

Novel Binuclear Copper (II) Complexes Of Tetradentate (NNNN) Functionalized Ligands : Synthesis And Characterizations

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ABSTRACT: In the present work, the synthesis of Copper (II) coordination compounds of tetradentate nitrogen donor ligand bis[2-hydroxyimino-1-(4-X.phenyl)1-ethylidene] benzidine (p-X.HINAP)₂ (X=H,Cl,Br,CH₃) is described. Their structures were determined based on elemental analysis, molar conductance, magnetic susceptibility, electronic and thermal analysis, ¹H-NMR and IR spectra. Based on analytical and molar conductance data it is revealing that the ligand (L) is coordinated in (N₄) fashion. The complex may be formulated as [Cu(X.INAP)₂bz.2H₂O]₂

KEYWORDS: copper (II), tetradentate, azomethine, oximino, molar conductance

I. INTRODUCTION

Schiff bases are organic compounds formed by the condensation of a primary amine with an aldehyde or ketone. They were characterized by presence of carbon-nitrogen double bond (C=N) functional group and are related to potential biological and pharmacological compounds having anticancer, anti-tubercular, anti-inflammatory and antimicrobial activities [1-3]. Their biological properties can be altered depending on the presence of different substituent groups present on the parent structural unit or by complexation with variable metal ions. The coordination chemistry of Schiff bases has undergone noticeable development due to ease of preparation and good chelating property. In recent years, there has been a growing interest in the synthesis, characterization and crystal structures of copper (II) Schiff base complexes, not only because they have interesting properties and structural diversity [4] but also because they have found important application in catalysis for the coupling of phenylacetylene with halobenzene [5], preparation of supramolecular assemblies [6,7], the design of single and double-stranded architectures [8,9] and the grid complexes [10,11]. Then, many efforts have been devoted to the design and synthesis of new Schiff base ligands that would be able to control the crystal structure of copper complexes [12, 13]. However, the Cu(II) complexes of Schiff base ligand bis[2-hydroxyimino-1-(4-X.phenyl)1-ethylidene] benzidine (p-X.HIPE)₂ (X=H,Cl,Br,CH₃) is not reported. In present communication, synthesis, spectral and thermal properties of Cu(II) complexes are incorporated.

II. EXPERIMENTAL

All chemical used in the project work were of AR grade. Benzidine was recrystallised while the solvent were purified and double distilled before use. The ligands bis[2-hydroxyimino-1-(4-X.phenyl)1-ethylidene] benzidine (p-X.HIPE)₂ bz (X=H,Cl,Br,CH₃) was synthesized in the laboratory by reported method [14]. Elemental analysis was done by using a thermal finger- flash CA, 112 series at IIT, Mumbai. Molar conductance was measured in DMF (10⁻³ M solution) on an ELICO Digital Conductivity meter Model CM-180. The IR spectra were recorded in KBr disc on a Perkin Elmer Model 1600 FTIR Spectrophotometer. The diffuse reflectance spectra of solid copper complexes were taken on a Carl-Zeiss VSU-2P spectrophotometer fitted with a reflectance assembly, with pure MgCO₃ used as a reference. The ¹H-NMR Spectra was recorded in DMSO on a VXR-300S Varian Supercon NMR Spectrometer using TMS as the internal reference. Magnetic Susceptibility measurements were carried out by employing the Gouy method using Hg [Co (SCN)₄] as a calibrant. The EPR spectra are recorded on a Varian E-Line, E-112 Electron Spin Resonance Spectrometer using TCNE as standard. Thermo gravimetric studies of the complex were done on Netzch-429 Thermoanalyser recording at a

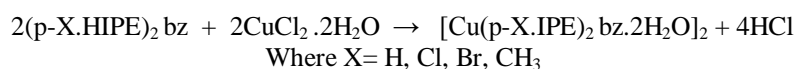
International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 3, March 2016

rate of 10 °C min⁻¹ Copper content of the complexes was done after decomposition of known amounts of the complexes and estimated by standard method [15]

2.1 Synthesis of complexes: A hot Dimethylformamide solution (DMF) of the ligands (0.01 mol) i.e. bis[2-hydroxyimino-1-(4-X.phenyl)1-ethylidene] benzidine (p-X.HIPE)₂ (X=H,Cl,Br,CH₃) and DMF solution (20mL) of the required metal salt (0.01 mol, 1.70g) were mixed together under constant stirring. These reaction mixtures were refluxed at 80 – 95 °C for 2 hours during which the colour of the solution changed. The solution was filtered and the filtrate was poured into crushed ice, when fine crystals of brown coloured complex were obtained. These were filtered, washed with 50% DMF-water mixture and dried in vacuum.



III. RESULTS AND DISCUSSION

The analytical and physical data of the copper complexes are presented in (Table:3.1). The complexes are brown in colored and thermally stable at least up to 150°C. They are insoluble in water and common organic solvents, but are somewhat soluble in DMF at room temperature. The analytical data of the complexes (Table:1) indicates that the complexes have 1:1 metal: ligand stoichiometry. The value of molar conductance in DMF solution at 10⁻³ M dilution are in the range of 0.14 – 0.20 ohm⁻¹ cm² mol⁻¹ suggesting a non-electrolyte nature of these complexes[16]. The ligands have four coordination sites but involvement of all to the same metal in the formation of a complex is sterically not favourable. However, linear dimers are possible and the structure of the complex may be represented as shown in (Fig.1) The analytical data of the complexes (Table-3.1) is consistent with their formulation as [Cu(p-X.IPE)₂ bz.2H₂O]₂ where p-X.IPE represents the deprotonated Schiff's base.

TABLE-3.1 PHYSICO-CHEMICAL CHARACTERISTIC OF COMPLEXES

Complexes	Yield %	Found (Calcd) (%)				Molar Cond. (Ω ⁻¹ cm ² mol ⁻¹)	μ _{eff} BM
		Cu	C	N	H		
[Cu(IPE) ₂ bz.2H ₂ O] ₂	75	11.52 (11.68)	61.56 (61.81)	10.20 (10.29)	4.24 (4.44)	0.142	1.741
[Cu(p-Cl.IPE) ₂ bz.2H ₂ O] ₂	78	10.12 (10.12)	54.34 (54.85)	8.92 (9.13)	4.02 (3.62)	0.153	1.752
[Cu(p-Br.IPE) ₂ bz.2H ₂ O] ₂	67	9.82 (9.05)	48.23 (47.91)	8.24 (7.98)	3.46 (3.16)	0.201	1.741
[Cu(p-CH ₃ .IPE) ₂ bz.2H ₂ O] ₂	72	11.01 (11.10)	63.46 (62.97)	10.00 (9.79)	5.12 (4.63)	0.164	1.657

The observed magnetic moment for the Cu(II) complexes are in the range of 1.65-1.75BM (Table-3.1). These are only slightly different from the spin only value of 1.73BM expected for a d⁹ system with one unpaired electron and are in the range normally found for Cu(II) complexes [17].

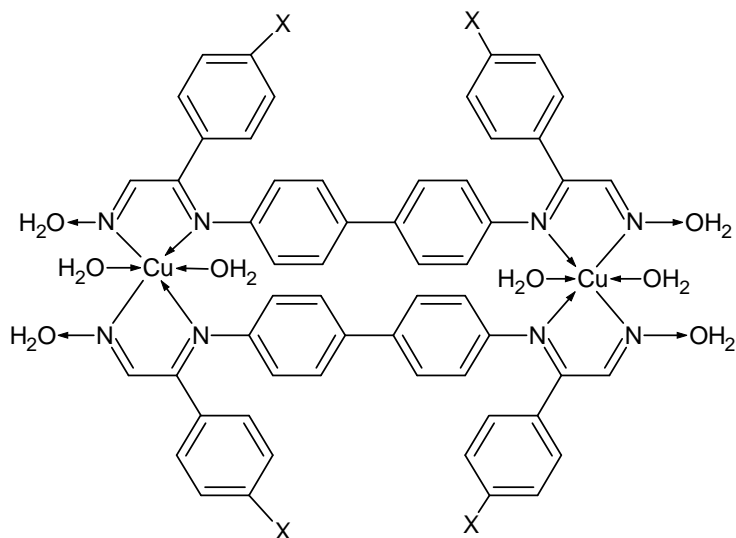


Fig:1 Structure of Cu(II) complexes of bis[2-hydroxyimino-1-(4-X.phenyl)1-ethylidene] benzidine (p-X.HIPE)₂

3.1 ¹H-NMR SPECTRA:

The ¹H-NMR spectrum of the ligands and complex are recorded in DMSO medium. Comparison of the ¹H-NMR spectra of the ligands and its complexes revealed that the ligand behaves as a tetradentate binegative NNNN donor; the disappearance of the signals at 11.9 ppm was ascribed to the fact that the ligands underwent deprotonation of the oximino group during complexation. A multiplet appearing in the region 6.6 – 7.2 ppm may be assigned to proton of biphenyl ring, where as phenyl proton show a multiplet at 7.4 – 8.0 ppm. The C-H proton of 1- ethylidene is at 8.4 ppm. This signal appears downfield shift by 0.2 – 0.4 ppm in the complexes indicating the coordination of hydroxyimino nitrogen. However, the position of other bands does not change appreciably because of the coordination of the metal ions with the ligand.

3.2 ELECTRONIC ABSORPTION SPECTRA:

All the Cu(II) complexes in solution exhibit intra ligand transition in the UV region. At least two bands are observed in the region around 32.67-36.23 kK and 47.62-48.78kK, and this may be ascribed to π - π^* transition which are observed at 35.21-35.74 kK and 47.62-48.31kK respectively in the electronic spectra of ligands (p-X.HIPE)₂ bz. The above observation indicates that π - π^* transition band in the metal complexes are observed at different position as compared to their position in the spectra of ligands , suggesting that the π electron system of the ligand undergoes considerable alteration on coordination to metal ion.

For a simple Cu(II) ion in octahedral field a simple spectrum corresponding to a single transition ${}^2E_g \rightarrow {}^2T_{2g}$ is expected. However, the complex Cu(II) ion with its unsymmetrically occupied E_g orbital is susceptible to Jahn-Teller distortion

The diffuse reflectance spectra of Cu(II) complexes of the ligand (p-X.HIPE)₂ bz shows two or three poorly defined band of different intensity in the range of 13.16-20.00kK constituting a broad band with clearly resolved spikes in some cases. The position and the assignment as referred in the Table-3.2 suggest that they are due to *d-d* transition in six- coordinated Cu (II) in a distorted octahedral environment [18].

TABLE-3.2 DIFFUSE REFLECTANCE SPECTRAL DATA FOR CU(II) COMPLEXES

complexes	Band kK	Assignments
[Cu(IPE) ₂ bz.2H ₂ O] ₂	13.160	² B _{1g} → ² B _{2g}
	15.384	² B _{1g} → ² A _{1g}
	20.000	² B _{1g} → ² E _g
	22.727	Charge transfer
[Cu(pCl.IPE) ₂ bz.2H ₂ O] ₂	14.285	² B _{1g} → ² B _{2g}
	17.850	² B _{1g} → ² E _g
	23.810	Charge transfer
[Cu(p-Br.IPE) ₂ bz.2H ₂ O] ₂	13.333	² B _{1g} → ² B _{2g}
	15.384	² B _{1g} → ² A _{1g}
	17.857	² B _{1g} → ² E _g
	23.809	Charge transfer
[Cu(p-CH ₃ .IPE) ₂ bz.2H ₂ O] ₂	13.157	² B _{1g} → ² B _{2g}
	16.129	² B _{1g} → ² E _g
	25.000	Charge transfer

3.3 INFRARED SPECTRA:

Several structurally significant vibrational bond have been evaluated based on infrared spectra of related compounds like imino complex of some carbonyl oximes[19] isonitrosoacetophenone and benzidine. The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation. The IR spectra data of the complexes are shown in Table 3.3. There are two types of (C=N) group (azomethine and oximino) are present in the complex.

TABLE -3.3 IMPORTANT IR SPECTRAL BANDS OF COPPER(II) COMPLEXES

Complexes	ν(O-H)	ν(C=N) azomethine	ν(C=N) oximino	ν(N-O)	ν(O-H) in-plane/ out plane	ν(M-N)	ν(M-O)
[Cu(IPE) ₂ bz.2H ₂ O] ₂	3341	1610	1577	1230	1275/1009	580	440
[Cu(pCl.IPE) ₂ bz.2H ₂ O] ₂	3348	1600	1551	1228	1277/1009	629	480
[Cu(p-Br.IPE) ₂ bz.2H ₂ O] ₂	3337	1590	1545	1244	1282/1008	609	449
[Cu(p-CH ₃ .IPE) ₂ bz.2H ₂ O] ₂	3350	1637	1580	1220	1284/1025	607	447

- A. The band around 1590 – 1620 cm⁻¹ are assigned to the azomethine group, whereas those around 1540 – 1580cm⁻¹ are attributed to oximino ν(C=N) vibrations. The azomethine and oxime ν(C=N) vibrational frequencies show either a positive or negative shift in metal complexes indicating coordination of the azomethine and oxime nitrogen donor atom to the metal ions
- B. The infrared spectra indicate that the ν(C=N) azomethine frequency is affected by substitution in the phenyl moiety of the present ligands. The ν(C=N) azomethine decreases in the order CH₃ > H > Cl > Br, this sequence is consistent with Hammett's σ values(CH₃ = -0.17, H =0, Cl =0.227, Br=0.232).The observed order is explained by the fact that the electron releasing substituents like CH₃ and H tend to increase the electron density on the nitrogen of the C=N group, thereby facilitating strong σ, but poor π interaction,
- C. The view is further supported by the appearance of the band corresponding to the metal-nitrogen (M-N) stretching vibration at 580-629 cm⁻¹ in all the complexes. A broad band at 3210 cm⁻¹ due to ν(NOH) in ligand was absent in all complexes indicating deprotonation of the oximino group during complexation.
- D. A new medium to strong intensity band observed in the region 1220 – 1244 cm⁻¹ in the spectra of all the complexes is ascribed to ν(N→O) appearing due to the formation of (N→O) linkage in the complex. This is indicative of bonding through oximino nitrogen atom leading to a five membered chelate ring formation.

- E. Bonding through oximino oxygen donor leading to formation of a six membered chelate ring is ruled out as $\nu(\text{N-O})$ due to O - coordinated oximino group expected to occur around 1000 cm^{-1} is not observed in the present complexes.
- F. The M-O stretching vibrational of the coordinated water molecules are observed at $440\text{-}480\text{ cm}^{-1}$ in the spectra. It may be noted that these bands are not present in the spectra of the respective ligands.
- G. The present studies indicate that the M-O stretching frequency are observed at lower frequency than the M-N vibrations this could be expected as $\nu(\text{M-O})$ bands are due to the coordinated water molecules [20,21]. Again, as inferred from the thermal studies that coordinated water molecules are lost before decomposition of the metal chelates indicating greater strength of the M-N bonds as compared to M-O [22,23]. The observed vibration spectral features therefore consistent with the proposed structure and with the results of the other physiochemical studies.

3.4 ESR SPECTRA:

The various ESR parameters are summarized in Table:3.4. The observed g_{\parallel} values are less than 2.3 in agreement with the covalent character of the metal-ligand bond [24]. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.003) observed for these complexes shows that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of Cu(II) ion and the spectral features are characteristic of axial symmetry, tetragonal elongated structure may be assumed for these Cu(II) complexes.

TABLE-3.4 ESR SPECTRAL PARAMETERS OF Cu(II) COMPLEXES

Complexes	g_{\perp}	g_{\parallel}	g_{av}	$A_1 \times 10^4$ (cm^{-1})	λ' (cm^{-1})	α^2	G
[Cu(IPE) ₂ bz.2H ₂ O] ₂	2.019	2.091	2.043	81.35	153.4	0.3650	4.78
[Cu(pCl.IPE) ₂ bz.2H ₂ O] ₂	2.025	2.106	2.052	81.93	208.9	0.3842	4.24
[Cu(p-Br.IPE) ₂ bz.2H ₂ O] ₂	2.030	2.130	2.063	74.58	245.6	0.3899	4.33
[Cu(p-CH ₃ .IPE) ₂ bz.2H ₂ O] ₂	2.025	2.118	2.056	70.52	205.0	0.3645	4.72

The axial factor G (given by $g_{\parallel}-2/g_{\perp}-2$) for these complexes are greater than 4, indicating exchange of coupling. The α^2 values obtained from Kivelson and Neiman's equation suggest appreciable covalency in these complexes. It is important to note that A_1 value is nearly half of the monomer value such a situation is expected for Cu dimer [24]. The covalent nature can also be ascertained from the value of spin-orbit coupling constant λ' . For octahedral d^9 ion, E ground term occur the spin-orbit interaction with higher T₂ term of the same multiplicity gives the following g_{av} value [24]

$$g_{av} = 2.00(1 - 2\lambda'/10Dq) \dots \dots (I)$$

The g_{av} value is obtained from the equation $g_{av} = 1/3(g_{\parallel} + 2g_{\perp})$ and $10Dq$ from the electronic spectrum. From Eq (I) the λ' values were calculated. The lower λ' values for the Cu(II) complexes compared to that of the free ion (-830 cm^{-1}) also suggest a considerable orbital overlap.

3.5 THERMAL STUDIES:

The weight loss between $150\text{-}240\text{ }^{\circ}\text{C}$ in the complexes of Cu(II) corresponds to the loss of coordinated water molecule. The observed and calculated weight loss for the metal complexes is presented in Table-3.5. Thus, the result of the thermal studies indicate the presence of coordinated water molecules in the metal complexes further corroborates the assumption made on the basis of infrared spectral studies

TABLE -3.5 THERMAL ANALYSIS OF COMPLEXES

Complexes	Wt. for Tg (mg)	Temp. °C	% of water loss Found(cacl.)	Decomposition temperature °C	% Wt. of CuO found (cacl.)
[Cu(IPE) ₂ bz.2H ₂ O] ₂	140	150-195	5.89(6.57)	200 to 750 °C	14.86 (14.51)
[Cu(pCl.IPE) ₂ bz.2H ₂ O] ₂	145	190-240	6.04(5.83)	250 to 700 °C	12.78 (12.89)
[Cu(p-Br.IPE) ₂ bz.2H ₂ O] ₂	154	150-200	5.35 (5.09)	200 to 630 °C	10.94 (11.27)
[Cu(p-CH ₃ .IPE) ₂ bz.2H ₂ O] ₂	159	180-210	5.26 (6.24)	220 to 770°C	12.96 (13.89)

The anhydrous complexes show rapid degradation presumably due to decomposition of organic constituent of the complex molecule as indicated by the steep fall in the percentage weight loss. The decomposition continues up to 770 °C and reaches to stable products in each complex as indicated by the consistency in weight in the plateau of the thermogram as seen in the Fig:2. This corresponds to the composition of their stable oxides. The decomposition temperature varies for different complexes as shown in Table-3.5.

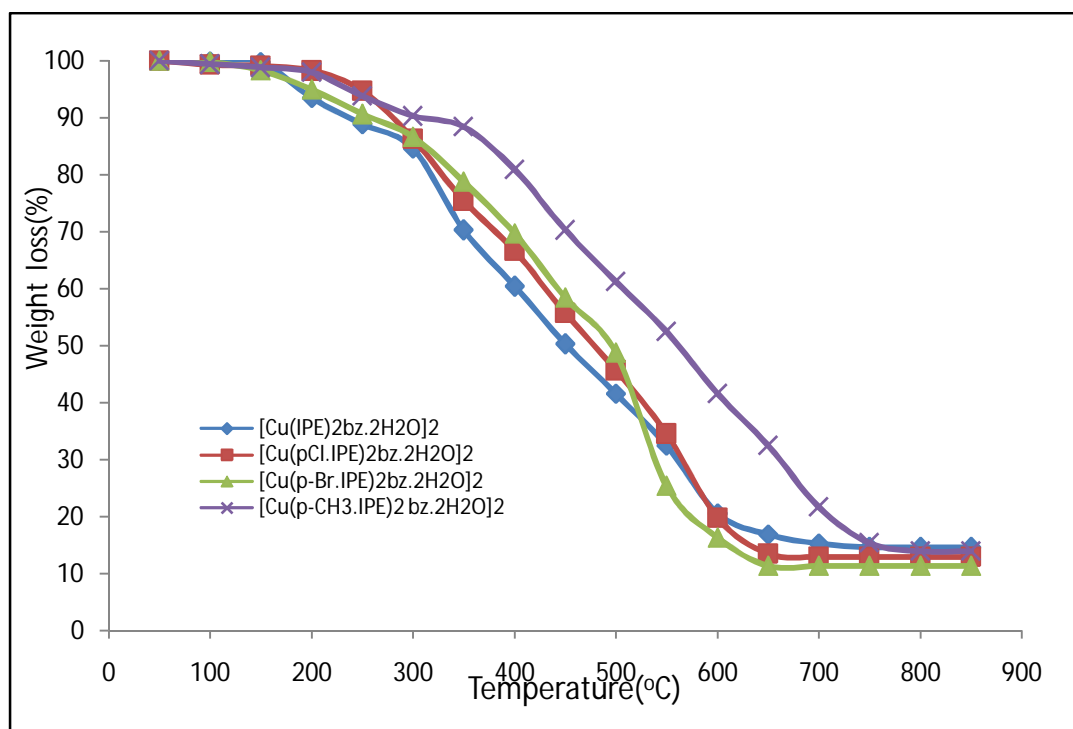


Fig:2 Thermogravimetric Curve of Cu(II) Complexes

IV CONCLUSION

The present study reveal octahedral geometry for the Cu(II) complexes . The ligands act in tetradentate manner coordinating with four nitrogen atoms of which two are of the azomethine and other two are of oximino group in NNNN fashion, which lead to a five member chelate ring formation. The satisfactory analytical data and all physio-chemical studies presented above suggest that these complexes may be formulated as [Cu(X.INAP)₂bz.2H₂O]₂ (X=H,Cl,Br,CH₃)

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 3, March 2016

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