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Synthesis of an Analytical Reagent, its Spectroscopic Characterization and Studies of its Complexation Behavior with Copper Metal Ion, its Application

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ABSTRACT

2-Hydroxy-4-n-propoxy-5-nitro [2'-methyl] propiophenone oxime (HnPNMPO) *has been used for the Spectrophotometric determination of Cu (II) at pH = 6.0. Job's method of continuous variation and Yoe and Jones Mole ratio method show metal: ligand ratio in the complex to be 1:2. The molar absorptivity of complex at 430 nm was found to be 4.450 x*10^3 *lit. mol*$^{-1}$*.cm*$^{-1}$ *and Sandell's sensitivity was found to be 0.0143µg/cm*^{2}*. The stability constant determined spectrophotometrically is found to be 3.9 x* 10^{11} *and Gibb's free energy change for complex formation reaction is calculated to be -15.91 k cal /mole. The Beer law is obeyed up to 2.54 ppm of Cu (II) ion at 430 nm. From TG studies, the energy of activation for the decomposition step has been calculated using broido method. It was found to be 21.996 k cal/mole. The reagent has been successfully applied for the determination of copper in drained microetch solution.*

Keywords: Spectrophotometric determination, propiophenone oxime, Gibb's free energy change, Energy of activation.

INTRODUCTION

Werner set forth the foundation of co-ordination chemistry. The formation of co-ordination compounds by organic reagents with metal ions has been extensively used in analytical chemistry. Organic reagents form chelate with metal ions. Reagents capable of forming chelates are highly selective in their action and hence offer attractive potentialities as analytical reagents. If the organic molecule is to form a chelate, it should contain an acidic group. Many organic reagents like o-hydroxy oxime [1-11], oxime [12-16], thiosemi carbazones [17-23], chalcone oxime [24], anilides [25], various heterocyclic compounds have been used as gravimetric and spectrophotometric reagent for various transition metal ions. o-hydroxy aldoximes and o-hydroxy ketoximes are very effective in forming chelates with metal ions. They are used to study the complexation behaviour for a variety of transition metal ions. It is interesting to study the complexation behavior of metal ion with 2-Hydroxy-4-n-propoxy-5-nitro [2'-methyl] propiophenone oxime (HnPNMPO). Also interesting to study the characterization by various spectral techniques.

MATERIALS AND METHODS

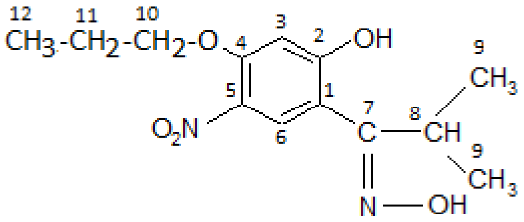
Instruments: Spectrophotometric measurements were done on Perkin-Elmer Lambada-35 UV-Visible spectrophotometer and all the pH measurement were done on electronic pH-meter (EQ-614). TG analysis was done using TA-Instrument SDTQ-600".

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 (A.R. Grade) in deionized water. Solutions of other ions were prepared by dissolving their salts (A.R) in deionized water.

Synthesis of Reagent [HnPNMPO] 2-Hydroxy-4-n-propoxy-5-nitro [2'-methyl] propiophenone oxime (HnPNMPO) was synthesized according to the method of H. Nogami [26], reaction between Resorcinol, Isobutyric acid and Anhydrous zinc chloride will give 2,4-Dihydroxy [2'-methyl] propiophenone (DHMP). Nitration of above ketone with 5.6 ml of ice cold nitric acid results in the formation of 2,4-Dihydroxy-5-nitro [2'-methyl] propiophenone (DHNMP), which was then treated with n-propyl bromide (0.01 mole) and potassium carbonate (1.25 gm) and was refluxed for 6 hours leads to the formation of 2-Hydroxy-4-n-propoxy-5-nitro [2'-methyl] propiophenone (HnPNMP). This nitro ketone derivative further refluxed with $NH_2OH.HCl$ in presence of sodium acetate forming the above reagent. Reagent was recrystalised in aqueous ethanol. M.P =169°C

RESULTS AND DISCUSSION

Characterization of Reagent: The thiosemicarbazone reagent under present investigation is characterized by following different analytical techniques.



2-Hydroxy-4-n-propoxy-5-nitro[2'-methyl] propiophenone oxime (HnPNMPO)

Elemental analysis: Elemental analysis of the reagent was done using "Carlo-Erba Elemental Analyzer Model 1106". The percentage elements, found are in agreement with its molecular formula. The results are given in the following Table 1.

Table 1: Elemental analysis of reagent HnPNMPO

Reagent	%Carbon [Calc.]	%Hydrogen [Calc.]	%Nitrogen [Calc.]
HnPNMPO	55.01% (55.32%)	6.11% (6.38%)	9.53% (9.93%)

TG Studies: The Thermo Gravimetric study of Chelate was done on TA-Instrument SDTQ-600".

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 227 nm that fall in UV region.

FT-IR Spectral studies: FT-IR spectrum of the reagent and its Chelate was recorded on "Simadzu 8400-S spectrophotometer" in KBr pallet. Absorption bands observed are shown in Table 2.

Table 2: FT-IR spectral studies reagent HnPNMPO and it's copper chelate

Reagent	**$\nu^{(O-H)}$ Phenolic (cm^{-1})**	**$\nu^{(O-H)}$ Oximino (cm^{-1})**	**Aromatic ether C-O-C (cm^{-1})**	**Gem-$(CH_3)_2$ Group (cm^{-1})**	**$\nu^{(C-H)}$ strec.of propoxy group (cm^{-1})**	**$\nu^{(C=C)}$ aromatic (cm^{-1})**	**νN=O strec. (cm^{-1})**	**$\nu^{(C=N)}$ (cm^{-1})**	**$\nu^{(N-O)}$ (cm^{-1})**
HnPNMPO	3377	3224	1227	1343	2881-2975	1600	1525	1624	946
Cu(II)-HnPNMPO	--	3178	1291	1385	2881-2975	1599	1513	1602	906

^{1}H and ^{13}C NMR Spectral Studies: The NMR spectrum of the reagent was taken in $CDCL_3$. The NMR spectrum was recorded on a BRUKER AVANCE II 400 NMR spectrometer using TMS as reference, Assignment of signals to different protons and carbons are given in Table 3 and Table 4.

Table 3: ^{1}H-NMR

Reagent	**Alkyl group**	**Methine & Methylene Proton**	**Methyl proton of propoxy group**	**Methylene proton of propoxy group near by oxygen**	**Phenolic (-OH)**	**Oximino (-OH)**	**Aromatic proton**
HnPNMPO ^{1}H -NMR	1.2285-1.3864 ppm (Doublet)	1.7091-2.1526 ppm (Multiplet)	0.9617-0.9851 ppm (Triplet)	4.2429-4.5787 ppm (Triplet)	12.0850 ppm	11.0918 ppm	6.4623-7.9311 ppm

Table 4: ^{13}C-NMR

HnPNMO	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**
^{13}C-NMR (δ ppm)	112.98	164.56	104.15	161.14	126.68	126.35	164.81	27.39	20.62	97.34	25.91	18.26

Spectrophotometric study of Cu(II) – HnPNMPO: 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 at the pH 6.0. The excess reagent was added to get complete precipitation of complex. It was extracted in three 5.0 mL portion of chloroform and final volume of this solution was adjusted to 25mL with chloroform. The absorbance was measured at 430 nm and plotted against the concentration of Cu (II). It was found that Beer's law was obeyed up to 2.54 ppm of Cu (II). Molar absorptivity and Sandell's sensitivity [27] were calculated from the graph and it was found to be 4.450×10^3 $lit.mol^{-1}.cm^{-1}$and 0.0143 µg cm^2 respectively. Job's method [28] of continuous variation and Yoe and Jones mole ratio method [29] 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 by thermogravimetric analysis. The stability constant was calculated using the formula,

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

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 two method is 3.9 x10^{11} and Gibb's free energy change for complex formation reaction was calculated using the formula $\Delta G° = -RT\ln K_S$ and found to be -15.91 k cal.mol^{-1} at 27°C.

Effect of diverse ion: Interference due to associated ions was examined in the determination of 2.54 ppm of Cu (II) at pH- 6.0 using the reagent. The tolerance limit was taken as the amount of foreign ion required to cause $\pm$ 2% error in the absorbance.

A 60 fold excess of Sr(II), Ba (II), Mg(II), Cd(II), Zn(II), K(I), Mn(II) ,Zr(IV) [24], Co(II) [25], Ni(II) [19] do not interfered. Fe (III) and Pd(II) interfered seriously. Chloride, bromide, nitrate, sulphate, citrate do not interfere in the determination, even when present in 150 fold excess.

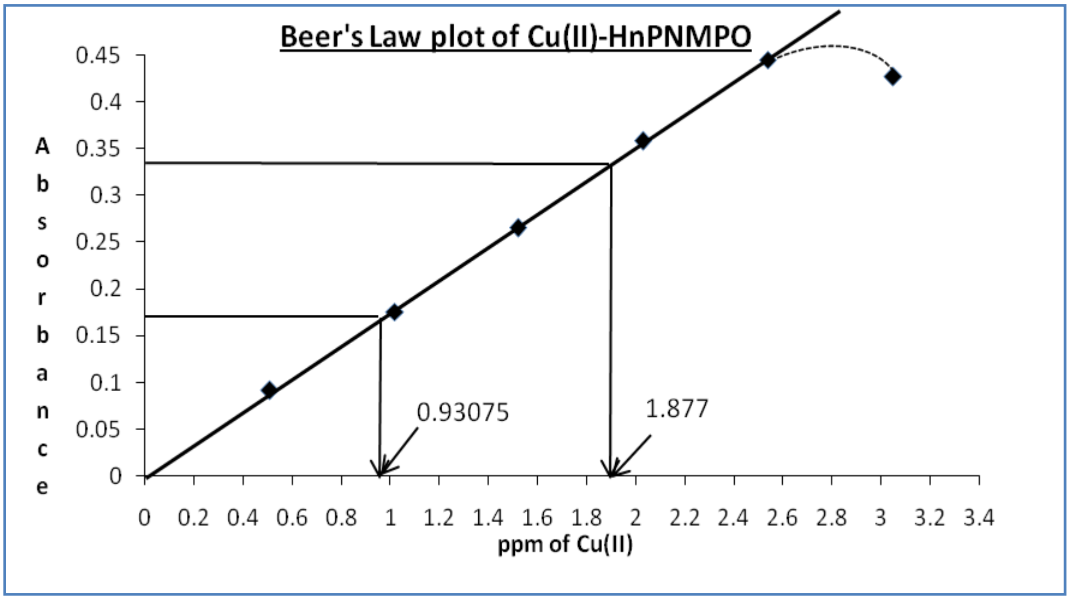
Thermo gravimetric analysis: Thermo gravimetric analysis of copper chelate was done on "TA-Instrument SDTQ-600". A definite quantity of chelate was taken in an alumina crucible and was put on a hanger of microbalance and crucible was kept in a furnace. The temperature of the furnace was raised from 30°C to 900°C in a programmed manner at the heating rate of 10°C min^{-1}.

From TG analysis of the Cu (II) chelate, it was found that there is no weight loss up to 180°C indicating that the chelate can be dried safely without decomposition at 110°C. Loss in weight from 180-900°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 Ea was calculated using Broido method [30] and found to be 21.996kcal mol^{-1} is necessary for the decomposition of complex.

IR Spectra: Interpretation of IR-spectra of the chelate shows that band around 3377 cm^{-1} disappears because of participation of hydroxy group in chelation. The weak band due to ν^{-OH} of Oximino group is found at 3324 cm^{-1} in ligand, is observed at nearly the same position in the complex. $\nu^{C=N}$ stretching band observed at 1624 cm^{-1} in ligand is shifted to 1602 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 946 to 906 cm^{-1}.

APPLICATIONS

Determination Of Copper In Drained Micro Etch Solution: Preanalysed sample of drain microetch solution containing 2.351% Cu (II) metal was taken to check the applicability of HnPNMPO. 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 1.0mL and 2.0mL were taken for complexation with 2.0mL of 0.001M ligand solution. Small amount of double distilled water was added and pH of the solution was adjusted to 6.0 with buffer solution.Complex was extracted in $CHCl_3$ and final volume was made 25mL. The absorbance was measured at 430nm and ppm of Cu (II) metal ion was calculated by using Beer's law plot. Absorbance values obtained were plotted in Beer's law plot.



Cu(II) taken in ml	Absorbance	ppm found	ppm taken	% found	% Error
1.0	0.165	0.93075	0.9404	2.3267	-1.03
2.0	0.330	1.877	1.8808	2.3463	-0.20

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