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Studies in Co(II), Cu(II) and Ni(II) Complexes with Substituted Pyrazoline and Pyrazole at 0.1 Ionic Strength pH-metrically

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The interaction of Co(II), Cu(II) and Ni(II) with 3-(2-hydroxy-5-methyl phenyl)-4-benzoyl-5-phenyl-1-pyridoyl-Δ^2-pyrazoline and 3-(2-hydroxy-3-bromo-5-methyl phenyl)-4-benzoyl-5-(4-methoxy phenyl)-1-pyridoyl pyrazole have been investigated by Bjerrum method as adopted by Calvin and Wilson. The stability constants of 1 : 1 and 1 : 2 complexes of Co(II), Cu(II) and Ni(II) have been studied at constant temperature (27 ± 0.1°C) and 0.1 M ionic strength (NaOH) in 70% DMF-water mixture. It is observed that formation of 1 : 1 and 1 : 2 complexes is occurring simultaneously.

INTRODUCTION

Metal chelates of 3-(*o*-hydroxyphenyl)-5-phenyl isoxazole with Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO_2(VI) have been investigated by Vithalrao *et al.*[1] The spectral properties of 3-(*o*-hydroxy phenyl)-5-phenyl isoxazole were reported by Murthy *et al.*[2] Metal ligand stability constants of lanthanides with some substituted pyrazolines and diketones are studied by Sawalakhe and Narwade[3]. Mandakmare *et al.*[4] have studied the metal-ligand stability constant of Cu(II) with some substituted coumarins pH-metrically in 70% dioxane-water mixture. Sondawale *et al.*[5] have determined metal-ligand stability constants and adiabatic compressibility of Cu(II)-peptide complexes recently. Gudadhe *et al.*[6] have performed the study of stability constants of Th(IV) complexes with some substituted pyrazolines.

In view of the analytical applications of pyrazolines and pyrazoles, it is of interest to study the physico-chemical properties such as stability constants of Co(II), Cu(II) and Ni(II) complexes with 3-(2-hydroxy-5-methyl phenyl)-4-benzoyl-5-phenyl-1-pyridoyl-Δ^2-pyrazoline and 3-(2-hydroxy-3-bromo-5-methyl phenyl)-4-benzoyl-5-(4-methoxy phenyl)-1-pyridoyl pyrazole. In the present investigation 70% DMF-water mixture is used as a solvent for preparation of solution.

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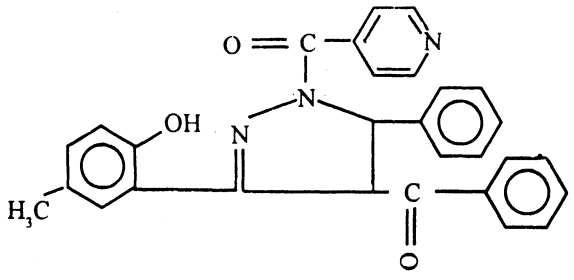
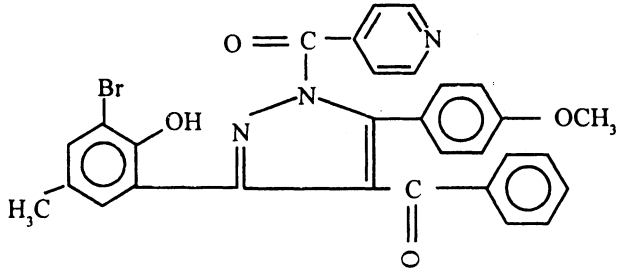


Ligand-1



Ligand-2

EXPERIMENTAL

All chemicals such as sodium hydroxide, nitric acid, potassium nitrate and metal salts of AnalaR grade were used in the present investigation.

3-(2-Hydroxy-5-methyl phenyl)-4-benzoyl-5-phenyl-1-pyridoyl-Δ^2-pyrazoline **(ligand-1)** and 3-(2-hydroxy-3-bromo-5-methyl phenyl)-4-benzoyl-5-(4-methoxy phenyl)-1-pyridoyl pyrazole **(ligand-2)** were prepared by following literature method. Both ligands were crystallized and their purity was checked by TLC before use. The solutions of purified ligands were prepared in DMF and standardised by potentiometric techniques.

ELICO pH-meter model LI-10 (accuracy ± 0.05 unit) with a glass electrode and saturated calomel electrode was used for the measurement of pH. It was calibrated by buffer of pH 4.0, 7.0 and 9.2 at 27°C before proceeding for titrations.

The experimental procedure involved pH-metric titrations of (i) free acid (0.01 M) (ii) free acid (0.01 M) and ligand (20×10^{-4} M) and (iii) free acid (0.01 M) + ligand (20×10^{-4} M) + metal ion (4×10^{-4} M) against standard NaOH solution. The ionic strength of all the solutions was maintained constant (0.1 M) by adding an appropriate quantity of 1 M potassium nitrate.

The titations were carried out in 100 mL pyrex glass beaker kept in a water bath maintained at constant temperature (27 ± 0.1°C). Nitrogen gas was slowly bubbled through the solution to remove the oxygen and carbon dioxide. The pH-meter readings were taken only after the gas bubbling was completely stopped. In aqueous-organic mixture pH values were corrected by use of Van-Utert and Hass equation.

RESULTS AND DISCUSSION

Proton-ligand formation constants: The deviation of acid-ligand curves from acid curves started around pH = 5.70 for both ligands and increased continuously up to pH 12.0. It shows that dissociation of —OH group occurs which is present in the ligand part of the complex structure. The values of $\bar{n}_A$ were calculated by Irving-Rossotti's expression. The pKa values for both systems were calculated by half integral and pointwise calculations which are presented in Table-1.

TABLE-1

S. No.	System	Constant pK	
		Half integral	Pointwise K-wise calculations
1.	3-(2-hydroxy-5-methyl phenyl)-4-benzoyl-5-phenyl-1-pyridoyl-Δ^2-pyrazoline	7.80	7.78 ± 0.05
2.	3-(2-hydroxy-3-bromo-5-methyl phenyl)-4-benzoyl-5-(4-methoxy phenyl)-1-pyridoyl pyrazole	7.40	7.45 ± 0.03

TABLE-2

S. No.	System	Constants			
		log K_1		log K_2	
		Half integral	Pointwise calculations	Half integral	Pointwise calculations
1.	Co(II) 3-(2-hydroxy-5-methyl phenyl)-4-benzoyl-5-phenyl-1-pyridoyl-Δ^2-pyrazoline	9.045	9.112 ± 0.02	8.159	8.059 ± 0.03
2.	Cu(II) 3-(2-hydroxy-5-methyl phenyl)-4-benzoyl-5-phenyl-1- pyridoyl-Δ^2-pyrazoline	8.045	8.095 ± 0.03	7.061	7.015 ± 0.04
3.	Ni(II) 3-(2-hydroxy-5-methyl phenyl)-4-benzoyl-5-phenyl-1- pyridoyl-Δ^2-pyrazoline	8.015	8.091 ± 0.03	6.995	6.905 ± 0.05
4.	Co(II) 3-(2-hydroxy-3-bromo-5-methyl phenyl)-4-benzoyl-5-(4-methoxy phenyl)-1-pyridoyl pyrazole	6.448	6.339 ± 0.05	5.855	5.789 ± 0.06
5.	Cu(II) 3-(2-hydroxy-3-bromo-5-methyl phenyl)-4-benzoyl-5-(4-methoxy phenyl)-1-pyridoyl pyrazole	6.978	6.398 ± 0.04	5.998	5.885 ± 0.03
6.	Ni(II) 3-(2-hydroxy-3-bromo-5-methyl phenyl)-4-benzoyl-5-(4-methoxy phenyl)-1-pyridoyl pyrazole	6.558	6.495 ± 0.07	5.565	5.495 ± 0.04

Metal-ligand stability constants: The values of $\bar{n}$ were evaluated 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 and pointwise calculation methods. These values are presented in Table-2. It could be seen from Table-2 that there is no differences

as such between the log K values for both the complexes. It showed that there must be simultaneously complex formations and not stepwise formation. The order of stability of metal-ligand complexes is Co(II) > Cu(II) > Ni(II) for pyrazoline ligand and Co(II) < Cu(II) < Ni(II) for pyrazole ligand. The lesser values of log K in case of pyrazole may be due to the presence of bromine atom as an electron withdrawing group.

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