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Chelation and extraction of copper(II) with 5-pyrazolone-based Schiff bases

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Copper(II) chelates of the Schiff bases (H_2L), obtained by condensation of 4-butyryl-3-methyl-1-phenyl-pyrazoline-5-one (HBMPP) with *o*-phenylene diamine (H_2L^1) and *p*-phenylene diamine (H_2L^2), have been prepared and characterized by elemental analyses, thermogravimetric analyses, magnetic measurements, diffuse reflectance spectra, IR and mass spectra, and conductance measurements. The extractability of copper(II) with H_2L in chloroform was examined. Effective extraction was observed with $1 \times 10^{-3} \text{ mol dm}^{-3}$ of ligands at pH 6.5 using H_2L^1 and pH 7.0 using H_2L^2 . The nature of the extracted species was ascertained by the slope analysis method. The ligand can effectively be used in solvent extraction of copper(II) from aqueous phase to organic phase.

Keywords: Ligands; Extraction; Schiff bases; 5-Pyrazolones; Copper(II)

1. Introduction

Schiff bases are important chelating agents toward metal ions for reversibly binding oxygen [1], catalytic activity [2, 3], DNA binding or cleavages [4], photochromic properties [5], and extraction of heavy metals [6]. Compounds containing C=N linkages have significant antifungal, antibacterial, and anticancer properties [3, 7]. In addition, solvent extraction of metal chelates has been used as a separation method, applicable to both trace and macro levels of metals [8].

Copper(II) is one of the essential elements in various biological species. However, larger concentration in the environment severely affects aquatic and human life. There are many extractants with special reference to β -diketones as chelating agents for metal ions. Acetyl acetone, dibenzoylmethane, and thenoyltrifluoroacetate have been extensively studied [9, 10]. Also five-membered heterocyclic β -diketones, particularly monothio benzoylmethane and dithiocarboxylate derivatives of 2-pyrazoline-5-one [11], have been used. Metal complexes of Schiff bases derived from substituted salicylaldehydes and various amines have been widely investigated [12–15]. 4-Acyl-3-methyl-1-phenyl-pyrazoline-5-ones and related compounds are good extractants toward a wide variety of metal ions [16, 17]. To the best of our knowledge,

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there is no report on extraction ability of Schiff bases derived from 5-pyrazolones. The derivatives of 5-pyrazolones have remained one of our focal points of research [18–20]. Therefore in this work we have synthesized two Schiff bases by the reaction of 4-butyryl-3-methyl-1-phenyl-pyrazoline-5-one with *o*- and *p*-phenylenediamines. Their copper(II) chelates were synthesized by template effect from the reaction of 4-butyryl-3-methyl-1-phenyl-5-pyrazolone (HBMPP) with corresponding aromatic diamines and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in ethanol. The extraction behavior of copper(II), from an aqueous phase to non-aqueous phase with these Schiff-base ligands (H_2L), was investigated.

2. Experimental

2.1. Reagents and solution

All the chemicals were analytical grade and used as received. The 4-butyryl-3-methyl-1-phenyl-pyrazoline-5-one (HBMPP) was prepared from the reaction of butyrylchloride with 3-methyl-1-phenyl-pyrazoline-5-one, $\text{Ca}(\text{OH})_2$ suspended in 1,4 dioxane as reported in the literature [21]. The stock solution 0.04 mol dm^{-3} in Cu^{2+} was prepared by taking 1.25 g of acetone dried pure copper foil, dissolved in 5.0 mL of fuming nitric acid with subsequent dilution to 1 L with doubly distilled water.

2.2. Physical measurements

Elemental analysis was carried out on a Perkin Elmer 2400 SERIES-II. Mass spectra were obtained on a JEOL SX-102(FAB) mass spectrometer at Sophisticated Instrumentation Center, CDRI, Lucknow, India. The gravimetric oxide method for estimation of metal was employed. Conductivity measurements were made with a “SYSTRONICS 305 conductivity bridge” at room temperature. Magnetic susceptibility measurements were made on a 7304 vibrating sample magnetometer, Lake Shore, USA. The molecular weight of the chelate of the ligand derived from *p*-phenylenediamine was determined using a K-7000 KNAUER vapor pressure osmometer in DMF, calibrated with benzil ($K=3000$). The thermograms of all the compounds were obtained from 25°C to 350°C using nitrogen flux with a SDT 2960 TA thermoanalyzer. Diffuse reflectance spectra (DRS) of solid compounds diluted with MgO (25%) were obtained on a BECKMAN-DK-2A recording spectrophotometer from 350 to 1700 nm with standard reflectance attachment. IR spectra of all the compounds were recorded with a NICOLET-400 D spectrophotometer ($400\text{--}4000 \text{ cm}^{-1}$) using KBr discs. ^1H NMR spectra were obtained in CDCl_3 on a Hitachi R 1500 FT-NMR spectrometer. Shimadzu 160 A (Japan) UV-Vis recording spectrophotometer was used to measure the absorbance of solution throughout the study. Photometric determination of copper(II) was made on a HACH model DR/2500 spectrophotometer by standard method. Elecon Digital pH meter was used to monitor the pH of solution.

2.3. Synthesis and characterization of Schiff-base ligands [H_2L]

A solution of 5 mmol of aromatic diamine (0.54 g) in 50 mL absolute ethanol with a few drops of acetic acid was added dropwise over 2 h to a stirred solution of HBMPP

(10 mmol, 2.44 g), Na_2SO_4 (24 mmol, 3.41 g) in 50 mL warm absolute ethanol and refluxed for 12 h. The colored product separated on cooling, after removing Na_2SO_4 and kept overnight. It was then filtered, washed with ether, and recrystallized from absolute ethanol.

[H₂L¹]: Yield: 2.1 g (75%), color: yellow, m.p.: 187–189°C. IR (cm^{-1}): 1629 $\nu(\text{C}=\text{N})$ (azomethine), 1595 $\nu(\text{C}=\text{N})$ (cyclic), 1320 $\nu(\text{C}-\text{O})$, 1240 $\nu(\text{O}-\text{H})$. ¹H NMR (ppm): $\delta = 6-7.8$ (phenyl multiplets) (m, 14H), $\delta = 0.6-2.5$ ($\text{CH}_2\text{CH}_2\text{CH}_3, -\text{CH}_3$) (m, 20 H), $\delta = 12$ (enolic OH) (s, 2H). Anal. Calcd for $\text{C}_{34}\text{H}_{36}\text{N}_6\text{O}_2$ (%): C, 72.83; H, 6.47; N, 14.99. Found (%): C, 72.78; H, 6.39; N, 14.91. FAB MS: (m/z) (%) = 560 av. Calcd 560.69.

[H₂L²]: Yield: 2.0 g (72%), color: almond black, m.p.: 250°C. IR (cm^{-1}): 1630 $\nu(\text{C}=\text{N})$ (azomethine), 1595 $\nu(\text{C}=\text{N})$ (cyclic), 1305 $\nu(\text{C}-\text{O})$, 1240 $\nu(\text{O}-\text{H})$. ¹H NMR (ppm): $\delta = 6-7.5$ (phenyl multiplets) (m, 14H), $\delta = 0.4-2.8$ ($-\text{CH}_2\text{CH}_2\text{CH}_3, -\text{CH}_3$) (m, 20H), $\delta = 11.8$ (enolic OH) (s, 2H). Anal. Calcd for $\text{C}_{34}\text{H}_{36}\text{N}_6\text{O}_2$ (%): C, 72.83; H, 6.47; N, 14.99. Found (%): C, 72.76; H, 6.39; N, 14.82. FAB MS: (m/z) (%) = 560 av. Calcd 560.69.

2.4. Synthesis and characterization of copper(II) chelates

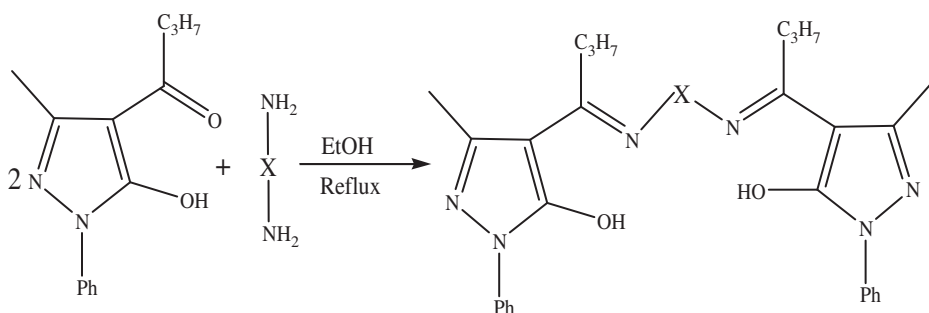
To a stirred solution of HBMPP (3.0 mmol, 0.72 g) and 1.5 mmol of diamine (0.162 g) in 50 mL of absolute ethanol was added dropwise the hydrated copper nitrate in absolute ethanol (50 mL) followed by the addition of sodium acetate (10 mg). After the addition was complete, stirring was continued under reflux for 3 h. A dark green precipitate was filtered and washed several times with water, diethyl ether, and then finally the product was dried in an oven at 60°C.

[Cu(L₁¹)(H₂O)₂]: Yield: 0.56 g (65%), color: blackish green, m.p.: 230°C. IR (cm^{-1}): 3100–3500 (m, H₂O) (coord.), 712 (m, $\rho_w\text{H}_2\text{O}$), 995 (m, $\rho_w\text{H}_2\text{O}$), 1240 (w, δOH), 1330 (sh, $\nu\text{C}-\text{O}$), 1625 (w, $\nu\text{C}=\text{N}$) (azomethine), 1595 (m, $\nu\text{C}=\text{N}$) (cyclic). Anal. Calcd for $\text{C}_{34}\text{H}_{38}\text{CuN}_6\text{O}_4$ (%): C, 62.04; H, 5.82; Cu, 9.65; N, 12.77. Found (%): C, 62.10; H, 5.90; Cu, 9.80; N, 12.78. FAB MS: (m/z) (%) = 657.12 av. Calcd 658.25. $A = 13.6 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$, $\mu_{\text{eff}} = 1.95 \text{ B.M. DRS: } 15,384 \text{ cm}^{-1}, 24,096 \text{ cm}^{-1}$ (charge transfer), $10 D_q$ (Calcd): 7692 cm^{-1} .

[Cu(L₂²)(H₂O)₂]: Yield: 0.51 g (59%) color: green, m.p.: 230°C. IR (cm^{-1}): IR (cm^{-1}): 3100–3500 (m, H₂O) (coord.), 713 (m, $\rho_w\text{H}_2\text{O}$), 993 (m, $\rho_w\text{H}_2\text{O}$), 1240 (w, δOH), 1330 (sh, $\nu\text{C}-\text{O}$), 1625 (w, $\nu\text{C}=\text{N}$) (azomethine), 1595 (m, $\nu\text{C}=\text{N}$) (cyclic). Anal. Calcd for $\text{C}_{68}\text{H}_{76}\text{Cu}_2\text{N}_{12}\text{O}_8$ (%): C, 62.04; H, 5.82; Cu, 9.65; N, 12.77. Found (%): C, 62.09; H, 5.88; Cu, 9.70; N, 12.80. FAB MS: (m/z) (%) = 1318 av. Calcd 1317. $A = 22.8 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$, $\mu_{\text{eff}} = 1.94 \text{ B.M. DRS: } 16,393 \text{ cm}^{-1}, 24,449 \text{ cm}^{-1}$ (charge transfer), $10 D_q$ (Calcd): 8196 cm^{-1} .

2.5. Extraction and analytical procedures

Equal volumes (25 mL) of chloroform, containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ of Schiff base (H₂L), and aqueous solution containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ of Cu^{2+} , $1 \times 10^{-1} \text{ mol dm}^{-3}$ of perchlorate, and required buffer ($1 \times 10^{-1} \text{ mol dm}^{-3}$ acetic acid, $1 \times 10^{-2} \text{ mol dm}^{-3}$



Where X = -C₆H₄(para)-, -C₆H₄(ortho)-

Scheme 1. Synthesis of Schiff base (H₂L).

acetate and hydrochloric acid or ammonia to adjust pH) were introduced into a stoppered flask and shaken for 0.5 h at $25 \pm 0.1^\circ\text{C}$. This period of shaking was enough to establish equilibrium between the two phases. The ionic strength (I) of the aqueous phase was kept at 0.1 mol dm^{-3} using appropriate amount of perchlorate. Two phases were separated by centrifuging and then the pH of the aqueous phase was determined and used in the calculation. The copper(II) ion content in equilibrated aqueous phase was determined spectrophotometrically by the HACH model DR/2500 spectrophotometer using CuVer[®] powder as standard reagent. The extracted species ($\lambda_{\text{max}} = 472 \text{ nm}$, $\varepsilon = 29,775 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in the non-aqueous phase was also measured in the same way after stripping with 2 mol dm^{-3} HCl solution.

3. Results and discussion

3.1. Analytical data

The formation of the Schiff bases, synthesized, and characterized by elemental analysis, IR, electronic spectra, magnetic measurements, molar conductivity, and mass spectra, can be expressed as shown in scheme 1.

3.2. IR spectra

IR spectra of free ligands show OH stretching frequency displaced to $3350\text{--}2800 \text{ cm}^{-1}$ due to internal hydrogen bonding of OH with $\text{N}=\text{C}$ [22, 23]. The ligands are relatively planar with intermolecular distance favoring hydrogen bond formation [23]. The electron donating groups on nitrogen also favor intra- or inter-molecular hydrogen bonding [23], suggesting that the ligands exist in enol form (scheme 1). The shifting of $\text{C}=\text{N}$ band ($1629\text{--}1635 \text{ cm}^{-1}$) in the ligands to a lower value ($1610\text{--}1630 \text{ cm}^{-1}$) in all the copper complexes suggests coordination might occur through ketimino nitrogen [24–26]. While the unaltered position of band (1595 cm^{-1} , due to cyclic $\text{C}=\text{N}$ of pyrazolone) observed in all the ligands in their corresponding copper chelates indicates

that there is no coordination *via* C=N (cyclic) [27]. Similarly the displacement of band due to C–O stretch ($1305\text{--}1330\text{ cm}^{-1}$) in complexation indicates the participation of OH of 5-pyrazolone in the coordination [22]. All the chelates show a broad band at $3500\text{--}3100\text{ cm}^{-1}$ due to the presence of water [28].

3.3. Thermogravimetric analysis

The thermograms of all the compounds were intended for finding out the nature and number of the water molecules in this study. The weight loss of 5.4% for all the chelates in the $110\text{--}190^\circ\text{C}$ range is assigned to two coordinated water molecules [29].

3.4. ^1H NMR spectra

^1H NMR spectra of the Schiff bases show phenyl multiplets at $6.6\text{--}7.40\text{ }\delta$ ppm. Three signals (triplet, multiplet, and triplet) between 0.7 and 2.5 ppm are assigned to propyl groups on pyrazolone. The enolic protons are observed at $12\text{--}14\text{ }\delta$ ppm.

3.5. Diffuse reflectance spectra

The presence of only one broad band at $16,000\text{--}20,000\text{ cm}^{-1}$ is attributed to only one spin allowed d–d transition $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ in a regular octahedral field. Highly Jahn–Teller unstable d^9 configuration also leads to tetragonal distortion (D_{4h}), which further splits $^2\text{E}_g$ and $^2\text{T}_{2g}$ into $^2\text{B}_{1g}$, $^2\text{A}_{2g}$ and $^2\text{B}_{2g}$, $^2\text{E}_g$, respectively. Thus the transitions may lie within one envelop or may resolve into two or three components. The broadness of the band may be attributed to three transitions lying within one envelop. If the splitting of the states due to tetragonal field follows barycentre rule, the approximate value of 10Dq may be calculated from the expression: $10\text{Dq} = \nu_3 - \frac{1}{2}\nu_1 - \frac{1}{3}(\nu_3 - \nu_2)$, where $\nu_1 = \nu_2 = \nu_3$ [30]. These values are 7692 and 8196 cm^{-1} for H_2L^1 and H_2L^2 , respectively. The absence of a band below $10,000\text{ cm}^{-1}$ ruled out the possibility of tetrahedral structure in solid state. The green color of the chelates also confirms the distorted tetragonal structure of Cu(II) chelates [18, 19, 30].

3.6. Magnetic and conductivity studies

The magnetic moment of all the chelates is in $1.94\text{--}1.95$ B.M. range, which corresponds to one unpaired electron [29]. The molar conductance (Λ) of all the chelates, $13.6\text{--}22.8\text{ }\Omega^{-1}\text{ mol}^{-1}\text{ cm}^{-2}$ range, indicates that the complexes are non-electrolytes [31].

3.7. Mass spectral characterization and V.P.O. study

The correlation of mass fragmentation pattern of all the Schiff bases and their respective copper(II) chelate with its V.P.O. study were used to assign the structure of the present compounds. It shows molecular ion peak at $m/z = 561$ (R.I. = 45%, Calcd mol. wt = 560) for ligand H_2L^1 . The fragment at $m/z = 335$ as base peak (R.I. = 100%, Calcd mol. wt = 334.2) may be due to $\text{C}_{20}\text{H}_{22}\text{N}_4$ ion. Rapture of different bonds inside

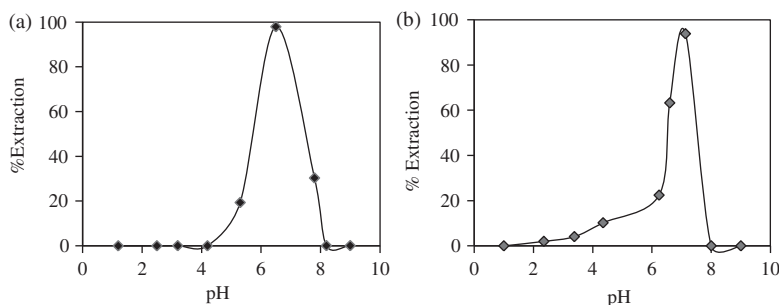


Figure 1. Percentage extraction vs. pH: (a) using H_2L^1 and (b) using H_2L^2 .

Table 1. The effect of pH^a on degree of extraction/distribution ratio.

pH	%E	D^b	pH	D^c
1.20	1.2	0.011	1	–
2.50	2.5	0.024	2.35	2.004
3.20	3.2	0.068	3.38	4.080
4.20	4.2	0.020	4.35	10.210
5.30	5.3	19.354	6.24	22.450
6.50	6.5	97.872	6.6	63.290
7.80	7.8	30.314	7.13	93.920
8.20	8.2	0.0100	8	–
9.10	9	0.01000	9	–

^aThe concentration of the ligand and Cu^{2+} were 1×10^{-3} and 1×10^{-3} mol dm⁻³, respectively.

^bDistribution ratio; average calculated for data obtained from three independent extraction experiments using H_2L^1 .

^cDistribution ratio; average calculated for data obtained from three independent extraction experiments using H_2L^2 .

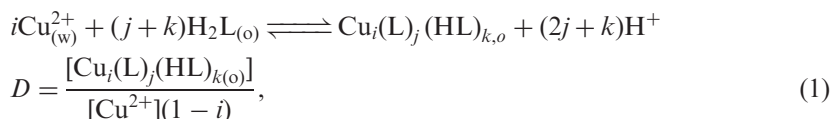
the molecule resulted in different molecular ion peaks. One appeared dominantly at $m/z = 227$ with R.I. of 40% may be assigned to $C_{14}H_{15}ON_2$ ion. Thus, there is a good agreement in the mass spectra of the ligand with the structure shown in scheme 1. The fragment in mass spectra of chelate of H_2L^1 at $m/z = 621$ (R.I. = 8%, Calcd 621.5) may be assigned to $C_{68}H_{72}Cu_2N_{12}O_6$ (M-2 H_2O) due to the elimination of water molecules.

For the complex of H_2L^2 , the peak at $m/z = 1318$ (R.I. = 7%, Calcd mol. wt = 1317) due to $C_{68}H_{76}Cu_2N_{12}O_8$ ion confirms the dimer nature of the chelate. The base peak at $m/z = 550$ with R.I. of 100% may be due to $C_{24}H_{22}Cu_2N_6O_2$ ion (M- H_2O - L^2 -propyl-Ph-Me). Also, in the V.P.O. measurements, the found molecular weight (1319) is very close to the calculated value, suggesting 2:2 metal to ligand stoichiometry.

3.8. Extraction studies

3.8.1. Distribution of copper(II). A plot of percentage extraction (%E) versus pH is shown in figure 1. The results are also expressed as distribution ratio (table 1). Assuming that no aqueous counter-ion ligands are involved in extraction, the probable extracted species can be designated as CuL^1 . The distribution ratio of divalent

copper(II) may be expressed based on the following extraction reaction:



where $\text{Cu}_i(\text{L})_j(\text{HL})_{k(o)}$ denotes extractable metal complex and i indicates the degree of polymerization, j the number of ligands that coordinate with both 5-OH donor sites of pyrazolone ring as a diprotic acid, k the number of ligands that coordinate with only one side of the 5-OH donor site as a monobasic acid.

From the above equation the relation between the extractant constant, k_{ex} and the distribution ratio, D can be expressed as

$$\log D - (i-1)\log[\text{Cu}^{2+}] = \log k_{\text{ex}} + (j+k)\log[\text{H}_2\text{L}] + \log i + (2j+k)\text{pH}. \quad (2)$$

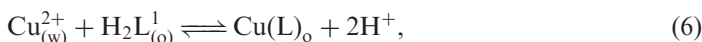
Evaluation of this equation by the slope analysis method allows the stoichiometry of the extracted species to be elucidated for each Schiff-base ligand system [32]. The following three partial derivative equations can be derived:

$$\partial(\log D)/\partial(\log[\text{Cu}^{2+}]) = i-1, \quad (3)$$

$$\partial(\log D - (i-1)\log[\text{Cu}^{2+}])/\partial(\text{pH}) = 2j+k, \quad (4)$$

$$\partial(\log D - (i-1)\log[\text{Cu}^{2+}])/\partial(\log[\text{H}_2\text{L}]) = j+k. \quad (5)$$

Generally, during chelation Cu(II) reacts with ligand to form a square-planar complex and is able to be extracted, depending upon the pH. As a tetradentate ligand, H_2L with two donor sites would affect mode and stoichiometry of the metal chelate. For instance, H_2L^1 , which has two 5-OH groups ortho to ketimonic carbon, is expected to form complex *via* ONNO donors. In this study, the slopes of the plots of $\log D$ versus $\log[\text{Cu}^{2+}]$, pH, and $\log[\text{H}_2\text{L}^1]$ are 0, 2, and 1, respectively. Consequently, the values of i , j , and k were obtained as 1, 1, and 0, respectively. Substituting these values in equations (1) and (2) yields:



$$\log D = \log k_{\text{ex}} + \log[\text{H}_2\text{L}] + 2\text{pH}. \quad (7)$$

According to equation (7), the plot of $\log D$ versus $\log[\text{H}_2\text{L}^1]_{(o)}$ at constant pH will give a straight line of slope equal to one and intercept as $\log k_{\text{ex}} + 2\text{pH}$. Hence, from the graph (figure 2) the extraction constant $p k_{\text{ex}}$ has been calculated as 11.22. From the results, the extraction equilibrium was found, as shown in equation (6). Thus, 1:1 Cu(II) to ligand stoichiometry is expected, as shown in figure 3. Both from quantitative evaluation of the equilibrium data and Job's method (figure 4), the chelates are 1:1 in metal to ligand stoichiometry $[\text{CuL}^1]$.

Another type of complex was observed for H_2L^2 at low concentration of Cu(II). The plot of $\log D$ versus $\log[\text{Cu}^{2+}]$ consists of two rectilinear sections with sharp discontinuity in slope at $3.2 \times 10^{-5} \text{ mol dm}^{-3} \text{ Cu}^{2+}$; the slope shifts from 0 to 1. In order to confirm the composition of the complex, the slope analysis was made in lower

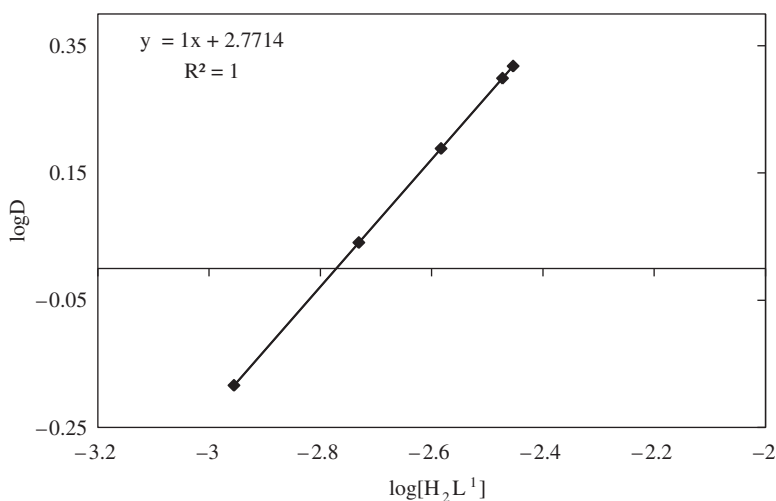


Figure 2. The plot of $\log D$ vs. $\log[H_2L^1]$.

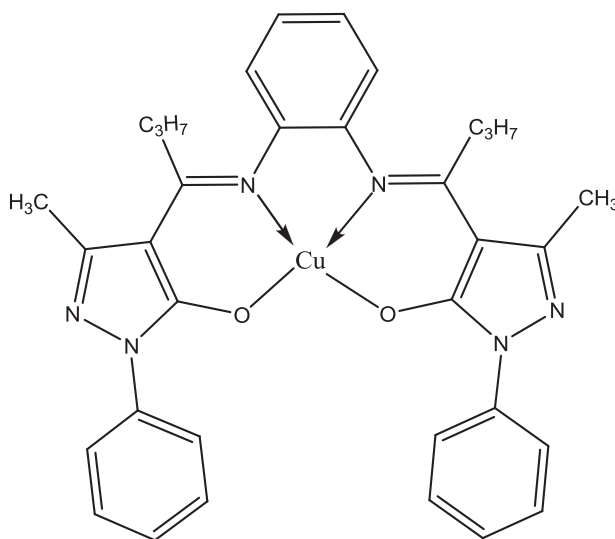
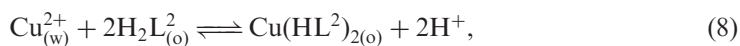


Figure 3. Suggested structure of extracted copper(II) chelate of 1 : 1 H_2L^1 to Cu(II) stoichiometry.

$[Cu^{2+}]$ range. Stoichiometry was deduced from the slope of the relevant section of plots of $\log D$ versus $\log[Cu^{2+}]$, pH, and $\log[H_2L]$ [32]. The slope of $\log D$ versus $\log[H_2L^2]$ is shown as figure 5. The observed values of the slopes were 0, 2, and 2, respectively, giving values of i , j , and k as 1, 0, and 2, respectively. Substituting these values in equations (1) and (2) yields:



$$\log D = \log k_{ex} + 2 \log[H_2L^2]_{org} + 2pH. \quad (9)$$

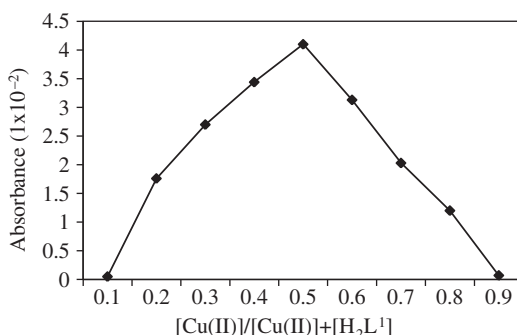
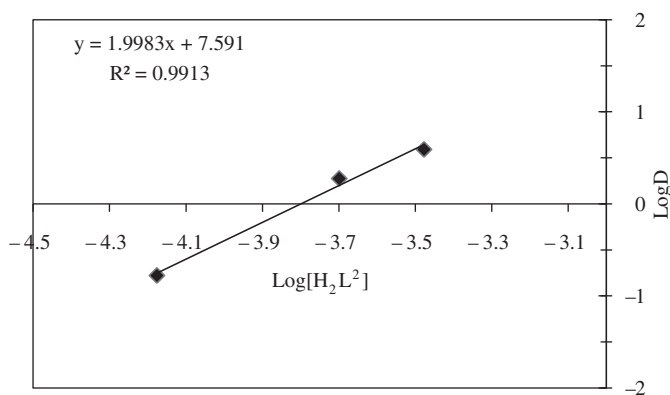


Figure 4. Job's method.

Figure 5. Plot of $\log D$ vs. $\log [H_2L^2]$.

Accordingly, the nature of extracted species may be 1:2 Cu(II) to ligand stoichiometry, where Cu(II) is coordinated through 5-OH donor of each of two ligands as monobasic acid, as shown in figure 6. Higher concentration of Cu(II) results in forming 2:2 type complexes, where the partial derivatives in equations (3)–(5) are 1, 4, and 2, respectively. From the intercept of plot $\log D$ versus $\log [H_2L^2]$ the value of pK_{ex} is calculated as 6.4.

This investigation at higher concentrations is not satisfactory, perhaps due to rigidity of the molecules in the solution. However from the V.P.O. study, the solid chelate derived from H_2L^2 is of type 2:2 metal to ligand stoichiometry. Thus our observation shows that H_2L^1 forms 1:1 and H_2L^2 1:2 complexes with copper(II). The dimer of H_2L^2 may be expected at higher concentration of copper(II).

4. Conclusion

From the elemental, physico-chemical, spectral, mass, TGA, V.P.O., and magnetic measurements the general structure of solid copper(II) chelates may be expressed

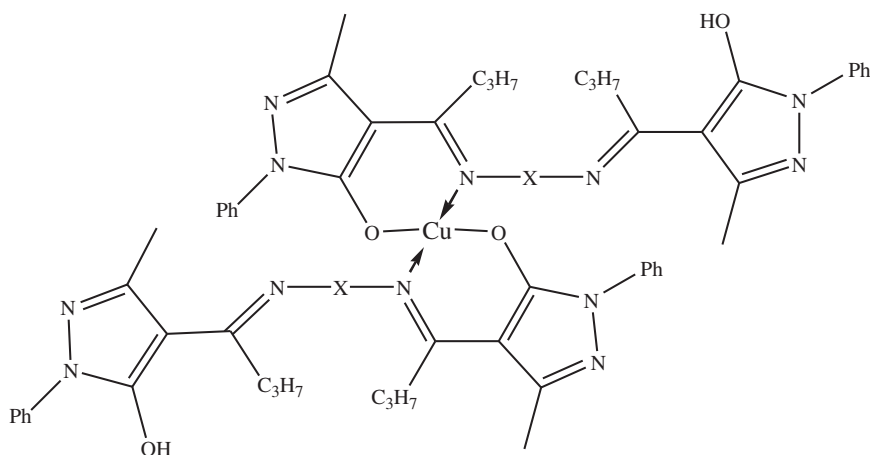


Figure 6. Suggested structure of extracted copper(II) chelate of 2:1 ligand to metal stoichiometry.

as $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]_n$, where $n = 1$ and 2 for H_2L^1 and H_2L^2 , respectively. The same ligands when employed for extracting copper from perchlorate aqueous medium into chloroform at pH 6.5 and 7, respectively, are $[\text{Cu}_i(\text{L})_j(\text{HL})_k]$, where $i = 1, j = 1, k = 0$ and $i = 1, j = 0, k = 2$ for complexes of H_2L^1 and H_2L^2 , respectively.

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