CHAPTER FOUR

INTERPRETATION OF THE RESULTS

An observation of the proton ligand stability constant values (Table III B) indicates that the basicities of the ligands are in the following order :

Pyridine < β-picoline < α-picoline < γ-picoline < 2:4-lutidine < 2-aminopyridine < 2:6-lutidine < 2:4:6-collidine < 2-amino-4-methyl pyridine.

Pyridine is a tertiary base with the basic nitrogen situated in the ring and hence its basicity is less than that of primary and secondary amines. As a matter of fact the simplicity and rigidity of the pyridine system render these heterocyclic bases particularly useful in the study of the role of steric effects on base strength. The introduction of a methyl group, ($-CH_3$) in to the 2-, 3- or 4- position of the pyridine results in an increase in the basicity[1]. This can be attributed to the increase in the charge density on the nitrogen atom due to the inductive (+ ve) and hyperconjugation effect of the methyl group. This effect felt is more from ortho- and para- positions[2-4]. Substitution at meta position is less effective in increasing the basicity. This explains the order of the basicities of the picolines. In case of lutidines and collidine increasing number of the $-CH_3$ groups increase the basicity still further. 2:6-lutidine is a base of large steric requirments, as shown by studies of its reactions with borine and boron fluoride[5]. However, the third methyl group sometimes results in a decrease instead of an increase. The decrease might be attributed to the steric interaction between the trimethylamine and trimethylboron portions of the addition compound (i.e. the F.strain). But when the boron atom is not in the side chain the third methyl substitution will definitely increase the basicity of the substituent. Lutidines and collidine are, therefore, more basic than picolines.

Aminopyridine has two basic centres, the ring nitrogen and the amino group, ($-NH_2$). It is naturally expected to have more basicity than the pyridine. Since there are two basic centres a question would arise as to which of the two basic groups, $-NH_2$ or $-N=$ would play the role of the principal basic centre. It has been observed that the ring nitrogen atom acts as the principal basic centre. The basic character of $-NH_2$ group becomes dormant after its entry in to the pyridine ring. As such the $P_{K_2}^{H}$ for 2-aminopyridine could not be found out even at low pH. In 2-amino-4-methylpyridine the effect of the $-CH_3$ group increases the electron density on the nitrogen and the $-NH_2$ groups resulting in greater basicity of the ligand; $P_{K_2}^{H}$ becomes measurable.

At higher temperature the thermal vibrations are expected to cause greater dissociation of the hydrogen ion from the protonated conjugate acid of the ligands. As a result of it the P_K^H values of the ligands go down (Table IIIB) at higher temperature.

The relationship between the basicity of the ligand and its tendency to form metallic complexes can be drawn by observing the formation constants of the complexes of Ni^{++}, Cd^{++} and Mg^{++} with the ligands studied. The order is found to be following in all the three cases :

Complexes with :

Pyridine $<$ β-picoline $<$ α-picoline $<$ γ-picoline $<$ 2:4-lutidine $<$ 2-amino-pyridine $<$ 2:6-lutidine $<$ 2:4:6-collidine $<$ 2-amino-4-methyl pyridine.

It is observed that the values of the metal ligand formation constants of the complexes studied (Table III D(i)-(iii)) are in general low. This may be expected from the fact that the tertiary amines used as ligands have low p_K^H values indicating lower basicity. Complex formation in Sidgwick sense is a phenomenon comparable to acid base reaction, where the ligand acts as a base. The formation constant is dependent upon the differences in the free energies of the products and that of the reactants in a standard state i.e. free energy change (ΔF) of the reaction. When the free energy change is negative the reaction can proceed spontaneously with the accomplishment of net work. The larger the amount of this work the farther removed is the reaction from equilibrium. Because of this, $-\Delta F$ has been called the driving force of the reaction. The higher the value of $-\Delta F$ the greater will be the stability constant as given by the relation :

mun ming ΔG

$$-\Delta F = 2.303 \, R \, T \log K \quad \ldots\ldots \qquad (4.1)$$

Greater the basicity of the ligand higher is the $-\Delta F$ and more is the value of the formation constant of the complexes. It is natural, therefore, to expect low values of ΔF in reactions of pyridine and substituted pyridines with metal ions. The formation constants of the complexes are in agreement with the basicities of the ligands. A plot of log K against log K_H of the ligand, however, does not show an exact linear relationship as expected from the equation[6]:

$$\log K = {}^{P}K_a + B \quad ..... \qquad (4.2)$$

This interesting relation between ln K and $^{P}K_a$ of the ligands has been studied by various authors.

Larson[7] found out the dissociation constants of various silver diamine ions and substituted ammonium ions and pointed out that a relation exists between $^{P}K_n^H$ and l_nK. Subsequent work by Bruehlman and Verholk[8] relating to aqueous media indicated that separate linear relations were obtained for primary, secondary and tertiary amines. From a review of other workers too it is found that $l_n K_n / {}^{P}K^H$ is essentially constant for a series of amines and a given metal ion. But these are only rough and are obtained for a series of structurally related ligands i.e. those forming same number of chelate rings and having similar π-bonding tendency. Schwarzenbach and coworkers[9] have, however, indicated positive deviation from the plots of this type. The deviation may be due to the steric hindrances and also may be ascribed to considerations of enthalpy and entropy changes.

The free energy change of a system involving complex formation is not defined completely by the basicity of the ligands alone but is dependent on enthalpy and entropy changes also.

$$\Delta F = \Delta H - T \Delta S \quad .... \qquad (4.3)$$

Since the factors determining entropy and enthalpy changes

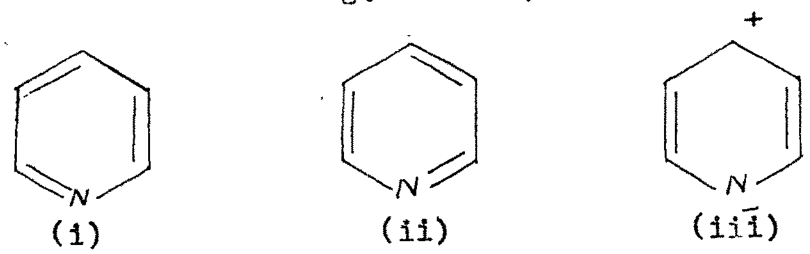
Gma wrong ΔG

are different, these functions must be considered to explain the divergence from the linear relationship.

If the metal ligand bond is purely σ - in character, the enthalpy change in a complex formation reaction may be expected to be proportional to the basicity of the ligands. The divergence from the linear relationship should therefore be sought in the π-bonding character of the M - L bond and the accompanying entropy change in the reaction. A reaction results in a more stable system if there is a positive entropy change or in other words the randomness in the resulting system is more. Since the ligands used in the present investigation are uncharged molecules, the ligation will not be accompanied by a reduction in the number of ions in solution or by neutralisation of the charge on the metal ion. The entropy changes will not, therefore, be significant during the complex formation. There may be a small positive entropy effect due to the fact that the neutral ligand molecules shield a coordinated metal from solvent contact and make solvent molecules less ordered around the complex ions than the arrangement around a free metal ion. However, the freedom gained by each water molecule is compensated by the loss of freedom by mono-dentate pyridine and its derivatives which get coordinated. In the case of bidentate aminopyridines the freedom gained by two water molecules is not completely compensated by the freedom lost by amine molecule. Thus the nature of the ligand determines the changes in entropy and consequently affects the formation constants.

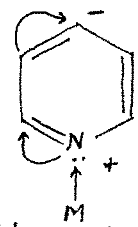
It will be interesting to compare the relative tendencies of magnesium, nickel and cadmium ions to combine with the tertiary bases. An observation of the values of the formation constants of these complexes indicates that the order of stability is Mg $<$ Cd $<$ Ni. The order can be explained by considering the possibility of π-interaction in the M – N bond. Pyridine normally exists in the following resonating forms :

Fig. IV 1 (i)-(iii)



In these forms the orbitals of the nitrogen atom are completely filled. However, when it combines with strong π-bonding metals it can take up the following ionic form

Fig. IV 2.

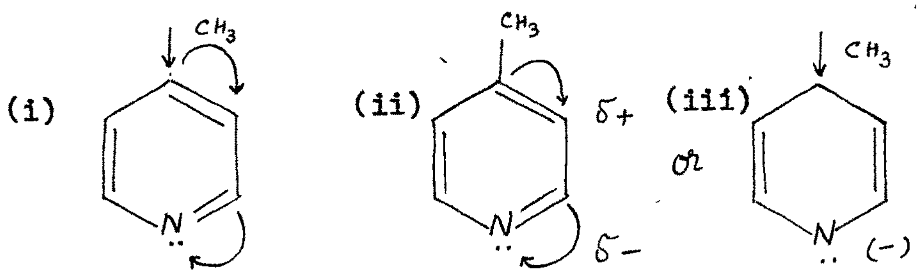


The π-orbitals of the nitrogen atom fall vacant and there can be $d\pi$ – $p\pi$ interaction by the donation of π-electrons from the metal ion to the vacant $p\pi$-orbitals of the nitrogen atom. This so called back donation of the electrons from metal to the ligands will not only serve to strengthen the bond but will also release the otherwise excessive negative charge on the metal ion due to L $\rightarrow$ M σ-bonding. The σ- and π-bonds mutually stabilize each other and this synergic effect in its turn stablizes the complex compound. The possibility of π-interaction in complexes of pyridine and its derivatives has also been indicated earlier.[10] To put in the words of R.J.P.Williams -

" We recognise here that although both F M L and F H L depend similarly upon one property of the ligand, the σ-donor (or acceptor) power they must differ in their dependance on its π-donor (or acceptor) character. Most strong σ-acceptor substituents in ligands are also π-donors e.g. methyl and most strong σ-acceptors are also π-acceptors e.g. nitro, so that a change of substituent in a ligand causes changes in and π-electron densities which are usually in the same direction ."

The transition metals nickel and cadmium with dπ-electrons can affect $d\pi - p\pi$ interaction between metal and nitrogen. This stabilizes metal-ligand bond and contributes more stability to the complexes. Cadmium with d^{10} configuration and a bigger size should have more tendency to form the π-bond than nickel with d^{8} configuration. The stabilities of nickel and cadmium are, however, near to one another. This may be because of the fact that cadmium with a bigger size forms less stable $L \rightarrow M$ σ-bond than in case of nickel. Magnesium being a non-transition element can not form π-bond and hence the stability should have been low. But since it has small size the $L \rightarrow M$ σ-bond is much stronger. The formation constant of magnesium complexes is not therefore, very much lower than that of Ni^{++} and Cd^{++} complexes.

The substitution of an electron repelling group releases charge in to the ring. It may therefore, be expected that all the methyl and amino substituted pyridines to have smaller tendency than pyridine to accept back coordination charge. The π-acceptor capacity, thus decreases from pyridine to monosubstituted pyridines and to polysubstituted pyridines. When an electron donor substitution is at position 4, the negative charge is likely to shift on the nitrogen atom as shown below : Fig. IV 3 (i)-(iii)



The effect of such a shift should possibly annual the stabilizing influence of the above resonating structure(Fig. IV 2. P.120), incidently weakening the π-interaction in M - N bond. Further, back coordination from M - L should localise the charge principally on 2-, 4- and 6-positions. Thus any substituent such as 3-alkyl, which directs charge to these positions will have the effect of inhibiting M - L π-bonding. Substitution at position 2- will have least effect in minimising π-bonding. Thus π-bonding capacity in picolines, lutidines and aminopyridine should be less than that in pyridine. Thus M - L π-interaction is also one of the factors affecting the linear relationship between the metal ligand formation constant and the basicity of the ligand in case of nickel and cadmium complexes where M - N π-interaction is possible.

The formation constants of metal ligand complexes in all the cases are observed to be lower at higher temperature.

This can be expected from the fact that the P_K^H values of the ligands go down at higher temperature resulting in a decrease in their tendency to form L $\rightarrow$ M bond. In other words, due to increased thermal vibrations, the M – L becomes less stable. Δ P_K^H of the ligands and Δ log β_2 of the complexes for the temperature range 35 to 45°C. have been tabulated in Table IV 1.

The decrease in the formation constant values of the complexes (log β_2) is observed to be nearly proportional to the decrease in the P_K^H values as observed by Bruehlhan and Verhock[11].

Table IV 1

Decreases in p_K^H and log β_2 values from 35° to 45°C.

Ligand	Δ log p_K^H	Δ log β_2		Δ log K_1 *
		Ni-complexes	Cd-complexes	Mg-complexes
Pyridine	0.07_0	0.16	0.14	0.07
α-picoline	0.09_5	0.19	0.16	0.17
β-picoline	0.10_5	0.19	0.16	0.09
γ-picoline	0.10_7	0.21	0.21	0.12
2:4-lutidine	0.12_0	0.23	0.25	0.13
2:6-lutidine	0.07_2	0.14	0.14	0.07
2:4:6-collidine	0.13_0	0.24	0.23	0.13
2-amino-pyridine	0.13_6	0.26	0.23	0.14
2-amino-4-methyl pyridine $p_{K_1}^H$	0.29_6	0.56	0.56	0.30
$p_{K_2}^H$	0.57_5			

* Magnesium forms only 1:1 complexes hence Δ log K_1 values have been given.

References -

1. Albert,A., Goldacre,R., and Phillips,J., J.Chem.Soc., 2240, (1948).
2. Conston and White, Amer.Chem.J., 29, 46, (1903).
3. Felsing and Biggs, J.Amer.Chem.Soc., 55, 3624, (1933).
4. Albert,A., and Goldacre,R., J.Chem.Soc., 706, (1946).
5. Brown,H.C., and Barbarad,G.K., J.Amer.Chem.Soc., 69, 1137, (1947).
6. Bjerrum,J., Chem.Rev., 46, 381, (1950).
7. Larson,E., Analyst, 77, 830, (1952).
8. Carlson,G.A., and Mc Reynold,V., J.Amer.Chem.Soc., 67, 1334, (1945).
9. Schwarzenbach,G., and Ackermann,H.P., Helv.Chim.Acta., 32, 1175, (1949).
10. Figgis,B.N., and Nyholm,R.S., J.Chem.Soc., 4190,(1958).
11. Bruchlhan,R.J., and Verhock,F.H., J.Amer.Chem.Soc., 70, 1402, (1948).