

Synthesis and characterization of bidentate mixed ligands of copper(II) complexes

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Abstract : Mixed ligand transition metal complexes play a significant role in biological processes by interacting with small molecules and activating the enzymes for nuclease activity. Two mixed ligand copper(II) complexes [Cu(5-nsal)(bipy)(ClO₄)] (1) and [Cu(2-hnap)(bipy) (ClO₄)] (2) (bipy = 2,2'-bipyridyl, 5-nsal = 5-nitrosalicylaldehyde and 2-hnap = 2-hydroxynaphthaldehyde) were successfully synthesized and physico-chemically characterized. The X-ray quality single crystals of copper(II) complexes showed that the copper atom was penta-coordinated with square- pyramidal geometry. The physicochemical characterizations of the copper(II) complexes also confirmed the formation of anticipated structures. The redox potentials of the complexes assessed by cyclic voltammetry showed a quasi-reversible redox behavior consistent with Cu(II)/Cu(I) reduction in the cathodic region.

(Keywords: Mixed ligand complexes; Solid state structures; Electronic spectra)

Introduction

Since the modern era of pharmacology, there exists a great scope for design of suitable new species for biomolecular interactions in the field of drug discovery. In the human body, the effect of a drug is mediated by its interactions with biological macromolecules like DNA, RNA and proteins¹⁻³. DNA being a storage and carrier molecule of genetic information, it is the major target for drug interaction as the DNA-bound drugs interfere strongly with transcription and/or replication of the cell. The first-row transition metal complexes were known for their stronger DNA interaction, especially copper due to its role

as a catalytic co-factor in cell physiology^{4,5}. Copper(II) complexes of mixed-ligands possess probable synergistic activity towards drug molecules and exhibit abundant biomolecular interactions⁶⁻⁸.

In mixed ligands, O, O chelating 2-hydroxy aldehydes and N, N chelating 2,22 - bipyridine, 1,10-phenanthroline, 2,22 - dipyridylamine ligands have been applied in both pure and applied chemistry⁹⁻¹². The mixed-ligand complexes show a wide range of applications in various medical fields such as biochemistry, toxicology and pharmacology^{13,14}. The hydroxy aldehydes ligands were monoanionic, the electron-rich aromatic system having strong coordination sites through oxygen and the bipyridyl ligands are rigid planar; hydrophobic [15], the electron-poor heteroaromatic system in which the nitrogen atoms were appropriately positioned to favour cation binding¹⁶.

The complexes of these type of ligands were proven as efficient DNA cleaving agents, novel anticancer agents and possess efficient antimicrobial properties¹⁷⁻¹⁹. In our previous studies, we reported that the electron withdrawing group on salicylaldehyde ligands result in greater biological activity than electron donating substituent and copper (II) complexes strongly influence on the interaction with biomolecules²⁰. In this current contribution, we investigate the influence of steric parameters and coordination chemistry of these compounds. Thus, in this article we report on the synthesis of

two new copper(II) based mixed ligand complexes bearing nitro salicylaldehyde/hydroxy naphthaldehyde and their bimolecular interactions.

Experimental

Materials used

Analytical reagent (AR) grade chemicals were used without any further purification. The commercial ethanol solvent was purified by standard procedures and other solvents of AR grade were used as received. The 5-nitrosalicylaldehyde (5-nsal) were purchased from Sigma-Aldrich (India); 2-hydroxynaphthaldehyde (2-hnap) and 2,2'-bipyridine (bipy) were purchased from Alfa Aesar (India).

Instrumentation

The UV-Visible spectra and absorption titrations for all complexes were recorded on a Shimadzu UV-3101 PC spectrophotometer. The FT-IR spectra were recorded on a Bruker EQUINOX - 55 spectrometer in 4000-400 cm^{-1} region and the EPR spectra were recorded on a Varian E-112 X-band spectrometer at room/liquid nitrogen temperature operating at 9-10 GHz (SAIF, IIT Bombay, India). The elemental composition of the complexes was evaluated on an Elementar Vario MACRO cube elemental analyzer. The redox potential of the complexes was measured on a Biologic CHI604D electrochemical analyzer using a three-electrode cell under nitrogen atmosphere where a glassy carbon, Ag/AgCl and a platinum wire were used as working electrode, a reference electrode and the auxiliary electrode, respectively.

Synthesis of copper(II) complexes

Synthesis of $[\text{Cu}(5\text{-nsal})(\text{bipy})\text{ClO}_4]$ (**1**)

To an ethanolic solution of copper perchlorate hexahydrate (0.74 g, 2.00 mM), 5-nitrosalicylaldehyde (0.28 g, 2.00 mM) and 2,2'-bipyridyl (0.35 g, 2.00 mM) in ethanol (10 mL) were added consequently with continuous stirring

at room temperature for 4 h. The removal of solvent from the resultant dark green solution obtained green precipitate was washed with water, ethanol, ether, and dried under vacuum. The obtained precipitate was recrystallized in acetonitrile solvent by slow evaporation giving X-ray quality single crystals after a few days. Yield: 1.00 g (75 %); m.p.: 284 °C. Anal. data for $\text{C}_{17}\text{H}_{12}\text{ClCuN}_3\text{O}_8$ Calc. (%): C, 42.07; H, 2.49; N, 8.66; Cu, 13.09; Found (%): C, 42.12; H, 2.40; N, 8.58; Cu, 13.02; IR (ν , cm^{-1}) (KBr Disc): 1633(ν C=O); 1609(ν C=N); 1573 (ν C-O); 622(ν Cu-O); λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) in DMF: : 624(198), 532 (984), 430 (144758), 372 (104638), 312 (100213), 264 (85070).

Synthesis of $[\text{Cu}(2\text{-hnap})(\text{bipy})\text{ClO}_4]$ (**2**)

Complex **2** were synthesized by a procedure similar to the synthesis of complex **1**. Copper perchlorate hexahydrate (0.74 g, 2.00 mM), 2-hydroxynaphthaldehyde (0.34 g, 2.00 mM) and 2,2'-bipyridyl (0.30 g, 2.00 mM). Recrystallization of the complex by a slow evaporation method in CH_3CN afforded green colored single crystals suitable for X-ray diffraction studies. Yield: 1.03 g (73 %). m.p.: 232 °C. Anal. data for $\text{C}_{21}\text{H}_{15}\text{ClCuN}_2\text{O}_6$ Calc. (%): C, 51.44; H, 3.08; N, 5.71; Cu, 12.96; Found (%): C, 51.38; H, 3.10; N, 5.68; Cu, 12.90; IR (ν , cm^{-1}) (KBr Disc): 1635(ν C=O); 1617(ν C=N); 1485 (ν C-O); 538(ν Cu-O), 436 (ν Cu-N); λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) in DMF: 619 (505), 504 (100), 407 (35042), 367 (47862), 311 (202465), 264 (187920).

X-ray diffraction studies

The bipyridyl based complexes were obtained as dark-green crystals suitable for X-ray diffraction studies. The crystal data were obtained from a Bruker Kappa apex II CCD diffractometer using single crystals of $0.50 \times 0.35 \times 0.30 \text{ mm}^3$ (**1**), and $0.45 \times 0.40 \times 0.40 \text{ mm}^3$ (**2**) dimensions in graphite monochromatized Mo-K α radiation. The crystal was kept at $T = 293(2) \text{ K}$ during data collection and processed using the

SAINT/XPREP software²¹. The structures were solved by SHELXS-97 and refined with SHELXL-2016/6²². The positions of the hydrogen atoms that bonded to carbon atoms were calculated and refined using a riding model. The hydrogen atom displacement parameters were restricted to be 1.2 (CH) or 1.5 (CH₃) Ueq of the parent carbon atom. The copies of crystallographic data for complexes **1** and **2** in CIF format (CCDC Nos. 985211 and 923549, respectively) are available free of charge from the CCDC, UK (<http://www.ccdc.cam.ac.uk>).

Computational details

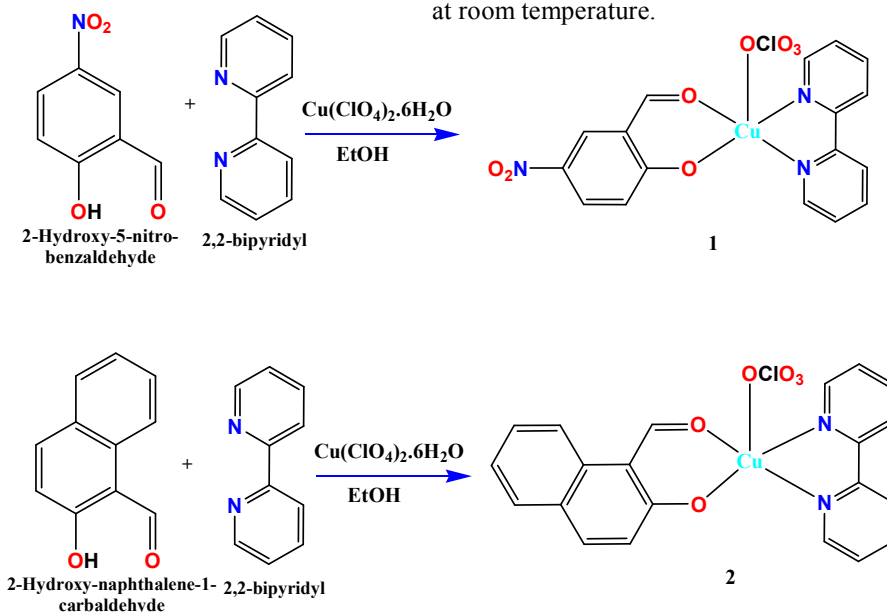
Doublet ground state geometry optimizations and molecular orbital generations of all the structure of complexes were carried out by Density Functional Theoretical (DFT) using the B3LYP functional method with the Los Alamos National Laboratory 2 Double-Zeta, LANL2DZ basis set in the gaseous phase [23]. This basis set uses effective core potentials in calculations which gives more reliable results than other basis sets [24]. Calculations were

performed using the Gaussian 09 program package, G09W [25] to get insight information about the ligands/complexes. The copper complexes were modelled at neutral charged species. The natural bond orbital (NBO) analysis [26] was performed to determine the spin densities and atomic charges of the complexes. All the four copper(II) complexes were modelled as neutral species of formal charge zero.

Results and Discussion

Synthesis of complexes

The copper(II) complexes **1** and **2** were synthesised by reactions of stoichiometric amounts of copper(II) perchlorate salt with respective bidentate-ligands in ethanol. The data obtained from physico-chemical characterizations of complex were consistent with the formation of complexes shown in Scheme 1. The neutral behaviour of complexes in solution revealed by their molar conductivity values. The synthesized complexes obtained as green solids were soluble in solvents like acetonitrile, dimethylformamide and were stable at room temperature.



Scheme 1 Schematic synthesis of complexes **1** and **2**.

Crystal structures description

The green coloured crystals of **1** and **2** suitable for X-ray diffraction analyses were got by recrystallization of complexes in acetonitrile (solvent). The ORTEP and PLATON view of complexes **1** and **2** were shown in Figures 1. The details of structural determination selected bond lengths and bond angles were presented in Table 1 and Table 2. In complexes **1** and **2**, the copper atom was coordinated with two O atoms of the mono-deprotonated aldehyde and two N atoms of 2,2'-bipyridyl in the basal plane and with one O atom of perchlorate in the axial plane to adopt a distorted square pyramidal geometry. The

complexes were observed as dimers with bridging of Cu–O1a (Cu1a–O1), Cu–O2a (Cu1a–O2) bonds at 2.799(4) and 2.821(4) Å, respectively which link the two monomeric units showing octahedral geometry. As the bond lengths of the characteristic bridging bond (2.799(4) and 2.821(2) Å) were observed at higher bond distances than the maximum value of 2.765 Å (Mean value 2.283 Å; obtained for accepted hits of 28 molecules (as on May 2018) with relevance 1.00 and z-score 1.322) for similar bridging molecules calculated by Mogul²⁷, the complexes correspond to monomeric species as observed in ORTEP.

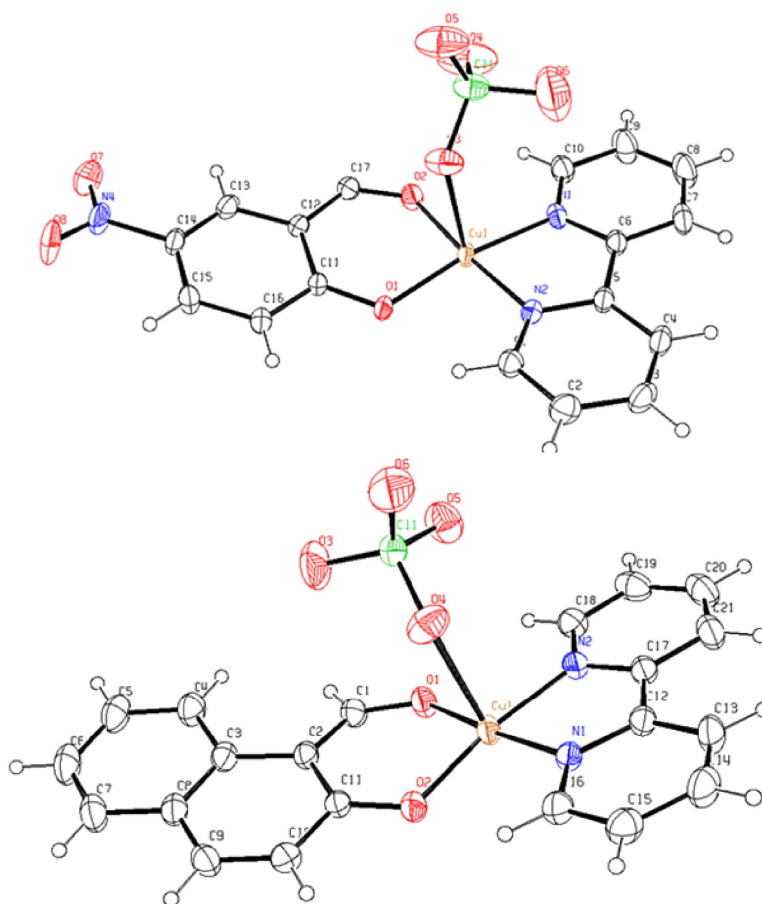


Figure 1 ORTEP view of complexes **1** and **2** with atoms shown as 50% thermal ellipsoids.

Table 1
Crystallographic data and structure refinement parameters for complexes **1** and **2**.

	1	2
Empirical formula	C ₁₇ H ₁₂ ClCuN ₃ O ₈	C ₂₁ H ₁₅ ClCuN ₂ O ₆
Formula weight	484.28	490.34
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
<i>a</i> (Å)	7.6580(9)	9.2486(5)
<i>b</i> (Å)	9.8005(12)	9.9350(4)
<i>c</i> (Å)	13.1107(16)	10.7519(5)
α (°)	76	85.226
β (°)	74	82.389
γ (°)	84	81.438
Volume (Å ³)	916.41(19)	966.29(8)
<i>Z</i> , calculated density (mg m ⁻³)	1, 1.755	1, 1.685
Absorption coefficient (mm ⁻¹)	1.392	1.313
<i>F</i> (000)	488	498
Crystal size (mm)	0.50 × 0.35 × 0.30	0.45 × 0.40 × 0.40
θ range for data collection (°)	2.15 to 28.23	1.91 to 28.26
Limiting indices, <i>h, k, l</i>	- 6 ≤ <i>h</i> ≤ 10, - 12 ≤ <i>k</i> ≤ 12, - 13 ≤ <i>l</i> ≤ 17	- 11 ≤ <i>h</i> ≤ 12, - 12 ≤ <i>k</i> ≤ 13, - 14 ≤ <i>l</i> ≤ 13
Reflections collected/ unique	7036 / 4226	7574 / 4488
Data / restraints / parameters	4226 / 0 / 271	4488 / 0 / 280
Goodness-of-fit on <i>F</i> ²	1.060	1.103
Final <i>R</i> indices [<i>I</i> > 2σ (<i>I</i>)]	<i>R</i> 1 = 0.0724, <i>wR</i> 2 = 0.2197	<i>R</i> 1 = 0.0323, <i>wR</i> 2 = 0.0887
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0825, <i>wR</i> 2 = 0.2303	<i>R</i> 1 = 0.0425, <i>wR</i> 2 = 0.1032
Largest difference peak and hole / e Å ⁻³	2.331 and - 1.019	0.404 and - 0.307

Table 2
Selected bond distances (Å) and bond angles (°) for complexes **1** and **2**.

	1		2
Cu(1)–N(1)	1.980(4)	Cu(1)–N(1)	1.9838(18)
Cu(1)–N(2)	1.985(4)	Cu(1)–N(2)	1.9899(19)
Cu(1)–O(1)	1.902(3)	Cu(1)–O(1)	1.9264(16)
Cu(1)–O(2)	1.973(4)	Cu(1)–O(2)	1.8994(16)
Cu(1)–O(3)	2.390(4)	Cu(1)–O(4)	2.501(2)
O(1)–Cu(1)–O(2)	92.45(15)	O(2)–Cu(1)–O(1)	91.97(7)
O(1)–Cu(1)–N(1)	170.75(16)	O(2)–Cu(1)–N(1)	92.84(7)
O(2)–Cu(1)–N(1)	93.85(16)	O(1)–Cu(1)–N(1)	175.04(7)
O(1)–Cu(1)–N(2)	91.98(15)	O(2)–Cu(1)–N(2)	171.81(7)
O(2)–Cu(1)–N(2)	175.47(14)	O(1)–Cu(1)–N(2)	93.56(7)
N(1)–Cu(1)–N(2)	81.87(17)	N(1)–Cu(1)–N(2)	81.53(8)

The equatorial Cu–N and Cu–O bonds of the complexes vary from 1.975(5) to 1.989(2) Å and 1.900(2) to 1.971(5) Å, respectively as that of similar Cu(II) complexes²⁸. The axial Cu–O (perchlorate) bond was observed to be lower for complex **1** due to the existence of nitro substituent (with strong electron withdrawing nature) in the ligand molecule. The dihedral angles between the mean planes of two bidentate ligands were in the range of 17.8(1)–18.2(4)°. The dihedral angles between the Cu, O1, O2 planes and Cu, N1, N2 planes were observed to be 6.5(1)–10.5(2)°. The monomeric complexes showed the structural index value (trigonality index) τ of 0.07 for **1** and 0.05 for **2** [$\tau = (\beta - \alpha)/60$, where α and β are two largest angles involved in geometry; for the entire square pyramidal and trigonal bipyramidal geometries the τ amounts are zero and unity, respectively] that were consistent with square-pyramidal geometry²⁹.

Spectral characterization

The IR spectra of copper(II) complexes showed a sharp band near 1690 cm⁻¹ due to the presence of C=O group of aldehydic ligands. A

strong band around 1000 – 1100 cm⁻¹ and a sharp band in the region around 625 cm⁻¹ were observed for all complexes due to the antisymmetric stretching and bending vibrations of the perchlorate ions, respectively.

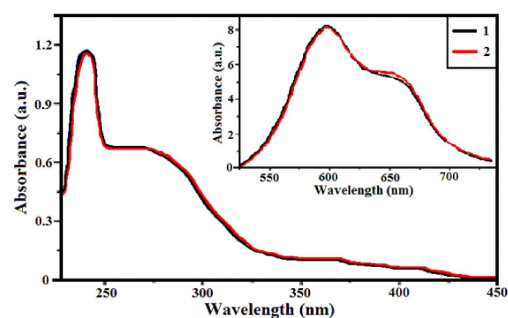


Figure 2 UV-vis spectra of complexes **1** and **2** (10^{-5} M) in DMF.

The absorption spectra of the copper(II) complexes were obtained experimentally in DMF solution. The peaks near 256 – 282 nm was attributed to $\pi \rightarrow \pi^*$ transition of coordinated ligands (Figure 2). In the UV region of

complexes, broad and slightly intense bands observed near 311 – 373 nm could be assigned to $n \rightarrow \pi^*$ transitions of coordinated ligands. The broad peak observed near 405–430 nm can assign for $O(\text{phenolate}) \rightarrow Cu^{II}$ (ligand-metal charge transfer) transitions^{30,31}. In the visible region of copper(II) complexes the absorption bands observed near 504 – 716 nm were ascribed to $d_{(x^2-y^2)} \rightarrow d_{xz}, d_{yz}$ transitions compatible for complexes with square pyramidal geometry around copper atom³².

Computational studies

The DFT calculated geometry-optimized structures and frontier orbital energy (highest occupied molecular orbital, HOMO and lowest unoccupied molecular orbital, LUMO) maps are summarized in Figure 3. The selected bond lengths and angles for complexes **1** and **2** from single crystal XRD were well comparable with DFT calculated results. The differences in their values within experimental results can be attributed to the environmental effects as well as the choice of the DFT method³³. The optimised geometries of the complexes revealed a distorted pentagonal planar structure which was in accordance with results of X-ray crystallographic analysis for the complexes **1** and **2**.

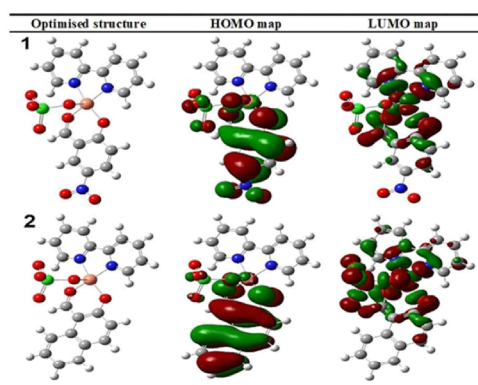


Figure 3 DFT-optimized structures, HOMO and LUMO maps for complexes **1** and **2** calculated by B3LYP/LANL2DZ method.

The DFT-calculated frontier orbital diagrams showed that most of the HOMO electron density was from π -system of the 5-nsal and 2-hnap ligand moiety, while the LUMO electron density was majorly from the d-orbitals on Cu(II) metal centre with a partial π -electronic cloud of the neighbourhood N and O atoms bonded to the metal. The HOMO-LUMO maps indicating the flow of electronic cloud from the ligand to metal, i.e., these systems are significantly ligand to metal charge transfer reactions. It was noticed that the present complexes are odd electron systems indicating its paramagnetic nature due to the presence of one unpaired electron in α molecular orbital (α MO). Thus, the HOMO in the present complex may be termed as singly occupied molecular orbital (SOMO) or α HOMO³⁴. The energy of α HOMO and α LUMO were associated with the electron-donating and electron-accepting abilities of the complexes, respectively

The energy difference between α LUMO and α HOMO ($\Delta E_{\alpha\text{LUMO-HOMO}}$) reflected on the reactivity/ binding ability of the complexes. Thus, the complex was showed relatively less $\Delta E_{\alpha\text{LUMO-HOMO}}$ value than other complexes with the reactivity order of **2** > **1**. Hard-soft- acid-base approximation³⁶ can also explain the biochemical reactivity of the complexes by its hard and soft nature of the complexes. The chemical/biological hard complexes have large ΔE value whereas for soft ones have small ΔE ³⁷. The activity was observed to be enhanced with the increase of softness value and decrease with hardness value according to the order of reactivity investigated for copper(II) complexes. The global electronegativity (χ) is also related to the freedom of electrons in the complex, indicating that the complexes with the lowest χ are highly active. The electron descriptors data for complexes were also corroborated well with the order of reactivity.

Redox behaviour of Cu(II) complexes

The redox behaviour of the copper(II)

complexes in DMF solution were analysed using cyclic voltammetry with a potential range of 0 to $\times 1.20$ V in presence of 10^{-1} M TBAP (supporting electrolyte). The cyclic voltammetric data were summarized in Table-3 and the cyclic voltammograms were shown in Figure-4. The controlled potential electrolysis displayed more negative response than the reduction wave, indicating one electron reduction per molecule. The mixed ligand Cu(II) complexes were associated with one quasi-reversible redox wave (the return wave with less amplitude than the forward wave) between $E_{pa} \times 0.63$ to $\times 0.77$ V and $E_{pc} \times 0.74$ to $\times 0.80$ V.

Table - 3
Electrochemical data of
copper(II) complexes

Complexes	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$ (V)	ΔE (mV)
1	- 0.80	- 0.77	- 0.79	80
2	- 0.78	- 0.65	- 0.72	130
3	- 0.76	- 0.62	- 0.69	140
4	- 0.74	- 0.63	- 0.69	110

The redox couple for all complexes agree with single electron transfer process attributed to Cu^{II}/Cu^I redox couples³⁸. The voltammetric data of copper(II) complexes confirm the existence of stabilized reduced copper ions which were held easily by the ligands in complexes. The ligand molecules did not show any redox wave near more negative region showed that the observed redox potentials are not due to the reactions of ligands³⁹. When the redox behaviour of copper(II) complexes with bipy and biim ligands were compared, biimidazole based complexes showed lower reduction potential than bipy based

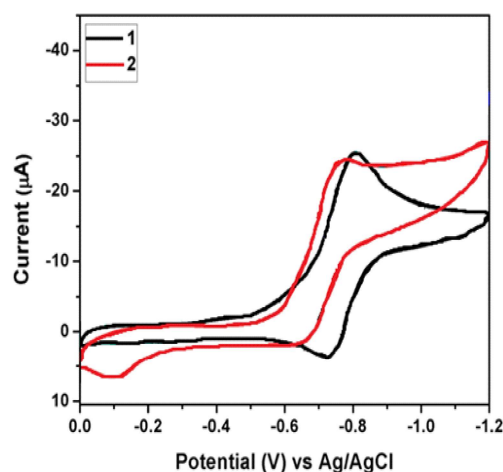


Figure 4 Cyclic voltammograms of copper(II) complexes **1** and **2**.

copper(II) complexes which are attributed to their ring size and nitrogen atoms forming different electron density around copper atom⁴⁰.

Conclusions

Two new mixed ligand copper(II) complexes were synthesized and characterized by spectral and physicochemical methods. The crystal structures of complexes **1** and **2** showed that the complexes exhibit a square-pyramidal geometry. The physicochemical characterizations of the copper(II) complexes also confirmed the formation of anticipated structures. The redox potentials of the complexes assessed by cyclic voltammetry showed a quasi-reversible redox behavior consistent with $Cu(II)/Cu(I)$ reduction in the cathodic region.

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