

Study of Transition Metal-Ligand Stability Constant with Some Substituted Pyrazolines-pH Metrically

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Complex formation between Cu(II), Co(II) and Ni(II) metal ions with 1-thiocarboxamido-3-(2-hydroxy-5-chlorophenyl)-4-bromo-5-(4-methoxy phenyl)pyrazoline (L_1), 1-thiocarboxamido-3-(2-hydroxy-5-chloro-phenyl)-4-bromo-5-phenyl pyrazoline (L_2) and 1-thiocarboxamido-3-(2-hydroxy-3-bromo-5-chloro-phenyl)-4-bromo-5-phenyl pyrazoline (L_3) have been investigated by employing Bjerrum-Calvin pH metric techniques at 27 °C in 70 % dioxane-water medium. The data obtained can be used for the determination of proton-ligand formation numbers (\bar{n}_A). From the formation curve, proton-ligand stability constant pK values have been evaluated using half integral method. The metal-ligand formation numbers (\bar{n}) are estimated by using Irving-Rossotti's expression. Metal-ligand stability constants for 1:1 and 1:2 complexes have been calculated which are designated by letters log K_1 and log K_2 , respectively.

Key Words: Substituted pyrazolines, Metal-ligand stability constant.

INTRODUCTION

The importance of pyrazoline lies in the fact that they can be effectively used as bactericidal¹, antiimplantation², insecticidal³, fungicidal⁴, herbicidal⁵ and pharmaceutical agents⁶. These are widely applicable in photography due to their excellent sensitivity.

In view of the analytical application of pyrazolines and confirmation of dissociable hydroxy group (-OH), it is necessary to know the physico-chemical properties such as proton-ligand and metal-ligand stability constant.

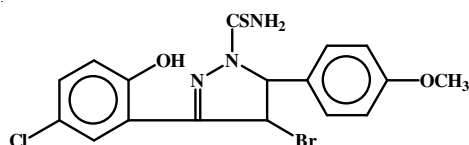
3-(2-Hydroxy phenyl)-5-(4-x-phenyl)pyrazolines with copper(II) and cobalt(II) have been synthesized and characterized by Natarajan *et al.*⁷. Kadu and Jamode⁸ have reported the stability constants of pyrazolines and pyrazoles pH-metrically.

EXPERIMENTAL

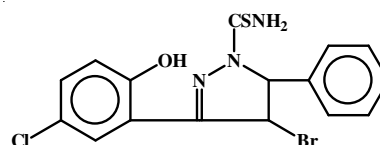
Carbon dioxide free conductivity water having pH about 6.94 was used in the present investigation. 0.1 solution of sodium hydroxide free from carbonate was prepared and standardized by titrating with standard oxalic acid solution. Desired amount of potassium nitrate was dissolved in conductivity water so as to prepare stock solution of 1 M.

Nitric acid (AR) was used for the preparation of 0.1 M HNO_3 and used as free acid solution. AR grade metal nitrates were used for preparing corresponding metal ion solutions and their concentrations estimated by standard procedure. The ligand solutions of 0.01 M were prepared in 70 % dioxane-water medium.

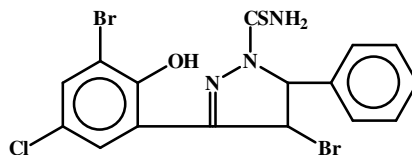
The following ligands were used for the study.



1-Thiocarboxamido-3-(2-hydroxy-5-chlorophenyl)-4-bromo-5-(4-methoxyphenyl)pyrazoline (L_1)



1-Thiocarboxamido-3-(2-hydroxy-5-chlorophenyl)-4-bromo-5-phenylpyrazoline (L_2)



1-Thiocarboxamido-3-(2-hydroxy-3-bromo-5-chlorophenyl)-4-bromo-5-phenylpyrazoline (L_3)

pH meter (accuracy ± 0.01 unit) along with saturated calomel electrode and glass electrode calibrated with buffer solution of pH 4, 7 and 9.2 at 27 °C was used for the pH measurements.

The titration were carried out in 100 mL pyrex glass beaker kept in water bath maintained at constant temperature (27 ± 0.1 °C), nitrogen was purged for chemically inert atmosphere. The pH meter readings were taken for each addition of 0.2 mL.

The experimental procedure involved the following titrations:

Free acid titration: A solution containing nitric acid (1.0×10^{-2} M) in 70 % dioxane-water mixture was titrated with standard NaOH solution (0.1 M).

Free acid-ligand titration: A solution containing nitric acid and ligand (20×10^{-4} M) in 70 % dioxane-water mixture was titrated against standard 0.1 M NaOH solution.

Free acid-metal-ligand titration: A solution containing nitric acid, ligand and metal ion (4×10^{-4} M) in 70 % dioxane-water mixture was titrated against 0.1 M NaOH solution. Data obtained from the titrations was used to plot a graph between volume of NaOH and pH values.

Following systems were studied: pK values of L_1 and L_2 in 70 % dioxane-water mixture at 27 °C; Log k values of Co(II), Cu (II) and Ni(II) with ligands L_1 , L_2 and L_3 were investigated.

RESULTS AND DISCUSSION

Proton-ligand dissociation constant (pK): The plot between volume of NaOH versus pH showed the (acid + ligand) curves and acid curves. The algebraic method has been used to determine the dissociation constants of ligands at 0.1 M ionic strength pH-metrically.

The deviation of (acid + ligand) curves from acid curves started at about 2.35 pH. It remains constant up to pH 5.8 and it increased continuously up to pH 12. This indicated the dissociation of -OH group, which is present in the ligand part of complex structure.

Proton-ligand formation numbers $\bar{\eta}_A$ were calculated from acid titration curve (A) and (A + L) by standard methods. It was found that values of $\bar{\eta}_A$ decreased with increasing pH of solution due to replacement of H⁺ ions from OH⁻ group.

Formation curves were constructed between $\bar{\eta}_A$ and pH. The proton-ligand stability constants pK, were calculated from half integral methods which are presented in Table-1.

TABLE-1
PROTON-LIGAND STABILITY CONSTANTS OF THE LIGANDS

Series	System	pK
1.	1-Thiocarboxamido-3-(2-hydroxy-5-chlorophenyl)-4-bromo-5-(4-methoxy phenyl)pyrazoline (L ₁)	6.8
2.	1-Thiocarboxamido-3-(2-hydroxy-5-chloro-phenyl)-4-bromo-5-phenyl pyrazoline (L ₂)	9.0
3.	1-Thiocarboxamido-3-(2-hydroxy-3-bromo-5-chloro-phenyl)-4-bromo-5-phenyl pyrazoline (L ₃)	7.6

From the formation curve, it appears that dissociation of these ligands occurred at higher pH. All the ligands showed their dissociation in the pH range 6-9. The pK value of L₁ is found to be less (*i.e.* 6.8) as compared to other values, this may be due to the presence of -OCH₃ electron withdrawing group in this structure. The proton-ligand stability constant of ligand L₃ is also less than the proton-ligand stability constant of ligand L₂ this is because of bromo electron withdrawing group nearer to -OH, that effects to dissociation of -OH group at low pH. Hence there is reduction in pK value of ligand L₃.

The deviation of (A + L + M) curve from (A + L) started at about pH 2.5. It indicated the commencement of complex formation. The metal-ligand formation numbers ($\bar{\eta}$) were calculated by standard methods, which increased with increasing pH.

The formation curves were plotted between $\bar{\eta}$ and pH. The metal-ligand stability constants were determined by half-integral method at $\bar{\eta} = 0.5$ and 1.5 showing 1:1 and 1:2 formation of complex. The metal-ligand stability constant values are given in Table-2.

TABLE-2
METAL-LIGAND STABILITY CONSTANTS

S. n.	System	Stability Constant		Difference in stability constant $\log K_1 - \log K_2$
1	Cu(II)-L ₁ complex	8.9444	7.1538	1.7906
2	Co(II)-L ₁ complex	8.0906	5.33	2.7606
3	Ni(II)-L ₁ complex	8.2445	5.7538	2.4907
4	Cu(II)-L ₂ complex	6.1445	3.8538	2.2907
5	Co(II)-L ₂ complex	6.7740	4.0538	2.6904
6	Ni(II)-L ₂ complex	5.9444	2.6532	3.2912
7	Cu(II)-L ₃ complex	7.0447	4.4538	2.5909
8	Co(II)-L ₃ complex	6.7447	5.2538	1.4909
9	Ni(II)-L ₃ complex	6.3447	4.0538	2.2909

It was observed from Table-2 that $\log K_1$ values are greater than $\log K_2$ values for all metal complexes. Cu(II)-L₁ complex and Co(II)-L₃ complex occurred simultaneously because there is no appreciable difference between $\log K_1$ and $\log K_2$ values. Rest of complexes occurred stepwisely due to sufficient difference between $\log K_1$ and $\log K_2$ values. The stability constant values of Co(II)-L₃ complex is found to be less, this may be due to presence of chloride and bromide electron withdrawing group in the structure of ligand.

Cu(II) with L₁ gives complex simultaneously due to the presence of -OCH₃ group which is electron withdrawing. Where as Cu with L₂ and L₃ formed complex stepwisely. Co(II) with L₂ and L₃ give complex stepwisely where as Co(II) with L₃ gives simultaneously due to the presence of electron withdrawing group, while all the ligands L₁, L₂ and L₃ form stepwise complexation with Ni(II).

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