



A new binuclear Cd(II)-containing ionic liquid: Preparation and electrocatalytic activities

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ARTICLE INFO

Article history:

Received 15 May 2009

Received in revised form 5 July 2009

Accepted 7 July 2009

Available online 31 July 2009

Keywords:

Metal-containing ionic liquid

Cadmium chloride

Crystal structure

Electrocatalysis

ABSTRACT

The present work reports on the synthesis, characterization and performance of a new metal-containing ionic liquid $[(C_{10}H_{21})_2\text{-bim}]_2[\text{Cd}_2\text{Cl}_6]$ (bim = benzimidazole) as an electrocatalyst of hydrogen peroxide and bromate. The structure of the Cd(II)-containing ionic liquid (Cd-IL) was characterized by X-ray crystallography, IR spectroscopy and elemental analysis. The molecular structure contained two independent cations of benzimidazolium and one binuclear anion of $\text{Cd}_2\text{Cl}_6^{2-}$. The cadmium atom had a tetrahedral geometry by coordinating to four chlorine atoms. The melting point of Cd-IL was 80 °C. Electrochemical properties of the Cd-IL had been investigated by preparing bulk-modified carbon paste electrode (Cd-IL/CPE), and Cd-IL was used as a binder and an electrocatalyst. This modified electrode showed good electrocatalytic activities toward the reduction of the hydrogen peroxide and bromate, and the results were reproducible with a lower detection limit than that mentioned in an earlier report. This work demonstrated that the Cd-IL may become a new kind of functional material in constructing chemicals and biosensors.

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1. Introduction

Since ionic liquids (ILs) have quite unique properties and can be used as solvents in organic synthesis, electrolytes in electrochemistry, and catalysts in catalysis chemistry, they recently gained a lot of attention from both chemists and physicists [1,2]. Metal-containing ionic liquids are regarded as promising new materials that combine the properties of ionic liquids with additional intrinsic magnetic, spectroscopic, or catalytic properties depending on the enclosed metal ion [3–6]. ILs of imidazolium salts composed of various metal components had been reviewed; some examples included halides of V, Fe, Co, Ni, Cu, Zn, Sn, In, Pt, Pd and Au and carbonyls of Co and Rh [7]. Many of these metal-containing ILs were air and moisture stable and had tunable Lewis acidity. These systems were capable of mediating a wide variety of synthetic reactions and exhibited great potential in organometallic chemistry and catalysis. Lin's group reported a series of metal-containing ionic liquids composed of N,N' -dialkylimidazolium salts of Pd(II) and Cu(II) and researched their liquid crystal properties [8]. Metal-containing ionic liquids $[\text{bmim}]\text{FeCl}_4$ (bmim = 1-butyl-3-methylimidazole) were reported for their magnetic behavior [9,10]. Seddon's group used $[\text{bmim}]_2[\text{PdCl}_4]$ as a catalyst in the Heck reaction conducted in a three-phase $[\text{bmim}][\text{PF}_6]/\text{hexane}/\text{water}$ system [11]. Martin's group reported a series of metal-containing ionic

liquid crystals formed by surfactant templating of molten metal halides (including Zn, Cd, Cu, Ni, Co, Fe and Mn)[12]. Tang synthesized two cyano-containing compounds, reacted them with cadmium chloride and obtained two new cadmium-containing ionic liquids [13].

Despite this, the reports on metal-containing ionic liquids composed of anionic cadmium chloride are still scarce. Especially, reports on using metal-containing ionic liquids as a bulk modifier to fabricate chemically modified carbon paste electrode and investigating the electrochemical properties of these modified electrodes are scarcer. The significance of our research work is to report the synthesis and crystal structure of $[(C_{10}H_{21})_2\text{-bim}]_2[\text{Cd}_2\text{Cl}_6]$, and use this new Cd-IL as a bulk modifier to fabricate the Cd-IL/CPE by direct mixing. The Cd-IL has double functions of a binder and an electrocatalyst. This modified electrode shows excellent electrocatalytic activity toward the reduction of the hydrogen peroxide and bromate, and the possible mechanisms are proposed.

2. Results and discussion

2.1. Crystal structure of the title complex

The molecular structure of the title complex with the atomic numbering scheme is shown in Fig. 1. Crystal data and structure refinement are listed in Table 1. Selected bond distances and angles are listed in Table 2. The molecular structure contained two

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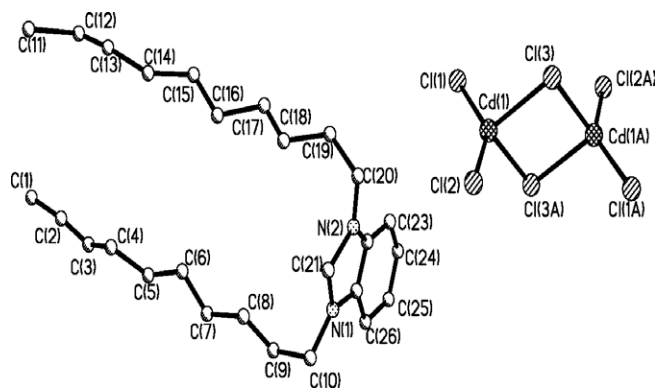


Fig. 1. ORTEP drawing of the title complex with partial atomic numberings.

Table 1
Crystal data and structure refinement for the title complex.

Empirical formula	C ₅₄ H ₉₄ Cd ₂ Cl ₆ N ₄
Formula weight	1236.83
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	
<i>a</i> (Å)	8.6419(8)
<i>b</i> (Å)	10.352(1)
<i>c</i> (Å)	18.717(2)
α (°)	99.869(2)
β (°)	90.935(2)
γ (°)	95.934(2)
<i>V</i> (Å ³)	1639.9(3)
<i>Z</i> , <i>D</i> _{calc} (Mg m ⁻³)	1, 1.252
Absorption coefficient (mm ⁻¹)	0.926
<i>F</i> (0 0 0)	644
Theta range for data collection (°)	2.01–25.50
Limiting indices	–10 ≤ <i>h</i> ≤ 10, –11 ≤ <i>k</i> ≤ 12, –22 ≤ <i>l</i> ≤ 25
Reflections collected/unique (<i>R</i> _{int})	9064/6072 (0.0227)
Completeness to theta = 25.50	99.2%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6072/21/294
Goodness-of-fit on <i>F</i> ²	1.035
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0927, <i>wR</i> ₂ = 0.2561
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1338, <i>wR</i> ₂ = 0.3003
Largest difference in peak and hole (e Å ⁻³)	1.004 and –0.883

Table 2
Selected bond lengths (Å) and angles (°) of the title complex.

Bond lengths (Å)	Bond angles (°)		
Cd(1)–Cl(2)	2.365(4)	Cl(2)–Cd(1)–Cl(3) ^{#1}	107.2(2)
Cd(1)–Cl(3) ^{#1}	2.648(4)	Cl(2)–Cd(1)–Cl(3)	100.7(2)
Cl(3)–Cd(1) ^{#1}	2.648(4)	Cl(3) ^{#1} –Cd(1)–Cl(3)	91.1(1)
N(1)–C(27)	1.47(2)	Cl(2)–Cd(1)–Cl(1)	139.5(2)
N(2)–C(22)	1.34(2)	Cl(1)–Cd(1)–Cl(3) ^{#1}	100.8(2)
Cd(1)–Cl(1)	2.369(5)	Cl(1)–Cd(1)–Cl(3)	107.6(2)
Cd(1)–Cl(3)	2.679(4)	Cd(1) ^{#1} –Cl(3)–Cd(1)	88.9(1)
N(1)–C(21)	1.37(2)	C(21)–N(1)–C(27)	110.0(1)
N(1)–C(10)	1.55(3)	C(27)–N(1)–C(10)	131.8(2)
N(2)–C(20)	1.42(2)	C(21)–N(1)–C(10)	116.2(2)

independent cations of benzimidazolium and one binuclear anion of Cd₂Cl₆²⁻. Each cation was composed of two decane chains and one benzimidazole head core. The cadmium center had a tetrahedral geometry by coordinating to four chlorine atoms. The angles around the Cd center were Cl(2)–Cd(1)–Cl(1) 139.5(2)°, Cl(2)–Cd(1)–Cl(3)^{#1} 107.2(1)°, Cl(1)–Cd(1)–Cl(3)^{#1} 100.8(2)°, Cl(2)–Cd(1)–Cl(3) 100.7(1)°, Cl(1)–Cd(1)–Cl(3) 107.6(2)°, and Cl(3)^{#1}–Cd(1)–Cl(3) 91.1(1)°. These values were in the range of

Cl–Cd–Cl angles known from previous studies [13]. Crystal packing drawing of the title complex viewed along the *a*-axis in Fig. 2. There was a potentially weak intermolecular C–H...Cl hydrogen bond interaction, and the donor and acceptor distance was 3.5651 Å for C(21)–H(21A)...Cl(1). In the solid state, the intermolecular interaction in this structure stabilized the crystal structure.

2.2. Thermal behavior

The DSC heating cooling trace is shown in Fig. 3. The first heating cycle exhibited three endothermic transitions at 80 °C, 111 °C and 130 °C. The first transition was one peak with a ΔH value of 11.37 kJ mol⁻¹, while the second transition peak had a ΔH value of 32.96 kJ mol⁻¹. The last peak had a ΔH value of 17.33 kJ mol⁻¹. When cooling it exhibited two exothermic transitions at 128 °C and 68 °C with the ΔH value of 1.08 kJ mol⁻¹ and 55.17 kJ mol⁻¹, respectively.

The TG/DTG curves of the title complex are presented in Fig. 4. We can see that there were two main steps of weight loss, and the decomposition events mainly took place at 381 °C and 566 °C. On the basis of weight changes, the weight loss around 381 °C corresponded to the loss of part of benzimidazolium (found 75.91% calc. 69.56%). The weight loss during 500–700 °C was attributed to decomposition of the part of benzimidazolium and cadmium chloride. From the weight loss, it can be suggested that the residue is Cd (found 11.82%, calcd. 18.17%).

2.3. Electrochemical behavior of Cd-IL/CPE

The electrochemical behavior of Cd-IL/CPE was investigated by cyclic voltammetry in the aqueous solution. Aqueous solution (0.1 M KCl), Britton–Robinson (B–R) buffer solution (0.1 M pH 7.0), and phosphates buffer solutions (0.1 M, pH 7.0) were chosen as the supporting electrolyte solutions. It was found that the modified electrode in B–R buffer solution has stronger current responses and symmetric peak shape. We then investigated the electrochemical behavior of modified CPE in the pH range from 4.0 to 8.0 in B–R buffer solution and found that the electrochemical signal was relatively stable at pH 6.1. So, the investigation on its electrochemical behavior and electrocatalytic properties were investigated in 0.1 M, pH 6.1, B–R buffer solution.

The cyclic voltammograms (CVs) of a bare CPE (curve a) and Cd-IL/CPE (curves b–g) are shown in Fig. 5. In the potential range of 0 to –1.5 V, there was no redox peak at the bare CPE (curve a). While at the modified Cd-IL/CPE, curve b had a couple of well-defined redox peaks at –0.746 V and –0.659 V when the scan rate was 0.05 V s⁻¹, with the formal potential (*E*⁰) being at approximately –0.703 V, corresponding to the electrochemical process of Cd(II)/Cd(I). The separation of the cathodic and anodic peak potential, $\Delta E = 0.087$ V, *i*_{pa}/*i*_{pc} = 1.02, indicated that the electrochemical behavior of the title complex on the electrode was a quasi-reversible process.

The effect of scan rates on the electrochemical behavior of the Cd-IL/CPE can be seen in Fig. 5. When the scan rate was varied from 0.05 to 0.10 V s⁻¹, the peak potentials changed gradually: the cathodic peak potentials shifted to a negative direction and the corresponding anodic peak potentials shifted to a positive direction with increasing scan rate. The plots of peak current vs. scan rates are shown in the inset of Fig. 5, the anodic and the cathodic currents are proportional to the scan rate, suggesting that the redox process was surface-confined process.

2.4. Electrocatalytic activity of the Cd-IL/CPE

2.4.1. Electrocatalytic effect on the reduction of hydrogen peroxide

Determination of hydrogen peroxide is practically important because peroxide hydrogen is the product of the reactions

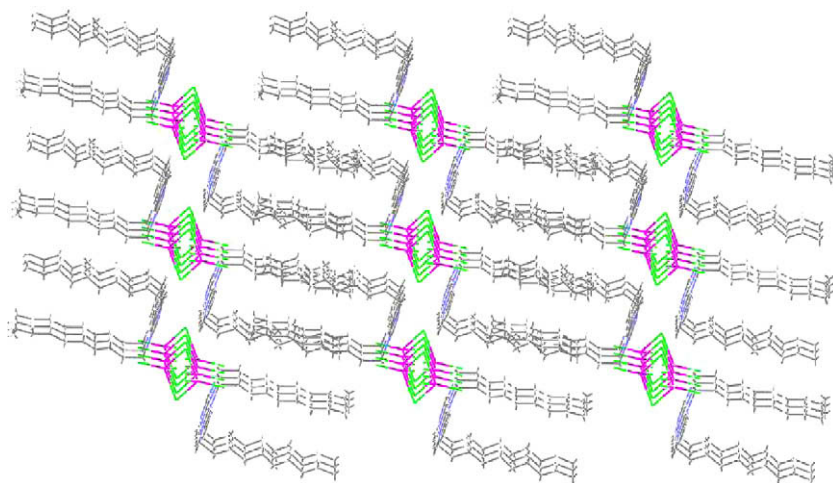


Fig. 2. Crystal packing drawing of the title complex viewed along the *a*-axis.

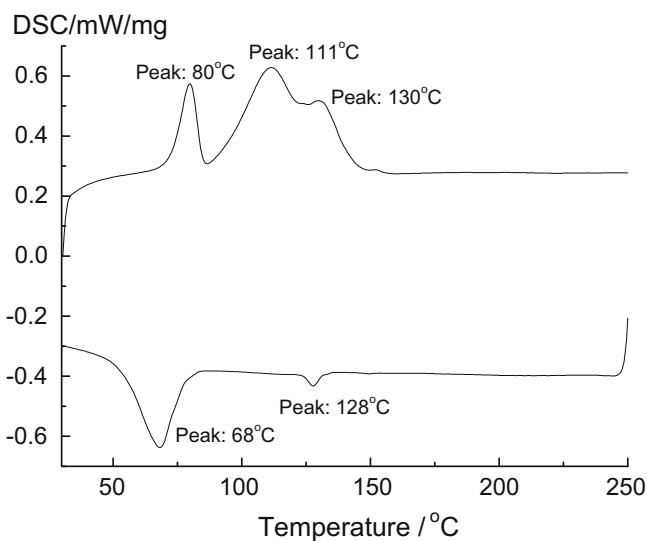


Fig. 3. DSC heating curve of the title complex.

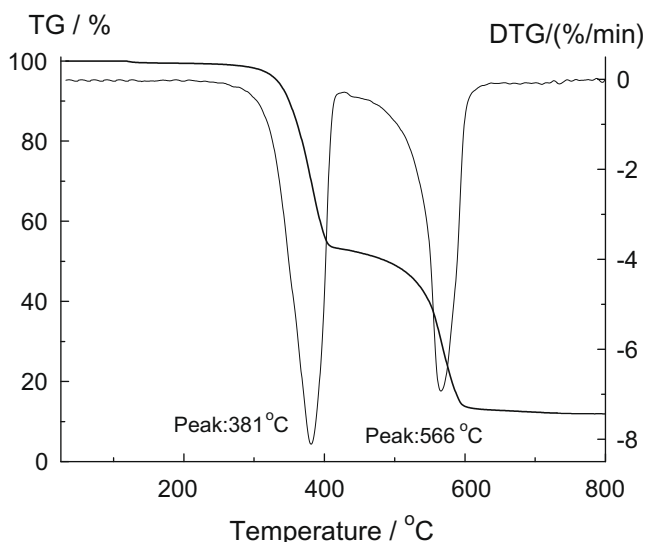


Fig. 4. TG/DTG curves of the title complex.

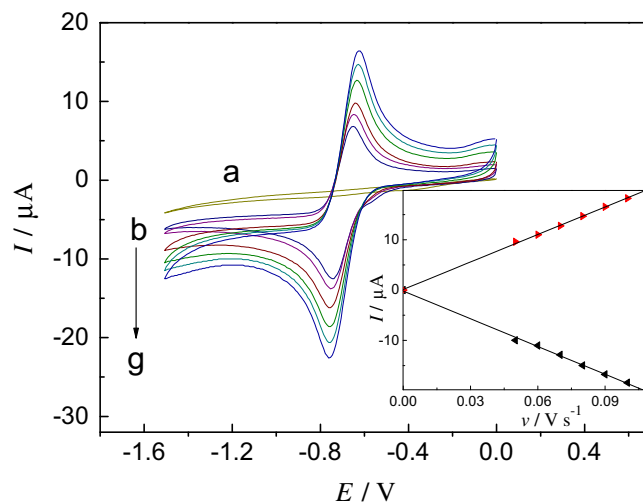
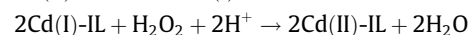
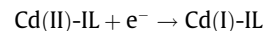


Fig. 5. CVs of (a) the bare CPE; (b–g) Cd-IL/CPE in 0.1 M, pH 6.1, B–R buffer solution, scan rates: 0.05, 0.06, 0.07, 0.08, 0.09, 0.10 V s^{-1} . Inset: the variation of peak currents vs. scan rate.

catalyzed by a large number of oxidases, and it is essential in food, pharmaceutical and environmental analyses [14]. As is known, the electroreduction of hydrogen peroxide requires a large overpotential and no obvious response is observed on a bare CPE.

The electrocatalytic activity of Cd-IL/CPE toward H_2O_2 had been investigated, which is shown in Fig. 6. With the addition of hydrogen peroxide (curves a–f), the peak potentials had little change, which suggested that the Cd-IL was still stable under this reaction. The reduction peak currents increased markedly while the corresponding oxidation peak decreased, which indicated that Cd-IL/CPE had a good electrocatalytic activity toward the reduction of hydrogen peroxide. The possible reaction processes could be described in the following equations [15,16]:



The inset of Fig. 6 shows that catalytic current is linear with hydrogen peroxide concentration in the range of 0.2–1.5 μM . The linear regression equation was $I_{\text{pc}} (\mu\text{A}) = -7.09C (\mu\text{M}) - 15.73$ with a correlation coefficient of 0.998, and the detection limit based on the signal-to-noise ratio of 3 was calculated to be 0.15 μM , which was

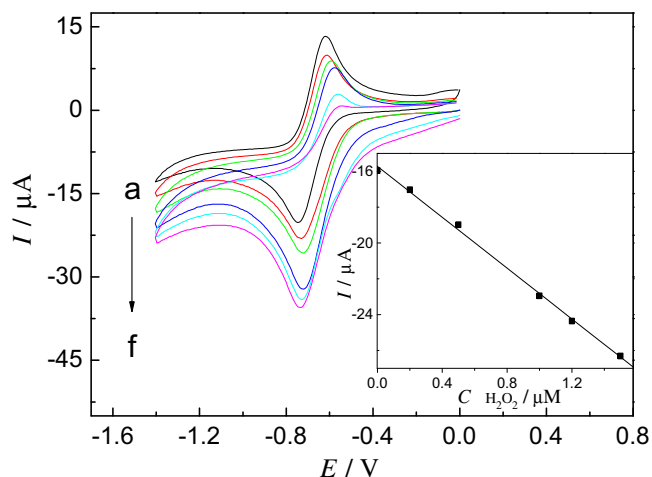


Fig. 6. CVs of Cd-IL/CPE in 0.1 M, pH 6.1, B-R buffer solution containing (a–f) 0, 0.2, 0.5, 1.0, 1.2, 2.0 μM H_2O_2 with the scan rate of 0.05 V s^{-1} . Inset: the variation of peak currents vs. H_2O_2 concentrations.

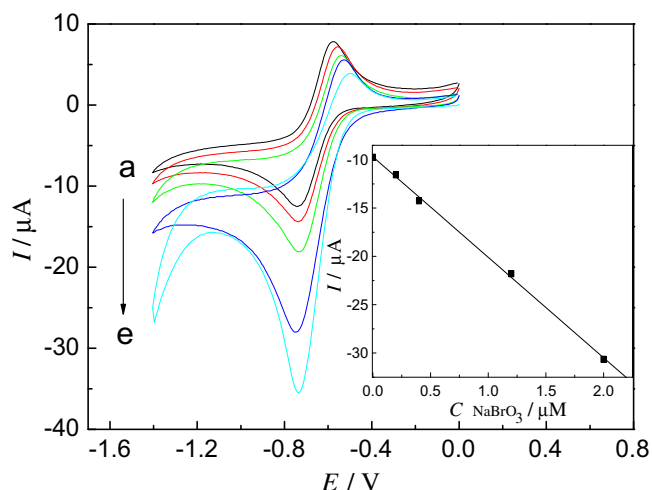
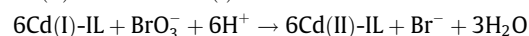
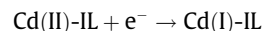


Fig. 7. CVs of Cd-IL/CPE in 0.1 M, pH 6.1, B-R buffer solution (a–e) containing 0, 0.02, 0.04, 0.12, 0.2 μM bromate with the scan rate of 0.05 V s^{-1} . Inset: the variation of peak currents vs. bromate concentrations.

much lower than that mentioned in the earlier report ($5 \mu\text{M}$) using other modified electrodes [17].

2.4.2. Electrocatalytic reduction toward bromate

Bromate is a disinfectant by-product contaminant found in drinking water, and is formed during the ozonation of source water containing bromide. The overpotential for bromate reduction is high and therefore an efficient electrocatalyst would be beneficial [18]. However, the reduction of bromate can readily be catalyzed by Cd-IL/CPE in 0.1 M, pH 6.1, B-R buffer solution. As shown in curves a–e in Fig. 7 Cd-IL/CPE has excellent electrocatalytic activity toward the reduction of bromate. With the addition of bromate, the peak potentials had little change, the reduction peak currents increased while the corresponding oxidation peak decreased. The possible reaction processes could be described in the following equations [15]:



The inset of Fig. 7 shows that catalytic current is linear with bromate concentration in the range of 0.02–0.2 μM . The linear regres-

sion equation was $I_{\text{pc}} (\mu\text{A}) = -103.9C (\mu\text{M}) - 9.74$ with a correlation coefficient of 0.999, and the detection limit based on the signal-to-noise ratio of 3 was calculated to be $0.019 \mu\text{M}$, which was much lower than that mentioned in the earlier report ($0.036 \mu\text{M}$) using other modified electrodes [19].

Compared with other modified film electrodes, the bulk-modified title complex showed high stability. In our experiment, after the electrocatalytic reaction, the Cd-IL/CPE was investigated in buffer solution under the same condition as shown in Fig. 5, we found that the peak potentials and peak currents had little change, which suggested that no new materials appeared. So I was sure that the Cd-IL was still stable and played the role of a catalyst during the reactions. When the potential range was maintained the same, it was stable over 200 cycles at a scan rate of 0.1 V s^{-1} and the current response remained almost unchanged. When the bulk-modified CPE was stored at room temperature for at least 2 months, the current response decreased by only 2.3%.

3. Experimental

3.1. Chemicals and measurement

All chemicals were of analytical reagent grade and used directly without further purification. Elemental analyses were measured with a Perkin–Elmer 1400C analyzer (USA). Infrared spectra were recorded on a Nicolet 170SX spectrometer (USA) using pressed KBr plates in the $4000\text{--}400 \text{ cm}^{-1}$ ranges. Thermal gravity (TG) was recorded on SDT 2980 simultaneously for the samples of ca. 10 mg under a nitrogen atmosphere (150 mL min^{-1}) at a heating rate of $10^\circ \text{C min}^{-1}$. Electrochemical measurements were performed on an Autolab PGSTAT-30 digital potentiostat/galvanostat, (EcoChemie BV, Utrecht, Netherlands). A three-electrode cell was used in the experiments. The working electrode was modified CPE. The counter electrode was a platinum wire. The reference electrode was an Ag|AgCl||KCl (1 M), and all potentials reported in this work were measured vs. this electrode (236.3 mV at 25°C). Supporting electrolytes used for electrochemical experiments were 0.1 M, pH 6.1, Britton–Robinson (B–R) buffer solution. All the solutions were deaerated by highly pure nitrogen for 30 min and kept at nitrogen atmosphere during the experiments. All measurements were performed at room temperature ($25 \pm 2^\circ \text{C}$).

3.2. The preparation and physical measurement of the title complex

Cadmium chloride (228 mg, 1 mmol) and $[(\text{C}_{10}\text{H}_{21})_2\text{-bim}]_2\text{Cl}$ (456 mg, 1 mmol) were dissolved in 50 mL ethanol, respectively. After stirring for 2 h, the resulting colorless precipitate of $[(\text{C}_{10}\text{H}_{21})_2\text{-bim}]_2[\text{Cd}_2\text{Cl}_6]$ was obtained by filtration. Recrystallization from THF gave a yield of 71%. The melting point of the title complex was 80°C . The C, H and N contents were determined by elemental analysis (Anal. Calc. for $\text{C}_{54}\text{H}_{94}\text{Cd}_2\text{Cl}_6\text{N}_4$: C, 52.43; H, 7.660; N, 4.530. Found: C, 52.41; H, 7.658; N, 4.532%).

In the IR spectra, the bands at 3072 and 749 cm^{-1} were assigned to the C–H (benzene ring) stretching vibration and bending vibration, respectively. The bands at 1604 and 1565 cm^{-1} were attributed to the vibration of benzene ring skeleton. The bands at 2922 , 2852 , 1464 , and 1377 cm^{-1} may be attributed to the C–H stretching vibration and bending vibration of the alkyl.

Reflection data and reflections for the unit cell determination were measured at 20°C using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite monochromator. The technique used was ω -scan with θ limits $2.01^\circ < \theta < 25.50^\circ$ for the title complex. Empirical absorption correction was carried out by using the SADABS [20] program. The structure of the title complex was solved by direct methods and refined by least squares on F_{obs}^2 by using the SHELXTL [21] software

package. The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* [22].

3.3. Preparation of Cd-IL/CPE

The traditional CPE was prepared by hand-mixing of graphite powder with paraffin at a ratio of 70:30 (w/w) in an agate mortar. The homogeneous carbon paste was packed into a cavity of a glass tube with an inner diameter of 3 mm. The electrical contact was provided by a copper stick. The Cd-IL/CPE was prepared according to the following procedure: 0.4 g of Graphite powder and 0.1 g of Cd-IL were mixed thoroughly in a mortar and heated at 100 °C to form a homogeneous carbon paste. A portion of the carbon paste was filled into one end of a glass tube (inner diameter 3 mm) and a copper stick was inserted through the opposite end to establish an electrical contact. The Cd-IL/CPE surface was smoothed on a piece of weighing paper just before use.

The amount of a modifier (Cd-IL) in the paste was optimized. We investigated the graphite powder and Cd-IL at the ratios of 6:1, 5:1, 4:1, and 3:1 (w/w), and found that the optimal preparation condition was 4:1. When the amount of the Cd-IL was too little, the bonding degree of graphite was bad, easy to fall off and smash. Conversely, the amount of the Cd-IL was too large, the mixture was so hard that it was difficult to shape it.

4. Conclusions

In summary, a new metal-containing ionic liquid of $[(C_{10}H_{21})_2\text{-bim}]_2[\text{Cd}_2\text{Cl}_6]$ was synthesized and the structure was characterized. The electrochemical behavior and electrocatalysis of the Cd-IL/CPE had been investigated. The Cd(II)-containing ionic liquid had double function of a binder and an electrocatalyst. This modified electrode showed excellent electrocatalytic activities toward the reduction of the hydrogen peroxide and bromate, and the results were reproducible with a lower detection limit, which was suitable for the quantitative analysis of environmentally hazardous materials. The advantages of the Cd-IL/CPE are its stability, excellent catalytic activity, low detection limit and simplicity of preparation in comparison with the other methods, which is important for practical application on electrochemical sensors. In this work, only the electrocatalytic activity of some small molecules at the

Cd-IL/CPE has been performed, and further investigation on the mediation of biomacromolecules is under way.

Acknowledgement

This work was supported by the Natural Science Foundation of Shandong Province (No. Z2007B01), PR China.

Appendix A. Supplementary data

CCDC 714078 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.07.012](https://doi.org/10.1016/j.jorganchem.2009.07.012).

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