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R. S. Thakur[a]; C. S. Bhandari[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

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Ternary Complexes in Solution. Mixed Ligand Complexes of Co(II) or Ni(II) with Bidentate Mercaptoacid Amides*

R. S. THAKUR and C. S. BHANDARI

Department of Chemistry
University of Rajasthan
Jaipur, India

ABSTRACT

The stability constants of ternary Co(II) or Ni(II) complexes containing 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen) as primary ligand and N-phenyl 2-mercaptoacid amide (PMA), N-(p-chloro)phenyl-2-mercaptoacid amide (CPMA), N-(p-tolyl)-2-mercaptoacid amide (TMA) or N-(p-anisyl)-2-mercaptoacid amide (AMA) as secondary ligand were determined in 70% (v/v) dioxane-water medium at 30 ± 1°C and 0.1 M (NaClO$_4$) ionic strength in a nitrogen atmosphere. A study of Co(II) or Ni(II) in the presence of an equimolar concentration of the two ligands showed the formation of mixed ligand complexes containing a 1:1:1 molar ratio of metal and the two ligands. These ternary complexes are more stable than would be expected on a statistical basis, i.e., the difference, $\Delta \log K_M = \log K^{MA}_{MAL} - \log K^{M}_{ML}$, is positive (A = bipy or phen, L = secondary ligand). Further results suggest that both the ligands are incompatible toward the metal ions and hence the mixed-ligand complexes formed are relatively more stable.

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*Dedicated to the late Dr. N. C. Sogani.

INTRODUCTION

Mixed ligand complexes have received considerable attention in recent years [1] where two or more different ligands, other than solvent molecules, bond to the central metal ion. Such ternary complexes are important in analytical chemistry [2] and metal ion catalyzed reactions [3, 4]. They appear in biological fluids and create specific structures [5]. 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 [6-8]. 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. In the present communication all the substituted mercaptoacid amides (PMA, CPMA, TMA, or AMA) as a second ligand, having sulfur and nitrogen as potentially binding sites, were taken for the study of mixed ligand complexes including their stability and their possible structure. All the ternary complexes are formed in a stepwise manner according to the equilibriums

$$M^{2+} + \text{bipy/phen} \rightleftharpoons [\text{M(bipy)/(phen)}]^{2+} \qquad (1)$$

$$[\text{M(bipy)/(phen)}]^{2+} + L^{-} \rightleftharpoons [\text{M(bipy)/(phen)L}]^{+} \qquad (2)$$

$$K^{\text{M(bipy)/(phen)}}_{\text{M(bipy)/(phen)L}} = \frac{[\text{M(bipy)/(phen)L}]}{[\text{M(bipy)/(phen)}][L]} \qquad (3)$$

The stability constants of binary and ternary complexes have been evaluated by the Irving-Rossotti pH-titration technique [9] in a 70% (v/v) dioxane-water medium (I = 0.1 M, $NaClO_4$, 30 ± 1°C).

EXPERIMENTAL

Material and Measurements

All the reagents 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 (in 70% dioxane) were prepared as usual. The ligands PMA, CPMA, TMA, and AMA were synthesized following the method of Mishra and Guha Sirkar [10] and their purity was checked by the iodine titration method [11] and thin-layer chromatography.

The titrations were carried out under nitrogen in 70% (v/v)

TABLE 1. Negative Logarithms of Acidity Constants of the Ligands and Logarithms of Stability Constants in 70% Dioxane ($I = 0.1$ M, $NaClO_4$, 30 ± 1°C)

Ligands	$pK^{H}_{H_2L}$	pK^{H}_{L}[a]	$\log K^{Co}_{CoL}$	$\log K^{CoL}_{CoL_2}$	$\log K^{Co}_{CoL_2}$	$\log K^{Ni}_{NiL}$	$\log K^{NiL}_{NiL_2}$	$\log K^{Ni}_{NiL_2}$
Bipy	-0.20[b]	3.36	4.24	3.85	8.09	4.29	4.07	8.36
Phen	-1.60[b]	4.11	4.94	4.46	9.40	4.99	4.55	9.54
PMA	9.96	12.63	8.12	6.84	14.96	8.44	7.65	15.09
CPMA	9.55	12.54	7.58	6.99	14.57	7.80	6.83	14.63
TMA	10.09	12.71	8.98	6.95	15.93	9.16	7.87	17.03
AMA	10.10	12.64	8.88	6.93	15.81	9.05	7.80	16.85

[a] Values used in calculations.

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

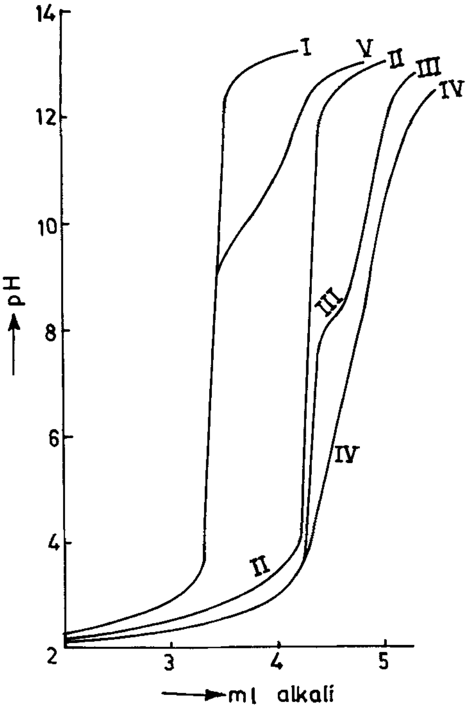

FIG. 1. Titration curves of the Ni(II)-bipy-PMA system. I: 0.012 M HCl_4, 0.1 M $NaClO_4$. II: 0.012 M $HClO_4$, 0.002 M bipy, 0.1 M $NaClO_4$. III: 0.012 M $HClO_4$, 0.002 M bipy, 0.002 M Ni(II) ion, 0.1 M $NaClO_4$. IV: 0.012 M $HClO_4$, 0.002 M bipy, 0.002 M PMA, 0.002 M Ni(II), 0.1 M $NaClO_4$. V: 0.012 M $HClO_4$, 0.002 M PMA, 0.1 M $NaClO_4$.

dioxane-water mixtures with an ionic strength of I = 0.1 ($NaClO_4$) at 30 ± 1°C with an E.C. model expanded scale pH-meter.

Procedure

The experimental procedure was the same as reported previously [12]. The constants due to binary and ternary complexes were evaluated using the Irving-Rossotti technique. The least-square method was employed to determine the precision of the stability constants of binary complexes. For ternary complexes, more precise values were obtained by plotting pA at each point against log $(1 - \bar{n})/\bar{n}$, which gave a straight line. Thus the average values were obtained. $K^{H}_{H_2L}$ values for bipy and phen were too low to be used in calculation (cf. Table 1), hence they were not used.

In all the mono-substituted mercaptoacid amides, it is the –NH proton which is deprotonated, and the sulfur of the sulfydryl group acts as the coordinating atom [13], hence only pK_{NH} values (cf. Table 1) were used in evaluating the stability constant data.

Figure 1 shows the experimental data for the Ni(II)-bipy-PMA system.

In all systems the ternary complexes are formed well before the hydrolyzing pH of the corresponding metal ions.

RESULTS AND DISCUSSION

Observation of Fig. 1 reveals that the metal-primary ligand Curve III diverges from the primary ligand Curve II at low pH, indicating the formation of a binary (1:1) complex. The binary (1:1) species is quite stable up to higher pH values. Metal-primary ligand-secondary ligand Curve IV and metal-primary ligand Curve III overlap each other at low pH. This indicates that the attachment of the secondary ligand with the binary (1:1) species does not take place in the low pH region. Curve IV diverges from Curve III, indicating the formation of a ternary species. Since dissociation of the primary ligand does not take place in the pH range of association with the secondary ligand, it can be inferred that the attachment of the secondary ligand with $[MA]^{2+}$, i.e., (1:1) species, has taken place. A superficial glance at the stability data due to binary complexes in Table 1 reveals that these complexes are more stable, as is to be expected. But a closer examination of the stability of these binary complexes shows that it is necessary to consider the somewhat different basicity of the imino group of these ligands. This can be achieved by plotting the stability constants against the acidity constants. For a series of structurally similar ligands, a straight line should be obtained [14-16]. In fact, a plot of the data in Table 1 results in a straight line, as seen in Fig. 2, which is straight within experimental error. Thus it is believed that all the binary complexes with secondary ligands in Table 1 have the same structure.

The stability of the mixed ligand complexes, [M(bipy)/(phen)L], also seems to be dependent on the nature of the imino group, as can be seen from the results presented in Table 2. Plots of the stability constants $\log K^{M(bipy/phen)}_{M(bipy/phen)L}$ versus the acidity constants pK^{H}_{HL} also give a straight line within experimental error.

Stability of the Mixed Ligand Complexes

The stability of the ternary complexes can be characterized by the difference in the stability constants $\Delta \log K_M$ in the equilibrium

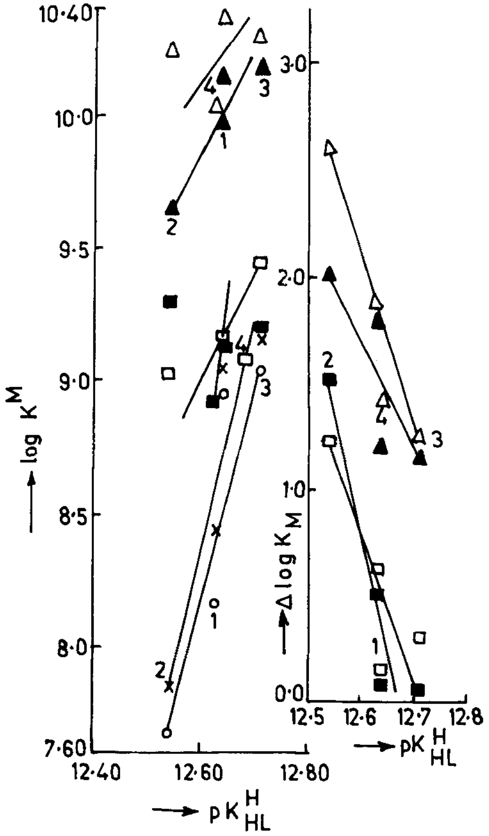

FIG. 2. Relation between pK^{H}_{HL} and ($\log K^{M}$ or $\Delta \log K_{M}$). (○) $\log K^{Co}_{CoL}$, (×) $\log K^{Ni}_{NiL}$, (□) $\log K^{Co(bipy)}_{Co(bipy)L}$, (△) $\log K^{Ni(bipy)}_{Ni(bipy)L}$, (■) $\log K^{Co(phen)}_{Co(phen)L}$, (▲) $\log K^{Ni(phen)}_{Ni(phen)L}$.

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

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

$$\Delta \log K_{M} \doteq \log K^{MA}_{MAL} - \log K^{M}_{ML} \tag{6}$$

TABLE 2. Logarithms of Stability Constants of Some Ternary Systems in 70% Dioxane (I = 0.1 M, $NaClO_4$, 30 ± 1°C)

Secondary ligand (L)	Co(II) ion with				Ni(II) ion with			
	bipy as primary ligand (A)		phen as primary ligand (A)		bipy as primary ligand (A)		phen as primary ligand (A)	
	$\log K^{MA}_{MAL}$	$\log K^{M}_{MAL}$	$\log K^{MA}_{MAL}$	$\log K^{M}_{MAL}$	$\log K^{MA}_{MAL}$	$\log K^{M}_{MAL}$	$\log K^{MA}_{MAL}$	$\log K^{M}_{MAL}$
PMA	9.13	13.37	9.15	14.09	10.08	15.37	10.06	15.05
CPMA	9.03	13.27	9.11	14.05	10.13	14.42	9.58	14.57
TMA	9.51	13.75	9.24	14.18	10.37	14.66	10.22	15.21
AMA	9.23	13.47	9.21	14.15	10.31	14.60	10.15	15.14

TABLE 3. Values of $\Delta \log K_M$ and log X of Some Ternary Complexes

Systems	log X	$\Delta \log K_M$
Co(II)-bipy-PMA	3.69	+1.01
Co(II)-bipy-CPMA	3.88	+1.45
Co(II)-bipy-TMA	3.48	+0.53
Co(II)-bipy-AMA	3.04	+0.35
Ni(II)-bipy-PMA	4.29	+1.64
Ni(II)-bipy-CPMA	5.85	+2.33
Ni(II)-bipy-TMA	3.93	+1.21
Ni(II)-bipy-AMA	3.99	+1.26
Co(II)-phen-PMA	3.82	+1.03
Co(II)-phen-CPMA	4.13	+1.53
Co(II)-phen-TMA	3.83	+0.26
Co(II)-phen-AMA	3.09	+0.33
Ni(II)-phen-PMA	4.46	+1.62
Ni(II)-phen-CPMA	4.97	+1.78
Ni(II)-phen-TMA	3.85	+1.06
Ni(II)-phen-AMA	3.89	+1.10

Generally $\Delta \log K_M$ is negative because usually $K^{M}_{ML} > K^{ML}_{ML_2}$ [17]. 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. To get a broader basis for the discussion and to be able to evaluate the specific influence of a ligand like bipy or phen on the stability of mercaptoacid amide complexes, one has to look at the comparative stability data of the binary and ternary complexes (cf. Tables 1 and 2).

In Table 3 the $\Delta \log K_M$ values for the systems investigated are given as calculated according to Eq. (6). In all the systems evaluated, the value of $\Delta \log K_M$ is positive. This is quite surprising since usually negative values are observed. In the present case the coordination of the $[M(bipy/phen)]^{2+}$ species and the sulfhydryl sulfur atom may result in a positive $\Delta \log K_M$ value which is generally seen in the case of ligands containing O-atoms as donors [6, 7, 18, 19]. Another, probably more convenient and surely more objective way to characterize the stability of the mixed ligand complexes is according to Eq. (8):

$$MA_2 + ML_2 \rightleftharpoons 2\,MAL; \qquad X = \frac{[MAL]^2}{[MA_2][ML_2]} \tag{7}$$

$$\log x = 2 \log \beta^M_{MAL} - (\log \beta^M_{MA_2} + \log \beta^M_{ML_2}) \tag{8}$$

For purely statistical reasons, one expects that the value of X will be 4, i.e., log x = 0.6 [20, 21]. The values obtained for log x (Table 3) are nearly of the same magnitude in all systems, indicating that all the mixed ligand complexes are stable.

Reproportionation Constant, K_d

The constant which correlates the stability of the mixed ligand complexes with the parent complexes formed with the same ligands is termed the reproportionation constant. The correlation between the formation constant and the reproportionation constant is given by

$$\beta_{ij} = K_d \beta^{i/m}_{m,o} \beta^{j/m}_{o,m} \qquad (m = i + j) \tag{9}$$

where K_d is the reproportionation constant, which gives a measure of the compatibility of different ligands in the inner sphere of a given metal ion. If the ligands are not compatible, then the mixed ligand complex formed will be less stable than the parent complex. In such cases the reproportionation constant should be smaller than unity. In the case of compatibility of ligands, this constant is larger than unity. The results presented in Table 4 indicate that the value of K_d is nearly unity, confirming the stability of all the ternary complexes. Moreover, the values of K_d in all the systems investigated are quite close to one another, which clearly indicates that Co(II) and Ni(II) ions behave in the same manner.

Bond Strengths of Ternary Complexes

The strength of the individual M–A bonds in the complex MA_iL_j can be calculated from the formation constants of the mixed ligand complexes and the parent complexes MA_i and ML_j by using

TABLE 4. Reproportionation Constants and Bond

	Co(II) ion						
Secondary ligands	K_d	Fx' (parent)	Fx (mixed)	(Fx - Fx')	Fy' (parent)	Fy (mixed)	(Fy - Fy')
PMA	0.83[a]	2940	1820[a]	-1120[a]	5629	4510[a]	-1119[a]
	0.77[b]		2069[b]	-871[b]		4274[a]	-1355[b]
CPMA	0.83[a]		1972[a]	-968[a]	5255	4288[a]	-967[a]
	0.78[b]		2243[b]	-697[b]		4073[b]	-1182[b]
TMA	0.84[a]		1653[a]	-1387[a]	6226	4940[a]	-1286[a]
	0.76[a]		1802[b]	-1138[b]		4603[b]	-1623[b]
AMA	0.82[a]		1591[a]	-1349[a]	6156	4808[a]	-1348[a]
	0.76[b]		1827[b]	-1113[b]		4558[b]	-1598[b]

[a] Systems with bipy as primary ligand.
[b] Systems with phen as primary ligand.

$$Fx = \frac{RT}{4i} \ln \beta_{ij} \frac{\beta_{i,o}}{\beta_{o,j}} \qquad (10)$$

Similarly, the M–L bond strength in the same complex is given by

$$Fy = \frac{RT}{4j} \ln \beta_{ij} \frac{\beta_{o,j}}{\beta_{i,o}} \qquad (11)$$

The strength of the metal-ligand bond in the parent complexes MA_m and ML_m can be calculated from their formation constants:

$$Fx' = \frac{RT}{2m} \ln \beta_{m,o}; \qquad Fy' = \frac{RT}{2m} \ln \beta_{o,m} \qquad (12)$$

Strengths (cal) of Various Mixed Ligand Complexes

Ni(II) ion

K_d	Fx' (parent)	Fx (mixed)	(Fx - Fx')	Fy' (parent)	Fy (mixed)	(Fy - Fy')
0.87^a	2974	2056^a	-918^a	5851	4933^a	-918^a
0.82^b		2291^b	-683		4983^b	-868^b
0.91^a		2295^a	-679^a	5408	4728^a	-680^a
0.81^b		2347^b	-627^b		4295^b	-1113^b
0.87^a		1907^a	-1067^a	6350	5283^a	-1067^a
0.80^b		2097^b	-877^b		4988^b	-1362^b
0.87^a		1924^a	-1050^a	6274	5224^a	-1050^a
0.80^b		2111^b	-863^b		4926^b	-1348^b

The differences in the free energies calculated from Eqs. (10), (11), and (12) characterize the change of the M–A and M–L bond energies which occur in the mixed complex formation. The results are presented in Table 4. They suggest the relative stability of mixed ligand complexes with either of the ligands that are incompatible for forming mixed complexes with Co(II) or Ni(II) ions. In mixed ligand complexes formed by such incompatible ligands, the free energies and the strength of all the metal-ligand bonds decreases [22], as is evident from the data in Table 4. This is probably due to the difference in the geometrical structure and bond type of the complexes [23].

Further, in addition to conventional σ-bond formation in the metal complexes, there exists a possibility of back-donation of π-electrons from the filled d-orbitals of the metal to empty d-orbitals of the ligand sulfur atom. In addition to the above, there also exists dπ-pπ, M → N bond interactions in ternary complexes due to the availability of π-delocalized orbitals of the bipy/phen molecule. As the coordinating sites in all the secondary ligands are identical, and the bridging groups between the two pyridyl moieties are also of the same nature, the observed difference in stability of the resulting ternary complexes for a given metal ion can be attributed solely to the preferential π-accepting properties of heteroaromatic N-base and the relative steric strain due to the secondary ligand moiety. Moreover, it can be concluded that these ternary complexes are more stable due to the better π-accepting properties of the participating heteroaromatic N-base.

The stability of the binary complexes and those of the mixed ligand complexes are somewhat different and are independent of the basicity of the N-aryl substituted mercaptoacid amides. Hence, if $\Delta \log K_M$ is plotted (Fig. 2) against pK^H_{HL}, a straight line is expected. Actually, a straight line between $\Delta \log K_M$ versus pK^H_{HL} for the structurally related ligands is obtained. However, in general no definite conclusion depending on the basicity of the ligands with regard to the stability may be drawn.

Having these aspects in mind and looking at the $\Delta \log K_M$ values in Table 3, one can draw some conclusion regarding the relative stabilities of the ternary complexes. In the present case, the ternary complexes formed by AMA or TMA with the $[M(bipy)/(phen)]^{2+}$ species seem to be quite stable in general (cf. $\Delta \log K_M$ values). Moreover, these ligands are comparatively more basic in nature, and consequently they influence the nature of the ternary complexes. Looking at Table 3, it is quite interesting to compare the stability of the ternary complexes of $[Co(bipy)]^{2+}$ or $[Ni(bipy)]^{2+}$ with the corresponding $[Co(phen)]^{2+}$ or $[Ni(phen)]^{2+}$ ternary complexes. For the latter case, $\Delta \log K_M$ is less positive. In other words, surprisingly more stability of the ternary complexes is lost when 2,2'-bipyridyl is replaced by phenanthroline. This is evidence that in these ternary complexes (unlike the binary systems), 2,2'-bipyridyl is more responsible for the higher stability and the ligand has an obvious stability increasing effect in the present study in comparison to phenanthroline.

Perhaps the π-acceptor qualities of the pyridyl group are more pronounced in 2,2'-bipyridyl or the incoming of the secondary ligand molecule to the $[M(phen)]^{2+}$ species is hindered due to its bulky molecule.

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