

Equilibrium studies on the formation of mixed-ligand complexes in solution—Part IV

V V RAMANUJAM* and V M SELVARAJAN

Department of Inorganic Chemistry, University of Madras, A.C. College Campus, Madras 600 025, India

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Abstract. Formation of ternary complexes of copper(II) with thiodiglycolic acid as primary ligand(A) and glycine, α -alanine, β -alanine, serine, ethylenediamine or malonic acid as secondary ligand(B) have been investigated in aqueous solution at 30°C employing pH-metric and spectrophotometric methods. The overall formation constants of the mixed-ligand complexes have been evaluated and the relative stabilities of the complexes are compared and discussed in terms of statistical considerations, nature of the donor atoms, steric effects and charge neutralisation as also the distribution of the different complex species present in the solution as a function of pH.

Keywords. Mixed-ligand complexes; copper(II); thiodiglycolic acid; amino acid; Ethylenediamine; malonic acid.

1. Introduction

Equilibrium studies on the formation of ternary complexes of metal ions in solution with sulphur containing ligands are not as abundant as those with oxygen and nitrogen donors (Marcus and Eliezer 1969; Sigel 1973). There are a few reports on the ternary complex formation of metal ions involving ligands such as thioglycolic acid and thiomalic acid (Panchal and Bhattacharyya 1972; Joshi *et al* 1973). Recently Shelke *et al* (1978a, b) and Shelke and Jahagirdar (1979) have studied the formation of mixed-ligand complexes of copper(II), nickel(II) and zinc(II) with thiodiglycolic acid and many multidentate ligands. The present paper reports the results of the studies of mixed-ligand complex formation by copper(II) with thiodiglycolic acid (TDGA) as primary ligand and glycine, α -alanine, β -alanine, serine, ethylenediamine (en) or malonic acid as secondary ligand using the spectrophotometric method of Newman and Hume (1957) in addition to the standard pH-metric technique.

2. Experimental

All the pH-titrations were carried out under an atmosphere of nitrogen at $30 \pm 0.1^\circ\text{C}$ and $\mu = 0.2 \text{ M}$ (NaNO_3).

The absorbance measurements were made with a single beam spectrophotometer with matched 1 cm glass cells, thermostatted at $30 \pm 0.1^\circ\text{C}$. In view of the high concentrations of the ligands employed in spectrophotometry, the ionic strength of the solutions was maintained at 0.6 M (NaNO_3).

* To whom all correspondence should be addressed.

3. Results

3.1 pH-metry

The ionisation constants of the ligands and the formation constants of the binary complexes were redetermined under the present experimental conditions using the methods of Irving and Rossotti (1953). The values are in good agreement with literature values (Martell and Sillen 1971). In pH-metric titrations involving the ternary system, the ratio, copper(II):primary ligand:secondary ligand was maintained at 1:1:1, the concentration of each being kept at 0.003 M. Typical titration curves are shown in figure 1 for copper(II)-TDGA and copper(II)-TDGA-glycine/ β -alanine/ethylenediamine/malonic acid systems. It is seen from the figure that for glycinate and ethylenediamine ternary systems (curves 2 and 4) the titration curves closely follow the curve for the binary system (curve 1) until 1.8 mol of base per mol of metal ion are added, indicating that the binary thiodiglycolate complexes predominate in this region. On further addition of alkali, the buffer region of complex formation is relatively

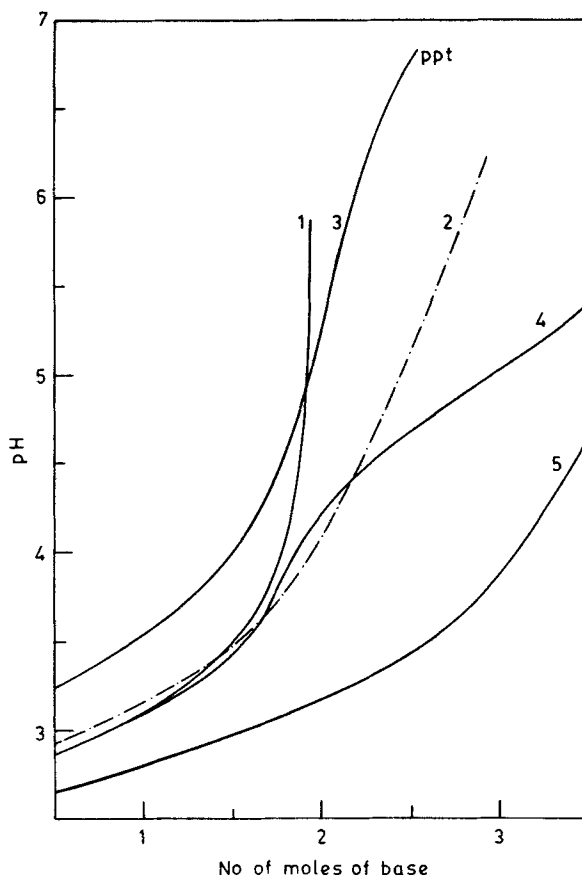


Figure 1. Copper(II)-TDGA-ligand B system. pH-metric titrations: 1. Cu(II)-TDGA (1:1), 2. Cu(II)-TDGA-glycine (1:1:1), 3. Cu(II)-tdga- β -alanine (1:1:1), 4. Cu(II)-tdga-en (1:1:1), 5. Cu(II)-tdga-malonic acid (1:1:1).

lowered compared to the binary system revealing the formation of ternary complex. In the malonate ternary system (curve 5) the buffer region of complex formation is lowered right from the beginning relative to the binary system indicating that both the ligands are simultaneously involved in complexation with the metal ion. The nature of the titration curve for the β -alaninate ternary system (curve 3) shows that appreciable ternary complex formation occurs only beyond pH 5. Calculations confirm this inference (figure 2).

The following mass balance equations were set up and the procedure of Martin and Paris (1964) was employed to evaluate the formation constants of the ternary complexes.

$$Cu_T = Cu + CuA + CuA_2 + CuB + CuB_2 + CuAB \quad (1)$$

$$A_T = A + HA + H_2A + CuA + 2 CuA_2 + CuAB \quad (2)$$

$$B_T = B + HB + H_2B + CuB + 2 CuB_2 + CuAB \quad (3)$$

$$H_T - C_B = 2 H_2A + HA + 2 H_2B + HB + H - OH \quad (4)$$

Cu_T , A_T , B_T and H_T represent the total concentrations of the metal ion, primary ligand, secondary ligand and hydrogen ions respectively. C_B is the concentration of the base added during the titration.

The above equations can be rearranged to arrive at a cubic equation in A, which can be solved to obtain the value of A. Substituting this value of A in equations (1)–(4) yields the values of B and M. Once A, B and M are evaluated, the formation constant of the ternary complex and the concentrations of the various species present in the solution can be calculated. The values of the formation constants are listed in table 1.

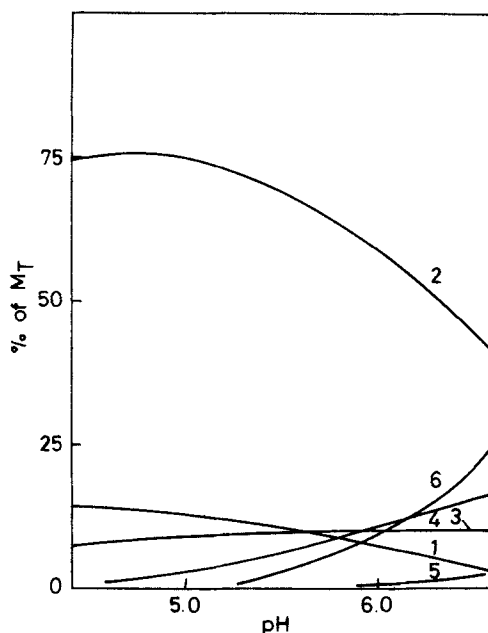


Figure 2. Copper(II)-thiodiglycolate(A)- β -alaninate(B) system. Distribution of complex species as a function of pH 1. Cu, 2. CuA, 3. CuA₂, 4. CuB, 5. CuB₂ and 6. CuAB.

Table 1. Formation constants of ternary complexes†.

Complex	log β_{MAB}		$\Delta \log K$	log X
	pH-metry ($\mu=0.2$ M)	Spectrophotometry ($\mu=0.6$ M)		
Cu(tdga)(gly)	11.67	11.54	-1.04	0.95
Cu(tdga)(ala)	11.64	11.42	-1.00	0.93
Cu(tdga)(bala)	10.65	10.49	-0.91	1.34
Cu(tdga)(ser)	11.35	11.24	-1.01	1.10
Cu(tdga)(en)	14.31	14.14	-0.73	1.51
Cu(tdga)(mal)	7.89	—	-1.60	—
Cu(imda)(gly)*	16.20	—	-2.50	—
Cu(imda)(ala)*	16.10	—	-2.53	—
Cu(imda)(bala)*	15.42	—	-2.13	—
Cu(imda)(ser)*	15.86	—	-2.49	—
Cu(imda)(en)*	18.65	—	-2.38	—
Cu(imda)(mal)*	12.73	—	-2.75	—

Abbreviations: imda = iminodiacetate; gly = glycinate; ala = α -alaninate; bala = β -alaninate; ser = serinate; mal = malonate.

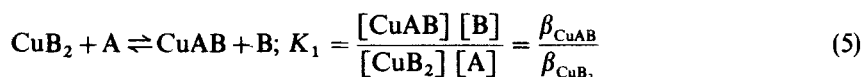
†The general accuracy of the results is ± 0.1 log unit. *Values from Ramanujam and Selvarajan (1981). Temp = $30 \pm 0.1^\circ\text{C}$.

Typical species distribution curves for copper(II)-TDGA- β -alaninate system are shown in figure 2. It is seen that at pH 4.5, 75% of copper(II) ions is present as Cu(TDGA), 15% as Cu(TDGA)₂ and 10% of copper(II) in the uncomplexed form. The formation of the ternary complex commences at pH 5.3 increases with pH reaching 25% at pH 6.5. The species Cu(bala) is also formed in significant amount, the concentration being 15% at pH 6.5, Cu(bala)₂ is formed in small amounts above pH 6.

3.2 Spectrophotometry

In all the experiments the concentration of copper(II) was kept at 0.01 M and that of each ligand in sufficient excess so that the metal ion is present in the form of the highest complex. Figure 3 gives the changes in the absorption when the pH of the solution containing copper(II) (0.01 M) and excess of thiodiglycolic acid (0.15 M) and glycine (0.04 M) is gradually varied. Since the two ligands differ widely in their tendencies to protonation in aqueous solution, the ratio of the deprotonated ligand concentrations could be varied by simply changing the pH of the solution. It is seen that at pH 5.38 the absorption of the solution (curve 2) is close to that of the binary copper(II)-TDGA complex (curve 1). At pH values less than 5 the absorption practically coincides with curve 1 indicating that only the thiodiglycolate binary complex is present at these pH values. Similarly above pH 7.5 the whole of copper(II) is present as the glycinate complex (curve 7). In the pH range 5 to 7 the absorption characteristics indicate that a mixture of binary and ternary complexes are present.

The formation of the ternary complex was investigated by the method of Newman and Hume (1957). The following equilibria were considered.



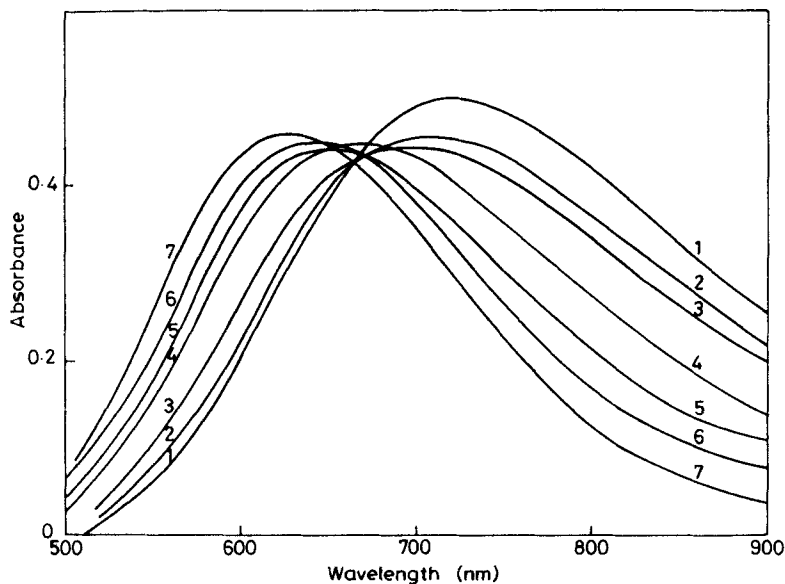
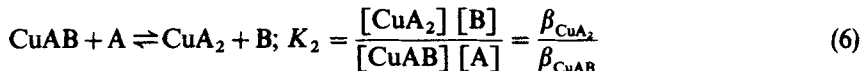


Figure 3. Copper(II)-thiodiglycolate(A)-glycinate(B) system. Absorbance characteristics of solutions containing binary and ternary systems. 1. Cu-A (1:15), pH = 5.81; 2. Cu-A-B (1:15:4), pH = 5.38; 3. Cu-A-B (1:15:4), pH = 5.83; 4. Cu-A-B (1:15:4), pH = 6.55; 5. Cu-A-B (1:15:4), pH = 6.97; 6. Cu-A-B (1:15:4), pH = 7.46; 7. Cu-B (1:10), pH = 7.12.



$$\beta_{\text{CuAB}} = \frac{[\text{CuAB}]}{[\text{Cu}][\text{A}][\text{B}]}; \beta_{\text{CuB}_2} = \frac{[\text{CuB}_2]}{[\text{Cu}][\text{B}]^2}; \beta_{\text{CuA}_2} = \frac{[\text{CuA}_2]}{[\text{Cu}][\text{A}]^2}$$

When the ratio of thiodiglycolic acid to the amino acid was large, it was assumed that only $\text{Cu}(\text{TDGA})_2$ and $\text{Cu}(\text{TDGA})$ aminocarboxylate are present in the solution and the following equation was applied to evaluate K_2 .

$$\bar{A} = K_2 (A_0 - \bar{A}) \frac{A}{B} + \varepsilon_{\text{CuAB}} \text{Cu}_T \quad (7)$$

\bar{A} is the absorbance of the solution, $\varepsilon_{\text{CuAB}}$ the molar absorptivity of the mixed-ligand complex and Cu_T the total metal ion concentration, A_0 is the absorbance when all the metal ion is present as CuA_2 . The A and B values can be calculated from a knowledge of the ionisation constants of A and B and their total concentrations in the solution. A plot of \bar{A} vs $(A_0 - \bar{A}) \frac{A}{B}$ gave a straight line, the slope of which is equal to K_2 . Typical data are given in table 2 for the copper(II)-TDGA-glycinate system. Substituting the K_2 value obtained as slope into (6), the β_{CuAB} value can be evaluated if β_{CuA_2} is already known.

Under favourable pH and concentration of the amino acid the species CuA_2 , CuAB and CuB_2 are present in the solution. It can be seen from figure 3 that the absorption of CuB_2 is not appreciable near 900 nm. In this wavelength region the following equation was employed to evaluate K_1 .

Table 2. Copper(II)-TDGA-glycinate system.

A (M)	B (M × 10 ⁶)	\bar{A}	$(A_0 - \bar{A}) \frac{A}{B}$
0.1485	9.14	0.410	650.0
0.1495	8.66	0.430	342.9
0.1492	9.97	0.432	268.9
0.1495	12.69	0.438	141.1
0.1490	10.04	0.413	532.7

Slope (K_2) = 5.53×10^{-5} ; $\log \beta_{\text{CuAB}} = 11.51$.

Evaluation of K_2 by the method of Newman and Hume $\text{Cu}_T = 0.01 \text{ M}$; $\mu = 0.6 \text{ M}$ (NaNO_3); Temp. = $30 \pm 0.1^\circ\text{C}$ CuA_2 and CuAB present and absorbing; $A_0 = 0.450$ at 780 nm.

$$K_2 (A_0 - \bar{A}) \frac{A}{B} - \bar{A} = \frac{1}{K_1} \bar{A} \frac{B}{A} - \epsilon_{\text{CuAB}} \text{Cu}_T \quad (8)$$

A plot of $K_2 (A_0 - \bar{A}) \frac{A}{B} - \bar{A}$ vs $\bar{A} \frac{B}{A}$ was linear, the slope of which gave the $1/K_1$ value.

Typical data are given in table 3 for the copper(II)-TDGA-glycinate system. Substituting the K_1 value in (5), β_{CuAB} can be evaluated if β_{CuB_2} is already known. The β_{CuAB} values obtained from (7) and (8) are in very good agreement with each other validating the assumptions made. The average values of β_{CuAB} evaluated at different wavelengths are given in table 1. These values are slightly lower than those obtained from pH-metry and this may be due to the higher ionic strength of the solutions maintained in spectrophotometry.

4. Discussion

Glycine forms the stablest mixed-ligand complex of all the α -amino acids employed because of the absence of any alkyl side chain which may produce an unfavourable steric effect in other α -aminoacids studied.

Table 3. Copper(II)-TDGA-glycinate system.

A (M)	B (M × 10 ⁵)	\bar{A}	$K_2 (A_0 - \bar{A}) \frac{A}{B} - \bar{A}$	$\left(\bar{A} - \frac{B}{A}\right) 10^5$
0.1498	5.88	0.171	-0.1584	6.57
0.1498	4.41	0.190	-0.1775	5.73
0.1496	2.68	0.216	-0.2033	3.87
0.1489	2.65	0.223	-0.2120	3.85
0.1499	1.89	0.234	-0.2241	2.96

Slope ($1/K_1$) = 1.9×10^3 ; $\log \beta_{\text{CuAB}} = 11.57$.

Evaluation of K_1 by the method of Newman and Hume $\text{Cu}_T = 0.01 \text{ M}$; $\mu = 0.6 \text{ M}$ (NaNO_3); Temp. = $30 \pm 0.1^\circ\text{C}$ CuA_2 , CuAB and CuB_2 present, CuA_2 and CuAB absorbing $A_0 = 0.256$ at 900 nm.

The extent of favoured formation of the ternary complexes (Sigel 1975) can be inferred from the $\Delta \log K$ values ($= \log K_{\text{CuAB}} - \log K_{\text{CuB}}$ where $K_{\text{CuAB}} = \frac{[\text{CuAB}]}{[\text{CuA}][\text{B}]}$ and $K_{\text{CuB}} = \frac{[\text{CuB}]}{[\text{Cu}][\text{B}]}$) as well as $\log X$ (where X represents the equilibrium constant for the disproportionation reaction $2 \text{CuAB} \rightleftharpoons \text{CuA}_2 + \text{CuB}_2$). On statistical grounds (Sigel *et al* 1971) the value expected for $\log X$ is 0.6. When one ligand is terdentate and the other is bidentate, the statistical value of $\Delta \log K$ is shown to be -0.7 for an octahedral environment around the metal ion (Ramanujam and Selvarajan 1981a). For metal ions like copper(II) forming distorted octahedral complexes the value will be less than -0.7 . The $\Delta \log K$ and $\log X$ values in table 1 indicate that they are close to or higher than the statistical values indicating that the formation of the ternary complexes is favoured.

The effect of charge neutralization is pronounced in the formation of the mixed chelates (Sigel 1975). The $\Delta \log K$ and $\log X$ values in table 1 also clearly indicate that the neutral ternary complex containing ethylenediamine is favoured to the charged mixed-ligand complexes involving amino acid or malonic acid. The $\log K$ values reveal that the ternary complexes involving thiodiglycolic acid are favoured to the corresponding complexes involving iminodiacetate, even though the chelating behaviour of both the ligands is alike, each capable of forming two five-membered rings on chelation. This may be due to the fact that the relatively 'soft' acid (Pearson 1963) copper(II) prefers a 'soft' base, sulphur, to the 'harder' nitrogen. Rizzarelli *et al* (1978) have also observed that the formation of Cu(bipy)(TDGA) is preferred to that of Cu(bipy)(TMDA).

Ternary complexes containing both nitrogen and oxygen donors with an equitable distribution of the two are preferred over those with only nitrogen or only oxygen donors (Griesser and Sigel 1970). The same is found in the present study also. The $\Delta \log K$ values indicate that in the copper(II)-thiodiglycolate-secondary ligand system, the formation of Cu(TDGA)(en) is the most favoured, since it contains two nitrogen, two oxygen and one sulphur as donors. Cu(TDGA)(mal) is not as favoured as the other ternary complexes, since it has four oxygen and one sulphur as donors. The $\Delta \log K$ values of Cu(TDGA)(aminocarboxylate) are intermediate between Cu(TDGA)(en) and Cu(TDGA)(mal) as they have one nitrogen, one sulphur and three oxygen donors.

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