Study of binary and ternary complexes of some binucleating ligands

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Stability constants of homobinuclear Cu(II) complexes of some binucleating ligands, having equivalent (N - O -) coordinating sites, viz., 4,4'-di-(o-hydroxybenzyl)diaminodiphenylmethane (H3A1) and 4,4'-di-(o-hydroxybenzyl)diaminodiphenylether (H3A2) and mixed ligand Cu(II) complexes with one of the above ligands and bipyridyl, glycine, α-alanine, phenylalanine, tyrosine or tryptophan as secondary ligands, have been determined potentiometrically in (50:50, v/v) water-dioxane medium using a computer program. The relative stabilities of the different complexes have been explained. The complexes [Cu2A2L2] (ClO4)2, [where, L=bipy or 1, 10 Phen, and A=4,4'-di-(o-hydroxybenzyl)diaminodiphenylmethane], have been isolated and characterized by elemental analysis, electronic, ESR spectral and magnetic studies.

Many binuclear complexes with equivalent or non-equivalent coordinating sites have been synthesized and structurally characterized1-5, to study the extent of the interaction between the two metal ion centres, and its dependence on the distance between the metal centres6-7, types of bridging ligands and also on the relative orientations of the metal ions8. Such studies are of importance from biochemical point of view, since they offer insight into the coordination chemistry of binuclear copper proteins9,10 and also their potential impact in catalysis.

The solution stability of complexes of binucleating biomolecules are however, confined to the ligands with two non-equivalent coordination sites, like L-dopa11, histidine12, 3-amino-l-tyrosine13, dipeptides like L-histidyl-glycine14, Beta-alanyl-L-histidine15 and others like DL-isoserine16, δ-hydroxy-lysine17 and ATP18. No work has been reported on the formation constants of binuclear complexes involving the ligands with two distant equivalent coordination sites.

The present paper reports the synthesis of new binucleating ligands 4,4'-di-(o-hydroxybenzyl)diaminodiphenylmethane (H3A1) and 4,4'-di-(o-hydroxybenzyl)diaminodiphenylether (H3A2) with two separate, well defined N - O - coordination sites, and the study of the formation constants of their binuclear binary and mixed-ligand Cu(II) complexes, with amino acids or Bipy as secondary ligands. The two mixed-ligand binuclear Cu(II) complexes involving the binucleating ligand 4,4'-di-(o-hydroxybenzyl)diaminodiphenylmethane and 1:10 Phen or bipy have been synthesized and characterized by microanalysis, UV, visible, IR and ESR spectral studies and magnetic moment measurements. The general structural formula of the binucleating ligands used for the present study is as shown below (Structure I).

![Structure I](image)

Materials and Methods

All the chemicals used were of AR grade. The binucleating ligands were synthesized by the following method.

Synthesis of new binucleating ligands

To an ethanolic solution of 4,4'-diamino diphenyl methane or 4,4'-diaminodiphenyl ether (2.5 mmol), a solution of salicylaldehyde in ethanol (5.0 mmol) was added with stirring. After some time a shining yellow coloured schiff base separated out. The mixture was refluxed for ~ 1 h and the schiff base filtered and dried. It was crystallized from benzene or chloroform. The schiff base, thus obtained, was reduced with solid NaBH₄ in a mixture of methanol/benzene (80:20 v/v) with stirring. The mixture was allowed to
stand for half an hour to complete the reduction. The volume of solvent was reduced to less than half and to this solution acidic water (20 ml dil. CH₃COOH in 40 ml water) was added in excess. A white solid separated out. This was filtered, washed with water and dried. The crude mannich base was crystallized several times in benzene and characterized by m.p., microanalysis and spectral studies.

All the titrations were carried out in water-dioxane (1:1, v/v) medium. The pH corrections were made using the method described earlier.¹⁹ The summary of other experimental parameters for the Cu(II) binary and mixed-ligand systems is given below.²⁰

**Ligand systems**

(a) 0.02 M HClO₄: 0.003 M lig. H₃A: 0.177 M NaClO₄.
(b) 0.02 M HClO₄: 0.002 M lig. H₃A: 0.178 M NaClO₄.

**Binary systems**

(a) 0.02 M HClO₄: 0.003 M CuClO₄: 0.0015 M lig. H₃A: 0.1755 M NaClO₄.
(b) 0.02 M HClO₄: 0.0045 M CuClO₄: 0.0015 M lig. H₃A: 0.174 M NaClO₄.

**Mixed ligand systems**

(a) 0.02 M HClO₄: 0.003 M CuClO₄: 0.0015 M lig. H₃A: 0.003 M lig. L: 0.1725 M NaClO₄.
(b) 0.02 M HClO₄: 0.0045 M (CuClO₄)_2: 0.0015 M lig. H₃A: 0.0045 M lig. L: 0.1695 M NaClO₄.

The ionic strength was maintained at 0.2 m dm⁻¹ (NaClO₄) and temperature was kept at 30°C.

The titrations were carried out in water-dioxane (1:1, v/v) using a GP Electronics pH meter (No. 8021, accuracy ± 0.01 pH unit). The formation constants were determined using SCOGS Computer program. The species considered for Cu(II) mixed ligand systems were AH₃, AH₂, AH, A, L, Cu(II) [CuAH₃] [CuACu] [CuL], [CuL₂], [LCuAH₃] and [LCuACuL].

The magnetic moment of the complexes were determined at room temperature and were found to be (1) 1.93, (2) 1.83, respectively. The electronic spectra were recorded on UV-Shimadzu-240 spectrophotometer. The ESR spectra of the complexes were recorded on BRUKER ESP-300;...
Table 1—Proton-ligand formation constants of the ligands and formation constants of homobinuclear complexes of Cu(II) in water-dioxan medium (50:50, v/v) [Temp. = 30°C; I = 0.2 M (NaClO₄)]

<table>
<thead>
<tr>
<th>Ligand (A)</th>
<th>Log $Kf^{II}$</th>
<th>Log $Kf^{III}$</th>
<th>Log $Kf^{IV}$</th>
<th>Log $K_{CuA}^{II}$</th>
<th>Log $K_{CuB}^{III}$</th>
<th>Log $K_{CuA}^{IV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2A^+$</td>
<td>10.84</td>
<td>10.63</td>
<td>4.84</td>
<td>8.58</td>
<td>8.09</td>
<td>16.67</td>
</tr>
<tr>
<td>$H_2A^-$</td>
<td>10.85</td>
<td>10.74</td>
<td>4.80</td>
<td>8.83</td>
<td>8.37</td>
<td>17.20</td>
</tr>
</tbody>
</table>

Table 2—Stability constants of mixed-ligand complexes [Cu(II)-$H_2A^-$-L system) in water:dioxane (50:50, v/v) medium [Temp. = 30°C; I = 0.2 M (NaClO₄)]

<table>
<thead>
<tr>
<th>Ligand (L)</th>
<th>Log $Kf^{Cu}_{Cl}$</th>
<th>Log $Kf^{Cu}_{ClAH}$</th>
<th>$\Delta \log Kf$</th>
<th>Log $Kf^{Cu}_{ClAH}$</th>
<th>$\Delta \log Kf$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>8.73</td>
<td>16.63</td>
<td>-0.68</td>
<td>15.67</td>
<td>-1.83</td>
</tr>
<tr>
<td>$\alpha$-alanine</td>
<td>9.16</td>
<td>17.24</td>
<td>-0.50</td>
<td>16.12</td>
<td>-1.63</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>8.96</td>
<td>17.72</td>
<td>+0.18</td>
<td>15.72</td>
<td>-1.15</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>8.92</td>
<td>17.82</td>
<td>+0.32</td>
<td>15.58</td>
<td>-1.15</td>
</tr>
<tr>
<td>Tryptophan</td>
<td>9.13</td>
<td>18.03</td>
<td>+0.32</td>
<td>15.66</td>
<td>-1.24</td>
</tr>
<tr>
<td>Bipyridyl</td>
<td>7.00</td>
<td>15.72</td>
<td>+0.14</td>
<td>13.60</td>
<td>-1.35</td>
</tr>
</tbody>
</table>

Cu(II)-$H_2A^-$-L Systems

<table>
<thead>
<tr>
<th>Ligand (L)</th>
<th>Log $Kf^{Cu}_{Cl}$</th>
<th>Log $Kf^{Cu}_{ClAH}$</th>
<th>$\Delta \log Kf$</th>
<th>Log $Kf^{Cu}_{ClAH}$</th>
<th>$\Delta \log Kf$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>17.16</td>
<td>-0.40</td>
<td>15.50</td>
<td>-2.00</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Alanine</td>
<td>17.67</td>
<td>-0.32</td>
<td>15.77</td>
<td>-2.08</td>
<td></td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>18.09</td>
<td>+0.30</td>
<td>15.73</td>
<td>-1.30</td>
<td></td>
</tr>
<tr>
<td>Tyrosine</td>
<td>18.10</td>
<td>+0.35</td>
<td>15.73</td>
<td>-1.21</td>
<td></td>
</tr>
<tr>
<td>Tryptophan</td>
<td>18.35</td>
<td>+0.39</td>
<td>16.25</td>
<td>-1.18</td>
<td></td>
</tr>
<tr>
<td>Bipyridyl</td>
<td>15.88</td>
<td>+0.05</td>
<td>14.07</td>
<td>-1.25</td>
<td></td>
</tr>
</tbody>
</table>

X-band spectrophotometer at room temperature as well as 77K in DMF phase.

Results and Discussion

The ligands have two phenolic --OH groups and two protonated --NH groups. The dissociation of all four protons takes place stepwise. At very low pH values, the dissociation of first proton from one --NH₂⁺ group takes place. The dissociation of second --NH₂⁺ proton occurs at pH ~ 4.00. The two phenolic --OH protons dissociate at pH above 10.

The earlier studies reveal that the ligands with two well separated coordination sites, behave like two individual ligands. The ligands synthesized for the present study also contain two separate coordination centres and hence, it is expected that both the coordination centres should behave like two individual ligands, as they are at a long distance. The values of the formation constants of the first Cu(II) coordination with one coordination site is comparable with the values of formation constants of second Cu(II) ion coordination with second (N--O⁻) site, as seen from the values...
of \( K_{CuAH} \) and \( K_{CuA} - K_{CuAH} \). It should, however be noted that the latter does not exactly correspond to the constant for coordination of Cu(II) to the second \( N - C \) - coordination site i.e., \( K_{CuA} - K_{CuAH} \) because \( K_{CuA} \) is different from \( K_{CuAH} \), and the former cannot be calculated in case of both the ligands \( (A^1) \) and \( (A^2) \). On coordination of first Cu(II) ion at one \( (N - O^-) \) site, the formation of complex \( [CuAH]^2 \) takes place, while the formation of the binuclear complex \( [CuACu] \) takes place on coordination of second Cu(II) to another \( (N - O^-) \) end of \( (A) \).

The equilibrium can be shown as follows:

\[
AH_4 \rightleftharpoons AH_3 + H^+ \\
Cu(II) + AH_3 \rightleftharpoons [CuAH]^2 + H^+ \\
[CuAH]^2 + Cu(II) \rightleftharpoons [CuACu] + 2H^+
\]

Mixed-ligand complexes

**Cu:** Bipy system

The species distribution curve (Fig. 1.1) indicates that at low \( pH \), only \( [CuBipy] \) complex formation takes place and it coordinates with one \( (N - O^-) \) end of lig. A, forming mixed-ligand complex \( [BipyCuAH] \). The formation of binuclear complex \( [BipyCuACuBipy] \) starts around \( pH \sim 5 \), on coordination of second \( [CuBipy] \) molecule to the second \( (N - O^-) \) site of \( (A) \). The reactions can be shown as,

\[
Cu(II) + L \rightleftharpoons [CuL] \\
[CuL] + AH_3 \rightleftharpoons [LCuAH]^2 + H^+ \\
[CuL] + [LCuAH]^2 \rightleftharpoons [LCuACuL] + 2H^+
\]

It has been observed that the values of formation constants of complexes \( [LCuAH] \) are higher i.e., \( \Delta \log K = [\log K_{CuAH} - (\log K_{CuA} + \log K_{CuL})] \) is positive. The positive values of \( \Delta \log K \) can be attributed to the \( \pi \)-acidic nature of Bipy, and to the presence of hydrophobic interactions between the Bipy aromatic ranges and the uncoordinated long chain of the ligand \( (A) \). The absence of this type of interaction can be seen in the binuclear mixed-ligand complexes \( [LCuACuL] \). These complexes are not extra stabilized, i.e., \( \Delta \log K' = [\log K_{CuACuL} - (\log K_{CuACu} + 2 \log K_{CuUL})] \) is negative.

**Cu:** A: Amino acid systems

In the ternary systems involving Cu(II), binucleating ligand and amino acids with and without side groups, it is interesting to see the effect of side groups on the stability of mono and binuclear complexes. It is observed that \( \Delta \log K \) values for the complexes \( [LCuAH] \), where \( L \) = phenylal,

The diffused reflectance spectra of the complexes exhibit a low intensity band at \( \sim 620 \) nm,
as observed in mononuclear square planar Cu(II) complexes, indicating that both the copper centres behave like two independent equivalent metal centres.

The IR spectral bands of the complexes in KBr phase corresponding to $-\text{ClO}_4^-$ have been used to establish its ionic nature. There is one band at $\sim 1100\text{ cm}^{-1}$, corresponding to $\nu_{asym}(\text{Cl} - \text{O})$. The absence of $\nu_{sym}(\text{Cl} - \text{O})$ at $\sim 900\text{ cm}^{-1}$ indicates $T_d$ symmetry and the presence of ionic ClO$_4^-$ moiety.

The room temperature magnetic moment measurements of the complexes show that $\mu_{eff}$ values correspond to one unpaired electron per Cu(II) atom and the absence of spin exchange interaction between the two metal centres. The X-band ESR spectra of the complexes in DMF at room temperature and at 77°K also exhibit $g_{||}=2.26$ and $g_{\perp}=2.06$, corresponding to distorted OIl' compounds. There is no half field transition at $g=4$, which further supports the absence of spin exchange between the metal centres.

References
1 Casellato U & Vigato P A, Coord chin Rev, 23 (1977) 91.
9 Sigel H, Metal ions in biological systems, Copper proteins, Vol. 13 (Marcel Dekker, New York) 1981.
21 (a) Sayce I G, Talanta, 11 (1968) 1377.
(b) Sayce I G, Talanta, 18 (1971) 653.
(c) Sayce I G & Sharma V S, Talanta, 19 (1972) 821.