



# The Formation Constants Of Certain Transition Metal Complexes 4-[(E)-{(2E)-[(3E)-3-(Hydroxyimino)Butan-2-Ylidene]Hydrazinylidene}Methyl]Phenol Were Determined In A Mixed Solvent System.

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## ARTICLE INFO

## ABSTRACT

A novel ligand, diacetyl monoximehydrazide-4-hydroxybenzaldehyde (HDM HpHB), was synthesized and reported for the first time in this study. Its acidity constant was determined potentiometrically in a mixed solvent system (dioxane + water) at different ionic strengths. Due to the interest in the ligand's coordinating behavior with various transition metal ions, similar potentiometric studies were conducted to determine the metal-ligand formation constants. The results indicated that the ligand behaves as a monobasic acid, despite having two potentially dissociable protons (the oximino and phenolic protons). The nature of this monobasic character was further examined. Metal complexes with Co(II), Ni(II), Cu(II), and Zn(II) revealed that the most stable species formed was the ML<sub>2</sub> complex.

**Keywords:** Ionic strength, stability constant, diacetylmonoximehydrazide-4-hydroxybenzaldehyde, metal ion complexes, potentiometric titration.

## INTRODUCTION

Oximino ketones and their derivatives have been extensively studied due to their diverse applications in fields such as analytical chemistry [1], bioinorganic systems [2], catalysis [3,4], and medicine [5,6]. This interest is largely attributed to the ambidentate nature of these ligands and the presence of multiple potential donor sites. Consequently, these ligands are known to form metal complexes with a variety of geometries, stabilities, and practical applications.

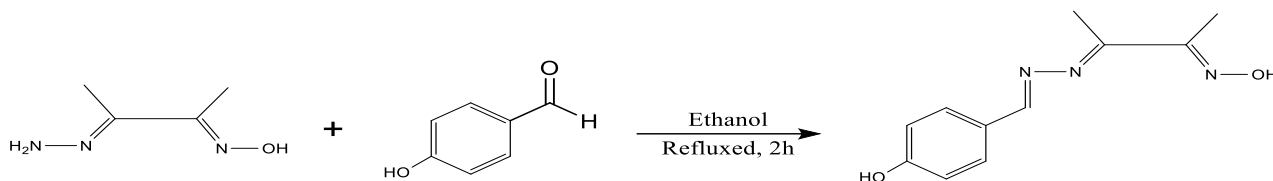
Oxime hydrazones [1-3] exhibit fascinating coordination chemistry due to the presence of multiple donor sites, including protonated or deprotonated oximino oxygen, the imine nitrogen from the hydrazone moiety, and an additional donor site (commonly N or O) provided by the Schiff base [4-5]. The coordination behavior of oxime complexes has been extensively studied from a structural perspective, revealing notable characteristics [6]. These compounds can coordinate with metal ions via nitrogen and oxygen atoms, enabling the formation of proximate-bridged extended networks [7-8]. The hydrogen atom of an oxime-OH group is capable of forming strong hydrogen bonds with other atoms or groups within or between molecules [9, 10]. As a result, metal complexes containing non-deprotonated oximes can establish expansive supramolecular networks through intermolecular hydrogen bonds, making them suitable as supramolecular synthons. The configuration of the oxime group in these molecules significantly influences the dimensionality of the extended network [11].

Additionally, trivalent oxime-hydrazones have been widely studied for their coordination chemistry, driven by their notable biological effects [12-15]. In this context, the current study presents a new ligand, diacetylmonoximehydrazide-4-hydroxybenzaldehyde (HDMHpHB), synthesized through the reaction of the hydrazone of diacetyl monoxime with salicylaldehyde. The research focuses on the formation studies of Co(II), Ni(II), Cu(II), and Zn(II) metal complexes in solution, using a mixed solvent system of dioxane and water (60:40 v/v) at varying ionic strengths. The goal was to understand the nature of the complexation, the stability of the complexes, and the influence of ionic strength on the complexation, leading to the determination of the thermodynamic stability constants for these metal complexes.

## EXPERIMENTAL SECTION

### SYNTHESIS OF LIGAND (HDMHpHB)

As previously reported, diacetylmonoximehydrazide-4-hydroxybenzaldehyde (HDMHpHB) was produced [16].



**Scheme 1: Preparation of HDMHpHB**

The structure of the ligand was verified using NMR, IR, and UV-Vis spectroscopic analyses.

### Reagents and Materials

A stock solution of the ligand (0.05M) was prepared by dissolving the required amount of the ligand in a minimal volume of dioxane and then diluting it to the final volume with dioxane. All chemicals used, including KCl, HCl, and KOH, were of analytical reagent (A.R.) grade. Metal ion solutions (0.01M) were prepared from metal chlorides and standardized volumetrically using a standard EDTA solution. The ionic strength was maintained at 0.05, 0.075, and 0.1 mol dm<sup>-3</sup> by adding a 1M KCl solution. A carbonate-free potassium hydroxide solution (0.1M) was prepared in double-distilled water and standardized against a standard succinic acid solution.

### Apparatus and Procedure

The pH meter (model EQ-610), equipped with a combined glass electrode and magnetic stirrer (accuracy  $\pm 0.01$ ), was used for the measurements. It was calibrated before each titration using buffer solutions of pH 4.00, 7.00, and 9.20, prepared from Qualigens buffer tablets. All pH-metric titrations were conducted at 28°C in an inert atmosphere by introducing oxygen-free nitrogen gas, which also facilitated stirring of the solution. The pH-metric titrations of the following solutions were carried out using a standard 0.1M KOH solution:

- Acid titration: 5cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HCl + 30 ml dioxane + 13 cm<sup>3</sup> distilled water.
- Ligand titration: 5 cm<sup>3</sup> of 0.100 mole dm<sup>-3</sup> HCl + 5cm<sup>3</sup> of 0.05 mol dm<sup>-3</sup> ligand + 25cm<sup>3</sup> dioxane + 13 cm<sup>3</sup> distilled water.
- Metal titration: 5cm<sup>3</sup> of 0.100 mole dm<sup>-3</sup> HCl + 5cm<sup>3</sup> of 0.05 mole dm<sup>-3</sup> ligand + 5cm<sup>3</sup> of 0.010 mole dm<sup>-3</sup> metal salt + 25cm<sup>3</sup> dioxane + 8.05cm<sup>3</sup> distilled water.

To maintain the ionic strength at 0.05, 0.075, and 0.1 mol, the appropriate amount of 1 mol dm<sup>-3</sup> KCl stock solution was added to the system. Each mixture was then brought to a total volume of 50 cm<sup>3</sup> using a 60:40 (V/V) dioxane-water medium. This solution was titrated against a standard alkali (0.104 M), and the titration was stopped when turbidity appeared, as indicated by a consistent drift in the pH meter readings. pH readings were taken at regular intervals once a stable value was obtained, and then pH versus the volume of alkali added was plotted [Fig. No. 1]. The proton-ligand dissociation constant was determined from the pH values using the Irving-Rosotti method.

## RESULTS AND DISCUSSION

**Table No.1: Proton-ligand Dissociation constant**

Sr. No.	Ionic Strength	Proton-ligand constant (LogK)		pK
		By Half integral method	By Graphical method	
1	0.05	10.59	10.59	10.59
2	0.075	10.54	10.56	10.55
3	0.1	10.48	10.50	10.49

**Table No. 2: Metal-Ligand Stability Constants of Metal Complexes**  
 $\mu=0.05$ ,  $pK=10.59$ ,  $\sqrt{0.05}=0.2267$

Sr. No.	Compound	LogK1		LogK2		log $\square = \text{Log}(K_1 + K_2)$
		By Half integral method	By Graphical method	By Half integral method	By Graphical method	
1	Co(II)	10.05	10.09	8.66	8.64	18.73
2	Ni(II)	10.14	10.12	8.73	8.75	18.87
3	Cu(II)	10.39	10.37	9.17	9.17	19.56
4	Zn(II)	10.32	10.34	9.03	9.05	19.37

**[A]  $\mu=0.075$   $pK=10.55$   $\sqrt{0.075}=0.2738$** 

Sr. No.	Compound	LogK <sub>1</sub>		LogK <sub>2</sub>		log $\square$ (K <sub>1</sub> + K <sub>2</sub> )
		By Half integral method	By Graphical method	By Half integral method	By Graphical method	
1	Co(II)	9.80	9.82	8.65	8.67	18.48
2	Ni(II)	9.82	9.84	8.81	8.79	18.64
3	Cu(II)	10.14	10.16	9.05	9.05	19.20
4	Zn(II)	10.02	10.04	8.87	8.89	18.91

**[c]  $\mu=0.1$   $pK=10.49$   $\sqrt{0.1}=0.3162$** 

Sr. No.	Compound	LogK <sub>1</sub>		LogK <sub>2</sub>		log $\square$ $\square = \text{Log}(K_1 + K_2)$
		By Half integral method	By Graphical method	By Half integral method	By Graphical method	
1	Co(II)	9.55	9.57	8.66	8.66	18.23
2	Ni(II)	9.75	9.75	8.72	8.70	18.35
3	Cu(II)	9.94	9.92	8.99	8.99	18.93
4	Zn(II)	9.66	9.68	8.80	8.82	18.49

**Table 7: Ionic strength and Metal stability constant**

Ionic Strength $\mu$	$\sqrt{\mu}$	Co Log $\beta$	Ni Log $\beta$	Cu Log $\beta$	Zn Log $\beta$
0.05	0.227	18.60	18.78	19.42	19.21
0.075	0.2738	18.41	18.58	19.14	18.89
0.1	0.3162	18.28	18.41	18.92	18.61

**FORMATION OF COMPLEXES IN SOLUTION**

The ligand appears colorless in a 60:40% (V/V) dioxane-water mixture. During the acid-ligand titration with 0.1 M KOH, a light-yellow color emerges at a low pH. As the titration progresses, the yellow color deepens around pH ~8.80, attributed to the dissociation of the proton from the oxime –OH group. Similarly, during metal ion titrations, varying colors are observed depending on the metal ions: cobalt yields a reddish color, nickel a brown color, copper a green color, and zinc a yellow color at different pH levels. These color changes suggest the formation of complexes.

**The proton-ligand dissociation constant**

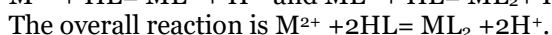
The ligand examined in this study can be regarded as a monobasic acid, containing a single dissociable proton from the oxime (-NOH) group. This characterization is supported by PMR, IR, and electronic spectral data, and the ligand is therefore represented as HL. The dissociation equilibrium can be expressed as follows.

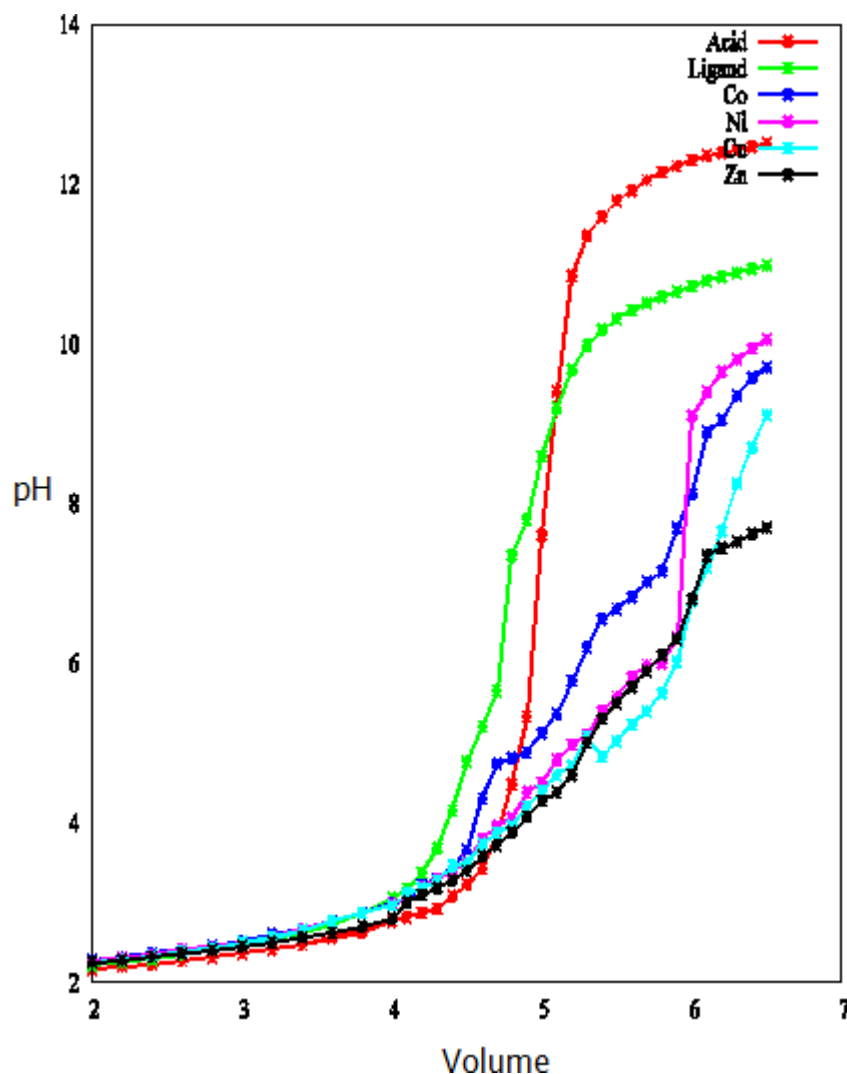


The proton-ligand formation number  $n_{An\_AnA}$  was determined using the Irving-Rossetti equation. The  $pK_a$  value of the ligand was calculated using both the half-integral method and graphical method, as reported in Table No. 2. It is evident that the  $pK_a$  values decrease with increasing ionic strength of the medium, consistent with Debye-Hückel theory.  $|A|$  value of less than 1.5 suggests that the ligand possesses only one dissociable  $H^+$  ion from the oxime group.

**Metal-ligand stability constant [Table No. 2]**

The titration curves for the metal-ligand solution demonstrate that the  $|A|$  values vary from 0 to 2. This suggests that there are at least two formation constants for the metal-ligand complex, indicating a two-step reaction process.





**Figure:1 Proton and metal-ligand titration curves**

1) The first step results in a  $\log K_1$  value, while the second step provides a  $\log K_2$  value for the stability of the metal-ligand bond. The curves also indicate that the metal-ligand titration curves consistently lie below the proton-ligand titration curves [Fig.No.1], suggesting that the metal-ligand complexes are more stable than the proton-ligand complexes.

2) The formation curves for the metal complexes were generated by plotting the average number of ligands attached per metal ion ( $\bar{n}$ ) against the free ligand exponent ( $\bar{n}_L$ ) according to the Irving and Rossotti method [14]. The  $\log K_1$  and  $\log K_2$  values were calculated at  $\bar{n}=0.5$  and  $\bar{n}=1.5$ , respectively, across different ionic strengths [Fig.No.2]. Higher  $\log K_1$  and  $\log K_2$  values indicate that the ligands function as strong chelating agents, and vice versa.  $\log K_1$  and  $\log K_2$  were also determined using a point-wise method:

3)  $\log (\bar{n} / (1-\bar{n}))$  vs.  $\bar{n}_L$

4)  $\log ((2-\bar{n}) / (\bar{n}-1))$  vs.  $\bar{n}_L$  [Fig.No.3].

5) The  $\log K_1$  and  $\log K_2$  values are presented in Table 2. From the data, the following observations were made:

6) The maximum value of  $\bar{n}$  was approximately two, indicating that only  $ML_2$  (metal: ligand) complexes are formed.

7) The stability constants of the metal complexes concerning the Schiff bases were found in the order: of  $Co(II) < Ni(II) < Cu(II) > Zn(II)$ , which aligns with the order proposed by Irving and Williams [18].

8) The stability constant decreases with increasing ionic strength, consistent with the Debye-Hückel theory.

9) The difference between  $\log K_1$  and  $\log K_2$  complexes is less than 2.5, indicating the simultaneous formation of both 1:1 and 1:2 complexes.

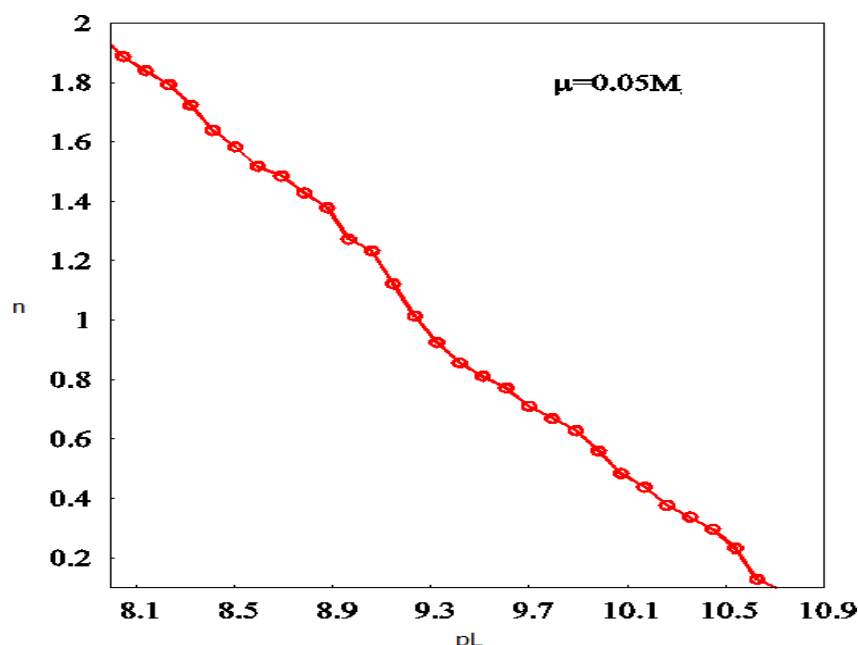


Figure:2 Formation of Cobalt complex

Calvin and Wilson [16] demonstrated that resonance can influence both the formation and stability of chelates. They examined the formation of  $\text{Cu}^{2+}$  complexes with acetylacetone, various  $\beta$ -diketones, substituted salicylaldehydes, as well as 2-hydroxy-1-naphthaldehyde and 3-hydroxy-2-naphthaldehyde. All of these compounds formed similar stable chelated rings, thus supporting their findings. Mellor et al. [17] investigated the stability of salicylaldehyde complexes in a 50:50 v/v dioxane-water mixture and found that the stability of the chelates followed the order:  $\text{Pd} > \text{Cu} > \text{Ni} > \text{Co} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Mg}$ .

Irving et al. [14] correlated their findings by plotting stability constants against the atomic numbers of the metals, observing the stability constant order to be  $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni} < \text{Cu} < \text{Zn}$ .

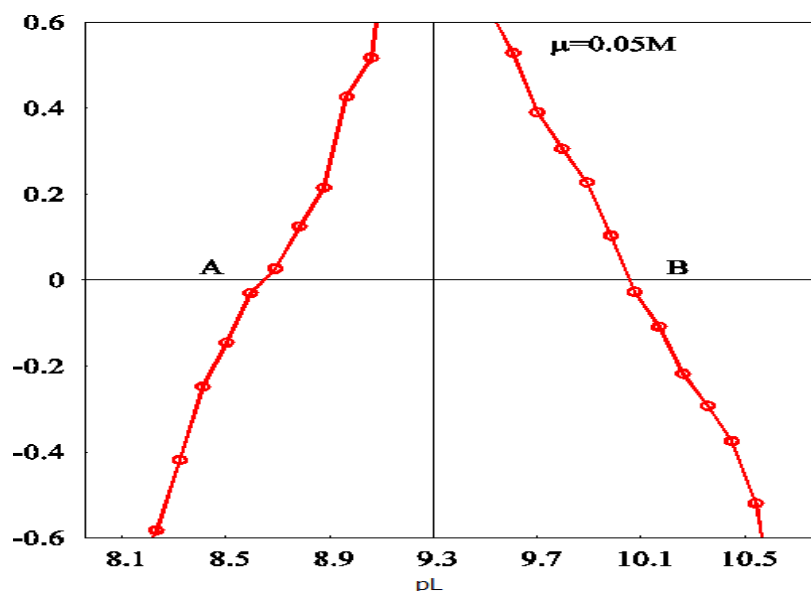


Figure:3 Graphical representation:  
A represents  $\log(n/(1-n))$  versus pL  
B represents  $\log(2-n/(n-1))$  versus pL

### CONCLUSION

The HDHMPH ligand is insoluble in water yet soluble in dilute alkali, indicating its acidic nature and solubility in common organic solvents. The dissociation constant of the ligand is approximately  $\text{pK} \sim 10.5$ . The stability and dissociation constants decrease as the ionic strength increases. In terms of metal ion stability constants, the order is  $\text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$ , which aligns with the natural order proposed by Irving and Williams.

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