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NOTE

pH-Metric Studies of Cu(II) and Th(IV) Complexes with Pyrazolines and Pyrazoles

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The interaction of Cu(II) and Th(IV) with 1-(3-chlorophenyl)-3-(2-hydroxy-5-methylphenyl)-5-phenylpyrazoline **(1)**, 1-(3-chlorophenyl)-3-(2-hydroxy-3-bromo-5-methylphenyl)-5-phenyl- pyrazoline **(2)** and 1-(3-phenylsulphonyl)-3-(2-hydroxy-3-bromo-5-methylphenyl)-5-(4-methoxyphenyl) pyrazole **(3)** have been investigated by Bjerrum method as adopted by Calvin and Wilson. The stability constants of complexes of Cu(II) and Th(IV) have been studied at constant temperature (27 ± 0.1°C) and 0.1 M ionic strength in 70% DMF-water mixture. It was observed that as the colour changes from light brown to darker shade there is complex formation between ligand and metal ion.

Key Words: pH-Metric studies, Cu(II), Th(IV), Complexes, Pyrazolines, Pyrazoles.

The study of stability constants of Th(IV) complexes with some substituted pyrazolines was reported by Gudadhe *et al.*[1] Mandakmare *et al.*[2] have studied the metal-ligand stability constants of Cu(II) with some substituted coumarins pH-metrically in 70% dioxane-water mixture. Metal-ligand stability of lanthanides with some substituted pyrazolines and diketones has been studied[3]. Metal-ligand stability constant and adiabetic compressibility of Cu(II)-peptide complexes have also been reported[4]. Some pyrazolines are found to be bactericidal[5] and fungicidal agents[6]. Pyrazoles are found to be hypolidermic agents[7]. Certain pyrazoles are antiinflammatory[8], anticonvulsant[9] and antihelmenthetic[10] in nature. In view of analytical applications of pyrazolines and pyrazoles, it was thought interesting to study the stability constants of Cu(II) and Th(IV) metal complexes with 1-(3-chlorophenyl-3-(2-hydroxy-5-methylphenyl)-5-phenylpyrazoline, 1-(3-chlorophenyl)3-(2-hydroxy-3-bromo-5-methylphenyl)-5-phenylpyrazoline and 1-(3-phenylsulphonyl-3-(2-hydroxy-3-bromo-5-methylphenyl)-5-(4-methoxyphenyl) pyrazole in 70% DMF-water mixture at fixed ionic strength, m = 0.1 M and temperature (27 ± 0.1°C).

In the present investigation, chemicals such as sodium hydroxide, perchloric acid, sodium perchlorate and metal salts (nitrates) used were of AR grade.

Ligands **1**, **2** and **3** were prepared according to literature methods. All ligands

were crystallized and their purity was checked by TLC before use. The solutions of ligands were prepared in DMF and standardized as per reported methods.

Systronics microprocessor based pH-meter with accuracy of ±0.01 unit with glass and saturated calomel electrode was used for the measurements. It was calibrated by buffer solutions of pH 4.00, 7.00 and 9.20 at 27° C before proceeding the titrations.

The experimental procedure involves pH-metric titration of (i) Free acid (0.01 M) (ii) Free acid (0.01 M) + Ligand (20×10^{-4} M) and (iii) Free acid (0.01 M) + Ligand (20×10^{-4} M) + Metal (4×10^{-1} M) against standard NaOH solutions. The ionic strength of these solutions was maintained constant (0.1 M) by adding an appropriate quantity of 1 M sodium perchlorate.

The titration was carried out in a 100 mL pyrex glass beaker kept in a water bath maintained at constant temperature (27 ± 0.1°C). Nitrogen gas was slowly purged into the solution to remove oxygen and carbon dioxide.

Proton-ligand Formation Constants: The deviation of (acid + ligand) curves from acid curves started at about pH 2.9 for each ligand and increased continuously up to pH 12.0. This indicates that the dissociation of —OH group occurs which is present in the ligand part of the complex structure. The proton-ligand formation number ($\bar{n}A$) was determined by Irving and Rossotti's expression. The values of pK (dissociation constant of —OH group) were estimated by noting the pH at $\bar{n}A = 0.5$ which were calculated by half integral method and presented in Table-1.

Metal-ligand Stability Constants: The deviations of (acid + ligand) curves from (acid + ligand + metal) curves were observed at about 3.0 pH in the media of 70% DMF-water mixture. This indicates the commencement of complex formation from this pH. During the titration process there is colour change of the solution from light brown to darker shade. This indicates the formation of complex between ligand and metal ion. The values of $\bar{n}$ (metal-ligand formation number) were calculated from Irving-Rossotti's expression which were used to calculate the metal-ligand stability constants. The metal-ligand stability constants for all the systems were calculated by Half integral method. These values are presented in Table-2. It could be seen from Table-2 that the difference between the values of log k_1 and log k_2 is sufficiently great. This shows the stepwise complex formation between ligand and metal ion. It could be seen from Table-1 that the order of pK values of the ligand **1** is greater than that of the value of ligand **2** and that of ligand **2** is greater than that of the value of ligand **3**. This may be due to the presence of bromo and bromomethoxy electron withdrawing groups of ligand **2** and ligand **3** respectively. The electron withdrawing groups reduce the pK values of the ligands. It is also seen from Table-2 that the values of metal ligand stability constants (log k_1 and log k_2) are greater for Cu(II) complexes than for Th(IV) complexes. It means that Cu(II) forms more stable complexes due to its smaller size than the complexes of Th(IV) with all three ligands. Moreever, transition metal ions form more stable complexes than the nuclear metal ions.

TABLE-1

S.N.	System	pK
1.	1-(3-chlorophenyl)-3-(2-hydroxy-5-methylphenyl)-5-phenylpyrazoline	8.10
2.	1-(3 -chlorophenyl)-3 -(2-hydroxy-3 -bromo-5-methylphenyl)-5-phenyl-pyrazoline	7.75
3.	1-(phenylsulphonyl)-3-(2-hydroxy-3-bromo-5-methylphenyl)-5-(4-methoxy-phenyl) pyrazole	7.60

TABLE-2

S.N.	System	log k_1	log k_2
1.	Cu(II)-1-(3-chlorophenyl)-3-(2-hydroxy-5-methylphenyl)-5-phenyl-pyrazoline	7.19	6.04
2.	Cu(II)-1-(3-chlorophenyl)-3-(2-hydroxy-3-bromo-5-methylphenyl)-5-phenylpyrazoline	8.53	6.25
3.	Cu(II)-1-(phenylsulphonyl)-3-(2-hydroxy-3-bromo-5-methylphenyl)-5-(4-methoxyphenyl) pyrazole	8.34	5.99
4.	Th(IV)-1-(3-chlorophenyl)-3-(2-hydroxy-5-methylphenyl)-5-phenyl-pyrazoline	5.45	4.04
5.	Th(IV)-1-(3-chlorophenyl)-3-(2-hydroxy-3-bromo-5-methylphenyl)-5-phenylpyrazoline	8.32	5.85
6.	Th(IV)-1-(phenylsulphonyl)-3-(2-hydroxy-3-bromo-5-methylphenyl)-5-(4-methoxyphenyl) pyrazole	8.51	5.92

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