Formation Constants of Some Ternary Complexes of Copper(II) with π-Bonding Ligands

SURESH PATEL & UMA CHUDASAMA*
Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda 390 002
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The formation constants of ternary complexes of the type CuAL [where A = dipyridyl (dipy), 1,10-phenanthroline (o-phen), 2-(2'-pyridyl)benzimidazole (PyBI), 2-(2'-pyridyl)imidazoline (PyIM), dipyridylamine (dpa), 5-nitro-1,10-phenanthroline (5-NO\textsubscript{2}-o-phen) and L = anthranilic acid] have been determined in 1:1 (v/v) dioxan-water medium at ionic strength \( \mu = 0.2 \) mol dm\(^{-3}\) (NaClO\textsubscript{4}) and temp. = 30°C. The effect of metal-ligand π-interaction and substitution on the tertiary amine has been discussed.

Formulation constants, \( K_{MAL}^{A} \), of ternary complexes of the type MAL where M = Cu(II) or Ni(II), A = tertiaryamine and L = σ-bonding ligand are greater than those expected from statistical consideration\(^{1}-^{3} \), due to M→A π-interaction\(^{4}-^{5} \). It was, therefore, thought of interest to study the ternary systems where L = anthranilic acid (in which the chelating amino and carboxylate groups are attached to an aromatic ring) and A = dipy, o-phen, 2-(2'-pyridyl) benzimidazole (PyBI), 2-(2'-pyridyl)imidazoline (PyIM), dipyridylamine (dpa) and 5-nitro-1,10-phenanthroline (5-NO\textsubscript{2}-o-phen) all of which coordinate through two nitrogens and have delocalised π-electrons.

All the reagents were of AR grade, except PyBI and PyIm which were prepared by a known method\(^{6} \).

The titrations were carried out in 1:1 (v/v) dioxan-water medium at \( \mu = 0.2 \) mol dm\(^{-3}\) (NaClO\textsubscript{4}) and temp. = 30°C, using a digital pH meter (accuracy ±0.01 pH units). The pH meter readings were corrected for the non-aqueous solvent by the method suggested by Van Uitert and Haas\(^{7} \).

The proton-ligand formation constants and the formation constants of the binary complexes CuL, CuL\(_2\), CuA, CuA\(_2\) were evaluated using the SCOGS computer programme as detailed earlier\(^{8} \).

For the determination of formation constants of ternary complexes, CuAL, the SCOGS computer programme was used under the following conditions:

(i) The ternary complex formation was assumed to occur by the reaction:

\[
[CuA]\textsuperscript{2+} + L \rightleftharpoons [CuAL]^{+}
\]

since formation of [CuA]\textsuperscript{2+} was complete in the lower pH range. The species considered to be present in the solution were L, LH, LH\(_2\), [CuA]\textsuperscript{2+} and CuAL. As Cu\textsuperscript{2+} and A were in equimolar proportions and as the formation of [CuA]\textsuperscript{2+} was complete, no free ligand species A, HA\textsuperscript{+} and H\(_2\)A\textsuperscript{2+} were considered. The formation constants of the ternary complexes CuPyBI.L and Cu.PyIm.L were determined using this programme. The formation constants of Cu.PyBI, Cu(PyBI)\(_2\), Cu.PyIm, and Cu(PyIm)\(_2\) could not be determined, as complete formation of [CuA]\textsuperscript{2+} was assumed.

(ii) The ternary complex formation was assumed to proceed by the reaction:

\[
Cu\textsuperscript{2+} + A + L \rightleftharpoons [CuAL]\textsuperscript{+}
\]

under the assumption that possible species in solution were LH\(_2\), LH, L, H\(_2\)A\textsuperscript{2+}, HA\textsuperscript{+}, A, Cu\textsuperscript{2+}, [CuL]\textsuperscript{+}, CuL\(_2\), [CuA]\textsuperscript{2+}, [CuA\(_2\)]\textsuperscript{2+} and [CuAL]\textsuperscript{+}.

The concentration-pH profile indicated that in the pH range ~2.0 to ~3.0, Cu(II) and CuA were the major species while in the pH region ~5.5 to ~7.0 the species CuA and CuAL predominated. The formation of CuA\(_2\), CuL\(_2\) and CuL was very less.

The values of ΔlogK, i.e. log\( K_{CuAL}^{CuA} \) – log\( K_{CuL}^{CuA} \) are small and negative (Table I) due to Cu→A π-interaction which reduces electron density around the metal ion in [CuA]\textsuperscript{2+} and makes it comparable to that in Cu\textsuperscript{2+}.

The formation constants log\( K_{CuAL}^{CuA} \) (see Table I) follow the order: Cu(5-NO\textsubscript{2}-o-phen)\(_2\)L > Cu(PyBI)L > Cu(dipy)L > Cu(o-phen)L > Cu(dpa)\(_2\)L > Cu(PyIm)L.

2-(2'-Pyridyl)imidazoline (PyIm) coordinates via one pyridine nitrogen and one of the imidazoline nitrogen atoms. In this case π-interaction is possible only with the pyridine ring, imidazoline ring being saturated is devoid of delocalised π-electron cloud. Enhanced stability of Cu(PyBI)L is due to additional π-
interaction involving nitrogen of benzimidazole ring. Cu(dipy)L and Cu(o-phen)L are of comparable stability because the extent of Cu→A π-interaction is comparable.

In the case of the complex Cu(dpa)L, chelating imino group of the ligand, situated in between two pyridine moieties, enhances the electron density on the ring because of the lone pair on imino nitrogen atoms. However, delocalisation of electron density in dpa occurs over a larger area than in dipyridyl which renders the ternary complexes Cu(dipy)L and Cu(dpa)L of comparable stability.

The highest stability of [Cu(5-NO_2-o-phen)L] is due to the nitro group which makes 5-NO_2-o-phen a stronger π-acid than o-phen.

It is observed⁵ that δlog_κ value of Cu-A anthranilate is more negative as compared to that of Cu-A-aminophenolate.

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References
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