Stabilities of Some Heterocyclic Amine Complexes

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The formation constants of Ni(II), Cd(II) and Mg(II) complexes with pyridine, α-, β- and γ-picoline have been determined by applying the two titration techniques of Irving-Rossotti. The values have been correlated with the nature of the metal ions and ligands.

The literature reveals that a large number of attempts have been made to prepare the tertiary amine-metal complexes[1-4] under different conditions. However, the studies of formation constants in solution are scarce[5,6]. In this investigation the formation constants of the complexes of Ni(II), Cd(II) and Mg(II) with the tertiary bases i.e., pyridine, α-, β- and γ-picoline have been attempted by Irving-Rossotti technique[7].

The titrations have been carried out as follows. Solutions containing perchloric acid (0·0588 M), Perchloric acid (0·0588 M)+ligand (0·05 M), perchloric acid+ligand+metal perchlorate solution (0·001 M), maintained at constant volume (50 ml). and constant ionic strength (0·2 M) by the addition of neutral salt $NaClO_4$ were titrated against standard alkali (0·5 M). The titrations have been performed at $35° \pm 0·1°$. The values of $\bar{n}_A$, $\bar{n}$ and pL were calculated from the equation in the original paper[7]. The proton ligand stability constants have been determined from the relationship

$$\log P^{H}k_1 = p\text{H} + \log \bar{n}_A/1 - \bar{n}_A$$

pH was plotted against $\log \bar{n}_A/1-\bar{n}_A$. At each point falling on the straight line the above relationship holds good. Average values have been presented in the following table. From the plots of $\bar{n}$ and pL (formation curve), values of formation constants $\log K_1$ and $\log K_2$ were obtained at $\bar{n} = 0·5$ and $1·5$ respectively.

The results were further confirmed by Irving-Rossotti's second method[7] for basic ligands. Two titrations are carried out in this method. Solution containing perchloric acid (0·4 M) and perchloric acid (0·4 M)+metal perchlorate (0·02 M), constant volume (50 ml.) and ionic strength (0·5 M) being maintained by addition of conductivity water and

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7. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904.

neutral salt $NaClO_4$, were titrated against ligand solution of 5 M strength. Values of $\bar{n}_A$ obtained by the first method have been used, $\bar{n}$ and pL were calculated by the equations given in the original paper[7]. At a particular pH $\bar{n}$ and pL obtained by both methods are same with difference in the third place of decimal. $\bar{n}$ and pL have an accuracy of ± 0.05. Since the spreading factor is low, the values of log K_1 and log K_2 obtained by half integral method are approximate. More accurate values have, therefore, been obtained by the method of successive approximation[8,9] and have been tabulated below :

TABLE 1

Values of $^PK^H$, log K_1 and log K_2

	$^PK^H$	Ni		Cd		Mg
		log K_1	log K_2	log K_1	log K_2	log K_1
Pyridine	1.07×10^5	2.40	1.85	2.24	1.79	2.08
α-picoline	6.42×10^5	2.91	2.43	2.61	2.15	2.59
β-picoline	4.10×10^5	2.82	2.37	2.54	2.09	2.44
γ-picoline	8.39×10^5	3.10	2.51	2.95	2.36	2.80

DISCUSSION

As revealed by proton ligand stability constant values the basicities of the ligands are in the order pyridine $< \beta$-picoline $< \alpha$-picoline $< \gamma$-picoline. The formation constants of the metallic complexes are in the order γ-picoline complex $>$ α-picoline complex $> \beta$-picoline complex $>$ pyridine complex, i.e., in the order of the basicities of the ligands. Plots of log K^H against log K, however, do not hold an exact linear relationship.

In solution magnesium forms 1 : 1 complexes, whereas nickel and cadmium exhibit 1 : 2 stoichiometry. The linking of greater number of ligand molecules with the transition metal ions may be due to some M-L π interaction.

Pyridine and its substituted derivatives have a resonating structure in which the nitrogen atom has a vacant $p\pi$ orbital.

The transition metals, Ni and Cd with $d\pi$ electrons can affect $d\pi$–$p\pi$ interaction between metal and nitrogen. This stabilises metal-ligand bond and contributes more stability to the complexes. Cadmium with d^{10} configuration and a bigger size should have more tendency to donate the π electrons than nickel with d^8 configuration. The stabilities of nickel and cadmium complexes are, however, near to one another. This may be because of the fact that cadmium with a bigger size forms less stable L-M σ bond than in case of nickel. The formation constants of Hg complexes as reported by Bjerrum[6] are little higher than that of cadmium (II). This is in agreement with the bigger size and greater π bonding tendency of the Hg(II) ion. Mg being a non-transition element can not form π

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9. J. Bjerrum, "Metal Amine Formation in Aqueous Solutions", P. Haase and Son, Copenhagen, 1941, 133.

bond and hence the stability should have been lower. But since it has small size the L-M σ bond is much stronger. Net effect of the σ and π bonds brings the stability constants of all the complexes nearer.

The substitution of $-CH_3$ group at different positions will have different effect in increasing the electron density at the nitrogen atom, thereby increasing the basicity but decreasing the $ML-\pi$ interaction. This accounts for the divergence in the linear relationship between the formation constants and basicities of the ligands.

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