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# Synthesis and Characterization of One Novel Copper(II) Complex with Bis(2-Pyridylcarbonyl)Amide

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*The preparation and spectral study of one copper(II) complex with the formula [Cu(bpca)(PHOD)]$ClO_4$1 [bpca = bis(2-pyridylcarbonyl)amide anion, PHOD = 1,10-phenathrolinedione] has been reported in this article. The structure of the complex has been determined by single-crystal X-ray diffraction. The crystal analysis shows that the mononuclear copper(II) complex is in five-coordinated surroundings with a tridentate bpca and a bidentate PHOD ligand, and two kinds of C–H···O hydrogen bonds connect the whole structure into three-dimensional network. Meanwhile, the complex has been characterized by infrared (IR), Uv-vis, Electron Paramagnetic Resonance (EPR) spectra, and cyclic voltammetric studies.*

**Keywords** Copper(II) complex; EPR spectra; spectral study

## Introduction

The highly stable bis(2-arylcarbonyl)amidocopper(II) species $[Cu(bpca)]^+$ can be exploited as building blocks for self-assembly, bpca can act as a tridentate ligand toward the copper(II) ion through the amidate nitrogen and two pyridyl (bpca) nitrogen atoms. Many mononuclear and polynuclear bpca-containing copper(II) complexes with various ligands were obtained and reported [1–7]. For some of these complexes, hydrogen bonding and $\pi$-$\pi$ stacking interactions may play important roles in the design of supramolecular systems.

In this article, we have used $[Cu(bpca)]^+$ unit as a building block to design and prepared one mononuclear copper(II) complex with 1,10-phenathrolinedione (PHOD), $[Cu(bpca)(PHOD)]ClO_4$, which also has been characterized by infrared (IR), Uv-vis, EPR spectra, and cyclic voltammetric studies.

## Results and Discussion

### *Synthesis and General Characterization*

The crystallographic data and processing parameters for structural analyses of complex 1 are summarized in Table 1; selected bond lengths and angles are listed in Table 2.

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**Table 1.** Experimental data for complex 1

| Empirical formula | $C_{24}H_{15}ClCuN_5O_{7.50'}$ |
|---|---|
| Formula mass (g/mol$^{-1}$) | 592.40 |
| Temperature (K) | 293(2) |
| λ (Mo$K\alpha$) (Å) | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | *Pbcn* |
| Unit cell dimensions | |
| $a$ (Å) | 14.265 (2) |
| $b$ (Å) | 17.056 (3) |
| $c$ (Å) | 20.601(3) |
| $\alpha$ ($^{o}$) | 90 |
| $\beta$ ($^{o}$) | 90 |
| $\gamma$ ($^{o}$) | 90 |
| $V$ (Å$^3$) | 5012.4 (13) |
| $\boldsymbol{Z}$ | 8 |
| $D_{calcd}$ (Mg/m$^3$) | 1.570 |
| Abs. coeff. (mm$^{-1}$]) | 1.035 |
| $F$ [000] | 2400 |
| Crystal size (mm) | 0.22 × 0.18 × 0.12 |
| 2$\theta$ range (°) | 2.11 to 25.01 |
| Limiting indices | $-15 \le h \le 16$ |
| | $-13 \le k \le 20$ |
| | $-23 \le l \le 24$ |
| Reflections collected | 23, 969 |
| Unique reflections | 4381 [$R$(int) = 0.1129] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 4381/302/456 |
| Completeness to $\theta$ (%) | 99.1 |
| Goodness-of-fit on $F^2$ | 1.096 |
| Max./min. transmission | 1.000000, 0.697352 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0660$, $wR2 = 0.1543$ |
| $R$ indices (all data) | $R1 = 0.1491$, $wR2 = 0.1989$ |
| Largest diff. peak hole (e Å$^{-3}$) | 0.591,−0.339 |

**Table 2.** The selected bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| Cu(1)–N(1) | 2.022(5) | Cu(1)–N(4) | 1.943(5) |
| Cu(1)–N(2) | 2.219(5) | Cu(1)–N(5) | 2.014(6) |
| Cu(1)–N(3) | 2.024(6) | N(1)–Cu(1)–N(3) | 98.8(2) |
| N(4)–Cu(1)–N(5) | 81.4(2) | N(4)–Cu(1)–N(2) | 111.2(2) |
| N(4)–Cu(1)–N(1) | 170.8(2) | N(5)–Cu(1)–N(2) | 99.1(2) |
| N(5)–Cu(1)–N(1) | 96.8(2) | N(1)–Cu(1)–N(2) | 77.93(19) |
| N(4)–Cu(1)–N(3) | 81.7(2) | N(3)–Cu(1)–N(2) | 93.46(19) |
| N(5)–Cu(1)–N(3) | 161.7(2) | | |

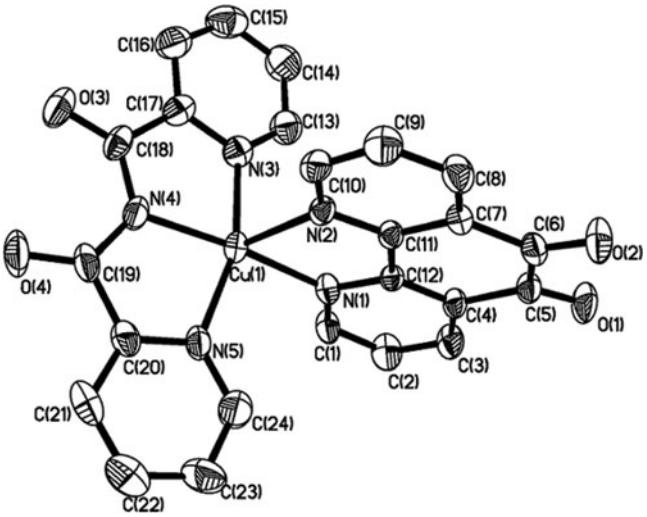


**Figure 1.** Molecular structure of the complex 1.

As shown in Fig. 1, the copper(II) is five coordinated with two nitrogen atoms from the PHOD group[N(1) and N(2)] and three nitrogen atoms from the bpca group[N(3), N(4), and N(5)] for mononuclear cationic $[Cu(bpca)(PHOD)]^+$ unit, and the dihedral angle of two five-membered rings formed by the bpca group and copper(II) [(N(5), C(20), C(19), N(4), and Cu(1); N(4), C(18), C(17), N(3), and Cu(1)] is 5.3°, which show that the bpca ligand is slightly distorted. The N(1), N(3), N(4), and N(5) atoms build the basal plane and the N(2) atom fills the apical position. The bond lengths of Cu(1)–N(1), Cu(1)–N(3), Cu(1)–N(4), and Cu(1)–N(5) in the basal plane are 2.022(5), 2.024(6), 1.943(5), and 2.014(6) Å, which are shorter than the bond length of Cu(1)–N(2) at the vertex with the value of 2.219(5) Å. The copper(II) ion is shifted by 0.1520 Å from its mean basal plane with $\tau$ values of 0.15, which shows that the copper is in slightly distorted square pyramidal surroundings.

One kind of C–H···O hydrogen bonds between the bpca ligands and uncoordinated perchlorate ligands (Fig. 2), where the bpca groups act as acceptors and the perchlorate ligands as donors, lead to a supramolecular two-dimensional layered structure. Another kind of C–H···O hydrogen bonds between the bpca ligands and PHOD ligands (Fig. 3),

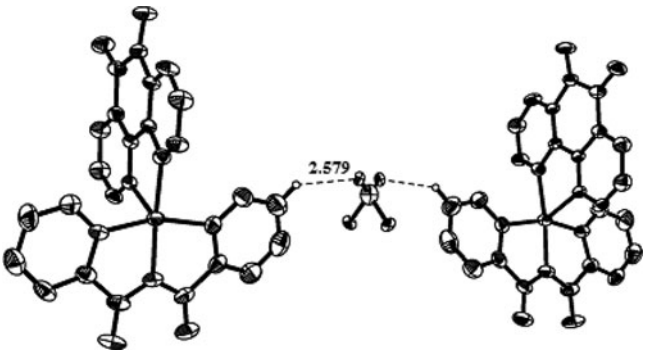


**Figure 2.** C–H···O hydrogen bonds between the bpca ligands and perchlorate ligands.

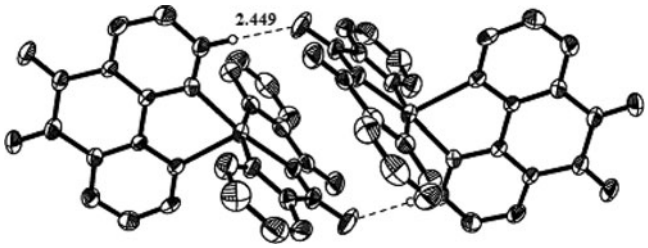


**Figure 3.** C–H· · ·O hydrogen bonds between the bpca ligands and PHOD ligands.

where the bpca groups act as donors and the PHOD ligands as acceptors, connect the whole structure into three-dimensional network.

### *Infrared Spectra*

The sharp and strong absorption peaks at 1707 $cm^{-1}$ and 1599 $cm^{-1}$ are associated with the asymmetric and symmetric stretching vibrations of carbonyl group from the bpca ligand.[8] Two characteristic peaks of perchlorate group at 1091 $cm^{-1}$ and 625 $cm^{-1}$ indicate that the perchlorate group is uncoordinated with the metal ions, but splits at 1091 $cm^{-1}$ also indicate the perchlorate group takes part in formation of the hydrogen bonds, which is consistent with the X-ray diffraction analysis.[9]

### *Uv-Vis Spectra*

The Uv-vis spectrum of complex 1 in DMSO was measured at room temperature, which is very similar to the Cu(bpca) complexes reported previously.[10–11] The electronic spectrum of complex 1 shows a weak absorption band at 619 nm (Fig. 4), which can presumably be assigned to the d-d transition of Cu(II). Gauss simulated results show two peaks (616 nm and 672 nm) may correspond to the transitions of $^2B_1 \rightarrow {}^2E$ and $^2B_1 \rightarrow {}^2B_2$.

### *EPR Spectra*

EPR experimental and simulation spectra of complex 1 at X-band microwave frequencies at room temperature in DMSO are shown in Fig. 5, with the values of $g$ tensor, $g_x = 2.06$, $g_y = 2.06$, $g_z = 2.16$, $g_\parallel > g_\perp > ge$, which show the copper(II) atom in an axial symmetry coordinated surroundings and the unpaired electrons occupies the $dx^2$-$y^2$ orbital.

### *Cyclic Voltammetric Studies*

The cyclic voltammogram of 1 (0.001M) in DMSO was carried out at a platinum disk working electrode, using $[Bu_4N][ClO_4]$ (Bu stands for butyl group, 0.1M) as supporting electrolyte (perchlorate salts are explosives and should be used with caution) and Ag/AgCl as reference electrod (Fig. 6), and the scanning range is from −1.5 V to 1.5 V in 0.1 $V.s^{-1}$. Two pairs of peaks on the negative potential sides of the cyclic voltammogram correspond to the reversible oxidation steps of the bpca ligand and Cu(I)/Cu(II), [12–13] with $E_{pa1} = -418$ mV, $E_{pc1} = -476$ mV, $\Delta E_{p1} = 58$ mV, $I_{pa1}/I_{pc1} = 1.1$ and $E_{pa2} = -652$ mV, $E_{pc2} = -711$ mV, $\Delta E_{p2} = 59$ mV, $I_{pa2}/I_{pc2} = 1.1$

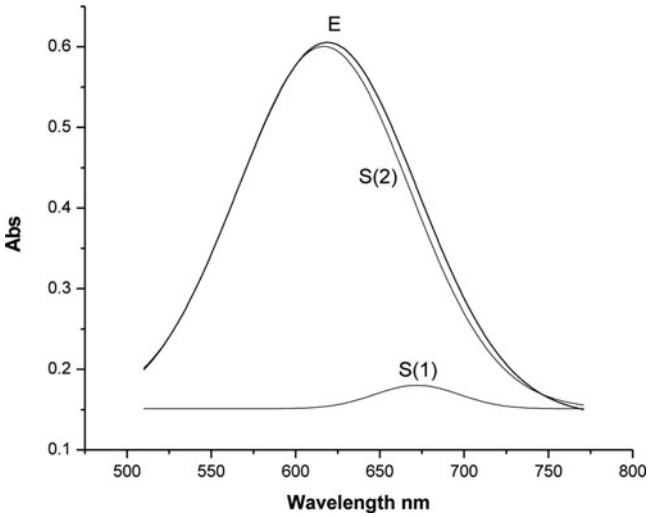


**Figure 4.** Uv-vis experimental spectrum (E) and Gauss simulated spectrum (S) of complex 1.

## Experimental Section

### *Materials and Methods*

$[Cu(bpca)(H_2O)_2(O_2CCH_3)]\cdot H_2O$ were synthesized according to the literature.[14] PHOD was reagent grade and used without further purification. C, H, and N elemental analyses were carried out with a Perkin-Elmer analyzer, model 240. Electronic spectra were recorded with a Shimadzu UV-2101PC spectrophotometer in the 200–2000 nm range at room temperature. The fourier transform (FT)-IR spectra were recorded with KBr pellets in the range 4000–400 $cm^{-1}$ with a Bio-Rad FTS 135 spectrometer.

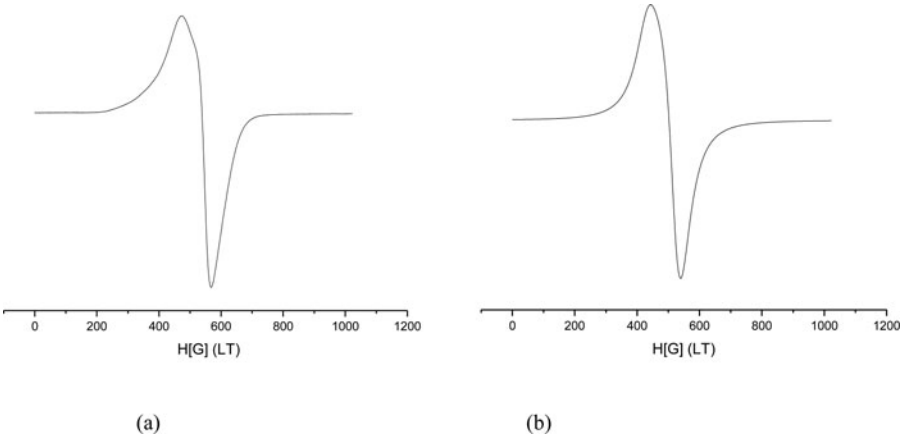


**Figure 5.** **(a)** EPR experimental spectrum of the complex 1 at 298 K. **(b)** EPR simulation spectrum of the complex 1 at 298 K.

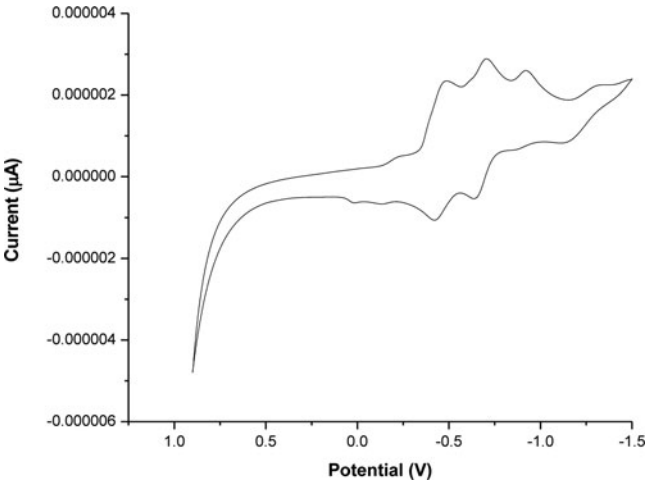


**Figure 6.** CV diagram of the complex 1 in DMSO.

### *Synthesis of [Cu(bpca)(PHOD)]ClO$_4$1*

An aqueous solution (10 ml) of [Cu(bpca)($H_2O$)$_2$($O_2CCH_3$)]·$H_2O$ (0.2 mmol) was added to an ethanol solution (12 ml) of PHOD (0.2 mmol), and then refluxed for more than 2 hr, the obtained bright green solution was filtered. Deep blue single crystals suitable for X-ray diffraction were obtained in several weeks by slow evaporation of filtrate. Elemental analysis (%) for $C_{24}H_{15}ClCuN_5O_{7.50}$ (Fw. 592.40): Anal. calc.: C = 48.42; H = 1.47; N = 11.65; Found: C = 48.58; H = 1.34; N = 11.80.

## Conclusions

One novel mononuclear copper(II) complex with $[Cu(bpca)]^+$ unit as building block has been synthesized and characterized by X-ray diffraction, IR, Uv-vis, EPR spectra, and cyclic voltammetric studies. Crystal data analysis shows that the complex is a supramolecular three-dimensional structure with two kinds of C–H$\cdots$O hydrogen bands, the study of EPR spectra also shows that the copper(II) atom is in a axial symmetry coordinated surroundings, and the cyclic voltammetric studies reveals the reversible oxidation steps of Cu(I)/Cu(II).

## Acknowledgment

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## Supplementary Data

X-ray Crystallographic Study: All measurements were made on a Bruker SMART diffractometer equipped with a graphite monochromator and Mo$K\alpha$ radiation ($\lambda$ = 0.71073 Å) source. The structure was solved by direct methods and refined by full-matrix least-squares. Hydrogen atoms were added geometrically and refined by mixed method. All calculations were performed using SHELEX-97 program.

CCDC 1013882 for complex 1 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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