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Synthesis Of An Analytical Reagent, its Spectroscopic Characterization And Studies Of Its Complexation Behaviour with Cu(II) Metal Ion And Its Applications

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ABSTRACT

Cu(II) was determined spectrophotometrically after precipitation with 2, 4 dihydroxy-5-iodo[2'-methyl] propiophenone oxime (DHIMPO) at room temperature at pH 5.0 in chloroform at 430nm. Beer's law was obeyed up to 8.13 ppm of Cu(II). Molar absorptivity and Sandell's sensitivity were found to be 7.03 x 10^2 lit $mol^{-1}cm^{-1}$ & 0.0903 $\mu g/cm^2$ respectively. Composition of chelate was determined using Job's method of continuous variation and Yoe and Jones mole ratio method which was found to be 1:2 (M:L). The stability constant determined spectrophotometrically was found to be 1.714 x 10^8. Gibb's free energy change for complex formation reaction was also calculated and found to be -11.30 k cal mol^{-1}. From TGA, the energy of activation was calculated using Broido method and found to be 35.85 k cal mol^{-1}. The reagent has been satisfactorily applied for the determination of copper in drain micro etch solution.

Keywords: Spectroscopic determination, Propiophenone oxime, DHIMPO.

INTRODUCTION

Organic reagents forms chelate with metal ions. Formation of coordination compounds by organic reagents with metal ions has been extensively used in analytical chemistry. It has been found that the reagents capable of forming chelates with metals are often specific or highly selective in their action and hence offer attractive potentialities as analytical reagents. Many organic reagents like o-hydroxy oximes[1-7], oximes[8-9], thiosemicarbazones[10-14], chalcone oxime[15], anilides[16], various heterocyclic compounds have been used for gravimetric and spectrophotometric determination of metal ions. Among the many systems used, the chelating system found in o-hydroxy aldoxime and ketoxime requires special mention due to the situation of groups in suitable position to form stable metal chelates. Oximes are selective and sensitive reagents for this purpose and hence here we had introduced a novel reagent (DHIMPO) for the determination of Cu(II).

MATERIALS AND METHODS

Reagents and solutions: DHIMPO was synthesized using the method of H. Nogami[17] by the condensation of resorcinol with isobutyric acid in presence of anhy. $ZnCl_2$ giving 2, 4 dihydroxy [2'-methyl] propiophenone. Iodination of the ketone was carried out using KIO_3 and KI which yield 2, 4 dihydroxy-5-iodo[2'-methyl] propiophenone. Iodo derivative was then converted to oxime by refluxing it with hydroxyl amine hydrochloride and sodium acetate. The oxime was re-crystallized from ethanol bearing M.P.85ºC.
Cu(II)-metal solution: A stock solution of copper(II) (0.05M) was prepared by dissolving an accurately weighed amount of copper sulphate penta hydrate in deionized water.

Characterization of reagent

Elemental analysis: Elemental analysis of the reagent was done using Elementar Vario EL III analyzer. The percentages are in agreement with its molecular formula. The results are represented in table 1.

Table 1: Elemental analysis of Reagent

Reagent	Percentage found (Calculated)		
	Carbon	Hydrogen	Nitrogen
DHIMPO	37.01% (37.383%)	3.25% (3.74%)	4.307% (4.361%)

UV-Visible spectral studies: The UV-Visible spectrum of reagent in ethanol was recorded on "Perkin-Elmer Lambada-35 UV-Visible spectrophotometer". Wavelength of maximum absorption is 227nm.

FT-IR Spectral studies: FTIR spectrum of the reagent was recorded on "Perkin Elmer-Spectrum RX-I" in KBr pellet. The bands which are observed are given in table 2.

Table 2: IR Spectra

Reagent	$\nu^{(O-H)}$ **Phenolic**	$\nu^{(O-H)}$ **Oximino**	$\nu^{(C-H)}$ **aliphatic**	$\nu^{(C=C)}$ **aromatic**	$\nu^{(C=N)}$	$\nu^{(N-O)}$
DHIMPO	3490 cm^{-1}	3328 cm^{-1}	2972 cm^{-1}	1573 cm^{-1}	1623 cm^{-1}	974 cm^{-1}
Cu(II)-DHIMPO	3493 cm^{-1}	3325 cm^{-1}	2927 cm^{-1}	1569 cm^{-1}	1616 cm^{-1}	765 cm^{-1}

^1H & ^{13}C NMR Spectral studies: The NMR spectrum was recorded on Brucker Avance-II 400 NMR spectrophotometer in $CDCl_3$ using TMS as reference. Assignment of signals to different protons is given in table 3.

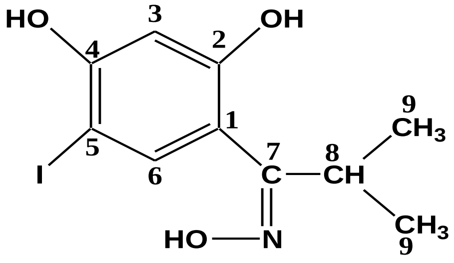

Table 3: ^{1}H & ^{13}C NMR Spectra

Chemical shift(δ) in ppm	Assignment
1.1426 ppm (Singlet)	Alkyl group
3.3549-3.4229 ppm (Multiplet)	Methine proton
12.9897 ppm	Phenolic –OH
10.973 ppm	Oximino –OH
6.5010-7.9981 ppm	Aromatic proton

Chemical shift(δ) in ppm	Assignment
115.07	C1
155.95	C2
103.80	C3
165.72	C4
73.54	C5
140.10	C6
160.90	C7
34.79	C8
19.43	C9

RESULTS AND DISCUSSION

pH study of Cu(II)-DHIMPO complex: To have the absorption spectra 1.0 ml (0.01M) metal ion solution and 2.0 ml (0.05M) reagent DHIMPO solution were taken in different beakers. pH of the solutions were adjusted with sodium acetate-acetic acid buffer in the range of 4.0 to 5.5. Complex obtained was extracted with three 5ml portion of $CHCl_3$. Finally it was diluted to 25 ml with $CHCl_3$. The spectra were recorded between 340nm to 800nm. It is observed from the graph (figure 1) that maximum absorption occurs at 430nm and the absorbance increases with increase in pH up to 5.0 and then decreases with increase in pH.

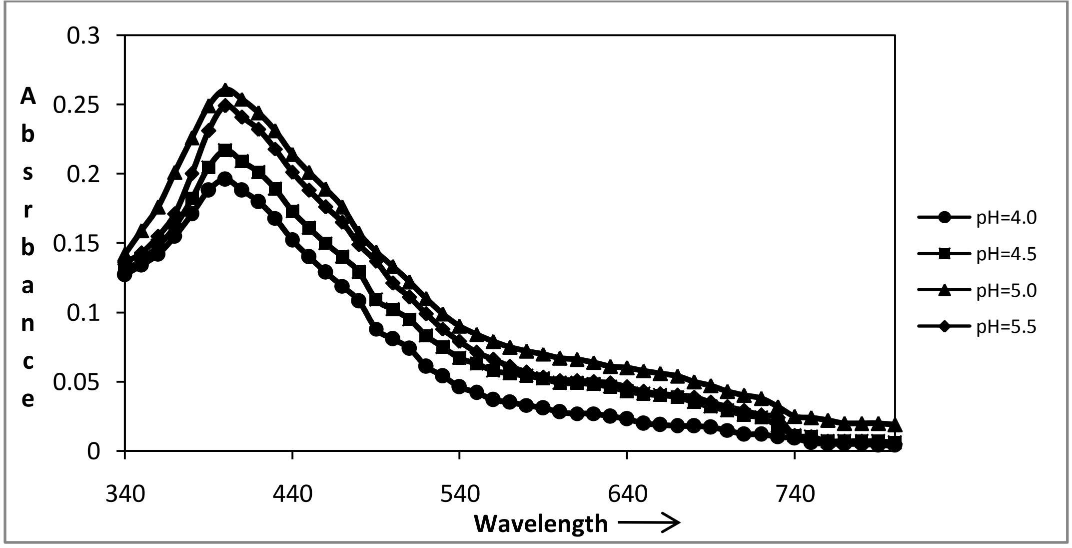

Figure-1: Absorbance spectra of Cu(II)-DHIMPO complex

Spectrophotometric study of Cu(II)-DHIMPO: In absorption spectra of Cu(II) complex in chloroform a shoulder band is obtained at 430nm and hence all spectrophotometric measurements were done at this wavelength. Different aliquots of Cu(II) solution were taken and buffer solution was added to maintain the pH 5.0. The excess reagent was added to get complete precipitation of complex. It was extracted in three 5.0ml portion of chloroform and final volume of this solution was adjusted to 25ml with chloroform. The absorbance was measured at 430nm and plotted against the concentration of Cu(II). It was found that Beer's law was obeyed upto 8.13 ppm of Cu(II). Molar absorptivity and Sandell's sensitivity were calculated form graph and it was found to be 7.03 x 10^2 lit mol^{-1} cm^{-1} & 0.0903 µg cm^{-2} respectively. Job's method of continuous variation[18] and Yoe and Jones mole ratio method[19] were used to determine the stoichiometry of the complex. It was found to be 1:2[M:L]. The stability constant was calculated using the formula,

$$K = \frac{1-\propto}{4 \propto^3 C^2} \quad , where \ \propto = \frac{Em - Es}{Em}$$

where, α= degree of dissociation, Em=maximum absorbance found from graph, Es =absorbance at the stoichiometric molar ratio of the metal to reagent in complex, C = concentration of complex

The average stability constant from the above two methods was found to be 1.714 x 10^8 and ΔG° for complex formation reaction at 27°C was found to be -11.30 k cal mol^{-1}.

Thermogravimetric analysis: Thermogravimetric analysis was done on "Perkin Elmer Diamond Instrument". The temperature of the furnace was raised from 30°C to 900°C in a programmed manner at the rate of 10°C min^{-1}. The atmosphere in the furnace was of static air. From TG analysis of the Cu(II) chelate, it was found that there is no weight loss upto 170°C indicating that the chelate can be dried safely without decomposition at 110°C. Loss in weight from 170-890°C is due to removal of organic ligand molecules. Observed loss and weight of copper oxide residue agrees well with the formula of the chelate in which M:L ratio is 1:2. Activation energy Ea was calculated using Broido method[20] and found to be 35.85 k cal mol^{-1}. (Figure-II)

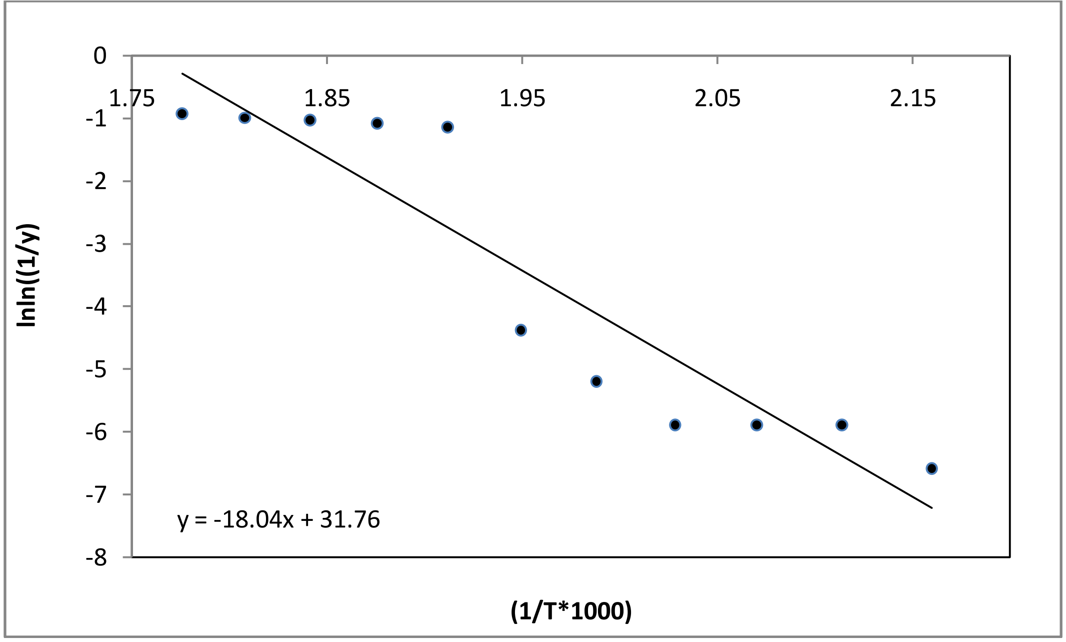

Figure-II: Broido method: Cu(II)-DHIMPO complex

IR Spectra: Interpretation of IR-spectra of the chelate shows weak band around 3493 cm^{-1} in comparison of ligand molecule. The weak band due to ν^{-OH} of oximino group is found at 3325 cm^{-1} in ligand, is observed at nearly the same position in the complex. $\nu^{C=N}$ stretching band observed at 1623 cm^{-1} in ligand is shifted to 1616 cm^{-1} in chelate, this indicates nitrogen is coordinately bonded with metal ion and covalently bonded with oxygen atom. It is also supported by the downward shift of ν^{N-O} group i.e. from 974 to 765 cm^{-1}.

APPLICATIONS

Spectrophotometric determination of Cu(II): Determination of Cu(II) was done in drain micro etch solution. From conventional titrimetric method % of Cu(II) was found to be 2.351% in original sample solution. To determine copper in this solution, 10ml of original solution was diluted to 100ml (0.2351g) (1ml=0.002351g). 1ml of this diluted solution was further diluted to 100ml (1ml=0.00002351g) (1ml=23.51µg). Two aliquots of 5.0ml & 7.0ml were taken for complexation with 3.0ml of 0.02M ligand solution. Small amount of double distilled water was added and pH of the solution was adjusted to 5.0 with buffer solution. Complex was extracted in $CHCl_3$ and final volume was made 25ml. Absorbance of both the solutions were measured against ligand blank and plotted on Beer's law plot and ppm were calculated. Results obtained are given in table 4 and figure 2.

Table 4. Determination of Cu(II) in drain micro etch solution

Cu(II) taken in ml	Absorbance	ppm found	ppm taken	% Found	% Error
5.0	0.131	4.676	4.702	2.3380	-0.55
7.0	0.182	6.559	6.583	2.3425	-0.36

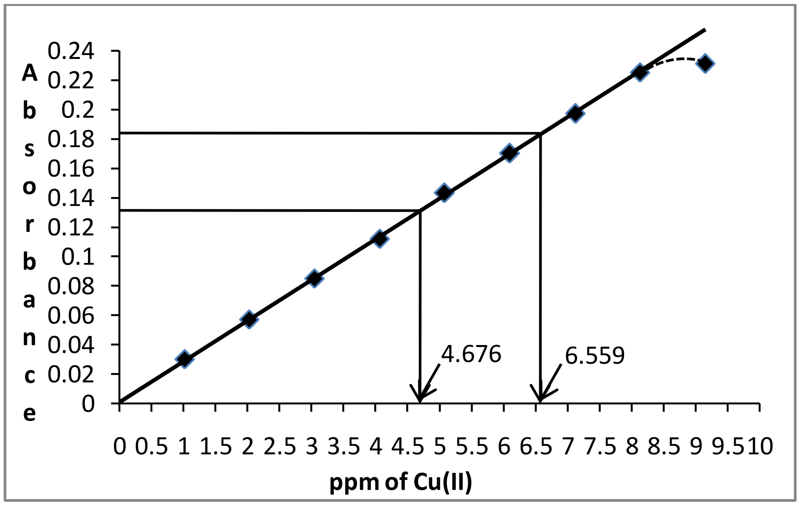

Figure 2. Beer's law plot of Cu(II)-DHIMPO

CONCLUSIONS

Reagent 2, 4 Dihydroxy-5-Iodo [2'-Methyl] Propiophenone Oxime [DHIMPO] can be successfully applied for the determination of various metal ions in trace amount in ores, alloys, synthetic mixtures and unknown samples. TGA indicates that the complex have good thermal stability and hence can be dried without fear of decomposition. The complex formed with the reagent is found to have good stability. The stability of the complex may be attributed to the presence of electron donating –OH group in position 4 to the ketoxime group. It may also be due to the presence of –OH group in position 2 which facilitate the formation of six membered hetrocyclic ring in the metal chelate. Complex can be extracted in organic solvents. This enable to do spectrophotometric determination of Cu-metal ion avoiding interference of some metal ions. Molar absorptivity of complex is also high to offer sensitivity.

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