Synthesis and characterization of some mixed ligand copper(II) complexes containing ONN donor Schiff base and bidentate ligands

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Abstract : Five new mixed ligand copper(II) complexes viz. Cu(PPS)(bipy)](ClO$_4$)$_2$ (1); [Cu(PPS)(phen)](ClO$_4$)$_2$ (2); [Cu(PPS)(dmp)](ClO$_4$)$_2$ (3); [Cu(PPS)(en)](ClO$_4$)$_2$ (4); [Cu(PPS)(temed)](ClO$_4$)$_2$ (5) [PPS = phenyl(pyridyl-2-yl)methanone-*N*-phenylsemicarbazone, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, dmp = 2,9-dimethyl-1,10-phenanthroline, en = ethylenediamine and temed = *N,N,N′,N′*-tetramethylethylenediamine] have been synthesized and characterized by means of elemental analysis, magnetic susceptibility, X-band EPR electronic spectroscopy and cyclic voltammetry. The superoxide dismutase activity of the present complexes have also been measured.
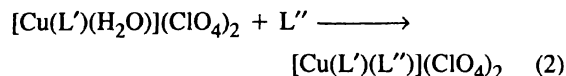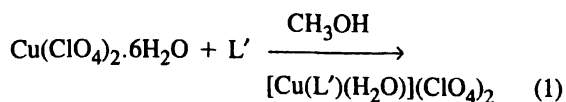
Keywords : Copper(II) complexes, Zn^{II} complexes, X-band, EPR, cyclic voltammetry.

Introduction

Heterocyclic semicarbazones or thiosemicarbazones Schiff bases derived from 2-benzoylpyridine and 4-phenylsemicarbazide are of particular interest due to their remarkable coordination properties and in biology owing to a wide spectrum of potential biological activities in the chemotherapeutic field[1,2]. The activity of semicarbazones depends very much on the α-(*N*)-heterocyclic aldehyde or ketones and is affected also by the presence of N(4) substitution[3–5]. Complexes of tridentate Schiff base bound by two nitrogen and one oxygen atoms of semicarbazones have been studied extensively because of their chemotherapeutic activities such as antimalarial, antibacterial, antiviral and antileishmanial activities[6,7]. Semicarbazones exist in tautomeric enol and keto forms. The enol form acts as a neutral bidentate ligand, whereas keto form can deprotonate and acts as an anionic ligand[8–10]. Herein, we present the synthesis and characterization of mixed ligand copper(II) complexes containing ONN donor Schiff base and diamine.

Results and discussion

All the present mixed ligand copper(II) complexes were synthesized by the following general sequential routes :

$$Cu(ClO_4)_2.6H_2O + L' \xrightarrow{\;CH_3OH\;}$$

$$[Cu(L')(H_2O)](ClO_4)_2 \quad (1)$$

$$[Cu(L')(H_2O)](ClO_4)_2 + L'' \longrightarrow$$

$$[Cu(L')(L'')](ClO_4)_2 \quad (2)$$

where, L′ = PPS = phenyl(pyridyl-2-yl)methanone-*N*-phenylsemicarbazone and L″ = bipy/phen/dmp/en/temed.

The Schiff base, PPS behaves as neutral tridentate ligand and all complexes are soluble in common organic solvents such as DMSO, DMF and in mixture of CH$_3$OH : CH$_3$CN, CH$_2$Cl$_2$: CH$_3$OH (1 : 1 v/v) solution but partially soluble in other organic solvents such as benzene, dichloromethane, chloroform and insoluble in aqueous media.

Magnetic susceptibility measurements :

All present ternary complexes 1-5 are paramagnetic in nature in the solid state at room temperature as expected from the d^9 electronic configuration of Cu^{II} ion. The observed magnetic moment values (μ_{eff}) of the complexes are 1.77 B.M. for 1; 1.79 B.M for 2; 1.98 B.M for 3; 2.1 B.M for 4 and 2.20 B.M for 5. These values are quite close to the other reported copper(II) complexes[11–13] and is in fair agreement with the spin only system S = ½.

EPR investigation :

X-Band EPR spectra of the present copper(II) com-

plexes were recorded in X-band frequency in the poly-crystalline state (298 K) and in solution (77 K). The detailed information of spectral data and various magnetic interaction parameter are summarised in Table 1. Some representative spectra are shown in Figs. 1 and 2. The exchange interaction parameter G, which is a measure of the exchange interaction between copper centers in the polycrystalline compound is calculated using the expression[14].

$G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ for axial spectra and for rhombic spectra

$G = (g_3 - 2.0023)/(g_{\perp} - 2.0023)$ and $g_{\perp} = (g_1 + g_2)/2$.

If $G > 4$, exchange interaction is negligible and if it is less than 4, considerable exchange interaction is indicated in the solid complex. The G values for the complexes found : 3.70 for 1, 3.69 for 2, 3.32 for 3, 3.15 for 4, 3.86 for 5 which is less than 4 and is suggesting ex-

Table 1. EPR and UV-Visible parameters of copper(II) complexes

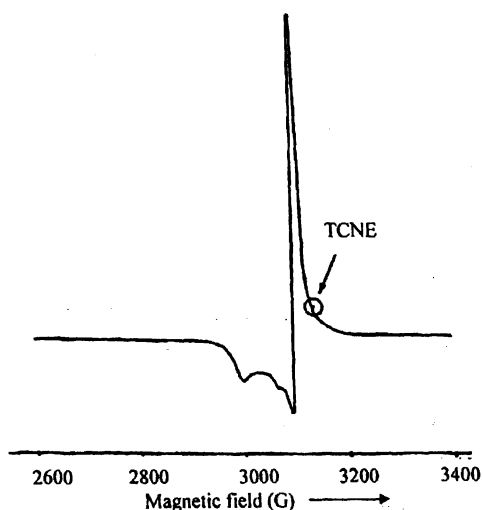| Parameter		[Cu(PPS)(bipy)] $(ClO_4)_2$ (1)	[Cu(PPS)(phen)] $(ClO_4)_2$ (2)	[Cu(PPS)(dmp)] $(ClO_4)_2$ (3)	[Cu(PPS)(en)] $(ClO_4)_2$ (4)	[Cu(PPS)(temed)] $(ClO_4)_2$ (5)
Polycrystalline	g_1	2.161	2.096	2.124	2.103	2.157
state (298 K)	g_2	2.048	2.016	2.055	2.055	2.068
	g_3	2.022		2.022	2.035	2.033
	g_{av}/g_{iso}	2.077	2.056	2.067	2.064	2.086
DMSO (77 K)	$g_{\parallel}$	2.268	2.279	2.214	2.162	2.221
	$g_{\perp}$	2.066	2.069	2.066	2.053	2.059
	$A_{\parallel}$ (G)	160	150	165	180	170
	G	3.70	3.69	3.32	3.15	3.86
	α^2	0.847	0.839	0.841	0.829	0.851
	β^2	0.185	0.189	0.177	0.151	0.174
	γ^2	0.192	0.196	0.195	0.1970	0.176
	$K_{\parallel}$	0.157	0.159	0.149	0.125	0.148
	$K_{\perp}$	0.163	0.165	0.164	0.141	0.150
	f (cm)	139	149	134	120	130
	λ_{max} (nm)	690	680	700	650	660

Fig. 1. EPR spectra of the complex [Cu(PPS)(en)](ClO₄)₂ (4) in polycrystalline state at RT.
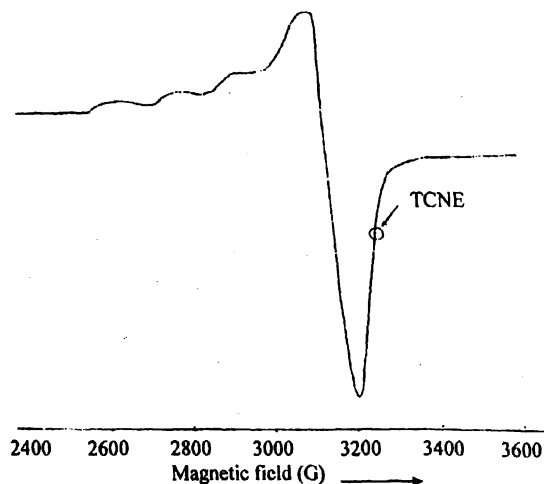

Fig. 2. EPR spectra (LNT) in 100% DMSO of the complex [Cu(PPS)(phen)](ClO₄)₂ (2).

change coupling interactions in the complex and consistent with a ground state in a square pyramidal geometry[15].

The EPR parameters and *d-d* transition energies were used to evaluate the bonding parameters α^2, β^2 and γ^2, which may be regarded as measure of the covalency of the in-plane σ-bonds and in-plane and out-of-plane π-bonds, respectively. The in-plane σ-bonding parameter α^2 was calculated using the expression of Kivelson and Neiman[16].

$$\alpha^2 = \left(\frac{A_{\parallel}}{0.036}\right) + (g_{\parallel} - 2.0023)$$

$$+ \frac{3}{7}(g_{\perp} - 2.0023) + 4.04$$

The orbital reduction factors $K_{\parallel}$ and $K_{\perp}$ were estimated from the expressions[17,18]

$$K_{\parallel}^2 = (g_{\parallel} - 2.0023)\,E_{d\text{-}d}/8\lambda_0$$

$$K_{\perp}^2 = (g_{\perp} - 2.0023)\,E_{d\text{-}d}/2\lambda_0$$

where, $K_{\parallel} = \alpha^2\beta^2$, $K_{\perp} = \alpha^2\gamma^2$ and λ_0 represent the one electron spin-orbit coupling constant for the free ion, equal to -828 cm^{-1}. Significant information about the nature of bonding in the copper(II) complexes can be derived from the magnitude of $K_{\parallel}$ and $K_{\perp}$. In case of a pure σ-bonding $K_{\parallel} \approx K_{\perp}$ ca. 0.77 whereas $K_{\parallel} < K_{\perp}$ implies considerable in-plane π-bonding while for out-of-plane π-bonding $K_{\parallel} > K_{\perp}$. Furthermore, α^2, β^2 and γ^2 have value much less than 1 (the value for 100% ionic bonding, this value decreasing with increasing covalent bonding). In all the complexes it is observed that $K_{\parallel} < K_{\perp}$, indicating the presence of significant in-plane π-bonding. The evaluated values of α^2, β^2 and γ^2 of present complexes are consistent with both strong in-plane σ and in-plane π-bonding. The $K_{\parallel}$ and $K_{\perp}$ values of the present complexes were found to be 0.157 and 0.163 for **1**, 0.159 and 0.165 for **2**, 0.149 and 0.164 for **3**, 0.125 and 0.141 for **4** and 0.148 and 0.150 for **5**.

UV-Vis absorption spectroscopy :

The electronic spectra of complexes **1-5** in DMSO solution representing typical *d-d* transition patterns of Cu^{II} complexes are shown in Fig. 3. Although it is difficult to predict solution structure of the Cu^{II} complexes from electronic spectroscopy alone because of a wide range of a possible geometrical distortions and the typically poor resolution of absorption band[19]. The shape of absorption
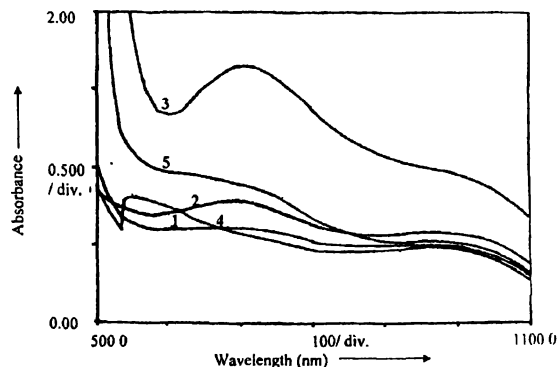

Fig. 3. The UV-Vis spectrum (0.003 mol^{-1} dm^{-3}) of the complexes 1-5.

suggests that more than one Cu^{II} species may exist in the solution. On the other hand, the ligand PPS may relax in solution under completion from the solvent molecule (DMSO) which may bind between tridentate Schiff base ligand and central metal ion. In any cases, the relatively lower energies of the absorption maxima for the above species are indicative of weak crystal fields in a distorted square pyramidal environment. By contrast, all five-coordinated complexes with the tridentate Schiff base ligand, PPS and *N,N*-bidentate ligand display two separate bands in the visible spectra with the intensity of the higher-energy band being markedly higher than the intensity of the lower-energy band. Such a pattern is characteristic for distorted square-pyramidal Cu^{II} complexes, is contrast to the trigonal bi-pyramidal geometry where the opposite intensity ratio is typical[16]. This finding suggests that the overall square-pyramidal coordination environment found in the solids is retained in solution. Similar spectra were reported for a number of other square-pyramidal Cu^{II} complexes[20-23]. The λ_{max} value of the present complexes found at 690 for **1**, 680 for **2**, 700 for **3**, 650 for **4** and 660 nm for **5**. All copper(II) complexes exhibit a moderately intense band in the range between 340 and 390 nm which may be assigned to metal-to-ligand charge-transfer (MLCT) transitions[24]. The spectra of all complexes as measured in frozen DMSO solution are axial with $g_{\parallel} > g_{\perp} > 2.0$, indicating a $d_{x^2-y^2}$ ground state[25] which is in agreement with the electronic spectroscopy assignments.

Cyclic voltammetric measurements :

The electron transfer properties of the present copper(II)

complexes were examined by cyclic voltammetry in DMSO solutions (0.1 M in NaClO$_4$) at platinum working electrode. The electrochemical response of the complexes was complicated by adsorption of the reduction products at the electrode surface, especially at the platinum working electrode. The potential and currents of adsorption peaks depends strongly on the experimental conditions, therefore a careful choice of optimal parameters was necessary to minimize such effects. The more information of CV results of these complexes are available in Table 2. A representative cyclic voltammograms of the complex **3** are depicted in Fig. 4. The redox behaviour of all com-

both peaks are complementory to each other. In all cases the peak potential differences increases as scan rate increases. In the redox process that the Cu^{II}/Cu^{I} potentials are mainly associated with the affinity between the donors and Cu^{II} ions[28–30].

Infrared study :

The IR spectra of the complexes show the ν(C=N) stretching shifted to 1610–1626 cm^{-1} while the ν(OH) stretching 2600–2800 cm^{-1} and ν(C=O) disappears in all the complexes indicating that the ligands are coordinated in their keto-enol tautomer form. New bands which are absent in the spectra of all the free ligands, were ob-

Table 2. Cyclic voltammetric measurements for copper(II) complexes in DMSO (0.001 mol dm^{-1}) containing 0.1 M NaClO$_4$ as supporting electrolyte

Complex	Scan rate	E_{pc} (mV)	I_{pc} (µA)	E_{pa} (mV)	I_{pa} (µA)	ΔE_p (mV)	$E^{0'}$	I_{pa}/I_{pc}
[Cu(PPS)(bipy)](ClO$_4$)$_2$ (1)	100	−460	2.0637	−142	0.09986	318	301	0.484
	200	−464	2.8989	−140	1.4018	324	302	0.483
[Cu(PPS)(phen)(ClO$_4$)$_2$ (2)	100	−601	1.4160	−345	0.8765	256	473	0.619
	200	−610	1.5392	−330	0.9638	280	470	0.626
[Cu(PPS)(dmp)](ClO$_4$)$_2$ (3)	100	−538	3.3295	−56	1.5564	482	297	0.467
	200	−544	12.5032	−54	5.8165	490	299	0.465
[Cu(PPS)(en)](ClO$_4$)$_2$ (4)	100	−432	1.8695	−122	0.9788	310	277	0.523
	200	−438	2.7532	−11ε	1.4436	320	278	0.524
[Cu(PPS)(temed)](ClO$_4$)$_2$ (5)	100	−448	2.2357	−160	0.9635	288	304	0.431
	200	−452	3.9446	−154	1.6735	298	300	0.424

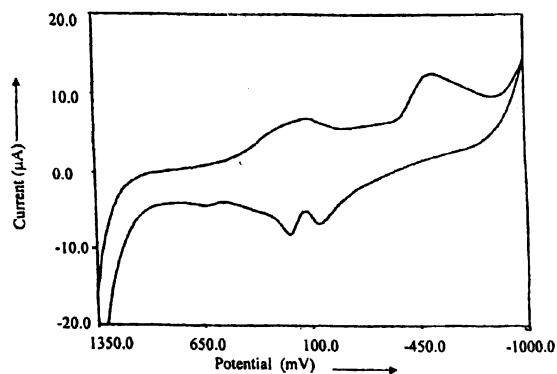$$E_p = E_{pa} - E_{pc}, \quad E^{0'} = \frac{E_p + E_{pc}}{2}.$$

Fig. 4. Cyclic voltammogram of the complex [Cu(PPS)(dmp)] (ClO$_4$)$_2$ (3) in 0.1 M NaClO$_4$ [scan rate : 100 mV/s].

plexes with PPS ligand are quite similar. In the different potential range at scan rate 100 mV/s and 200 mV/s yielded an irreversible couple corresponding to Cu^{II}/Cu^{I} redox process[26,27]. Constancy of $E^{0'}$ shows that in all cases

served at 1535 and 1557 cm^{-1}, attributable to the coordinated ν(C–O) mode[31,32] and in the 450–670 region assigned to the M–O and M–N bands. When compared to complex 1 and 2 spectra two new absorption bands which are characteristic of the presence of chelating phen[33] (725 and 855 cm^{-1}) for **2** and bipy[34] (775 and 739 cm^{-1}) for **1**. The IR spectra of the complexes containing perchlorate anions were dominated by the very strong stretching vibrations characteristic of ClO$_4^-$ (1087–1111 and 619–623 cm^{-1}) in all the cases.

Superoxide dismutase activity :

The superoxide dismutase mimetic activities of the present complexes **1-5** were examined with assayed by the use of alkaline-DMSO as a superoxide anion generating system in association with nitroblue tetrazolium chloride as a Scavenger of superoxide[35]. The complexes in the present study exhibit catalytic activity towards the

dismutation of superoxide anion. It is interesting that the SOD activity of the present copper(II) complexes decreases in the order **1 > 2 > 3 > 4 > 5** where it appears that the inclusion of the nitrogen donor ligands reduce the SOD activity. The inclusion of the N,N-donor ligands like 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) in the copper(II) complexes significantly increased catalytic activity. The chromophore concentration value required to yield 50% inhibition of the reduction of NBT (IC$_{50}$) of the present complexes 60 μmol dm^{-3} for **1**, 54 μmol dm^{-3} for **2**, 45 μmol dm^{-3} for **3**, 42 μmol dm^{-3} for **4** and 40 μmol dm^{-3} for **5** are higher than the value exhibited by the native enzymes (IC$_{50}$ = 0.04 μmol dm^{-3}) on a molar base. These higher values may be due to the strong ligand field created by the tridentate Schiff base ligand which opposes the interaction of the complexed copper with superoxide radical and the geometry of copper in the SOD enzymes also changes from distorted square pyramidal.

Experimental

Materials and methods :

Copper(II) perchlorate hexahydrate (Aldrich), 2-benzoylpyridine (s.d. fine chem.), 4-phenylsemicarbazide (Across), 2,2′-bipyridine (s.d. fine chem.), 1,10-phenanthroline (s.d. fine chem.), 2,9-dimethyl-1,10-phenanthroline (s.d. fine chem.), ethylenediamine (s.d. fine chem.), N,N,N',N'-tetramethylethylenediamine (s.d. fine chem.), CH$_3$OH (s.d. fine chem.), DMSO (s.d. fine chem.), nitroblue tetrazolium chloride (s.d. fine chem.) and dipotassium hydrogen phosphate (s.d. fine chem.). All the chemicals were of AR grade and were used as supplied. Elemental analyses (C, H, N) of new copper(II) complexes were performed on an Elementar Vario ELIII Carlo Erba 1108 analyser. Fast Atom Bombardment (m/z) spectra of the complexes were recorded on Jeol S-102/DA 6000 mass spectrometer using Xenon (6 KV, 10 mA) as the FAB gas. The magnetic susceptibility measurements were carried out on Gouy balance at room temperature using mercury(II) tetrathiocyantatocobaltate(II) (χ_g = 16.44 × 10^{-6} cgs unit) as the calibrant. The electronic spectra were recorded at ambient temperature on a Schimadzu UV-Visible recording spectrophotometer UV-160 in quartz cells in the desired wave length region. The IR spectra (400–4000 cm^{-1}) of the complexes were re-

corded on a Varian 3100 FTIR Excalibur series spectrophotometer with samples prepared as KBr pellets. EPR spectra were recorded on a Varian E-line Century Series EPR spectrometer employing X-band radiations and a cylindrical cavity with 100 KHz magnetic field modulation. TCNE (g_e = 2.00277) was used as field marker. A BAS 100 Epsilon electrochemical analyzer was used for cyclic voltammetric experiments in a DMSO solution of the complex containing NaClO$_4$ as the supporting electrolyte. The three electrode measurement was carried out at 298 K under a nitrogen atmosphere with a platinum working electrode, a platinum wire auxiliary electrode and a silver/silver chloride reference electrode (Ag/AgCl).

Synthesis of the Schiff base (PPS) :

A solution of 4-phenylsemicarbazide (10.0 mmol, 1.51 g) in 10 mL ethanol was refluxed with a ethanolic solution of 2-benzoylpyridine (10.0 mmol, 1.83 g) continuously for 6 h after adding 1–2 drops of acetic acid. On cooling the solution pale yellow crystals separated which were filtered and washed with methanol. The empirical formula given for the ligand, C$_{19}$H$_{16}$N$_4$O was confirmed by elemental analysis. Yield ~60% (Found : C, 72.08; H, 5.08; N, 17.72. Calcd. for C$_{19}$H$_{16}$N$_4$O (PPS) : C, 72.06; H, 5.06; N, 17.70%).

Synthesis of [Cu(PPS)(bipy)](ClO$_4$)$_2$ (1) :

Complex **1** was prepared in high yield from the reaction of copper(II) perchlorate hexahydrate (1.0 mmol, 0.37 g) with the multidentate Schiff base (PPS) ligand (1.0 mmol, 0.32 g) dissolved in 20 mL of methanol. To this solution, 2,2-bipyridine (1.0 mmol, 0.16 g) was added dropwise and the resulting green precipitate, separated out were collected by filtration, washed with diethylether, dried in air and stored in CaCl$_2$ desiccator. Yield ~80%. The complex has been characterized from analytical and physico-chemical data. The empirical formula given for the complex **1** C$_{29}$H$_{24}$Cl$_2$N$_6$O$_9$ was confirmed by elemental analyses (Found : C, 47.33; H, 3.23; N, 11.40. Calcd. for **1** : C, 47.35; H, 3.26; N, 11.43%); FAB-mass (m/z) : Calcd. : 535.11, Found : 536.

Synthesis of [Cu(PPS)(phen)](ClO$_4$)$_2$ (2), [Cu(PPS)-(dmp)](ClO$_4$)$_2$ (3), [Cu(PPS)(en)](ClO$_4$)$_2$ (4) and [Cu(PPS)-(temed)](ClO$_4$)$_2$ (5) :

All of these complexes were synthesized as complex **1** described by employing, phen (1.0 mmol, 0.19 g), dmp

(1.0 mmol, 0.21 g), en (1.0 mmol, 0.06 ml) and temed (1.0 mmol, 0.1 ml) in place of bipy (Found : C, 47.89; H, 3.37; N, 10.83. Calcd. for $C_{31}C_{26}Cl_2N_6O_9$ (2) : C, 47.87; H, 3.35; N, 10.81%); FAB-mass (m/z) : Calcd. : 578.14, Found : 579; (Found : C, 50.33; H, 4.08; N, 10.69. Calcd. for $C_{33}H_{32}Cl_2N_6O_9$ (3) : C, 50.31; H, 4.06; N, 10.67%); FAB-mass (m/z) : Calcd. : 588.19; Found 589 (Found : C, 39.47; H, 3.79; N, 3.17. Calcd. for $C_{21}H_{24}Cl_2N_6O_9$ (4) : C, 39.45; H, 3.76; N, 3.15%); FAB-mass (m/z) : Calcd. 439.92; Found 440 (Found : C, 43.18; H, 4.60; N, 12.00. Calcd. for $C_{25}H_{32}Cl_2N_6O_9$ (5) : C, 43.16; H, 4.60; N, 12.08%) : FAB-mass (m/z) : Calcd. 496.13; Found : 497.

Acknowledgement

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