

pH-Metric Study of Metal-Ligand Stability Constants of Co(II), Cu(II) and Zn(II) Complexes with Substituted β -Diketones

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The interactions of Co(II), Cu(II) and Zn(II) with 1-(2'-hydroxy-5'-chlorophenyl)-3-(4'-chlorophenyl)-1,3-propanedione (1) and 1-(2'-hydroxy-3'-nitro-5'-methylphenyl)-3-(4'-chlorophenyl)-1,3-propanedione (2) have been studied by Bjerrum method as adopted by Calvin and Wilson. The stability constant of 1 : 1 and 1 : 2 complexes of Co(II), Cu(II) and Zn(II) have been studied at constant temperature ($27 \pm 0.1^\circ\text{C}$) and 0.1 M ionic strength (NaOH) in 70% dioxane-water mixture. It is observed that formation of 1 : 1 and 1 : 2 complexes is occurring simultaneously

Key Words: pH-Metric study, Co(II), Cu(II), Zn(II), Metal-ligand stability constant, Substituted β -diketones

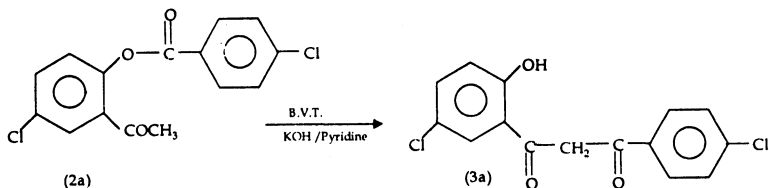
INTRODUCTION

Since the last four decades, considerable research work has been done on the study of complexes in solution^{1,2}. Bjerrum's dissertation³ has taken the initiative to develop the field. Some of the important characteristics added to the drugs play an important role in biological activities, *e.g.*, low dissociation constant, special redox potential, electron distribution and solubilities which has been imparted by the metal complex formation. The effect on solubilities of the drug in the lipids and their transfer through the cell membrane have been marked by these characteristics. The group transfer reactions, bond formation, bond cleavage are the natural processes which have been processed by metal-complex formation. Metal complexations not only bring the reacting molecules together to give activated complex⁴ but also polarize electrons from the ligands 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 the ligands as well as stability. The stability of the complexes is determined by the nature of central metal atom and the ligands. The stability of the complex compounds is influenced by the most important characteristics like the degree of oxidation, the radius and electronic structure. Stability of the complexes depends on the same characteristics of the ligand as considered for the cation as complexes reacted with monoatomic ligands. In addition, the strength of binding for ligand molecules and polyatomic ions depends on the ligand molecule and the nature of the atoms which is directly linked to the central atom or ion.

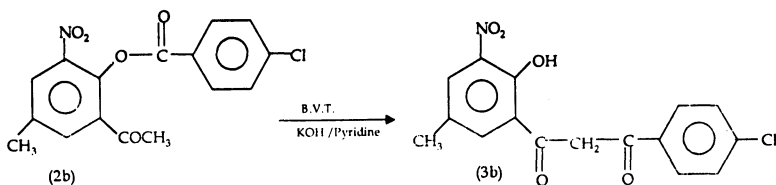
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By comparing the ionic radius and second ionization potentials of the metal ions, the stability order of metal complexes of transition metal ions was studied by Irving and Williams⁵ because it is valid for most nitrogen and oxygen donor ligands. In stability of complexes, the size and number of chelating ring plays an important role. The structure of chelating agents determines the size of chelating ring and the number of rings formed on chelation. The work on amino acid chelates and identification of five and six-membered rings as the most stable is reported by Ley⁶. In the past a number of workers⁷⁻²² have reported their results on metal-ligand chemistry.

In the present work, substituted diketones have been synthesized in view of analytical applications and biological activities. Additional to fungicidal activity, diketones, especially chloro diketones are found to possess antihelminthic activities. It is reported that the substituted diketones which are different in nature act as antimicrobial agents, anti-inflammatory agents, insecticides, bactericides, pharmaceuticals and fungicides.



Ligand 1



Ligand 2

EXPERIMENTAL

All chemicals such as NaOH, HNO₃, KNO₃ and metal salts of AR grade were used in the present work.

1-(2'-Hydroxy-5'-chlorophenyl)-3-(4'-chlorophenyl)-1,3-propanedione (1) and 1-(2'-hydroxy-3'-nitro-5'-methylphenyl)-3-(4'-chlorophenyl)-1,3-propanedione (2) were synthesized by literature method. Both ligands were crystallized and their purity was checked by TLC before use. The solutions of purified ligands were prepared in 70% dioxane-water mixture and standardized by pH-metric techniques.

Systronics microprocessor based instrument with accuracy ± 0.01 unit with glass electrode and saturated calomel electrode was used for the measurements. It was calibrated by buffer solution of pH 4.00, 7.00 and 9.20 at 27°C before processing the titrations.

The experimental procedure involved potentiometric titration of:

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

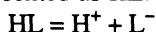
The ionic strength of all the solutions was maintained constant (0.1 M) by adding appropriate quantity of 1 M KNO_3 solution.

The titrations were carried out in 100 mL pyrex glass beaker kept in a ice-cold water bath maintained at constant temperature ($27 \pm 0.1^\circ\text{C}$). Nitrogen gas was purged for chemically inert atmosphere. The readings were recorded for each addition of 0.5 mL. The graph of volume of alkali against pH were plotted. The pH-meter readings were taken only after the gas bubbling completely stopped.

RESULTS AND DISCUSSION

Determination of proton-ligand stability constants

The dissociation constants of substituted diketones (1, 2) were determined at 0.1 M ionic strength pH-metrically. The reagents or ligands used in the present investigation are monobasic acids having only one dissociable H^+ ion from OH group and can therefore be represented as HL.



The titration curves of the acid and the ligand deviate at about pH 1.5 and then increase upto pH 7.5. The deviations between acid curve from ligand for all the systems showed the dissociation of H^+ ions from —OH groups of the ligands.

Proton-ligand formation numbers ($\bar{\eta}_A$) were calculated by the Irving and Rossotti expression.

$$\bar{\eta}_A = \gamma - \frac{(\text{E}^\circ + \text{N}) \Delta V}{(\text{V}_0 + \text{V}_1) \text{T}_L^\circ}$$

where V_0 = Initial volume of solution (50 mL)

N = Normality of sodium hydroxide

T_L° = Concentration of ligand in 50 mL solution

E° = Initial concentration of free acid (HNO_3)

γ = Number of dissociable protons from ligand.

$(\text{V}_2 - \text{V}_1) = \Delta V$ = Volumes of alkali consumed by acid and ligand on the same pH

The pKa values for both systems were calculated by half integral calculation which are presented in Table-1.

TABLE -1
PROTON-LIGAND STABILITY CONSTANTS

System	pK
Ligand-1: 1-(2'-hydroxy-S'-chlorophenyl)-3-(4'-chlorophenyl)-1,3-propanedione;	6.84
Ligand-2: 1-(2'-hydroxy-3-nitro-5-methylphenyl)-3-(4'-chlorophenyl)-1,3-propanedione	6.50

TABLE-2
METAL-LIGAND STABILITY CONSTANTS (log K)

System	Metal-ligand stability constant	
	log K ₁	log K ₂
Ligand-1 Co(II)	8.13	6.75
Ligand-1 Cu(II)	8.81	6.41
Ligand-1 Zn(II)	8.55	6.51
Ligand-2 Co(II)	7.30	5.97
Ligand-2 Cu(II)	6.69	5.59
Ligand-2 Zn(II)	8.07	6.51

Conclusion

It is observed from the titration curves between (acid + ligand) and (acid + ligand + metal) for all the systems that the deviation between the curves is found to be at about pH 1.5. This indicates the commencement of complex formation from this pH. During the titration process, solution colour is changed from light brown to dark brown. This also shows the formation of complex between ligand and metal ion.

It could also be seen from Table-1 that the order of pK values of the ligands is found to be as:

$$\text{pK ligand 1} > \text{pK ligand 2}$$

This may be due to the fact of the presence of nitro ($-\text{NO}_2$) electron withdrawing groups in **2**. The electron withdrawing group reduces the pK values of the ligand.

It is observed from Table-2 that the difference between the values of log K₁ and log K₂ is sufficiently large. This indicates the stepwise complex formation between ligand and metal ions. The values of metal-ligand stability constants (log K₁ and log K₂) are greater of Cu(II) complexes than Co(II) and Zn(II) complexes. It means Cu(II) forms more stable complexes than the complexes of Co(II) and Zn(II) with ligand **1** but less stable in case of ligand **2**.

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