-type polyoxometalates containing mixed transition metals,  $[Cd_2Zn_2(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ : Syntheses, spectrochemical characterization and its electrocatalytical activity comparison with  $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$  (M = Cd<sup>2+</sup> and Zn<sup>2+</sup>) and  $[P_2W_{15}O_{56}]^{12-}$ 

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#### ARTICLE INFO

Article history: Received 27 August 2015 Received in revised form 8 January 2016 Accepted 16 January 2016 Available online 23 January 2016

Keywords: Polyoxometalate Sandwich complexes Cadmium Electrochemistry

## ABSTRACT

The mixed-metal sandwich-type polyoxometalate  $[Cd_2Zn_2(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$  (abbreviated  $Cd_2Zn_2P_4W_{30}$ ) has been synthesized and characterized by FT-IR, <sup>31</sup>P NMR, <sup>113</sup>Cd NMR spectroscopies, cyclic voltammetry (CV) and elemental analysis. The electrochemical behavior of this sandwich-type complex in aqueous solution has been investigated, and also systematic comparisons of that have been made by  $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$  ( $M = Cd^{2+}$  and  $Zn^{2+}$ ) (abbreviated  $M_4P_4W_{30}$ ) and  $[P_2W_{15}O_{56}]^{12-}$  (abbreviated  $P_2W_{15}$ ). All these compounds show successive reduction processes of the tungsten centers in a negative potential range, but in some cases, the electrochemistry involves redox reactions originating from cadmium ions. These sandwich-type complexes have efficient electrocatalytic activities towards the reduction of nitrite. However, there is a significant decrease in efficiency as the number of cadmium centers in the complex increases.

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# 1. Introduction

Polyoxometalates (POMs) and their transition metal substituted derivatives (TMSPs) are a multifaceted and huge group of metaloxygen anionic clusters with applications in catalysis, medicine, materials science and molecular magnetism [1–5]. Among known POM structural types, sandwich complexes are the largest class of TMSPs due to the number (2, 3, 4 or 6) and the nature of the metal centers that could be included between 2 or 3 multivacant POM fragments [6–17]. The structural properties of sandwich compounds derived from  $B-\alpha$ -[ $P_2W_{15}O_{56}$ ]<sup>12–</sup> are among the most well known because they are more amenable to NMR studies (such as <sup>31</sup>P NMR) than are the analogous Keggin (i.e.  $B-\alpha$ -[ $XW_9O_{34}$ ]<sup>*n*–</sup>) species. These complexes are composed of a central M<sub>4</sub>O<sub>16</sub> unit encapsulated by two  $B-\alpha$ -[ $X_2W_{15}O_{56}$ ]<sup>12–</sup> (X = P<sup>V</sup> or As<sup>V</sup>) trivacant POMs (Fig. 1) [18–22].

In 1983, the first Wells–Dawson derivatives  $[M_4(OH_2)_2(P_2W_{15} O_{56})_2]^{16-}$  (M = Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) was informed by Finke et al. [23]. Kirby and Baker, in 1995, published the first article about cadmium-containing Wells–Dawson sandwich-type polyoxometalate as  $[Cd_4 (OH_2)_2 (P_2W_{15}O_{56})_2]^{16-}$  [24]. After few years, the first

\* Corresponding author. E-mail addresses: f.zonoz@hsu.ac.ir, fzmohamadi@yahoo.com (F.M. Zonoz). arsenic (V) analogues of the Wells–Dawson type,  $[M_4 (OH_2)_2 (A_5_2W_{15}O_{56})_2]^{16-}$  (M = Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>) was reported by Bi et al. [25]. The first sample of a sandwich-type compounds with less than four transition metals was published by Hill et al. in 2001 [26]. They reported that  $[Fe_2O_{14}(NaOH_2)_2]$  unit was sandwiched between two Wells–Dawson  $[P_2W_{15}O_{56}]^{12-}$  fragments and formed  $[(NaOH_2)_2Fe_2 (P_2W_{15}O_{56})_2]^{16-}$  mixed-metal polyoxometalate. In this compound, the two similar internal locations are occupied by Fe<sup>III</sup> centers, while two similar external positions are occupied by sodium ions (Fig. 1B). In 2001, Hill et al. was reported two asymmetric diferric complexes of sandwich-type mixed-metal polyoxoanions as  $[TM^{II}Fe_2^{II}(P_2W_{15}O_{56})(P_2TM_2^{II}W_{13}O_{52})]^{16-}$ , TM = Cu or Co. These compounds were formed by the reaction of  $[(NaOH_2)_2Fe_2 (P_2W_{15}O_{56})_2]^{16-}$ unit with Cu<sup>2+</sup> or Co<sup>2+</sup> ions in aqueous solution [27].

From then till now, a lot of reports have been published based on mixed-metal sandwich-type polyoxometalates. For instance, the mixed-metal complexes  $[(MOH_2)_2Fe_2(P_2W_{15}O_{56})_2]^{16-}$ , where  $M = Ni^{II}$ ,  $Mn^{II}$ ,  $C0^{II}$  or  $Zn^{II}$  can be synthesized by the addition of several first row transition metal cations on  $[(NaOH_2)_2Fe_2(P_2W_{15}O_{56})_2]^{16-}$  [19,28,29]. These mixed-metal compounds have valuable significance because of their properties can be easily adjustable by changing the number and/or nature of metals "sandwiched" in the tetra nuclear cluster. The preparations of new POMs probably play a main role in catalytic and electrocatalytic reactions [30]. Actually,



**Fig. 1.** (A) Polyhedral representation of  $B-\alpha-[P_2W_{15}O_{56}]^{12-}$ . (B) Polyhedral representation of  $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ . (C) Wells–Dawson-based sandwich-type structure, with the cluster off our metal atoms and two water molecules (ball-and-stick) between two  $[P_2W_{15}O_{56}]^{12-}$  fragments (polyhedra). Typically, green and blue spheres are referred to as external and internal positions, respectively. (Color online.)

it was found that the nature, number and location of the d metal centers in the POM framework may affect the interactions between redoxactive centers within the molecule. In 2004, Nadjo et al. reported that the electroreduction of dioxygen by  $[Fe_y(X_2W_{15}O_{56})_2]^{n-}$  (where X = As or P and y = 2, 3 or 4) improved when the number of Fe atoms was increased. It is well established that mixed-metal sandwichtype POMs catalyze the reduction of NO<sub>2</sub><sup>-</sup> [22,32,33].

In the present article, we report the synthesis of a new cadmium-containing Wells–Dawson sandwich-type polyoxometalate. Several attempts to prepare single crystal of  $Cd_2Zn_2P_4W_{30}$  were unsuccessful. Therefore, this compound has been characterized by elemental analysis, cyclic voltammetry and spectrochemical methods (FT-IR, <sup>31</sup>P and <sup>113</sup>Cd NMR). The electrochemical properties of this compound and electrocatalytic reductions of nitrite have been investigated in detail by using cyclic voltammetry and its results have been compared with  $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$  $(M = Cd^{2+} \text{ and } Zn^{2+}) \text{ and } [P_2W_{15}O_{56}]^{12-} \text{ complexes.}$ 

# 2. Experimental

## 2.1. Materials and general methods

All reagents were of analytical grade and were used as received from commercial sources without further purification. The  $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$  (M = Cd<sup>2+</sup> and Zn<sup>2+</sup>) and  $[P_2W_{15}O_{56}]^{12-}$ compounds were prepared according to the published methods and characterized by elemental analysis and FT-IR spectroscopy [23,24,34]. FT-IR spectra were recorded in the range of 4000-400 cm<sup>-1</sup> on Shimadzu 8400S FT-IR spectrophotometer using a KBr pellet. The NMR spectrum was recorded on a Bruker BRX-300 AVANCE Spectrometer. The resonance frequencies for the <sup>31</sup>P and <sup>113</sup>Cd nuclei are 202.46 and 110.92 MHz, respectively. Chemical shifts for <sup>31</sup>P and <sup>113</sup>Cd NMR spectra were externally referenced relative to 85% H<sub>3</sub>PO<sub>4</sub> and 0.1 M cadmium perchlorate, respectively. Elemental analyses were carried in an Integra XL Inductively Coupled Plasma Spectrometer. 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 10 min by bubbling pure N<sub>2</sub> and kept under N<sub>2</sub> 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 (GC) electrode. A platinum electrode was used as counter electrode and an Ag/AgCl (3 M KCl) electrode was used as reference electrode. All potentials were measured and reported versus the Ag/AgCl electrode. All voltammetric experiments were carried out at room temperature.

## 2.2. Synthesis

# 2.2.1. Synthesis of Na<sub>16</sub>[Cd<sub>2</sub>Zn<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]·50H<sub>2</sub>O

A variation on the method described by Finke et al. was used to prepare this complex [23]. A 2.50 g (0.625 mmol) of  $P_2W_{15}$  was dissolved in 25 ml of 1 M NaCl solution. To this suspension at 50–60 °C was added a mixture of 0.187 g (0.625 mmol) of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and 0.185 g (0.625 mmol) of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O respectively. After heating and stirring for approximately 30 min, the colorless solution was allowed to stand overnight in a



**Fig. 2.** Comparison of the IR spectra of the hydrated sandwich heteropolyanions  $P_2W_{15}$ ,  $Cd_4P_4W_{30}$ ,  $Cd_2Zn_2P_4W_{30}$ ,  $Zn_4P_4W_{30}$  and  $P_2W_{18}$ .



Fig. 3. <sup>31</sup>P NMR of Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub> (A) and Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> (B) polyoxometalates.

refrigerator at 5 °C. After 1 day, the white powder which formed was collected, recrystallized by 0.5 M NaCl aqueous solution and dried in air. Yield: 1.23 g (0.135 mmol, 43.3%). IR (KBr, cm<sup>-1</sup>): 1081, 1045 (P-O stretching bonds), 925 (W-O<sub>term</sub> stretching bonds), 881 (W-O<sub>b</sub> stretching bonds), 773, 720 (W-O<sub>c</sub> stretching bonds), <sup>31</sup>P NMR (D<sub>2</sub>O), ( $\delta$ : ppm): -4.47, -14.59. <sup>113</sup>Cd NMR (D<sub>2</sub>O), ( $\delta$ : ppm): 42.38. Elemental *Anal.* Calc. for Na<sub>16</sub>[Cd<sub>2</sub>Zn<sub>2</sub>(H<sub>2</sub>-O)<sub>2</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]·50H<sub>2</sub>O: Requires Na, 4.04; Cd, 2.47; Zn, 1.43; P, 1.36; W, 60.6; H<sub>2</sub>O, 9.88. Found: Na, 4.14; Cd, 2.58; Zn, 1.30; P, 1.45; W, 61.3; H<sub>2</sub>O, 10.04%.

# 3. Results and discussion

## 3.1. IR characterization

The IR spectrum of  $Cd_2Zn_2P_4W_{30}$  is shown in Fig. 2 and is compared to  $Cd_4P_4W_{30}$ ,  $Zn_4P_4W_{30}$ ,  $\alpha$ - $P_2W_{15}$  and  $\alpha$ - $P_2W_{18}$  polyoxometaltes. These compounds show the spectral patterns characteristic of the Dawson POM framework (Fig. 2) [35].

Besides the W-O and W-O-W bands appeared at lower than 1000 cm<sup>-1</sup>, the IR spectra of phosphorus centered polyoxotungstates have been defined by well-separated P-O stretching vibrations between 1200 and 1000 cm<sup>-1</sup> [36]. By considering to the local symmetry of the PO<sub>4</sub> unit, the triply-degenerate mode  $F_2$  (for  $T_d$  symmetry) may split into two or three absorption bands by decreasing symmetry (the splitting depends on the deviation from ideal symmetry). In phosphotungstate Keggin-type lacunary anions and for the substituted metallophosphate of first row transition metals it was presented that the splitting  $\Delta v$  declines when the transition metal interacts more strongly with the oxygen atom of the PO<sub>4</sub> tetrahedron [37]. For lacunary or substituted unsymmetrical Wells-Dawson POMs, this situation is more complicated because of the overlap of vibrational absorption bands deriving from two different PO<sub>4</sub> tetrahedra; although, in desirable instance, it is feasible to distinguish between the bands deriving from the unperturbed subunit PW<sub>9</sub> and those deriving from the PW<sub>x</sub>M<sub>y</sub> segment [38].

As seen in Fig. 2, it is notable that only two bands of (P-O) stretching vibration are observed at 1090 and 1022 cm<sup>-1</sup> in the  $\alpha$ -P<sub>2</sub>W<sub>18</sub> heteropolyanion (assigned to PW<sub>9</sub>), whereas three bands are observed at 1130, 1087 and 1010 cm<sup>-1</sup> in the  $\alpha$ -P<sub>2</sub>W<sub>15</sub> heteropolyanion. The additional band at 1130 cm<sup>-1</sup> can be referred to the PW<sub>6</sub> subunit [20]. The IR spectra of the Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub>, Zn<sub>4</sub>P<sub>4</sub>W<sub>30</sub> and Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> are almost identical, which indicates a structural similarity. Moreover, the stretching bands between 950 and 720 cm<sup>-1</sup> are attributed to terminal W-O and bridging W-O-W bands which are at lower wavenumbers than for the parent saturated  $\alpha$ -P<sub>2</sub>W<sub>18</sub> anion.

# 3.2. <sup>31</sup>P NMR characterization

<sup>31</sup>P NMR is a well-suited technique to characterize the POMs and it is suitable to evaluate the purities of POM species. The <sup>31</sup>P NMR spectra of Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub> and Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> are reported in Fig. 3 and their data as well as some results of phosphotungstate Dawson-type POMs are given in Table 1. Two remarkably different types of <sup>31</sup>P NMR are observed in the symmetrical Wells–Dawson sandwich-type polyoxometalate ( $C_{2h}$  symmetry) [19].

In Table 1, P(1) refers to the resonance attributed to the P atom closer to the  $M_4O_{16}$  metal centers (PW<sub>6</sub>M<sub>3</sub> subunits) and P(2) refers P atom far away from the  $M_4O_{16}$  metal centers (PW<sub>9</sub> subunits) (Fig. 1C). The <sup>31</sup>P NMR spectrum of the diamagnetic compound

Tab	ie i							
<sup>31</sup> P	NMR	chemical	shift	patterns	for	some	phosphotungstate	Dawson-type
poly	/oxome	talates.						

	δP (1), ppm	δP (2), ppm	Refs.
$\alpha - P_2 W_{15}$	+0.5	-13.8	[20]
$\alpha - P_2 W_{15}$	+0.1	-13.3	[34]
$Zn_4P_4W_{30}$	-3.92	-13.95	[20]
$Zn_4P_4W_{30}$	-4.31	-14.30	[23]
$Cd_4P_4W_{30}$	-3.60	-14.36	[20]
$Cd_4P_4W_{30}$	-4.20	-14.90	This work
$Cd_2Zn_2P_4W_{30}$	-4.47	-14.59	This work

Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub> shows two lines, consistent with the presence of a single isomer (Fig. 3A). The most shielded line, at  $\delta = -14.9$  ppm, is related to P(2) of the PW<sub>9</sub> unit. The deshielded line, at  $\delta = -4.20$  ppm, corresponds to P(1) in the PW<sub>6</sub>M<sub>3</sub> unit; its integrated intensity appears smaller than that of P(2) due to a slower relaxation rate (large *T*<sub>1</sub>). The <sup>31</sup>P NMR spectrum of mixed-metal Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> shows two peaks (P(1):  $\delta = -4.47$  ppm and P(2):  $\delta = -14.59$  ppm) which has a remarkable agreement with M<sub>4</sub>P<sub>4</sub>W<sub>30</sub> (M = Cd and Zn) Dawson sandwich complexes (Fig. 3B). This pattern suggests *C*<sub>2h</sub> symmetry for Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> in which various metallic centers (Cd and Zn) occupy identical positions in M<sub>4</sub>O<sub>16</sub> metal center framework [28]. The little difference of chemical shifts between Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> with M<sub>4</sub>P<sub>4</sub>W<sub>30</sub> (M = Cd and Zn) can be attributed to the different size and effective nuclear charge of Cd<sup>2+</sup> and Zn<sup>2+</sup> ions.

# 3.3. <sup>113</sup>Cd NMR characterization

Due to the diamagnetic nature of cadmium, Cd NMR (<sup>113</sup>Cd and <sup>111</sup>Cd NMR) is a practical technique for characterizing cadmiumcontaining POMs. The Cd NMR data for some cadmium-containing POMs are given in Table 2. According to the results of Kortz et al. the <sup>111</sup>Cd NMR spectrum of  $[Cd_4Cl_2(B-\alpha-AsW_9O_{34})_2]^{12-}$  shows two singlet peaks that the upfield signal is very broad which is

 Table 2

 <sup>113</sup>Cd NMR chemical shift patterns for some cadmium-containing POMs.

	δCd <sub>in</sub> <sup>a</sup> , ppm	δCd <sub>ex</sub> <sup>b</sup> , ppm	Refs.
$Cd_4P_4W_{30}^{c}$	-49	-79	[24]
$Cd_4P_2W_{18}$	52.76	26.25	[39]
$Cd_4As_2W_{18}^d$	57	11.1	[40]
CdZn <sub>3</sub> P <sub>2</sub> W <sub>18</sub>	-	30.52	[41]
$Cd_2Zn_2P_2W_{18}$	-	29.16	[41]
$Cd_4P_4W_{30}$	70.21	38.14	This work
$Cd_2Zn_2P_4W_{30}$	-	42.38	This work

<sup>a</sup> Internal Cd in M<sub>4</sub>O<sub>16</sub> metal centers.

<sup>b</sup> External Cd in M<sub>4</sub>O<sub>16</sub> metal centers.

<sup>c</sup> Acidified 2 M CdCl<sub>2</sub>·2.5H<sub>2</sub>O was used as an external standard.

d 111Cd NMR.

probably due to the quadrupolar moment of the chloro ligand. Thus, they assigned this signal to the external cadmium ions in  $[Cd_4Cl_2(B-\alpha-AsW_9O_{34})_2]^{12-}$  whereas the other, sharp signal corresponds to the internal cadmium centers. And also, they assigned the upfield signal at 11.1 ppm to the external cadmium ions and the downfield signal at 57.0 ppm to the internal cadmium ions of  $[Cd_4(H_2O)_2(B-\alpha-AsW_9O_{34})_2]^{10-}$  [40]. By considering Table 2, the <sup>113</sup>Cd NMR of Cd<sub>4</sub> $P_4W_{30}$  shows two singlet peaks (Fig. 4A). In analogy to the works of Kortz et al., in 2005, the upfield signal at 38.14 ppm can be assigned to the external Cd ions in  $Cd_4P_4W_{30}$ , while the downfield signal at 70.21 ppm can be referred to the internal Cd ions in Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub>. These results are also in good agreement with the <sup>113</sup>Cd NMR study of  $[Cd_4(H_2O)_2(B-\alpha-PW_9O_{34})_2]^{10-1}$ by Alizadeh et al. in which they observed two singlet peaks with different intensities [39]. By attention to the mentioned result, one singlet peak in <sup>113</sup>Cd NMR of  $Cd_2Zn_2P_4W_{30}$  (Fig. 4B) can be attributed to the cadmium ions which are located in external position at M<sub>4</sub>O<sub>16</sub> metal centers in Dawson-type sandwich POMs. These results are also in proper agreement with <sup>113</sup>Cd NMR of mixed-metal Keggin-type sandwich POMs in the report of Shojaie et al. [41].

### 3.4. Electrochemistry

#### 3.4.1. Electrochemical behavior

In 2002, Ruhlmann et al. investigated the electrochemical behavior of  $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$  (M = Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, or Cd<sup>II</sup>) in aqueous solution by cyclic voltammetry at different pH values [20]. And also, redox behavior and electrocatalytic properties of  $[Cu_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$  was studied by Nadjo et al. in 2003 [42]. Moreover, in 2007, Herring and his group reported the application of  $H_{12}[(P_2W_{15}O_{56})_2Fe^{II}_{4I}(H_2O)_2]$  as electrocatalyst materials for fuel cells [43]. In addition, Ruhlmann and his coworkers investigated electrochemical behavior of mixed-metal Dawson sandwich complexes { $Na_{16}[M^{II}Co_3(H_2O)_2 (P_2W_{15}O_{56})_2]$  (M = Mn, Co, Ni, Zn and Cd)} in aqueous solution (pH = 3.5) [44]. Recently, Mbomekalle et al. reported the electrochemical behavior of mixed d metal-iron containing Wells–Dawson sandwich-type complexes:  $[(FeOH_2)_2 M_2(P_2W_{15}O_{56})_2]^{n-}$  and  $[(MOH_2)_2Fe_2(P_2W_{15}O_{56})_2]^{n-}$  (M = Cr<sup>III</sup>, Mn<sup>III</sup>,



Fig. 4. <sup>113</sup>Cd NMR of Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub> (A) and Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> (B) heteropolyanions.



Fig. 5. (A) Cyclic voltammograms of Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub>, Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> and Zn<sub>4</sub>P<sub>4</sub>W<sub>30</sub>. (B) The comparison of cyclic voltammograms of Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub> and Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> compounds.

#### Table 3

Electrochemical data of the Wells–Dawson and sandwich complexes obtained from cyclic voltammetry (scan rate = 50 mVs<sup>-1</sup>) in 0.5 mol L<sup>-1</sup> acetate buffer (pH = 4.7). All redox potentials  $E^{\circ}$ , approximated by (*E*ap + *E*cp)/2 for the reversible steps, are given in V vs. Ag/AgCl.

	W(1) <sup>a</sup>	W(2) <sup>a</sup>	W(3) <sup>a</sup>	W(4) <sup>a</sup>	W(5) <sup>a</sup>	Refs.
$\alpha - P_2 W_{18}^{b}$	+0.02	-0.15	-0.52	-0.67	-0.90	[34]
$\alpha - P_2 W_{15}^{b}$	-0.52	-0.78	_	-	-	[34]
$Cd_4P_4W_{30}$	-0.49	-0.61 <sup>c</sup>	-0.79	-	-	This work
$Cd_2Zn_2P_4W_{30}$	-0.48	-0.62 <sup>c</sup>	-0.84	-	-	This work
$Zn_4P_4W_{30}$	-0.44	-0.67	-0.83	-0.98	-	This work

<sup>a</sup> In parentheses: number of exchanged electron(s) *n* and  $\Delta E_p = |E_p^a - E_p^c|$ .

<sup>b</sup> Redox potentials are given V vs. SCE.

<sup>c</sup> These waves correspond to the redox potential of W and Cd centers.

Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup> and n = 12 or 14) in 1.0 M LiCH<sub>3</sub>COO + CH<sub>3</sub>COOH (pH = 6.0) and 0.5 M Li<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH = 3.0) [22].

In this work, the electrochemical behavior of  $Cd_4P_4W_{30}$ , Zn<sub>4</sub>P<sub>4</sub>W<sub>30</sub> and Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> in aqueous solution (0.5 M acetate buffer, pH = 4.7) have been compared by cyclic voltammetry. The CVs of 0.5 mM  $Cd_4P_4W_{30}$ ,  $Zn_4P_4W_{30}$  and  $Cd_2Zn_2P_4W_{30}$  in 0.5 M acetate buffer are presented in Fig. 5. All electrochemical data are collected in Table 3. By considering these data and cyclic voltammograms in Fig. 5A, it is clear that the waves in the range of -0.4 to -0.6 V in  $Cd_4P_4W_{30}$  and  $Cd_2Zn_2P_4W_{30}$  corresponds to tungsten and cadmium centers and the wave at about -0.8 V can be attributed to tungsten centers [33,45]. The current intensity of wave II in Cd<sub>2</sub> Zn<sub>2</sub>  $P_4W_{30}$  is the half of that in Cd<sub>4</sub> $P_4W_{30}$ . This result has a proper agreement with the number of cadmium atoms in these compounds. The cyclic voltammograms of the compounds Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub>, and Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> are compared in Fig. 5B. The slight cathodic potential shift of wave I in Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> to positive potentials and the decreasing of current intensity in Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> are the major differences in this pattern, which can be attributed to the replacing of internal cadmium ions by zinc in the equatorial metal cluster of  $Cd_4P_4W_{30}$  compound [15,31].

Fig. 6 shows the cyclic voltammograms of the  $P_2W_{15}$ ,  $Cd_4P_4W_{30}$ , Zn<sub>4</sub>P<sub>4</sub>W<sub>30</sub> and Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> at different scan rates in the 0.5 M acetate buffer solution. When the scan rate varied from 25 to 750 mV/s, the cathodic peak potentials shifted to the negative direction and the corresponding anodic peak potentials shifted to the positive direction with increasing scan rate. The plots of peak (II) current versus scan rates are shown in the insets of Fig. 6. As shown in this Figure, at scan rates lower than 100 mV/s, the anodic currents of  $P_2W_{15}$ ,  $Cd_4P_4W_{30}$  and  $Cd_2Zn_2P_4W_{30}$  compounds are proportional to the square root of the scan rate, which indicates that the redox process is diffusion-controlled; however, at scan rates higher than 100 mV/s, the anodic currents of these compounds are proportional to the scan rate, suggesting that the redox process is surface-confined. On the other hand, by considering to Fig. 6D at scan rates lower than 100 mV/s, the anodic currents of  $Zn_4P_4W_{30}$  are proportional to the scan rate, suggesting that the redox process is surface-confined; but, at scan rates higher than



**Fig. 6.** The cyclic voltammograms of P<sub>2</sub>W<sub>15</sub>(A), Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub>(B), Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub>(C) and Zn<sub>4</sub>P<sub>4</sub>W<sub>30</sub>(D) in 0.5 M acetate buffer solutions at different scan rates (from inner to outer: 25–750 mV s<sup>-1</sup>). The inset shows plots of the anodic peak currents of wave II against scan rates.

100 mV/s, the anodic currents of this compound are proportional to the square root of the scan rate, which indicates that the redox process is diffusion-controlled [46].

#### 3.4.2. Electrocatalysis of $NO_2^-$ reduction

As is known, POMs have been applied extensively in electrocatalytic reductions [2]. Direct electroreduction of nitrite ion needs a large overpotential at most electrode surfaces, but the reduction can be catalyzed in aqueous solution by various transition metal complexes [47–50]. In these catalysts, the transition metals show considerable roles as active sites, and are coordinated to NO forming transition metal nitrosyl complexes as principal intermediates followed by multi-electron reduction processes [51]. The real catalytic process yielding ammonia occurs by reduction of this metal-nitrosyl derivative at more negative potentials where the necessary number of electrons is provided by the W framework. It is well-known that  $HNO_2$  can disproportionate to form NO and  $NO_{3}^-$ ,

## $3HNO_2 \rightarrow NO_3^- + 2NO + H^+ + H_2O$

To ensure that the effect of this reaction is minimal, experimental data relevant to nitrite catalysis have been always obtained from freshly prepared solutions, and also our experiments have been carried out at pH = 4.7 in order to avoid complications associated with the possible disproportionate of HNO<sub>2</sub> [52]. Catalytic efficiency is defined as CAT =  $100 \times \{[I_p(\text{POM}, \text{NaNO}_2) - I_p(\text{POM})]/I_p(\text{POM})\}$ , 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 NaNO<sub>2</sub>, respectively.

The polyoxometalates  $P_2W_{15}$ ,  $Cd_4P_4W_{30}$ ,  $Zn_4P_4W_{30}$  and  $Cd_2Zn_2P_4W_{30}$  are tested at pH = 4.7 for their activity in the reduction of nitrite ion (Fig. 7). Clearly, with the addition of NaNO<sub>2</sub> to the solution, even for small values of the excess parameter  $\gamma$  ( $\gamma$  is the excess parameter defined here as  $\gamma = C_{(NO_x)}^0/C_{(POM)}^0$ ), cathodic current of all waves rose and the corresponding anodic current declined indicated the existence of an electrocatalytic process in the examined potential area. The insets of Fig. 7 present three or four straight lines over a wide range of concentrations with different slopes, indicating that wave III or IV (the last tungsten wave) has higher catalytic activity than other waves.

By comparison to previous works, the catalytic efficiency (CAT) of NaMn<sub>3</sub>P<sub>4</sub>W<sub>30</sub>, NaCo<sub>3</sub>P<sub>4</sub>W<sub>30</sub> and Co<sub>4</sub>P<sub>4</sub>W<sub>30</sub> decreases with increasing pH. For example, in NaCo<sub>3</sub>P<sub>4</sub>W<sub>30</sub> compound the catalytic efficiency, CAT, was 300%, 220%, 88%, 28%, and 0% at pH = 0.59, 1.77, 2.52, 3.00, and 3.50, respectively; while, no catalytic effect was seen at pHs  $\ge 3.5$  [32,33]. Moreover, for Cu<sub>4</sub>P<sub>4</sub>W<sub>30</sub> the catalytic efficiency in the reduction of nitrite ion was observed in pH = 5 (in the high quantity value of  $NO_2^-$  concentration) which can be related to the transition metal's nature [42]. On the other hand, the maximum CATs (in the low quantity value of NO<sub>2</sub><sup>-</sup> concentration) for the last tungsten wave of P<sub>2</sub>W<sub>15</sub>, Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub>,  $Cd_2Zn_2P_4W_{30}$  and  $Zn_4P_4W_{30}$  in the same  $\gamma$  at pH = 4.7 are 37.2%, 14.2%, 36.6% and 174.7% respectively. The graphs of CATs vs.  $\gamma$ and CATs vs. cadmium numbers of Cd<sub>4</sub>P<sub>4</sub>W<sub>30</sub>, Cd<sub>2</sub>Zn<sub>2</sub>P<sub>4</sub>W<sub>30</sub> and  $Zn_4P_4W_{30}$  are shown in Fig. 8. According to this figure, by reducing the number of cadmium ions in the central tetranuclear cluster of sandwich-type POMs, catalytic efficiency increases. These results have a suitable agreement with the electrochemical behavior of cadmium-containing monolacunary Wells-Dawson polyoxometalates [53].



**Fig. 7.** Cyclic voltammograms (scan rate: 75 mV s<sup>-1</sup>) for the electrocatalytic reduction of  $NO_2^-$  with a 5 × 10<sup>-4</sup> M solution of polyoxometalates in a 0.5 M acetate buffer solution: (A)  $P_2W_{15}$  (from up to bottom  $\gamma$  = 0, 1, 2, 4), (B)  $Cd_4P_4W_{30}$  (from up to bottom  $\gamma$  = 0, 1, 2, 5), (C)  $Cd_2Zn_2P_4W_{30}$  (from up to bottom  $\gamma$  = 0, 1, 2, 5) and (D)  $Zn_4P_4W_{30}$  (from up to bottom  $\gamma$  = 0, 1, 2, 3, 4). The excess parameter defined as  $\gamma = C^0 (NO_2^-)/C^0$  (POM). Inset: the relationship between catalytic current and  $NO_2^-$  concentration.



**Fig. 8.** (A) The CAT quantities comparison of  $Zn_4P_4W_{30}$ ,  $Cd_2Zn_2P_4W_{30}$  and  $Cd_4P_4W_{30}$  versus  $\gamma$  number. (B) The plot of CAT quantities versus Cd number for  $Zn_4P_4W_{30}$ ,  $Cd_2Zn_2P_4W_{30}$  and  $Cd_4P_4W_{30}$  in  $\gamma = 2$ .

## 4. Conclusion

Mixed-metal sandwich-type compounds based on Wells–Dawson fragments  $[P_2W_{15}O_{56}]^{12-}$  constitute a novel class of POMs that has been discovered very recently. Only very few compounds of this type have been described and fully characterized. This work presents the compound  $[Cd_2Zn_2(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ , which has been synthesized and characterized by FT-IR, <sup>31</sup>P NMR, <sup>113</sup>Cd NMR spectroscopy, cyclic voltammetry (CV) and elemental analysis. The <sup>31</sup>P NMR pattern of  $[Cd_2Zn_2(H_2O)_2(P_2W_{15}O_{56})_2]^{16}$ suggests  $C_{2h}$  symmetry for  $Cd_2Zn_2P_4W_{30}$  in which various metallic centers (Cd and Zn) occupy identical positions in  $M_4O_{16}$  metal center framework and the <sup>113</sup>Cd NMR result of this compound demonstrates that the cadmium ions are located at the external position of  $M_4O_{16}$  metal centers in Dowson-type sandwich POMs.

The electrochemical behavior of the  $Cd_4P_4W_{30}$ ,  $Zn_4P_4W_{30}$  and  $Cd_2Zn_2P_4W_{30}$  compounds has been investigated systematically in aqueous solution (0.5 M acetate buffer, pH = 4.7) by cyclic

voltammetry. The electrochemistry of  $Cd_2Zn_2P_4W_{30}$  exhibits three steps redox waves attributed to the tungsten-oxo and cadmium-oxo redox processes.

The compounds studied in this article exhibit remarkable electrocatalytic activities for the reduction of nitrite ion. By reducing the number of cadmium ions in the central tetranuclear cluster of sandwich-type POMs, catalytic efficiency increases.

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