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Ternary Complexes in Solution: Mixed Ligand Complexes of Co(II), Ni(II), Zn(II), or Cd(II) with N, S Donor Ligands*

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ABSTRACT

The stability constants of ternary Co(II), Ni(II), Zn(II), or Cd(II) complexes containing 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen) as a primary ligand and N-phenyl-2-mercaptopropionamide (PMP) as a secondary ligand in a 1:1:1 molar ratio were determined using the Irving-Rossotti pH-titration technique in a 70% (v/v) dioxane-water mixture ($I = 0.1$ $\underline{M}$ $NaClO_4$; $30 \pm 1°C$) in an inert atmosphere. The stability of these ternary complexes is discussed on the basis of π-accepting qualities of the sulfur ligand and the participating heteroaromatic N-base.

INTRODUCTION

The study of mixed ligand complexes has received considerable attention in recent years [1], where two or more ligands, other than the solvent molecule, combine with the metal ion either simultaneously or in a different pH range. Martell et al. [2] studied the mixed ligand system where two ligands combine in a different pH range and

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*Dedicated to the late N. C. Sogani.

the first ligand does not dissociate, even at higher pH. These ternary complexes are important in analytical chemistry [3] and metal ion catalyzed reactions [4, 5]. They appear in biological fluids and create specific structures [6]. The ligands containing O and N as donor atoms have shown that the stability of the mixed ligand complexes is strongly dependent on the kind of donor atoms and the possibility of π-bond formation [7-9]. Since S is also one of the more important donor atoms, being able to form both σ- and π-bonds, it is of considerable interest to learn something about the binding behavior of this atom in ternary complexes. The present communication deals with the mixed complexes of Co(II), Ni(II), Zn(II), or Cd(II) metal ions with 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen) as a first ligand and N-phenyl-2-mercaptopropionamide (PMP) as a second ligand. The stability constants of the binary and ternary complexes have been evaluated by the Irving-Rossotti pH-titration technique [10] in a 70% (v/v) dioxane-water mixture (I = 0.1 M, $NaClO_4$; 30 ± 1°C).

EXPERIMENTAL

Material and Measurements

All the reagent used were of Analytical Grade. Metal solutions were prepared in double distilled water and estimated by standard methods. Solutions of sodium hydroxide (0.2 M), sodium perchlorate (1.0 M), bipy, and phen (70% dioxane) were prepared as usual. Dioxane was purified by refluxing with sodium wire for 36 h and was freshly distilled over sodium before use. PMP was synthesized following the method of Guha and Sirkar [11] and its purity was checked by the iodine titration method [12] and thin-layer chromatography.

The titrations were carried out at 30 ± 1°C in a 70% (v/v) dioxane-water mixture with an E.C. model expanded scale pH meter in conjugation with a glass and calomel electrode assembly (0-14 pH range) and was standardized with potassium-hydrogen phthalate and phosphate buffers.

Procedure

For the mixed ligand system five mixtures were prepared in 70% (v/v) dioxane-water. In each case the total volume was kept at 50 mL and the ionic strength was maintained at 0.1 M $NaClO_4$ at 30 ± 1°C. The Irving-Rossotti method was employed for evaluating the stability constant for the binary and ternary systems.

For the Cd(II) ion the concentration of metal:primary ligand: secondary ligand was taken as half of that used in other metal ion systems to obtain heterogeneity at a higher concentration.

TABLE 1. Negative Logarithms of the Acidity Constants of the Ligands in 70% Dioxane (I = 0.1 M NaClO₄; 30 ± 1°C)

	bipy	phen	PMP
$K^H_{H_2L}$	-0.20[a]	-1.60[a]	10.12
K^H_{HL} [b]	3.36	4.11	12.72

[a] R. H. Linnell and A. Kaczmarzyk, J. Phys. Chem., 65, 1196 (1961).

[b] Values used in calculations.

The Acidity Constants of the Ligands

$K^H_{H_2L}$ values for bipy and phen were taken from a report by Linnell and Kaczmarczyk (reference in Table 1). K^H_{HL} values for bipy and phen, and $K^H_{H_2L}$ and K^H_{HL} values for PMP were determined using the Irving-Rossotti method under identical conditions. The values for PMP are in good agreement with the values reported from our laboratories [13].

Stability Constants of the Binary and Ternary Complexes

The stability constants for binary complexes were determined by titrating 50 mL of a 70% (v/v) dioxane-water mixture (0.012 M $HClO_4$; 0.1 M $NaClO_4$) in the presence and absence of the metal ion and the ligand in a ratio of 1:1 with 0.2 M NaOH under nitrogen. The titrations for the ternary systems were performed in the same way with metal:primary ligand:secondary ligand in a 1:1:1 ratio. The exact concentration in the different systems is given in Fig. 1.

Evaluation of Titration Data

$K^H_{H_2L}$ values for bipy and phen are too low and exist only in strongly acidic solution, hence are not used in the calculations. In the case of PMP, the K^H_{HL} value is used because the –NH proton is deprotonated during complexation and the sulfur of the sulfhydryl group acts as a coordinating atom [13, 14].

Plots of pH against the volume of alkali added are obtained.

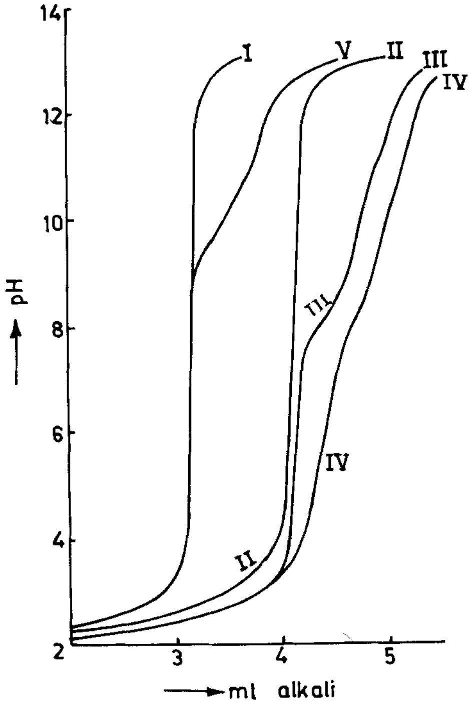

FIG. 1. Titration curves of the Co(III)-bipy-PMP system. I: 0.012 M $HClO_4$ and 0.1 M $NaClO_4$. II: 0.012 M $HClO_4$, 0.002 M bipy, and 0.1 M $NaClO_4$. III: 0.012 M $HClO_4$, 0.002 M bipy, 0.002 M Co(II) ion, and 0.1 M, $NaClO_4$. IV: 0.012 M $HClO_4$, 0.002 M bipy, 0.002 M PMP, 0.002 M Co(II) ion, and 0.1 M $NaClO_4$. V: 0.012 M $HClO_4$, 0.002 M PMP, and 0.1 M $NaClO_4$.

$\bar{n}$ and pA values are obtained using the Irving-Rossotti method, and the formation constants for binary and ternary systems are evaluated from the formation curves ($\bar{n}$ versus pA) corresponding to $\bar{n} = 0.5$.

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

Figure 1 shows one set of experimental data for the Co(II) ion with bipy and PMP.

RESULTS AND DISCUSSION

bipy or phen reacts with the metal ions at a lower pH as is evident from the titration Curve III (MA). The titration Curves IV (MAL) and

TABLE 2. Logarithms of the Equilibrium Constants of the Binary System in 70% Dioxane (I = 0.1 M $NaClO_4$; 30 ± 1°C)

Metal ions	$\log K^{M}_{M(bipy)}$	$\log K^{M}_{M(phen)}$	$\log K^{M}_{M(PMP)}$
Co(II)	4.24	4.94	10.89
Ni(II)	4.29	4.99	9.24
Zn(II)	4.18	4.83	10.14
Cd(II)	4.15	4.79	11.14

III (MA) overlap in the lower pH range, indicating that PMP does not combine with the metal ion in this pH range. At higher pH, one observes a divergence of Curve IV from Curve III, showing the coordination of PMP with the $[MA]^{2+}$ species. The $[MA]^{2+}$ species is quite stable up to the higher pH range where the attachment of PMP takes place, forming the ternary species MAL.

Stability of the Mixed Ligand Complexes

Stability of the mixed ligand complexes can be characterized by the difference in the stability constant of binary and ternary complexes (i.e., $\Delta \log K_M$) which is referred to the equilibrium

$$M + L \rightleftharpoons ML; \qquad K^{M}_{ML} = \frac{[ML]}{[M][L]} \tag{1}$$

$$MA + L \rightleftharpoons MAL; \qquad K^{MA}_{MAL} = \frac{[MAL]}{[MA][L]} \tag{2}$$

$$\Delta \log K_M = \log K^{MA}_{MAL} - \log K^{M}_{ML} \tag{3}$$

Perusal of Table 3 shows that the values of $\Delta \log K_M$ are negative in all systems since $K^{M}_{ML} > K^{ML}_{ML_2}$ [15]. This is due to the fact that more coordination positions are available for bonding of the first ligand to a given metal ion than for the second ligand.

Perhaps in the presence of significant M→S, π-interaction the value of K^{MA}_{MAL} is significantly lower than K^{M}_{ML} due to the fact that metal ions having donated π-electrons to the bipy or phen molecule have a

TABLE 3. Logarithms of the Equilibrium Constants of the Ternary Systems and Related Data in 70% Dioxane (I = 0.1 M NaClO$_4$; 30 ± 1°C)

Metal ions	bipy as primary ligand (A)			phen as primary ligand (A)		
	$\log K^{MA}_{MAL}$	$\log K^{M}_{MAL}$	$\Delta \log K_M$	$\log K^{MA}_{MAL}$	$\log K^{M}_{MAL}$	$\Delta \log K_M$
Co(II)	9.93	14.17	-0.96	9.63	14.57	-1.26
Ni(II)	8.83	13.12	-0.41	8.52	13.51	-0.72
Zn(II)	10.05	14.23	-0.09	9.98	14.81	-0.16
Cd(II)	10.45	14.60	-0.69	10.34	15.13	-0.80

much smaller tendency to form M→S, π-bonds. M→S, π-bonding, if present, should be reduced significantly in [M(bipy/phen)L] compared to ML_1, thus resulting in a lower value of K^{MA}_{MAL}.

The ternary complexes of PMP with the $[M(phen)]^{2+}$ species is less stable than with the $[M(bipy)]^{2+}$ species (cf. Table 3) as also observed from $\Delta \log K_M$ values. This may be due to the larger size of the $[M(phen)]^{2+}$ species than the $[M(bipy)]^{2+}$ species, and hence may cause steric hindrance to the incoming PMP moiety. The trend in the stability constant values of the ternary metal chelates has been found to be Cd(II) > Zn(II) > Co(II) > Ni(II), which does not agree with the sequence of metal chelate stability given by Irving and William for divalent metal ions. For ligands containing sulfur as the coordinating atom [16-18], a plausible explanation can be the back-donation tendency of electrons to go from the metal dπ-orbitals to the vacant d-orbitals of the coordinating sulfur atom [9, 19], and the π-accepting qualities of the heteroaromatic N-base (bipy or phen) in the case of Co(II) ternary complexes, which is especially less stable than Zn(II), unlike in the binary system. Perhaps in this case the participation of a heteroaromatic N-base with good π-acceptor properties does enhance the ternary complexes with Co(II) considerably less than it favors the one with Zn(II) ion.

Moreover, the strength of the donor π-electron depends on the mobility of d-electrons which can be characterized by the energy required for further ionization of the metal ion in question. Thus, the lower the third ionization potential, the more stable is the donor π-bond. However, no uniform generalization for the donor-acceptor relationship of the metal-sulfur link based on electronegativity, polarizability, dπ-pπ, or dπ-dπ bonding, and ligational free energy [20] has yet been evolved.

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