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Mixed Ligand Chelates of Transition Metal Ions with [(1-Phenyl-3-methyl-5-oxodihydropyrazol-4-yl)phenylimino]-2′,3′-dimethylaniline as a Primary Ligand and 2-Hydroxy-1-naphthaldehyde as a Secondary Ligand

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Binary and ternary complexes of the type M-Y and M-X-Y [M = Cu(II), Zn(II), Mn(II), Ni(II), Co(II), X = [1-Phenyl-3-methyl-5-hydroxopyrazol-4-yl)phenylimino]-2',3'-dimethyl-aniline, Y = 2-hydroxy-1-naphthaldehyde have been examined pH metrically at 29 ºC and μ = 0.1 M (KCl) in a (75:25) % (v/v) dioxane-water medium. The values of formation constants for M-Y and M-X-Y systems [M = Cu(II), Zn(II), Ni(II), Co(II), Mn(II)] are calculated.

Key Words: Ternary complexes, Mixed ligand, Stability constant.

INTRODUCTION

Metal complexes of Schiff bases have occupied a central role in the development of coordination chemistry[1]. Many attempts have been made to evaluate different factors affecting the stability of metal chelates along with their stability constants[2-4].

In present studies, the results of the studies on mixed ligand complexes of Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} with [1-phenyl-3-methyl-5-oxodihydro-pyrazol-4-yl)phenylimino]-2',3'-dimethylaniline (HPMPZP)dma-the Schiff base as the primary ligand and 2-hydroxy-1-naphthaldehyde (HNA) as a secondary ligand in (75:25 %) v/v dioxane-water medium are reported by employing modified pH-metric titration technique[5-7]. Under identical conditions the formation of binary metal complexes of HNA have also been investigated.

EXPERIMENTAL

The pH titrations were carried out by pH meter model No. EQ-614 supplied by equiptronics, a precesion research pH meter with a wide range of glass electrode and calomel reference electrode. The pH meter was stan-

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dardized with potassium hydrogen phthalate and phosphate buffers before perfomring the titrations.

Synthesis of Schiff base: 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone was synthesized by reported method. It was recrystallized from ethanol. The pure crystals of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and 2,3-dimethylaniline were taken in round bottom flask in 1:1 stoichiometric proportion. The resulting mixture was refluxed in presence of 2 mL conc. HCl for 4-5 h. The reaction was monitored by TLC. The reaction mixture was concentrated for partial removal of solvent, the crystals of Schiff base *i.e.*, (HPMPZP)dma separated out which were filtered under suction.

The solutions of ligands were prepared in dioxane. All the metal ion solutions were prepared in distilled water and standardized by using conventional procedures[7]. A solution of KOH (0.2 M) was prepared in double distilled water and standardized with standard solution of succinic acid.

The titrations were carried out in an inert atmosphere of nitrogen. All the measurements were carried out at temperature 29 ± 0.5 ºC. The method of Bjerrum and Calvin as modified by Irving and Rossotti[5,6] was used to determine ñ and pL values. All the solvents and chemicals used were of analytical grade.

pH metric titrations: For the determination of proton ligand stability constant of the secondary ligand and metal ligand stability constants of binary and ternary complexes, the following sets of solutions were prepared keeping the total volume V_o = 40 mL. All titrations were carried out at the ionic strength of 0.1 M (KCl) in (75:25) % v/v dioxane-water medium against standard 0.2 M KOH solution.

Binary system: (i) 4 mL HCl (0.16 M) + 3.36 mL KCl (1 M) + 2.64 mL distilled water + 30 mL 1,4-dioxane (ii) 4 mL HCl (0.16 M) + 3.36 mL KCl (1 M) + 2.64 mL distilled water + 4 mL secondary ligand HNA (0.04 M) + 26 mL 1,4-dioxane (iii) 4 mL HCl (0.16 M) + 3.24 mL KCl (1 M) + requisite volume of metal chloride solution (to maintain the concentration in total volume as equal to 0.001 M) + requisite volume of distilled water + 4 mL secondary ligand HNA (0.04 M) + 26 mL 1,4-dioxane.

Ternary system: (i) 4 mL HCl (0.16 M) + 3.24 mL KCl (1 M) + requisite volume of metal chloride solution (to maintain the concentration in total volume as equal to 0.001 M) + requisite volume of distilled water + 4 mL of secondary ligand HNA + 22 mL of dioxane.

The ratio of metal (M):secondary ligand (Y) was maintained at (1:4) in the binary system. In ternary system the ratio of metal (M):primary ligand (X):secondary ligand (Y) was maintained at 1:1:1.

RESULTS AND DISCUSSION

Proton-ligand stability constant: The plots of volume of alkali (KOH) against pH-meter readings were used to evaluate the proton ligand stability constants of secondary ligand. The deviation between free acid titration curve and secondary ligand titration curve was used to evaluate the formation constant $\tilde{n}_A$. The proton ligand formation curve was then obtained by plotting the values of $\tilde{n}_A$ *vs.* pH-meter readings. From the graphs, the value of log K_1^H and log K_2^H were evaluated by half integral method (A) and in a similar way log K_1^H and log K_2^H were evaluated using graphical method (B) by plotting the graph log $\tilde{n}_A/1\text{-}\tilde{n}_A$ against pH and log 2-ñ/1-ñ against pH, respectively.

The metal-ligand stability constants of binary complexes were evaluated assuming the polynuclear complexes and hydrolyzed product formation does not take place. The examination of titration curves indicates that complex formation takes place in solution on the following grounds: (i) the metal titration curves showed displacement with respect to ligand titration along the volume axis. This indicates the affinity of ligand to metal ions which release protons and produce volume different V‴-V″; (ii) the colour change of ligand in presence of metal ion appeared showing the formation of new species, due to co-ordination; (iii) the hydrolysis of the metal ions was suppressed due to the complex formation and precipitation did not appear during the titrations.

From the ligand and metal titration curves the values of ñ and subsequently the values of pL were evaluated. The formation curves obtained were used to evaluate metal-ligand stability constants by method A and B. The results are presented as follows:

TABLE-1
PROTON LIGAND STABILITY CONSTANTS

Ligand	$\log K_1^H$	
	Method A	Method B
HNA	8.4	8.5

The variation of ñ was found to be between 0-2 for the binary complexes of the above mentioned metals, which indicates that the composition of complexes was 1:2 in solution. Table-2 shows the metal-ligand stability constants and the log β values of the binary complexes. The log K_1 values for the binary complexes of metals are in the following order;

Mn(II) > Cu(II) > Co(II) > Ni(II) > Zn(II)

TABLE-2
METAL LIGAND STABILITY CONSTANTS FOR BINARY SYSTEMS

Metal complexes	log K_1		log K_2		log β	
	Method A	Method B	Method A	Method B	Method A	Method B
[Mn-HNA]	5.8	5.7	3.6	3.4	9.4	9.1
[Co-HNA]	5.5	5.5	3.5	3.4	9.0	8.9
[Ni-HNA]	4.4	4.5	3.3	3.3	7.7	7.8
[Cu-HNA]	5.6	5.5	4.1	4.1	9.7	9.6
[Zn-HNA]	4.3	4.3	3.1	3.2	7.4	7.5

Metal-ligand stability constants of ternary complexes: The metal-ligand stability constants of ternary complexes were evaluated assuming that the formation of polynuclear complexes and hydroxy products does not take place. An examination of the titration curves indicated that the ternary complexes formation has taken place in solution on the following grounds: (i) the ternary complexes titration curves show displacement with primary complexes titration curves. The horizantal distance was measured between ternary curves and secondary ligand curve. The positive difference shows the earlier release of protons in the formation of ternary complex; (ii) the hydrolysis of metal ions was suppressed and precipitation did not result. The values of ñ varies from 0-1, thus confirming the formation of 1:1:1 mixed ligand complexes. The values of $\log^{Pri}_{MXY}$ have been evaluated from the formation curves (ñ *vs.* pL) [method A] as shown in Fig. 1a-1e at ñ = 0.5, in the formation curve pL = log K. The log K values were also evaluated by graphical method (B) as shown in Fig. 2a-2e.

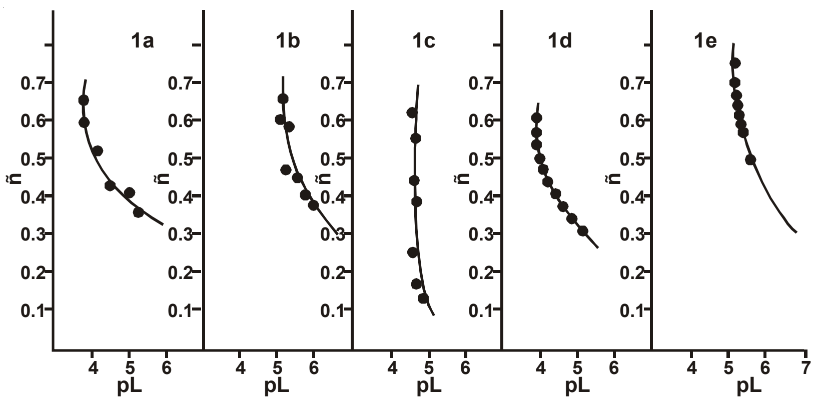

Fig. 1a-e. Ternary system (HPMPZP)dma-M-HNA
where M = Ni, Cu, Co, Zn, Mn

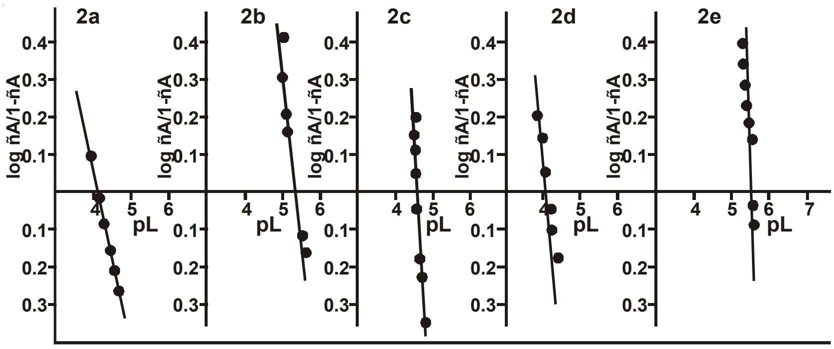

Fig. 2a-e. Ternary system (HPMPZP)dma-M-HNA
where M = Ni, Cu, Co, Zn, Mn

The metal ligand stability constants of ternary complexes are shown as follows:

TABLE-3
METAL-LIGAND STABILITY CONSTANTS OF TERNARY COMPLEXES

Ternary system	log K	
	Method A	Method B
Mn(II)-(HPMPZP)dma-HNA	5.5	5.50
Co(II)-(HPMPZP)dma-HNA	4.5	4.55
Ni(II)-(HPMPZP)dma-HNA	4.0	4.10
Cu(II)-(HPMPZP)dma-HNA	5.3	5.30
Zn(II)-(HPMPZP)dma-HNA	3.9	3.90

The values for metal-ligand stability constants $\log^{Pri}_{MXY}$ are found to be lower than their corresponding binary complexes. This is because, in the formation of ternary complexes lesser no of sites are available for incoming ligands groups as compared to binary complexes.

It is also observed that 1:1 complex is formed at low pH for M-X and stable upto higher pH. The mixed ligand complex formation takes place only after complete formation of binary complex with primary ligand. The formation curves of ternary complex coincides with the binary curves upto pH 5.8-6.0, after this the ternary curves of all above mentioned metals deviate which again confirms that there is first the formation of primary complex MX and above pH 6 the secondary ligand introduces itself and combines to form mixed ligand complex.

The relative stability of ternary complexes with corresponding binary complexes can expressed in many different ways. In this discussion, relative stabilities are shown in terms of $\Delta \log K_T$.

The Δ log K_T values for all the metals in the present system are negative indicating that the secondary ligands bind better to M(II) ions than to combine with the metal ion already bound with ligand X. [Δ log K_T = $\log K^{MX}_{MXY} - \log K^{M}_{MY}$].

The log K values for the ternary complexes are in the following order:

Mn(II) > Cu(II) > Co(II) > Ni(II) > Zn(II)

TABLE-4
Δ log K_T VALUES OF DIFFERENT METAL IONS FOR MY AND MXY SYSTEM

Metal ion	Δ log K	
	Method A	Method B
Ni(II)	-0.40	-0.40
Zn(II)	-0.40	-0.40
Mn(II)	-0.30	-0.20
Co(II)	-1.00	-0.95
Cu(II)	-0.30	-0.20

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