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Stability Constants of Pr(III), Nd(III) and Sm(III) Chelates with Some Substituted Pyrazolines

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The interaction of Pr(III), Nd(III) and Sm(III) metal ions with 3(2-hydroxy-3-iodo-5-methyl-phenyl)-1,5-diphenyl-pyrazoline (ligand **1**); 3(2-hydroxy-3-bromo-5-methyl-phenyl)-1-phenyl-5-(4-methoxy-phenyl)-pyrazoline (ligand **2**) and 3(2-hydroxy-3-chloro-5-methyl-phenyl)-5-(4-methoxy-phenyl)-pyrazoline (ligand **3**) have been investigated by pH-metric technique at 0.1 M ionic strength at 27 ± 0.1°C in 70% alcohol (methanol)-water mixture. The data obtained were used to estimate the values of proton-ligand stability constant (pk) and metal-ligand stability constants (log K). It is observed that Pr(III), Nd(III) and Sm(III) metal ions formed 1 : 1 and 1 : 2 complexes with all the ligands.

INTRODUCTION

Pyrazolines are weak bases and are good complexing agents due to presence of donor nitrogen. Complexes of 3(2-hydroxy-phenyl)-5(4-phenyl)-pyrazoline with Cu(II) and Co(II) have been synthesised and characterised by Natarajan *et al.* Metal chelates of 3(2-hydroxy-phenyl)-5-phenyl isoxazoline with Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO_2(II) have been investigated by Khadikar *et al.*[1] Narwade *et al.*[2] have studied the stability constants of complexes of Th(IV) with some substituted pyrazolines potentiometrically. Mahajan *et al.*[3] have studied Cu(II) complexes with sulphonic acid potentiometrically. The interaction between Cu(II) chelates with 2-hydroxy aromatic ketones and alkyl monomines is studied by Rabindranath[4]. Sawalakhe *et al.*[5] have studied the interactions of metals with 1,3-diketones, pyrazole and pyrazolines spectrophotometrically. Sondawale *et al.*[6] have studied the confirmation of complex formation and determination of conditional stability constants of Cu(II) complexes with some amino acid peptides spectrophotometrically. Recently Shety *et al.*[7] have studied the determination of stability constants of some rare earth metal complexes derived from 3-phenyl salicylaldehyde. The study of the stability constants of Pr(III), Nd(III) and Sm(III) complexes with substituted pyrazolines are still lacking. It was therefore thought of interest to study the chelating properties of some substituted pyrazolines under suitable conditions potentiometrically.

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EXPERIMENTAL

Metal nitrates (BDH) were dissolved in perchloric acid and their concentrations were estimated by standard method[8]. Substituted pyrazolines are insoluble in water and hence 70% alcohol-water (v/v) was used as a solvent. Methanol was purified by standard method[9] and its purity was checked.

pH measurements were carried out with ELICO pH-meter (accuracy ± 0.05 unit) using glass and calomel electrodes at 27 ± 0.1°C. The B values (pH-meter readings in 70% alcohol-water mixture) were converted to (H^+) values by applying the corrections proposed by Van Uitert and Hass[10]. The overall 0.1 M. ionic strength of solution was calculated by the expression $\mu = \frac{1}{2} \sum_{i=1} c_i z_i^2$. The contribution of the other ions in addition to Na^+ and ClO_4^- was also taken into considerations.

RESULTS AND DISCUSSION

Proton ligand stability constants

Substituted pyrazolines may be considered as monobasic acids having one replaceable H^+ ion from phenolic —OH group and can therefore be represented as HL, *i.e.*, $HL \rightleftharpoons H^+ + L^-$. The titration data were used to construct the cuves between volume of NaOH *vs.* pH.

It is observed from the titration curves that the ligand curves start deviating from the free acid curves at about pH 3.35 for ligand **1**, at about pH 4.75 for ligand **2** and pH 4.25 for ligand **3**. The derivation increased continuously up to pH 11.00. It indicated that —OH group starts to dissociate at about 3.50 and complete its dissociation at about pH 11.00.

The average number of protons associated with the ligand ($\bar{n}A$) was determined from ligand titration curves employing the equation of Irving and Rossotti[11]. The pK values were estimated from formation curves ($\bar{n}A$ *vs.* pH) by noting the pH at which $\bar{n}a = 0.5$. The accurate values of pK were estimated by pointwise calculation which are presented in Table-1. The pK values are found to decrease in the following order of ligands.

ligand **1** < ligand **2** < ligand **3**

TABLE-1
DETERMINATION OF PROTON-LIGAND STABILITY CONSTANTS (pK) OF SOME SUBSTITUTED PYRAZOLINES AT 0.1 M IONIC STRENGTH

Systems	Constants pK Half integral	pointwise calculation
Ligand 1	10.85	10.90 ± 0.05
Ligand 2	12.10	12.20 ± 0.05
Ligand 3	12.40	12.40 ± 0.05

It may be attributed to the increasing electron releasing tendencies of the group —CH_3.

Metal-ligand stability constants

Metal-ligand stability constants of Pr(III), Nd(III) and Sm(III) complexes with some substituted pyrazolines were determined by employing Bjerrum-Calvin pH-titration technique as adopted by Irving and Rossotti.

The formation of chelates between Pr(III), Nd(III) and Sm(III) and the substituted pyrazolines was indicated by:

(i) The significant departure, starting from pH 2.90 for Pr(III), pH 2.80 for Nd(III) and pH 2.90 for Sm(III) complex system.

(ii) The change in colour from yellow to dark yellow and then brown as pH was raised from 3.00 to 11.00

The log K values were directly read from the formation curves ($\bar{n}$ *vs*. PL) using half integral method.

The most accurate log K values were calculated by pointwise calculations. Methods are presented in Table-2 for all the systems. The log K_1 and log K_2 values follow the oder as Pr(III) < Nd(III) < Sm(III). It could be seen (Table-2) that log K values follow increasing trend. This is due to the effect of electron releasing group (Cl^-, Br^-, I^-). The values of log K, (log $K_1 - \log K_2$), and (log K_1/log K_2) are presented in Table-3. It is observed that the smaller difference may be due to *trans*-structure.

TABLE-2
METAL-LIGAND STABILITY CONSTANTS (Log K) OF Pr(III), Nd(III) AND Sm(III) COMPLEXES WITH SUBSTITUTED PYRAZOLINES AT 0.1 M IONIC STRENGTH

System	Constants	
	log K_1	log K_2
Pr(III) Ligand 1	10.45	9.77
Pr(III) Ligand 2	10.15	9.60
Pr(III) Ligand 3	12.00	8.11
Nd(III) Ligand 1	9.90	8.50
Nd(III) Ligand 2	11.05	8.55
Nd(III) Ligand 3	12.45	10.57
Sm(III) Ligand 1	10.60	7.50
Sm(III) Ligand 2	10.70	8.75
Sm(III) Ligand 3	12.45	11.97

The results show that the ratio $\frac{\log K_1}{\log K_2}$ is positive in all cases. This implies that there is little or no steric hindrance to the addition of secondary ligand molecule.

TABLE-3
METAL-LIGAND STABILITY CONSTANTS AT 0.1 M IONIC STRENGTH

System	$\log K_1 - \log K_2$	$\log K_1/\log K_2$
Pr(III) Ligand 1	0.68	1.069
Pr(III) Ligand 2	0.55	1.057
Pr(III) Ligand 3	3.89	1.080
Nd(III) Ligand 1	1.40	1.164
Nd(III) Ligand 2	2.05	1.292
Nd(III) Ligand 3	3.10	1.777
Sm(III) Ligand 1	3.10	1.413
Sm(III) Ligand 2	1.95	1.222
Sm(III) Ligand 3	0.48	1.040

Validity of $\log K = a\,pK + b$ relation:

The linear relationship $\log K = a\,pK + b$ has been found out by some workers[12] to hold for transition metal complex of series of closed related ligands.

The stability of the metal complexes of subsituted pyrazolines follows the order Pr(III) < Nd(III) < Sm(III).

The plot of $\log K_1/\log K_2$ *vs.* pK shows satisfactory linear relationship giving slope values of 1.00 and 1.05 respectively. The partial molar free energies of metal-ligand and proton-ligand complexes exactly compensate each other, when log K *vs.* pK plot is linear with a slope of unity.

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