

两个基于苯并咪唑还原席夫碱的双核铜(II) 配合物的合成、晶体结构和电化学性质

赵海燕* 李 娜 杨晓东

(河北科技大学理学院, 石家庄 050018)

摘要: 在甲醇体系中, 分别将苯并咪唑还原席夫碱 HL 与四氟硼酸铜和硝酸铜进行配位反应得到 2 个结构类似的双核铜配合物 $[\text{CuL}(\text{CH}_3\text{OH})]_2(\text{BF}_4)_2$ (**1**) 和 $[\text{CuL}(\text{NO}_3)_2]_2$ (**2**) (HL=2-(((2-(2-benzimidazolyl) ethyl)amino)methyl)phenol), 并用元素分析、红外光谱、紫外-可见光谱和单晶 X 射线衍射对其结构进行了表征。结构分析表明: 2 个配合物均属于单斜晶系, $P2_1/c$ 空间群, 为酚氧桥联的双核铜结构, 其中每个 Cu(II) 处于 N_2O_3 的畸变四方锥构型。配合物中的氢键将配合物 **1** 和配合物 **2** 分别连接成一维和三维网络结构。采用循环伏安法测定了双核配合物的氧化还原电位, 表明 2 个配合物均显示 2 个准可逆单电子还原过程。

关键词: 双核铜(II)配合物; 还原席夫碱; 晶体结构; 氧化还原性质

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Two Binuclear Cu(II) Complexes of Reduced Schiff Base Ligand Containing Benzimidazole Ring: Syntheses, Structures and Electrochemical Properties

ZHAO Hai-Yan* LI Na YANG Xiao-Dong

(College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, China)

Abstract: Two binuclear copper(II) complexes of the reduced Schiff base, namely, HL=2-(((2-(2-benzimidazolyl) ethyl) amino)methyl)phenol (HL) have been synthesized and characterized by C, H and N microanalyses, spectroscopic (FT-IR, UV-Vis) as well as electrochemical techniques and single-crystal X-ray diffraction. The crystal structures of $[\text{CuL}(\text{CH}_3\text{OH})]_2(\text{BF}_4)_2$ (**1**) and $[\text{CuL}(\text{NO}_3)_2]_2$ (**2**) show that the Cu(II) atoms are bridged by two phenolato oxygen atoms in the dimers. The geometries around Cu(II) atoms are distorted square pyramid with the Addison parameters (τ) of 0.31 and 0.35 for **1** and **2**, respectively. Furthermore, the complex units in **1** and **2** are linked into 1D and 3D supramolecular networks by H-bonding in the solid state, respectively. The electrochemical studies of **1** and **2** show two quasi-reversible one electron reduction processes. CCDC: 2276305, **1**; 2276307, **2**.

Keywords: binuclear copper complexes; reduced Schiff base ligand; crystal structure; redox properties

0 Introduction

Binuclear copper(II) complexes are of ongoing interest due to their interesting magnetic, catalytic, electrochemical properties and a wide variety of biological applications as catechol oxidase, antibacterial

species, DNA binding and cleaving agents^[1-11]. Among these binuclear complexes, the phenolate bridged binuclear copper complexes with tunable stereochemistry are often five-coordinated in which Cu(II) ions are in distorted square pyramid with different Addison parameter (τ). Structural properties of the Cu_2O_2 core,

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*通信联系人。E-mail: hbhaiyanzh@163.com; 会员登记号: S06N6511M1009。

such as the coordination geometry of the copper ions, the Cu···Cu distances, Addison parameter (τ) and torsion angles have been postulated to influence the spectral and electrochemical properties of the binuclear copper complexes, which offer a great scope of design for species that are suitable for magnetic, catalytic properties and biological activities^[3-4,12-14]. Hence, it would be interesting to find a relationship between the geometries and properties of newly designed phenoxo bridged binuclear copper complexes.

Herein, we report the synthesis, crystal structures, and electrochemical properties of two binuclear copper complexes $[\text{CuL}(\text{CH}_3\text{OH})]_2(\text{BF}_4)_2$ (**1**) and $[\text{CuL}(\text{NO}_3)_2]_2$ (**2**) of the newly designed reduced Schiff base ligand HL (HL=2-(((2-(2-benzimidazolyl) ethyl)amino) methyl)phenol). The ligand HL is considered to be more flexible compared to the Schiff base due to the reduction of the rigid azomethine ($-\text{CH}=\text{N}-$) fragment to less constrained $-\text{CH}_2\text{-NH}-$ moiety^[15] and therefore has the potential to form binuclear complexes through a bridging phenolate group.

1 Experimental

1.1 Materials and physical measurement

All chemicals were of reagent grade and used as received. 2-(Aminoethyl)-benzimidazole dihydrochloride was performed by a method described by Cescon et al^[16]. FT-IR spectra (KBr pellet) were obtained on a FT-IR 170 SX (Nicolet) spectrometer in the range of 4 000~400 cm^{-1} . Elemental analyses were taken using a Perkin-Elmer 240C analyzer. ^1H NMR was performed on a Bruker Avance 500MHz spectrometer using trimethyl silicon as internal standard. The electronic absorption spectra UV-Vis spectroscopy were recorded on a spectrophotometer using DMF as solvent. Cyclic voltammograms were run on a CHI model 750B electrochemical analyzer in a DMF solution containing tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. A three-electrode cell was used, which was equipped with a glassy carbon-working electrode, a platinum wire as the counter electrode and a saturated Ag/AgCl electrode as the reference electrode.

1.2 Synthesis of HL

The ligand was synthesized by a condensation reaction between 2-(aminoethyl)-benzimidazole dihydrochloride (3.16 g, 13.5 mmol), previously neutralized with NaOH (1.08 g, 27 mmol), and salicylaldehyde (1.4 mL, 13.5 mmol) in 75 mL of methanol. The reaction mixture was refluxed for approximately two hours and then reduced by slow addition of NaBH_4 (0.5 g, 13.5 mmol) at 0 $^\circ\text{C}$. The reaction mixture was concentrated under reduced pressure and the product was extracted with three portions of CHCl_3 (60 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure resulting in a white powder. Yield (2.56 g, 68%). m.p. 147~149 $^\circ\text{C}$. Anal. Calcd. for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}$ (%): C, 71.89; H, 6.41; N, 15.72. Found(%): C, 71.52; H, 6.37; N, 15.96. ^1H NMR: δ 7.21~7.55 (4H, $\text{CH}_{\text{benzimid}}$), 6.76~7.20 (4H, CH_{ar}), 3.99~4.04 (2H, N-CH_2), 3.08~3.19 (2H, CH_2). IR (KBr, cm^{-1}): 3 316(m), 2 855(w), 1 598(s), 1 455(s), 1 275(s), 1 094(m), 1 031(m), 922(m), 751(s), 617(w).

1.3 Syntheses of the complexes

1.3.1 Synthesis of $[\text{CuL}(\text{CH}_3\text{OH})]_2(\text{BF}_4)_2$ (**1**)

A solution of HL (26.6 mg, 0.1 mmol) and NEt_3 (0.014 mL, 0.1 mmol) in 7 mL methanol was added to a solution of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (34.5 mg, 0.1 mmol) in 3 mL water. The resulting dark green solution was stirred for two hours at room temperature. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of the solvent at 4 $^\circ\text{C}$. Yield: 65%. Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{BCuF}_4\text{N}_3\text{O}_2$ (%): C, 45.51; H, 4.49; N, 9.36. Found(%): C, 45.62; H, 4.52; N, 9.49. IR (KBr, cm^{-1}): 3 647(m), 3 120(w), 1 599(s), 1 545(m), 1 483(s), 1 457(s), 1 419(w), 1 394(w), 1 293(s), 1 251(s), 1 083(s), 880(m), 854(m), 764(s), 753(s).

1.3.2 Synthesis of $[\text{CuL}(\text{NO}_3)_2]_2$ (**2**)

A solution of HL (26.6 mg, 0.1 mmol) and NEt_3 (0.014 mL, 0.1 mmol) in 5 mL methanol was added to a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (24.1 mg, 0.1 mmol) in 5 mL methanol. The resulting dark green solution was stirred for two hours at room temperature. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of the solvent at room temperature.

Yield: 47%. Anal. Calcd. for $C_{16}H_{16}CuN_4O_4$ (%): C, 49.05; H, 4.12; N, 14.30. Found(%): C, 49.39; H, 4.06, N, 14.21. IR (KBr, cm^{-1}): 3 119(w), 1 598(s), 1 484(m), 1 456(m), 1 384(s), 1 256(m), 1 025(w), 857(w), 751(s).

1.4 X-ray crystallography

Diffraction intensities for complexes **1** and **2** were collected on a Bruker Smart 1000 CCD area detector using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071\ 073\ nm$) with φ - ω scan mode at 293(2) K. Unit cell dimensions were obtained with least-squares refinements and semi-empirical absorption corrections were applied using SADABS program^[17]. For complex **1** all fluorine atoms from BF_4^- are disordered and were

refined isotropically with occupancy with 0.6 and 0.4. All the structures were solved by direct method and non-hydrogen atoms were obtained in successive difference Fourier syntheses. All the structures were solved by direct method and the refinements were performed by full-matrix least-squares methods on F^2 with SHELXTL program package^[18]. Hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms. The crystal data and structure refinement parameters of complexes are listed in Table 1 while Table 2 lists selected bond distances and angles.

CCDC: 2276305, **1**; 2276307, **2**.

Table 1 Crystal data and structural refinement parameters for complexes **1** and **2**

Complex	1	2
Formula	$C_{17}H_{20}BCuF_4N_3O_2$	$C_{16}H_{16}CuN_4O_4$
Formula weight	448.71	391.87
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / nm	0.845 7(6)	0.809 6(4)
b / nm	1.738 4(11)	1.058 2(5)
c / nm	1.311 0(8)	1.929 1(10)
$\beta / (^\circ)$	99.443(12)	94.756(9)
V / nm^3	1.901(2)	1.647 1(15)
$D_c / (g \cdot cm^{-3})$	1.567	1.580
Z	4	4
Absorption coefficient / mm^{-1}	1.204	1.356
$F(000)$	916	804
Crystal size / mm	0.28×0.20×0.16	0.24×0.20×0.18
θ range / $(^\circ)$	1.96~25.01	2.12~26.42
Limiting indices	$-10 \leq h \leq 9, -18 \leq k \leq 20, -14 \leq l \leq 15$	$-10 \leq h \leq 9, -12 \leq k \leq 13, -15 \leq l \leq 24$
Reflection collected, unique	9 642, 3 343 ($R_{int}=0.086\ 0$)	9 229, 3 351 ($R_{int}=0.035\ 8$)
Reflection with $I > 2\sigma(I)$	2 009	2 467
Data, restraint, parameter	3 343, 68, 291	3 351, 2, 234
Goodness of fit on F^2	1.005	1.010
Final R indices [$I > 2\sigma(I)$]	$R_1=0.069\ 9, wR_2=0.174\ 5$	$R_1=0.035\ 5, wR_2=0.077\ 3$
R indices (all data)	$R_1=0.125\ 0, wR_2=0.209\ 4$	$R_1=0.060\ 4, wR_2=0.086\ 9$
Largest diff. peak and hole / $(e \cdot nm^{-3})$	793 and -991	336 and -422

Complex **1**: $w=1/[\sigma^2(F_o^2)+(0.123\ 5P)^2]$, with $P=(F_o^2+2F_c^2)/3$; Complex **2**: $w=1/[\sigma^2(F_o^2)+(0.041\ 6P)^2+0.447\ 0P]$, with $P=(F_o^2+2F_c^2)/3$.

Table 2 Selected bond distances (nm) and angles ($^\circ$) for **1** and **2**

Complex 1					
Cu1-N1	0.195 2(6)	Cu1-N3	0.202 0(5)	Cu1-O1	0.195 3(4)
Cu1-O2	0.228 0(6)	Cu1-O1 ⁱ	0.197 4(4)		

Continued Table 2

N1-Cu1-N3	91.8(2)	N1-Cu1-O1	175.3(2)	N1-Cu1-O1 ⁱ	99.7(2)
N1-Cu1-O2	88.3(2)	N3-Cu1-O2	101.5(2)	O1-Cu1-N3	92.6(2)
O1-Cu1-O1A	76.83(19)	O1-Cu1-O2	89.1(2)	O1A-Cu1-N3	156.0(2)
O1A-Cu1-O2	99.7(2)	Cu1-O1-Cu1 ⁱ	103.17(19)		
Complex 2					
Cu1-N1	0.202 0(2)	Cu1-N2	0.195 5(2)	Cu1-O1	0.192 29(18)
Cu1-O2	0.258 0(3)	Cu1-O1 ⁱⁱ	0.198 20(19)		
N2-Cu1-N1	92.48(9)	N2-Cu1-O1 ⁱⁱ	98.75(8)	O1-Cu1-N1	93.10(9)
O1-Cu1-N2	174.05(8)	O1-Cu1-O1 ⁱⁱ	77.03(8)	O1A-Cu1-N1	153.25(8)
O2-Cu1-N1	103.036(80)	O2-Cu1-N2	93.199(80)	O2-Cu1-O1	83.544(70)
O2-Cu1-O2 ⁱⁱ	100.494(74)	Cu1-O1-Cu1 ⁱⁱ	102.97(8)		

Symmetry codes: ⁱ $-x+1, -y+1, -z+2$ for **1**; ⁱⁱ $-x, -y+1, -z+1$ for **2**.

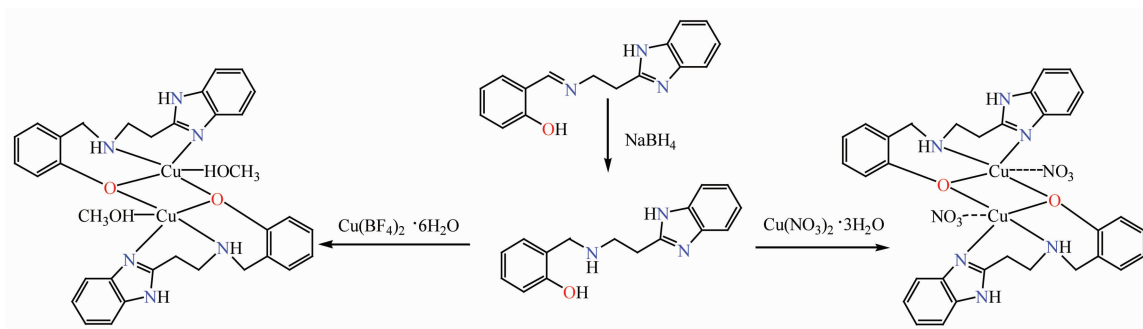
2 Results and discussion

2.1 Synthesis and characterization

The condensation of 2-(aminoethyl)-benzimidazole dihydrochloride in 1:1 molar ratio with salicylaldehyde afforded the Schiff bases, *N*-salicylidine-2-aminoethylbenzimidazole which on reduction with sodium borohydride readily produced the reduced Schiff base, HL. HL on reaction with copper(II) tetrafluoroborate hexahydrate and copper(II) nitrate trihydrate in 1:1 molar ratios yielded complexes **1** and **2**, respectively (Scheme 1). Unlike its Schiff base counterpart, the reduced Schiff base has flexible backbones. Two phenolic oxygen atoms bind two metals to form a dimer, in which one four-membered ring, four six-membered rings are formed as shown in Scheme 1.

The characteristic IR bands (4 000~400 cm^{-1}) for the free ligand, when compared with those of its copper (II) complexes, provided positive indications with regard to the bonding sites of the ligand. The

presence of one medium intensity broad band between 2 500 and 3 200 cm^{-1} in the free ligand hints toward the existence of hydrogen bonding between NH of benzimidazole and other electronegative atoms^[19]. The broad band remains almost unchanged in the two complexes, indicating that the N-H of benzimidazole ring does not participate in the coordination^[20]. In the spectrum of the free ligand the band of the stretching vibrational modes of the phenolic OH around 3 316 cm^{-1} , disappeared from the spectra of the two complexes indicating the deprotonation of the ligand. Additionally, the bands originating from the C-O stretching vibrations at 1 205 cm^{-1} , in the complexes exhibited positive shifts at 1 251 cm^{-1} for complex **1** and 1 256 cm^{-1} for complex **2**, respectively, denoting coordination through the phenolic oxygen of the ligand^[21]. Furthermore, the reduction of the imine group is very clearly indicated by the absence of the strong band due to imine vibration which appeared in the region of 1 620~1 650 cm^{-1} for the free ligand and the two complexes^[22]. Several new



Scheme 1 Synthesis of the reduced Schiff base ligand and the complexes **1** and **2**

bands presented in the region $400\sim600\text{ cm}^{-1}$ in the spectra of the complexes were assigned to the Cu-N and Cu-O stretching vibrations^[23].

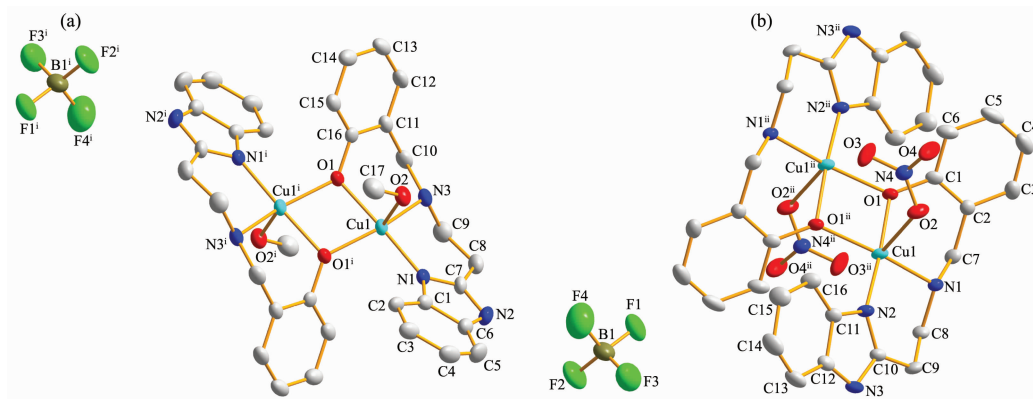
Characteristic stretching frequencies for the anions are observed. The presence of the bands at near $1\ 100$ and 522 cm^{-1} in complex **1** confirmed the presence of non-coordinated tetrafluoroborate anions and point to a lack of strong deviation from tetrahedral symmetry^[24]. Furthermore, the BF_4^- group vibration near $1\ 083\text{ cm}^{-1}$ splitting into a peak at $1\ 083\text{ cm}^{-1}$ and a shoulder at $1\ 063\text{ cm}^{-1}$ approximately, indicated BF_4^- anions involved hydrogen bonding, which is consistent with the crystal structures^[25]. Appearance of a strong sharp band at $1\ 384\text{ cm}^{-1}$ demonstrated the presence of nitrate in complex **2**^[26].

The electronic absorption spectra of the ligand HL and the two complexes in DMF were recorded at room temperature. UV bands at 275 and 285 nm were observed for the free ligand HL, which are characteristic of the benzimidazole group and arise from a $\pi\text{-}\pi^*$ transition. These were blue-shifted upon coordination and were observed at 272 and 278 nm for the two complexes^[27], respectively. The complexes display a broad $d\text{-}d$ band in the region of $560\sim680\text{ nm}$. The position of this band suggests that the geometry about each Cu(II) atom is best described as square pyramidal^[28]. In addition, one charge transfer band due to a LMCT transition between the bridging phenoxo and Cu(II) atoms in the region of $400\sim420\text{ nm}$ was also observed. Similar UV-Vis features have been previously observed for several related phenolate bridged

binuclear copper(II) complexes^[29].

2.2 Crystal structure

Fig.1 gives the crystal structures of **1** and **2** with atomic labeling scheme, respectively. X-ray diffraction studies revealed that both complexes **1** and **2** crystallize in monoclinic system with $P2_1/c$ space group. In complexes **1** and **2**, two phenoxo groups bridge two Cu(II) atoms giving the binuclear structure, containing an exactly planar Cu_2O_2 core owing to the crystallographic inversion symmetry. The stereochemistry around each Cu(II) is best described as a distorted square pyramidal with a value of τ being 0.31 for **1** and 0.35 for **2**, respectively. The equatorial positions are occupied by benzimidazolyl nitrogen atom, the amine nitrogen atom, phenolate oxygen atom and the bridging phenoxo oxygen atom from the symmetry related molecule. The Cu-O bridge distances are in the range of $0.192\ 29(18)\sim0.198\ 20(19)\text{ nm}$, with Cu1-O1-Cu1^i bridging angles of $103.17(19)^\circ$ for **1** and Cu1-O1-Cu1^{ii} of $102.97(8)^\circ$ for **2**, falling within the normal range for diphenoxo-bridged copper(II) complexes^[3-4,12-14]. The average Cu-N_{imine} and Cu-N_{benzimidazole} bond lengths are $0.202\ 0$ and $0.195\ 4\text{ nm}$, which are similar to the Cu-N bond distance found for similar copper/reduced Schiff system and copper/benzimidazole system, respectively^[27,30]. In **1**, the axial position is occupied by oxygen O2 of the monodentate coordinating methanol molecule with the Cu-O2 distance of $0.228\ 0(6)\text{ nm}$, suggesting a weak axial interaction. While in **2**, the fifth position is occupied by a nitrate oxygen at a semi-coordination distance of $0.258\ 0\text{ nm}$ for Cu1-O2 ,



H atoms are omitted for clarity; Symmetry codes: $i: -x+1, -y+1, -z+2$ for **1**; $ii: -x, -y+1, -z+1$ for **2**

Fig.1 Molecular structures of **1** (a) and **2** (b) with 30% probability level along with the atom numbering scheme

Equatorial bond angles deviate from the expected value of 90° , the largest deviation being 13.17° , and the sum of the equatorial angles at Cu(II) are nearly 360° for both **1** and **2**. The Cu \cdots Cu distances between the two metal ions are 0.308 5 nm for **1** and 0.305 6 nm for **2**, which are almost close to other symmetric bis(μ -phenoxo) bridged binuclear copper(II) complexes^[3-4,12-14].

In complex **1**, the binuclear moieties are linked with pairs of tetrafluoroborate anions by hydrogen bonds into 1D chain (Fig.2). Each tetrafluoroborate acts as hydrogen bond acceptor and forms two hydrogen bonds with one methanol molecule and one benzimidazole NH group (N2–H2A \cdots F4 and O2–H2 \cdots F1ⁱⁱⁱ, Symmetry codes: ⁱⁱⁱ $x, -y+1, -z+1$). The interatomic distances of N2 \cdots F4 and O2 \cdots F1ⁱⁱⁱ are 0.280 5 and

0.288 9 nm, respectively, both being in the range of moderate hydrogen bond distances. The H \cdots F separations are 0.212 3 and 0.213 1 nm and hydrogen bond angles are 135.89° and 137.96° , respectively.

In complex **2**, each nitrate acts as hydrogen bond acceptor and forms two hydrogen bonds with one amine group (N1–H1 \cdots O2^{iv}, Symmetry codes: ^{iv} $-x+1, -y+1, z+1$) and one benzimidazole NH group (N3–H3A \cdots O4^v, Symmetry codes: ^v $x, 0.5-y, z-0.5$) (Fig. 3a). The interatomic distances of N1 \cdots O2^{iv} and N3 \cdots O4^v are 0.315 6 and 0.288 5 nm, respectively. The H \cdots O separations are 0.238 2 and 0.204 9 nm and hydrogen bond angles are 151.03° and 165.33° , respectively. As a result, a 3D hydrogen-bonded network is formed (Fig.3b).

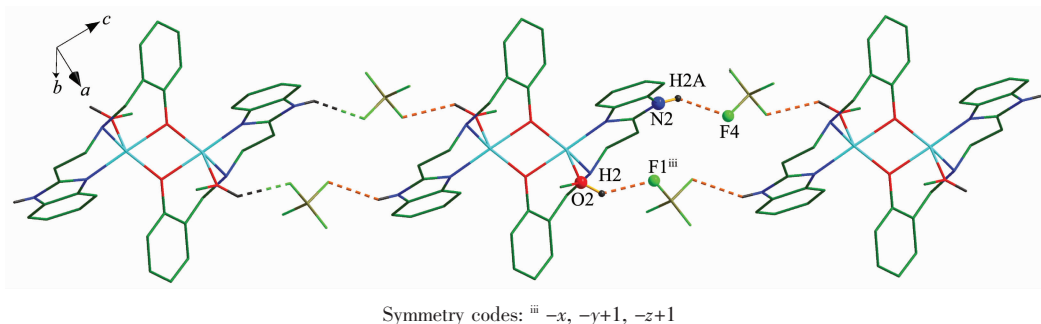


Fig.2 One dimensional chain in **1** formed through N–H \cdots F and O–H \cdots F hydrogen-bonding interactions along the *a*-axis

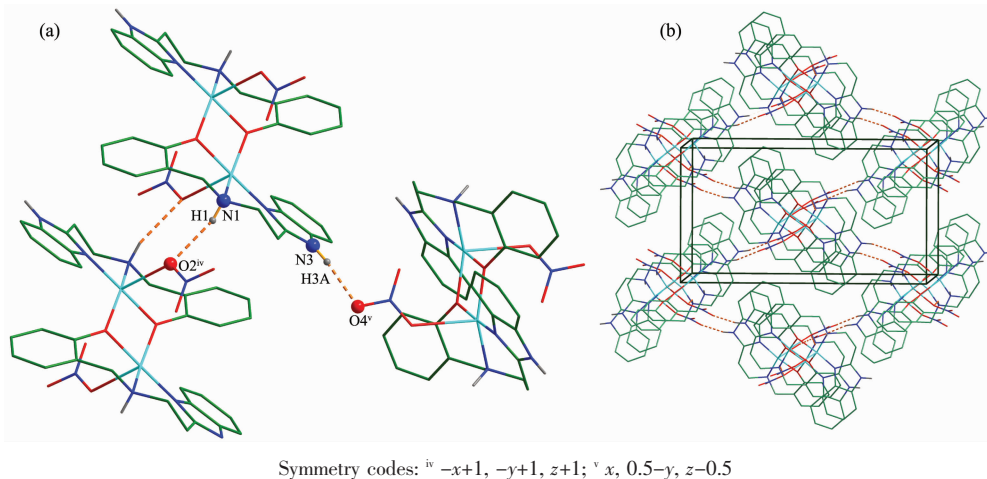


Fig.3 (a) Packing diagram showing the hydrogen-bonded interactions in **2**; (b) 3D framework for **2** built by hydrogen bond

2.3 Electrochemical characterization

Cyclic voltammetric studies were carried out for the copper(II) complexes at $1 \text{ mmol} \cdot \text{L}^{-1}$ concentration, dissolved in DMF containing $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBAP as a supporting electrolyte. The cyclic voltammetric data

for the binuclear complexes **1** and **2** are shown in Table 3. The cyclic voltammograms (CV) of **1** and **2** were almost identical, suggesting similar environments around the Cu(II) ions in **1** and **2** (Fig.4). This is consistent with the single crystal X-ray diffraction

Table 3 Cyclic voltammetric data for 1 mmol·L⁻¹ solution of **1** and **2** in DMF containing 0.1 mol·L⁻¹ TBAP as supporting electrolyte

Complex	E_{pc}^1 / V	E_{pa}^1 / V	$E_{1/2}^1$ / V	ΔE^1 / mV	E_{pc}^2 / V	E_{pa}^2 / V	$E_{1/2}^2$ / V	ΔE^2 / mV	K_{con}
1	-0.47	-0.35	-0.41	120	-0.91	-0.78	-0.85	130	2.73×10^7
2	-0.41	-0.36	-0.38	50	-0.92	-0.78	-0.85	140	1.91×10^8

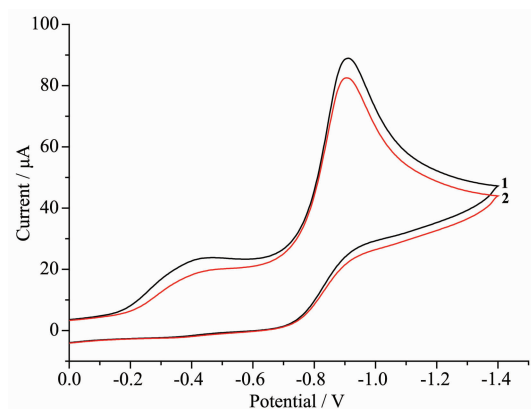


Fig.4 CV of the complexes **1** and **2** in DMF

results. The CV of the two complexes showed two quasi-reversible reduction waves at $E_{1/2}^1 = -0.41$ V and $E_{1/2}^2 = -0.85$ V for **1** and $E_{1/2}^1 = -0.38$ V and $E_{1/2}^2 = -0.85$ V for **2**. The first process corresponds to the $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightleftharpoons \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ reduction couple and the second process corresponds to the $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \rightleftharpoons \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ reduction couple. The negative potentials observed in **1** and **2** are due to the factors such as the steric hindrance of the benzimidazole ring and the hard nature of the phenoxide atoms in the ligand, which will stabilize the copper(II) oxidation state, making the Cu(II) to Cu(I) conversion difficult. Similar observations are also reported for benzimidazole copper complexes and phenoxo copper complexes, which reduced in the range of $-0.87 \sim -1.40$ V^[31-33].

The observed two well-separated one electron reductions for **1** and **2** can be substantiated from a stability consideration of the mixed-valence species, $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$. The stability of mixed valence form can be quantified by the comproportionation equilibrium constant (K_{con}), $\lg K_{con} = 16.9(\Delta E_{1/2})$, where $\Delta E_{1/2} = (E_{1/2}^1 - E_{1/2}^2)$ ^[34]. It is observed that the larger $\Delta E_{1/2}$ is, the greater is the stability of the mixed-valence species with respect to comproportionation. The magnitude of the constant, K_{con} was determined to be 2.73×10^7 for **1** and 1.91×10^8 for **2**, respectively, which can be compared

to the value of K_{con} for phenoxo bridge copper(II) complexes^[32]. The large K_{con} values indicated that the addition of a second electron is more difficult than of the first electron and the $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ mixed valence species is stable with respect to comproportionation^[35].

3 Conclusions

In this work, one unsymmetrical tridentate Schiff base ligand has been reduced by NaBH_4 . The reduced ligand was more flexible compared to the Schiff base and used to form two phenoxo bridged binuclear copper complexes, which differ by the anions. The Addison parameters (τ) of both complexes indicated that the environment around the copper ions is a distorted square pyramidal geometry. The binuclear moieties are linked with pairs of tetrafluoroborate anions by the $\text{N2-H2A} \cdots \text{F4}$ and $\text{O2-H2} \cdots \text{F1}^{\text{iii}}$ hydrogen bonds in complex **1** while in complex **2** a 3D hydrogen-bonded network is formed by the $\text{N1-H1} \cdots \text{O2}^{\text{iv}}$ and $\text{N3-H3A} \cdots \text{O4}^{\text{v}}$ hydrogen bonds. The two complexes show two quasi-reversible one electron reduction processes in cyclic voltammetry.

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