



2-Chloro-2'-Hydroxy-4'-Chloro-5'-Methoxychalcone Oxime [CHCMCO] As An Analytical Reagent: Studies On Ni (II) Chelate

KEYWORDS

Analytical reagent, Ni (II) chelate, 2-Chloro- 2'-hydroxy-4'-chloro-5'-methylchalcone oxime (CHCMCO)

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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 Ni (II) ion. In the pH range of 7.0 to 7.5, this reagent gives light green colored complex with Ni (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 obedience of Beer's law was studied and the molar absorptivity was found to be $1.25 \times 10^2 \text{ lit.mol}^{-1}\text{cm}^{-1}$. The reagent and its complex have been characterized by elemental analysis and IR spectra. The magnetic susceptibility measurement (4 ampere and 2980 K) of the chelate has been calculated. The complex is diamagnetic in nature.

Introduction:

In the current scenario, large numbers of organic reagents have been employed for the detection and quantitative determination of metal ions. They include o-hydroxy ketoximes¹⁻², phenyl hydrazones, thiosemicarbazones, chalcone oximes³⁻⁹ 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 Ni (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 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.05 M) was prepared by dissolving 2.971 gm of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (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 standardization¹⁰ with EDTA.

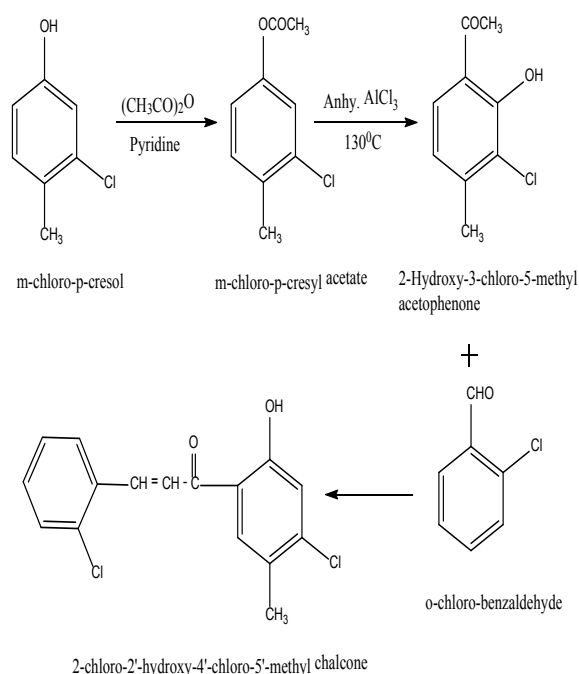
Synthesis of Reagent [CHCMCO] :

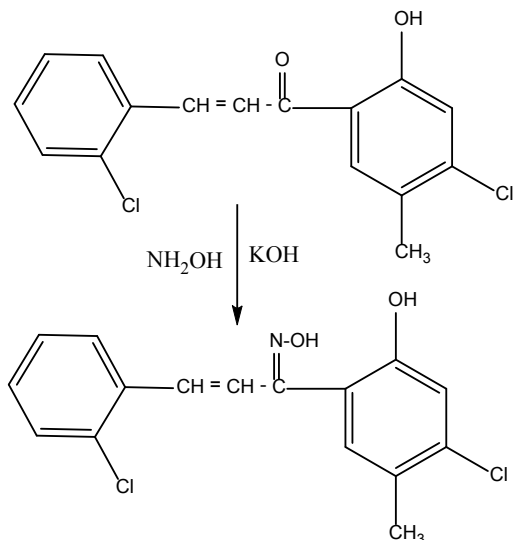
m-chloro-p- cresyl acetate was prepared¹¹ from m-chloro-p-cresol, glacial acetic acid and pyridine was heated on water bath for 4 hours. The reaction mixture was poured over crushed ice containing hydrochloric acid. The liquid separated was washed with a solution of NaHCO_3 and then with water. It was then extracted with ether, dried over anhydrous sodium sulphate, ether was removed and then distilled as colorless liquid at 220°C.

m-chloro-p- cresyl acetate was mixed slowly with anhydrous AlCl_3 at room temperature, and then heated at 130°C 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-chlorobenzaldehyde 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 :





2-chloro-2'-hydroxy-4'-chloro-5'-methyl chalcone oxime

Gravimetric determination of Ni (II):

Nickel Chloride solution (0.05 M, 10 ml) was taken in a clean beaker and diluted to about 100 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 7.0 - 7.5 using HCl/NaOAc buffer. A light green 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_1) 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°C in hot air oven, cooled and weighed as Ni ($C_{32}H_{24}O_4N_2Cl_4$). 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 : 1 GRAVIMETRIC DETERMINATION OF NI(II) USING CHCMCO

pH: 7.0-7.5 Drying temperature: 100-105°C
Salt : $NiCl_2 \cdot 6H_2O$

Ni(II) taken in g	Ni(II) complex in g	Ni(II) found in mg	Error in mg
0.00735	0.08817	0.00733	-2×10^{-5}
0.01467	0.17633	0.01463	-4×10^{-5}
0.02202	0.26462	0.02205	$+3 \times 10^{-5}$
0.02936	0.35270	0.02930	-6×10^{-5}

Conversion factor = Ni (II)/Ni (II) complex=0.08322

Spectrophotometric study of Ni (II) - CHCMCO chelate:

The chelate of Ni (II) with the chalcone oxime was extracted in chloroform and the absorption spectra were recorded in the range of 340 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 410 nm and hence all measurements were carried out at 410 nm.

Verification of Beer's law and optimum concentration range :

A definite amount 0.05 g. of the dried metal chelate was dissolved in 100 mL chloroform. This solution was taken in definite volumes and diluted to 10 mL, thereafter the absorbance of these solutions was measured at 410 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 obedience of Beer's law is obtained. The standard graph thus obtained was used for the determination of Nickel in unknown solution using 2-chloro-2'-hydroxy-4'-chloro-5'-methylchalcone oxime.

Stoichiometry of complex:

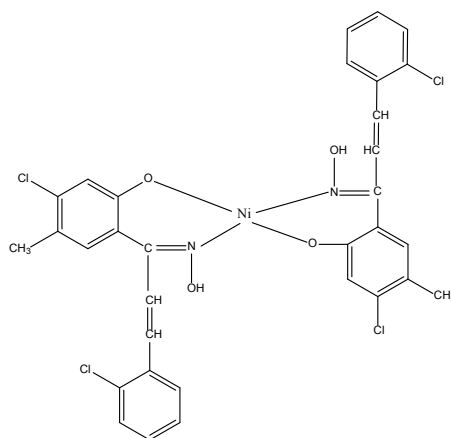
Job's method of continuous variation¹² and Yoe and Jones mole ratio method¹³ were used to determine the stoichiometry of the Ni(II)- CHCMCO complex. From both the methods, it was found to be 1:2 [M:L] ratio. This is in agreement with the stoichiometry found from gravimetry. The stability constant (Ks) found from two methods is 1.7×10^7 .

Magnetic Susceptibility Measurements:

Gouy method¹⁴ was used to measure the magnetic moment of the crystallized Ni (II)-Chalcone oxime. The effective Magnetic moment (μ_{eff}) indicates that the complex is diamagnetic.

IR Spectra:

Examinations of the IR spectra of the chelates show that the band due to O-H phenolic group disappears in the Ni (II)-CHCMCO complex. This results in revealing of two bands due to oximino -OH group at 2850 cm^{-1} and 3000 cm^{-1} in Ni (II) complex. The band due to the -C=N stretching which is observed at 1600 cm^{-1} in ligand is shifted to 1610 cm^{-1} in complex. The C-Cl stretching band observed at 750 cm^{-1} shifted to 760 cm^{-1} in the complex.



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

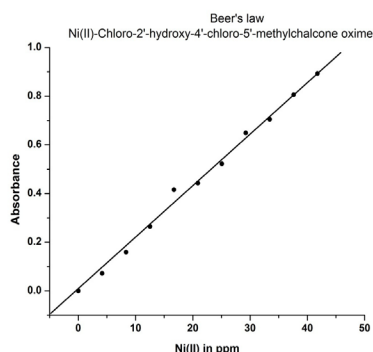


Figure 1: Beer's law plot for Ni (II)-CHCMCO complex

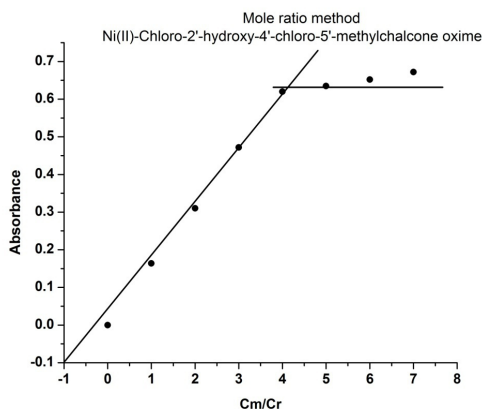


Figure -2. Yoe and Jones mole ratio method for Ni(II)-CHCMCO complex Plots of Yoe and Jones mole ratio method for determination of M:L ratio 0.002 M Ni(II), 0.002 M CHCMCO; pH = 7.0-7.5; λ_{\max} = 410 nm.

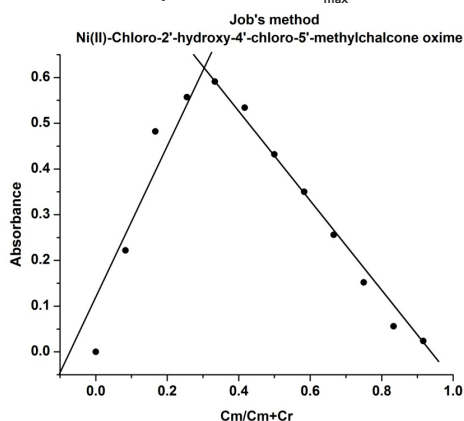


Figure -3. Job's method for Ni (II)-CHCMCO complex Plots of Job's method of continuous variation for determination of M:L ratio 0.002 M Ni(II), 0.002 M CHCMCO; pH = 7.0-7.5; λ_{\max} = 410 nm.

Conclusion:

2-chloro-2'-hydroxy-4'-chloro-5'-methylchalcone oxime (CHCMCO) is suitable reagent for the gravimetric and spectrophotometric determination of Ni (II). The complex is diamagnetic in nature.

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