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Determination of Stability Constant of La (III), Pr (III) and Nd (III) Chelates with Some Substituted Pyrazole

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ABSTRACT

Substituted pyrazoles such as 1-phyenyl-3-(2-hydroxy-4-methyl phenyl)-5- methyl pyrazole – L1 &4-(benzole)-3-(4-chlorophenyl)-5-(o-hydrohydroxy phenyl) pyrazole – L2are synthesized in laboratory. The interaction of the above substituted pyrazoles have been studied with La (III), Pr (III), Nd (III) and Metal - ligand stability constants have been evaluated in 70 % dioxane-water mixture at 0.1 ionic strength. The ratio logK1 / logK2 is positive in all cases. This implies that there is little or no steric hindrance to the additions of secondary ligand molecule

KEYWORDS: Pyrazole, Lanthanide metal ions, Dioxane.

I. INTRODUCTION

Metal complexes containing pyrazole-based have been the subject of much research interest owing to their rich coordination chemistry and a number of established and potential application area[1,2]. It has been known that pyrazole and substituted pyrazole possess numerous chemical, biological, medicinal and agricultural applications because of their versatile biological activities appearing as antimicrobial[3], antiviral[4], antitumer[5], antiinflammatory[6], antihistaminic[7], antifungal[8] and antiherbicide[9]. Similarly, pyrazolines have been reported to show a broad spectrum of biological activities including antibacterial[10], antifungal[11], antiinflammatory[12] and antidepressant[13] activities. The pyrazoline function is quite stable and has inspired to study for their complex formation. In the literature, the numerous metal complexes have been investigated for a long time in the study of complexes and measurement of complex stabilities. The many methods that have been used to determine stability, describes in detail the often-intricate calculation and gives a remarkable thorough bibliography of work in this field. It concerns itself with ionic and molecular association inall their forms. The nitrogen ligand metal complexes are used as catalyst for olefin polymerization[14], which modified to give different microstructures and high molecular weights. The zinc pyrazole complexes work as luminescent[15] that exhibit blue emission at room temperature.

Substituted pyrazoles fall in the class of aromatic compounds and have the structural features involving two nitrogen atoms in a ring, which make them interesting ligands.

The study of proton-ligand stability constants and metal-ligand stability constants of La (III), Pr(III) and Nd (III) complexes withsome substituted pyrazoles is still remaining. It was therefore interesting to study the chelating properties of some substituted pyrazoles (mentioned above) under suitable condition pH metrically.

II. EXPERIMENTAL

The ligands used in the present work are synthesized by standard known literature methods[16,17]. 0.01 M stock solution of each ligand was prepared by dissolving the requisite amount in dioxane (100%) solvent.

All the pH measurement was carried out with EQUIP-TRONICS digital pH-meter (model EQ-610) equipped with combined glass electrode and magnetic stirrer (accuracy ± 0.005 units).

Calvin-BjerrumTitration :-

The experimental procedure involved pH-metric titrations of solutions of (i) free acid i.e. HNO_3 (A) (ii) free acid + ligand (A+L) (iii) free acid + ligand + metal ion (A+L+M) against standard alkali solution (i.e. NaOH). The ionic strength of each solution was adjusted a constant volume (0.1 M) by addition of appropriate amount of 1 M KNO_3 solution. The glass beaker placed in a water bath to maintain a constant temperature 27 ± 0.1°C.

The titrating solution was allowed to attain the bath temperature before commencement of the titration. The titration vessel and its contents were purged with nitrogen for five minutes and then titration was begun. The pH meter readings were taken only after the gas bubbling and magnetic stirring were stopped. At the point, when the meter readings raised suddenly i.e. at the neutralization point of HNO_3, the rate of bubbling was increased to allow the reading to become steady more quickly, normally, it took about two/three hours to complete one titration.

The optical densities of the ligand solutions and their metal complexes have been measured by UV-VIS spectrophotometer model 1700 (Shimadzu, Japan) and accuracy = ± 0.005. The spectral range of the instrument was from 180 nm to 1100 nm.

Irving and Rossotti[18] have proposed a relation between the stability of the complexes and basicity of the ligand by equation.

$\log k = a\,pK + b$

III. RESULTS AND DISCUSSION

The relation $\log K = a\,pK + b$ was, therefore, examined for 1:1 and 1:2 complexes of La (III), Pr(III) and Nd (III) metal ions with ligands by plotting $\log K_1$ or $\log K_2$ against $pK_1 + pK_2$ having straight line graph.

The result obtained during the work is tabulated in following tables.

pH-METRIC TITRATION DATA

SYSTEM :Ligand (L_1)

Medium : 70% Dioxane-Water.

E^0=0.01 M $T_L^0 = 20.00 \times 10^{-4}$ M $T_M^0 = 4.00 \times 10^{-4}$ M

V_0=50 ml N = 0.20 N Temp. = $27^0C \pm 1^0C$ μ = 0.1M

Table 1:

Titration of					
Volume of Alkali added(ml)	Free Acid	Free Acid + Ligand 1	Free Acid + Ligand 1 + Metals		
			La(III)	Pr(III)	Nd(III)
	pH	pH	pH	pH	pH
0.0	2.15	2.15	2.15	2.15	2.15
0.2	2.16	2.16	2.16	2.16	2.16
0.4	2.19	2.19	2.19	2.19	2.19
0.6	2.21	2.21	2.21	2.21	2.21
0.8	2.23	2.23	2.23	2.23	2.23
1.0	2.26	2.26	2.26	2.26	2.26
1.2	2.29	2.29	2.29	2.29	2.29
1.4	2.31	2.31	2.31	2.31	2.31
1.6	2.34	2.34	2.34	2.34	2.34
1.8	2.37	2.37	2.37	2.37	2.37
2.0	2.39	2.39	2.39	2.39	2.39
2.2	2.43	2.43	2.43	2.43	2.43
2.4	2.46	2.46	2.46	2.46	2.46
2.6	2.51	2.51	2.51	2.51	2.51
2.8	2.57	2.57	2.57	2.57	2.57
3.0	2.61	2.61	2.61	2.61	2.61
3.2	2.66	2.66	2.66	2.66	2.66
3.4	2.74	2.74	2.74	2.74	2.74
3.6	2.85	2.85	2.85	2.85	2.85
3.8	2.97	2.97	2.97	2.97	2.97
4.0	3.10	3.10	3.10	3.10	3.10
4.2	3.25	3.25	3.25	3.25	3.25
4.6	3.50	3.50	3.38	3.46	3.58
4.8	5.75	4.50	3.95	4.06	3.80
5.0	9.47	7.41	6.39	6.70	6.25
5.2	10.25	8.25	7.60	7.25	7.45
5.4	10.73	9.10	7.87	8.05	7.73
5.6	10.90	9.35	8.14	8.45	8.00
5.8	11.00	9.59	8.72	8.90	8.57
6.0	11.10	9.85	9.30	9.25	9.15

pH-METRIC TITRATION DATA

SYSTEM : Ligand (L_2) Medium : 70% Dioxane-Water.

E^0=0.01 M $T_L^0 = 20.00 \times 10^{-4}$ M $T_M^0 = 4.00 \times 10^{-4}$ M

V_0=50 ml N = 0.20 N Temp. = $27^0C \pm 1^0C$ μ = 0.1M

Table 2:

Titration of					
Volume of Alkali added(ml)	Free Acid	Free Acid + Ligand 2	Free Acid + Ligand 2 + Metals		
			La(III)	Pr(III)	Nd(III)
	pH	pH	pH	pH	pH
0.0	2.15	2.20	2.20	2.20	2.20
0.2	2.16	2.22	2.22	2.22	2.22
0.4	2.19	2.24	2.24	2.24	2.24
0.6	2.21	2.26	2.26	2.26	2.26
0.8	2.23	2.29	2.29	2.29	2.29
1.0	2.26	2.31	2.31	2.31	2.31
1.2	2.29	2.34	2.34	2.34	2.34
1.4	2.31	2.36	2.36	2.36	2.36
1.6	2.34	2.38	2.38	2.38	2.38
1.8	2.37	2.41	2.41	2.41	2.41
2.0	2.39	2.45	2.45	2.45	2.45
2.2	2.43	2.48	2.48	2.48	2.48
2.4	2.46	2.52	2.52	2.52	2.52
2.6	2.51	2.57	2.57	2.57	2.57
2.8	2.57	2.62	2.62	2.62	2.62
3.0	2.61	2.67	2.67	2.67	2.67
3.2	2.66	2.73	2.73	2.73	2.73
3.4	2.74	2.79	2.79	2.79	2.79
3.6	2.85	2.85	2.85	2.85	2.85
3.8	2.97	2.93	2.93	2.93	2.93
4.0	3.10	3.05	3.05	3.05	3.05
4.2	3.25	3.20	3.20	3.20	3.17
4.6	3.50	3.45	3.40	3.42	3.39
4.8	5.75	4.95	4.71	4.85	4.05
5.0	9.47	7.00	6.98	6.95	6.10
5.2	10.25	7.44	7.29	7.39	6.95
5.4	10.73	7.88	7.60	7.70	7.64
5.6	10.90	8.31	8.00	8.10	7.96
5.8	11.00	8.74	8.41	8.51	8.29
6.0	11.10	9.25	8.74	8.84	8.64

Table 3: Metal-Ligand stability constants (log K)

System	Ligand (L_1)				Ligand (L_2)			
	log K_1	log K_2	log K_1- log K_2	log K_1/log K_2	log K_1	log K_2	log K_1- log K_2	log K_1/log K_2
La(III)-	8.9447	5.2538	3.6909	1.7025	8.6647	4.0938	4.5709	2.116542
Pr (III)	6.5047	2.9536	3.5511	2.202296	7.3447	3.0938	4.2509	2.374006
Nd (III)	5.7447	2.5539	3.1908	2.249383	5.7447	1.2139	4.5308	4.732433

IV. CONCLUSION

The above observations & results revealed that the change in colour during pH metric titration also indicate the formation of complex between ligand and metal ions. The departure between acid curve and ligand curve indicate the dissociation of phenolic -OH groups. The formation of straight line between pKvs log K hold good the relationship between log K = a.pK + b.

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