Chemical Concepts

International Journal of Chemical Concepts
ISSN:2395-4256 **www.chemconsai.com**
Vol.06, No.01, pp 01-07, 2020

2-Chloro-2'-hydroxy-4'-chloro-5'-methoxychalcone Oxime [CHCMCO] as an Analytical Reagent: Studies on Cu (II) Chelate

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Abstract: The ligand 2-Chloro- 2'-hydroxy-4'-chloro-5'methylchalcone oxime (**CHCMCO**) was developed as a new analytical reagent for the gravimetric and spectrophotometric analysis of Cu (II) ion. In the pH range of 6.0 to 6.5, this reagent gives buff colored complex with Cu (II). Job's method of continuous variation and Yoe and Jone's mole ratio method revealed the stoichiometry of the complex to be 1:2 [M: L]. The obeyance of Beer's law was studied, the molar absorptivity was found to be $1.07x10^2$lit.mol^{-1}cm^{-1}. The reagent and its complex have been characterized by elemental analysis and IR spectra. The magnetic susceptibility measurement (4 ampere and 298^o K) of the chelate reveals the paramagnetic nature of the complex.
Key words: Analytical reagent, Cu (II) chelate, 2-Chloro- 2'-hydroxy-4'-chloro-5'methylchalcone oxime **(CHCMCO**)

Introduction:

In the current scenario, large number of organic reagents have been employed for the detection and quantitative determination of metal ions. They include o-hydroxy ketoximes[1-2], phenyl hydrazones, thiosemicarbazones, chalcone oximes[3-8] etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. Here, we report the use of 2-Chloro- 2'-hydroxy-4'-chloro-5'methylchalcone oxime (**CHCMCO**) as an analytical reagent for Cu (II)

Experimental:

Instruments:

Spectrophotometric measurements were done on a "Baush and Laumb" Spectrophotometer working on a Doran's mains unit connected to 220V/50 cycles and "Spectronic-20". The IR spectra were recorded on "Perkin-Elmer" IR Spectrophotometer (Model No.377) in KBr pallet. All pH measurements were done on Elico pH meter .Magnetic Susceptibility measurement was carried out on "Gouy" method.

Stock solution:

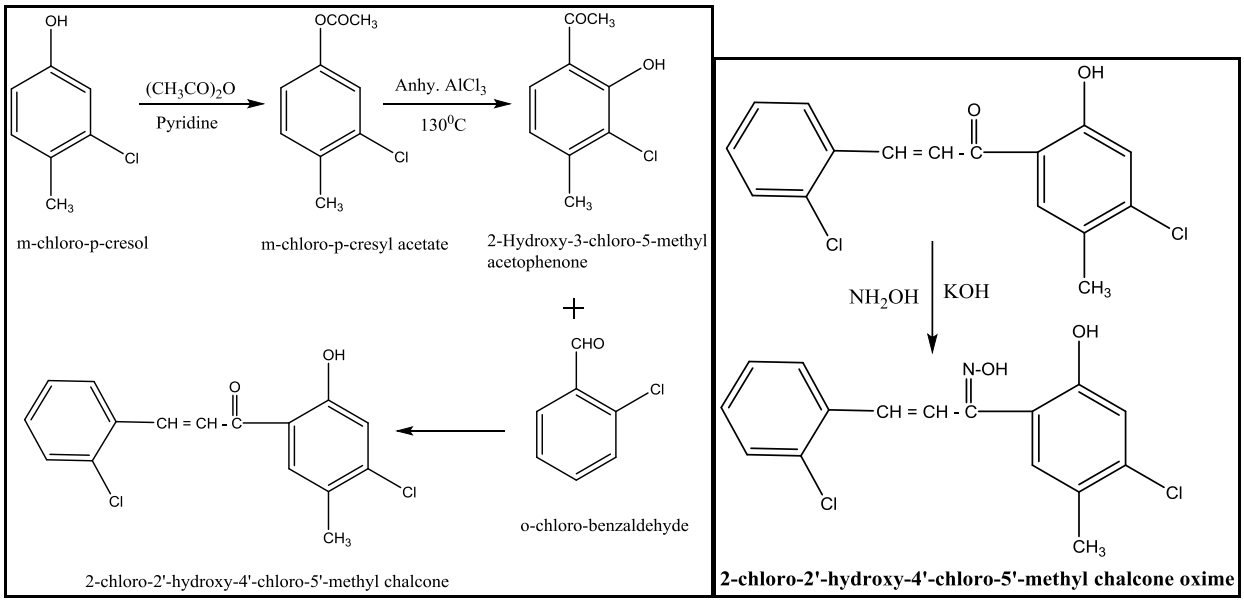
Stock solution of $CuSO_4.5H_2O$ (0.05 M) was prepared by dissolving 3.121 gm of $CuSO_4.5H_2O$ (A.R.) in minimum quantity of water and diluted to 250 ml with doubly distilled water. Concentrated sulphuric acid was added in little amount to prevent the hydrolysis of the salt. It was used after standardization[9] with EDTA.

Synthesis of Reagent [CHCMCO**]:**

m-chloro-p- cresyl acetate was prepared[10] from m–chloro-p-cresol, glacial acetic acid and pyridine was heated on water bath for 4 hours.The reaction mixture was poured over crushed ice containing hydrochloric acid. The liquid separated was washed with a solution of $NaHCO_3$and then with water. It was then extracted with ether, dried over anhydrous sodium sulphate, ether was removed and then distilled as colorless liquid at 220^oC.

m-chloro-p-cresyl acetate was mixed slowly with anhydrous $AlCl_3$ at room temperature, and then heated at 130^oC on an oil bath for 4 hours. The reaction mixture was cooled and decomposed with ice and concentrated hydrochloric acid.2-hydroxy-4-chloro-5-methyl acetophenone was separated and washed with a solution of $NaHCO_3$ and then with water. The solid separated was collected and crystallized from petroleum ether as colorless needles. The 2-hydroxy-4-chloro-5-methyl acetophenone was converted to 2-chloro-2'hydroxy-4'chloro-5'methylchalcone by its condensation with 2-cholrobenzaldehyde in presence of aqueous KOH for 18 hours at room temperature. The 2-chloro-2'-hydroxy-4'-chloro-5'-methylchalcone was converted to its oxime using hydroxylamine hydrochloride and sodium acetate. On crystallization from alcohol pure oxime in the form of colorless crystals with m.p.195°C was obtained. Stock solution of reagent (1%) was prepared by dissolving in 60% aqueous ethanol.

Reaction :



Gravimetric determination of Cu (II):

Copper Sulphate solution (0.05 M, 10 ml) was taken in a clean beaker and diluted to about100 ml with distilled water. A little excess of reagent solution was added (0.05 M, 22 ml). The pH of the solution was adjusted between 6.0 -6.5 using suitable acid buffer. A buff precipitate obtained was digested on water-bath for 60 minutes at 60°C. The precipitate were filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water followed by 60% aqueous ethanol to remove excess of the reagent. The chelate was dried to constant weight at 105-110$^{\circ}C$ in hot air oven, cooled and weighed as Cu ($C_{32}H_{24}O_4N_2Cl_4$). Duplicate experiments were performed. The results are given in Table 1. The experiment was also repeated with different aliquots, keeping the optimum pH value to evaluate its applicability. The error in any case did not exceed 1.0%.

Table : 1gravimetric Determination Of CU(II) using Chcmco

pH:6.0-6.5Drying temperature = 100-105^{o}CSalt = $CuSO_4.5H_2O$

Cu(II) taken in g	Cu(II) complex in g	Cu(II) found in mg	Error in mg
0.00794	0.0883	0.00796	$+2 \times 10^{-5}$
0.01588	0.1768	0.01592	$+4 \times 10^{-5}$
0.002382	0.2654	0.002390	$+8 \times 10^{-5}$
0.003176	0.3540	0.003188	$+12 \times 10^{-5}$

Conversion factor = Cu (II)/Cu (II) complex=0.09005

Spectrophotometric study of Cu (II) –CHCMCO chelate:

The chelate of Cu (II) with the chalcone oxime was extracted in chloroform and the absorption spectra were recorded in the range of 330 to 1000 nm. It was observed that the absorbance of the colored solution of chelate increases continuously towards the shorter wavelength. A band of absorbance curve is observed at 400 nm and hence all measurements were carried out at 400 nm.

Verification of Beer's law and optimum concentration range:

A definite amount 0.0915 g. of the dried metal chelate was dissolved in 15 mL chloroform. From this, 5 mL of the solution was diluted to 50 mL to get 0.8523×10^{-3} M solution and 45 mL of this solution was diluted to 100 mL to get a solution of 0.3870×10^{-3}M. This solution was taken in definite volumes and diluted to 10 mL, thereafter the absorbance of these solutions were measured at 400 nm against chloroform as the blank sample. Absorbance values were plotted against metal concentration expressed in ppm. A straight line passing through the origin, indicating obeyance of Beer's law is obtained. The standard graph thus obtained was used for the determination of copper in unknown solution using 2-chloro-2'-hydroxy-4'-chloro-5'methylchalcone oxime.

Stoichiometry of complex:

Job's method of continuous variation[11] and Yoe and Jones mole ratio method[12] were used to determine the stoichiometry of the Cu (II)-CHCMCO complex. From both the methods, it was found to be 1:2 [M: L] ratio. This is in agreement with the stoichiometry found from gravimetry. The stability constant (Ks) found from two methods is 1.9×10^{7}.

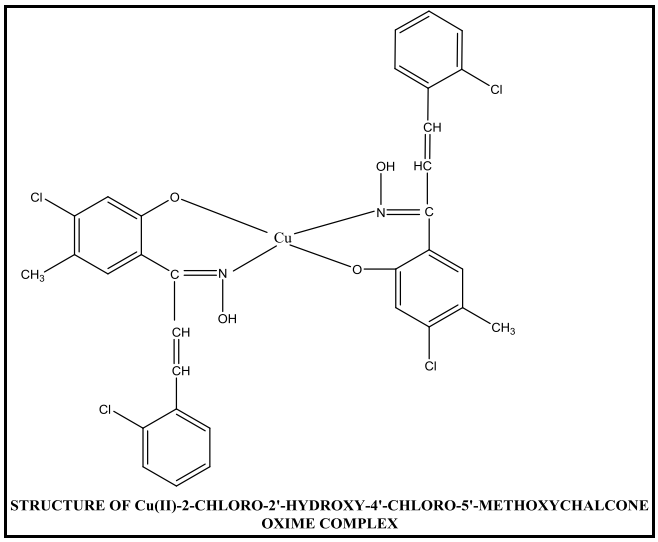
Magnetic Susceptibility Measurements:

Gouy method[13] was used to measure the magnetic moment of the crystallized Cu (II)-Chalcone oxime. The calculated (298^{o}K and 4 ampere) effective Magnetic moment (μ_{eff})was 1.89.

Name of the Complex	Gram magnetic susceptibility Ã χ_g x 10 $^{-6}$ in emu	Molar magnetic susceptibility Ã χ_m x 10 $^{-6}$ in emu	Effective magnetic susceptibility Ã μ_{eff}
Copper-2-chloro-2'-hydroxy-4'-chloro-5'-methylchalcone oxime	2.1154	1496.69	1.89

IR Spectra:

Examinations of the IR spectra of the chelates show that the band due to O-H phenolic group, group disappears in the Cu (II)-CHCMCO complex. This results in revealing of two bands due to oximino -OH group at 3110 cm^{-1} and 3140 cm^{-1} in Cu (II) complex.The band due to the -C=N stretching which is observed at1600 cm^{-1} in ligand is shifted to 1610 cm^{-1} in complex. The C-Cl stretching band observed at 750 cm^{-1}remains as it is in the complex.



STRUCTURE OF Cu(II)-2-CHLORO-2'-HYDROXY-4'-CHLORO-5'-METHOXYCHALCONE OXIME COMPLEX

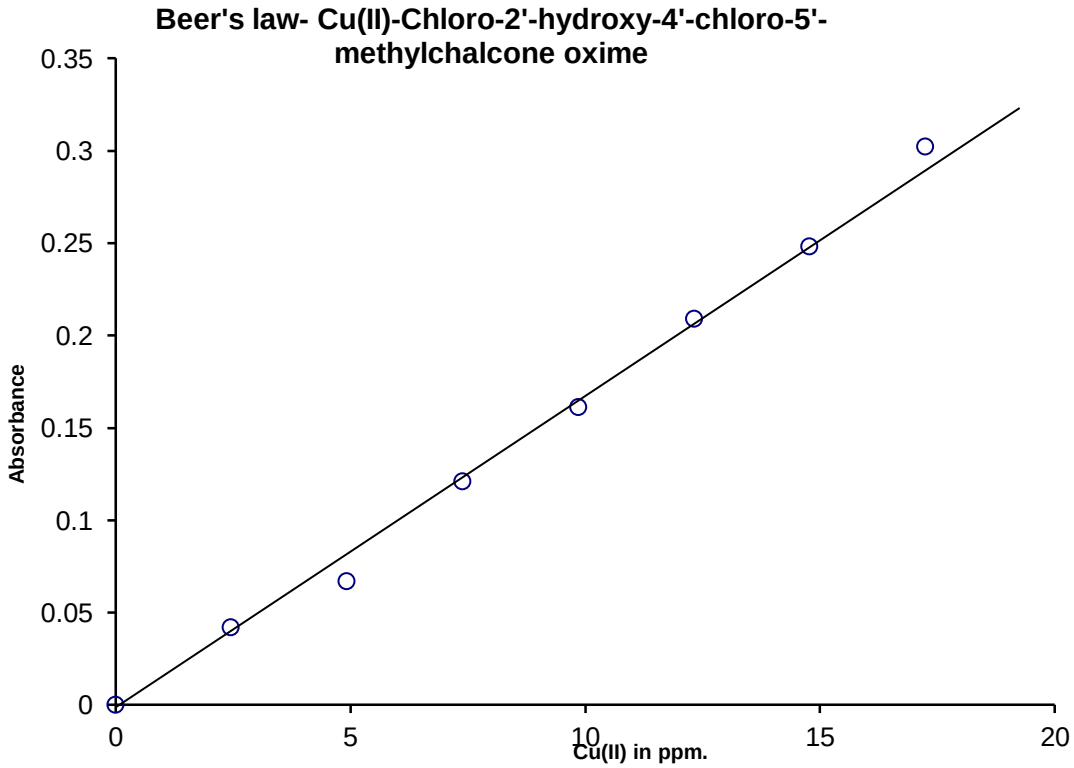


Figure 1: Beer's law plot for Cu (II)-CHCMCO complex

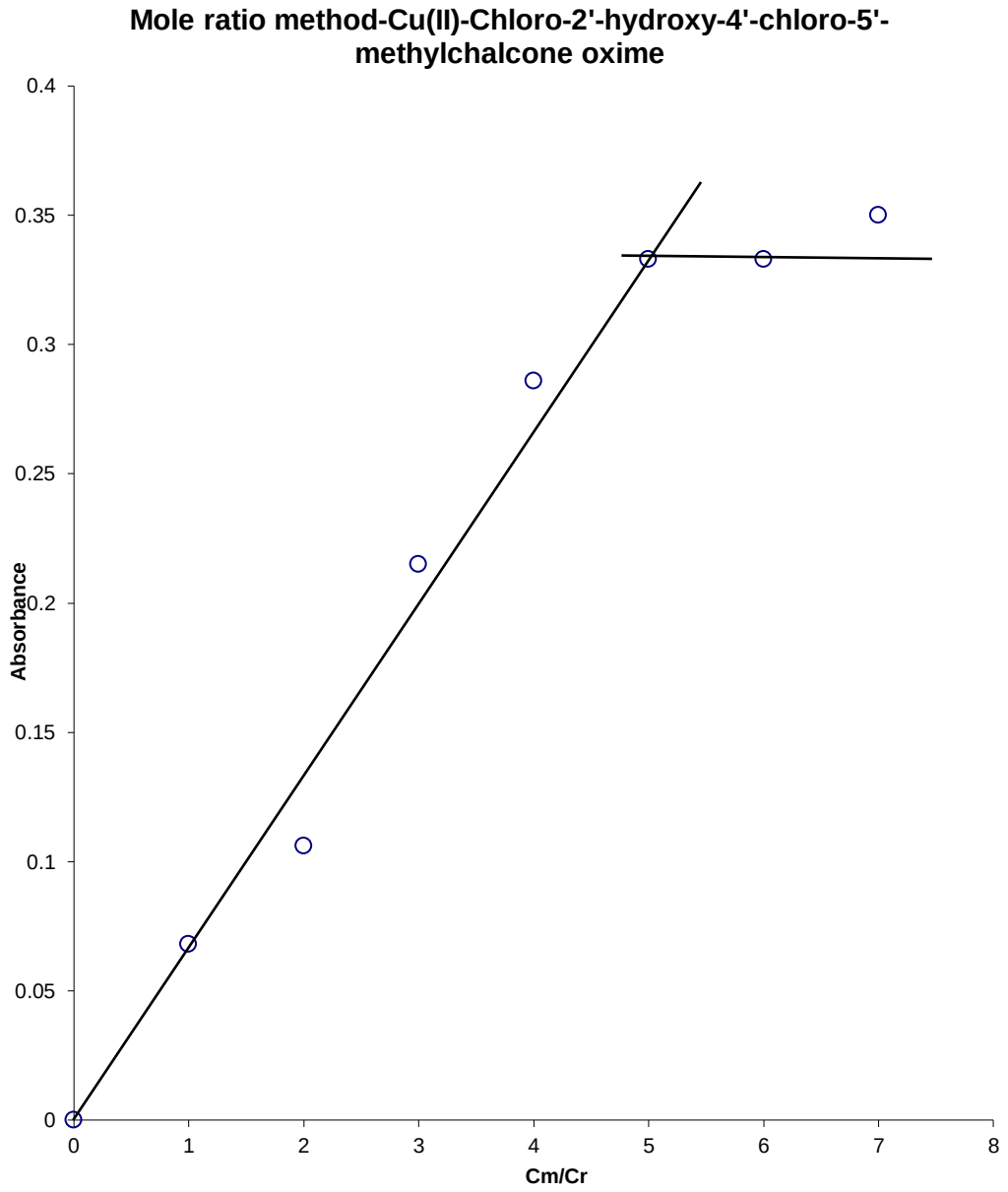


Figure -2. Yoe and Jones mole ratio method for Cu(II)-CHCMCO complex

Plots of Yoe and Jones mole ratio method for determination of M:L ratio0.002 M Cu(II), 0.002 M CHCMCO;pH = 6.0-6.5; λ_{max}= 400 nm.

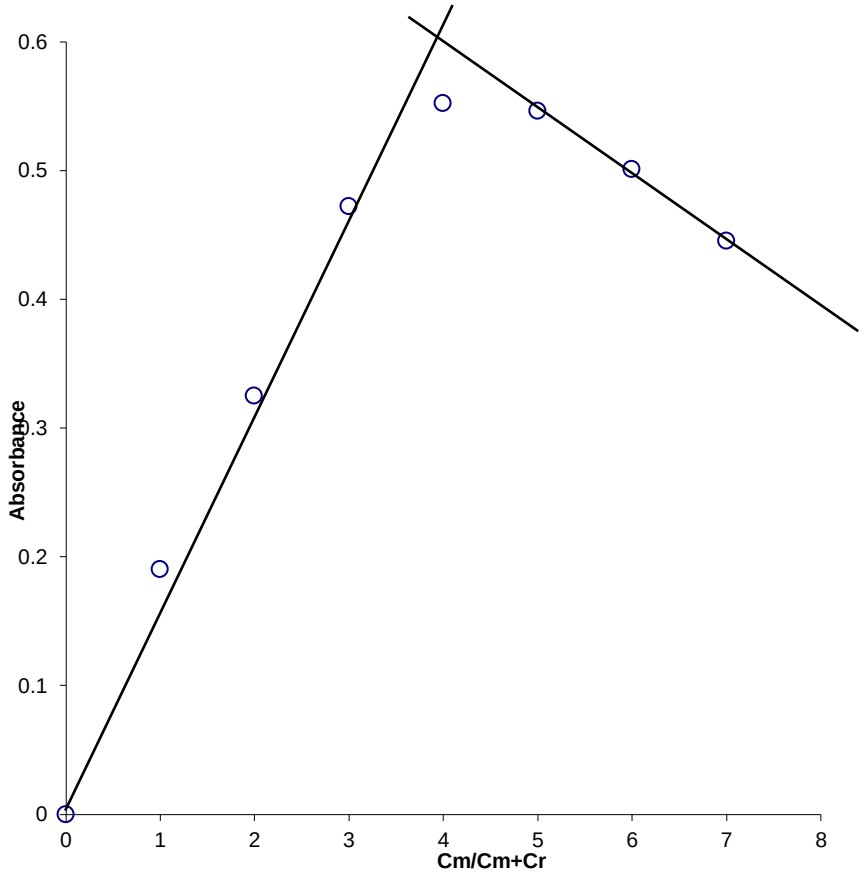


Figure -3. Job's method for Cu (II)-HBCO complex

Plots of Job's method of continuous variation for determination of M:L ratio 0.002 M Cu(II), 0.002 M CHCMCO;pH = 6.0-6.5 ;λ_{max}= 400 nm.

Conclusion:

Based on the results and discussion, followings are the concluding remarks.

1. 2-chloro-2'-hydroxy-4'-chloro-5'methylchalcone oxime (CHCMCO) is suitable reagent for the gravimetric and spectrophotometric determination of Cu (II).
2. The complex is paramagnetic in nature which indicates the presence of one unpaired electron in d-orbital and confirms the removal of two electrons, one from 3d orbital and one from 4s orbital. Thus 3d and 4s orbitals are involved in the formation of the chelate.

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