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Determination of stability constant of some transition metal ions chelates with substituted pyrazoles

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ABSTRACT

The stability constants of the complexes of Cu (II), Co (II) and Ni (II) ions with 3-(3'-nitrophenyl)-4-(4''-chlorobenzoyl)-5-(2-hydroxyphenyl) pyrazole (L_1), 3-(4'-chlorophenyl)-4-(4''-chlorobenzoyl)-5-(2-hydroxyphenyl) pyrazole (L_2), 3-(4'-methoxyphenyl)-4-benzoyl-5-(2-hydroxyphenyl) pyrazole (L_3), 3-(4-bromophenyl)-4-furoyl-5-(2-hydroxyphenyl) pyrazole (L_4) have been determined by the pH-metric method at 0.1M ionic strength at 28 ± 0.1^{0}C in 70% dioxane-water mixture. The data obtained were used to estimate the values of proton-ligand (pK) and metal-ligand (logK) stability constants. It is observed that Cu (II), Co (II) and Ni (II) metal ions form 1:1 and 1:2 complexes with all the ligands.

Key words: Stability constants, Pyrazoles, metal chelates, dioxane-water.

INTRODUCTION

Pyrazoles are heterocyclic aromatic compounds containing two adjacent nitrogen atoms, as heteroatoms, which enhance the chelation and makes them as interesting ligands[1-3]. The metal ligand stability constants of Pr (III) and Nd (III) ions complexes with some substituted pyrazoles have been reported[4]. The influence of ionic strength on the stability constants of transition and lanthanide metal ions complexes with substituted pyrazoles reported by Agrawal *et. al.,*[5]. The interactions of some lanthanide metal ions with substituted isoxazolines at 0.1M ionic strength have been reported pH-metrically[6-9]. Mokhles *et. al.,*[10] investigated the formation of 3-H complexes of pyrazoles with Chromium and Tungsten. Recently Naik *et.al*[11] carried out pH-metric studies on formation constant of the complexes of substituted pyrazoles with some lanthanide metal ions and the influence of ionic strengths on complex equilibria in 70% Dioxane-water mixture.

Hence an attempt has been made to study the determination of proton-ligand stability constant and metal-ligand stability constants of Cu (II), Co(II) and Ni (II) complexes with L_1, L_2, L_3 and L_4 at 28 ± 0.1^{0}C in 70% Dioxane-water mixture pH-metrically.

EXPERIMENTAL

Substituted Pyrazoles were synthesized in the laboratory by standard method[12]. The pyrazoles are insoluble in water, hence 70% Dioxane-water (V/V) was used as solvent, Cu (II), Co (II) and Ni (II) metal nitrates were dissolved in double distilled water and their concentration estimated by standard method (13). Sodium hydroxide, Nitric acid and Potassium nitrate used are of AR grade. Dioxane was purified by the method described by Vogel (14). pH measurement were carried out with ELICO pH-meter (accuracy ± 0.05 units) using combined electrode at 28 ± 0.1^{0}C .

Calvin Bjerrum Titration Technique

The titrations were carried out in an inert atmosphere of nitrogen. The ionic strength of solution was maintained constant by adding an appropriate amount of 1 M KNO_3 solution. The values were recorded by pH-meter. These values converted to $[H^+]$ values by applying the correction proposed by Van, Uitert and Hass (15). The overall 0.1 M ionic strength of solution was calculated by expression.

$$\mu = \frac{1}{2}\sum_{i=1} C_i Z_i'$$

The contribution of the other ions in addition to K^+ and NO_3^- also taken into consideration.

RESULT AND DISCUSSION

The titration data were used to construct the curve between volume of NaOH and pH. They are called as acid titration curve, ligand titration curve and metal titration curve. The pK values of ligand and log K values of Cu (II), Co (II) and Ni (II) complexes at 0.1 M ionic strength were calculated by Irving and Rossotti's method[16].

Proton-Ligand Stability Constants

Substituted pyrazole may be considered as monobasic acids having one replaceable H^+ ion from phenolic –OH group and can therefore be represented as HL.

$$HL \rightleftharpoons H^+ + L^-$$

The titration data were used to construct the curves between volume of NaOH vs pH. It is

Table 1: pH-Deviation of various Ligands

S. No	Ligands	pH of Deviation
1	L_1	3.48
2	L_2	2.80
3	L_3	2.72
4	L_4	2.70

Table 2: Determination of Proton-Ligand stability Constants (pK) of Ligands at 0.1M ionic Strength

Ligand	Proton-Ligand Stabilty Constant (pK)	
	Half Integral Method	Point wise Method
L_1	10.40	10.35 ± 0.03
L_2	11.00	10.35 ± 0.05
L_3	11.40	11.55 ± 0.03
L_4	12.70	12.60 ± 0.04

Table 3: Metal-Ligand Stability Constants of Cu (II) and Ni (II) complexes with ligands at 0.1 M ionic strength

System	M-L Stability Constant		Log K_1 – log K_2	Log K_1 / log K_2
	LogK_1	LogK_2		
Cu (II) L_1	10.7969	8.0198	2.7771	1.3463
L_2	7.5969	3.1198	4.4771	2.4351
L_3	10.3969	4.9198	5.4771	2.1137
L_4	9.7969	5.0198	4.7771	1.9517
Ni (II) L_1	9.3969	2.7198	6.6771	3.4549
L_2	7.0969	3.8198	3.2771	1.8579
L_3	8.5969	4.9198	3.6771	1.7474
L_4	8.6969	4.0198	4.6771	2.1635
Co (II) L_1	8.7969	3.7198	5.0771	2.3649
L_2	7.2969	3.2198	4.0771	2.2663
L_3	8.1969	5.7198	2.4771	1.4331
L_4	8.3969	4.9198	3.4771	1.7068

observed from the titration curve that the ligand curves stand deviating from free acid curve at about pH 3.48 for L_1, pH 2.80 for L_2, pH 2.72 for L_3 and pH 2.70 for L_4. The deviation increased continuously up to pH 12.50. It indicates that OH^- group starts to dissociate at about pH 2.70 and complete its dissociation at about pH 12.50. It can be summarized in Table 1.

The average number of proton associated with the ligand ($\bar{n}_A$) was determined from ligand titration curve employing the equation of Irving and Rossotti (16). The pK values were estimated from formation curve (vs pH) by noting the pH at which = 0.5. The accurate values of pK were estimated by point wise calculations, which are presented in Table-02. The pK values of ligands increases in the following order.

$$L_1 < L_2 < L_3 < L_4$$

It could be seen from the values, the more reduction in pK values of ligand L_1 may be due to presence of nitro and chlorobenzoyl groups which acts as stronger electron withdrawing groups.

Metal-Ligand Stability Constant

Metal-Ligand stability constant of Cu (II), Co (II) and Ni (II) complexes with some substituted pyrazoles were determined by employing Calvin – Bjerrum pH-metric titration technique (17). The formation of chelates between Cu (II), Co (II) and Ni (II) with substituted pyrazoles was indicated by

- The significant departure starting from pH 3.5 in case of L_1, 2.8 in case of L_2, 2.72 incase of L_3 and 2.70 in case of L_4.
- The change in colour from blue to dark green for Cu (II) complexes, dark red to purple in case of Co (II) complexes and green to dark green in case of Ni (II) complexes on raising the pH 3.5 to 12.00.

The logK values were directly read from the formation curves ($\bar{n}$ Vs PL) using half-integral method. The most accurate logK values were calculated by pointwise calculation method is presented in Table-03 for all the system. The logK_1 and logK_2 values follow the order as

Co (II) < Ni (II) < Cu (II)

It could be seen that log K values follow increasing trend. This is due to the electron-releasing group. The values of log K, (log K_1 - logK_2) and log K_1 / log K_2) are in good agreement with expected values.

The difference between log K_1 and log K_2 is greater in all systems. Its seems there, that both 1:1 and 1:2 complexes are formed in a stepwise process and not simultaneously. Further the result shows that, the ratio of log K_1 / log K_2 is positive in all cases. This implies that there is little or no steric hindrance to the additions of secondary ligand molecule.

Vality of LogK = apK + b

The linear relationship logK = apK + b has been found(18) to hold good transition metal complexes of series of closely related ligands. The stability of the metal complexes of substituted pyrazoles follows the order Co (II) < Ni (II) < Cu (II). The plot of log K_1 Vs Pk shows satisfactory linear relationship giving slop values of 0.16, 0.21 and 0.36 respectively. The partial exactly compensate with each other.

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