

## Studies on Interaction between Cu (II), Co (II) and Ni (II) metal ions and novel chalcones at 0.1M ionic strength pH metrically

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**Abstract:** The interaction of Cu (II), Co(II) and Ni(II) metal ions with 3-bromo-2-hydroxy-5-Methyl chalcone (L1) and 3-Bromo-(2-hydroxy-5-methyl benzoyl) -4-phenyl-1, 3-butadine chalcones (L2) have been studied at 0.1M ionic strength in 70% Dioxane-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Sm(III) and Nd(III) metal ions from 1:1 and 1:2 complexes with ligands (L1 & L2). The data obtained were used to estimate and compare the values of proton-ligand stability constant ( $pK$ ) and metal-ligand stability constants ( $\log K$ ). The effect of substituents was studied from estimated data ( $pK$  &  $\log K$ ).

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### I. Introduction:

The consider research work has been done on the study of complexes (1-2.) The many workers (3-7) have reported their results on metal – ligand stability constants. With the view to understand the bio-inorganic chemistry of metal ions.

**The studies in metal** – ligand complexes in solution of number of metal ions with carboxylic acids, oximes, phenols, etc would be interesting which throw a light on the mode of storage and transport of metal ions in biological kingdom.

Bejerrums's [B] dissertation has taken the initiative to develop the field. Metal complexation not only bring the reacting molecules together to give activated complex [g] but also polarised electrons from the ligands is indicated towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy change value. Bulkier group increases the basicity of ligands as well as stability. The stability of the complexes is determined by the nature of central metal atom and ligand. The stability of the complexes is influenced by the most important characteristics like degree of oxidation, radius and electronic structure. Irvin and Williams [10] have studied the order of stability of metal complexes of transition metal ions by comparing the ionic radius and second ionisation potential of metal ions, as it is valid for most nitrogen and oxygen donor ligands.

Tekade et al [11] have investigated stability constants of some substituted pyrazoline, isoxaline and diketone. Prasad et al [12] have studied mixed ligand complexes of alkaline earth metals, Mg[II], Ca[II], Sr[II] & Ba[II] complexes with 5 – nitrosalicylaldehyde and  $\beta$  – diketones.

In present work an attempt has been made to study the interaction between Cu(II), Co(II) and Ni(II) and novel chalcones (L1 & L2) at 0.1M ionic strength pH-metrically in 70% dioxane – water mixture.

### II. Experimental

The chemicals used in present work were novel chalcone (Ligand 1&2) were synthesized by literature method in laboratory.

The chemicals used in present work were of AR grade. Chalcones [ligands L1 & L2] used were synthesized by literature method in laboratory. The solutions of ligands were prepared in purified 70% dioxane-water mixture and standardised by pH metric technique.

Systronic microprocessor based instrument with accuracy of  $\pm 0.01$  unit with glass and saturated calomel electrode was used for the titrations. It was calibrated by buffer solution of pH 7.00 and 9.20 at  $28 \pm 0.1$  °C, before processing the titrations.

Titrations were carried out in an inert atmosphere by bubbling a constant flow of nitrogen gas. The experimental procedure involved the titrations of –

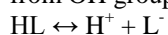
1. Free acid  $HClO_4$  (0.01 M)
2. Free acid  $HClO_4$  (0.01 M) and ligand ( $20 \times 10^{-4}M$ )
3. Free acid  $HClO_4$  (0.01M) and ligand ( $20 \times 10^{-4}M$ ) and metal ion ( $4 \times 10^{-4}M$ ) against standard NaOH solution.

The ionic strength of all the solution were maintained constant (0.1 M) by adding appropriate amount of NaClO<sub>4</sub> solution. All the titrations were carried out in 70% dioxane – water mixture and the reading were recorded for each 0.1 ml addition. The graph of volume of alkali (NaOH) against pH were plotted.

### III. Results And Discussions:

#### Proton – ligand stability constants :

The chalcones used in present investigations are monobasic acid having only one dissociable H<sup>+</sup> ion from OH group. It can therefore, be represented as HL



The titrations curves of the acid and ligand deviate at about 3.0 pH.

The deviation between acid curve from ligand for all the systems showed the dissociation of H<sup>+</sup> ions from –OH group of ligands. The proton - ligand formation number (n-A) were calculated by Irvin and Rossotti expressions:

$$\bar{n}A = \gamma - \frac{(E_0 + N)(V_2 - V_1)}{(V_0 + V_1)T_0L}$$

Where,

V<sub>0</sub> – Initial volume of solution (50ml)

E<sup>0</sup> – Initial concentrations of free acid (HClO<sub>4</sub>)

T<sup>0</sup>L – Concentration of ligand in 50 ml solution

N – Normality NaoH solution

γ – Number of dissociable protons from ligand

(V<sub>2</sub> – V<sub>1</sub>) – Volume of alkali (NaoH) consumed by acid and ligand on same pH

The pk values were calculated from the formation curves between pH Vs nA noting the pH at which nA=0.5 (half integral method) and point wise calculations which are represented in table 1.

**Table 1 Proton – ligand stability constants pK**

Sr No	System	pK	
		Half Integral method	Pointwise method
1	L1:[Beomo-2-hydroxy-5-methyl chalcone]	6.7506	6.8536
2	L2:[3-Bromo-(2-hydroxy-5-methyl benzoyl)-4-phenyl-1, 3-butadine chalcones	5.5423	5.5555

It is observed that the order of pK values of ligands is found to be as pK ligand 1 > pK ligand 2.

The reduction in pK values of ligand 2 may be due to strong inductive effect and resonance effect of benzyl group.

#### Metal – ligand stability constants:

The stepwise formation constants of Cu(II), Co(II) and Ni(II) metal ions with ligands (L1 & L2) in 70% dioxane – water mixture were determined. The values of log K<sub>1</sub> and log K<sub>2</sub> were directly computed from the formation curves (-nVspL) using half integral method. The most accurate values were calculated by pointwise calculations which are represented in table 2.

**Table 2 Metal – ligand stability constants (log K)**

System	Metal - ligand stability constants	
	log K <sub>1</sub>	log K <sub>2</sub>
Cu(II)-ligand -1	10.2237	9.7533
Co(II)-ligand -1	10.3729	10.0791
Ni(II)-ligand -1	10.352	9.7786
Cu(II)-ligand -2	9.4016	8.8542
Co(II)-ligand -2	9.5567	9.1151
Ni(II)-ligand -2	9.4852	9.2141

#### IV. Conclusion:

From the titration curves, it is observed that the departure between (acid + ligand) curve and (acid + ligand + metal) curve for all systems started from pH=3.0 this indicated the commencement of complex formation. Also change in colour from yellow to brown in the pH range from 3 to 10 during titration showed the complex formation between metal and ligand.

**Table 3 – Metal – ligand stability constants (logK)**

Cu(II)-ligand-1	0.4704	1.0482
Co(II)-ligand-1	0.2938	1.0291
Ni(II)-ligand-1	0.5734	1.0586
Cu(II)-ligand-2	0.5474	1.0634
Co(II)-ligand2	0.4416	1.0484
Ni(II)-ligand-2	0.2711	1.0294

From the table 2 and 3, It shows that the difference between log k1 and log k2 values in these ligands is very less, indicated Cu(II)Co(II) and Ni(II) complexes are occurring simultaneously.

The value of log k1 and log K2 (table 2) for Co(II) ligand-1 complex are higher than Cu(II) and Ni(II) ligand 1, indicates that Co(II) forms stable complex with ligand 1 than Cu (II) and Ni(II) metal ions.

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