Distribution of Cu(II) between Buffered Aqueous Phases and Organic Phases Containing N,N'-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine (H$_2$PrEtP) in Chloroform

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Authors’ contributions

This work was carried out in collaboration amongst all authors. Author FCN did the synthesis of the ligands and extraction of the metal ions. Authors VIEA and PACO designed, wrote the protocol and supervised the work. Author FCN preformed the statistical analysis, managed the literature search and wrote the first draft of the manuscript with assistance author JG. All authors read and approved the final manuscript.

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ABSTRACT

Complexation of Copper (II) ions from aqueous media into chloroform solution of N,N'-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H$_2$PrEtP) Schiff base in chloroform was studied. Effect of various parameters for the extraction such as pH of aqueous media, concentration of the ligands and concentration of Cu(II) were all investigated.
alongside the synergistic effect of 4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HPrP) under a well-defined extraction condition. Complexation of Copper (II) ions was found to be highly dependent on pH of aqueous media and occurred more readily in acidic media. Single ligand complexation gave a pH½ (pH at which 50% extraction occurred) of 4.57 with the partition coefficient statistically determined to be $\log D_{CuHPrEtP} = 1.56 \pm 0.01$ and extraction constant $\log K_{exCuHPrEtP} = -3.25 \pm 0.10$. Complexation with mixed ligand system gave a pH½ of 3.0, partition coefficients $\log D_{CuHPrEtP/HPrP}$ of $1.70 \pm 0.05$ and extraction constant $\log K_{exCuHPrEtP/HPrP}$ of $-3.12 \pm 0.10$ showing that the complexation of Cu(II) was slightly higher in the mixed ligands system. Optimum concentration of $3.5 \times 10^{-2} \text{M} H_{2}PrEtP$ which gave 97.61% E was observed on varying the ligand concentration in the absence of the synergist while in the presence of the synergist, optimum concentration of $4.0 \times 10^{-2} \text{M}$ which corresponds to 98.53% E was observed for the main ligand. Variation in synergist concentration gave optimum result of 97.85% E at $2.25 \times 10^{-2} \text{M HPrP}$. Analysis of slope was used to predict stoichiometry of the extraction reactions and to propose extracted metal complexes structure in both single and mixed ligands system as $\text{Cu(HPrEtP)}o$ and $\text{Cu(HPrEtP.HPrP)o}$ respectively.

**Keywords:** Complexation; copper (II) ions; effect of Synergist; pH and ligands concentration.

### 1. INTRODUCTION

Schiff bases have been widely used as ligands because of the high stability of their coordination compounds and their solubility in common solvents [1]. Schiff bases are typically formed by the condensation of primary amines and a ketone or an aldehyde [2]. The resultant functional group $R\equiv C\equiv N\equiv R$ is called an imine [3], and it is regarded as one of the most important chelators for easy formation of new metal chelates [4] via the $N\equiv -$ atom lone pair especially when in combination with one or more donor atom to form a polydentate ligand [3,5]. The mechanism of imine formation begins as a nucleophilic addition to carbonyl group; in this case, the nucleophile is the amine which reacts with the aldehyde or ketone to give an imine [6]. Schiff bases with N and O donor atoms arranged in $Ar-OH$ and $-CH=NH-$ group tends to show high selectivity towards Cu(II) and Fe(III) ions [7]. Metal complexes of Schiff base are studied extensively due to synthetic flexibility of these compounds and their selectivity as well as their sensitivity towards the central metal atom [8,9,10,11]. The $\pi\equiv$-System in Schiff bases often impose a geometrical constrain and affect the electronic structure as well [1]. The thermodynamic, theoretical and catalytic aspects of this class of compounds have been extensively investigated [12]. Complexes containing Schiff base ligands and their derivatives play important roles in oxidation chemistry for instance; (Salen) Chromium (V) oxo complexes are active oxidants for the stoichiometric and catalytic epoxidation of olefins [12]. Schiff bases have been used in catalysis, antibacterial activity, anti-oxidative activity, medicine as antibiotics, anti-inflammatory agents [13] and on the industrial scale for anti-corrosion properties, dyes and pigments [14]. They are also very important sensory molecules for fabricating cation and anion selective electrodes and have been used for the enrichment and separation of trace amount of metals ions [13,14]. The selective transport of metal ions across a membrane is known to play an essential role in many biological processes [15]. Dinuclear copper complexes containing two metal centers in close proximity are the subject of recent extensive investigation as a result of its structural involvement in a variety of important biochemical processes such as oxygen transport and oxygen activation by oxidase and monoxygenase enzymes [16]. Copper-Schiff bases complexes have been reported for the catalytic oxidation of alcohols and phenols [17]. Solvent extraction of Copper (II) and Lithium (I) using Cyanex272 in synergism with TBP has been reported [11]. In continuation of our work on the synthesis, characterization of 1-phenyl-3-methyl-4-acylpyrazolone-5 derivatives and their application in the extraction of bivalent transition metal ion such as Ni(II) [8] and Co(II) [18]. We report the use of the Schiff base $N,N'$-ethylenbis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) as a potential extractant for Copper(II) ions.

### 2. MATERIALS AND METHODS

All reagents were of analytical grade. $H_{2}PrEtP$ (Schiff base) was synthesized by the method reported elsewhere [9,12]. The ligands purity after recrystallizations from aqueous ethanol were determined by elemental analysis for C, H.
and N; analysis of IR and NMR spectral data at Institute for Inorganic Chemistry Technology, University of Dresden Germany [9,12].

All other reagents used were purchased from Aldrich and BDH.

Doubly distilled deionized water was used in all dilutions. Stock solution of 0.05 M H$_2$PrEtP was prepared by dissolving the required amount of the ligand in chloroform. 0.05 M solution of HPrP was similarly prepared in chloroform. Stock solution of 1.57×10$^{-2}$ M of Cu(II) were also prepared by dissolving Copper(II) Tetraoxosulphate(VI) Pentahydrate in 0.1 ml of 10 M HNO$_3$ and making up to mark in a 50 ml volumetric flask with deionized water. Buffer solutions of pH range 1 to 10 were prepared with; 0.1 M HCl/0.1 M NaCl (pH 1.0 to 2.9), 0.1 M CH$_3$COOH/0.1 M NaCl (pH 3.0 to 3.5), 0.1 M CH$_3$COOH/0.1 M CH$_3$COONa (pH 3.6 to 5.6), 0.1 M KH$_2$PO$_4$/0.1 M NaOH (pH 5.7 to 10.0). The pH of buffered solutions was measured using a digital labtech pH meter.

### 2.1 Extraction Procedure

A buffered solution (2 ml) containing 7.87×10$^{-4}$ M of Cu(II) ions at the required pH was prepared in a 10 ml extraction bottle. Equal volume (2 ml) of 0.05 M solution of H$_2$PrEtP in chloroform was added. For the mixed ligand complexation, the organic phase was 0.05 M H$_2$PrEtP and 0.05 M HPrP solution in chloroform mixed in the ratio of 9:1 by volume. The mixture was mechanically agitated for 30 minutes at room temperature to enable the attainment of equilibrium. The phases (aqueous and organic) were allowed to settle and separated with the aid of a micropipette. Concentration of Cu(II) ions in the aqueous phase was determined with a Buck Scientific Atomic Absorption Spectrophotometer (AAS) at 324.7 nm. The concentration of Cu(II) ion complexed into the organic phase was determined by the difference between the concentration of Cu(II) ion in the aqueous phase before and after the extraction. The distribution ratio (D) can be expressed as $C_{org}/C_{aq}$ where $C_{org}$ and $C_{aq}$ are the concentrations of Copper (II) in the organic and the aqueous phase, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of Buffer Solution on Complexation of Copper (II) ions

Distribution of Cu(II) from aqueous solution into chloroform phase having the Schiff base H$_2$PrEtP can be represented by the Eqn. (1)

$$Cu^{2+}(aq) + H_2PrEtP_{(org)} \leftrightarrow Cu(PrEtP)_{(org)} + 2H^+_{(org)}$$

Eqn. (1) is based on the assumption that the Cu(II) from aqueous solution is extracted into chloroform solution of the Schiff base by forming a complex with the Cu(II) ion in 1:1 mole ratio. Thus the extraction constant (Kex) can be expressed by Eqn. (2).

$$[Cu(PrEtP)_{(org)}][H^+]^2/[Cu^{2+}_{(aq)}][H_2PrEtP]$$

#### Fig. 1. Plot of log D against pH for the complexation of 7.87×10$^{-4}$ M Cu(II) ions from buffered aqueous solution into chloroform solution of 0.05 M H$_2$PrEtP
The plot in Fig. 1 shows the effect of pH of aqueous solution on the distribution of Cu(II) into chloroform solution of H$_2$PrEtP. A slope of approximately one was obtained from the graph indicating that 1 mole of hydrogen ion was displaced and confirmed that there was ligand-metal interaction through the oxygen atoms of the hydroxyl functional groups of ligand. The distribution ratio (D) of the metal ions between the two liquid phases becomes;

$$D = \frac{[\text{Cu(HPrEtP)}]_{\text{org}}}{[\text{Cu}^{2+}]_{\text{aq}}}$$  \hspace{1cm} (3)

Substituting D into eqn. 2 after rearrangement gives

$$\log D = \text{Log} K_{\text{ex}} + \log [\text{H}_2\text{PrEtP}] + \text{pH}$$  \hspace{1cm} (4)

Equation (4) showed that the extraction of copper (II) ions into chloroform solution of H$_2$PrEtP increased with increase in pH of aqueous solution and reached a peak at pH 6.10, where a percentage extraction of 97.38% was achieved. Thereafter, further increase in pH resulted in a decrease in percentage extraction of the metal. The partition coefficient, log$D$ was determined statistically from the plot to be 1.56±0.01. The pH½ was 4.57.

### 3.2 Effect of Addition of HPrP (synergist) on the Complexation of Cu(II) ions

On addition of HPrP, quantitative extraction of 98.23% was obtained at pH 6.10. The pH½ was significantly lowered from pH 4.57 (acidic) to a more acidic pH of 3.0. The partition coefficient was found to be 1.70±0.05 and was determined statistically from the plot as shown in Fig. 2. Plot of Log$D$ against pH in the mixed ligands system also gave a slope of approximately 1, indicating that 1 mole of hydrogen ion were displaced during the extraction process. Thus, the possible reaction equation for the extraction may be written as:

$$\text{Cu}^{2+} + \text{H}_2\text{PrEtP}^+ + \text{HPrP}^+ \leftrightarrow \text{Cu(HPrEtP)}^+ + \text{H}_2\text{PrEtP} + \text{H}^+$$  \hspace{1cm} (5)

$$K_{\text{ex}} = \frac{[\text{Cu(HPrEtP)}^+][\text{H}_2\text{PrEtP}]_{\text{org}}}[\text{Cu}^{2+}]_{\text{aq}}[\text{H}^+]$$  \hspace{1cm} (6)

### 3.3 Effect of Ligand (H$_2$PrEtP) and Synergist (HPrP) Concentrations on the Complexation of Cu(II) ions at Different pH

All extraction processes studied showed that the extraction of Cu(II) into chloroform solution of H$_2$PrEtP and HPrP increased as the ligands concentrations increased. The extractions followed similar trends on variation of the concentrations of either the ligand (H$_2$PrEtP) or the Synergist (HPrP) as shown in Figures 3, 4 and 5. On varying the ligand concentration in the absence of the synergist from 2.5×10$^{-3}$M to 4.0×10$^{-3}$M at a constant pH of 5.0, the %E increased rapidly from 81.50% observed at 2.5×10$^{-3}$M H$_2$PrEtP to 97.37% at 4.0×10$^{-3}$M H$_2$PrEtP concentration. Variation of the ligand concentration at constant pH of 6.0 also gave the least percentage extraction of 81.86% E at H$_2$PrEtP concentration of 2.5×10$^{-3}$M, while peak extraction of 97.50% E was observed at H$_2$PrEtP concentration of 3.5×10$^{-3}$M. At constant pH of 7.0 variation of the ligands concentration gave least extraction of 94.06% E at H$_2$PrEtP concentration of 2.5×10$^{-3}$M while highest percentage extraction of 97.61% E was observed at H$_2$PrEtP concentration of 3.5×10$^{-2}$M. Variation of the ligand in the presence of the synergist at three different pH values of 4.7, 5.3 and 6.0 also showed similar trend in percentage extractions of copper (II) ions. At pH 4.7, the least extraction of 96.26% E was observed at H$_2$PrEtP concentration of 5.0×10$^{-3}$M while peak extractions were achieved at H$_2$PrEtP concentration of 3.0×10$^{-3}$M and 4.0×10$^{-3}$M where percentage extraction of 98.22% was achieved. Similarly, varying the ligand in the presence of the synergist at pH 5.3 gave least extraction of 95.40% E at H$_2$PrEtP concentration of 2.5×10$^{-3}$M while highest extraction of Cu(II) was observed at H$_2$PrEtP concentration of 2.0×10$^{-6}$M and 4.0×10$^{-3}$M which gave 98.28% E. At pH of 6.0, the least percentage extraction was observed at ligand concentration of 2.5×10$^{-3}$M while the peak extraction of 98.53% E for copper occurred at 4.0×10$^{-3}$M H$_2$PrEtP.

Variation of the synergist concentration in the presence of the ligand from 2.5×10$^{-3}$M to 2.25×10$^{-3}$M at pH values of 4.7, 5.3 and 6.0 also showed similar results as observed for ligand variations. At pH 4.7, least percentage extraction of 94.30% was observed at HPrP concentration of 2.5×10$^{-3}$M while maximum extraction of copper occurred at 2.0×10$^{-3}$M HPrP concentration which gave 97.67%E. Varying the synergist at pH 5.3 gave least extraction of 94.04% E at HPrP concentration of 2.5×10$^{-3}$M while maximum extraction of 97.85% E occurred at HPrP concentration of 2.25×10$^{-3}$M. At pH 6.0, the least extraction was observed at HPrP concentration of 3.50×10$^{-3}$M while peak extraction of 97.50% E for copper occurred at 2.0×10$^{-3}$M and 2.25×10$^{-3}$M.
5.4 Effects of Metal ions (Cu(II)) Concentrations

Figs. 6 and 7 showed the effect of copper concentration on the extraction of copper (II) ions. The results showed that concentrations had insignificant effect on the extraction hence a slope of zero was obtained for the extractions in both mixed and single ligand systems. Variation of the metal concentrations from 3.15×10^{-4} M to 4.72×10^{-4} M at three different pH values of 5.0, 6.0 and 7.0 in the absence of HPrP all gave similar result. Percentage extraction of copper for the three pH values fluctuated around 96% E. Least extraction of 96.02% E was observed at Cu(II) concentration of 3.46×10^{-4} M for pH 6.0 while maximum extraction of 96.96% E occurred at Cu(II) concentration of 3.93×10^{-4} M for pH 5.0.

In the presence of HPrP, varying the metal concentration at three different pH values of 4.7, 5.3 and 6.0 gave its highest extraction of 97.43% E at Cu(II) concentration of 3.46×10^{-4} M while the least extraction of 96.56% E were observed at Cu(II) concentration of 3.15×10^{-4} M and 3.93×10^{-4} M pH 5.3.
Fig. 4. Plot of logD against log\([H_2PrEtP]\) for the extraction of 7.87\times10^{-4} \text{ M} of Cu(II) from aqueous solutions into chloroform solution of \(H_2PrEtP\) with \(HPrP\) kept constant.

Fig. 5. Plot of logD against log[HPrP] for the extraction of 7.87\times10^{-4} \text{ M} of Cu(II) from aqueous solutions into chloroform solution of \(H_2PrEtP\) with \(HPrP\) kept constant.
Fig. 6. Plot of LogD against Log $[\text{Cu(II)}]$ for the extraction of Cu(II) from buffer solution into chloroform solution of 0.05 M $\text{H}_2\text{PrEtP}$

Fig. 7. Plot of LogD against Log $[\text{Cu(II)}]$ for the extraction of Cu(II) from buffer solution into chloroform solution of 0.05 M $\text{H}_2\text{PrEtP}$ and 0.05 M $\text{HPrP}$ in 9:1 ratio

Fig. 8. Proposed structure for Cu($\text{HPrEtP}$)$_{\text{org}}$X

Fig. 9. Proposed structure for Cu($\text{HPrEtP.HPrP}$)$_{\text{org}}$
3.5 Proposed Structures for Copper (II) complexes with H₂PrEtP and H₂PrEtP/HPrP

Based on the results and statistical analyses of data, we proposed the structures in Figs. 8 and 9 for copper (II) complexes with H₂PrEtP and H₂PrEtP/HPrP respectively where X is anionic species from the buffer incorporated to stabilize the charge on the copper ion.

4. CONCLUSION

On studying the complexation of Copper (II) in buffered aqueous medium with chloroform solution of H₂PrEtP, a pH½ of 4.57 was observed. The synergistic effect of HPrP shifted the pH½ from pH 4.57 to a more strongly acidic pH of 3.0. The partition coefficients were H₂PrEtP D₁ 1.56±0.01 and H₂PrEtP/HPrP D₂ 1.70±0.05 for single and mixed ligands extractions respectively, indicating that there is a slight difference in the distribution of the metal ions into chloroform solution of H₂PrEtP and into mixture of H₂PrEtP/HPrP. The extraction constants KexCu₁ is -3.25±0.10 and KexCu₂ was found to be -3.12±0.10. The values indicated that Cu(II) distributes better into the mixed ligands system from the buffered media. From all the observations, we concluded that the extraction of Cu(II) ion is more effective in a strong to moderately acidic medium.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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