

Stability Constants of Ternary Complexes of Copper(II) with Phthalic Acid & O⁻,O⁻; O⁻,N & N,N Donor Ligands

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The equilibria involved in the formation of ternary complexes of Cu(II) with different ligands in the presence of a O⁻,O⁻ donating ligand (phthalic acid) have been studied by pH-titration technique at 25° and $\mu=0.1$ M KNO₃ in aqueous medium. The ligands used are: (i) O⁻,O⁻ donating ligands: oxalic, maleic, fumaric, salicylic acids and pyrocatechol; (ii) O⁻,N donating ligands: 8-hydroxyquinoline and *o*-aminophenol and (iii) N,N donating ligands: 2,2'-bipyridyl and ethylenediamine. The stability constants of the ternary complexes have been evaluated by different methods depending on the equilibria involved in the complex formation and have been compared and discussed in terms of donating atoms, size of the chelated rings, electrostatic considerations and $d\pi-p\pi$ interactions.

The importance of ternary complexes in biological processes¹⁻⁵ prompted inorganic chemists to study the complexes of Cu(II) containing imidazole and aminoacids. In the present investigation, the formation constants of the ternary complexes of Cu(II) with phthalic acid and O⁻,O⁻; O⁻,N and N,N donating ligands such as oxalic acid (OA), maleic acid (MA), fumaric acid (FA), salicylic acid (SA) pyrocatechol (PC), 8-hydroxyquinoline (8-HQ), *o*-aminophenol (*o*-AP), 2,2'-bipyridyl (bipy) and ethylenediamine (en) have been determined potentiometrically in aqueous medium at 25°C and $\mu=0.1$ M KNO₃.

Materials and Methods

All the chemicals used were of AR grade. The ligands were recrystallized/distilled before use and their purity checked. The Cu(II) solution was prepared by dissolving required amount of cupric nitrate in CO₂-free doubly distilled water and standardized as usual.

An ITL digital pH-meter model DPH-14 with glass and calomel electrode (accuracy ± 0.01 pH unit) assembly was used for pH measurements. The instrument was standardized with standard buffers of pH 4.00 and 9.20 before each titration. The following sets of solutions were titrated against 0.2 M NaOH at 25° and $\mu=0.1$ M KNO₃:

(i) HNO₃ (1×10^{-2} M); (ii) i + ligand A (2×10^{-3} M); (iii) ii + Cu(II) (2×10^{-3} M); (iv) i + ligand L (2×10^{-3} M); (v) iv + Cu(II) (2×10^{-3} M); (vi) iii + ligand L (2×10^{-3} M).

Results and Discussion

The formation of a ternary complex of metal ion in

the presence of ligands A and L occurs in the following steps (1-5):



The formation of the mixed-ligand complexes in solution was established initially by noting the pH of precipitation for MA, ML and MAL and by comparing the mixed-ligand titration curve with the composite curve (Fig. 1). The composite curve was drawn theoretically by the graphical addition of 1:1 MA/ML curve to the titration curve of the free ligand (L/A). It is evident from Fig. 1 that the formation of ternary complex takes place at low pH region by the interaction of OA, MA, FA, SA, 8-HQ and PhA simultaneously with the metal ion, whereas the Cu(II)-PhA species which exists in the lower pH region interacts with the second ligand (PC/*o*-AP) forming the ternary complex in a stepwise manner. The bipy and en are found to form binary complexes at much lower pH region than PhA. Therefore, in these cases also a stepwise formation of ternary complex is observed.

The required ionization constants of ligands and the

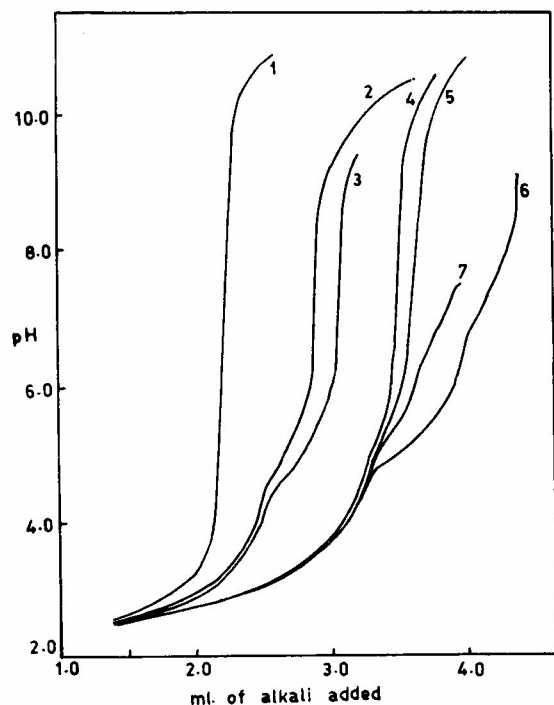


Fig. 1—Titration curves of binary and ternary complexes of Cu(II) with PhA and *o*-aminophenol [(1), HNO₃; (2), (1) + *o*-AP; (3), (2) + Cu(II); (4), (1) + PhA; (5), (4) + Cu(II); (6), (3) + PhA; (7) Composite curve]

Table 1—Stability Constants of Binary Complexes

Ligand	pK_{a1}	pK_{a2}	$\log K_1$	$\log K_2$
PhA	2.98	5.35	3.49	2.59
OA	1.40	4.13	4.28	3.97
MA	1.80	5.85	4.02	2.82
FA	3.07	4.58	3.19	—
SA	2.57	13.60	10.83	8.05
PC	8.61	11.25	11.28	8.62
8-HQ	5.12	10.00	12.85	10.86
<i>o</i> -AP	3.66	9.45	7.81	6.92
bipy	4.40	—	8.00	5.60
en	6.80	9.74	10.31	8.60

Table 2—Stability Constants of Ternary Complexes of Cu(II)

System	β_{MAL}	$\log K_{reprop.}$	$\log K_{MAL}^{MA}$	$\log K_{MLA}^{ML}$	$\log K$
Cu(II)-PhA-OA	7.94	+1.55	4.45	3.66	+0.17
Cu(II)-PhA-MA	8.15	+3.38	4.66	4.13	+0.64
Cu(II)-PhA-FA	6.75	+0.97	3.26	3.56	+0.07
Cu(II)-PhA-SA	9.45	-6.06	5.96	-1.38	-4.87
Cu(II)-PhA-PC	11.16	-3.66	7.67	0.12	-3.61
Cu(II)-PhA-8-HQ	14.06	-1.67	10.57	1.21	-2.28
Cu(II)-PhA- <i>o</i> -AP	7.35	-6.11	3.86	-0.46	-3.95
Cu(II)-PhA-bipy	12.13	+4.58	8.64	4.13	+0.64
Cu(II)-PhA-en	9.98	-5.03	6.49	-0.33	-3.82

formation constants of binary complexes were evaluated by Irving and Rossotti method⁶ and are presented in Table 1. These values were compared with the literature values⁷. The formation constants of ternary complexes determined by different methods depending on the nature of the titration curves along with $\Delta \log K$ and $\log K_{reprop.}$ values are presented in Table 2 (accuracy $\pm 0.1 \log$ units).

O⁻, O⁻ Donor Ligands

The $\Delta \log K$ value ($= \log K_{MAL}^{MA} - \log K_{ML}^M = \log K_{MLA}^{ML} - \log K_{MA}^M$) is the measure of the stability of a ternary complex. From statistical considerations it is reported that its value will be negative for the formation of a stable ternary complex. It can be seen from Table 2 that the $\Delta \log K$ values for the systems containing Cu(II)-PhA and OA/MA/FA are positive. Though the formation of ternary complexes occurs simultaneously in these systems, it is clear from the titration curves and from the calculations of the stability constants of binary systems, that the complexes Cu(II)-PhA and Cu(II)-L are first formed at lower pH region, which then disproportionate to give ternary complex as (Eq. 6)



The positive $\Delta \log K$ values obtained in these cases may be due to the favourable shift of the equilibrium in forward direction.

The maleic acid complex is more stable than that of oxalic acid or fumaric acid even though the maleate ion forms a five-membered ring in the ternary complex whereas oxalate forms a five-membered ring. This may be due to the fact that strain involved in the Cu(II)-PhA-OA chelate may be more than that in Cu(II)-PhA-MA due to greater repulsion between O^- , O^- of PhA and of OA. Further, the $d\pi$ - $p\pi$ interactions in Cu(II)-MA complex make the resulting ternary complex more stable. The fumaric acid due to its *trans*-geometry may involve greater strain in chelate formation and thus forms less stable ternary complex.

The $\Delta \log K$ value of the ternary complex with SA is more negative than that with PC indicating that the former complex is more stable. The mixed-ligand complexes are generally considered to be formed by the simultaneous or stepwise replacement of water molecules from the coordination sphere of the metal ions with the formation of $M-O/N$ bonds. The observed trend in the case of SA and PC complexes may be explained as follows: unlike the phenolate oxygen the carboxylate oxygen in SA is not directly bound to the benzene. It may therefore, adjust stereochemically more easily than the phenolate oxygen. In SA one donor atom is carboxylate oxygen and the other is a phenolate oxygen, while in the

pyrocatechol both the donor atoms are phenolate oxygens, thus resulting in less stable ternary complex.

O⁻, N Donor Ligands

The $\Delta \log K$ of 8-HQ ternary complex is less negative than that of *o*-AP complex indicating that the *o*-AP complex is more stable. But in this case the $\Delta \log K$ does not give the measure of stability. The 8-HQ complexes are quite stable when compared to those of *o*-AP^{7,8}. The 8-HQ, a heterobicyclic compound containing a tertiary nitrogen forms a stable five-membered ring chelates, coordinating through phenolate oxygen and pyridine nitrogen. In the ternary complexes involving such ligands, the interaction of ligand $p\pi$ and metal ion $d\pi$ orbitals renders retention of the same electron density around the metal ion as in Cu(II). Thus the tendency to form a ternary complex is not significantly lower, hence $\Delta \log K$ has a small negative value, as compared to that of *o*-AP complex in which the π -interaction does not occur to that extent. The $\log K_{\text{reprop.}}$ [$= 2 \log K_{\text{MAL}}^{\text{M}} - (\log K_{\text{MA}_2}^{\text{M}} + \log K_{\text{ML}_2}^{\text{M}})$] therefore, gives the measure of stability of ternary complexes in these two cases. It is less negative in the case of Cu(II)-PhA-8-HQ complex (-1.67) as compared to that (-6.11) of Cu(II)-PhA-*o*-AP complex indicating that the former complex is more stable.

N, N Donor ligands

The titration curves indicate that the metal ion first interacts with either bipy or en than with PhA. The $\Delta \log K$ value in the case of Cu(II)-bipy-PhA complex is positive. In general in the formation of a binary

complex there will be electron repulsion between the metal ion $d\pi$ -electrons and lone pair of electrons (if any) present on the coordinating atom of L, making $\Delta \log K (= \log K_2 - \log K_1)$ negative. However, in the case of ternary complexes of Cu(II)-bipy, the repulsions are reduced to minimum, due to back donation of metal $d\pi$ electrons to the tertiary amine molecule. Thus, the resulting ternary complex will be more stable with positive $\Delta \log K$. There is no such π -interaction in the case of en, as it is an open chain, saturated neutral molecule, hence $\Delta \log K$ value is negative. The high $\log K_{\text{reprop.}}$ value (4.58) of Cu(II)-bipy-PhA system indicates that it is the stable complex among all complexes studied in the present investigation.

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