



**MIXED LIGAND COMPLEXES OF BIVALENT METAL IONS WITH 2-HYDROXY METHYL PYRIDINE  
IN PRESENCE OF KOJIC ACID, MALTOL, ACETYL ACETONE  
AND TRIFLUORO ACETYL ACETONE - pH METRY**

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**ABSTRACT**

Stability constants associated with mixed ligand complexes of bivalent metal ions with 2-hydroxy methyl pyridine in presence of other O-O donors (viz., maltol, kojic acid, acetylacetone and trifluoroacetylacetone) was evaluated potentiometrically at  $T=30^{\circ}\text{C}$  and  $I=0.1\text{ M KNO}_3$  in aqueous medium. Stability trend is discussed in terms of nature of donor atoms and substituent groups present on ligands. Distributions of various species as a function of pH are also drawn using BEST Computer program.

**Keywords:** Hydroxy methyl pyridine, Ligand, Metal Ions

**1. INTRODUCTION**

Hydroxy methyl pyridine (HMP) are valuable intermediates and have promising application, for example, in the synthesis of pharmaceuticals and agrochemicals, such as mefloquine hydrochloride and pirofenone [1] carbonyl derivatives of transition metals, on the other hand, are useful intermediates in the synthesis of important coordination compounds [2-5] and have applications in catalysis of important reactions such as epoxidation, carbonylation, hydrogenation and hydroformylation reactions [6-9]. For example, the complex  $[\text{Rh}(\text{CO})_2\text{Cl}(\text{HMP})]$  was synthesized and characterized. It showed higher efficiency as catalyst for carbonylation of methanol to yield acetic acid and methyl acetate. It proved to be much better than the industrially used species  $[\text{Rh}(\text{CO})_2\text{I}_2]$  [10].

In view of its catalytic activity, the present potentiometric work is undertaken to explore its binding tendency with different metal ions. The 2-hydroxy methyl pyridine (HMP) was allowed to react with different metal ions in presence of other ligands viz., maltol (MA), kojic acid (KA), acetyl acetone (AA) and trifluoro acetyl acetone (TFAA). The stabilities of the thus formed ternary complexes are evaluated and compared to check the factors by which they are governed.

**2. EXPERIMENTAL**

**2.1. Reagents**

The ligands, maltol, kojic acid, acetyl acetone were obtained from Fluka (Switzerland). Trifluoroacetylacetone and 2-hydroxymethyl pyridine obtained from Sigma-Aldrich. The metal salts of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are of AnalaR grade and their solution are standardized volumetrically by titration with the sodium salt of EDTA [11].

**2.2. Apparatus and Instruments**

Potentiometric measurements are carried out at  $30^{\circ}\text{C}$  in aqueous medium (with  $0.1\text{ mol dm}^{-3}$  ( $\text{KNO}_3$ ) as background electrolyte) using Control dynamics pH meter. The pH meter readings are plotted against "a" (moles of base added per mole of ligand) or "m" (moles of base added per mole of metal ion). Calculations are carried out with the help of computer program - BEST [12].

**3. RESULTS AND DISCUSSION**

**3.1. Acid Dissociation Constants**

(a) 2-Hydroxy methyl pyridine: the free ligand titration curve ( $\text{H}_2\text{L}^+$ ) of this ligand show inflection at  $a=1$ , followed by a buffer region in higher pH. The  $\text{pK}_a$  and  $\text{pK}_{2a}$  are calculated in the region  $a=0$  to  $a=1$  and  $a=1$  to  $a=2$  respectively.

(b) Maltol/Kojic acid/acetyl acetone/trifluoroacetylacetone: Free ligand titration curves of all these ligands show a single inflection at  $a=1$ . The constants calculated in the buffer region  $a=0$  to  $a=1$  are presented in Table 1. The values are good agreement with values found in literature (13). The free ligand titration curves of MA, KA and AA, TFAA (trifluoro acetyl acetone) and 2-hydroxy methyl pyridine are given in Fig.1 along with other curves.

**3.2. Binary Complexes**

(a)  $\text{M}^{2+}$ -2-Hydroxy methyl pyridine:

Potentiometric titration curves of  $\text{M}^{2+}$ -2-hydroxymethyl pyridine (diprotonated) in 1:1 ratio shows a feeble inflection at  $m=1$  followed by a buffer region. The separation of (M-L) curve from the free ligand curve is small for all metals, suggesting complex formation with low stability constants. The protonated constants are calculated in the buffer

region of  $m=0$  to  $m=1$ . The stability constants obtained and presented in Table I.

(b)  $M^{2+}$ -Maltol/Kojic acid/acetyl acetone/trifluoro acetyl acetone: Potentiometric titration curves of  $M^{2+}$ -Maltol/Kojic acid/acetyl acetone/trifluoroacetyl acetone in 1:1 ratio show a

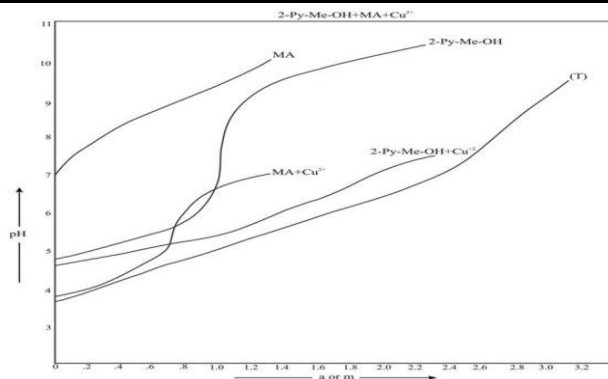
single inflection at  $m = 1$ . The stability constants calculated in the buffer region  $m=0$  to  $m=1$  are presented in Table-1. The values have good matching with literature values.

**Table 1: Logarithms of the stability constants of different systems at T: 30°;  $\mu= 0.1$  M ( $KNO_3$ ), aqueous medium.**

Ligands	pKa	pK <sub>2a</sub>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	
Maltol	8.48± 0.02	-	5.33± 0.01	5.48± 0.02	7.15± 0.02	5.59± 0.08	
Kojic acid	7.89± 0.03	-	4.83± 0.01	5.01± 0.09	6.67± 0.01	5.08± 0.01	
Acetyl acetone	8.95± 0.03	-	5.24± 0.01	5.67± 0.01	7.43± 0.09	4.86± 0.01	
Trifluoro acetyl Acetone	6.53± 0.03	-	3.60± 0.02	3.73± 0.02	4.93± 0.01	2.86± 0.04	
2-Hydroxy Methyl pyridine (HMP)	5.29± 0.02	9.74± 0.02	2.71± 0.01	2.92± 0.04	3.17± 0.03	2.35± 0.03	(Protonated complex)
	-	-	2.81± 0.02	2.40± 0.08	6.88± 0.01	4.25± 0.02	(Normal complex)

### 3.3. Ternary Complexes

$M^{2+}$ -Maltol / Kojic acid/acetylacetone / trifluoroacetylacetone: The potentiometric titration curves of the ternary complexes in 1:1:1 ratio show an inflection at  $m = 3$  indicating the simultaneous coordination. The constants are calculated in the buffer region  $m=1$  to  $m=3$ , using the pK<sub>a</sub> and pK<sub>2a</sub> of 2-hydroxy methyl pyridine and pKa of KA (or) MA (or) AA (or) TFAA. The values then obtained are presented in Table 2. A representative curve for (Cu+2-hydroxy methyl/pyridine+MA) is shown in Fig. 1.



**Fig.1: Potentiometric titration Curves of Ternary Complex [HMP-Cu<sup>2+</sup>-MA]**

**Table 2: Logarithms of the stability constants of ternary complexes of bivalent metal ion at T: 30°;  $\mu= 0.1$  M ( $KNO_3$ ), aqueous medium**

Ligand combinations	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
HMP + Maltol	8.57± 0.05	8.51± 0.05	14.78± 0.06	10.52± 0.05
HMP + Kojic acid	7.97± 0.07	7.92± 0.07	14.23± 0.05	9.91± 0.06
HMP + Acetyl acetone	8.36± 0.09	8.49± 0.08	14.82± 0.05	9.45± 0.05
HMP + Trifluoro acetyl acetone	6.42± 0.01	6.18± 0.01	11.92± 0.12	7.20± 0.05

### 3.4. The Concept of $\Delta \log K$

The relative stability of the ternary metal complexes (MLA) as compared to that of the corresponding binary complexes have been quantitatively expressed in terms of the parameter  $\Delta \log K$ , given by the Eq. 1.

$$\Delta \log K = [\log K_{MLA} - (\log K_{MLA} + \log K_{MLA})]L1$$

In case of 2-hydroxymethyl pyridine (HMP) complexes, 2-HMP binds to the metal through oxygen and nitrogen. The statistically expected  $\Delta \log K$  value for the Interaction of two different bidentate ligands with square planar (or) distorted octahedral metal ion are -0.6 or 0.9 respectively.

The  $\Delta \log K$  values for ternary complexes containing maltol, kojic acid or acetylacetone and trifluoroacetylacetone are more positive (Table 3) than values expected on the

statistical grounds, reflecting the extensive stabilization of these complexes. This stabilization may be due to (a) nature of donor atoms; O-O donors form better complexes with N-O donors, (b) formation of a neutral complex: the resultant ternary complex is neutral, (c)  $\pi$ - $\pi$  interactions: The ligand HMP and MA, KA, AA or TFAA are capable of forming  $\pi$  - interactions, (d) the lowest stability of trifluoro acetylacetone is attributed to the electron withdrawing groups present on the ligand, which lowers the basicity and stability of metal complexes as is expected.

The sequence of stability of ternary complexes with respect to their ligands decrease in the order: maltol > kojic acid > acetyl acetone > trifluoro acetyl acetone. The tentative structure of ternary complex is shown in Fig.2.



Fig.2: Tentative structure of ternary complex having HMP,  $M^{2+}$  and MA

Table 3:  $\Delta \log K$  values of ternary complexes of bivalent metal ions

Ligand combinations	$Co^{2+}$	$Ni^{2+}$	$Cu^{2+}$	$Zn^{2+}$
HMP + Maltol	+0.43	+0.63	+0.75	+0.68
HMP + Kojic acid	+0.33	+0.51	+0.68	+0.58
HMP + Acetyl acetone	+0.31	+0.42	+0.51	+0.34
HMP + Trifluoro acetyl acetone	+0.01	+0.05	+0.11	+0.09

### 3.5. Distribution Diagrams

From the knowledge of proton-ligand and metal-ligand formation constants, the distribution of the total metal among the various metal-ligand species as a function of pH has been calculated by a computer program BEST [13-18]. As a representative case, the distribution diagram for (2-hydroxy methyl pyridine + Cu + MA) system is given in Fig.3.

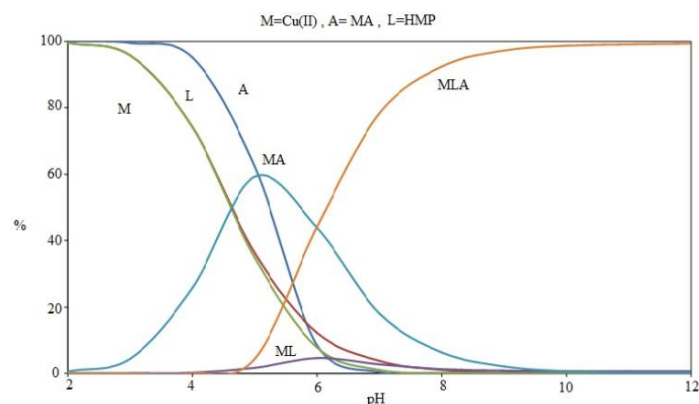


Fig.3: BEST (SPE) computed distribution of complex species with pH for [HMP- $Cu^{2+}$ -MA] complex

The maximum percentage of the Cu-MA (or) ML is 16.2 at pH=5. As the pH increase the percentage of ML reaches minimum. The other binary species (Cu-2-HMP) has attained maximum percentage of 72.5 at pH 5.6. After pH 4 the formation of ternary complex has started (appearance of curve MLA) and percentage goes on increasing with increase in pH with simultaneous decrease in percentage of both binary species (i.e., MA and ML). The ternary species is the only predominant species in higher pH.

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The stability constants of ternary complexes of bivalent metal ions is in the order  $Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$ . This order is comparing with Irving-William's natural order of stabilities.

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