Synthesis, Characterization, Crystal Structure, and Electrochemical Property of Copper(II) Complexes with Schiff Bases Derived from 5-Halogenated Salicylaldehyde and Amantadine¹

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Abstract—A mixture of copper(II) chloride dihydrate and ligands derived from amantadine and 5-halogenated salicylaldehyde in anhydrous methanol generated two novel complexes $C_{34}H_{38}Cl_2CuN_2O_2$ (I) and $C_{34}H_{38}Br_2CuN_2O_2$ (II), respectively. The complexes were characterized by melting point, elemental analysis, molar conductance, IR, UV-Vis, and single-crystal X-ray diffraction (CIF files nos. 1435429 (I), 1435430 (II)). Single-crystal X-ray diffraction analysis reveals that both complexes crystallize in monoclinic system, $P_{2_1/c}$ space group. Each asymmetric unit consists of two mononuclear copper(II) complex molecules and each complex molecule includes one copper(II) atom two corresponding deprotonated ligands. The central copper(II) atom is four-coordinated via two nitrogen atoms and two oxygen atoms from the corresponding Schiff base ligands, forming a distorted tetrahedral geometry. Electrochemical properties of the complexes were studied by cyclic voltammetry.

Keywords: copper(II) complexes, amantadine, Schiff base, synthesis, crystal structure, cyclic voltammetry **DOI:** 10.1134/S1070328417110033

INTRODUCTION

Recent years, Schiff bases have been widely investigated owing to their biological activity [1, 2]. Schiff bases also brought about many metal-based pharmaceuticals for their complexation characteristics [3]. Copper is one of the prevalent trace elements and an important enzyme active site in human body [4, 5]. Copper(II) complexes have a wider range of coordination geometries than any other transition metal ions [6]. Some copper(II) complexes exhibit significantly enhanced antibacterial and antifungal activity as compared to their corresponding Schiff base ligands [7].

In many countries, amantadine (SymmetrelTM) and rimantadine (FlumadineTM) have been regarded as being efficacious for the prevention and treatment of infections with influenza A because they could inhibit the early stages of virus replication by blocking

the ion channel, which formed by the M2 protein of influenza A viruses [8-12]. Salicylaldehyde and its derivatives, especially one or more halo-atoms on the benzene ring, exhibited antibacterial and antiviral activity and were used to produce efficient herbicides, insecticides and fungicides [13–16]. In view of these points above, we designed and managed to synthesize a series of complexes containing both copper(II) ions and the ligands derived from amantadine and halogenated salicylaldehyde. As an extension of our previous work on metal complexes with bulky Schiff bases [17– 23], in this work, two novel four-coordinated copper(II) complexes bis(2-(1-adamantyliminomethyl)-4-chlorophenolato-N,O)-copper(II) C₃₄H₃₈Cl₂Cu- N_2O_2 (I) and bis(2-(1-adamantyliminomethyl)-4bromophenolato-N,O)-copper(II) C₃₄H₃₈Br₂Cu- N_2O_2 (II) with ligands derived from amantadine and 5-halogenated (Cl, Br) salicylaldehyde (HL¹, HL²), respectively, were synthesized.

¹ The article is published in the original.





Their structures were characterized by the means of IR, UV-Vis, elemental analysis, molar conductance, and single-crystal X-ray diffraction. More over, the electrochemical behavior of the complexes was investigated by cyclic voltammetry in dimethylformamide (DMF). The biological activity studies of two complexes are in progress and will be reported later.

EXPERIMENTAL

Materials and methods. All chemicals and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd, they were analytical grade and used without any further purification. Elemental analysis was carried out on Perkin Elmer Flash EA 1112. Chemical shifts (δ) for ¹H NMR spectra were recorded at 300 MHz on a Varian Mercury-Vx300 spectrometer in CDCl₃ solvent containing TMS as an internal standard. IR spectrum was scanned in the range 4000-400 cm⁻¹ with KBr pellets on a Nicolet NEXUS FT-IR 5700 spectrophotometer. UV-Vis spectrum was measured on a Perkin Elmer Lambda 25 spectrophotometer. Melting points were measured on a WRS-1B micro melting point apparatus which were uncorrected. The molar conductance of the complexes in DMF (1.0 \times 10⁻³ M) was measured on a DDS-11A conductometer.

Synthesis of ligands. Two Schiff base ligands were prepared analogously to the literature [19]. Adamantaneamine 3.03 g (0.02 mol) in 20 mL anhydrous alcohol was added to a solution 2.0 mM 5-halogenated salicylaldehyde in 50 mL anhydrous alcohol. The mixture was refluxed for 1 h and then cooled to room temperature. A colored solid was filtered off and washed with anhydrous alcohol three times and air dried.

HL¹: 440 mg, yield 76%, yellowish powder, m.p. 131.5–132.2°C. UV-Vis (hexane, $c = 0.67 \times 10^{-4} \text{ mol/L}$): $\lambda_{\text{max}} = 228$ (1.614), 254 (0.597), 328 (0.239); $\lambda_{\text{min}} = 244$ (0.496), 290 (0.032). IR (KBr; v, cm⁻¹): 3502 w, 2917 s, 2848 m, 1629 s, 1607 m, 1576 m, 1512 w, 1484 s, 1455 w, 1389 w, 1369 w, 1343 m, 1311 w, 1278 s, 1226 w, 1196 m, 1121 m, 1103 m, 1089 s, 983 w, 944 w, 916 w, 877 m, 825 s, 792 m, 752 m, 694 w, 649 w, 565 w. ¹H NMR (CDCl₃; 300 MHz; δ , ppm): 14.51 (s., 1H, Ar–OH); 8.24 (s., 1H, CH=N); 6.87

(d., ${}^{3}J = 9.6$, 1H, Ar–H); 7.27–7.15 (m., 2H, Ar–H); 2.19 (s., 3H, CH, adam. H); 1.83 (s., 6H, CH₂, adam. H); 1.79–1.67 (m., 6H, CH₂, adam. H).

For C ₁₇ H ₂₀ NOCl	(M = 289.80)		
Anal. calcd., %:	C, 70.46;	H, 6.96;	N, 4.83.
Found, %:	C, 70.40;	H, 7.01;	N, 4.80.

HL²: 521 mg, yield 78%, yellow powder, m.p. 142.5–143.2°C. UV-Vis (hexane, $c = 0.67 \times 10^{-4}$ mol/L): $\lambda_{max} = 230$ (1.460), 252 (0.522), 328 (0.199); $\lambda_{min} = 248$ (0.494), 290 (0.036). IR (KBr; v, cm⁻¹): 3463 w, 2913 s, 2848 m, 2349 w, 1627 s, 1604 m, 1571 w, 1480 s, 1345 w, 1310 w, 1279 m, 1192 m, 1118 m, 1088 m, 985 w, 881 m, 819 m, 788 w, 744 w, 626 w, 561 w. ¹H NMR (CDCl₃, 300 MHz; δ , ppm): 14.55 (s., 1H, Ar–OH), 8.23 (s., 1H, CH=N), 7.36 (s., 1H, Ar–H); 7.34 (d.d., ³*J* = 8.7, ⁴*J* = 2.4, 1H, Ar–H); 6.83 (d.d., ³*J* = 8.1, ⁴*J* = 1.2, 1H, Ar–H); 2.19 (s., 3H, CH, adam. H); 1.83–1.67 (m., 12H, CH₂, adam. H).

For
$$C_{17}H_{20}NOBr$$
 (*M* = 334.25)

Anal. calcd., %:	C, 61.09;	Н, 6.03;	N, 4.19.
Found, %:	C, 61.01;	H, 6.05;	N, 4.10.

Synthesis of complexes. Two complexes were prepared in a similar procedure starting from their corresponding newly synthetic Schiff base ligands, NaOH and copper(II) chloride dihydrate in anhydrous methanol, respectively.

A solution of NaOH (80 mg, 2.0 mmol) in 10 mL of anhydrous methanol was added gradually to a solution of a ligand (2.0 mmol) in 10 mL of anhydrous methanol. The mixture was stirred at 30°C for 10 min, then copper(II) chloride dihydrate (170 mg, 1.0 mmol) in 10 mL of anhydrous methanol was added dropwise. The mixture was refluxed for about 1.5 h, and then cooled to room temperature. The pearlescent solids were suction filtered, washed with small amount anhydrous methanol and dried under vacuum.

I: 372 mg, yield 58%, brown powder, m.p. 225.8°C. UV-Vis (hexane, $c = 0.25 \times 10^{-4} \text{ mol/L}$): $\lambda_{\text{max}} = 258$ (0.942), 324 (0.357), 388 (0.627), 502 (0.112); $\lambda_{\text{min}} =$ 304 (0.311), 344 (0.284), 466 (0.105). IR (KBr; v, cm⁻¹): 2907 s, 2850 m, 2341 m, 1610 s, 1528 m, 1461 s, 1388 m, 1344 w, 1325 m, 1269 w, 1242 w, 1189 m, 1173 m, 1131 w, 1105 w, 1075 m, 931 w, 874 w, 819 m, 785 w, 756 w, 694 w, 661 w, 550 w.

For $C_{34}H_{38}N_2O_2Cl_2Cu$ ($M = 641.10$)			
Anal. calcd., %:	C, 63.64;	Н, 5.93;	N, 4.37.
Found, %:	C, 63.73;	Н, 5.94;	N, 4.36.

II: 415 mg, yield 57%, taupe powder, m.p. 207.9°C. UV-Vis (hexane, $c = 0.25 \times 10^{-4}$ mol/L): $\lambda_{max} = 258$ (0.907), 317 (0.390), 385 (0.647), 501 (0.112); $\lambda_{min} = 309$ (0.387), 343 (0.342), 467 (0.105). IR (KBr; v, cm⁻¹): 2904 m, 2849 w, 1608 s, 1542 w, 1524 m, 1461 s, 1387 m, 1324 m, 1267 w, 1189 m, 1172 m, 1132 w, 1105 w, 1072 m, 926 w, 874 w, 818 m, 747 w, 647 w, 606 w, 551 w.

For C ₃₄ H ₃₈ Br ₂ Cu	$N_2O_2 (M = 7)$	(30.02)	
Anal. calcd., %:	C, 55.89;	H, 5.21;	N, 3.84.
Found, %:	C, 55.93;	Н, 5.27;	N, 3.83.

X-ray crystallography. The crystals of two complexes suitable for X-ray analysis developed from a solution of $CH_3OH-CH_2Cl_2$ (1 : 1 v/v) through slow evaporation. The crystallographic data collections were conducted on a Bruker Smart Apex II CCD with graphite-monochromated Mo K_{α} radiation (λ = 0.71073 Å) using the ω -scan technique. The data were integrated by using the SAINT program, which also corrected the intensities for Lorentz and polarization effect [24]. An empirical absorption correction was applied using the SADABS program [25]. The structures were solved by direct methods using the program SHELXS-97 and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix leastsquares technique using the SHELXL-97 crystallographic software package [26]. The hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELXL-97 crystallographic software package. The details of the crystal parameters, data collection and refinement are summarized in Table 1. Selected bond lengths and angles with their estimated standard deviations are given in Table 2. The molecular structures for the complexes were generated with the XP feature of SHELXTL.

Electrochemical studies. The complexes were investigated by cyclic voltammetry. They were prepared with concentration of 1.0×10^{-3} mol/L in DMF. Electrochemical data was collected using a CHI 660E Electrochemical Workstation (Shanghai Chenhua). A three-electrode cell was used for all electrochemical experiments. This system consisted of glassy carbon (working), platinum wire (counter) and Ag/AgCl (reference) electrodes. Test solutions contained 1 mM copper(II) complex and 0.15 M tetrabutylammonium perchlorate (TBAP) in DMF. During the cyclic voltammetry measurement, a constant flux of N_2 was kept over the solution surface in order to check the diffusion of atmospheric oxygen into the solution. All measurements were carried out at room temperature. The electroactivity range for this system was 3.0 V (from -1.5 to 1.5 V vs. SCE) at a scan rate of 100 mV s⁻¹. The data were integrated by using the OriginPro 8 program.

RESULTS AND DISCUSSION

By analyzing the presence of C, H, and N contents, it turned out to be that both complexes consist of one copper(II) and two corresponding deprotonated ligands. All compounds were soluble in both dichloromethane and chloroform; however, the complexes were less soluble than the ligands in other solvents such as ethanol, tetrahydrofuran, benzene and ethyl acetate. The molar conductance values (Λ_M) for I and II were 3.50 and 4.11 S cm² mol⁻¹, which were much less than 18 S cm² mol⁻¹, indicating non-electrolyte behavior of the complexes [27].

The OH stretching vibration of phenol was mostly reported to be 3657 cm⁻¹ [28, 29], which red-shifted to 3502 and 3463 cm^{-1} in free ligands, indicating that intramolecular hydrogen bonding was formed. These bands disappeared after the coordination of copper, proving that the hydrogen of phenol was substituted with the copper(II) ion and these bands vanished naturally in complexes. The spectra of the free ligands HL^1 and HL^2 showed strong bands at 1629 and 1627 cm^{-1} which assigned to the C=N stretching vibration. These bands red-shifted towards lower wavenumber of 1610 cm^{-1} for I and 1608 cm^{-1} for II in compared with ligands indicating a coordination of azomethine nitrogen to chelation with the copper(II) ion. The spectra of ligands displayed strong bands at 1278 and 1279 cm⁻¹, was assigned to the C–O stretching vibration. These bands also occurred in complexes at lower frequency 1173 and 1172 cm⁻¹. The absorption peak at 550 cm⁻¹ for I and 551 cm⁻¹ for II were attributed to Cu-O vibration, indicating that oxygen atoms of the ligands were coordinated to metal ions.

UV-Vis spectra of the ligands are shown in Fig. 1. Two complexes exhibited significant changes in the ultraviolet and visible spectra compared to their corresponding ligands. Bands at 228 nm for HL¹ and 258 nm for I were attributed to $\pi - \pi^*$ transitions of the benzene ring. Bands at 328 nm for HL¹ were attributed to $n-\pi^*$ transitions of the $p-\pi$ conjugation. Bands at 324 nm for I were assigned to $n-\pi^*$ transitions from the ligands to copper(II) $(n-\pi^*$ transition) of N \rightarrow Cu and O \rightarrow Cu. Bands at 230 nm for HL² and 258 nm for II were attributed to $\pi-\pi^*$ transitions of the benzene ring. Bands at 328 nm for HL² and 258 nm for II were attributed to $\pi-\pi^*$ transitions of the benzene ring. Bands at 328 nm for HL² and 258 nm for HL and 258 nm for HL² and 258 nm for II were attributed to $\pi-\pi^*$ transitions of the benzene ring. Bands at 328 nm for HL² mere attributed to $n-\pi^*$ transitions of the benzene ring. Bands at 328 nm for HL² mere attributed to $n-\pi^*$ transitions of the benzene ring. Bands at 328 nm for HL² mere attributed to $n-\pi^*$ transitions of the $p-\pi$ conjugation. Bands at 317 nm

Table 1.	Crystallographic	data and and	structure refinement	for complexes I and II
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Derometer	Value			
Parameter	Ι	П		
Fw	641.10	730.02		
Crystal size, mm	$0.40 \times 0.30 \times 0.20$	$0.18 \times 0.16 \times 0.14$		
Crystal system	Monoclinic	Monoclinic		
Space group	$P2_1/c$	$P2_{1}/c$		
a, Å	21.8285(17)	21.944(10)		
b, Å	11.5879(7)	11.620(5)		
<i>c</i> , Å	25.2549(17)	25.549(11)		
β, deg	106.344(7)	106.767(4)		
V, Å ³	6130.0(7)	6238(5)		
Ζ	8	8		
<i>F</i> (000)	2680	2968		
Index ranges	$-25 \le h \le 19,$	$-24 \le h \le 25,$		
	$-13 \le k \le 12,$	$-13 \le k \le 137$,		
	$-25 \le l \le 30$	$-30 \le l \le 30$		
ρ , g cm ⁻³	1.389	1.555		
μ, mm ⁻¹	0.920	3.300		
Reflections collected/unique (R_{int})	23816/10783 (0.042)	33736/10657 (0.056)		
Data/restraints/parameters	10783/0/739	10657/0/739		
GOOF	1.126	1.058		
<i>Т</i> , К	298(2)	293(2)		
$R_1/wR_2 (I \ge 2\sigma(I))^*$	0.0923/0.1794	0.0763/0.1912		
R_1/wR_2 (all data)	0.1307/0.1962	0.1028/0.2130		
Largest difference peak and hole, $e \text{ Å}^{-3}$	2.17/-0.58	2.62/-0.75		

* $R_1 = \Sigma ||F_0| - |F_c||/|F_0|; wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}.$

for **II** were assigned to $n-\pi^*$ transitions from the ligands to copper(II) $(n-\pi^* \text{ transition})$ of N \rightarrow Cu and O \rightarrow Cu. Broad peaks at 388 nm for I and 385 nm for **II** could be caused by $d \rightarrow d^*$ transition of copper(II), which could not be found in the ligands. These changes between the ligands and complexes, as we predicted, displayed different colors due to distinguishing structural features themselves.

The molecular structures for the complexes are shown in Fig. 2. The central copper(II) atom in I and II lies on a twofold rotation axis and is bonded to the oxygen and nitrogen donor atoms of the two bidentate ligands molecules in a *trans*-arrangement. The geometry around copper(II) in I and II is intermediated between square planar and tetrahedral, where the dihedral angle between the two coordination planes defined by O(1)Cu(1)N(1) and O(2)Cu(1)N(2) is 51.35° for I, by O(1)Cu(1)N(1) and O(2)Cu(1)N(2) is 52.12° for II [30]. The two phenyl rings are in the intersecting planes with a dihedral angle defined by C(1)C(6)C(5) and C(19)C(18)C(23) of 55.54° for I and defined by C(3)C(4)C(5) and C(19)C(20)C(21)of 54.56° for II. Bond angles also show that the coordination geometry about the copper atom in I is distorted tetrahedral ($\tau_4 = [360 - (\alpha + \beta)]/141^\circ = 0.57$) with O(2)Cu(1)O(1) (α) and N(2)Cu(1)N(1) (β) angles of $142.10(3)^{\circ}$ and $137.44(9)^{\circ}$, respectively. Complex II is distorted tetrahedral ($\tau_4 = [360 - (\alpha +$ β)]/141° = 0.54) [31] with N(2)Cu(1)N(1) (α) and O(2)Cu(1)O(1) (β) angles of 142.60(2)° and $141.90(2)^{\circ}$, respectively. Complexes I and II are expected for a typical Schiff base ligand (containing a short C=N bond distance of 1.289 Å for I and 1.284 Å for II) coordinated to a metal centre, where the imine form is predominant. The distinctly shortened Cu(1)-O(1) and elongated Cu(1)-N(1) bonds in I and II are 1.873–1.900 and 1.992–2.015 Å, respectively (the normal bond length of them are about 1.940 and 1.960 Å), so the coordination geometry around the copper(II) ion reflects Jahn-Teller effect [32]. The distances of two neighboring copper atoms along the y axis are 6.895 Å in I and 6.839 Å in II. The bidentate coordi-

Bond	<i>d</i> , Å	Bond	d, Å
	1	I	1
Cu(1)–O(1)	1.878(5)	Cu(2)–O(3)	1.880(5)
Cu(1)–O(2)	1.891(5)	Cu(2)–O(4)	1.900(5)
Cu(1)–N(1)	2.009(6)	Cu(2)–N(3)	2.000(6)
Cu(1)–N(2)	2.015(6)	Cu(2)–N(4)	2.010(6)
N(1)–C(7)	1.286(8)	N(3)–C(41)	1.292(8)
N(2)-C(24)	1.289(8)	N(4)-C(58)	1.294(9)
	I	й	1
Cu(1)–O(1)	1.888(5)	Cu(2)–O(3)	1.873(5)
Cu(1)–O(2)	1.880(5)	Cu(2)–O(4)	1.891(5)
Cu(1)–N(1)	2.009(5)	Cu(2)–N(3)	1.995(6)
Cu(1)–N(2)	1.992(5)	Cu(2)–N(4)	2.012(5)
N(1)–C(7)	1.284(8)	N(3)–C(41)	1.296(8)
N(2)-C(24)	1.300(8)	N(4)-C(57)	1.280(8)
Angle	ω, deg	Angle	w, deg
		I	
O(1)Cu(1)O(2)	142.1(3)	O(3)Cu(2)O(4)	141.5(3)
O(1)Cu(1)N(1)	93.6(2)	O(3)Cu(2)N(3)	93.8(2)
O(1)Cu(1)N(2)	98.5(2)	O(3)Cu(2)N(4)	98.8(2)
O(2)Cu(1)N(2)	95.3(2)	O(4)Cu(2)N(4)	95.4(2)
O(2)Cu(1)N(1)	95.9(2)	O(4)Cu(2)N(3)	95.9(2)
N(1)Cu(1)N(2)	143.7(2)	N(3)Cu(2)N(4)	143.2(2)
	·	Ш	
O(1)Cu(1)O(2)	141.9(2)	O(3)Cu(2)O(4)	141.5(2)
O(1)Cu(1)N(2)	96.2(2)	O(3)Cu(2)N(4)	98.4(2)
O(1)Cu(1)N(1)	95.5(2)	O(3)Cu(2)N(3)	94.0(2)
O(2)Cu(1)N(1)	98.2(2)	O(4)Cu(2)N(3)	96.1(2)
O(2)Cu(1)N(2)	94.1(2)	O(4)Cu(2)N(4)	95.8(2)
N(1)Cu(1)N(2)	142.6(2)	N(3)Cu(2)N(4)	142.5(2)

Table 2. Selected bond length (Å) and angles (deg) in complexes I and II



Fig. 1. UV-Vis spectra of complexes I (a) and II (b) (hexane, $c = 2.5 \times 10^{-5} \text{ mol/L}$).



Fig. 2. Molecular structures of I (a) and II (b). Thermal ellipsoids are drawn at 50% probability.

nation mode of complexes refrains themselves from forming intramolecular hydrogen bonds because of the deprotonated ligands, but there also exists two sixmembered rings through a copper(II) ion, two oxygen atoms and two nitrogen atoms in I and II [33]. Two complexes are found not to possess intermolecular hydrogen bonding in stacking, however the intermolecular aromatic $\pi \cdots \pi$ interaction is presented between approximate parallel phenyl rings from different complex molecules (Fig. 3). The distances between centroids of two phenyl rings are 3.671 Å for I and 3.647 Å for II.

The study of the electrochemical behavior of I and II was carried out in DMF with TBAP as supporting



Fig. 3. Intermolecular aromatic $\pi \cdots \pi$ interaction for I (a) and II (b). Hydrogens are omitted for clarity.

electrolyte. The cyclic voltammogram of I (-1.5 to 1.5 V) at a scan rate of 100 mV s⁻¹ shows a quasireversible peak in the negative region, characteristic of the Cu(II) \rightarrow Cu(I) couple at $E_{pc} = -0.875$ V of peak A with associated anodic peak at $E_{\rm pa} = -0.7232$ V for Cu(I) \rightarrow Cu(II) of peak B. The $\Delta E_{\rm p} = (E_{\rm pa} - E_{\rm pc})$ value was 151.8 mV and the $i_{\rm pa}/i_{\rm pc} = 1.72$ relationship was far from unity [34]. This finding shows the quasi-reversibility of this redox process. It's been reported that the Cu(II)L₂/[Cu(I)L₂] reaction in most CuN₂O₂ coordination complexes is quasi-reversible in nature due to the fact that the [Cu(I)L₂] species are chemically decomposed to a copper ion, which subsequently is reduced to copper metal [35]. Similar results were obtained for II (with $E_{\rm pc} = -1.1759$ V, $E_{\rm pa} = -1.0381$ V, $\Delta E_{\rm p} = 139.9$ mV, $i_{\rm pa}/i_{\rm pc} = 1.861$). In the Fig. 4, two oxidation peaks were also observed.

Thus, two novel complexes were obtained from copper(II) chloride dihydrate and two ligands derived from amantadine and 5-halogenated salicylaldehyde, respectively. The electrochemical properties of the copper(II) complexes revealed the quasi-reversible one electron transfer redox process. Single-crystal X-ray diffraction analysis reveals that both complexes consist of one copper(II) and two deprotonated Schiff base ligands. Each Schiff base ligand serves as a bidentate ligand coordinating through an oxygen atom and a nitrogen atom to copper(II) atom. The geometry around copper(II) atom in complexes is distorted square planar.

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Fig. 4. Cyclic voltammogram for complexes I (a) and II (b) in DMF solution.

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