

Synthesis and Spectroscopic Studies of Mononuclear Mixed Ligand Schiff Base Complexes of Cu(II) Involving Conjugated Heterocyclic Nitrogen Base and N-PhOHA or N-PhDHA

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Mononuclear complexes of Cu(II) have been prepared by reacting a 1:1:1 molar ratio of N- phOHA or N-phDHA, dipy or phen and cupric chloride where, N-phOHA = N-phenyl-O-hydroxyacetophenonimine, N-phDHA = N-phenyl-2,4-dihydroxyacetophenonimine, dipy = 2,2'-bipyridil, phen = 1,10-phenanthroline. All complexes were characterized on the basis of their microanalysis data, molar conductance, magnetic moment at room temperature, UV-Vis, IR, ¹H NMR, and ESR spectra. The monomeric and ionic nature of complexes was confirmed by their magnetic moment data and molar conductance values. The ESR spectra of metal chelates in polycrystalline and solution state at 300 K and 77 K were recorded and their silent features are reported. The ESR spectra of the metal chelates provided information about their structure on the basis of Hamiltonian parameters of the complexes and also degree of covalency.

Keywords: Mixed ligand, Schiff base, Spectroscopy, Copper(II)

INTRODUCTION

Metal complexes of Schiff bases have played a central role in the development of coordination chemistry. From the survey of existing literature [1-7], it appears that Cu(II) Schiff bases have been extensively used as biologically active complexes and as catalyst in chemical and the petrochemical industries [8-10]. Keeping the above facts in mind, we continue our research work [11] on transition metal complexes with Schiff bases.

The present study describes the preparation and characterization of Schiff base-Cu(II) complexes of type [(N-phOHA) or (N-phDHA) Cu (phen) or (dipy)] ClO₄.

EXPERIMENTAL

Methanol, ethanol, acetone, and diethyl ether were used after purification using the standard method described in literature [12]. 2-Hydroxy acetophenone, 2,4-dihydroxyacetophenone, 2,2'-dipyridyl, and 1,10-phenanthroline (E-Merck) were used as received. Aniline (BDH) was distilled before use. The metal salt cupric chloride was of BDH made.

Synthesis of N-Phenyl-2-hydroxyacetophenonimine or N-Phenyl-2,4-dihydroxyacetophenonimine

N-phenyl-2-hydroxyacetophenonimine or N-phenyl-2,4-dihydroxyacetophenonimine were prepared by condensation of O-hydroxyacetophenone or 2,4-dihydroxyacetophenone and aniline using acetic acid as catalyst according to the following procedure:

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Into a 1 l two neck bottom flask equipped with a reflux condenser was placed an ethanolic solution of O-hydroxyacetophenone (0.01 mol, 1.203 ml) or 2,4-dihydroxyacetophenone (0.01 mol, 1.507 g). To this solution was added aniline drop wise (0.01 mol, 0.091 ml), within of about 2-3 min, using a separating funnel and a few drops of acetic acid were added. The reaction mixture was then refluxed for 1 h on a sandbath. During this period, the color of the reaction mixture was turned to red. After purring the reaction mixture into an ice bath, shining yellow or red orange colored Schiff base compounds were isolated. Both the Schiff base compounds were re-crystallized from methanol and dried under vacuum.

Synthesis of Mono-Nuclear Cu(II) Complexes

N-Phenyl-2-hydroxyacetophenonimine (0.01 mol, 2.11 g) or N-phenyl-2,4-dihydroxyacetophenonimine (0.01 mol, 2.27 g) and 2,2'-dipyridyl (0.01 mol, 1.56 g) or 1,10-phenanthroline (0.01 mol, 1.98 g) were dissolved in methanol (50 ml) by warming and then added to the metal solution (30 ml, 0.01 mol, 1.70 g). The pH of solution was raised up to 4 by adding sodium acetate solution. The reaction mixture was then refluxed on a water-bath for 1 h and after that saturated solution of sodium perchlorate was added. The complex was precipitated out and further refluxed on water-bath for 1 h. Colored compound thus separated was filtered under suction and washed successively with water and ethanol to remove unrelated ligands and then air dried.

Apparatus

Elemental analyses (C, H, N) were performed on a CDRI, Lucknow apparatus. FT-IR spectra in the spectral region 4000-400 cm^{-1} were obtained, using KBr discs, on a Parkin Elmer IR Spectrophotometer (No. 1310). Electronic spectra in the 200-800 nm region were obtained in acetone on a Shimadzu UV 160A instrument, using quartz cells of 1 cm^3 optical path. Magnetic measurements were carried out at room temperature by the Gouy method, using $\text{Hg}[\text{Co}(\text{SCN})_4]$ for calibration. Molar conductances of the Schiff base complexes were determined on a Systronics direct reading conductivity meter type CM-82T. ESR spectra of all complexes were recorded by X-band ESR at RSIC, IIT, Mumbai, at room temperature and liquid nitrogen temperature for polycrystalline and solution

state.

RESULTS AND DISCUSSION

The newly synthesized Schiff base ligand and its complexes are very stable at room temperature in solid state. The ligand and complexes are soluble in common organic solvents. The analytical data of all the compounds are presented in Table 1. The analytical data are in good agreement with the proposed Schiff base complexes of Cu(II). Condensation of 2-hydroxy acetophenone or 2,4-dihydroxy acetophenone with aniline gives the corresponding imine, which is easily identified by its IR, ^1H NMR spectra (Fig. 1) Schiff base complexes were obtained from reaction of 1:1:1 molar ratio of metal ions, N-phOHA or N-phDHA and (dipy) or (phe) (Fig. 2).

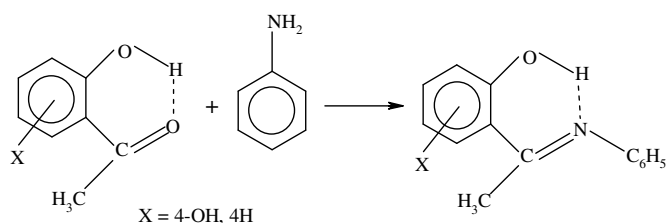


Fig. 1. Synthesis scheme for the preparation of the ligand N-phOHA and N-phDHA.

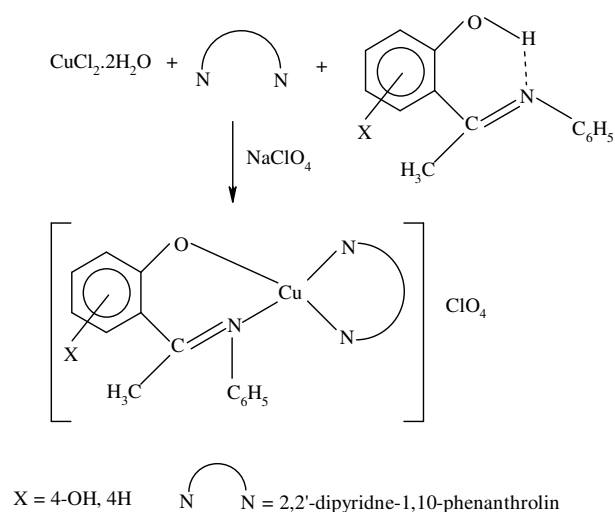


Fig. 2. Synthesis of Mono-nuclear Schiff base complexes of Cu(II).

Table 1. Physical and Analytical Data of Mononuclear Cu(II) Complexes

Compound abbreviation	Mol. Wt.	Color	Yield (%)	M.p. (°C)	%Found (Calcd.)				μ_{eff} B.M
					C	H	N	Metal	
[(N-phOHA)(dipy)Cu(II)]ClO ₄	514.04	Green	75	230	49.32 (49.82)	3.09 (3.12)	7.9 (7.96)	12.07 (12.26)	1.93
[(N-phOHA)(phen)Cu(II)]ClO ₄	553.04	Green	78	230	57.41 (57.92)	2.94 (3.01)	6.68 (6.96)	11.27 (11.48)	1.88
[(N-phDHA)(dipy)Cu(II)]ClO ₄	545.04	Green	82	272	5.41 (52.84)	3.41 (3.66)	7.56 (7.70)	11.81 (11.65)	1.93
[(N-phDHA)(phen)Cu(II)]ClO ₄	569.04	Green	79	252	54.98 (54.82)	3.22 (3.51)	7.86 (7.38)	11.43 (11.16)	1.92

Molar Conductance Studies

The molar conductance of the mononuclear complexes is observed in the range 36 to 50 moh cm² mol⁻¹, which is close to that expected for a 1:1 electrolyte in acetone. This shows the presence of ClO₄⁻ as the counter ion in the outer sphere of the complexes.

Magnetic Measurement Studies

The room temperature magnetic moment values obtained are reported in Table 1. The room temperature magnetic moment of mixed ligand mononuclear complexes of Cu(II) = 1.72-1.80 B.M. almost agree with the a spin only value of 1.73 for $S = \frac{1}{2}$, as usually observed for Cu(II) complexes.

¹H NMR Spectral Studies

The ¹H NMR spectra of the Schiff base ligand show slightly broad and medium resonance peak at 14.63 and 10.00, 9.44 δ due to 2-OH-N protons. In the Schiff base ligand N-phOHA one more sharp and single peak was observed in the low field region, i.e. at 12.67 ppm due to 4 -OH group present in the phenyl group. In the high field region, the -CH₃ proton appears as sharp and singlet peaks at 2.33 and 2.53 ppm in Schiff base ligands N-phOHA and N-phDHA, respectively. The phenyl multiplets of the ligand was observed in the range 6.86-7.64 ppm and 6.35-7.06 ppm in the case of N-phOHA and N-phDHA, respectively. The different position of -OH and -CH₃ protons and phenyl multiplet are due to the presence of one more -OH group at 4th position in the phenyl

group.

FT-IR Spectral Studies

There is a strong and very broad band centered around 3434 and 3315 cm⁻¹, which is characteristic of strong hydrogen bonded O-H vibration in both Schiff base ligand. The infrared spectra of mixed ligand (mononuclear) complexes of the type [MLL']ClO₄, where L = N-phOHA or N-phDHA, L' = 2,2'-dipyridyl or 1,10-phenanthroline show no partially broad bands centered at 3434 and 3315 cm⁻¹ indicating that ν O-H, which strongly hydrogen bonded of the N-phOHA or N-phDHA respectively, gets dissociated after complexation. All the spectra show medium absorptions at 3070-3050 cm⁻¹ and 2930-2860 cm⁻¹ due to aromatic and aliphatic C-H stretching, respectively. The ligands N-phOHA and N-phDHA shows characteristic band at 1625-1615 cm⁻¹, however this band is lowering in the frequency (10- 12 cm⁻¹) when the complex formation is take place [13,14]. The other bands in the region 1600-1300 cm⁻¹ are due to ring deformation modes. A characterization band of intermediate intensity is found at 1205 cm⁻¹ which may be assigned to $\nu_{\text{C-O}}$ [15,16].

In mononuclear case, the perchlorate gives rise to two IR bands, a weak band at 935-926 cm⁻¹ due to symmetric stretching mode (IR-forbidden) and an asymmetric stretching mode at 1190- 1090 cm⁻¹ (IR-allowed). This shows that ClO₄⁻ ion has T_d-symmetry and is ionic [17]. The FT-IR data were summarised in Table 2.

Table 2. Characterization IR (cm^{-1}) and Electronic Spectral Data of Complexes

Compounds	$\nu_{\text{O-H}}$ H bond	ν_{OH} of H_2O	$\nu_{\text{C-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	λ_{max} (cm^{-1})	
						d-d transition	Charge transfer band
[(N-phOHA)(dipy)Cu(II)]ClO ₄		3450(b)	3010(m)	1600	1205	15936	32680, 32010, 29498, 28802
[(N-phOHA)(phen)Cu(II)]ClO ₄		3450(b)	3050	1600	1200	16103	33738, 32237, 30285, 28802
[(N-phDHA)(dipy)Cu(II)]ClO ₄	3495(b)	3150(b)	-	1600	1200	16807, 16273	32509, 32216, 32051, 28802, 26968
[(N-phDHA)(phen)Cu(II)]ClO ₄	3470(b)	3150(b)	3140(b)	1600	1210	16260	32216, 28802, 26371

Table 3. g and G Values of the Powder ESR Spectra of Mononuclear and Binuclear Cu(II) at R.T. and L.N.T.

Complexes	R.T.				L.N.T.			
	g	g _⊥	g ^a	G ^b	g	g _⊥	g ^a	G ^b
[(N-phOHA)(dipy)Cu(II)]ClO ₄	2.20	2.04	2.11	4.08	2.27	2.10	2.13	4.30
[(N-phOHA)(phen)Cu(II)]ClO ₄	2.19	2.03	2.08	4.8	2.33	2.08	2.16	4.07
[(N-phDHA)(dipy)Cu(II)]ClO ₄	2.20	2.04	2.09	4.27	2.34	2.08	2.17	4.13
[(N-phDHA)(phen)Cu(II)]ClO ₄	2.19	2.04	2.09	4.20	2.39	2.07	2.18	4.87

$$^a |g| = 1/3 (g_{||} + g_{\perp}). \quad ^b G = (g_{||} - 2.002)/(g_{\perp} - 2.002).$$

Electronic Spectra Studies

The electronic spectra studies in solution state of present mixed ligand Cu(II) complexes the broad band observed in between 16807-15823 cm^{-1} , which is attributed to a combination of three transition is square planer stereochemistry [18,19]. The electronic spectra are given in Table 2. There is no much difference of band positions in the electronic spectra of dipyrindyl and 1,10-phenanthroline mixed ligand complexes, which indicates that the ligand field around Cu(II) is equal in these complexes.

The UV-Vis spectra of ligands and their complexes have been taken in DMSO solution between 5000-25000 cm^{-1} . The

Schiff base ligand N-phOHA exhibits four bands at 32985, 32216, 28892, and 27382 cm^{-1} whereas N-phDHA exhibits three bands at 32216, 28802, and 27041 cm^{-1} . In both ligands, the inner ligand transitions such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ are common due to the presence of C=N, C=O, C=C and C-O groups in the ligands' structures [19]. In the metal complexes, the inter ligand transition remains as it is. New bands at higher wavenumbers 33738-326787 cm^{-1} support the formation of strong M-N bonds [11].

ESR Studies

As we could not get well-shaped single crystals, the EPR

spectra of the Schiff base complexes were recorded only for the powder and solution samples at RT and LNT, and the results are described in Table 3. All the powder sample spectra were recorded in quartz tubes to avoid Mn(II) or Fe(II) impurities and the solution spectra were recorded in pyridine:toluene (60:40) mixture in capillary tubes. The recorded solution spectra confirmed that the complexes do not undergo any structural change in solution.

The ESR spectra of mixed mononuclear complexes at RT and LNT are in identical nature showing a normal feature with $g_{||} > g_{\perp}$, g -values (Figs. 3 and 4 and Table 3). The complexes gave an axial symmetry; principal axes aligned parallel, which would be consistent with square coplanar stereochemistry. In these axial spectra, the values are related by the expression given in [18]. If $G < 4.0$, the ligand forming the copper(II) complex is regarded as a strong field ligand.

The ESR spectra of the mononuclear complexes were recorded in a mixed solvent system such as pyridine-toluene (60:40) at room temperature. Four asymmetric but equally spaced hyperfine line characterizes a copper(II) nuclear hyperfine interaction. In frozen solution spectra of mononuclear complexes, only three hyperfine components were resolved in the parallel region with no resolution of the hyperfine splitting observed in the perpendicular region.

Molecular orbital coefficient, α^2 (covalent in-plane, σ -bonding) and β^2 (covalent in-plane, π -bonding) were calculated by using the following equations [20,21].

$$\alpha^2 = -(A_{||}/0.036) + (g_{||} - 2.0023) + 3/7 (g_{\perp} - 2.0023) + 0.04$$

$$\beta^2 = (g_{||} - 2.0023) E / -8\lambda\alpha^2$$

The values of bonding parameters obtained from the ESR spectra are reported in Table 5. The α^2 value account for a fraction of the unpaired electron density on the copper(II) ion. The smaller the value of α^2 , the higher the covalent bonding. The β^2 value is regarded as in-plane π -bonding parameter. For the present mononuclear Schiff base complexes, the α^2 values calculated from $A_{||}$ lie between 0.77-0.79, which indicate the moderately covalent nature of complexes [22]. The β^2 values for mononuclear complexes are in the range 0.88-0.91, indicating that there is no back donation is present in these

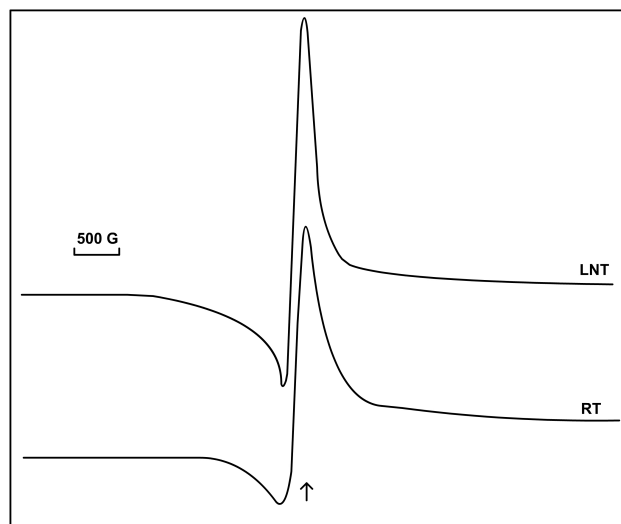


Fig. 3. X-band ESR spectra of $[\text{Cu}(\text{PMFP-EA})(\text{dipy})]\text{ClO}_4$ complex in polycrystalline form at RT and LNT.

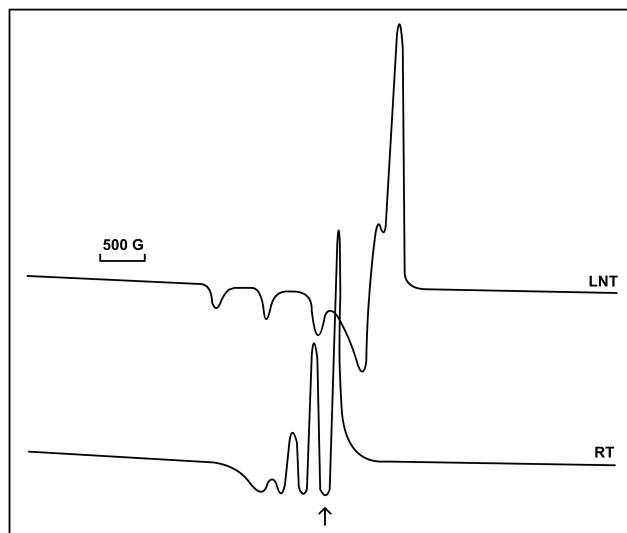


Fig. 4. X-band ESR spectra of $[\text{Cu}(\text{PMFP-EA})(\text{dipy})]\text{ClO}_4$ complex in solution at RT and LNT.

complexes. The K values were calculated from the experimental data as follows. After deriving the g_{iso} and A_{iso} parameters from liquid solution spectra at RT, the K value was calculated from the relation,

$$K = -A_{\text{iso}} + p (g_{\text{iso}} - 2.0023) (1 + f)$$

Table 4. g and A Values of the Solution^a Mononuclear and Binuclear Cu(II) Complexes

Complexes	$g_{ }$	g_{\perp}	$ g ^b$	$A_{ } \times 10^{-4}$ (cm^{-1})	$A_{\perp} \times 10^{-4}$ (cm^{-1})	$ A ^c \times 10^{-4}$ (cm^{-1})	$g_{ }/A_{ }$
[(N-phOHA)(dipy)Cu(II)]ClO ₄	2.28	2.01	2.10	157.70	24.0	69.0	145.0
[(N-phOHA)(phen)Cu(II)]ClO ₄	2.31	2.04	2.13	162.45	26.49	71.81	142.0
[(N-phDHA)(dipy)Cu(II)]ClO ₄	2.29	2.07	2.14	160.99	24.75	70.16	142.7
[(N-phDHA)(phen)Cu(II)]ClO ₄	2.31	2.02	2.11	162.74	26.34	71.14	142.0

^a(60% pyridine + 40% toluene). ^b $|g| = 1/3(g_{||} + g_{\perp})$. ^c $|A| = 1/3(A_{||} + A_{\perp})$

Table 5. Bonding Parameter of Mononuclear and Binuclear Cu(II) Complexes

Complex	α^2	β^2	$K \times 10^{-4}$ (cm^{-1})
[(N-phOHA)(dipy)Cu(II)]ClO ₄	0.78	0.89	107
[(N-phOHA)(phen)Cu(II)]ClO ₄	0.79	0.91	123
[(N-phDHA)(dipy)Cu(II)]ClO ₄	0.77	0.88	125
[(N-phDHA)(phen)Cu(II)]ClO ₄	0.78	0.89	115

α^2 and β^2 were calculated by using $P = 0.036 \text{ cm}^{-1}$ and $\xi = -828 \text{ cm}^{-1}$.

where $f = 0.067$ and $p = 0.036$. The K values obtained are also included in Table 5. We found no particular correlation between α^2 and K values.

Thermal Analysis

The mononuclear and binuclear complexes were subjected to the thermogravimetric analysis, to determine the presence of water molecule in their structures. However, in the presence of OHA or 2,4-DHA ligands, the compounds at higher temperatures give cracking noise and bumping out from the container. As a result of this, we could not take any TGA thermogram.

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