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# Equilibrium Studies on Mixed Ligand Complexes of Some Bivalent Metal Ions with 2,2′-Bipyridyl or 1,10-Phenanthroline and N-Methylaminothioformyl-N′-phenylhydroxylamine

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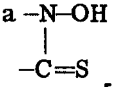
## ABSTRACT

Equilibrium studies on mixed ligand complexes of some bivalent metal ions, viz., Cu(II), Zn(II), Cd(II), Co(II), or Ni(II) with 2,2′-bipyridyl (Bpy) or 1,10-phenanthroline (Phen) as primary ligand and N-methylaminothioformyl-N′-phenylhydroxylamine (MATPH) as secondary ligand have been made using the Irving-Rossotti pH titration method in 50% aqueous-dioxane medium at 35 ± 0.5°C and 0.1 $\underline{M}$ ($NaClO_4$) ionic strength in an inert atmosphere. Formation constants, characteristic of mixed ligand complexes, have been calculated in the system

$$M + A \rightleftharpoons MA; \qquad MA + L \rightleftharpoons MAL$$

where M = Cu(II), Zn(II), Cd(II), Co(II), or Ni(II); A = 2,2′-bipyridyl or 1,10-phenanthroline, L = N-methylaminothioformyl-N'-phenylhydroxylamine. In all the systems, the $\Delta \log K_M$ values are negative which is due to the discriminating qualities of the heteroaromatic N-base. It is suggested that the S-ligand may also have $\pi$-accepting qualities with a greater influence on the stability of the complexes. Further results indicate that MATPH and Bpy or Phen are incompatible ligands toward the metal ions mentioned above and hence the mixed ligand complexes formed have lower stability than binary complexes of MATPH.

## INTRODUCTION

In mixed ligand complexes, two or more different ligands other than solvent molecule bond with the central metal ion either simultaneously [1] or at a different pH range [2], where the first ligand does not become dissociated even up to higher pH values. Mixed ligand complexes of transition metal ions [3-6] with amines and aminoacids are of biological importance and have been studied in detail. The analytical suitability of the reagent (MATPH) has been extensively studied in our laboratories [7-10]. MATPH possesses a  $-\underset{\underset{-C=S}{|}}{N}-OH$ group which is reported to be responsible for antimicrobial activity [11]. The biological activities of Bpy or Phen ligands have long been recognized. For the present study these ligands have been selected as the primary ligands because they form very stable complexes (1:1) with Cu(II), Zn(II), Cd(II), Co(II), and Ni(II) at low pH, whereas the attachment of MATPH takes place at considerably higher pH values. Thus the possibility of the ligand exchange is negligible, i.e., the reaction

$$M(Bpy/Phen) + MATPH \rightleftharpoons M(MATPH) + Bpy/Phen$$

does not occur.

The primary ligands, being neutral, also minimize electrostatic repulsion toward the incoming secondary ligand (MATPH).

## EXPERIMENTAL

### Material and Measurements

All chemicals used were of analytical grade. Metal solutions were prepared in double distilled water and estimated by standard methods.

Solutions of sodium hydroxide (0.1 M), sodium perchlorate (1.0 M), 2,2'-bipyridyl, or 1,10-phenanthroline (in 50% dioxane) were prepared as usual.

MATPH was synthesized following the method of Bhandari [12] and its purity was established. A Cambridge bench-type pH meter was used for all pH measurements. It was standardized with suitable buffers. Nitrogen gas freed from carbon dioxide and oxygen was continuously passed over the solution to provide an inert atmosphere.

The titrations were carried out at 35 ± 0.5°C in a 50% (v/v) dioxane-water mixture at constant ionic strength (0.1 M, $NaClO_4$). The Irving-Rossotti pH titration technique [13] was employed for evaluating the stability constants of all the systems.

## The Acidity Constants of the Ligands and Stability of Binary Systems

The diprotonated forms of Bpy and Phen exist only in strongly acidic medium (cf. Table 1) and do not take part in complexation with metal ions. Hence $pK^H_{H_2A}$ values for Bpy and Phen have not been used in the calculations. For the evaluation of stability constants for the binary systems of each metal ion with primary and secondary ligands (in a 1:2 ratio), the titrations were performed under similar conditions using the same technique. The values for the binary system (1:2) have been computed by the least-squares method.

## Stability Constants of the Ternary Systems

For mixed ligand systems, five titration mixtures were prepared taking 1:1:1 as the metal primary ligand-secondary ligand ratio. Stability constant values have been evaluated using the Irving-Rossotti method.

In all systems the complexes are formed well before the hydrolyzing pH of the corresponding metal ion is reached.

The plots of pH against volume of alkali in the binary and ternary systems were obtained. $\bar{n}$ and pA values were obtained using the Irving-Rossotti method, and the formation constants were evaluated from the formation curves ($\bar{n}$ vs pA) corresponding to $\bar{n} = 0.5$. More precise values were obtained by plotting pA at each point against log $(1 - \bar{n})/\bar{n}$, which afforded a straight line. The average values thus obtained are listed in Tables 2 and 3.

# RESULTS AND DISCUSSION

## Reproportionation Constant, $K_d$

The constant which correlates the relative stability of the mixed ligand complexes with the parent complexes formed with the same

TABLE 1. Negative Logarithms of the Stability Constants of the Ligands in 50% Dioxane (I = 0.1 M NaClO₄; 35 ± 0.5°C)

| pK | Bipy | Phen | MATPH |
|---|---|---|---|
| $pK^{H}_{H_2L}$[a] | -0.50 | -1.60 | - |
| $pK^{H}_{HL}$ | 3.65 | 4.60 | 11.40 |

[a] W. A. E. McBryde, Can. J. Chem., 43, 2472 (1965).

ligand is termed the "reproportionation constant." It is obtained by the relation

$$\beta_{ij} = K_d \beta_{mo}^{i/m} \beta_{om}^{j/m} \qquad (m = 1 + j)$$

This constant gives a measure of the compatibility of either ligand in the inner sphere of the central metal ion. If the ligands are not compatible, the mixed ligand complexes so formed will be less stable than the parent complexes and the constant $K_d$ should be smaller than 1.

The results obtained are presented in Table 4. The values for $K_d$ in all systems suggest that the mixed ligand complexes are less stable since the values of $K_d$ are less than 1.

## Bond Strengths of M-Bpy/phen-MATPH Complexes

The strength of the individual M–A bonds in the complex $MA_iL_j$ can be calculated from the values of $\beta_{ij}$ (i.e., log $K^{MA}_{MAL}$) of the mixed complex and the parent complexes $MA_i$ and $ML_j$ using the equation

$$F_x = \frac{RT}{4_i} \ln \beta_{ij} \frac{\beta_{io}}{\beta_{oj}} \qquad (1)$$

Similarly, the M–L bond strengths in the same complex are given by

$$F_y = \frac{RT}{4_j} \ln \beta_{ij} \frac{\beta_{oj}}{\beta_{io}} \qquad (2)$$

The strength of the metal-ligand bonds in the parent complexes $MA_m$ and $ML_m$ can be obtained from

TABLE 2. Logarithms of the Equilibrium Constants of Binary Systems in 50% Dioxane (I = 0, 1 M, $NaClO_4$; 35 ± 0.5°C)

| Metal ions | Bipy as ligand | | | Phen as ligand | | | MATPH as ligand | | |
|---|---|---|---|---|---|---|---|---|---|
| | Log $k_1$ | Log $k_2$ | Log $k_1k_2$ | Log $k_1$ | Log $k_2$ | Log $k_1k_2$ | Log $k_1$ | Log $k_2$ | Log $k_1k_2$ |
| Cu(II) | 6.65 | 5.42 | 12.07 | 7.05 | 6.20 | 13.25 | 10.26 | 9.35 | 19.61 |
| Cd(II) | 4.54 | 3.15 | 7.69 | 5.62 | 4.85 | 10.47 | 9.86 | 9.60 | 19.46 |
| Zn(II) | 4.85 | 4.05 | 8.90 | 5.90 | 4.95 | 10.85 | 10.35 | 7.50 | 17.85 |
| Co(II) | 5.15 | 4.45 | 9.60 | 5.80 | 4.71 | 10.51 | 8.80 | 7.01 | 15.81 |
| Ni(II) | 6.05 | 5.02 | 11.07 | 6.50 | 5.28 | 11.78 | 9.70 | 6.78 | 16.48 |

TABLE 3. Logarithms of the Equilibrium Constants of Ternary Systems and Related Data in 50% Dioxane (I = 0.1 M $NaClO_4$; 35 ± 0.5°C)

| Metal ions | Bipy as primary ligand | | | | Phen as primary ligand | | | |
|---|---|---|---|---|---|---|---|---|
| | Log $K^{MA}_{MAL}$ | Log $K^{M}_{MAL}$ | $\Delta$ log $K_M$ | Log X | Log $K^{MA}_{MAL}$ | Log $K^{M}_{MAL}$ | $\Delta$ log $K_M$ | Log X |
| Cu(II) | 9.44 | 16.09 | -0.82 | +0.50 | 9.68 | 16.73 | -0.58 | +0.60 |
| Cd(II) | 9.12 | 13.66 | -0.74 | +0.17 | 9.45 | 15.07 | -0.41 | +0.21 |
| Zn(II) | 8.58 | 13.43 | -1.77 | +0.11 | 8.65 | 14.55 | -1.70 | +0.40 |
| Co(II) | 7.70 | 12.85 | -1.10 | +0.29 | 7.85 | 13.65 | -0.95 | +0.98 |
| Ni(II) | 7.91 | 13.96 | -1.79 | +0.37 | 8.12 | 14.62 | -1.58 | +0.98 |

TABLE 4. Reproportionation Constants of Ternary Complex, Bond Strengths (cal) of the Binary and Ternary Complexes

| Metal | $K_d$ | $F_{x'}$ M-A (Parent) | $F_x$ M-A-MATPH (Mixed) | $F_x - F_{x'}$ | $FY'_{\text{M-MATPH}}$ (Parent) | $FY_{\text{M-A-MATPH}}$ (Mixed) | FY - FY' |
|---|---|---|---|---|---|---|---|
| Cu(II) | 0.61[a] | 4253[a] | 2054[a] | -2199[a] | 6910 | 4598[a] | -2312[a] |
| | 0.60[b] | 4669[b] | 2280[b] | -2389[b] | | 4542[b] | -2368[b] |
| Cd(II) | 0.74[a] | 2710[a] | 1339[a] | -1371[a] | 6857 | 5088[a] | -1769[a] |
| | 0.66[b] | 3689[b] | 1836[b] | -1853[b] | | 4824[b] | -2033[b] |
| Zn(II) | 0.68[a] | 3136[a] | 1085[a] | -2051[a] | 6290 | 4958[a] | -1332[a] |
| | 0.62[b] | 3823[b] | 1480[b] | -2343[b] | | 4616[b] | -1674[b] |
| Co(II) | 0.63[a] | 3383[a] | 1427[a] | -1956[a] | 5571 | 3999[a] | -1572[a] |
| | 0.61[b] | 3703[b] | 1709[b] | -1994[b] | | 3823[b] | -1748[b] |
| Ni(II) | 0.59[a] | 3901[a] | 1501[a] | -2400[a] | 5807 | 4073[a] | -1734[a] |
| | 0.58[b] | 4151[b] | 1734[b] | -2417[b] | | 3988[b] | -1819[b] |

[a] Values for the systems with Bpy.
[b] Values for the system with Phen.

$$F_{x'} = \frac{RT}{2m} \ln \beta_{mo}; \qquad F_{y'} = \frac{RT}{2m} \ln \beta_{om} \tag{3}$$

The difference in the free energies calculated from Eqs. (1), (2), and (3) provides the changes of the M–A and M–L bond energies which occur in the mixed-ligand complex formation. The results of these investigations are reported in Table 4.

Perusal of Table 4 shows that the free energy and strength of all the metal-ligand bonds decreases. Thus a change in the geometry and type of bond in the formation of mixed ligand complexes from parent one does influence the stability of the mixed ligand complexes.

The stability of the mixed ligand complexes can also be characterized in two ways which are independent of basicity of Ligands A and L. The mixed ligand complex can be formed according to the equilibrium

$$M + A \rightleftharpoons MA; \qquad K^{M}_{MA} = \frac{[MA]}{[M][A]} \tag{4}$$

$$MA + A \rightleftharpoons MA_2; \qquad K^{MA}_{MA_2} = \frac{[MA_2]}{[MA][A]} \tag{5}$$

$$M + L \rightleftharpoons ML; \qquad K^{M}_{ML} = \frac{[ML]}{[MA][L]} \tag{6}$$

$$ML + L \rightleftharpoons ML_2; \qquad K^{ML}_{ML_2} = \frac{[ML_2]}{[ML][L]} \tag{7}$$

$$MA + L \rightleftharpoons MAL; \qquad K^{MA}_{MAL} = \frac{[MAL]}{[MA][L]} \tag{8}$$

The values of $\Delta \log K_M$, i.e., $\log K^{MA}_{MAL} - \log K^{M}_{ML}$, give an idea about the stability of the mixed ligand complex. Generally, the value of $\log K_M$ is negative since it usually holds [14] that $K^{M}_{ML} > K^{ML}_{ML_2}$. This is due to the fact that more coordination sites are available for bonding of the first ligand to a given metal ion than for the second ligand.

In the present case, $\Delta \log K_M$ values in all the systems investigated are negative, especially so in the case of Zn(II), Ni(II), and Co(II).

One expects to observe values for $\Delta \log K_M$ of about -1 to -2 log units for bidentate ligands [15]; for monomdentate ligands about 0.5 to 0.8 log unit. The results presented in Table 3 are in agreement with the above values except in the case of Cd(II). This may be due to some discriminating qualities of Bpy or Phen. Thus the $\Delta \log K_M$ values generally depend upon the coordination number of the metal ion and the denticity of the ligands.

Another, probably more convenient and surely more objective way to characterize the stability of the mixed ligand complexes is according to

$$MA_2 + ML_2 \rightleftharpoons 2MAL; \qquad X = \frac{[MAL]^2}{[MA_2][MB_2]} \tag{9}$$

$$\log X = 2 \log \beta^{M}_{MAL} - (\log \beta^{M}_{MA_2} + \log \beta^{M}_{ML_2}) \tag{10}$$

For purely statistical reasons, one expects that the value of X = 4, i.e., log X = 0.6 [16, 17].

The values obtained for log X (cf. Table 3) are nearly of the same magnitude (0.2 to 0.98), indicating the greater stability of the Cu(II), Ni(II), and Co(II) complexes.

In general, it can be argued that in the presence of M–S $\pi$-interaction [18-21], the values of $K^{MA}_{MAL}$ are significantly lower than $K^{M}_{ML}$, which may be due to the fact that the metal ions, having donated $\pi$-electrons to the Bpy or Phen molecule, have a much smaller tendency to form the M–S $\pi$-bond. Therefore, the M–S bonding, if present, should have reduced significantly the [M(Bpy)/(Phen)L] thus resulting in a lower value of $K^{MA}_{MAL}$.

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