Study of some mixed ligand complexes of tertiary diimines and bidentate amide ligands

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Stability constants of the ternary complexes of copper(II) with tertiary diimines [bis(2-pyridylamine) (A') and 5-nitro-1,10-phenanthroline (A'')] as primary ligands and bidentate amides [MeCOCH₂CONHPh (HL¹), MeCOCH₂CONHC₆H₄Me⁻(o) (HL²), MeCOCH₂CONHC₆H₄OMe⁻(o) (HL³), PhCOCH₂CONHPh (HL⁴), salicylamide (HL⁵), salicylanilide (HL⁶) and 5-bromosalicylamide (HL⁷)] as secondary ligands have been determined by potentiometric titrations at 30°C in 50% (v/v) aqueous dioxane at 0.2 M [NaClO₄]. The \( \log K_{MAL} \) values have been determined using the computer programme SCOGS. The complexes have been isolated in solid state and characterized by elemental analyses, conductivity and magnetic measurements and electronic and IR spectral studies. The order of stabilization in the ternary complexes (i.e. \( \Delta \log K = \log K_{MAL} - \log K_{ML} \) values) has been explained on the basis of the electron repulsion concept. This has also been correlated with the shift in energy of the ligand field transition in the ternary complexes from the average value for the corresponding binary complexes.

Recent studies on the factors affecting the stability of ternary complexes are mainly directed towards the correlation of the characteristics of ligands and the ternary complex stability. Most of the earlier work describing the effect of the nature of the ligand on the stability of the complexes has been excellently reviewed. The effects of intramolecular interligand interactions and non-interacting substituents in the ligands on the stability of the ternary complexes are the major topics of current interest. In continuation of our work on the effect of substitution in ligands on the stability of ternary complexes, we report here the results of our study on some mixed ligand complexes involving β-ketoanilides (general structures I).

Materials and Methods

Bis(2-pyridyl)amine (A') (Fluka), 5-nitro-1,10-phenanthroline (A '') (Sigma), acetoacetanilide (L¹), acetoacet-\( \sigma \)-toluidide (L²), acetoacet-\( \sigma \)-anisidide (L³) (all U.C., U.S.A.), salicylamide (L⁴) (Riedel), and salicylanilide (L⁵) (BDH) were of AR grade and were used without further purification. Benzoylacetonilide (L⁶) was prepared by the literature method (m.p. 106, reported 106-106.5°). 5-Bromosalicylamide was prepared by the bromination of salicylamide with N-bromosuccinimide in N,N-dimethyl formamide (m.p. 232, reported 232°C). Purity of both these compounds was checked by elemental analyses and TLC.

Formation constants of the ternary complexes [CuAL]⁺ have been determined potentiometrically using the computer programme SCOGS, as detailed earlier, in 1:1 (v/v) dioxane-water medium at 30°C and 0.2 M [NaClO₄]. The values of the protonation constants of the ligands and the binary formation constants (\( \log K_{ML} \)) under similar conditions together with the formation constants, \( \log K_{MAL} \) of the ternary complexes and \( \Delta \log K = \log K_{MAL} - \log K_{ML} \) values have been recorded in Table 1.

Preparation of [CuAL]ClO₄

A hot methanolic solution containing 2.5 mmol
Table 1 – Stability constants of ternary complexes [CuAL] in aqueous dioxane (1:1 v/v) medium at 30°C, 
I = 0.2 M[NaClO₄]

<table>
<thead>
<tr>
<th>Ligand (L)</th>
<th>pKᵢ⁺</th>
<th>log Kᵢ⁺</th>
<th>A⁺ = dpa</th>
<th>A⁺ = N-phen</th>
<th>A⁺ = phen</th>
<th>A⁺ = bipy</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>dpa</td>
<td>6.54</td>
<td>7.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-phen</td>
<td>2.56</td>
<td>6.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acac</td>
<td>9.81</td>
<td>9.65</td>
<td>8.45 ± 0.11</td>
<td>-1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sal</td>
<td>8.55</td>
<td>5.92</td>
<td>6.03</td>
<td>+0.11</td>
<td>6.43</td>
<td>+0.51</td>
<td></td>
</tr>
<tr>
<td>L¹</td>
<td>10.98 ± 0.20</td>
<td>7.69 ± 0.07</td>
<td>6.61 ± 0.70</td>
<td>-1.08 8.62 ± 0.05</td>
<td>+0.93 8.76 ± 0.03</td>
<td>+1.07 9.30 ± 0.30</td>
<td>+1.61</td>
</tr>
<tr>
<td>L²</td>
<td>10.27 ± 0.06</td>
<td>6.85 ± 0.06</td>
<td>6.32 ± 0.30</td>
<td>-0.53 7.85 ± 0.05</td>
<td>+1.00 8.00 ± 0.08</td>
<td>+1.15 8.46 ± 0.10</td>
<td>+1.61</td>
</tr>
<tr>
<td>L³</td>
<td>10.14 ± 0.03</td>
<td>7.11 ± 0.08</td>
<td>7.89 ± 0.06</td>
<td>+0.77 8.08 ± 0.02</td>
<td>+0.97 8.12 ± 0.03</td>
<td>+1.01 8.69 ± 0.20</td>
<td>+1.58</td>
</tr>
<tr>
<td>L⁴</td>
<td>9.78 ± 0.05</td>
<td>7.07 ± 0.06</td>
<td>7.32 ± 0.07</td>
<td>+0.25 8.50 ± 0.06</td>
<td>+1.43 8.08 ± 0.01</td>
<td>+1.01 8.96 ± 0.20</td>
<td>+1.89</td>
</tr>
<tr>
<td>L⁵</td>
<td>9.33 ± 0.02</td>
<td>5.64 ± 0.09</td>
<td>5.99 ± 0.10</td>
<td>+0.35 6.41 ± 0.08</td>
<td>+0.76 6.82 ± 0.08</td>
<td>+1.18 6.81 ± 0.03</td>
<td>+1.17</td>
</tr>
<tr>
<td>L⁶</td>
<td>8.55 ± 0.01</td>
<td>4.54 ± 0.08</td>
<td>5.40 ± 0.09</td>
<td>+0.86 5.54 ± 0.06</td>
<td>+1.00 5.72 ± 0.08</td>
<td>+1.18 5.72 ± 0.09</td>
<td>+1.18</td>
</tr>
<tr>
<td>L⁷</td>
<td>8.42 ± 0.01</td>
<td>5.14 ± 0.05</td>
<td>5.78 ± 0.05</td>
<td>+0.64 5.92 ± 0.05</td>
<td>+0.78 5.74 ± 0.10</td>
<td>+0.60 5.82 ± 0.04</td>
<td>+0.68</td>
</tr>
</tbody>
</table>

*a* acac = pentane-2,4-dione; *b* sal = salicylaldehyde; *c* this work

of ligand A and 2.5 mmol of ligand L was added to an aqueous solution containing equimolar amount of copper acetate monohydrate. To the resulting solution (total volume ~ 70 ml), concentrated solution of sodium perchlorate was added till the precipitation was complete. The solid with the mother liquor was digested on a water bath for about 10-15 min, cooled, filtered, washed with water and ethanol and dried at ~ 50°C. The metal contents of the complexes were determined voltammetrically.

Analyses of the compounds are given in Table 2 together with the room temperature magnetic moment and molar conductivity values. The instruments used for these and the spectral measurements were the same as described earlier.

**Results and Discussion**

The value of log $K_{MA/L}$, determined by assuming the complete formation of MA at pH where it starts combining with L, agree well with the values determined by considering simultaneous existence of all the species, AH⁺, A, LH, L⁻, Cu²⁺, [CuA]²⁺, [CuA₂]²⁺, [CuL]⁺, [Cu₂L⁻] and [CuAL]⁺. (Here onwards the charges on the species are omitted for convenience). This indicates that the formation of [CuAL] takes place in steps, Cu + A → [CuA] and [CuA] + L → [CuAL], which is also evident from the species distribution (plot of concentrations of the various species) as function of pH (Fig. 1).

As the protonation constants indicate, the β-ketoanilides are more basic than β-diketones. However, the former form less stable binary complexes with copper. This is because in the latter case there is a possibility of M-β-diketone π-interaction with consequent pseudoaromatic character of the β-diketone complexes. In β-ketoanilides, +N = C =O resonance form (mesomeric electron release by amide N) makes the amide oxygen less susceptible to accept electrons from the metal ion and hinders the delocalization of π-electrons over the chelate ring. Thus, there is
only a slight possibility of \( \pi \)-interaction of these ligands with the metal ion.

Formation constant values in Table 1 reveal that the ternary complexes of copper(II) with tertiary diimines as primary ligands and \( \beta \)-ketoanilides as secondary ligands are more stable than the corresponding binary complexes of the ligands leading to more positive \( \Delta \log K \) \((= \log K_{MA}^{M} - \log K_{ML}^{M})\) values than the values expected on the basis of the statistical considerations. Also, \( \Delta \log K \) values are more positive than the corresponding values in the case of \( \beta \)-diketone complexes. This can be explained as follows:

In \( \beta \)-ketoanilides, electron-releasing \(-\text{NH} \) group increases the electron density over the ligand. Hence, there is more repulsion between metal \( \pi \)-electrons and the ligand electrons and thus binary \( \beta \)-ketoanilides are less stable than the binary metal \( \beta \)-diketonates. However, in the ternary complex the electron density over the metal ion gets reduced due to \( M \rightarrow A \) \( \pi \)-interaction and, hence, the electrons in ligand \( L \) face less repulsion while combining with \( MA \) than with free metal ion. Thus, the lowering of repulsion\(^{13,20} \) in the ternary complex results in its greater stabilization and less negative \( \Delta \log K \) values than those in the corresponding complexes of \( \beta \)-diketones.

The order of stabilization of the ternary complexes is reverse to that in the case of the complexes of salicylaldehyde and its derivatives\(^{14,16} \). The \( \Delta \log K \) values (Table 1) of different \( \beta \)-ketoanilides follow the order: \([Cu \text{ dpa L}] < [Cu \text{ bipy L}] > [Cu \text{ phen L}] > [Cu N-phen L] \). This may be because greater withdrawal of electron density by the diimine \( A \) from the metal ion imparts to it more of class-A character which demands a second ligand with strong \( \sigma \) basic sites for coordination. The \( O \rightarrow O \) coordinating ligands like salicylaldehyde or \( \beta \)-ketoanilides may not be able to provide such strongly \( \sigma \) coordinating sites. Hence, the complexes \([Cu A \beta \text{-ketoanilide}]\) will be less stable, when \( A \) has electron withdrawing substituents like \( -\text{NO}_2 \) on it and \( M \rightarrow A \) \( \pi \)-interaction is stronger. Further, \([Cu \text{ dpa L}] \) complexes, which have two six-membered chelate rings, are less stable than \([Cu \text{ bipy L}] \) having one five-membered and one six-membered chelate ring\(^{21} \).

The order of stabilization of ternary complexes with respect to the secondary ligands is in accordance with the above explanation. \( \sigma \) basicity and \( \pi \)-bonding ability of the amide oxygen increases and decreases, respectively, with greater electron releasing nature of the anilide ring. This results in the formation of less stable binary and more stable ternary complexes and, hence, more positive \( \Delta \log K \) values.

As far as salicylamide is concerned, it fits well in the order of stabilities of complexes of the other salicylaldehyde derivatives\(^{14,16} \). \( \Delta \log K \) value for \([Cu A \text{ salicylamide}]\) is more positive than that for the corresponding salicylaldehyde containing ternary complexes. In the ternary complexes containing salicylamide like ligands, \( \Delta \log K \) values for the complexes with different primary ligands are almost similar within the uncertainty range of the values.

**Isolation of the ternary complexes in solid state**

Analyses of the complexes correspond to the general formula \([CuAL] \text{ ClO}_4\) (Table 2). The structure of a representative complex can be shown as follows:

![Complex Structure](image-url)
**Table 3 - Ligand field bands of [CuAL] complexes (\(\tilde{\nu}\) in 10^3 cm^{-1})**

<table>
<thead>
<tr>
<th>L</th>
<th>(\tilde{\nu}) in [CuL]</th>
<th>A = (\tilde{\nu})</th>
<th>(\Delta\tilde{\nu})</th>
<th>(\tilde{\nu}) in [CuL]</th>
<th>A = (\tilde{\nu})</th>
<th>(\Delta\tilde{\nu})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d.r.s. (50% (v/v) aq. dioxane)</td>
<td>acq. dioxane</td>
<td>d.r.s. (50% (v/v) aq. dioxane)</td>
<td>acq. dioxane</td>
<td>d.r.s. (50% (v/v) aq. dioxane)</td>
<td>acq. dioxane</td>
</tr>
<tr>
<td>(A^1)</td>
<td>15.20</td>
<td>25.19</td>
<td>16.03</td>
<td>0.76</td>
<td>16.95</td>
<td>19.61</td>
</tr>
<tr>
<td>(A^2)</td>
<td>14.28</td>
<td>(210) (^b)</td>
<td>(69)</td>
<td>(42)</td>
<td>(51)</td>
<td></td>
</tr>
<tr>
<td>(L^1)</td>
<td>15.34</td>
<td>25.38</td>
<td>15.97</td>
<td>0.68</td>
<td>17.09</td>
<td>19.61</td>
</tr>
<tr>
<td>(L^2)</td>
<td>15.20</td>
<td>25.32</td>
<td>16.00</td>
<td>0.80</td>
<td>16.92</td>
<td>19.68</td>
</tr>
<tr>
<td>(L^3)</td>
<td>15.27 (^c)</td>
<td>15.97</td>
<td>16.00</td>
<td>0.81</td>
<td>17.24</td>
<td>21.74</td>
</tr>
<tr>
<td>(L^4)</td>
<td>14.75</td>
<td>25.00</td>
<td>15.75</td>
<td>0.78</td>
<td>16.83</td>
<td>23.81</td>
</tr>
<tr>
<td>(L^5)</td>
<td>14.79</td>
<td>23.53</td>
<td>16.67</td>
<td>0.68</td>
<td>16.66</td>
<td>23.53</td>
</tr>
<tr>
<td>(L^6)</td>
<td>14.97</td>
<td>23.81</td>
<td>15.62</td>
<td>0.54</td>
<td>16.61</td>
<td>23.81</td>
</tr>
</tbody>
</table>

(a) \(\tilde{\nu}_c\) values have been used for the calculation of \(\Delta\tilde{\nu}\),
(b) Molar absorbance values are given in parentheses,
(c) in methanol

Molar conductivities of one millimolar methanolic solutions of the complexes correspond to 1:1 electrolytes indicating ionic nature of the perchlorate. Magnetic moment values correspond to one unpaired electron and thus rule out any intermolecular interaction leading to spin-spin coupling, except in the case of [Cu\(AL^2\)]ClO_4 where the magnetic moment is observed to be slightly less than the spin-only value. This may be because of the weak intermolecular interaction between the O^- of one molecule with the Cu^{II} centre in another molecule.

IR spectra of the complexes in KBr phase exhibit the bands characteristic of the primary ligand and the aromatic part of the secondary ligands in the region 600-1700 cm^{-1}. A strong band at \(\sim 1100\) cm^{-1} is observed corresponding to the asymmetric \(v\)Cl-O of the perchlorate. This band and the absence of any absorption at 920 cm^{-1} corresponding to the symmetric \(v\)Cl-O support the non-coordinate nature of perchlorate anion.

Free salicylamide ligands exhibit \(v\)C=O at 1670-1680 cm^{-1}. The \(\beta\)-ketoanilides exhibit two bands at 1705-1725 and 1660-1680 cm^{-1} corresponding to the \(v\)C=O of the ketone and \(v\)C=O of amide, respectively. In ternary complexes, \(v\)C=O of the amide is lowered and occurs at \(\sim 1600-1640\) cm^{-1}. The lowering is due to the coordination of amide 0 with the metal ion. The band corresponding to ketone >C=O stretch disappears on complexation indicating enolization of the keto group. The \(v\)N-H bands at \(\sim 3350\) and \(\sim 3200\) cm^{-1} and \(\Delta\)N-H at \(\sim 1590\) cm^{-1} of the amide group remain almost unaffected in the complexes indicating non-participation of NH in coordination and supporting the fact that these ligands coordinate through bidentate O^-O sites.

Electronic spectra of the complexes in 50% aqueous dioxane and the diffuse reflectance spectra are almost identical. The complexes exhibit two low intensity bands, one at 400-450 nm (\(\epsilon_{\text{max}}\) \(\sim 100-500\)) and the other, a broad band, at 630-650 nm (\(\epsilon_{\text{max}}\) \(\sim 100\)). The bands can be assigned to the three possible transitions in a \(d^6\) metal ion. In these complexes because of the M-L pi-bonding, energies of the \(d_{xy}\) and \(d_{yz}\) orbitals of the metal ion are lowered whereas \(d_{yz}\) (\(b_{2g}\)) orbital is raised in energy. This results in the shift of the \(E_g \rightarrow B_{1g}\) transition to higher energy whereas the other two transitions, \(B_{2g} \rightarrow B_{1g}\) and \(A_{1g} \rightarrow B_{1g}\) remain merged resulting in a broad band at \(\sim 620\) nm. The latter is lightly shifted towards higher energy (\(\sim 590-600\) nm) in the d.r.s. indicating very weak intermolecular interaction in the axial direction in the solid state. The energies of the bands also indicate slight distortion from planarity in the geometry around the metal ion.

The relative positions of the bands are recorded in Table 3. They all are at higher energies...
than the positions estimated from the average of the energies of the corresponding binary complexes. The lower energy band $\tilde{\nu}$ in the ternary complexes of $\text{CuAL}$ corresponding to $A_{1g} \rightarrow B_{1g}$ and $B_{2g} \rightarrow B_{1g}$ transitions can be considered to correspond, roughly, to $10 D_{eq}$. If $\tilde{\nu}_1$ and $\tilde{\nu}_2$ are the positions of $\tilde{\nu}$ bands in $[\text{CuA}_{2}]$ and $[\text{CuL}_{2}]$, stabilization or destabilization of the ternary complex with respect to the corresponding binary complexes can be expressed as $\Delta \tilde{\nu}$ (Eq. 1).

$$\Delta \tilde{\nu} = \tilde{\nu}_c - (\tilde{\nu}_1 + \tilde{\nu}_2)/2 \quad \ldots (1)$$

$\Delta \tilde{\nu}$ values (Table 3) are all positive, which indicate that the ternary complexes are more stable than expected from average field created by the two ligands in their corresponding binary complexes. Although, both spectrophotometrically determined $\Delta \log K$ values, and potentiometrically determined $\Delta \log K$ values, are measures of the stability of the ternary complex and their orders are comparable to some extent, a linear correlation between the two does not exist. This is because $\Delta \tilde{\nu}$ is related only with the crystal field created by the ligands whereas both enthalpy and entropy factors affect $\Delta \log K$ values.

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References

17 Allen C F H & Humphlett W J, Org synth, Coll Vol. 4, p. 80.
19 (a) Sayce I G, Talanta, 15 (1968) 1397; (b) Sayce I G, Talanta, 18 (1971) 653; (c) Sayce I G & Sharma V S, Talanta, 19 (1972) 831.