CHAPTER I

GENERAL INTRODUCTION

During the past few decades there has been a phenomenal increase in the study of the chemistry of transition metal complexes. The interest in the metal complexes now embraces areas ranging from purely academic synthesis to large scale industrial production. X-ray crystallography, magnetic studies and various spectral techniques such as Mössbauer, NMR, ESR, Electronic and IR have been extensively used for the elucidation of structures of metal complexes. In fact, this has been mainly responsible for the renaissance of coordination chemistry. The development of ligand field and molecular orbital theories has also been of immense help to those working in this rapidly growing area of inorganic chemistry(1).

The present investigation was undertaken with a view to making a modest contribution to the coordination chemistry of silver, the 47th element in the periodic table. The coordination chemistry of silver is interesting because of the ability of this metal to form complexes with different coordination numbers and also of its tendency to form poly-nuclear complexes.

Because of its high polarising power and lower position in the electrochemical series of elements, silver has a strong
tendency towards complex formation even in the monovalent state. The compounds of silver, when the metal is in its higher valency states, owe their existence with a few exceptions to the stabilising effect of complex formation. The reluctance on the part of silver to form complexes with oxygen donor ligands is evidenced by the fact that very few hydrates of silver salts are known. This may be attributed to the fact that the link of oxygen might be too weak to resist the electrostriction in crystals (2). Because of this low affinity for oxygen, only few oxygen coordinated complexes of silver are known.

Silver is one of the few metals to exhibit coordination number two characteristically when in the monovalent state. This may be due to the relatively small energy difference between the filled $d_{z^2}$ and the unfilled 's' orbitals which enables them to hybridise easily. In addition to linear coordination, compounds with coordination numbers 3, 4 and 5 are also common. Such compounds have a wide range of geometries and are often of low symmetry and may be polymeric. Majority of the complexes of silver(I) investigated during the past few years are with nitrogen and sulphur donor ligands and rarely of oxygen donors. Chelation in silver complexes is rare and is limited to systems where sulphur and oxygen or sulphur and nitrogen are the donor atoms (3).
STEREOCHEMISTRY OF SILVER(I) COMPLEXES

Coordination number 2

This is characterised usually by a linear structure about the silver atom produced by 'sp' hybridisation exemplified by the structure of silver cyanide (4), silver cyanate (5) and silver fulminate (6). However, if sulphur is the donor atom the linearity of the structure about silver is lost, possibly due to 'd' electron contribution to the expected 'sp' hybridisation scheme (7-10).

Coordination number 3

This is the most common coordination number for silver and examples are known for most of the common donor atoms. The bonding present in these complexes has been suggested to involve both $\sigma$ and $\pi$ bonds, but subsequent work indicates that the $\pi$ bond contribution is much less significant than was originally supposed (11). Some typical examples are the complexes between thiourea and Ag$^+$ in aqueous solutions (12), substituted pyridine complexes of the type $[\text{Ag}(L_2)X]$ (where $L$ = substituted pyridine and $X$ = NO$_3^-$ or ClO$_4^-$) (13), AgBr$_3^-$ in fused salts and the complexes with tertiary phosphines (14).

Coordination number 4

For univalent silver ion with its outer most electronic shell, a filled 4d level tetrahedral complex formation using
$\text{sp}^3$ hybrid bonds of 5s and 5p levels might be expected to constitute the bulk of silver(I) complex chemistry. Since tetrahedral configuration corresponds to minimum electrostatic potential energy, this is in fact the favoured configuration for four coordinated complexes in which the ligand-central metal atom bonds are of largely ionic character. However, for complexes in which bonding is more of a covalent nature, the preferred orientation is square planar involving $\text{dsp}^2$ hybridisation. Compounds of phosphines (15), arsines, thiourea (16), olefines (17), triazoles (18) etc. are some of the typical examples.

Coordination number 5

This most unusual coordination number for silver(I) is found in the trithiane complex, $(C_3H_6S_3)\text{AgNO}_3$ which contains two crystallographically different kinds of Ag cations one tetra and the other penta coordinated (19).

DONOR ATOMS IN LIGANDS

Silver ion behaves as a strong 'class b' acceptor in the Irving-Williams sense. According to Gonick et.al. (20) who determined the formation constants of a series of sulphur and nitrogen containing chelates with ions of various transition metals, sulphur is a stronger donor than nitrogen for silver ion. In fact, majority of the coordination compounds of Ag(I) isolated so far are with nitrogen and sulphur donor ligands.
They may be of pure nitrogen donors, pure sulphur donors, sulphur-nitrogen donors or oxygen-nitrogen donors. A few compounds with pure oxygen donors have also been reported. The electronegativities of sulphur, nitrogen and oxygen are 2.5, 3.0 and 3.5 on Pauling's scale (20). Due to the lone pair-lone pair repulsion, the two lone pairs of oxygen get flattened. Hence, nitrogen with one lone pair, can more effectively concentrate its electron on the metal atom. This factor along with lower electronegativity makes nitrogen donor ligands generally stronger than oxygen donor ligands. Though the lone pair-lone pair repulsion as well as the effect of the larger size of sulphur atom may reduce the donor capacity of sulphur compared to nitrogen, the availability of vacant 3d orbitals in sulphur atom for possible back donation of electrons from the metal ions is an additional factor which increases the ligand capacity of 'S' donor ligands.

A BRIEF SURVEY OF THE EARLIER WORK ON COMPLEXES OF SILVER

Majority of the complexes investigated in detail in the past few years were with nitrogen and sulphur donor ligands. Complexes with ligands containing donor atoms like phosphorus, arsenic and oxygen have also been reported. Some olefinic complexes and a few complexes containing metal ions themselves acting as ligands are also known (21).
HYDROCARBON COMPLEXES

Complexes of silver(I) with olefins have probably been more extensively studied by quantitative methods than those of any other metal ion. Compounds of silver nitrate, perchlorate and fluoborate with straight and branched chain aliphatic olefins, cyclic olefins, diolefins, oxygenated olefin derivatives and aromatic hydrocarbons have been investigated (22).

In aqueous solution the reaction to form ethylenic complexes was found to be reversible and fast. It was also noticed that the more deeply buried the double bond the less stable is the resulting complex (23). Bonding is thought to be a resonance hybrid structure of

\[
\begin{align*}
\text{C} & \equiv \text{C} \\
\text{Ag} & \\
\text{C} & \equiv \text{C} \\
\text{Ag} & \\
\text{C} & \equiv \text{C} \\
\text{Ag} & \\
\end{align*}
\]

The stability constants of silver(I) complexes have been found to be much smaller than those of the corresponding Pt(II) and Cu(II) complexes in cases where the comparison has been made (24,25). The increased stability of Pt(II) complexes is thought to be due to much stronger Pt(II) - ligand \( \pi \) bond produced by the overlap of metal 5d 6s 6p\(^2\).
hybrid orbitals with the olefin $\pi$ electron (26) than the Ag(I) - ligand $\pi$ bond produced by the overlap of the 4d orbital of silver(I) with the olefin $\pi^*$ orbital (27).

Solid silver-olefin complexes can be obtained from aqueous solution by mixing solutions of silver salt and the ligand if the complex is sparingly soluble (28). Anhydrous conditions have been employed in cases where the complex is found to be water soluble. In some cases the olefin complexes decompose in water and this property has been employed for purifying certain olefins (29).

ACETYLENES

Acetylene with aqueous solutions of silver salts give unstable complexes of the type $(C_2Ag_2)_n(AgX)_p$ where $X = NO_3^-$, $ClO_4^-$, $F^-$, $SiF_6^{2-}$, $AsO_4^{2-}$, $CrO_4^{2-}$, $SeO_4^{2-}$ and $WO_4^{2-}$ (30). Several complexes with substituted alkynes have also been prepared, usually obtained as white or yellow powder at room temperature. In the majority of the cases, side reactions and the ready loss of alkyne on exposure to air produce products of variable stoichiometry (31). Several complexes of the general formula $M\angle Ag(C=CR)_{2-\gamma}$ where $M = K$ or Ba are known. They are prepared by the reaction between Ag and K (or Ba) acetylides in liquid ammonia. They are often photosensitive and sensitive to moisture (32).
AROMATIC COMPOUNDS

Silver forms well defined complexes with many types of aromatic compounds ranging from benzene itself through molecules of increasing complexity up to polycondensed benzenoid hydrocarbons (33), and non condensed polynuclear benzenoid hydrocarbons (34-36). From a study of the crystal structure of silver perchlorate-benzene complex, it is evident that polarisation of the $\pi$-bonding system leads to an increase of electron density near silver ions and this effect is far more important than charge transfer bonding in determining electron densities within the ring (37).

NITROGEN DONOR ATOMS

Cyanide complexes: The strong tendency for complex formation between Ag(I) and CN$^-$ ions forms the basis of the cyanide process and also of the use of cyanides in electroplating baths where a low Ag$^+$ concentration is required to obtain a coherent deposit. Complexes of the types $\text{M}^+ \left\langle \text{Ag(CN)}_2^- \right\rangle$ and $(\text{M}^+)_2 \left\langle \text{Ag(CN)}_3^- \right\rangle$ are known (38), but the 4-coordinate complex known for cuprous ion, is unknown for silver (39). The $\left\langle \text{Ag(CN)}_2^- \right\rangle$ ion has been shown by X-ray analysis to have a perfect linear structure with an Ag-N distance of 3.29 Å (40).

Complexes between Ag(I) and acetonitrile (41,42) and succinonitrile (43) have been prepared. Silver tricyanomethide,
Ag C(CN)_3 is also known and a crystal structure study indicates that each Ag atom is coordinated in a flat pyramid to 3N atoms at 2.11 ± 0.06 Å (1 N atom) and 2.25 ± 0.04 Å (2 N atoms). One N-Ag-N bond angle is 99.7° and while the other two are 123.9° (44).

Isonitrile complexes of the type AgCN·R·CN have been reported (45). They are colourless crystalline compounds which on heating liberate a mixture of the nitrile and the isonitrile. They are insoluble in water and most organic solvents, but dissolve readily in alcohol. Decomposition occurs in strong acids and boiling dilute alkalis.

Nitro complexes

Both 2,3- and 4-nitrobenzoic acids form 1:1 and 1:2 complexes with silver. The values of the stability constants are in the sequence expected from ligand affinities for H⁺ ions (46) and are less than those of the corresponding copper complexes (47,48). A complex nitrite, Cs[^Ag(NO₂)₂]·7·2H₂O has also been described (49).

Ammines

The dissolution of silver halides in ammonia solution is due to the formation of an ammine complex salt. Several complex salts containing 2 or 3 ammonia molecules (but not more than 3) per silver atom have been prepared. The[^H₃N — Ag — NH₃]⁺ ion is linear (49).
Amines behave similarly (50,51) and 4-coordinate complexes have been isolated with amines like aniline and toluidine. With 2-allylpyridine, a 1:1 complex is formed, the olefinic group and the pyridine nitrogen coordinating to the metal (52).

Patel and Rao and Misra and Rao (13) have prepared 1:2 complexes of silver(I) nitrate and perchlorate with substituted pyridines like 2-methyl, 3-methyl, 4-methyl, 4-vinyl, 3-chloro, 4-cyano and 2,6-dimethylpyridine and 3,5-lutidine having the general formula $\text{AgL}_2\text{ClO}_4$ and $\text{AgL}_2\text{NO}_3$ (where L = substituted pyridine) and characterised. Some $\alpha$-picoline complexes of cyanide, thiocyanate and cyanate of silver are also known (53). Silver complexes of pyridine, 2,2′-bipyridyl, 2,2′-bipyridyl-N-oxide, 1,10-phenanthroline, 2,2′-bipyridylamine and 2-aminopyridine and its derivatives (54,55) are known. Silver chloride, bromide and iodide complexes of 1,10-phenanthrolins and bipyridyls have also been reported (56). The structure analysis of the complex $\text{Ag(en)}\text{ClO}_4$ formed from solutions of silver perchlorate and 1,2-diaminoethane reveals a linear coordination of silver with the ligand acting as a bridge to form a long chain polymer (57). In solutions at higher concentration the species $\text{Ag}_2\text{(en)}_2^{2+}$ predominates (58). Lately, the IR spectra of silver(I) complexes of 4,4′-bipyridyl, methylpyrazine, quinoxaline, 4,4′-bipyridyl N-oxide, 1,3-bis(4-pyridyl) propane, hexamethylenetetramine (59,60) and 6-amino-5-nitroso uracil and its methyl derivatives (61) have been
investigated.

Silver(I) readily forms eight membered ring systems. The structure of the nitrate complex of methyl cystosine-a DNA base - is a limit consisting of two bidentate ligands and two silver atoms to give a ring (Fig 1) (62). The limits are stacked so that the cross linking occurs between them and silver coordination rises to 4.

![Figure 1](image)

In some imidazole complexes from solutions of 3M sodium perchlorate and imidazole, the species $\left[ AgL \right]^+$ predominates at high concentrations and the species $\left[ Ag(OH)L \right]$ at low concentrations (63).

X-ray studies in solution of the diammine complexes indicate that there are two nitrogen-silver bonds of length $2.22 \pm 0.02 \text{ Å}$ (64). The nature of coordination of two ammine groups to silver has been probed by solid state NMR studies of $\left[ Ag(NH_3)_2 \right]$, $\left[ Ag(NO_2)_2 \right]$ (65) and AgSO$_4 \cdot 4NH_3$ (66). Both indicate rapid reorientation of the ammine groups about the essentially linear species.
Silver(I) ions can form complexes with nucleic acids (67) probably by the involvement of \( \sigma \) -electron pairs of nitrogen atoms of the purine and pyrimidine moieties though \( \pi \) -bonding also is a possibility (68,69). They are similar to corresponding copper complexes at low silver ion concentrations, but at higher silver ion concentrations another complex consisting of a silver ion combined with two nucleotide residues was obtained (70).

PHOSPHOROUS AND ARSENIC DONOR ATOMS

The addition compounds, \( \text{AgX} \cdot \text{P(OEt)}_3 \) (\( X = \text{halogen} \)) were described as early as 1905 (71). Silver halide complexes with trialkyl phosphine and arsine, which are very similar to their cuprous analogues, are also known (72). They are all 4 coordinate complexes, the 4-coordination being conferred by polymerisation as evidenced by molecular weight determinations. Recently, the complexes \( \text{Ph}_3 \text{P} \cdot \text{AgX} \) and \( (\text{Ph}_3 \text{P})_3 \cdot \text{AgX} \) (\( X = \text{halogen and BH}_4^- \)) have been prepared as crystalline white solids (73). The 1:1 and 2:1 complexes between vinyldiphenylphosphine and silver nitrate have also been reported (74). In vinyldiphenylphosphine complexes, coordination occurs between Ag(I) and both the phosphorous atom and the vinyl double bond.

The reaction of \((1,8\text{-naphthalenedicarboxylato)disilver(I)}, \ (\text{C}_{12}\text{H}_6\text{O}_4)\text{Ag}_2 \) with a variety of phosphines gives novel complexes
of the type \( (\text{C}_{12}\text{H}_{16}\text{O}_{4})_2(\text{L}\text{Ag})_4 \) where \( \text{L} = \text{PPh}_3 \). The \( \text{PPh}_3 \) complex has been shown to contain a cave of four silver atoms bridged in a complex manner by the carboxylate ligands; the phosphine groups being coordinated to silver outside the cave (75). With the multidentate ligand (II), the results are somewhat more predictable with a tridentate coordination of (II), the 4th site being occupied by a phosphine (76). However, when phosphine is bidentate, a bridged structure is formed (Fig III) and (II) behaves as a bidentate ligand.

![Figure II](image)

The complexes of silver with phosphines, arsenes and stibines are four coordinate pseudo-tetrahedral (77) in nature.
In the compounds \((\text{Ph}_3\text{P})_2\text{Ag(BH}_4)\) and \((\text{Ph}_3\text{P})_3\text{Ag(H}_3\text{BCO}_2\text{R})\) (\(\text{R} = \text{C}_2\text{H}_5\) or \(\text{H}\)) the boron hydride is coordinated to the metal in a monodentate fashion. This is the least well characterised of the expected modes of boron hydride coordination (78). In the complex, \(\text{M}_2\text{S}_8 \left[\text{Ag(PPPh}_3\right]_4\) (\(\text{M} = \text{Mo or W}\)) (79,80) a most unusual structure is revealed, a system of two six membered rings. In this, one phosphine is attached to each silver atom (Fig IV).

The crystal structure analysis of dimeric chloro bis(triphenylphosphine) silver(I) reveals as expected, the presence of two bridging groups (81).

**OXYGEN DONOR ATOM**

The poor affinity of silver for oxygen is shown by the fact that very few hydrates of silver salts are known. In solution the silver ion may be hydrated, and tetra-aquo silver ion has been postulated with two molecules held firmly.
and two loosely (82). But this postulate is not substantiated by entropy data (83) and the species present is probably \( \text{Ag(OH}_2\text{)}_2^- \) (84).

Although the linear ion, \( \text{Ag(OH)}_2^- \) (log \( k_1 = 2.3 \), log \( k_2 = 1.9 \)) is known, the complexing power of Ag(I) with monodentate oxygen ligands is low (85) and the behaviour when oxygen is part of a chelating ligand is not clear. Among the few silver(I) complexes with the oxygen donor ligands are those with dioxan (\( \text{AgClO}_4 \cdot 3\text{C}_4\text{H}_8\text{O}_2 \)) and octamethylpyrophosphoramide (OMPA) \( \text{Ag(CMe}_2\text{N)}_2\text{PO.0.0P(NMe}_2\text{C)}_2^- \) (86-88). In the latter complex, OMPA can satisfy the maximum coordination number of the metal ion even though spectral evidence indicates weak bonding. OMPA is believed to form 6-membered rings with the metal ion in which the phosphoryl oxygens are the donor sites (Fig V).

Specific triangular coordination is found in tris[1-phenyl-3,5-dimethylypyrazole]silver(I) nitrate. Ag is regarded as two
and three coordinated in AgBaGeS$_4$ (89).

In recent years an oxygen donor ligand, semicarbazide has been used as a new reagent for the detection of silver (90). Some adducts of unipositive silver with oxygen donor ligands have been prepared and their IR spectra examined. Dimethylacetamide, N-methylacetamide, dimethylformamide, dimethylurea, tetramethylurea, triethylphosphate, hexamethylphosphoramide, pyridine-N-oxide and dimethylsulphoxide have been used as ligands towards silver(I). The complexes are, in most of the cases, hygroscopic and photosensitive (91).

SULPHUR DONOR ATOM

The affinity of silver for sulphur is much greater than that for oxygen and correspondingly larger number of complexes of sulphur donors are known. They are of two main types (1) addition compounds with thioethers and (2) addition compounds with thiourea and its derivatives and other compounds containing C=S grouping (92-95).

Stability of silver thiourea complexes in solution decreases as the substitution increases (96). Silver is sufficiently soft to react with coordinated 'S' and will form a complex with $\left[\text{en}_2\text{CoC\text{SCH}_2\text{COOH}}\right]^{-}$ without breaking the Co-S bond (97). With 2-methylthiomethylpyridine, silver(I) forms a complex probably containing a dimeric cation $\left[\text{Ag}_2(\text{mmp})_2\right]^{2+}$ (98) (Fig VI).
Thiazolidine-2-thione (99) and deprotonated 2-mercapto benzoxazole (100) complexes of Ag(I) have been prepared. They were found to be linear having a 1:1 metal ligand stoichiometry. The 1,2,4-triazole-3-thiol complex of univalent silver Ag(C$_2$H$_2$N$_3$S) has been characterised on the basis of IR and analytical data (101). For the silver(I) complex of 3-methyl and 3-ethyl-4-amino-5-mercapto, 1,2,4-triazole, a polymeric structure having 1:1 stoichiometry is expected (102). The silver(I) complex of 3-diphenylaminomethyl-5, o-hydroxyphenyl-1,3,4-oxadiazole-2-thione, has the composition Ag$\left(\text{C}_{21}\text{H}_{17}\text{N}_{3}\text{O}_{2}\text{S}\right)\text{NO}_{3}$$\cdot$$2\text{H}_2\text{O}$. The water molecules are removed at 150°C without the decomposition of the complex indicating noncoordinated nature of the water molecules. The compound is linear and diamagnetic (8). Complexes of 2-furaldehydethiosemicarbazone (103), and mercapto-benzothiazole (104) have also been prepared. Saheb et.al. have examined the reactions of 2-thiopyrrole-1,2-dicarboxamide and N-carb mcylpurrole-2-thiocarboxamide with Ag(I) and many other transition metals (106). The nature of the M-S bond
was extensively studied. The structure (VII) is assigned to the silver complexes

Complexes of 5-benzylthio-1,2,4-triazole (107), 2-amino-1,3,4-thiadiazole, 2-ethylamino-1,3,4-thiadiazole (105), N-benzoyl-N-(2-pyridyl)thiourea (108), thiourea and dimethylol-thiourea (109) with silver(I) have also been investigated.

The dithiocarbamate complexes of silver(I) exist as hexamers in solution (110). The crystal structures of $\text{[Ag} \text{n-Pr}_2\text{Dtc]}_6$ (111) and $\text{[AgEt}_2\text{Dtc]}_6$ (112) have been determined.

Akerstrom investigated the reaction of univalent dithiocarbamates with tetraalkylthiocarbamoyldisulfides and determined the stoichiometries for oxidants of $\text{[Ag} \text{R}_2\text{Dtc]}$ (113, 114). The Ag(II) and Au(II) complexes have not been isolated so far. However, their presence has been detected in solution using EPR and electronic spectra.

Vanngard and co-workers investigated the EPR spectrum of $\text{[Ag} \text{i-Pr}_2\text{Dtc]}_2$ in benzene solution (115, 116) and detected
the hyperfine structure in the EPR spectrum due to the naturally abundant $^{33}$S, which was not observed in the EPR spectrum of $\text{Ag(PipDtC)}_2$ (117).

Very interesting temperature dependence was observed in the EPR spectrum of Ag($\text{Et}_2\text{DtC}$)$_2$. At 295 K the spectrum consisted of a doublet ($g = 2.020 \pm 0.001; A = 2.76 \times 10^{-3} \text{ cm}^{-1}$) and a triplet ($g = 2.040 \pm 0.001; A = 12.50 \text{ e}$). At 373°C the triplet becomes unobservable and the peak intensity of the doublet increases by a factor of 10. The triplet reappeared on cooling and at 243 K the two signals were of equal intensity. Further cooling to 223 K resulted in the complete disappearance of the doublet. These data were interpreted as due to the equilibrium.

$$\text{Ag}^{I}(R_2\text{DtC}) + \frac{1}{2}(R_2\text{DtC}) \rightleftharpoons \text{Ag}^{II}(R_2\text{DtC})_2$$

The doublet arises from the Ag(II) complex while the triplet is due to $R_2\text{DtC}$ radical. It is interesting to note that no such behaviour was found with the complex $\text{Ag(BzDtC)}_2$ which showed only one doublet signal (118). Recently, the equilibrium, silver(I) dithiocarbamate - silver(II) dithiocarbamate in chloroform solutions was studied spectrophotometrically and by EPR spectroscopy (119). The data obtained confirm the existence of polymers in the silver(I) dithiocarbamate complexes, hexamers being the dominating species. The values obtained on Ag(II) dithiocarbamates indicate
mostly monomer formation, but dimer formation can also be expected to a smaller extent (119).

HALIDE DONOR ATOMS

Existence of complex ions of the type $\text{AgX}_2^-$, $\text{AgX}_3^-$ and $\text{AgX}_4^-$ (X = halide ion) has been reported by various workers in aqueous solutions of AgX and alkalimetal halides (120,121). Complexes of the types $\text{M}_2\text{AgI}_3$ and $\text{MAg}_4\text{I}_5$ (M = $\text{K}^+$, $\text{Rb}^+$, $\text{NH}_4^+$) have been obtained on cooling molten mixtures of AgI and MI. $\text{RbAg}_4\text{I}_5$ is remarkable for its ionic conductivity (0.12 ohm$^{-1}$ cm$^{-1}$ at room temperature) which exceeds that of all known solid ionic conductors. Several studies have been made on the solubility of halide and silver ions in alkali nitrate melts and the results interpreted in terms of complex ion formation. The complex ions postulated include $\text{AgBr}_2^-$, $\text{AgBr}_3^-$, and $\text{AgBr}_6^-$ (122-124).

Silver halide complexes of substituted 1,10 phenanthroline and related dipyridyls were studied extensively by Hall et.al. (125). Complexes of the type $\text{AgLX}$ (where L = substituted phenanthrolines and X = F, Cl, Br and I) have also been investigated (56).

CHELATE COMPLEXES

Very few chelate complexes of silver are known and these usually involve at least one sulphur donor atom. Some
exceptions do occur and an example of oxygen-oxygen chelate is the colourless salt, $K(\text{AgCO}_3)$ which crystallizes from a solution of silver carbonate in aqueous potassium carbonate. An X-ray analysis indicates the presence of a ring structure (Fig VIII) (126). The octamethylpyrophosphoramide complex described earlier also contain oxygen chelation.

\[
\begin{array}{c}
\text{Ag} \\
\text{O} \\
\text{C=O} \\
\text{O} \\
\end{array}
\]

More common is the sulphur-oxygen chelates which are of great importance in photography. The solubilizing action of the thiosulphate ion on silver halides is due to the formation of sulphur-oxygen chelate. The precise composition of the thiosulphate complex obtained is dependent on the reaction conditions (127) and a typical possible structure of $\text{Na}_2\text{[Ag(S}_2\text{O}_3)_2]}$ is shown in Fig IX (128). However, infrared evidence suggests that the thiosulphate ions in this complex is acting as a monodentate ligand only (129).
Much less common than the sulphur-oxygen chelation is sulphur-nitrogen chelation. Nevertheless it does occur. A typical S-N chelating ligand, \(2\text{(methylthiomethyl)pyridine(MMP)}\) yields the complex \(\text{Ag(MMP)ClO}_4\). The complex probably contains the dimeric cation, \(\text{Ag}_2\text{(MMP)}_2^{2+}\) (98).

**COMPLEXES OF SILVER(II)**

Argentic ion is stabilized by coordination, particularly with nitrogen containing heterocycles. The complexes formed are usually four coordinate square planar (some times distorted) (130) produced by \(d_{sp}^2\) hybridisation (131). Compounds with higher coordination numbers are also known (132,133).

In this oxidation state silver ion has the electronic configuration \(4d^9\) and hence exhibits paramagnetic properties. Ag(II) complexes are usually magnetically dilute (134,135) showing magnetic moment values of 1.7-1.8 BM. This corresponds to spin only contribution of one unpaired electron with almost complete quenching of the orbital angular momentum.

ESR measurements have indicated the existence of two classes of Ag(II) complexes (134). (1) Inorganic salts of complex cations including compounds in which the ligand molecules are nitrogen containing bases. In this class of complexes the unpaired electron is not localized on the silver ion and no hyperfine splitting due to the silver nucleus is observed. The hybridisation in this case could
be $4d\ 5s\ 5p^2$. (2) Inner complexes which include the complexes of the derivatives of pyridine carboxylic acids. In these the presence of negatively charged ligands tends to localize the unpaired electron on the silver ion thus giving a less quenched orbital angular momentum. Hybridisation in this case could be $5s\ 5p^2\ 5d$.

The argentic ion will give fairly stable aqueous solutions when strongly acidified with non-reducing acids. For example, acidic solutions of argentous salts can be oxidised by persulphate ion, fluoride or ozone to argentic ion (136,137). The solutions are coloured and paramagnetic, the colour being dependent on the nature of the acid used to acidify the argentous salt solution (136). The colour effect together with the results of the kinetic studies (138) suggests that the anion is coordinated to argentic ion in solution.

Some of the Ag(II) complexes are very stable. Ag(II) complexes with pyridine $[\text{Ag(Py)}_4]^+X_2$ (139), dipyridyl $[\text{Ag(dipy)}_2]^+X_2$ (133), tripyridyl $[\text{Ag(tripy)}X]^+_X$ (140), ortho-phenanthroline $[\text{Ag(o-phen)}_2]^+_X$ (141) and pyridine mono, di and tri carboxylic acids (142,143) have been reported. The pyridinecarboxylic acid series is interesting. In general the stabilities of these complexes vary as $(\text{mono}) > (\text{di}) > (\text{tri})$. The spacial distribution of the carboxylic acid groups on the pyridine nucleus also affects
the stability of the resultant complexes and it has been postulated that steric effects which could hinder (or distort) a planar dsp$^2$ configuration around the silver ion would produce complexes of reduced stability (143).

Ligand field spectra of some complexes of bivalent silver were investigated by Banerjee and Basu (144). These compounds are rather unstable in solutions, the bivalent silver getting reduced to monovalent state. In the presence of excess of persulphate, the bis-bipyridyl compound was found to be stable for several hours and measurement of solution spectra was possible. All the compounds studied were tetracoordinated having either tetrahedral or square planar geometry. In the tetrahedral case the d orbitals split into a triply degenerate less stable $t_{2g}$ and a doubly degenerate stable $e_g$ stage. In the case of square planar structure, on the other hand the d orbitals split into four levels, the energies being in the order $d_{x^2-y^2} > d_{xy} > d_z^2$, $d_{xz}$, $d_{yz}$. In the $d^9$ case there can be only one transition involving the $t_{2g}$ and $e_g$ levels for tetrahedral configuration while there will be at least three transitions $d_{x^2-y^2} \rightarrow d_{xy}$, $d_{x^2-y^2} \rightarrow d_z^2$, $d_{x^2-y^2} \rightarrow d_{xz}$, $d_{yz}$ for a square planar structure (assuming positron excitation). The experimental data show that the absorption bands could be resolved into three Gaussian components in all the cases, thereby indicating that the bivalent silver is taking a square planar configuration in these tetra coordinated complexes (144).
Spectral, magnetic and X-ray studies of a number of carboxylic acid complexes of silver(II) have been made in detail (145-153). Majority of these complexes are four coordinated whose stereochemistry approximates to square planar.

SILVER(III) COMPLEXES

In this oxidation state silver has the electronic configuration 4d^8. It is extremely doubtful whether the uncomplexed Ag^{3+} ion can exist. The stability of Ag(III) is greatly increased when complexed with ethylenebidiguanide (Fig X) and stable salts with composition \( [\text{AgEn(BigH)}_2]X_3 \) (where \( X = \text{HSO}_4^-, \text{ClO}_4^-, \text{NO}_3^-, \) and \( \text{OH}^- \)) have been obtained (Fig XI) (154). These compounds are obtained as beautiful needle shaped crystals. When \( X = \text{OH}^- \), the crystals are violet red and stable at ordinary temperatures. They can be recrystallised from warm dilute nitric acid in which solvent the stability of the complex cation has been determined (155). These complexes are
diamagnetic. Crystal structure of the nitrate complex has been elucidated (156). En(BigH)_2 acts as a tetradentate ligand forming two coordinate and two covalent bonds through four nitrogen atoms. This results in the formation of one 5-membered and two six membered rings. Each ring is planar but the rings subtend angles between one another so that the whole molecule is not planar and is analogous to the copper complex (157). The non planarity results in distortion of the dsp^2 configuration about silver. Salts of Ag(III) are stabilized by coordination with ethylenebiguanide (Fig XII) forming complexes of the formula \( \text{Ag(III)}(\text{EnBigH}_2)\_X_3 \) (Fig XIII) where X = \( \frac{1}{2} \text{SO}_4^{2-}, \text{NO}_3^-, \text{ClO}_4^-, \) and \( \text{OH}^- \).

These complexes are similar to ethylenebiguanide complexes (158). They are also deep red diamagnetic crystals.

Stabilization of Ag(III) with simple biguanide C_2H_7N_5 has also been achieved and the brown sparingly soluble crystalline compound Ag(C_2H_7N_5)_2(OH)SO_4\_7H_2O is obtained by K_2S_2O_8 oxidation of a cold aqueous solution of silver nitrate.
and biguanide sulphate at pH 6.5-7.0. Treatment with dil nitric acid yields a complex in which OH$^-$ is replaced by NO$_3^-$. The suggested structure of the complex ion is (XIII) (159).

SCHIFF BASES, IMIDAZOLES, DITHIOCARBAMATES AND THIOSEMICARBAZONES AS LIGANDS

Schiff bases have the general structure RN=C-R' where R and R' are aryl, alkyl, cyclo alkyl or heterocyclic groups which may be variously substituted. They are often referred to as anils, imines or azomethines and are prepared by the condensation of a primary amine with an active carbonyl group. Schiff bases which are effective as coordinating ligands bear a functional group, usually OH, sufficiently near the site of condensation so that five or six membered chelate ring can be formed upon reaction with the metal ion. Schiff bases are known to possess tubercidostatic (160,161), bactericidal, fungicidal (163,164), antimicrobial (165,166) and anticancer (167,168) activities. The possibility of using them in chemical analysis (169), selective separation and enrichment of certain metals (170,171), catalysis and gas chromatography (172,173) and also in stabilising polyolefines against oxidation and ultraviolet light deterioration (174) is being explored. Metal derivatives of schiff bases are known since 1840 (175). Both synthesis
and properties of schiff base complexes are very often related to the associated metal and these aspects have been discussed in detail by Lindoy and Layer (176,177). Various aspects of their chelating characteristics are discussed by Dewer and Mellor and Saul Patai (178,179). Schiff bases derived from salicylaldehyde and various amines are most thoroughly studied (180,162) Yamada et.al. have reviewed the developments in the stereochemistry of schiff base metal complexes (181). A survey of literature shows that no silver complex with schiff bases has been investigated in detail so far (182).

Imidazole is generally regarded as aromatic and the molecule is planar as expected for an aromatic system (183). When the aromaticity is taken into consideration there is only one pair of electron as lone pair, the pair of N₃ and the π electrons of N-1 are part of the aromatic sextet. Protonation of N-3 takes place at pKₐ = 7.1 in acid solutions. Imidazole as a ligand can be quantitatively compared to ammonia and pyridine. The order of increasing basicity Pyr < ImH < NH₃, is also order of decreasing π electron acceptor capability which is nil for ammonia. Some combination of these two properties make imidazole an excellent donor molecule. Very little work on silver complexes of imidazoles, benzimidazoles and other substituted imidazoles has been done so far (184-186).
Dithiocarbamates (the products obtained by the reaction of carbon disulphide with the nucleophile, RNH form chelate complexes with metal ions coordinating through both the sulphur atoms, giving rise to a 4-membered stable ring system. It has been reported that in certain cases it can act as a monovalent monodentate ligand also. Dithiocarbamic acids and their metal complexes have application in various fields and this has stimulated much research work in this field. A review of the analytical applications and the chemistry of dithiocarbamates and other dithioacids is available (187). Except the pioneering synthetic studies by Akerstrom, Hesse Nilson and Cras et.al., no other systematic work on dithiocarbamate complexes of silver has been reported so far.

Thiosemicarbazide (H₂NCSNHNH₂) reacts with aliphatic as well as aromatic compounds containing active carbonyl group to yield thiosemicarbazones (H₂NCSNHNCR₁R₂). They are strong complexing agents and give rise to a large number of chelate complexes with metal ions by bonding through sulphur and hydrazinic nitrogen. Monodentate behaviour where coordination is through the sulphur atom alone also has been observed. The interesting chemistry of thiosemicarbazones has been reviewed by Akbar Ali et.al. (188) and Campbell (189).

Many of the complexes of thiosemicarbazones possess antitubercular (190) and antimalarial (191) activity. They
are also found to be active against influenza (192), protozoal maladies (193), small pox (194) and certain kinds of tumour (195). They have been reported to possess pesticidal and fungicidal properties also (196,197). 5-Hydroxypyridine-2-carboxaldehydethiosemicarbazone is one of the most active anti-lukaemia agents used (198). These findings have led to an increased interest in the chemistry of transition metal complexes of thiosemicarbazones (199). A perusal of literature revealed that very little work has been done on silver complexes of thiosemicarbazones.

SCOPE OF THE PRESENT INVESTIGATION

During the present study the donor behaviour of several dithiocarbamates, thiosemicarbazones, imidazoles and isonicotinoylhydrazones towards silver(I) has been examined. Many of these ligands are of considerable biological as well as industrial importance. It is well known that the biological activity is often enhanced several fold when these organic molecules are complexed with metal ions. This makes a detailed study of the metal complexes of such ligands all the more important. Several new complexes of silver(I) with the ligands mentioned above have been prepared in the solid state and characterised. The complexes studied include a few complexes of silver(I) containing fluoride as the counter anion. Complexes of silver(I) of this
type are prepared for the first time.

For convenience of the thesis is divided into nine chapters as detailed below.

Chapterwise arrangement of the thesis

Chapter I gives a review on the chemistry of silver(I), a brief survey of the relevant aspects of the chemistry of carbodithioates, thiosemicarbazones, schiff bases and imidazoles. It also briefly outlines the scope and significance of the present investigation.

The reagents used, methods of preparation of the ligands, the physico-chemical techniques employed and some procedural details are described in chapter II.

Chapter III deals with the preparation and characterisation of silver(I) complexes of the dithiocarbamates derived from the heterocyclic secondary amines, morpholine, piperidine, 1,2,3,4-tetrahydroisoquinoline, N-methylpiperazine and pyrrolidine.

The preparation and characterisation of thiosemicarbazone complexes of silver(I) are described in chapter IV. Thiosemicarbazones of salicylaldehyde, o-hydroxyacetophenone, benzaldehyde and piperonaldehyde have been used as ligands.
In chapter V the preparation and characterisation of silver(I) nitrate and perchlorate complexes of the Schiff bases derived from isonicotinoylhydrazide and 2-hydroxyacetophenone, furfural, benzaldehyde decyclohexanone, 2-acetylfuran, 4-hydroxybenzaldehyde, 4-methylbenzaldehyde, 4-methoxybenzaldehyde, 4-chlorobenzaldehyde, 4-nitrobenzaldehyde, 4-dimethylaminobenzaldehyde or 2-nitrobenzaldehyde are described.

Chapter VI deals with the preparation of the silver(I) fluoride complexes of the ligands, 8-hydroxyquinoline, 1,10-phenanthroline, 4,4′-bipyridyl, pyridine carboxylic acid and pyridine-2,6-dicarboxylic acid and their characterisation.

Chapter VII comprises the work on the silver(I) fluoride complexes of the Schiff bases derived from isonicotinoylhydrazide and salicylaldehyde, 2-hydroxyacetophenone, benzaldehyde, furfural or 2-acetylfuran.

Chapter VIII deals with the studies on the complexes of silver(I) with the Schiff bases derived from pyridine-2-aldehyde and phenylhydrazine, benzoylhydrazide, isonicotinoylhydrazide or thiosemicarbazide.

The last chapter (Chapter IX) deals with the preparation and characterisation of the silver(I) complexes of the imidazole derivatives, 2-coumarinylbenzimidazole and benzimidazole-2-thiol.