

Synthesis, crystal structure, and electrocatalytic properties of a copper(II) complex of 1,2-bis(2-benzimidazolyl)benzene

Yue-Yi Deng · Fa-Qian Liu · Yan-Ling Jin

Received: 29 October 2011 / Accepted: 6 January 2012 / Published online: 4 April 2012
© Springer Science+Business Media B.V. 2012

Abstract A new copper(II) complex based on the rigid ligand OBimB (OBimB = 1,2-bis(2-benzimidazolyl)benzene) has been synthesized and structurally characterized by X-ray single-crystal diffraction. In the structure of the complex, each Cu(II) atom is coordinated by four N atoms from two twisted V-shaped OBimB ligands in a square-planar geometry. The complex has been used as a bulk modifier to fabricate a carbon paste electrode (Cu-CPE). Electrochemical studies of the Cu-CPE in 0.1 M pH 2.0 phosphate buffer solution reveal that the $\text{Cu}^{2+}/\text{Cu}^{+}$ redox process is quasi-reversible. Electrocatalytic studies of the Cu-CPE indicate that it has good electrocatalytic activities toward reduction of bromate, hydrogen peroxide, and nitrite.

Introduction

Bis(2-benzimidazolyl) compounds and their metal complexes have attracted much attention in recent years. They exhibit biological properties such as antivirus activities [1, 2] and control of liver diseases [3], as well as potential applications as proton sponges [4], selective ion-exchange resins [5, 6], polymerization catalysts [7–9], and electron transfer agents [10]. The coordination chemistry of these species has been focused on matters such as geometrically constraining ligands [11], supramolecular aggregates

formed with transition metals [12, 13], and modeling of biological systems [14, 15].

Transition metal complexes can be used as electron transfer mediators for modification of different kinds of electrode materials owing to their electrochemical reversibility [16]. Some metal complexes have also received great interest as catalysts for electrochemical reactions in recent years [16–19]. The electron transfer mediator complexes can be dispersed and stabilized in different supporting carbon materials to give low background currents, wide potential windows, chemical inertness, and low cost [20]. The electrochemical and electrocatalytic properties of copper complexes with some polycarboxylate and N-containing heterocyclic ligands have been investigated [21–26], but studies on the complexes based on bis(2-benzimidazolyl) ligands are scarce [26]. In this paper, we report the synthesis and crystal structure of a new copper(II) complex containing the OBimB rigid ligand, namely $[\text{Cu}(\text{OBimB})_2](\text{NO}_3)_2 \cdot (\text{EtOH})_2$. In addition, the electrochemical properties of the complex bulk-modified carbon paste electrodes (Cu-CPE) have been investigated and reveal that the modified electrode exhibits excellent electrocatalytic activities toward the reduction of bromate, hydrogen peroxide, and nitrite.

Experimental

All the reagents for synthesizing the ligand OBimB and the title complex were purchased commercially and used without further purification. K_2HPO_4 and KH_2PO_4 were used for the preparation of 0.1 M phosphate buffer solution, and hydrochloric acid was used for pH adjustment. Elemental analyses (C, H and N) were carried out on a Perkin–Elmer 1400C analyzer. IR spectra were recorded in

Y.-Y. Deng (✉) · F.-Q. Liu · Y.-L. Jin
Key Laboratory of Rubber-plastics, Ministry of Education,
College of Polymer Science and Engineering, Qingdao
University of Science and Technology, No. 53, Zhengzhou
Road, Qingdao 266042, People's Republic of China
e-mail: dengyyqust@hotmail.com

the range of 400–4,000 cm^{-1} on a Nicolet 170SX spectrometer with pressed KBr pellets. UV–Vis spectra were recorded on a Perkin–Elmer UV–Vis spectrometer. Voltammetry was performed using a CHI 832B electrochemical analysis system (China) with a three-electrode system consisting of the modified electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. All the electrochemical measurements were carried out in a 10 mL electrolyte cell with 0.1 M pH = 7.0 or 2.0 phosphate buffer solutions as electrolyte.

Preparation of the complex

OBimB was synthesized by condensing *o*-diaminobenzene with *o*-phthalic acid according to the literature method [27] with minor revisions. *o*-Diaminobenzene (4.7 g, 44 mmol) and *o*-phthalic acid (3.3 g, 20 mmol) were finely ground together and heated to 230 °C in polyphosphoric acid (40 mL) with stirring for 4 h. The reaction mixture was allowed to cool to 100 °C and then poured into ice water with vigorous stirring. The precipitate was then filtered off and stirred in a saturated sodium bicarbonate solution for 12 h. The raw solid was recrystallized from hot methanol to give the light yellow product (yield, 3.0 g, 38%). IR(KBr): 3,049(w), 2,878(w), 1,620(w), 1,534(w), 1,441(s), 1,317(m), 1,280(m), 1,007(m), 764(s).

Synthesis of $[\text{Cu}(\text{OBimB})_2](\text{NO}_3)_2 \cdot (\text{EtOH})_2$

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.072 g, 0.3 mmol) and OBimB (0.09 g, 0.3 mmol) were added to ethanol (20 mL) and acetonitrile (10 mL), and the mixture was stirred and refluxed for 30 min. The resulting blue solution was filtered, and the filtrate was kept at ambient temperature for a period of about 3 days, to give blue block crystals (31% yield based on Cu) suitable for structural determination. Anal. Calcd(%) for $\text{C}_{44}\text{H}_{40}\text{CuN}_{10}\text{O}_8$: C 58.7, H 4.5, N 15.6; found(%): C 58.7, H 4.5, N 15.6. IR(KBr, cm^{-1}): 3,425(br), 1,629(w), 1,578(w), 1,462(m), 1,390(s), 1,283(m), 1,229(w), 893(w), 815(w), 748(m), 682(w).

Preparation of the modified CPE

The CPE electrode modified by the complex was fabricated by the following steps. Graphite powder (0.3 g) and complex (0.03 g) were ground together with an agate mortar and pestle for about 30 min to give an even mixture. Paraffin oil (0.1 mL) was added to the mixture and stirred for about 20 min. Then, a 3-mm inner diameter glass tube was packed to a length of about 0.8 cm with the homogenized mixture, and a copper stick was used as the electrical contact. The surface of the modified CPE was polished on a

piece of weighing paper to achieve a mirror finish before use.

X-ray crystallographic study

A block shaped crystal with dimensions of $0.20 \times 0.15 \times 0.10$ mm was mounted on a Bruker SMART 1000 CCD area detector X-ray single-crystal diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm) and a φ/ω scanning mode at 293(2) K. Intensities were corrected for Lorentz and polarization effects, and empirical absorption. The structure was solved by direct methods using the SHELXS 97 program [28] and refined by full-matrix least-squares on F^2 via SHELXL 97 [29]. The correct positions for the copper atoms were deduced from the E-map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Restraints were applied to the N–H bond lengths of the imidazole rings (DFIX restraints, N2–H2N = 0.86 nm, N4–H4N = 0.86 nm). H atoms were positioned geometrically (C–H = 0.093 and 0.096 nm) and allowed to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$. The complex crystallizes in triclinic system, $P1$ space group, with the cell parameters: $a = 0.8707(15)$ nm, $b = 1.14994(19)$ nm, $c = 1.2181(2)$ nm, $\alpha = 62.765(4)^\circ$, $\beta = 77.320(4)^\circ$, $\gamma = 73.633(4)^\circ$, $V = 1.0346(3)$ nm³, $Z = 1$, and $D_c = 1.445$ g cm⁻³, the final $R_1 = 0.071$, $wR_2 = 0.1831$.

Results and discussion

Characterization of the complex

An ORTEP view of the complex dication $[\text{Cu}(\text{OBimB})_2]^{2+}$ with the atomic numbering scheme and selected bond distances and bond angles is shown in Fig. 1, showing 30% probability displacement ellipsoids. The central Cu atom in the complex is coordinated by four N atoms from two OBimB ligands in a square-planar geometry. The *trans* angles are all 180° for symmetry requirement, and the *cis* angles are 89.63(17)° and 90.37(17)° for N1–Cu–N3 and N1–Cu–N3¹ (symmetry code: $i, -x + 1, -y + 1, -z + 1$), respectively. The Cu–N distances are 1.963(4) and 1.974(4) Å, which are close to those of the structurally analogous complex $[\text{Cu}(\text{bmbz})_2](\text{CF}_3\text{SO}_3)_2$ (bmbz = 1,2-bis(*N*-methylbenzimidazol-2'-yl)benzene, Cu–N = 1.961(3) and 1.981(3) Å) [30]. Each OBimB ligand affords two coordination sites and chelates a Cu(II) atom to form a seven-membered ring, resulting in the construction of a ML_2 complex. The overall structure of the ligand can be described as a twisted V-shaped conformation, so that the two coordinated N atoms of the benzimidazoles are more exposed for metal binding. The dihedral angles of the benzimidazolyl

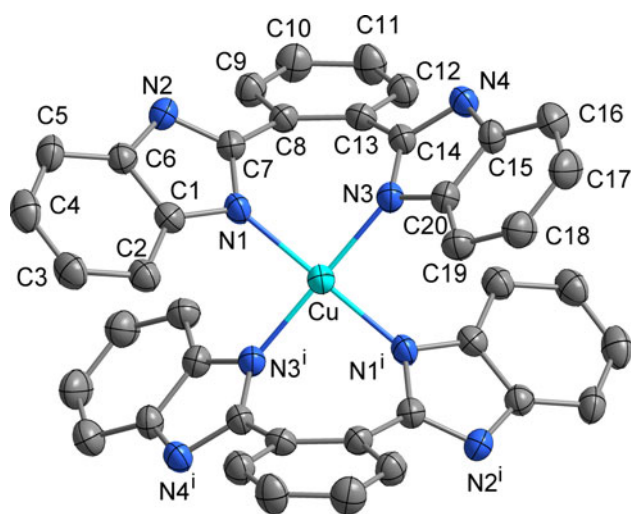


Fig. 1 Structure of the complex $[\text{Cu}(\text{OBimB})_2]^{2+}$ at 30% probability displacement ellipsoids with atomic numbering scheme (anions and hydrogen atoms are omitted for clarity). Selected bonds and angles (\AA , $^\circ$): Cu–N1 1.963(4), Cu–N3 1.974(4), N1–Cu–N1ⁱ 180.0, N1–Cu–N3ⁱ 90.37(17), N1–Cu–N3 89.63(17); symmetry code: i, $-x + 1, -y + 1, -z + 1$

ring planes (comprising imidazole ring atoms N1, C1, C6, N2, N7 designated as plane 1 and N3, C14, C15, N4, C20, as plane 2) with the central phenyl ring plane (comprising atoms C8–C13) are very similar, at 39.05° and 39.07° , respectively. The dihedral angle between the planes (planes 1 and 2) of the benzimidazolyl groups in the ligand is 56.33° , which is smaller than that in the complex $[\text{Cu}(\text{bmbz})_2](\text{CF}_3\text{SO}_3)_2$ (70.2°) [30]; the difference may be ascribed to the alkylation of the benzimidazoles in bmbz.

In the complex, the two amine NH groups of the OBimB ligand are involved in hydrogen bonding with an ethanol molecule and NO_3^- anion (N2ⁱⁱⁱ–O2, 2.792(8) \AA , N4ⁱⁱ–O4, 2.738(8) \AA ; symmetry code: ii, $-x + 1, -y + 2, -z + 1$, iii, $x - 1, y, -z$), and there is also a weak hydrogen bonding between the ethanol molecule and NO_3^- anion (O4–O2, 2.798(8) \AA). These hydrogen bonds link the complex units into a one-dimensional chain (Fig. 2). The 1-D chains are further extended into a 2-D layer network by $\pi \cdots \pi$ stacking interactions among the imidazole rings of the OBimB ligands, with a $\text{Cg}(1) \cdots \text{Cg}(1)^{\text{iv}}$ distance of ca. 3.885 \AA (Cg(1) is the centroid of the imidazole ring N1, C1, C6, N2, C7; symmetry code: iv, $-x, -y + 1, -z + 1$) and intermolecular C–H $\cdots\pi$ interactions with a $\text{C4} \cdots \text{Cg}(2)^{\text{iv}}$ distance of 3.542 \AA (Cg(2) is the centroid of the imidazole ring N3, C14, C15, N4, C20; symmetry code: iv, $-x, -y + 1, -z + 1$) (Fig. 3).

The infrared spectrum of the complex shows characteristic absorptions for the OBimB ligand with slight shifts due to coordination. A strong absorption band at $1,390 \text{ cm}^{-1}$ is assigned to the ν_{as} vibration of the nitrate anion. A band at $3,425 \text{ cm}^{-1}$ in the spectrum of the complex can be assigned to $\nu_{\text{N-H}}$ of the OBimB ligand, and the

broadness of this band indicates that hydrogen bonds exist in accordance with the crystal structure analysis. The UV–Vis spectrum of the complex in ethanol solution shows two intense transitions around 224 and 280 nm, which can be assigned to intramolecular charge transfer transitions and $\pi \rightarrow \pi^*$ transitions in the ligands. The weak absorbance band at $\sim 390 \text{ nm}$ is assigned to $n \rightarrow \pi^*$ transitions in the ligands.

Electrocatalytic reduction of bromate at a Cu-CPE electrode

Because of the electrochemical reversibility of the modified electrode (Cu-CPE), using the complex as a redox mediator in acidic media, the Cu-CPE can be used as an electrocatalytic electrode material. Bromate is a toxic pollutant of drinking water, which is formed by ozonation of source waters containing bromide. The direct electroreduction of bromate requires a large overpotential, which can be decreased by a suitable catalyst. Hence, the catalytic reduction of bromate by our Cu-CPE electrode has been investigated. The electrochemical behavior of the Cu-CPE in pH 2 phosphate buffer solution is shown in Fig. 4. The Cu-CPE displays a pair of well-defined redox peaks with large currents; an anodic peak is observed at 0.341 V and a cathodic peak at 0.186 V. The mean peak potential $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ is 0.263 V, corresponding to the $\text{Cu}^{2+}/\text{Cu}^+$ electrochemical process [16, 31]. The separation of the cathodic and anodic peak potentials, $\Delta E = 0.155 \text{ V}$, indicates that the electrochemical behavior of the Cu-CPE is a quasi-reversible process. The anion peak current is larger than the cathodic current ($i_{\text{pc}}/i_{\text{pa}} = 0.66$), indicating a slow electron transfer process. With the addition of bromate, there is a dramatic enhancement of the cathodic peak current while the anodic peak current decreases (Fig. 5), which indicates a strong catalytic effect. The possible catalytic processes can be described by the following equations [32, 33]:

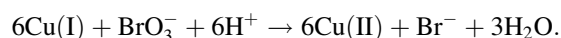
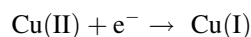


Figure 6 shows that catalytic current is proportional to the concentration of bromate. The plot of catalytic current versus bromate concentration is linear in the concentration range of 1–5 mM, which is fitted by the equation $I (\mu\text{A}) = 3.5513[\text{BrO}_3^-] + 3.2197 \mu\text{A}$ with $R^2 = 0.9927$.

Electrocatalytic reduction of hydrogen peroxide and nitrite at a Cu-CPE electrode

The catalytic activity of the Cu-CPE toward hydrogen peroxide has also been investigated, as shown in Fig. 7.

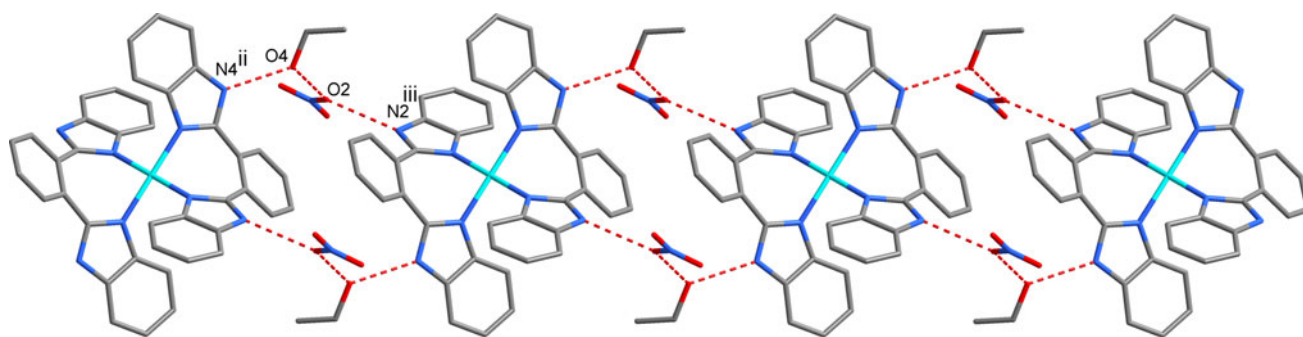


Fig. 2 1-D chain formed by N–H...O and O–H...O hydrogen bonds; symmetry code: ii, $-x + 1, -y + 2, -z + 1$; iii, $x - 1, y, -z$

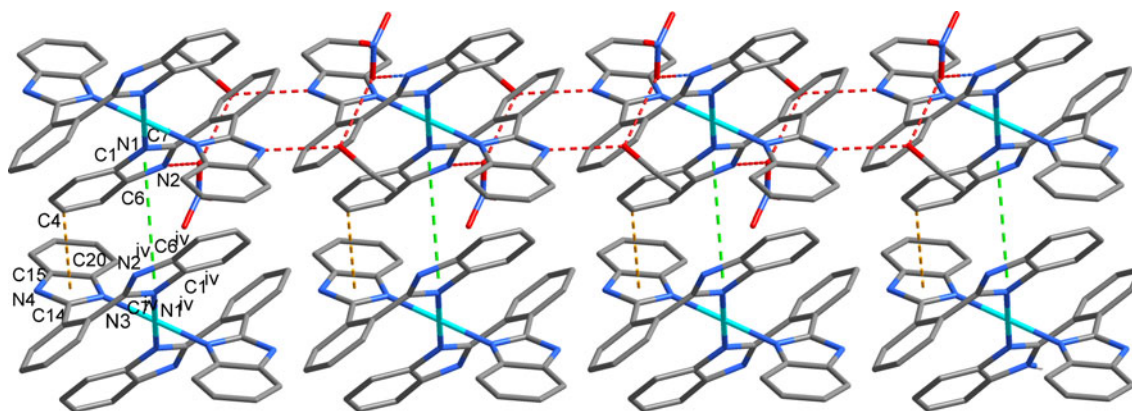


Fig. 3 2-D layer formed by π ... π and C–H... π interactions between the 1-D chains; symmetry code: iv, $-x, -y + 1, -z + 1$

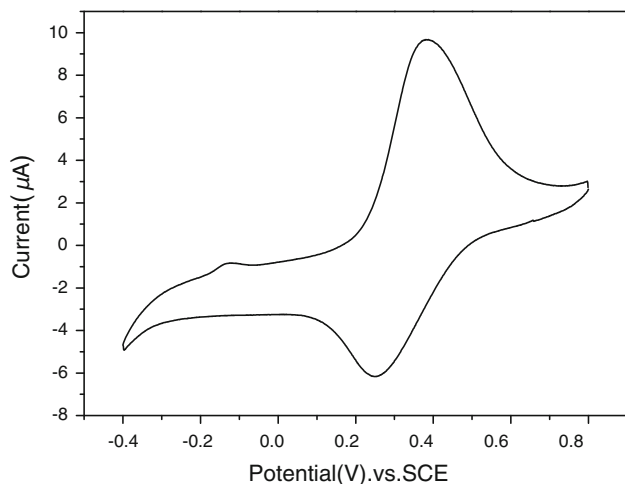


Fig. 4 Cyclic voltammogram of Cu-CPE in 0.1 M pH 2.0 phosphate buffer solution at a scan rate of 0.1 V s^{-1}

When H_2O_2 is added to the buffer solution, the cathodic peak current increases and the anodic peak current decreases (Fig. 7b). With increasing H_2O_2 concentrations, the reduction peak currents are dramatically enhanced (Fig. 7c, d), which indicates that the Cu-CPE has good electrocatalytic activity toward the reduction of H_2O_2 . The dependence of peak current response on the concentration

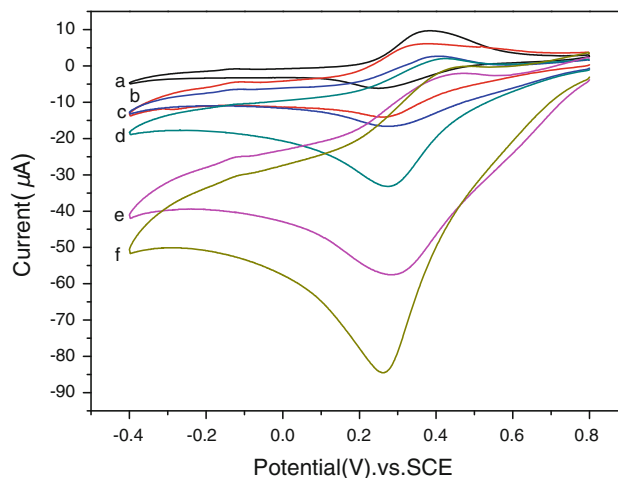


Fig. 5 Cyclic voltammograms of Cu-CPE in 0.1 M pH 2.0 phosphate buffer solution at a scan rate of 0.1 V s^{-1} with increasing BrO_3^- concentrations 0(a), 1(b), 2(c), 3(d), 4(e), 5 mM (f)

of H_2O_2 is linear in the range 1–5 mM, as shown in the inset of Fig. 7. The catalytic reduction of H_2O_2 can be described by the following equation [25]:



Figure 8 shows the cyclic voltammograms of Cu-CPE in buffer solutions containing different concentrations of

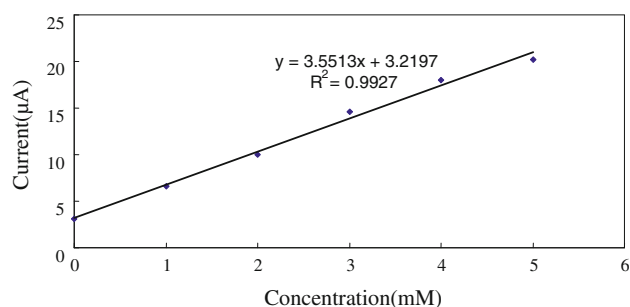
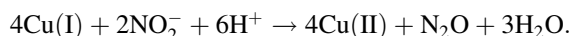


Fig. 6 The plot of cathodic peak current versus bromate concentration

nitrite. With the addition of nitrite, the reduction peak currents increase significantly, accompanied by a decrease in the oxidation peak currents. The inset of Fig. 8 shows that the catalytic current varies in a linear fashion with nitrite concentration up to 6 mM. A similar mechanism for the catalytic reduction of nitrite can be proposed as [22]:



The Cu-CPE exhibits high stability. Thus, after the electrocatalytic reaction, the Cu-CPE was investigated in 0.1 M pH 2.0 phosphate buffer solution at a scan rate of 0.1 V s^{-1} and showed little change in the peak potentials and currents. When the Cu-CPE was continuously scanned for 1 h, the peak current decreased 10%. When the Cu-CPE was stored at room temperature for 2 months, the current response decreased only by 3.5%. The good stability of the Cu-CPE can be ascribed to the poor solubility of the copper(II) complex and to the strong adsorption of the complex on graphite powder.

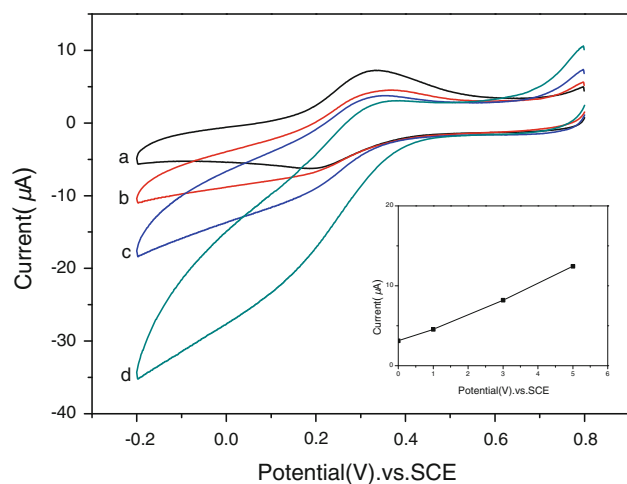


Fig. 7 Cyclic voltammograms of Cu-CPE in 0.1 M pH 2.0 phosphate buffer solution at a scan rate of 0.1 V s^{-1} with increasing hydrogen peroxide concentrations 0(a), 1(b), 3(c), 5 mM (d). Inset: the variation of cathodic peak currents versus hydrogen peroxide concentrations

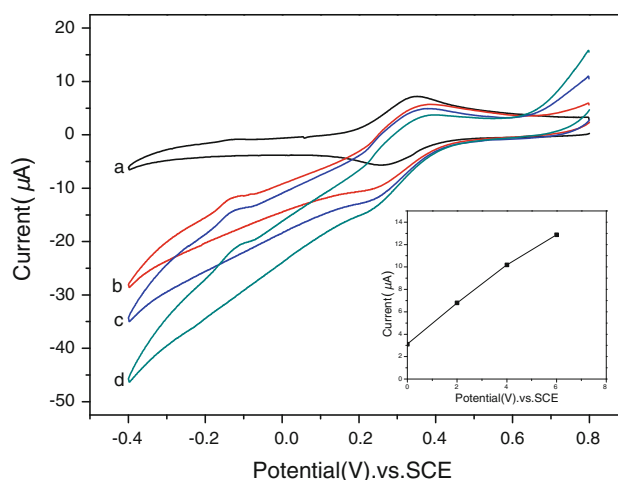


Fig. 8 Cyclic voltammograms of Cu-CPE in 0.1 M pH 2.0 phosphate buffer solution at a scan rate of 0.1 V s^{-1} with increasing NO_2^- concentrations 0(a), 2(b), 4(c), 6 mM (d). Inset: the variation of cathodic peak currents versus nitrite concentrations

Conclusion

A new copper(II) complex based on a rigid ligand containing bis(2-benzimidazolyl) groups, $[\text{Cu}(\text{OBimB})_2](\text{NO}_3)_2 \cdot (\text{EtOH})_2$, had been synthesized and structurally characterized by X-ray diffraction analysis. In the structure of the complex, two ligands with twisted V-shaped conformations chelate the copper(II) center, resulting in a square-planar geometry. The bulk-modified carbon paste electrode incorporating the complex exhibits good electrocatalytic activity toward reduction of bromate, hydrogen peroxide, and nitrite, indicating that the modified electrode has potential applications in the field of electrocatalysis.

Supplementary data

CCDC 837393 contains the supplementary crystallographic data for the complex. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments The supports of Natural Science Foundation of China (No. 20871072), Doctoral Foundation of Shandong Province (No. 2007BS04023), and Qingdao University of Science & Technology are gratefully acknowledged.

References

- Poeta MD, Schell WA, Dykska CC, Jones S, Tidwell RR, Czarny A, Bajic M, Kumar A, Boykin D, Perfect JR (1998) *Antimicrob Agents Chemother* 42:2495

2. Salunke NM, Revankar VK, Mahale VB (1994) *Transit Met Chem* 19:53
3. Tidwell RR, Jones SK, Naiman NA (1993) *Antimicrob Agents Chemother* 37:1713
4. Stibrany RT, Schugar HJ, Potenza JA (2002) *Acta Crystallogr Sect E* 58:o1142
5. Hoorn HJ, de Joode P, Driessen WL, Reedijk J (1995) *React Funct Polym* 27:223
6. Hoorn HJ, de Joode P, Dijkstra DJ, Driessen WL, Kooijman H, Veldman N, Spek AL, Reedijk J (1997) *J Mater Chem* 7:1747
7. Stibrany RT, Schulz DN, Kacker S (2003) *Macromolecules* 36:8584
8. Patil AO, Zushma S, Stibrany RT, Rucker SP, Wheeler LM (2003) *J Polym Sci Part A Polym Chem* 41:2095–2106
9. Stibrany RT, Kacker S (2002) US Patent No 6479425
10. Xie B, Elder T, Wilson LJ (1999) *Inorg Chem* 38:12
11. Stibrany RT, Lobanov MV, Schugar HJ (2004) *Inorg Chem* 43:1472
12. Chen CL, Tan HY, Yao JH, Wan YQ, Su CY (2005) *Inorg Chem* 44:8510
13. Meng FY, Zhou YL, Zou HH, Zeng MH, Liang H (2009) *J Mol Struct* 920:238
14. Bouwman E, Driessen WL, Reedijk J (1990) *Coord Chem Rev* 104:143
15. Albada GA, van Smeets WJJ, Spek AL (1999) *Inorg Chim Acta* 288:220
16. Salimi A, Alizadeh V, Hadadzadeh H (2004) *Electroanalysis* 16:1984
17. Gao GG, Xu L, Wang WJ, An WJ, Qiu YE, Wang ZQ, Wang EB (2005) *J Phys Chem B* 109:8948
18. Yamazaki H, Shouji A, Kajita M, Yagi M (2010) *Coord Chem Rev* 254:2483
19. Zagal JH, Griveau S, Silva JF, Nyokong T, Bedioui F (2010) *Coord Chem Rev* 254:2755
20. Valentini F, Amine A, Olanducci S, Terranova ML, Palleschi G (2003) *Anal Chem* 75:5413
21. Kulesza PJ, Roslonek G, Faulkner LR (1990) *J Electroanal Chem* 280:233
22. Chen SM (1998) *J Electroanal Chem* 457:23
23. Wang X, Zhao H, Lin H, Liu G, Fang J, Chen B (2008) *Electroanalysis* 20:1055
24. Jiang XE, Guo LP, Du XG (2003) *Talanta* 61:247
25. Wang XL, Lin HY, Liu GC, Zhao HY, Chen BK (2008) *J Organomet Chem* 693:2767
26. Zhuang RR, Jian FF, Wang KF (2009) *J Mol Struct* 938:254
27. Carina RF, Williams AF, Bernardinelli G (2001) *Inorg Chem* 40:1826
28. Sheldrick GM (1992) *Acta Crystallogr Sect A* 46:467
29. Sheldrick GM (1997) SHELXL-97, Program for X-ray Crystal Structure Refinement. University of Göttingen, Germany
30. Gilbert JG, Addison AW, Prabakaran P, Butcher RJ, Bocelli G (2004) *Inorg Chem Commun* 7:701
31. Santra BK, Reddy PAN, Neelakanta G, Mahadevan S, Nethajia M, Chakravartya AR (2002) *J Inorg Biochem* 89:191
32. Li YX, Lin XQ, Jiang CM (2006) *Electroanalysis* 18:2085
33. Salimi A, Mamkhezri H, Hallaj R, Zandi S (2007) *Electrochim Acta* 52:6097