

PUBLICATIONS

- (1) Ternary Complexes of Cu(II) with 2,2'-dipyridyl as the Primary Ligand and β -ketoanilides as Secondary Ligands

Indian J. Chem., 18, 459, 1979.

Modified Irving-Rossotti titration technique has been used to study the formation constants of binary and ternary complexes of the type $[CuL]$ and $[Cu.dipyridyl.L]$, where L = acetoacetanilide, acetoacet-o-toluidide, acetoacet-o-anisidide or benzoatoacetanilide. It has been found that the values of the formation constants of the ternary complexes, K_{CuAL}^{CuA} , are higher than those of the corresponding binary complexes, K_{CuL}^{Cu} . This shows that π delocalization exists in Copper. β -ketoanilide ring.

- (2) Mixed-Ligand Complexes of Copper(II) with Tertiary Amines and β -diketones or β -ditoanilides

J. Indian Chem. Soc., 56, 445, 1979.

A number of mixed-ligand complexes of Copper(II) of the type $[CuAL]$, where A = 2,2'-dipyridyl and 1,10-phenanthroline and L = β -diketones and β -ketoanilides have been synthesized. The complexes have been characterized by elemental analyses, visible and infrared spectra, from which bonding modes have been suggested.

(3) Studies in Some Mixed-Ligand Complexes Containing
 β -dicarbonyls. Part-IV

J. Indian Chem. Soc., 56, 751, 1979.

Mixed-ligand complexes of the type $[\text{CuLL}']$, where
 LH = acetoacetanilide or derivatives and
 L'H = salicylaldehyde or 2-hydroxyacetophenoneimine have
 been synthesised. These complexes undergo amine exchange
 over the schiff base on treatment with methylamine,
 ethylamine and ethanolamine. The complexes have been
 characterised by elemental analyses, TLC, conductance,
 magnetic moment and spectral studies.

(4) Studies of Some Ternary Complexes of Copper(II)
 Involving π bonding Ligands

J. Chem. Soc., Dalton, 543, 1981.

The formation constants of complexes of the type
 $[\text{CuAL}]^+$, where A = 1,10-phenanthroline, 2-(2'-pyridyl)-
 benzimidazole or 2-(2'-pyridyl)imidazoline and
 L = acetoacetanilide (L^1), acetoacet-o-toluidide (L^2),
 acetoacet-o-anisidide (L^3) or benzoatoacetanilide (L^4) have
 been determined in dioxan-water (1 : 1 v/v) solutions and
 0.2M NaClO_4 at 30 °C. The value of

$\Delta \log K = \log K_{\text{CuAL}}^{\text{CuA}} - \log K_{\text{CuL}}^{\text{Cu}}$ is positive except when A
 is 2-(2'-pyridyl)imidazoline. Ultraviolet spectral studies

of these complexes have also been carried out and show that there is no significant interaction between the two ligands through the metal $d\pi$ orbitals in the mixed-ligand complexes. Positive $\Delta \log K$ values may be due to a lowering in repulsion between metal $d\pi$ electrons and ligand π electrons in the mixed-ligand complex.

(5) Studies of Some Ternary Complexes of Copper(II)

Involving π bonding Ligands : Part II

J. Chem. Soc., Dalton, (In press)

The proton-ligand formation constants of LH, binary complexes $[\text{CuL}]^+$ and $[\text{CuL}_2]$, and ternary complexes $[\text{CuAL}]^+$, where A = 2,2'-dipyridyl, 1,10-phenanthroline, 2-(2'-pyridyl)benzimidazole, or 2-(2'-pyridyl)imidazoline and L = salicylamide ion, salicylanilide ion, 5-bromosalicylamide ion or 5-bromosalicylanilide ion have been determined in dioxan-water (1 : 1 v/v) solutions and 0.2M NaClO_4 at 30 °C. The mixed-ligand stability constants $K_{\text{CuAL}}^{\text{CuA}}$ have been calculated by three methods, viz. graphical linear plot, computer calculations considering complete formation of $[\text{CuA}]^{2+}$ prior to the formation of $[\text{CuAL}]^+$, and also considering all possible species to be present in solution. The values so obtained are nearly same and the concentration plot confirms that the major

species present in the solution are only $[\text{CuA}]^{2+}$ and $[\text{CuAL}]^+$. The value of $\Delta \log K = \log K_{\text{CuAL}}^{\text{CuA}} - \log K_{\text{CuL}}^{\text{Cu}}$ is positive, except when A is 2-(2'-pyridyl)imidazoline.

Majority of the mixed-ligand complexes have been synthesized and characterized. Electronic spectra confirm that there is no significant interaction between the two ligands through the metal $d\pi$ orbitals in the mixed-ligand complexes. The greater stability of the ternary complexes may be due to a lowering of repulsion between metal $d\pi$ electrons and the ligand electrons in the ternary complex.