SECTION - II

CHEMISTRY OF BIVALENT SILVER COMPLEXES WITH STERICALLY HINDERED HETEROAROMATIC LIGANDS
CHAPTER -1

INTRODUCTION TO BIVALENT SILVER CHEMISTRY
A general introduction to bivalent silver chemistry:

The sub-group of coinage metals is unique among transition metal groups in that each member has a different stable oxidation state in water.

\[ \begin{align*}
2 \text{Cu}^+ & \iff \text{Cu}^{2+} + \text{Cu} \quad \quad \text{... 1.} \\
2 \text{Ag}^+ & \iff \text{Ag}^{2+} + \text{Ag} \quad \quad \text{... 2.} \\
3 \text{Au}^+ & \iff \text{Au}^{3+} + 2 \text{Au} \quad \quad \text{... 3.}
\end{align*} \]

Cu\(^+\) and Au\(^+\) disproportionate readily (equations (1) and (3), K for copper is \(5 \times 10^5\) m\(^{-1}\) l at 25°C) while for silver, the disproportionation (equation 2) is not detectable. The major factors that decide the stability of the oxidation states are the difference in the size of the ions in different oxidation states and the differences in the ionization energies of the atoms\(^1,2\). Thus the Cu\(^{2+}\) ion, being much smaller than Cu\(^+\) ion, has a much larger hydration energy and this is responsible for the ready disproportionation of Cu\(^+\) in water. Silver on the other hand has a much larger second ionization energy while the heats of hydration are not very different. For silver the stable oxidation state in water is +1. The difference between silver and gold is mainly due to the lesser value for the third ionization energy of gold and the crystal field stabilisation of d\(^8\) configuration in square-planar geometry.

The redox potentials are profoundly influenced by ligands. Thus, Ag\(^+\) undergoes disproportionation according to equation (2) in the presence of porphyrins. Complexes are known for most of the +1, +2 and +3 ions. However Au(II) complexes have been rather elusive\(^1,3\).
Numerous Ag(II) complexes are known. Some of them are isolable in the solid state like Ag(bpy)$_2$S$_2$O$_8$ while some are obtained only in solution or in mixed crystals, for example, Ag(dedtc)$_2$. Silver salts catalyse several oxidation reactions and they are believed to involve Ag$^{2+}$ as the electron transfer intermediary. In the following sub-sections the silver(II) chemistry involving heteroaromatic ligands is reviewed so as to provide the necessary background for the novel complexes and electron transfer reaction to be presented in the subsequent chapters.

Survey of bivalent silver complexes with heteroaromatic ligands:

Several reviews in the past$^4$ as well as in the recent past$^5$ have highlighted the synthetic and structural aspects of Ag(II) chemistry. The salient features of the complexes with pyridyl, bipyridyl and related ligands only are discussed in this sub-section.

The Agpy$_4$S$_2$O$_8$ was originally prepared by Barbieri$^6$. This has been reexamined by several workers$^7$ and e.s.r. was studied$^8$. Evidence for more than four pyridines coordinating with bivalent silver was not seen even in neat pyridine solution. In frozen nitric acid solution, formation of Agpy$_2$(NO$_3$)$_2$ was suggested$^7$ which was not confirmed by recent authors$^9$. E.s.r. of this complex as polycrystalline solid solution at 1% concentration in Cdpy$_4$S$_2$O$_8$ showed hyperfine structure corresponding to an axial symmetry. All the pyridine complexes are reported$^9$ to be magnetically dilute except polymeric Agpy$_2$S$_2$O$_8$, which is antiferromagnetic$^{10}$. The electronic spectrum$^{11}$ of Agpy$_4^{2+}$ suggests square-planar configuration with much larger energy compared to 10-12 kK expected for a tetrahedral
complex. The silver hyperfine and nitrogen superhyperfine structures were observed\textsuperscript{37} for Agpy\textsubscript{2}(NO\textsubscript{3})\textsubscript{2} in frozen nitric acid solution at 77 K. Number of substituted pyridine complexes were also studied\textsuperscript{13}.

Perhaps the most popularly studied complex is Ag(bpy)\textsuperscript{2+} which was isolated\textsuperscript{14} with S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}, ClO\textsubscript{4}\textsuperscript{-}, HSO\textsubscript{4}\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, ClO\textsubscript{3}\textsuperscript{-}, CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{3}F\textsuperscript{-} anions. Tris(bipyridine) silver (II) reported\textsuperscript{15} earlier was shown not to exist\textsuperscript{16} but the presence of this bivalent silver species was suggested as an intermediate in the electrochemical studies of the Ag\textsuperscript{+}/Ag\textsuperscript{2+} system in propylene carbonate containing excess of bipyridine\textsuperscript{17}. X-ray structure of Ag(bpy)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2} \cdot H\textsubscript{2}O was determined\textsuperscript{18} which showed a distortion of \textasciitilde28\degree from square-planar AgN\textsubscript{4} unit with a weak axial interaction with two bridging nitrates to form a chain structure. In neutral solution Ag(bpy)\textsuperscript{2+} is present but in nitric acid Ag(bpy)(NO\textsubscript{3})\textsubscript{2} is produced\textsuperscript{19} which was also structurally characterised\textsuperscript{20}. It has a distorted square-planar structure with a chelating bipyridine ligand and two cis-monodentate nitrate groups with long axial contacts to two farther nitrate groups.

Similar complexes with phen as ligand are also known\textsuperscript{21}. They are found less soluble compared to bipyridine complexes and in nitric acid solution \textbrackets Ag(phen)(NO\textsubscript{3})\textsuperscript{+} was expected\textsuperscript{22} to form. With 2, 2', 2''-terpyridine the 1:1 complexes are prepared\textsuperscript{23} easily and probably are four-coordinate. Dark brown Ag(terpy)\textsubscript{2}S\textsubscript{2}O\textsubscript{8} \cdot 3H\textsubscript{2}O was obtained from AgNO\textsubscript{3}, K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} and excess terpyridine. Based on p.a.s and electronic spectra which show absorption at much lower energy than Ag(terpy)X\textsubscript{2}, it was suggested to be six-coordinate.
Secondary-ion mass spectra of bivalent silver complexes have been reported recently. Bivalent silver pyridine, bipyridine and pyrazine complexes have been analysed.

Very recently, \( \text{AgTPP}^{2+} \), was structurally characterised by x-ray data confirming the planar geometry.

Another class of nitrogen donor ligands which form Ag(II) complexes readily are pyridine carboxylic acids. They are all expected to form 2:1 planar complexes analogous to their Cu(II) complexes. However, no x-ray data is available. Most of the complexes are expected to be magnetically dilute except Ag(nicotin)\(_2\) being antiferromagnetic.

Survey on copper and silver complexes of sterically hindered ligands:

Structural studies of Cu(dmp)\(_2\)NO\(_3\), Cu(dmp).NO, and Cu(dmp)\(_2\)ClO\(_4\) and also Cu(tmbp)\(_2\)ClO\(_4\) and Cu(dmbp)\(_2\)BF\(_4\) were reported. Unlike other copper(I) complexes which are air-sensitive and are synthesised in inert atmosphere, these complexes were reported to have formed in organic solvents. In these complexes Cu-N distances showed considerable variations, ranging from 2.02-2.08 Å for dmp complexes and 2.018-2.076 Å for the substituted bipyridine complexes suggesting that for some ligands Cu-N bond lengths are significantly different. They were found to exhibit pseudotetrahedral geometry which prefers Cu(I) to Cu(II). The metal to ligand charge transfer band for Cu(dmbp)\(_2^+\) was found at a lower energy than in Cu(bpy)\(_2^+\) and the former complex will have a greater preference for tetrahedral geometry because the Cu-N bond length is expected to increase due
to the presence of methyl groups.

Compared to the Cu(II) complexes of the unsubstituted ligand which are quite stable in organic solvents, Cu(II) complexes of 6, 6'-substituted bipyridine ligands are observed\textsuperscript{28} to undergo autoreduction in non-aqueous solvents, without the need of reducing agents. Cu(dmbp)\textsuperscript{2+} was found to undergo reduction in ethanol and a reduction in the intensity of the metal to ligand charge transfer band with time was observed.

Ag(dmp)NO\textsubscript{3} complex was prepared and its i.r. data reported\textsuperscript{29}. Recently x-ray structure for Ag(tmbp)\textsubscript{2}BF\textsubscript{4} was reported\textsuperscript{30}. This was found to be isomorphous and isostructural with Cu(tmbp)\textsubscript{2}ClO\textsubscript{4}. A twist angle of 70\degree for silver compound was obtained compared to 75\degree for the copper analogue. The characteristic flattening distortion from tetrahedral geometry was ascribed to lattice effect of the stacking interactions involving the heteroaromatic ligands, rather than due to the participation of the Jahn-Teller active charge transfer excited state.