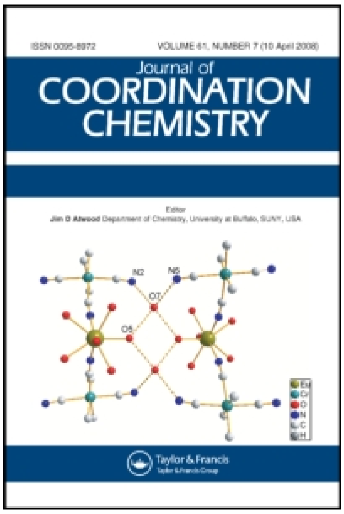

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Hydrothermal synthesis, crystal structure, and electrochemical property of a new 3-D coordination polymer based on benzene-1,2,4,5-tetracarboxylate bridging ligand: $[Cu_2(btec)(en)_2]_n$

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A new 3-D copper(II) complex, formulated as $[Cu_2(btec)(en)_2]_n$ (**1**) [H_4btec = benzene-1,2,4,5-tetracarboxylate, and en = ethylenediamine], was hydrothermally synthesized and structurally characterized by elemental analysis, IR spectroscopy, thermal gravimetric analysis, and single crystal X-ray diffraction. The structural analysis of **1** reveals that copper(II) connect by μ_6-bridging btec to form a 3-D coordination polymer, in which four carboxylates of btec show monodentate and bidentate coordination. Complex **1** was used as solid bulkmodifier to fabricate renewable carbon paste electrode (**1**-CPE) by direct mixing method. The cyclic voltammogram of **1**-CPE displayed one-electron quasi-reversible redox waves in potential range 300 to −300 mV due to Cu(II)/Cu(I). Moreover, **1**-CPE showed electrocatalytic activity toward the reduction of nitrite.

Keywords: Copper complex; Hydrothermal synthesis; Crystal structure; Electrochemical property

1. Introduction

Coordination polymers have achieved considerable progress due to their intriguing structural diversity and potential functions in catalysis, molecular adsorption, and magnetic materials [1–6]. Judicious selection of ligands is important because the changes in organic building blocks such as length, flexibility, and symmetry can dramatically change the structural motifs of these coordination polymers. Multibenzenecarboxylate ligands have been explored in the design of metal–organic polymers with desired topologies owing to their rich coordination modes [7–12]. A number of metal–organic coordination polymers based on benzene-1,2,4,5-tetracarboxylate (H_4btec) have been successfully prepared [13–17]. However, compared with the rich coordination chemistry exhibited by benzenedicarboxylate and 1,3,5-benzenetricarboxylate, the studies on

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H_4btec are less presumable due to the steric reasons with all the four carboxyl groups unlikely to engage in coordination with metal ions [13].

The electrochemical and electrocatalytic properties of Cu^{II} complexes with various ligands have attracted our attention. NO_2^-, BrO_3^-, and SO_2 can be electrocatalytically reduced by one-electron-reduced species of copper [9, 18–21]. As an extension of our study of copper/carboxylates/N-containing ligand hybrid systems, we have been focusing on designing the metal–organic frameworks used as electroactive materials [9, 19], especially assembly reactions of H_4btec with copper ions *via* the hydrothermal synthetic methods in the presence of other auxiliary ligands. In this article, we report a new copper complex with btec and ethylenediamine (en), $[Cu_2(btec)(en)_2]_n$ (**1**). In addition, the electrochemical behavior and electrocatalytic reduction of NO_2^- on the surface of the copper complex bulk-modified carbon paste electrode (**1**-CPE) has been examined.

2. Experimental

2.1. *Materials and methods*

All reagents employed were commercially available and used as received. FT-IR spectrum (KBr pellets) was taken on a Magna FT-IR 560 Spectrometer and elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C elemental analyzer. Thermal gravimetric analysis (TGA) was carried out with a Pyris Diamond TG-DTA instrument. Electrochemical experiments were carried out using a CHI 440 Electrochemical Quartz Crystal Microbalance. A conventional three-electrode cell was used at room temperature. The modified electrode was used as a working electrode. A saturated calomel electrode and a platinum wire were used as the reference and auxiliary electrodes, respectively.

2.2. *Synthesis*

2.2.1. Synthesis of $[Cu_2(btec)(en)_2]_n$ (1). A mixture of $CuCl_2 \cdot 2H_2O$ (0.034 g, 0.2 mmol), H_4btec (0.0254 g, 0.1 mmol) and H_2O (12 mL) was stirred for 30 min in air and then the pH was adjusted to *ca* 6.8 with ethylenediamine. The mixture was then transferred to and sealed in a 25 mL Teflon reactor and heated at 160°C for 6 days, leading to the formation of blue block crystals of **1** (19% yield based on Cu). Anal. Calcd (%) for $C_7H_5CuN_2O_4$: C 34.33, H 2.06, N 11.44%. Found (%): C 34.48, H 2.22, N 11.23%. IR (KBr, cm^{-1}): 3427s, 3090m, 2367m, 2335m, 1624s, 1570s, 1485m, 1423s, 1361s, 1380s, 1231w, 1144m, 1074m, 818m, 775s, 737s, 644w, 617w, 574w, 471w.

2.3. *Preparation of modified CPEs*

The modified CPE were fabricated as follows: 0.3 g of graphite powder and 0.02 g of **1** were mixed and ground together by agate mortar and pestle for approximately 30 min to achieve an even, dry mixture; to the mixture 0.13 mL paraffin oil was added and stirred with a glass rod; then the homogenized mixture was used to pack 3 mm inner diameter glass tubes to a length of 0.5 cm. The electrical contact was established with the copper stick, and the surface of the modified CPE was wiped with weighing paper. The same procedure was used for the preparation of bare CPE without copper complex.

2.4. *X-ray crystallographic study*

Crystallographic data for **1** were collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) by ω scan mode. The structure was solved by direct methods using SHELXS of the SHELXTL package and refined by full-matrix least-squares with SHELXL [22, 23]. Metals in the complex were located from the *E*-maps, and all non-hydrogen atoms were refined anisotropically. The hydrogens of the ligand were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. A summary of crystal data and structure refinement for the title complex is provided in table 1. Selected bond lengths and angles are listed in table S1.

3. Results and discussion

3.1. *Structure description*

X-ray study reveals that **1** is a 3-D coordination polymer network constructed from bridging btec and chelating ethylenediamine. As shown in figure 1, each Cu(II) is five-coordinate *via* three oxygens from two different btec ligands and two nitrogens from one ethylenediamine to form a distorted square pyramid. The Cu–O bond lengths range from 1.959(4) to 2.520(4) Å, which is within the range of those found

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_7H_5CuN_2O_4$
Formula weight	244.68
Crystal system	Monoclinic
Space group	*P21/n*
Unit cell dimensions (Å, °)	
a	6.6407(13)
b	7.4905(14)
c	17.429(3)
β	96.018(2)
Volume (Å^3), *Z*	862.2(3), 4
Calculated density (g cm^{-3})	1.885
Absorption coefficient (mm^{-1})	2.520
F(000)	488
θ_{max} (°)	26.08
Total data	7169
Unique data	1710
R_{int}	0.1145
Final *R* indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0471$
(all data)	$wR_2{}^b = 0.1142$
Goodness-of-fit on F^2	0.968
Largest difference peak and hole (e Å^{-3})	0.625 and −0.760

$^a R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $^b wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

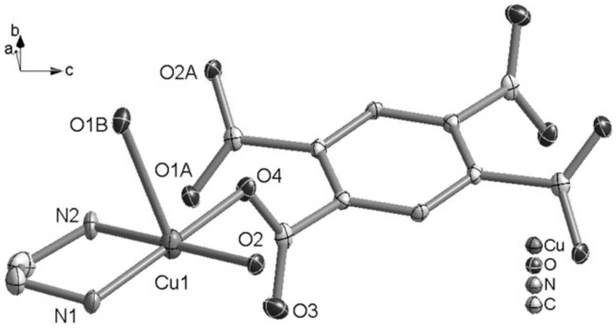

Figure 1. ORTEP diagram showing the coordination environment for Cu(II) in **1** (at 30% probability level).

in related octahedral Cu(II) coordination polymers. The Cu–N bond lengths [Cu(1)–N(1) = 1.978(4) Å, Cu(1)–N(2) = 1.995(4) Å] are similar to that in a 3-D Cu–btec complex [16, 24]. In **1**, all carboxyls of btec are deprotonated. The four carboxylates show deviations from the plane of the central aromatic ring due to the rotation of the OCH_2 groups, and they are arranged "above" and "below" the plane (figure S1). The four carboxylates show two different coordinations. Two carboxylates are monodentate with one oxygen bonding Cu, while the other two are bidentate bridging, linking two Cu ions. Hence, btec serves as a μ_6-bridge, linking six Cu centers through its four arms in different coordination modes forming an infinite 3-D polymer network (figure 2). The presence of terminal ethylenediamine is similar to previous reports [25, 26].

To understand the framework topology, it is necessary to simplify the building blocks from the 3-D polymer network. The overall 3-D network is described in terms of two subnets. The first subnet is composed of Cu(II), connected with three different btec's as three-connected nodes. The second subnet is formed by btec's, which bridge copper ions into a six-connected network. Then the total topology of **1** can be considered to be a well-known 3,6-connected topology [27], as shown in figure 3.

3.2. *Thermal gravimetric analysis*

TGA was carried out from 30°C to 650°C (figure S2). The TG curve of **1** reveals that there is only one obvious weight loss step, occurring between 310°C and 480°C and attributed to the loss of btec and ethylenediamine. The observed 67.09% weight loss is in agreement with the calculated value of 67.30%. The remaining 32.91% corresponds to CuO (32.70%).

3.3. *Electrochemical behavior of 1-CPE*

Electrochemical studies of **1** modified CPE (**1**-CPE) was carried out in 0.1 M phosphate buffer solution (pH = 2.3). Figure 4 shows the cyclic voltammograms at a bare CPE and the modified CPE. In the potential range 300 to −300 mV, there is no redox peak for bare CPE. At **1**-CPE, a quasi-reversible redox couple was observed, the mean peak potential $E_{1/2} = (E_{pa} + E_{pc})/2$ of −22.67 mV, attributed to Cu(II)/Cu(I) [28–32]. $[Cu(phen)_2(H_2O)](ClO_4)_2$ in DMF and 50 mM Tris–HCl/0.1 M KCl buffer solution

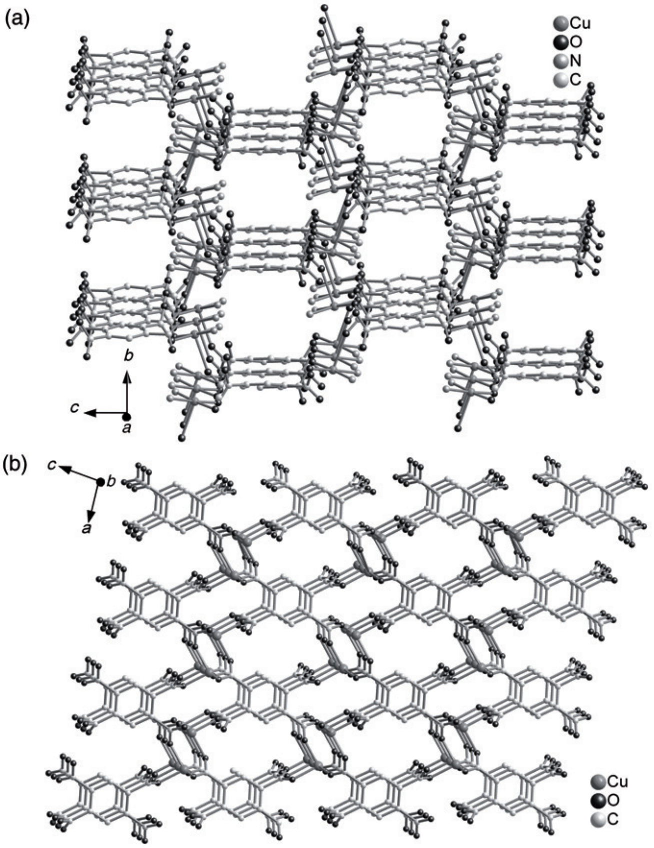

Figure 2. (a) 3-D polymeric network of **1** along *a*-axis (all H and C atoms of ethylenediamine are omitted for clarity); (b) 3-D polymeric network of **1** along *b*-axis (all hydrogens and ethylenediamine molecules are omitted for clarity).

gives peaks with a $E_{1/2}$ value of $-33.00\,\text{mV}$ [32]. The oxidation potential of our complex shifts to lower potential and its reduction potential shifts to higher potential, due to the influence of btec and ethylenediamine.

Scan rate effect on the electrochemical behavior of **1**-CPE was investigated in the potential range of $+300$ to $-300\,\text{mV}$ in 0.1 M pH 2.3 phosphate buffer aqueous solution, as shown in figure 5. When the scan rate was varied from 40 to $450\,\text{mV}\,\text{s}^{-1}$, the peak potentials changed gradually as the cathodic peak potentials shifted to negative and the corresponding anodic peak potentials shifted to positive with increasing scan rate. The plots of peak current *versus* scan rate, inset of figure 5, show the anodic and cathodic currents were proportional to scan rate, suggesting that the redox process for **1**-CPE was a surface-confined process.

3.4. *Electrocatalytic reduction of 1-CPE toward nitrite*

Direct electroreduction of nitrite requires a large overpotential at most electrode surfaces and no obvious response is observed at bare CPE. The electrocatalytic

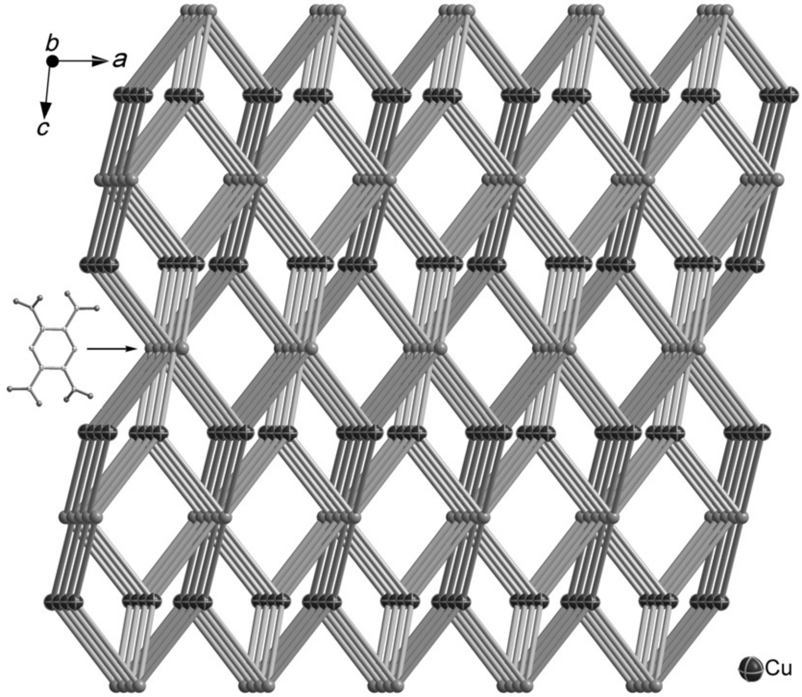

Figure 3. The topology of **1**.

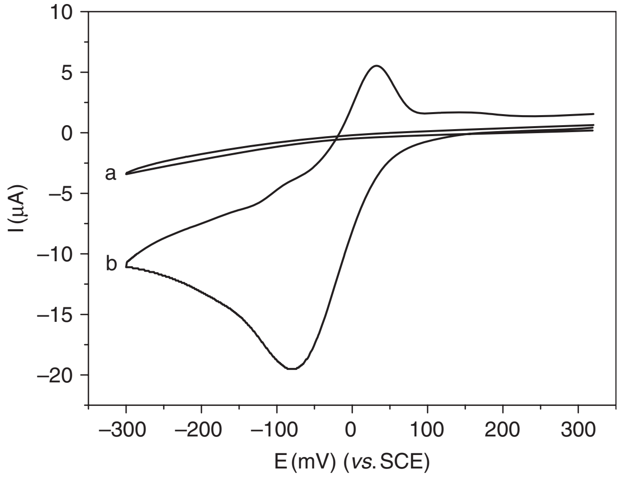

Figure 4. Cyclic voltammograms of (a) bare CPE and (b) **1**-CPE in 0.1 M pH 2.3 phosphate buffer solution in the potential range 300 to −300 mV. Scan rate: 50 mV s^{-1}.

reduction of nitrite at the surface of **1**-CPE has been studied (figure 6). Curve *c* in figure 6 shows the cyclic voltammograms of **1**-CPE in phosphate buffer solution containing 5 mM NO_2^-. With the addition of nitrite, the reduction peak currents increase markedly while the corresponding oxidation peak currents

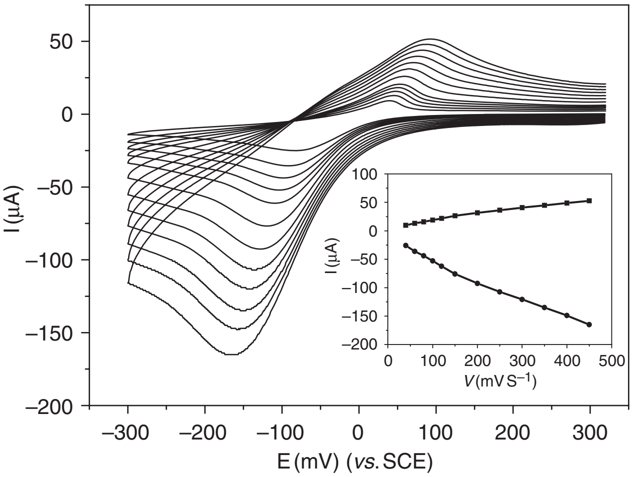

Figure 5. Cyclic voltammograms of **1**-CPE in pH 2.3 phosphate buffer solution at different scan rates (from inner to outer) 40, 60, 80, 100, 120, 150, 200, 250, 300, 350, 400, and 450 mV s^{-1} of **1**-CPE. The inset shows the plots of the anodic and the cathodic peak currents *vs.* scan rates.

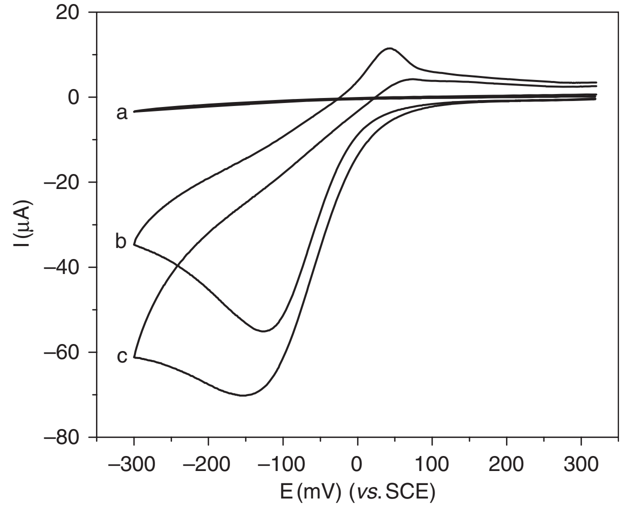

Figure 6. Cyclic voltammograms of a bare CPE in phosphate buffer solution with pH of 2.3 containing 2 mM $NaNO_2$ (a) and **1**-CPE in phosphate buffer solution containing NO_2^- concentrations of 0.0 mM (b), 5 mM (c). Scan rate: 80 mV s^{-1}.

decrease markedly. Similar voltammograms have been obtained for copper(II) bis(5-amino-1,10-phenanthroline)-modified glassy carbon electrode in an aqueous buffer solution (pH 1.5) [18], confirming that NO_2^- is the active species on the surface of **1**-CPE. Our results indicate that **1**-CPE has remarkable electrocatalytic activity toward the reduction of nitrite in phosphate buffer solution with pH 2.3, and the electrochemical catalytic pathway is probably the reduction of NO_2^- to NO and then further reduction to N_2O in the acidic aqueous solution. The electrochemical behavior and the electrocatalytic activities of **1**-CPE are similar to that of our previous reports [9, 19], and the slight difference of peak potential might be attributed to the different structure of copper complexes.

4. Conclusion

A new copper(II) complex formulated as $[Cu_2(btec)(en)_2]_n$ has been hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction. Complex **1** is a 3-D coordination polymer network based on bridging btec and terminal ethylenediamine. Complex **1** was employed to fabricate a bulk-modified carbon paste electrode (**1**-CPE) due to its insolubility. The **1**-CPE displays a quasi-reversible redox couple attributed to Cu(II)/Cu(I) in 0.1 M phosphate buffer solution (pH = 2.3) and shows good electrocatalytic activity toward the reduction of nitrite. These preliminary results indicate that copper(II) complexes may be the good candidates for electrochemical and electrocatalytic materials.

Supplementary material

CCDC 688247 for **1** contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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