

## Research Article

# Synthesis, Spectroscopic, and Electrochemical Studies on Some New Copper(II) Complexes Containing 2-{[(Z)-Phenyl (Pyridine-2-yl) Methylidene] Amino} Benzenethiol and Monodentate Ligands

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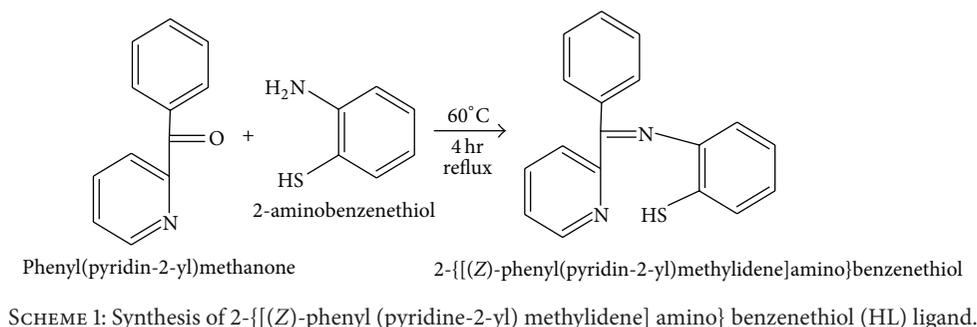
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Five new mononuclear copper(II) complexes, namely, [Cu(L)(ImH)]·ClO<sub>4</sub> **1**; [Cu(L)(Me-ImH)]·ClO<sub>4</sub> **2**; [Cu(L)(Et-ImH)]·ClO<sub>4</sub> **3**; [Cu(L)(2-benz-ImH)]·ClO<sub>4</sub> **4**; [Cu(L)(benz-ImH)]·ClO<sub>4</sub> **5**, where HL = 2-{[(Z)-phenyl (pyridine-2-yl) methylidene] amino} benzenethiol; ImH = Imidazole; Me-ImH = Methylimidazole; Et-ImH = Ethylimidazole; 2-benz-ImH = 2-methyl-benzimidazole; benz-ImH = benzimidazole, have been synthesized and characterized by various physicochemical and spectroscopic techniques. Magnetic moments, electronic spectra, and EPR spectra of the complexes suggested a square planar geometry around Cu(II) ion. The synthesized HL ligand behaves as monobasic tridentate Schiff base bound with the metal ion in a tridentate manner, with N<sub>2</sub>S donor sites of the pyridine-N, azomethine-N, and benzenethiol-S atoms. The redox behaviour of the copper complexes has been studied by cyclic voltammetry. Superoxide dismutase activity of these complexes has been revealed to catalyse the dismutation of superoxide (O<sub>2</sub><sup>-</sup>) and IC<sub>50</sub> values were evaluated and discussed.

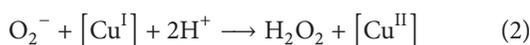
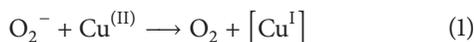
## 1. Introduction

Transition metal complexes coordinated to tridentate Schiff base ligands have been studied extensively mainly because of their ease of preparation, flexibility, and versatility in terms of chemical properties, geometry, coordination sites, and ease of substitution. Ternary complexes formed between metal ions and two different types of bioligands, namely, heteroaromatic nitrogen bases and Schiff base, may be considered as models for substrate metal ion-enzyme interactions and other metal ion mediated biochemical interactions. Among those compounds, copper(II) complexes with Schiff base ligands have been of great interest due to their importance as essentially biologically active [1–4] models for metalloproteins [5, 6]. Copper is an important trace element for plants and animals

and is involved in mixed ligand complex formation in a number of biological processes [7]. Imidazole and its derivatives are very important from a biological point of view [8]; namely, benzimidazole as the 5,6-dimethyl derivative is present in vitamin B<sub>12</sub> and related biomolecules [9] and other benzimidazole compounds have found wide use as anthelmintic agents for both human and veterinary purposes [10]. In addition, it has been reported that several copper complexes with benzimidazole derivatives show inhibitory effects on helminth parasites [11]. Imidazole is also one of the most biologically important ligands. It behaves like a monodentate ligand at lower pH and at higher pH it serves as a bridging ligand. The deprotonated form of imidazole is involved in the active site of bovine erythrocyte superoxide dismutase (BESOD) [12]. It bridges copper(II) and zinc(II) ions. Oberley



and Buettner [13] have reported that cancer cells had less superoxide dismutase (SOD) activity than normal cells. These SODs disproportionate the  $\text{O}_2^-$  radical to molecular oxygen and hydrogen peroxide [14]. All SODs employ the two steps Ping-Pong mechanism shown as follows:



As an extension of our previous work [15] on 2-[(Z)-(5-bromo-2-hydroxyphenyl) methylidene] amino} benzoic acid ligand, herein we now report synthesis, spectroscopic, and electrochemical studies on some new copper(II) complexes possessing tri- and monodentate ligands. The complexes were formulated as  $[\text{Cu}(\text{L})(\text{ImH})]\cdot\text{ClO}_4$  **1**;  $[\text{Cu}(\text{L})(\text{Me-ImH})]\cdot\text{ClO}_4$  **2**;  $[\text{Cu}(\text{L})(\text{Et-ImH})]\cdot\text{ClO}_4$  **3**;  $[\text{Cu}(\text{L})(2\text{-benz-ImH})]\cdot\text{ClO}_4$  **4**;  $[\text{Cu}(\text{L})(\text{benz-ImH})]\cdot\text{ClO}_4$  **5**. 2-[(Z)-phenyl (pyridine-2-yl) methylidene] amino} benzenethiol (HL) behaves as monobasic tridentate Schiff base (Scheme 1) having  $\text{N}_2\text{S}$  donor sites. The SOD activities of the complexes have also been investigated.

## 2. Experimental

**2.1. Materials Used for Synthesis.**  $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ , phenyl (pyridine-2-yl) methanone, and 2-aminobenzenethiol were purchased from Across Organics. All other chemicals used were of synthetic grade and used without further purification. Imidazole and its derivatives were purchased from S.D. Fine Chemicals, India.

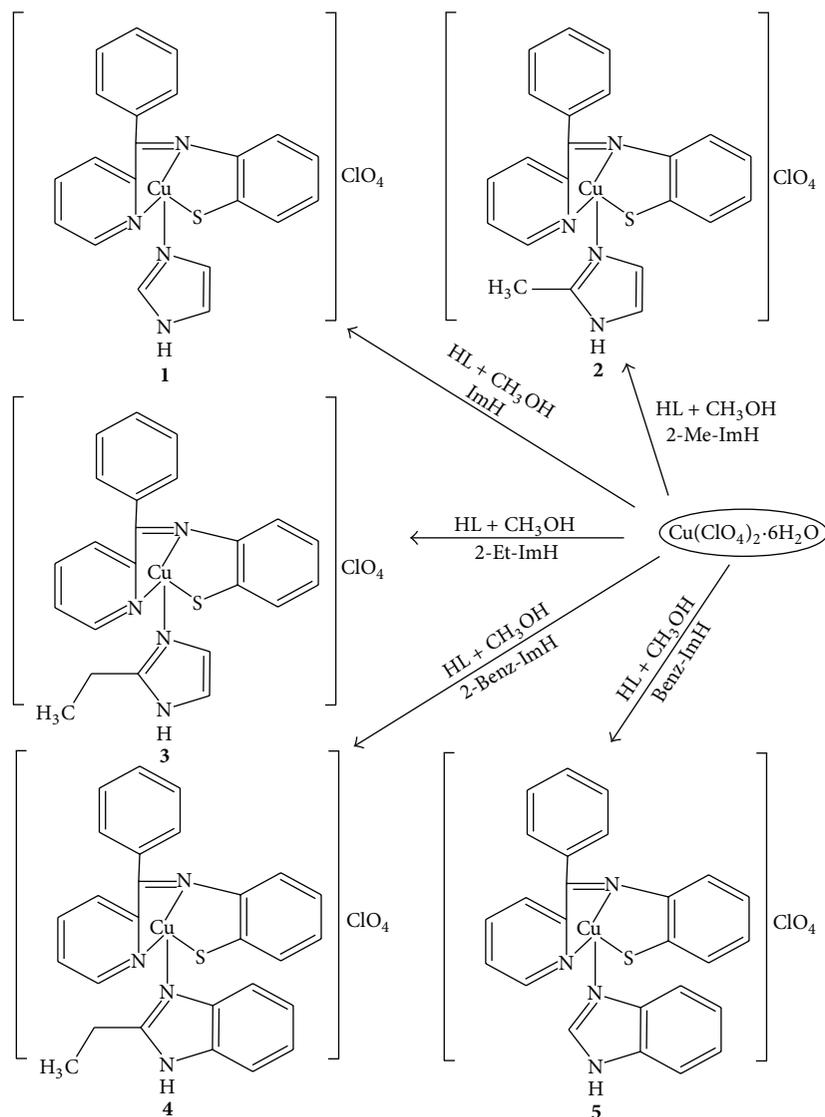
**2.2. Physical Measurements.** Elemental analyses were performed on an Elementar Vario EL III Carlo Erba 1108 analyzer. FAB mass spectra were recorded on a JEOL SX 102/DA 6000 Mass Spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. Magnetic susceptibility measurements were performed on a Gouy balance at RT using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the calibrant ( $x_g = 16.44 \times 10^{-6}$  c.g.s. units). Diamagnetic corrections were applied in compliance with the Pascal constant. The molar conductance measurements were realized using  $10^{-3}$  M solution of

the complexes in DMSO on a Systronics conductivity bridge TDS meter 308 at RT. The electronic spectra (in DMSO) were recorded on a Shimadzu UV-Vis spectrophotometer. FT-IR spectra were recorded in KBr discs on a Perkin-Elmer 783 spectrophotometer in wave number range  $4000\text{--}400\text{ cm}^{-1}$ . X-band EPR spectra were recorded at room temperature on a Varian E-line Century Series Spectrometer operating in the X-band region with 100 kHz modulation frequency, 5 mW microwave power and 1G modulation amplitude [21] was using tetracyano-ethylene (TCNE) as the internal standard. Cyclic voltammetry was performed with a BAS-100 Epsilon electrochemical analyser using a three-electrode electrochemical cell. Ag/AgCl was used as a reference electrode, glassy carbon as the working electrode, and a platinum wire as the auxiliary electrode. 0.1 M  $\text{NaClO}_4$  was used as the supporting electrolyte and DMSO as the solvent. All measurements were performed at room temperature under a nitrogen atmosphere. The solution was deoxygenated by purging nitrogen gas.

The *in vitro* SOD activity was measured using alkaline DMSO as a source of superoxide radical ( $\text{O}_2^-$ ) and nitro blue tetrazolium chloride as  $\text{O}_2^-$  scavenger [16]. In general, 400  $\mu\text{L}$  sample to be assayed was added to a solution containing 2.1 mL of  $0.2\text{ mol L}^{-1}$  potassium phosphate buffer (pH 8.6) and 1 mL of  $56\text{ }\mu\text{mol L}^{-1}$  alkaline DMSO solution was prepared under similar condition in DMSO (except NaOH). A unit of SOD activity is the concentration of complex, which causes 50% inhibition of alkaline DMSO-mediated reduction of NBT.

**2.3. Preparations.** Schiff base was prepared by standard literature procedure and recrystallized from ethanol or methanol.

**2.3.1. Synthesis of 2-[(Z)-Phenyl (Pyridine-2-yl) Methylidene] Amino} Benzenethiol (HL) Ligand.** The 2-[(Z)-phenyl (pyridine-2-yl) methylidene] amino} benzenethiol (HL) ligand was synthesized by refluxing equimolar quantities of phenyl (pyridine-2-yl) methanone (1.0 mmol, 0.18 g) and 2-aminobenzenethiol (1.0 mmol, 0.12 mL) dissolved in ethanol (Scheme 1). The resulting reaction mixture was refluxed on a water bath for 4 h and then allowed to cool overnight. The colored crystalline solid of the obtained Schiff base was filtered, washed with cold ethanol several times, dried in air



SCHEME 2: Synthesis of Schiff base copper(II) complexes 1-5.

at room temperature, and finally preserved under reduced pressure in a desiccator. Yield: 75%. Anal. Found (%): C, 74.48; H, 4.83; N, 9.65. Calcd for  $C_{18}H_{14}N_2S$  (%): C, 46.74.48; H, 4.85; N, 9.67.

2.3.2. *Synthesis of Complexes.* The complexes were prepared by the following general procedure.

2.3.3. *Synthesis of  $[Cu(L)(ImH)]ClO_4$  1;  $[Cu(L)(Me-ImH)]ClO_4$  2;  $[Cu(L)(Et-ImH)]ClO_4$  3;  $[Cu(L)(2-benz-ImH)]ClO_4$  4;  $[Cu(L)(benz-ImH)]ClO_4$  5.* Complexes 1 were prepared by mixing 50 mL of a 10 mM ethanolic solution of  $Cu(ClO_4)_2 \cdot 6H_2O$  (1.0 mmol, 0.370 g) with 50 mL of a 10 mM ethanolic solution of the H L (1.0 mmol, 0.289 g), and a ethanolic solution (20 mL) of ImH (1.0 mmol, 0.068 g) was added in a 1:1 (metal-ligand) ratio (Scheme 2). The resulting mixture was refluxed on a water bath for 3–5 h. A coloured

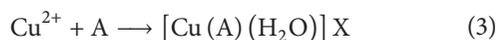
product appeared on standing and cooling the solution. The precipitated complex was filtered, washed with ether, recrystallized several times from ethanol, and dried under reduced pressure over anhydrous  $CaCl_2$  in a desiccator. They were further dried in an electric oven at 50–60°C. Yield: 72%. Anal. Found (%): C, 48.55; H, 3.46; N, 10.78. Calcd (%) for  $C_{21}H_{18}ClCuN_4O_4S$  (1): C, 48.58; H, 3.49; N, 10.81. FAB-mass ( $m/z$ ): Obs. (Calcd) 519.54(520). Complexes 2, 3, 4, and 5 were also synthesized in a similar fashion described above as 1 by employing Me-ImH (1.0 mmol, 0.07 g); Et-ImH (1.0 mmol 0.08 g); 2-benz-ImH (1.0 mmol, 0.12 g); benz-ImH (1.0 mmol; 0.13 g), respectively, in place of imidazole (ImH). Yield varied in range 75–90%. Anal. Found (%): C, 49.53; H, 3.75; N, 10.50. Calcd for  $C_{22}H_{19}ClCuN_4O_4S$  (2): C, 49.56; H, 3.78; N, 10.53. FAB-mass ( $m/z$ ): Obs. (Calcd) 532 (533). Anal. Found (%): C, 50.45; H, 4.02; N, 10.23. Calcd for  $C_{23}H_{21}ClCuN_4O_4S$  (3): C, 50.48; H, 4.05; N, 10.26. FAB-mass ( $m/z$ ): Obs. (Calcd) 546 (547). Anal. Found (%): C, 54.27; H, 4.03; N, 9.38. Calcd for

$C_{27}H_{23}ClCuN_4O_4S$  (**4**): C, 54.30; H, 4.06; N, 9.41. FAB-mass ( $m/z$ ): Obs. (Calcd) 597 (596). Anal. Found (%): C, 52.85; H, 3.17; N, 9.86. Calcd for  $C_{25}H_{19}ClCuN_4O_4S$  (%): C, 52.86; H, 3.18; N, 9.87. FAB-mass ( $m/z$ ): Obs. (Calcd) 569 (568).

**Caution.** Although no problems were encountered in this work, perchlorate salts of metal complexes are potentially explosive. They should be synthesized in small quantity and handled with great care.

### 3. Results and Discussion

**3.1. Synthesis and Characterization.** The mononuclear complexes were prepared in high yield by reacting copper(II) salt with 2-[[*Z*]-phenyl (pyridine-2-yl) methylidene] amino} benzenethiol and monodentate ligands in 1:1 molar ratio to give complexes of general composition [Cu (A) (B)]. The reactions possibly proceed in the following manner (Scheme 2):



where A = HL, B = monodentate ligands and X =  $ClO_4^-$ . The 2-[[*Z*]-phenyl (pyridine-2-yl) methylidene] amino} benzenethiol (HL) ligand was prepared by refluxing equimolar quantities of phenyl (pyridine-2-yl) methanone and 2-aminobenzenethiol in ethanol for 4 h at 60°C. In the present paper, the coordination behaviour of Schiff base (Scheme 1) derived from the condensation of phenyl (pyridine-2-yl) methanone with 2-aminobenzenethiol towards Cu(II) ion is described, which may help in understanding more the mode of chelation of ligand towards copper(II) complexes. The proposed structures of the Schiff base 2-[[*Z*]-phenyl (pyridine-2-yl) methylidene] amino} benzenethiol (HL) ligand and their complex  $[Cu(L)(ImH)ClO_4]$  **1** are presented in Figures 1 and 2, respectively. All the copper complexes were coloured, solid, and stable towards air and moisture at RT. They decompose on heating at high temperature and were more or less soluble in common organic solvent. IR spectra suggest that the 2-[[*Z*]-phenyl (pyridine-2-yl) methylidene] amino} benzenethiol (HL) bound with the Cu(II) ion in a tridentate manner, with SNN donor sites of the benzenethiol-S, azomethine-N, and pyridine-N atoms. Such metal complexes may be stereo selective and stereo active in nature and thus applicable in various catalytic reactions. Molar conductivity in DMSO shows nonconductor behaviour [17] ( $14 \Omega^{-1} cm^{-1} mol^{-1}$ ) for **2**,  $17 \Omega^{-1} cm^{-1} mol^{-1}$  for **3**,  $10 \Omega^{-1} cm^{-1} mol^{-1}$  for **5** and 2:1 electrolyte ( $145 \Omega^{-1} cm^{-1} mol^{-1}$ ) for **1**, and ( $150 \Omega^{-1} cm^{-1} mol^{-1}$ ) for **4**. The present copper(II) complexes are paramagnetic in solid state at room temperature as expected from  $d^9$  electronic configuration of Cu(II) ion. The observed magnetic moments ( $\mu_{eff}$ ) of the copper(II) complexes were found at the range 1.72–1.79 B.M. The effective magnetic moment values of 1.72, 1.77 and 1.79 B.M. might indicate antiferromagnetic interactions at room temperature, suggesting dimeric structures, that is, bridging of the  $Cu^{II}$  ions through the deprotonated

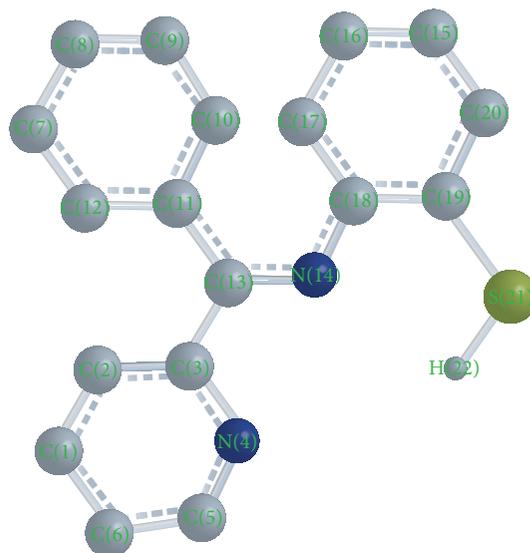


FIGURE 1: Structure of 2-[[*Z*]-phenyl (pyridine-2-yl) methylidene] amino} benzenethiol (HL) ligand.

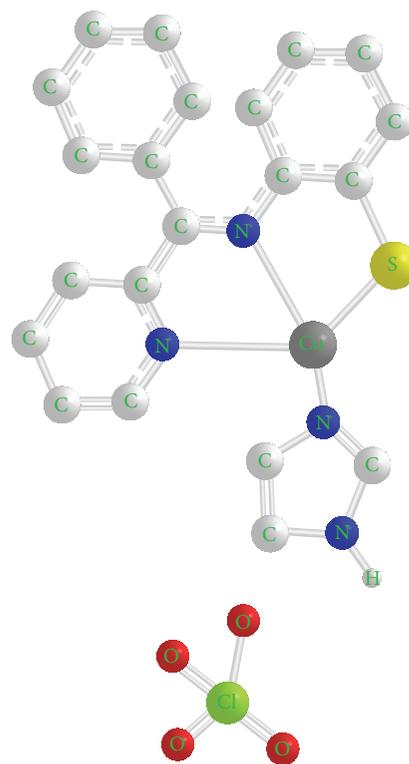


FIGURE 2: Structure of Schiff base copper(II) complex  $[Cu(L)(ImH)]ClO_4$  **1**.

sulphur atom. Be more specific about the other reported copper(II) complexes [17, 18] and are consistent with spin only magnetic moment of 1.732 B.M. for a  $S = 1/2$ .

**3.2. Electron Paramagnetic Resonance.** The EPR spectra of the complexes in the polycrystalline state at 298 K and in

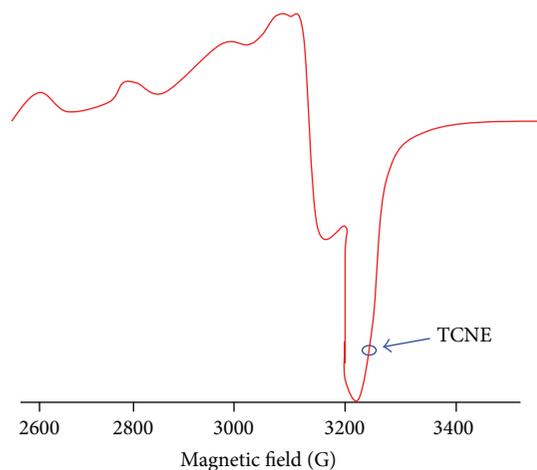


FIGURE 3: EPR spectrum of the complex  $[\text{Cu}(\text{L})(\text{ImH})(\text{ClO}_4)] \mathbf{1}$  ( $3 \times 10^{-3}$  M) at 77 K in DMSO.

solution at 77 K were recorded in the X-band region, using 100 KHz field modulation and the  $g$  factors were quoted relative to the standard marker TCNE ( $g = 2.00277$ ). Some representative EPR spectra are shown in Figure 3. The electron paramagnetic mononuclear copper(II) complexes display X-band EPR spectra in 100% DMSO at 77 K giving  $g_{\parallel} > g_{\perp} > 2.0023$  indicating  $d_{x^2-y^2}$  ground state in a square planar geometry.

The EPR spectra of the complexes revealed two  $g$  values ( $g_{\parallel}$  and  $g_{\perp}$ ). Since the  $g_{\parallel}$  and  $g_{\perp}$  values were closer to 2 and  $g_{\parallel} > g_{\perp}$ , a tetragonal distortion around the Cu(II) ion is suggested. The trend  $g_{\parallel} > g_{\perp} > g_e$  (2.0023) shows that the unpaired electron is localized in the  $d_{x^2-y^2}$  orbital in the ground state of Cu(II) and spectra were characteristic of axial symmetry. The value of  $g_{\parallel} > 2.3$  is characteristic of an ionic environment and  $g_{\parallel} < 2.3$  indicates a covalent environment in metal-ligand bonding. The  $g_{\parallel}$  values for the complexes were less than 2.3, suggesting the environment was covalent.

The exchange coupling interaction between two Cu(II) ions is explained by the Hathaway expression [22]:

$$G = \frac{(g_{\parallel} - 2.0023)}{(g_{\perp} - 2.0023)}. \quad (5)$$

According to Hathaway [23], if the value  $G$  is greater than 4 ( $G > 4.0$ ), the exchange interaction is negligible, whereas when the value of  $G$  is less than 4 ( $G < 4.0$ ), a considerable exchange coupling is present in a solid complex. The  $G$  values for the complexes were less than four (2.30 for **1**, 2.80 for **2**, 2.83 for **3**, 2.74 for **4**, 2.45 for **5**) indicating considerable exchange interaction in the complexes.

The solution EPR spectra of the complexes were recorded in DMSO at 77 K. The spectra typically indicate a  $d_{x^2-y^2}$  ground state ( $g_{\parallel} > g_{\perp} > 2.0023$ ). No nitrogen super hyperfine splitting could be observed. These spectral features are characteristic of axial symmetry [24]. The EPR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and the energies of the d-d transition were used to evaluate the bonding parameters  $\alpha^2$ ,  $\beta^2$ , and  $\gamma^2$ , which

may be regarded as measures of the covalence of the in-plane  $\sigma$ -bonds, in-plane  $\pi$ -bonds, and out-of-plane  $\pi$ -bonds, respectively. The value of the in-plane  $\sigma$ -bonding parameter  $\alpha^2$  was calculated using the following expression [25]:

$$\alpha^2 = \left( \frac{A_{\parallel}}{0.036} \right) + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04. \quad (6)$$

The orbital reduction factors  $K_{\parallel} = \alpha^2\beta^2$  and  $K_{\perp} = \alpha^2\gamma^2$  were calculated using the following expression [26]:

$$K_{\parallel}^2 = (g_{\parallel} - 2.0023) \frac{E_{d-d}}{8\lambda_0}, \quad K_{\perp}^2 = (g_{\perp} - 2.0023) \frac{E_{d-d}}{2\lambda_0}, \quad (7)$$

where  $\lambda_0$  is the spin-orbital coupling constant, with a value of  $-828 \text{ cm}^{-1}$  for a copper(II)  $d^9$  system. According to Hathaway [23], for pure  $\sigma$  bonding,  $K_{\parallel} \approx K_{\perp} \approx 0.77$  and for in-plane  $\pi$  bonding  $K_{\parallel} < K_{\perp}$ , while for out-of-plane  $\pi$  bonding,  $K_{\parallel} > K_{\perp}$ . In all of the present copper(II) complexes, it is observed that  $K_{\parallel} > K_{\perp}$ , which indicates the presence of significant out-of-plane  $\pi$ -bonding. The evaluated values of  $\alpha^2$ ,  $\beta^2$ , and  $\gamma^2$  of the complexes are consistent with both strong in-plane  $\sigma$  and out-of-plane  $\pi$ -bonding. The empirical factor  $f = g_{\parallel}/A_{\parallel} \text{ cm}^{-1}$  is an index of tetragonal distortion and its value may vary from 105 to  $135 \text{ cm}^{-1}$  for small to extreme distortions in square planar complexes and it depends on the nature of the coordinated atoms [27]. The  $f$  values of these complexes are found to be in the range 120–145  $\text{cm}^{-1}$ , indicating significant distortion from planarity.

**3.3. Electronic Spectral Study.** The significant electronic absorption bands in the spectra of the complexes were recorded in DMSO at 25°C. For square planar complexes with a  $d_{x^2-y^2}$  ground state, three spin allowed transitions are possible, namely,  ${}^2B_{1g} \rightarrow {}^2A_{1g}(d_{x^2-y^2} \rightarrow d_{z^2})$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}(d_{x^2-y^2} - d_{xy})$  and  ${}^2B_{1g} \rightarrow {}^2E_g(d_{x^2-y^2} \rightarrow d_{xy}, d_{yz})$ . Since the four d orbitals lie very close together, each transition cannot be distinguished by its energy and hence it is very difficult to resolve the bands into separate components. The spectra of complexes **1–5** each exhibit a broad band centered at 710–740 nm, similar to those reported for copper(II) ions in a square planar environment [28, 29]. Due to the broadness of the band, the other expected transitions in this range could not be assigned. The ligand to metal charge transfer band for the complexes appeared at 415–419 nm with a shoulder at 455–465 nm.

**3.4. Infrared Spectral Study.** The IR spectra of the complexes were compared with those of the free ligand in order to determine the involvement of the coordination sites in the chelation. Characteristic peaks in the spectra of the ligand and complexes were considered and compared. IR spectrum of the HL ligand exhibited the most characteristic bands at  $1665 \text{ cm}^{-1}$   $\nu(>\text{C}=\text{N}, \text{azomethine})$ ,  $1497 \text{ cm}^{-1}$   $\nu(>\text{pyridine-N})$ , and  $1680 \text{ cm}^{-1}$   $\nu(>\text{benzenethiol-S})$ . The formation of

the Schiff base, 2-[[*(Z)*-phenyl (pyridine-2-yl) methylidene] amino] benzenethiol, was noted from the absence of C=O and NH<sub>2</sub> peaks in the ligand. The band 1665 cm<sup>-1</sup> due to the azomethine group of the Schiff base was shifted to lower frequency (1615–1580 cm<sup>-1</sup>) after complexation, indicating the azomethine nitrogen to the metal ions. This can be explained by the donation of electrons from nitrogen to the empty d-orbital of the metal atom [30]. νN–H band arises at 3180 cm<sup>-1</sup> due to the imidazole. There was no appreciable change in the ν(C=N) at 1665 cm<sup>-1</sup> in ligand on complex formation, which indicate that the pyridine ring in nitrogen does not participate in the coordination. Complexes 1–5 showed a broad feature that is split into three bands at the ranges 1080, 1110, and 1140 cm<sup>-1</sup> and is assigned to ionic perchlorate [29]. In the low frequency region, the band of weak intensity [31] observed in the spectra of the complexes in the region 447–455 cm<sup>-1</sup> is attributed to Cu–S and in the region 480–490 cm<sup>-1</sup> to Cu–N. The IR data of ligand and their copper(II) complexes showed that the Schiff base was coordinated to the metal ion in a tridentate manner (NNS).

**3.5. Cyclic Voltammetry.** The electrochemical properties of the present complexes have been studied by cyclic voltammetry (CV) under a nitrogen atmosphere in DMSO solution containing 0.1 M NaClO<sub>4</sub> as the supporting electrolyte at a platinum working electrode. The electrochemical properties of metal complexes particularly have been studied in order to minor spectral changes accompanying electron transfer. These complexes 1–5, a negative scan initiated at 1200 mV in the potential range 1500 to –1200 mV, yielded a quasi-reversible on electron reduction (Cu<sup>II</sup>/Cu<sup>I</sup>) process [32, 33] in the potential range 0.458 to 0.575V against Ag/AgCl electrode. In each case, the cathodic peak potential and difference increase as the scan rate is increased. Constancy of *E*<sup>o'</sup> shows that in all the cases both peaks are complementary to each other. The pertinent redox couples are represented in the following electron transfer series (8):



**3.6. Superoxide Dismutase Activity.** SOD mimetic activities of the present complexes have also been measured. The SOD mimetic activities of the present complexes were examined by the NBT assay, following kinetically the reduction of NBT to MF<sup>+</sup> at 562 nm. Superoxide was enzymatically supplied from alkaline DMSO. The count fraction causing 50% inhibition of NBT reduction is called IC<sub>50</sub> concentration, equivalent to one unit of SOD activity (IC<sub>50</sub> values), together with the IC<sub>50</sub> values of native SOD that are given in Table 1. The IC<sub>50</sub> values of these complexes are 38 μmol dm<sup>-3</sup> for 1, 40 μmol dm<sup>-3</sup> for 2, 36 μmol dm<sup>-3</sup> for 3, 39 μmol dm<sup>-3</sup> for 4, and 37 μmol dm<sup>-3</sup> for 5. The observed SOD (IC<sub>50</sub>) value is higher than the value exhibited by the native enzyme (IC<sub>50</sub> = 0.04 μmol dm<sup>-3</sup>) (note that the smaller the IC<sub>50</sub> value, the higher the SOD activity). The SOD activity of present mononuclear complexes increases in the order 3 < 5 < 1 < 4 < 2. The difference in IC<sub>50</sub> values of these complexes may be

TABLE 1: Superoxide dismutase activity of some copper(II) complexes.

S. number	Complex	IC <sub>50</sub> (μmol dm <sup>-3</sup> )	Reference
1.	Native SOD	0.04	[16]
2.	[Cu(glygly)]·3H <sub>2</sub> O	132	[16]
3.	[Cu(glygly)(Phen)]·3H <sub>2</sub> O	32	[16]
4.	[Cu(L <sup>I</sup> )(phen)]	61	[15]
5.	[Cu(SAT)(bipy)]	58	[17]
6.	[Cu(SAA)(MeImH)]	35	[18]
7.	[Cu(L)(bipy)]	25	[19]
8.	[Cu(L)Cl <sub>2</sub> ]	22	[20]
9.	[Cu(L)Br <sub>2</sub> ]	18	[20]
10.	[Cu(L)(ImH)]·ClO <sub>4</sub> 1	38	In this study
11.	[Cu(L)(Me-ImH)]·ClO <sub>4</sub> 2	40	In this study
12.	[Cu(L)(Et-ImH)]·ClO <sub>4</sub> 3	36	In this study
13.	[Cu(L)(2-benz-ImH)]·ClO <sub>4</sub> 4	39	In this study
14.	[Cu(L)(benz-ImH)]·ClO <sub>4</sub> 5	37	In this study

ascribed to the imidazoles (HL) and copper ion. These values are comparable with other reported copper(II) complexes [19, 20, 34]. These higher values may be due to the strong ligand field created by the tridentate Schiff base 2-[[*(Z)*-phenyl (pyridine-2-yl) methylidene] amino] benzenethiol ligand which opposes the interaction of the complexes copper with the superoxide radical and another important factor is the ability of the ligand to accommodate the reduced copper(I) centre in a tetrahedral-like or linear environment.

## 4. Conclusion

Five new copper(II) complexes, namely, [Cu(L)(ImH)]·ClO<sub>4</sub> 1; [Cu(L)(Me-ImH)]·ClO<sub>4</sub> 2; [Cu(L)(Et-ImH)]·ClO<sub>4</sub> 3; [Cu(L)(2-benz-ImH)]·ClO<sub>4</sub> 4; [Cu(L)(benz-ImH)]·ClO<sub>4</sub> 5, have been synthesized and characterized by various physicochemical and spectroscopic techniques. The IR data, magnetic susceptibility measurement, and spectroscopic data of copper complexes 1–5 indicate square planar geometry. The IC<sub>50</sub> values of copper complexes are higher than the value exhibited by the native enzyme (IC<sub>50</sub> = 0.04 μmol dm<sup>-3</sup>) on a molar base. Copper(II) complexes display X-band EPR spectra in 100% DMSO at 77 K giving *g*<sub>||</sub> > *g*<sub>⊥</sub> > 2.0023 indicating d<sub>x<sup>2</sup>-y<sup>2</sup></sub> ground state. The synthesized 2-[[*(Z)*-phenyl (pyridine-2-yl) methylidene] amino] benzenethiol (HL) ligand bound with the metal ion in a tridentate manner, with NNS donor sites of the benzenethiol-S, azomethine-N, and pyridine-N atoms. The present copper(II) complexes undergo quasi-reversible on electron reduction (Cu<sup>II</sup>/Cu<sup>I</sup>) redox process.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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