

Studies of Some Ternary Complexes of Copper(II) Involving 2,2'-Bipyridyl as a Primary Ligand

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The formation constants of the complexes of the type $[CuAL]$, where $A=2,2'$ -bipyridyl and $L^1=2$ -[benzoylamino]benzoic acid, $L^2=2$ -[(phenylamino)carbonyl]benzoic acid, $L^3=2$ -[2'-aminobenzoylamino]benzoic acid and $L^4=2$ -[2'-aminobenzoyl]benzoic acid have been determined in methanol-water (1:1 v/v) medium at $\mu=0.1 M KNO_3$ and $30^\circ C$. The formation constants and the stability constants of binary and ternary systems have been evaluated using Irving-Rossotti titration technique. The values of $\Delta \log K$ are found to be positive. This trend is ascribed to the decreased repulsion between the ligand π -electrons and the metal d_{π} -electrons in ternary complexes.

The participation of Cu(II)-L-histidine-albumin ternary complex as an intermediate in the exchange of Cu(II) in blood between a macromolecule such as albumin and low molecular weight substance like an amino acid¹ has generated interest amongst inorganic chemists to prepare model compounds which closely resemble the naturally occurring compounds. As a part of such studies, detailed investigations have earlier been carried out on the mixed-ligand complexes, involving aromatic tertiary amines, because of the similarity of these compounds with imidazole which commonly occurs in metalloenzymes^{2,3}. It has also been observed that the tertiary amines have a discriminating effect over the second ligand.

The present paper describes the formation constants of the ternary complexes of Cu(II)-bipy with other ligands such as 2-[benzoylamino]benzoic acid (L^1), 2-[(phenylamino)carbonyl]benzoic acid (L^2), 2-[2'-aminobenzoylamino]benzoic acid (L^3) and 2-[2'-aminobenzoyl]benzoic acid (L^4). These ligands have two potential binding atoms, O and N, for complexation with metal ions.

Materials and Methods

All the reagents used were of AR grade. The ligands L^1 to L^3 were prepared by known methods⁴⁻⁶ and the ligand L^4 was obtained from Aldrich Chemical Company (USA). These were recrystallized twice from methanol. The stock solutions of the ligands were prepared in methanol, and all other solutions in doubly distilled water.

The proton ligand formation constants and metal-ligand stability constants of binary complexes were obtained in methanol-water (1:1 v/v) solution at $\mu=0.1 M (KNO_3)$ and $30^\circ C$, using the Irving-Rossotti titration technique⁷. The formation constants of the

ternary complexes $[CuAl]^+$ were determined by an extension⁸ of the same technique. An ITL digital pH-meter model DPH-14 fitted with calomel and glass electrodes and having an accuracy of ± 0.01 pH was used for pH measurements. The pH meter was standardized against standard buffers of pH 4.00 and 9.20 before each titration the pH-meter readings in aquo-organic mixture were corrected by Van-Uitert and Haas method⁹. The calculations of mixed ligand formation constants were carried out in the pH range 4-6 and hence hydroxo-complex formation was not considered.

The binary and ternary complex stability constants obtained from formation curve data were refined by plotting pL at each point against $\log(1 - \bar{n}/\bar{n})$ such a plot was linear. At each point on the linear curve $\log K_{MAL}^{ML} = pL - \log(1 - \bar{n}/\bar{n})$. The refined values are presented in Table 1.

Results and Discussion

The proton-ligand formation constants and the metal-ligand stability constants are presented in Table 1. Potentiometric titration curves of the ligands L^1 and L^2 show one inflexion while L^3 , L^4 (protonated ligands) show two inflexions indicating the dissociation equilibria as:

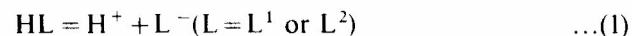
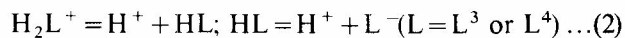


Table 1— Proton-ligand Constants of Ligands and Stability Constants of Binary and Ternary Complexes of Cu(II)

[Methanol-water (1:1 v/v); $\mu=0.1 M KNO_3$; temp = $30^\circ C$]					
Ligand	K_1^H	K_2^H	$\log K_{ML}^H$	$\log K_{MAL}^{MA}$	$\Delta \log K$
L^1	4.07	—	3.02	4.20	+1.18
L^2	5.04	—	2.76	3.61	+0.85
L^3	4.63	2.86	2.81	3.63	+0.82
L^4	5.17	2.53	2.82	3.47	+0.65



The titration curves of ternary systems indicate that the complexation of Cu(II) with the ligands occurs in a stepwise manner (Fig. 1). The formation tendency of ternary complexes has been expressed by $\Delta \log K$ values (Table 1), which are positive. From Table 1 it can be seen that the ternary complex stability constant is more than that of the binary complex, indicating that the association of the second ligand to [MA] is more facile than that to the aquo-complex. This may be due to the existence of inter-ligand π -interaction of the two ligands as shown, though not conclusively, by Sigel *et al.*¹⁰.

The stability constant and $\Delta \log K$ values of [CuAl¹] is more than those of other complexes under investigation. The ligand L¹ is coordinating through O and N atoms while L² through two O atoms. From earlier investigations^{2,3} it can be expected that the ternary complex involving the ligand L² should be more stable, with greater positive $\Delta \log K$ value. The higher stability of the complex with L¹ is due to the formation of a six-membered chelate compared to a seven membered chelate with L². The same is also observed in the case of L³ and L⁴ complexes.

The ternary complexes of the ligands L¹ and L² (bidentate ligands) are more stable than those of L³

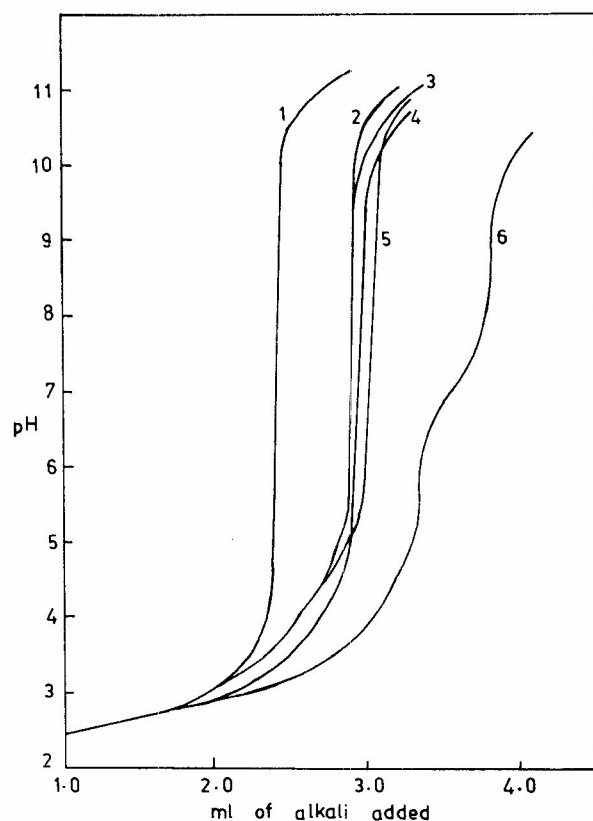


Fig. 1—The plots of pH against volume of alkali added. [(1) H⁺; (2) H⁺ + L¹; (3) H⁺ + A; (4) H⁺ + A + Cu(II); (5) H⁺ + L¹ + Cu(II); and (6) H⁺ + A + L¹ + Cu(II)]

and L⁴ (tridentate ligand). This is due to the fact that in [CuAl¹]⁺ and [CuAl²]⁺ the four coordination sites of the Cu(II) ion are occupied by the two ligands A and L and no strain is involved in the formation of ternary complexes, while in the case of [CuAl³]⁺ and [CuAl⁴]⁺ the water molecule on tetragonally distorted [CuA]²⁺ complex needs to be replaced by one of the coordinating atoms of the ligand L³ or L⁴.

Electronic spectra

In order to see the possibility of interligand π -interaction through the metal d_x orbitals the electronic spectra of the ligands (A and L), binary complexes (CuA and CuL) and ternary complexes (CuAL) were recorded in 1:1 (v/v) methanol-water solution. Solution of CuA was prepared by mixing Cu(II) and A in 1:1 ratio and adjusting the pH to 3.5. Solutions of CuL and CuL₂ were prepared by mixing metal ion and ligand in 1:1 and 1:2 ratios and adjusting the pH to 4.5 and 5.5 respectively. The spectra of these solutions were identical. For [CuAL], the metal ion and two ligands were mixed in the ratios 1:1:1 and the pH raised to 6.0, since the concentration of CuAL was maximum at this pH.

Bipyridyl exhibits bands at 47169, 42372 and 35460 cm⁻¹. The bands in the lower region correspond to $\pi \rightarrow \pi^*$ transitions. The complex [Cu(bipy)]²⁺ displays bands at 47230, 42372, 33670, 32258 and 13560 cm⁻¹. The appearance of a new band and the shift in the $\pi \rightarrow \pi^*$ transition show that there is interaction between π -orbitals of Cu(II) and those of the bipyridyl molecule. The ligand L¹ exhibits bands at 42735 and 32894 cm⁻¹ and its Cu(II) complex at 42372, 32894, 24691 and 13020 cm⁻¹. The presence of a new band at 24691 cm⁻¹ indicates the interaction of ligand π -orbital and metal ion π -orbitals. Similar spectral data have been obtained for other binary complexes. The spectral data thus clearly indicate that there is considerable interaction of the π -orbitals of the ligand and metal ion in all the binary complexes. The spectrum of ternary complex [CuAl¹]⁺ exhibits bands at 42735, 32894, 32258, 24000 and 15900 cm⁻¹ showing all the transitions of [CuA]²⁺ and [CuL]⁺ without much significant shift. Similar behaviour is exhibited by the ternary complexes of the ligands L², L³ and L⁴. Thus, although there is metal-ligand interaction between [CuA]²⁺ and [L⁻], which is evident from the stability constant data and the shift in $d-d$ transitions, there is no significant change in the π -orbital energies due to mixed-ligand complexation. These data cast doubt on the interligand π -interaction, as postulated by Sigel.

This may be explained alternatively as follows: The ligands L¹ to L⁴ have a lone pair of electrons on either O or N atom which are not involved in coordination.

Because of this π -electron density, there is repulsion between the ligand π -electrons and the Cu(II) d_{π} electrons. This repulsion is more in binary complexes but is decreased in $[\text{CuAL}^{1-4}]^+$ complex due to the delocalization Cu(II) d_{π} -electrons over the vacant π -orbitals in bipyridyl molecule. This leads to a positive value of $\Delta \log K$ in the $[\text{CuAL}]^+$ complexes³. Thus, the stabilization of the ternary complexes is due to the decreased repulsion between the ligand π -electrons and the metal d_{π} -electrons, with no significant interligand π -interaction.

Further, the $d-d$ transition bands of $[\text{CuA}_2]^{2+}$ (13560 cm^{-1}), $[\text{CuL}_2]$ (13020 cm^{-1}) and $[\text{CuAL}^1]^+$ (15900 cm^{-1}) clearly show that the crystal field in the mixed-ligand complex is greater than in the corresponding binary complex. Normally in a mixed-ligand complex there should be creation of an average field compared to the field in the binary complexes. The deviation from this expectation can be due to special behaviour of 2,2'-bipyridyl, which accepts the metal d_{π} -electrons, thus reducing the electron density over the metal ion. The second ligand, therefore, is repelled to a lesser extent in the mixed-ligand complex compared to the binary complexes. In other words, the

second ligand can create a stronger field in the ternary complex and this is responsible for the shift of $d-d$ transition bands to higher energy in the mixed-ligand complex¹¹.

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