



2, 4 Dihydroxy-5-Bromo[2'-Methyl] Propiophenone Oxime as an Analytical Reagent: Studies on Cu(II) Chelate

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ABSTRACT

Cu(II) was determined spectrophotometrically after co-precipitation with 2, 4 Dihydroxy-5-bromo[2'-methyl] propiophenone oxime (DHBMPPO) at room temperature. Obeyance of Beer's law was found and from that Molar absorptivity and Sandell's sensitivity were calculated. Composition of chelate was determined using Job's method of continuous variation and Yoe and Jones mole ratio method. The stability constant and Gibb's free energy change were also determined spectrophotometrically. From TGA, the energy of activation was also calculated using Broido method for the first and second step decomposition. The reagent has been satisfactorily applied for the determination of copper in drain micro etch solution.

Key words: Propiophenone oxime, DHBMPPO, Chelate.

INTRODUCTION

Several organic compounds with phenolic protogenic group and a suitably placed electron donating atom like nitrogen, oxygen or sulphur are found to interact with metal ions giving precipitation or coloration due to complex formation. Many organic reagents like o-hydroxy oximes¹⁻⁹, oximes¹⁰⁻¹¹, thiosemicarbazones¹²⁻¹⁶, chalcone oxime¹⁷, anilides¹⁸, various heterocyclic compounds have been used for gravimetric and spectrophotometric determination of metal ions. Oximes are selective and sensitive reagents for this purpose and hence here we had introduced a novel reagent (DHBMPPO) for the determination of Cu(II).

EXPERIMENTAL

DHBMPPO was synthesized using the method of H. Nogami¹⁷ by the condensation of resorcinol with isobutyric acid in presence of anhy. $ZnCl_2$ giving 2, 4 dihydroxy [2'-methyl] propiophenone. It was then brominated with Bromine in acetic acid giving 2, 4 dihydroxy-5-bromo[2'-methyl] propiophenone. Bromo derivative was then converted to oxime using hydroxyl amine hydrochloride and sodium acetate. The oxime was re-crystallized from ethanol bearing M.P. 162.1^o C.

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.

Solutions of other diverse ions were prepared by dissolving their salts (A.R.) 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

UV-Visible spectral studies

The UV-Visible spectrum of reagent in ethanol was recorded on "Perkin-Elmer Lambda-35 UV-Visible spectrophotometer". Wavelength of maximum absorption is 226 nm.

FT-IR Spectral studies

FTIR spectrum of the reagent was recorded on "Perkin Elmer-Spectrum RX-I Spectrophotometer" in KBr pellet. The bands which are observed are given in Table 2

¹H-NMR Spectral studies

The NMR spectrum of the reagent was taken in DMSO. The NMR spectrum was recorded on Bruker Avance-II 400 NMR spectrophotometer using TMS as reference. Assignment of signals to different protons is given in Table 3.

RESULTS AND DISCUSSION

Gravimetric determination of Cu(II)

A 0.05 M solution of the reagent in 50% aqueous ethanol was used. Copper sulphate solution (0.05 M, 10ml) was taken in a clean beaker. A (0.05 M, 22ml) ligand solution was added and diluted with double distilled water. Different sets were prepared and studied within the pH range of 3.0-6.0. pH of the solution was adjusted using Sodium acetate-acetic acid buffer. A buff precipitate were obtained were digested on water-bath for 60 minutes at 60°C. The precipitate were filtered through a previously weighed sintered glass crucible (G4) and washed with warm water followed by 50% aqueous ethanol to remove excess of the

Table 1 : Elemental analysis of Reagent

Reagent	Percentage found (Calculated)		
	Carbon	Hydrogen	Nitrogen
DHBMPO	43.55% (43.79%)	4.367% (4.379%)	5.020% (5.109%)

Table 2: IR Spectra

Reagent	$\nu^{(O-H)}$ Phenolic	$\nu^{(O-H)}$ Oximino	$\nu^{(C-H)}$ aliphatic	$\nu^{(C=C)}$ aromatic	$\nu^{(C=N)}$	$\nu^{(N-O)}$
DHBMPO	3484 cm ⁻¹	3389 cm ⁻¹	2965 cm ⁻¹	1599 cm ⁻¹	1633	927

Table 3: NMR Spectra

Reagent	Alkyl group	Methine Proton	Phenolic (-OH)	Oximino (-OH)	Aromatic proton
DHBMPO	1.3680-1.3855 ppm (singlet)	3.3836-3.4531 ppm (multiplet)	12.9897 ppm	11.2118 ppm	7.5682 ppm

reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115°C in hot air oven, cooled and weighed. The experiment was repeated at different pH of solution. The results obtained are given in Table:4

Effect of diverse ion

To study the effect of foreign ions on gravimetric determination of Cu(II), 8 to 10 mg of various cations were added to a solution containing 31.77 mg of Cu(II) at pH 4.0 and gravimetric estimation were carried out. It was observed that Mg(II), Sr(II), Mn(II), Cd(II), Ca(II), Ni(II), Zn(II), Ba(II) do not interfere at this pH but Fe(III) and Pd(II) interfered seriously. Interference of Fe(III) can be removed by masking it with H_3PO_4 . Many common anions like nitrate, nitrite, sulphate, chloride, bromide and iodide were not found to interfere.

Table 4: Gravimetric determination of Cu(II)-DHBMPPO

pH	Cu(II) complex in gm	Cu(II) found in mg	Error in mg	%
3.0	0.3016	31.4388	-0.3312	-1.04
3.0	0.3013	31.4075	-0.3625	-1.14
3.5	0.3018	31.4596	-0.3104	-0.98
3.5	0.3020	31.4805	-0.2895	-0.91
4.0	0.3041	31.6994	-0.0706	-0.22
4.0	0.3043	31.7202	-0.0498	-0.16
4.5	0.3064	31.9391	+0.1691	+0.53
4.5	0.3068	31.9808	+0.2108	+0.66
5.0	0.3073	32.0330	+0.2630	+0.83
5.0	0.3077	32.0746	+0.3046	+0.96
5.5	0.3085	32.1580	+0.3880	+1.22
5.5	0.3086	32.1685	+0.3985	+1.25
6.0	0.3094	32.2519	+0.4819	+1.52
6.0	0.3093	32.2414	+0.4714	+1.48

Conversion factor: 1gm complex= 104.24mg Cu(II)

Spectrophotometric study of Cu(II)-DHBMPPO

In absorption spectra of Cu(II) complex in chloroform a shoulder band is obtained at 410nm 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 4.0. 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 410nm and plotted against the concentration of Cu(II). It was found that Beer's law was obeyed upto 25.42 ppm of Cu(II). Molar absorptivity and Sandell's sensitivity were calculated from graph and it was found to be $2.7 \times 10^3 \text{ lit mol}^{-1} \text{ cm}^{-1}$ & $0.0234 \mu\text{g/cm}^2$ respectively. Job's method of continuous variation¹⁸ and Yoe and Jones mole ratio method¹⁹ were used to determine the stoichiometry of the complex. It was found to be 1:2[M:L]. This is in agreement with stoichiometry determined from gravimetric analysis. The stability constant was calculated using the formula,

$$K = \frac{1-\alpha}{4\alpha^3 C^2}, \text{ where } \alpha = \frac{E_m - E_s}{E_m}$$

where, α = degree of dissociation

E_m = maximum absorbance found from graph.

E_s = 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 1.85×10^{10} and "G° for complex formation reaction at 27°C was found to be -14.0934 k cal/mol.

Thermogravimetric analysis

From TG analysis of the Cu(II) chelate, it

Table 5: Determination of Cu(II) in drain micro etch solution

Cu(II) taken in ml	Absorbance	ppm found	ppm taken	% Cu(II) found	% Error
2.5	0.492	11.65	11.755	2.3300	-0.89
3.5	0.696	16.35	16.457	2.3357	-0.65

was found that there is no weight loss upto 191°C indicating that the chelate can be dried safely without decomposition at 110°C. Loss in weight from 191°-860°C is due to removal of organic ligand molecules. Observed loss and weight of metal

residue agrees well with the formula of the chelate in which M:L ratio is 1:2. Activation energy E_a was calculated using Broid method²⁰ and found to be 27.897 k cal/mol for first step and 2.998 k cal/mol for second step decomposition.

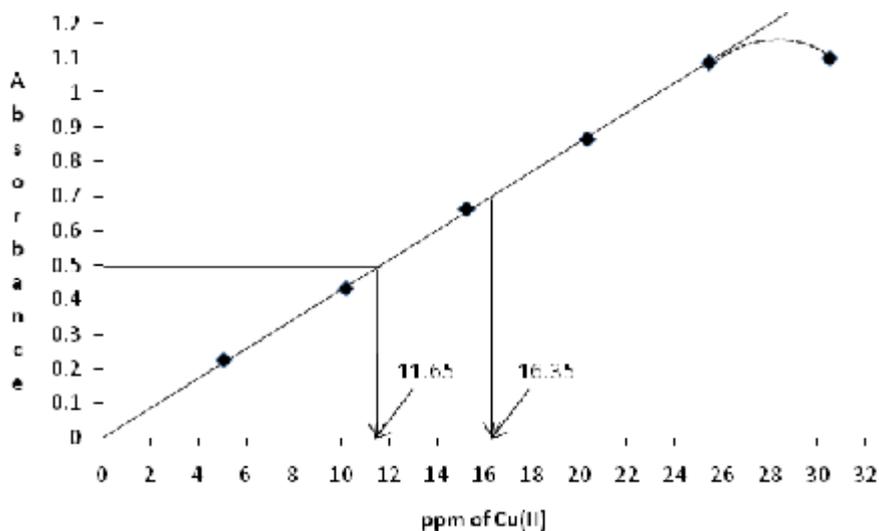


Fig. 1: Beer's law plot of Cu(II)-DHBMPO

IR Spectra

Interpretation of IR-spectra of the chelate shows weak band around 3485 cm^{-1} in comparison of ligand molecule. The weak band due to ν^{OH} of oximino group is found at 3389 cm^{-1} in ligand, is observed at nearly the same position in the complex. $\nu^{\text{C=N}}$ stretching band observed at 1633 cm^{-1} in ligand is shifted to 1617 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 $\nu^{\text{N-O}}$ group i.e. from 927 to 880 cm^{-1} .

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. 10ml of stock solution was diluted to 100ml. 10ml of this solution was further diluted to 100ml. From that 25ml of solution was

finally diluted to 50ml. A 2.5ml and 3.5ml aliquots of this diluted sample was taken in two different beakers containing 4.0ml (0.01M) of reagent solution each. Small amount of double distilled water was added and pH of the solution was adjusted to 4.0 with sodium acetate and acetic acid buffer. Complex was extracted in CHCl_3 and final volume was made 25ml. The absorbance was measured and ppm of Cu(II) was calculated by using Beer's law plot. Results obtained are given in Table 5 and Fig.1.

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