Ternary Complexes in Solution: Mixed Ligand Pb(II) Complexes with 2,2'-Bipyridyl or 1,10-Phenanthroline and Some Bivalent Mercapto Acid Amides

R. S. Thakur[a]; S. P. Mathur[a]; C. S. Bhandari[a]

[a] Department of Chemistry, University of Rajasthan, Jaipur, India

PLEASE SCROLL DOWN FOR ARTICLE

Ternary Complexes in Solution: Mixed Ligand Pb(II) Complexes with 2,2′-Bipyridyl or 1,10-Phenanthroline and Some Bivalent Mercapto Acid Amides

R. S. THAKUR, S. P. MATHUR, and C. S. BHANDARI

Department of Chemistry
University of Rajasthan
Jaipur, India

ABSTRACT

The stability constants of ternary Pb(II) complexes containing 2,2'-bipyridyl (Bipy) or 1,10-phenanthroline (phen) as the first ligand and N-phenyl-2-mercapto acid amide, N-(p-chloro)phenyl-2-mercapto acid amide, N-(p-tolyl)-2-mercapto acid amide, N-(p-anisyl)-2-mercapto acid amide, or N-phenyl-2-mercapto-propionamide as the second ligand were determined in 70% v/v dioxane-water medium at $30 \pm 1°C$ and constant ionic strength (0.1 M $NaClO_4$) in a nitrogen atmosphere. The results give evidence that all these complexes have the same structure and therefore the binding sites of the ligands have to be the imino nitrogen and sulfur of the sulfhydryl group. The stability difference between the ternary and the binary complexes are in good agreement with this interpretation. It is of interest to note that these ternary complexes are significantly more stable than expected from statistical reasons, i.e., the difference; $\Delta \log K_M^M = \log K_{MAL}^{MA} - \log K_{ML}^{M}$ is positive (except for PMP) (where A = Bipy or phen and L is the second ligand). In addition, the enhanced stability of the ternary complexes is suggested on the basis of the π-accepting qualities of the hetero aromatic N-base. The effect of the chelate ring size is discussed.

INTRODUCTION

In recent years there has been increased interest in the study of mixed ligand complexes [1] in which two or more different ligand molecules, other than the solvent molecule, combine with the metal ion. These are important in analytical chemistry [2] and metal-ion catalyzed reactions [3, 4]. They appear in biological fluids and create specific structures [5]. The ternary complexes containing ligands with oxygen as a coordinating atom are found to be more stable [6]. In other words, a positive Δ log K_M as defined by Eq. (3) is obtained.

The ligands containing O and N as donors have shown that the stability of the mixed ligand complexes is strongly dependent on the kind of donor atoms available and the possibility of π-bond formation [6, 7].

Sulfur is also one of the more important donor atoms, being able to form both σ- and π-bonds. It is of considerable importance to learn something about the binding behavior of this atom in ternary complexes. In the present communication all the substituted mercapto acetamides used have sulfur and N-atoms as potential binding sites; hence they are used for the study of the stability and structure of mixed ligand complexes. The acidity constants of the ligands and the stability constants of binary and ternary complexes were determined using the Irving-Rossotti pH titration technique [8] in a 70% (v/v) dioxane medium (I = 0.1 $\underline{M}$ NaClO$_4$, 30 $\pm$ 1°C) under a nitrogen atmosphere.

EXPERIMENTAL

Material and Measurements

All the chemicals used were of analytical grade. Metal solutions were prepared in double distilled water and estimated by standard methods. Solutions of sodium hydroxide (carbonate free, 0.2 $\underline{M}$), sodium perchlorate (1.0 $\underline{M}$), Bipyridyl, and phenanthroline were prepared as usual. Ligands N-phenyl-2-mercapto acid amide (PMA), N-(p-chloro)phenyl-2-mercapto acid amide (CPMA), N-(p-tolyl)-2-mercapto acid amide (TMA), N-(p-anisyl)-2-mercapto acid amide (AMA), and N-phenyl-2-mercaptopropion amide (PMP) were synthesized following the method of Guha Sirkar [9] and their purity was checked by the iodine titration method [10] and thin-layer chromatography.

The pH meter (E.C. model, expanded scale) was calibrated before and after each titration set with suitable buffer solutions (pH 4.0 and 7) and the direct readings for pH were used in the calculations. No corrections were applied for the change in solvent (70% dioxan-water medium, I = 0.1 $\underline{M}$ NaClO$_4$, 30 $\pm$ 1°C).

Procedure

For the mixed ligand systems five mixtures were prepared in 70% (v/v) dioxane (cf. Fig. 1). In each case the total volume was kept at 50 mL and the ionic strength was kept at 0.1 $\underline{M}$ (NaClO₄) at 30 ± 1°C.

The Acidity Constants of the Ligands

$K^H_{H_2L}$ values for Bipy and phen are taken from a report of Linnell (see footnote reference in Table 1). K^H_{HL} values for Bipy and phen, and $K^H_{H_2L}$ and K^H_{HL} values for all the secondary ligands were determined in 70% (v/v) dioxane under identical conditions using the Irving–Rossotti method. The values for secondary ligands are in close agreement with the reported values from our laboratories [11].

Stability of Binary and Ternary Complexes

The stability constants of binary systems were evaluated from the titration of 50 mL of a 70% (v/v) dioxane-water mixture (0.012 $\underline{M}$ HClO₄, 0.1 $\underline{M}$ NaClO₄) in the presence and absence of the metal ion and the ligand in the ratio of 1:1 under nitrogen with 0.2 $\underline{M}$ NaOH. The titrations for ternary systems were performed in the same way with the metal ion, primary ligand, and secondary ligand present in the ratio 1:1:1. The exact concentrations in the different systems evaluated are given in Fig. 1.

Evaluation of the Titration Data

$pK^H_{H_2L}$ values for Bipy and phen are very low and exist in strongly acid solution. Therefore these values are not taken into account in the calculations. All the secondary ligands are structurally similar and the −NH proton is deprotonated in them, whereas the sulfur atom in these ligands acts as a coordinator. Hence only pK_{NH} was used in evaluating the stability constants data (cf. Table 1).

Plots of pH against the volume of the alkali added were obtained. $\bar{n}$ and pA values are evaluated using the Irving–Rossotti pH titration technique. The formation constants for binary and ternary systems were obtained from formation curves ($\bar{n}$ versus pA) corresponding to $\bar{n} = 0.5$.

In all the systems the binary and ternary complexes are formed before the hydrolyzing pH of the Pb(II) ion.

Figure 1 shows one set of experimental data for Pb(II) with Bipy and PMA. Other data of a similar nature are not shown.
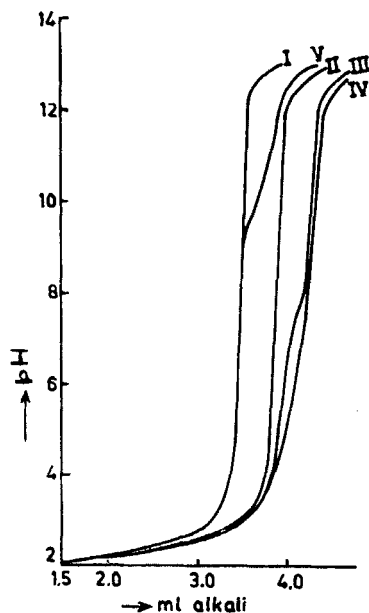
FIG. 1. Titration curves of the Pb(II)-Bipy-PMA system. I: 0.012 M HClO$_4$, 0.1 M NaClO$_4$. II: 0.012 M HClO$_4$, 0.002 M Bipy, 0.1 M NaClO$_4$. III: 0.012 M HClO$_4$, 0.002 M Bipy, 0.002 M Pb(II) ion, 0.1 M NaClO$_4$. IV: 0.012 M HClO$_4$, 0.002 M Bipy, 0.002 M PMA, 0.002 M Pb(II), 0.1 M NaClO$_4$. V: 0.012 M HClO$_4$, 0.002 M PMA, 0.1 M NaClO$_4$.

RESULTS AND DISCUSSION

Observation of Fig. 1 reveals that the metal-Bipy Curve III diverges from the M-Bipy Curve II at a low pH, indicating the formation of a 1:1 complex which is complete below pH 3.5 in nearly all cases. The 1:1 species is quite stable up to a higher pH. Curve IV (metal:Bipy:second ligand) overlaps with Curve III (metal:Bipy) at a lower pH, indicating no attachment of secondary ligand with the 1:1 species at a lower pH. Curve IV diverges from Curve III, indicating the formation of a mixed ligand complex. As a 1:1 complex does not dissociate in the pH range of association of a secondary ligand, it can be inferred that the secondary ligand combines with the 1:1 species to form a mixed ligand complex.

Bipy and phen are neutral molecules. Both N-atoms are coordinating with the metal ion in them whereas in N-aryl monosubstituted

TABLE 1. Negative Logarithms of Acidity Constants of the Ligands and Logarithms of the Stability Constants of Binary Pb(II) Complexes in 70% Dioxane (I = 0.1 $\underline{M}$ NaClO$_4$, 30 ± 1° C)

Ligands, L	$pK^H_{H_2L}$	pK^{Ha}_{HL}	$\log K^{Pb}_{PbL}$	$\log K^{Pb}_{Pb}c$
Bipy	-0.20[b]	3.36	4.20	-
phen	-1.60[b]	4.11	4.68	-
PMA	9.96	12.63	11.22	9.37
CPMA	9.55	12.54	11.40	8.80
TMA	10.09	12.71	11.70	9.35
AMA	10.10	12.64	11.10	8.96
PMP	10.12	12.72	11.39	-

[a]Values used in calculations.
[b]R. H. Linnell and A. Kaczmarzyk, J. Phys. Chem., 65, 1196 (1961).
[c]N-Aryl monosubstituted 3-mercaptopropion amide (unpublished results). For PMA, N-phenyl-; for CPMA, N-(p-chloro)phenyl-; for TMA, N-(p-tolyl)-; for AMA, N-(p-anisyl)-.

mercapto acid amides as well as in PMP the −NH proton is replaced during complexation and the sulfur atom of the sulfhydryl group acts as a coordinating atom. The following possible Structures A and B for the resulting binary and ternary complexes are proposed:
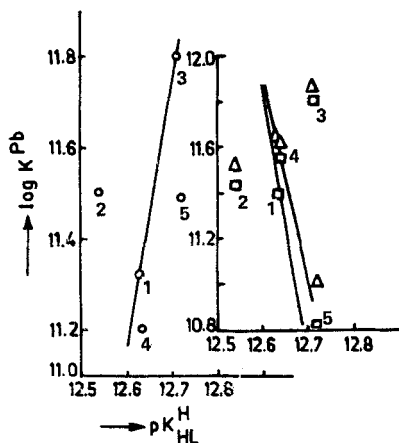

(−5 membered ring)

(−6 membered ring)

A   B
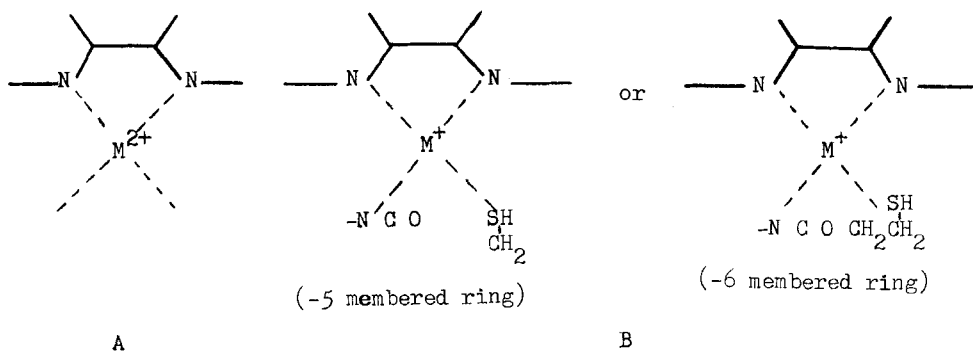
FIG. 2. Relation between log K^{Pb} and pK_{HL}^H: ($\circ$) log K_{Pb}^{Pb}, ($\square$, $\triangle$) log $K_{Pb(Bipy)}^{Pb(Bipy)}$.

The results for binary complexes in Table 1 indicate that these complexes are more stable,* as expected [12]. For a closer examination of the stability of these binary complexes, it is necessary to consider the somewhat different basicity of the imino group of these substituted ligands. This can be achieved by plotting the stability constants against the acidity constants. For a series of structurally similar ligands, a straight line is expected [13-15]. In fact, a plot of the data in Table 1 results in a line which is straight within experimental error (Fig. 2). Thus the binary complexes with the ligands in Table 1 have the same basic structure, and the carbonyl oxygen of the ligands has no role in the stability of the metal complexes. It is quite interesting to observe that if there is a long tail, i.e., in an aryl monosubstituted 3-mercapto propionamide (−NHCOCH$_2$CH$_2$SH), with the carbonyl oxygen in the potential binding site and the functional sulfhydryl proton remaining the same, it affects the stability of the metal complexes. By knowing the stability constants data for N-aryl substituted 3-mercapto propionamide (cf. Table 1), one can conclude that the stability is lowered in these cases
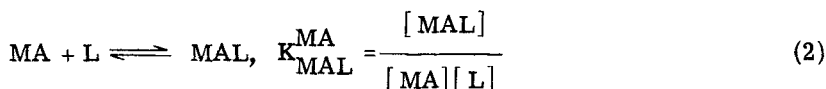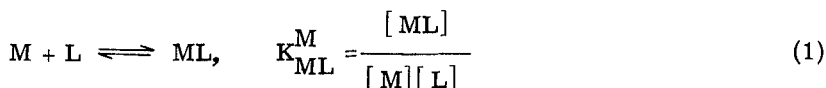
---

*An intramolecular hydrogen bonding between the −NH hydrogen and the sulfur of the sulfhydryl group in the N-aryl monosubstituted mercapto acid amide and propion amide is obtained; i.e., in such a situation the detachment of the −NH proton becomes more difficult, thus raising the pK$_{NH}$ values. Consequently, the complex formed is more stable if the −NH proton is being pushed away by the metal ion.

and can be thought to be due to the six-membered chelate ring which is less stable than a five-membered ring in the case of N-aryl mono-substituted mercapto acid amides. Thus an increase in the length of the side chain significantly decreases the stability of the metal complexes where the basicity of the binding site is a dominating factor.

The main difference between the ternary and binary complexes is that only two coordination positions of an M^{2+} ion are occupied by a primary ligand and the remaining two are left for interaction with the secondary ligand. The stability of the mixed ligand complexes seems to be dependent on the nature of the –NH imino group, as can be seen from the data in Table 2. When the stability constants of the mixed ligand complexes are plotted against the acidity constants of the ligands, a line which is straight within experimental errors results. This again suggests the same principal structure for the resulting mixed ligand complex in solution, i.e., Structure C.

Stability of the Mixed-Ligand Complexes

The stability of mixed ligand complexes can be characterized by the difference in their stability constants, $\Delta \log K_M$, according to

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

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

where A = Bipy or phen, and L is a secondary ligand.

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

Generally the value of $\Delta \log K_M$ is negative because $K^M_{ML} > K^M_{ML_2}$ [16] since more coordination positions are available for the first ligand to be bound to the M^{+2} aq ion than for the second ligand. To get a broader basis for discussion and to be able to draw conclusions regarding the specific influence of ligands such as Bipy or phen on the N-aryl substituted mercapto acid amide complexes, it is necessary to compare the stability data of binary and ternary complexes (cf. Table 2). Except in the case of PMP ligand, the $\Delta \log K_M$ values for all the systems investigated are positive. This is quite interesting since generally the values of $\Delta \log K_M$ are negative. In this case the

TABLE 2. Logarithms of the Stability Constants of Ternary Pb(II) Complexes and the Values of log K_M in 70% Dioxane (I = 0.1 M NaClO₄), 30 ± 1°C)
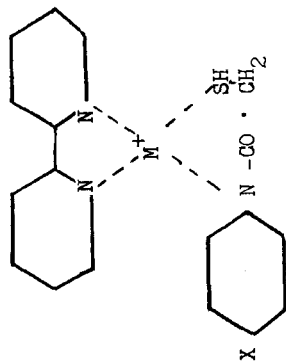
Secondary ligands	log $K^{Pb(Bipy)}_{Pb(Bipy)L}$	log $K^{Pb}_{Pb(Bipy)L}$	log K_M	log $K^{Pb(phen)}_{Pb(phen)L}$	log $K^{Pb}_{Pb(phen)L}$	log K_M
PMA	11.39	15.59	+0.17	11.63	16.31	+0.41
CPMA	11.44	15.64	+0.04	11.53	16.21	+0.13
TMA	11.81	16.01	+0.11	11.86	16.54	+0.16
AMA	11.55	15.75	+0.45	11.62	16.30	+0.52
PMP	10.83	15.03	-0.56	11.08	15.76	-0.31
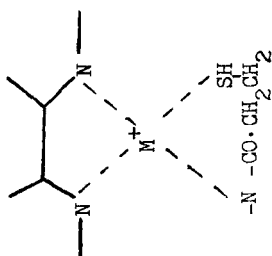
(-1 five and 1 six membered ring)
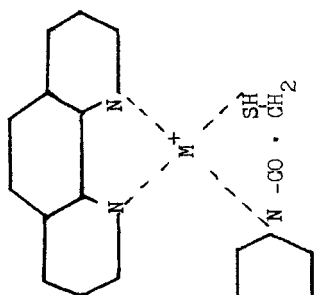
(2 five membered rings)

or

c

$[X = H, -Cl, -CH_3$ or $-CCH_3]$

positive $\Delta \log K_M$ values indicate relatively more stability of these
ternary complexes. Moreover, the coordination of $[MA]^{2+}$ species
with the secondary ligands, where a sulfur atom of the sulfhydryl group
is one of the coordinating sites, may result in more stable ternary
complexes. Similarly, a positive $\Delta \log K_M$ is also observed in ligands
containing O-donor atoms [17, 18]. It may also be that for a positive
$\Delta \log K_M$ value, the geometry of $[MA]^{2+}$ is such that it has a greater
preference for the secondary ligands than for the aquo metal $[M(H_2O)_2]^{2}$
species. Consequently, due to the resultant π-interaction in the M → N
bond, the electronegativity around the metal ion in the $[MA]^{2+}$ complex
does not increase significantly. Hence the electronegativity around
the metal ion in MA^{2+} is almost the same as in $[M(H_2O)_n]^{2+}$, thus
giving a positive $\Delta \log K_M$ value. Further, in addition to conventional
σ-bond formation in the metal complexes, there exists a possibility
of back-donating of π-electrons from the filled d-orbitals of the metal
to empty d-orbitals of the ligand sulfur atom. Additionally, there also
exist $d\pi$-$p\pi$, M → N bond interactions in ternary complexes, and MAL
is due to the availability of π-delocalized orbitals of Bipy or phen
molecules.

As the coordinating sites of all the secondary ligands are identical,
and bonding of the Bipy or phen moieties are also of the same nature,
the observed difference in the stability of the ternary complexes for
the Pb(II) metal ion is due to the π-accepting properties of the hetero
aromatic N-base and the relative steric strain due to the secondary
ligand moiety. The $-\Delta \log K_M$ value in the case of the PMP ligand
can be attributed to the formation of a six-membered ring because of
the longer side chain. Consequently the resulting ternary complex is
less stable than the ternary complexes formed with the remaining
secondary ligands where a more stable five-membered chelate ring is
formed.

ACKNOWLEDGMENTS

REFERENCES

[1] Y. Marcus and I. Eliezer, Coord. Chem. Rev., 4, 273 (1969).
[2] T. S. West, Talanta, 17, 13 (1970); A. K. Babko, Ibid., 15, 721,
      735 (1968).

[3] D. S. Sigman and C. T. Jorganson, J. Am. Chem. Soc., 94, 1724
     (1972).
[4] A. E. Martell, Artificial Enzymes, in Metal Ions in Biological
     Systems, Vol. 2 (H. Sigel, ed.), Dekker, New York, 1973, p. 207.
[5] H. Sigel and D. B. McCormick, Acc. Chem. Res., 3, 201 (1970).
[6] R. Griesser and H. Sigel, Inorg. Chem., 9, 1238 (1970); 10, 2229
     (1971). P. R. Huber, R. Griesser, and H. Sigel, Ibid., 10, 945
     (1971).
[7] D. D. Perrin, I. G. Sayce, and V. S. Sharma, J. Chem. Soc., A,
     p. 1755 (1967); p. 446 (1968); p. 2060 (1969).
[8] H. M. Irving and H. S. Rossotti, Ibid., p. 2904 (1954).
[9] R. N. Mishra and S. S. Guha Sirkar, J. Indian Chem. Soc., 32,
     127 (1955); 33, 329 (1956).
[10] D. Sen, Ibid., 13, 268 (1936).
[11] C. S. Bhandari and N. C. Sogani, Bull. Acad. Pol. Sci., Ser. Sci.
     Chim., 20, 377 (1972).
[12] C. S. Bhandari, U. S. Mehnot, and N. C. Sogani, Ibid., 20, 91
     (1972).
[13] B. R. Rabin, Trans. Faraday Soc., 52, 1130 (1956).
[14] A. E. Martell and M. Calbin, Chemistry of Metal Chelate Com-
     pounds, Prentice-Hall, Englewood Cliffs, New Jersey, 1952.
[15] R. Griesser, B. Prijs, H. Sigel, W. Fory, L. D. Wright, and
     D. B. McCormick, Biochemistry, 9, 3285 (1970).
[16] L. G. Sillen and A. E. Martell, Stability Constants of Metal Ion
     Complexes, Special Publication 17, The Chemical Society,
     London, 1964.
[17] H. Sigel, P. R. Huber, R. Griesser, and B. Prijs, Inorg. Chem.,
     12, 1199 (1973).
[18] B. E. Fischer and H. Sigel, Ibid., 18, 425 (1979).