PHYSICO-CHEMICAL STUDIES
IN METAL COMPLEX FORMATION
PART: ONE

PHYSICO CHEMICAL STUDIES OF ARGENTATION EQUILIBRIA IN SOLUTION WITH SOME HETERO-
CYCLIC LIGANDS-PYRAZOLE AND SOME METHYL
SUBSTITUTED PYRAZOLE
SECTION A

MODERN TRENDS IN THE STUDY OF ARGENTATION

EQUILIBRIA
The element silver (Ag), one of the most well-known elements from the ancient times, is a member of second transition series as well as a member of the noble metal family. It (atomic number 47) has a single 5-electron outside a completed d-shell (4d\(^{10}\) 5s\(^{1}\)) and thus the argentous state Ag(I')-compounds is the normal and predominant oxidation state of silver.

The metal ion exists as a well-defined colourless argentous ion (Ag\(^{+}\)) in aqueous solution. Schmidt and Kellér\(^{1}\) in 1929 and later on Bathe\(^{2}\) reported that in aqueous solution of strongly dissociated silver salts, Ag(I) is present as a diaquo complex. The nature of the solvation shell is, however, not known with certainty. Both ionic and covalent characters are exhibited by Ag(I) compounds. Salts such as AgNO\(_{3}\), Ag\(_{2}\)SO\(_{4}\),
AgOCOCH₃ etc. appear to be primarily ionic on the basis of the Ag-O distances. On the other hand, although AgCl, AgBr have the NaCl structures, there appears to be appreciable covalent character in the Ag ...... X bonding.

For Ag(I), the stereochemistry is sensitive to the nature of the ligand and although the predominant co-ordination number is 2, there are some types of ligands with whom co-ordination number 4 is attained.

Metal ions having characteristic co-ordination number 2, usually have linear configuration of their complexes. This has been evidenced by X-ray analysis of silver diamine complex by Corey and Wyckoff. Both π-bonding and non-π-bonding ligands form complexes in solution with Ag(I). Most of these stable complexes usually have linear structures like (I-A-1).

\[
\begin{array}{c}
\text{L} & \text{Ag} & \text{L} \\
(\text{I-A-1})
\end{array}
\]

and as such chelating ligands cannot form such simple ions and hence tend to form polynuclear complex ions. For monodentate ligands, all the species AgLn (where n = 1 to 4) may exist in solution, but in most of the cases the high stability
constant values for the complexes with \( n = 1 \) and \( 2 \) in comparison to those with \( n = 3 \) and \( 4 \) point towards the predominance of the linear complexes. The possibilities of \( \text{Sp}^2 \) and \( \text{Sp}^3 \) bonding in addition to linear hybridisation are, however, sensitive to the nature of the ligand. The exceedingly small tendency of the complexes of Ag(I) to change from linear configuration to a configuration with 4 valency bonds has been viewed by many workers to be due to the possibility that the tetra complexes actually are tetrahedral or have a configuration with 2 oppositely placed strongly bound and 2 more loosely bound ligands. For ligands with \( d\pi \) bonding potential, especially S, Se, P and As donor ligands, the three and four coordinated species can predominate\(^4\).

Orgel\(^5\) suggested that the pronounced tendency for the most Ag(I) complexes to exhibit linear 2-fold co-ordination is due to a relatively small energy difference between the filled d-orbitals and the unfilled S-orbital which permits extensive hybridisation of the \( dz^2 \) and S-orbitals and further that of \( p_z \) orbitals. This favours formation of two hybrid orbitals suitable for forming a pair of linear covalent bonds.

The complexation reactions of Ag(I) indicate that the ligand studied are of three main types viz.,
(1) ligands with little or no dπ-bonding capacity, which show a marked inflexion or a limiting value at \( n = 2 \) in the complex constant curves e.g. \( \text{NH}_3 \) gives only \([\text{Ag(\text{NH}_3)}_2]^+\) even in the highest concentration of \( \text{NH}_3 \).

(2) ligands having strong dπ-bonding capacity which have a limit at \( n = 1 \) or \( n = 3 \) such as P, As or I and

(3) ligands of intermediate dπ-bonding capacity which show uniform formation upto \( n = 4 \). Complexes of this type viz. \([\text{AgL}_4]\text{ClO}_4\) can be obtained with phosphines\(^7\) and with certain phosphites\(^8\). The unusual tertiary

\[
\begin{align*}
\text{CH}_2 & \quad \text{P.C}_6\text{H}_5 \\
\text{CH}_2 &
\end{align*}
\]

\((\text{I-A-2})\)

phosphine, 2-phenyl phosphindoline (I-A-2) forms several types of Ag(I) complexes\(^9\). With ethylene-diamine, different types of complexes depending on the conditions of the reactions result but 2-co-ordination of Ag(I) appears to be preserved either by bridging (I-A-3)

\[
\begin{align*}
\text{Cl} & \quad \text{Ag} \quad \text{NH}_2. \text{CH}_2. \text{CH}_2. \text{NH}_2 \quad \text{Ag} \quad \text{Cl}
\end{align*}
\]

\((\text{I-A-3})\)
or by polymerisation\textsuperscript{10}.

Study of the argentation equilibria has been attempted since the end of the last century\textsuperscript{11-15}. Although it includes the determination of stability constants of Ag(I) complexes in solution and studies on various factors affecting the stability on one hand and studies on the thermodynamics of these complexation reactions on the other hand, a thorough investigation is lacking on the latter aspect of study. As such, without dividing the present discussion in two parts, the relevant observations on the study of thermodynamics of argentation equilibrium will be discussed in the proper position.

Both inorganic and organic ligands\textsuperscript{16} drew the attention of chemists for the above studies. Of these neutral dipolar molecules have the advantage that in the investigation of such metal-complex systems, it is apparent that the electrostatic effect is almost eliminated and salt concentration in the medium has only a small influence upon the consecutive constants. As such the effect of the ligand may be directly calculated from the experimentally found equilibrium constants and may then be compared. This is evident from the studies of Bjerrum\textsuperscript{17} with complexation reactions with ammonia.
At high concentrations of ligands, complexes of Ag(I) do not exist as fully saturated mononuclear complexes but they show a tendency to be transformed into tri- or tetra-ligated, often polynuclear, species. This fact is apparent from the complexity constant of Ag(I) complexes with CN', SCN' and \( S_2O_3^{2-} \), which though not permitted calculation of either the ligand effect or the respective total effects, still showed indirectly that the formation curve must have a 'stop' after the binding of the first two ligands.

In the case of Ag(I) - cyanide system the Ag(I) binds more than 3 CN' in 1N cyanide solution. Using this, Bjerrum has shown that while Zn (II) system is a normal system with the characteristic co-ordination number 4, the Cu (I), Ag (I) and Hg (II) have abnormally high ligand effects. This is, of course, due to the asymmetry of the formation curve after the uptake of the first two ligands. The normal cyanide and thiocyanate complexes are believed to have linear chain structures (I-A-4):

![Diagram of linear chain structure I-A-4]
Halide complexes of Ag (I), \([\text{Ag}^\text{XrQ}^{1+n}]^{(1+n^-)}\) are known\(^{16}\) with values of \(n\) up to 5. Erber and Schühly\(^{20-22}\) reported that the silver (I) - bromide and silver (I) - iodide systems formed the binuclear complexes \([\text{Ag}^\text{I}_2\text{Br}_6]^{4^-}\), although other workers differed on the composition of the species. The fluoride and chloride systems have been investigated by Connick and Paul\(^{23}\) and by Jonte and Martin\(^{24}\) under conditions of controlled media. The remaining work on these systems\(^{20-22,25}\) and that for iodide complexes were done under conditions of varying media. While the relative stabilities of halogeno complexes\(^{26}\) indicate that the sequence of stability constants is \(F > Cl > Br > I\) for most of the metal ions, it is reversed for Ag (I). The large value of \(\log K_1/K_2\) for Ag (I)-iodide system may be done to \(\pi\)-bonding\(^{27}\). Thermodynamics of cyanide complexation of Ag (I) in solution have been investigated by Izatt et al.\(^{28}\) using calorimetry and those of thiocyanate complexation by Jaenicke\(^{29,30}\) and Golub\(^{31}\). Thermodynamic data\(^{32}\) are also being accumulated for poly-nuclear halogeno and thiocyanato Ag (I) complexes.

The evaluation of the complexity constants for the hydroxo Ag (I) - systems has also been attempted\(^{33,34}\). Although a large number of authors assumed a direct or an indirect
splitting off of the hydroxyl hydrogen of the amphoteric metal hydroxides forming oxo-complexes, Bjerrum\textsuperscript{17} considered the process as a direct uptake of hydroxyl ions.

$$\text{AgOH} + \text{OH}^- \rightarrow \text{Ag(OH)}_2^-$$

and calculated the ligand effect of the system.

Of all the ligands with which the argentation equilibria have been investigated the ligands having N-donor atoms occupy the top position. Ammonia and amines are typical among them. There is available at present a lot of data on the investigations of the complexation equilibria of Ag (I) with NH\textsubscript{3} and various amines. Reychler\textsuperscript{12}, Konowaloff\textsuperscript{13}, Bodländer and Fittig\textsuperscript{35}, Bodländer and Öberlein\textsuperscript{36}, Euler\textsuperscript{37} showed that in ammoniacal solution Ag (I) forms a complex ion with coordination number 2. That Ag (I) forms diamine complexes with amines in general was first shown by Euler\textsuperscript{37} and this was later more closely investigated by Pawelka\textsuperscript{38}, Job\textsuperscript{39} and Britton and co-workers\textsuperscript{40-42}, Larsson\textsuperscript{43} pointed out that the formation of the diamine complex proceeds through the formation of the monoamine complex, but he was of the opinion that the monoamine species is not present in demonstrable
amount in the equilibrium. The most effective investigation of Ag (I) ammine complexes is, however, due to Bjerrum\textsuperscript{17} by glass electrode potentiometric technique. His work showed that it was not possible to prove the presence of ammine complexes with more than two ammonia molecules in Ag (I)-NH\textsubscript{3} systems\textsuperscript{17}. This may, however, be due either to the great instability of such complexes or due to the fact that such ammine complexes do not exist. The probable existence of a triammine complex salt in ammoniacal AgCl at high concentration of NH\textsubscript{3}, as suggested by Jarry\textsuperscript{15} does not necessarily mean that NH\textsubscript{3}-richer complexes are present in the solution in analytically demonstrable quantities.

A quite good agreement exists between the results of several early workers\textsuperscript{29,44-46}, who measured the heat of formation of the Ag\textsuperscript{2+}-diammine complexes (\(\Delta H_2\)) by a variety of methods. In particular, the calorimetric values obtained by Smith et al\textsuperscript{46} appear reliable. Fyfe\textsuperscript{47} has obtained a value for \(\Delta H_2\) by a calorimetric method at 'room temperature'.

After Britton and Wilson\textsuperscript{40} reported the formation of a strong complex base \([\text{Ag(NH}_3)_2\text{OH}]\) when silver oxide is dissolved in ammonia, Britton and Williams\textsuperscript{41} attempted to find out the nature of the bases, by replacing ammonia by amines
like mono-, di- and trimethylamines and the corresponding ethylamines. Their aim was to correlate the strength of these bases with their tendencies to form co-ordination linkages with Ag (I). Both conductometric and potentiometric methods as well as solubility measurements in different amines were carried out with Ag₂O for the determination of stability constants. Similar type of bases AgB₂OH, where B's are the corresponding amines resulted. Although no relationship between the structure of the bases and the stability of the resulting complex cations appeared apparent, the order of the co-ordinating ability with Ag (I) was found to be in the order, primary amines > secondary amines > tertiary amines.

Before Bjerrum⁴⁸ published his review on the studies of metal ion complex equilibria in solution (1950) some studies have been made on the amine complexes of Ag (I) and of these the work of Verhoek et al.⁴⁹,⁵⁰ and Tamisier⁵¹ are worth mentioning. Bjerrum⁴⁸ arranged a number of organic bases including various amines in the order of their increasing basic strength and showed that the tendency towards complex formation increased on the whole in the same order as the basicity. The constancy in the log Kₐg⁺/log K_H⁺ (where log Kₐg⁺ = mean complexity constant of the complexes formed
with the corresponding bases) showed that there exists at least a rough proportionality between the two quantities in the entire series. The greatest deviations from the average value of the above ratio found with amines occur in cases with tertiary amines. With secondary amines this ratio is, distinctly too small. All the secondary amines studied have a value of \( \sim 0.29 \) for this ratio. These deviations from the average value formed the basis of Bruehlman and Verhoek's graphical representation which indicated separate linear relations for primary, secondary and tertiary amines. The linear relationship between \( pK_{NH} \) of amine ligands and \( \log \beta_2 \) for Ag (I)-complexes was, however pointed out by Larsson as early as in 1934.

Bjerrum showed that the tertiary amine, hexamethylene tetra amine has a relatively high affinity for Ag (I) and fall into the same group as \( \text{NH}_3 \) and the primary amines. This may undoubtedly be due in part to the fact that this tertiary base has a spatial configuration which is far more favourable to coordination with a metal ion than the more space-requiring configurations of the other tertiary and secondary amines. That the steric factors are indeed the reasons for the too little tendency of the bases to form complexes is evidenced by the relatively high value of \( K_1 \) as compared with that of \( K_2 \).
negative values of log $K_1/K_2$ for various Ag(I)-amines further indicate the special stability of linear Sp hybrid structures.

Using the data of Bodländer and Fitting\textsuperscript{11} on the solubility of AgCl and AgBr in aqueous NH$_3$, CH$_3$NH$_2$ and C$_2$H$_5$NH$_2$, Seth and Dey\textsuperscript{52,53} concluded that the principal complex ion formed in the system, is [AgRNH$_2$]$^+$ when $R = H$, CH$_3$ or C$_2$H$_5$.

While Armeanu and Luca\textsuperscript{54} were attempting to find out the influence of substituents in the ammonia molecule on the stability of Ag(I) complexes formed with the respective amines, the parallelism between the basicity of the primary amines and the stability of the complex ions formed was confirmed. The stronger the base, the greater is the stability in solution of the complex ions formed therein. Only amines which have a basicity exponent $< 12$ form complex ions in solution. The others like Ph$_2$NH do not form Ag(I) complexes. The deviation of secondary and tertiary amines from this parallelism conforms with Brower's hypothesis\textsuperscript{55} of steric effects. An attempt was made by some investigators\textsuperscript{54} to give an electronic explanation for the observed phenomena and to discern the inductive, the conjugation and the steric effects in cases of the amines under investigation. Although the formation of diamine complexes was the general trend, presence of mono-amine and sometimes the
Some more attempts\textsuperscript{56-58} have also been made to rationalise separate linear correlations of $\log K(ML)$ against $\log K(HL)$ for primary, secondary and tertiary amines from considerations of steric factors. Brown\textsuperscript{56} has described an F-strain as arising from face to face interference between H (or M) and ligand L and a B-strain which arises through enforced crowding at the back of the ligand. Both effects will be larger for the metal ions than the protons and this would suggest that Ag(I)-complexes with secondary and especially tertiary amines would be less stable than what might be expected from the basicity of the ligands.

Popa, Luca and Magearu\textsuperscript{59} studied the effect of the solvents on the stability of complex combination of Ag(I)-amines. The stability constants of the complexes were found to increase with the increase in the alcohol content of the solvent mixture, though not linearly. Initially, it increased gradually, then attained almost constant values and subsequently rose gradually.

Complex formation between Ag(I) and n-alkyl amines $\text{CH}_3\cdot(\text{CH}_2)_n\text{NH}_2$ ($n = 1$ to $5$) and amino n-alkyl alcohols,
NH₂·(CH₂)ₙ·OH (n = 1 to 5) has been studied by Alner, Lansbury and Smeeth to obtain information regarding the effect of chain length on the donating power of the nitrogen atom. Formation curves indicated the absence of polynuclear complexes and showed the normal sigmoid shape with limiting \( n = 2 \).

The \( \beta_2 \) values for alkyl amines suggest that the order of increasing electron repulsion is as expected, although this effect was not evident from the corresponding pKₐ values. This is possibly a \( \Delta H \) effect. The anomalous behaviour of 1-amino propane is yet to be explained. With amino alcohols, both log \( \beta_2 \) and pKₐ values increase regularly thus showing the clear trend in log \( \beta_2 \) and pKₐ. Several general correlations emerge from a consideration of all these results. There exists a constancy in the ratio \( \log K_1/pK_a \) for all the ligands which is in agreement with similar constancies found by others and secondly \( K_2 \geq K_1 \) as found by Bjerrum and others. An increase in the chain length of the ligand molecule appears to increase the stability of the Ag(I) complexes, whereas the introduction of a hydroxy group results in the decrease of the stability of the complexes.

Association equilibria study of Ag(I) with Tris(hydroxy methyl)-amino methane [tris], a compound used in connection
with a titrimetric method for the determination of sulphydryl group in proteins excludes the possibility of interaction between Ag(I) and the oxygen atom of the ligand. It is suggested that the substituent groups do not interfere with the reactivity of the N-atom, because intramolecular H-bonding between hydroxy methyl groups leads to a highly symmetrical structure (I-A-5).

Gonick, Fernelius and Douglas, studying with 2-thenyl, 2-furfuryl- and benzyl amines, established that the S and the O atoms in the former two ligands are not effective in co-ordination with Ag(I) ions. The ligands rather behave like NH$_3$ and other amines. A similar study with 2-amino ethyl phosphate by Dutta and Grzybowski excluded the possibility of interaction with phosphate group. Complexation rather appeared to occur by the basic form of the amino group.

Thermodynamic behaviour of Ag(I)-amines has not been thoroughly investigated. Seth and Dey calculated the free
energy changes for the reactions of Ag(I) with methyl and ethyl amines. Fyfe\textsuperscript{65} reported the measurements of entropies with methyl-, dimethyl-, ethyl- and di-ethyl amines and was of the opinion that the steric effect has an important role in controlling the thermodynamic values. Another investigation by Trotman and Dickenson\textsuperscript{66} reports that the entropy changes accompanying either the association of protons with amines or the formation of Ag(I)-amine complexes decrease in the order NMe\textsubscript{3} > HNMMe > H\textsubscript{2}NMMe > NH\textsubscript{3}. Fernelius and co-workers\textsuperscript{67} in a subsequent thermodynamic study with some oxygenated amines showed that for the silver (I) complexes of both ethanol amine and 2-methoxethanol amine the \( \Delta G \) values are somewhat greater than half of those for some typical diamines\textsuperscript{68}. The terminal oxygen atoms in these compounds are evidently too weakly bound to the metal ion to have a significant effect on the stability of the complexes.

Polyamines and amino acids are interesting because of their ability to form chelate ring with metal ions. While Britton and co-workers\textsuperscript{41,42} reported quite stable complexation between Ag(I) and ethylenediamine, Bjerrum\textsuperscript{48} reported a normal value for the ratio \( \log K_{Ag+/log K_{H^+}} \) but an abnormally high value for the ratio between the successive constants of Ag(I)-ethylenediamine complexes. This shows ethylenediamine molecule taken
up primarily must be assumed to be bound in a chelate through both of its amino groups, regardless of the fact that the Ag$^+$ has linear valencies and thus cannot act as a constituent of a five-membered ring without some co-ersion. Bjerrum further indicated that in co-ordinating the second molecule of ethylene-diamine, it must be assumed that the ring is opened and at any rate this explains why a normal value is obtained for the ratio between the mean complexity constant and the basic strength of the amine.

Controversy arose when Job showed that Ag(I) binds not one but two ethylene diamine molecules and with a strength of the same order of magnitude as that with which the Ag(I) binds with NH$_3$ or monodentate amines. Since the characteristic co-ordination number 2 of Ag(I) with a valency angle of 180° makes the system unfit for forming chelate complexes, it was suggested that ethylene diamine molecule co-ordinates to Ag(I) with one of the amine groups only. This idea has been corroborated by the results of X-ray analysis by Corey and Wyckoff. Instances are known where ethylene diamine occupies only one co-ordination position and ethylene diamine complex of Ag(I) may be an example of such a type. The possibility that Ag(I) is capable of forming chelates cannot, however, be ignored
due to the maximal co-ordination number 4 of the metal ion.

In solutions containing ethylene diamine (en) and Ag(I) ion, Schwarzenbach and co-workers, however detected the complex species like \([\text{Ag(en)}]^2+\), \([\text{Ag}_2\text{en}]^2+\), \([\text{Ag(en)}_2]^+\) and surprisingly \([\text{Ag}_2(\text{en})_2]^2+\). The existence of the dimeric form of \([\text{Ag en}]^+\), probably a 10-membered ring compound (I-A-6) has been proved also by these workers by cryoscopic measurements of the crystalline sulfate \([\text{Ag}_2\text{en}]_2\text{SO}_4\).

Although values of \(K_d\) for the displacement of two NH\(_3\) ligands by one en, are positive for a number of metal ions,

\[
[\text{M(NH}_3)_2]^+ + \text{en} \rightleftharpoons [\text{M en}] + 2\text{NH}_3
\]

the value is negative for Ag(I). It seems likely that the
linear Sp hybrid orbital of Ag(I) is distorted on co-ordination with en and that the five-membered ring is strained. A negative entropy change for such reaction further signifies a strained ring formation. It has been seen that the stability of the aliphatic diamine complexes of Ag(I) increases with the increasing ring size and is explained by the hypothesis that ring strain due to bridging the Sp orbital of the metal ion decreases.

In 1950, Schwarzenbach and co-workers carried out investigations on the complex equilibria of Ag(I) with a series of polyamines. The detectable species in those investigations were mainly AgZ, AgHZ, and bimetallic complexes Ag2Z and only in few cases AgH2Z, where Z represents a molecule of the respective neutral amines. The stability order of the corresponding complexes have been compared.

The stability constant values with ligands like 1,3 diamino-2-propanol (H2NCH2)2CHOH have close agreement to those with 1,3 diamino propane (H2N.CH2)2.CH2 and 2,2-Dimethyl 1,3 propane diamine (H2N.CH2)2.C(CH3)2. This suggests that -OH group is not participating in co-ordination in the complexes.

With 2-aminomethyl 1,3 diamino propane Anderegg found that the formation of complexes is limited to 1:1 species, as
Steric hindrance plays an important role in reducing the stability of higher complexes. While other metal ions form complex ions like $MH_2L$, $MHL$, $ML$ etc., Ag(I) forms an exceptionally stable complex through co-ordination of all the three amino groups.

The $\Delta H$ value for the reaction between Ag(I) and 1,4 butane diamine (−10.7 Kcal) is less negative than that for 1,3 propane diamine (−14.6 Kcal) reflecting the greater basicity of the latter amine. This effect is, however, almost completely compensated by the more favourable entropy change for the formation of the seven-membered ring with 1,4 butane diamine. Experimental results further show that the thermodynamic character of the complexation reaction of Ag(I) with 1,3 diamino propanol is intermediate between those of 1,3 propane diamine and 1,4 butane diamine. Fernelius and co-workers also studied thermodynamic aspects of Ag(I) complexation reaction with some complex diamines like 1,8 diamino 3,6 dioxaoctane and 1,8 diamino 3-oxa-6-thio-octane.

The formation of Ag(I) complexes with glycine and alanine was reported by Keefer and Reiber in 1941 and by Albert in 1951 from the solubility studies. 1:1 chelate
complexes like \( R \cdot CH_2 \cdot COO \cdot N \cdot Ag \) were assumed to be formed and the alaninato complex was found to be more stable than the glycinate complex. Bjerrum, however, mentioned that in Ag(I) complexes of this type, the ligand is bound to the metal only through its amino group. Flood and Loràs supported the view of Bjerrum and contended that the glycinate Ag(I) complex is not a chelate but is co-ordinated only by nitrogen.

Azizov and co-workers and Dutta and Grzybowskii, from the study of the Ag(I)-complexation with a series of amino acids like glycine, \( \alpha \)- and \( \beta \)-alanines, norleucine, serine, methionine, \( \beta \)-phenyl \( \alpha \)-alanine and aspargine also arrived at the same conclusion that the co-ordination of the amino acids to the Ag(I) takes place only through the nitrogen atoms, except in the case with methionine. Methionine gives only one complex (AgL) of great stability compared with the other complexes of this composition and hence a chelation through the nitrogen and sulphur atoms of the ligand molecule has been suggested.

Alner and co-workers as well as Thiels and co-workers studied the complex formation between Ag(I) and a series of amino n-alkyl carboxylic acids, \( H_2N(CH_2)_nCO_2H \)
(n = 1 to 5) to find out the effect of chain length on the donating power of the nitrogen. The log $\beta_2$ values for amino acid complexes follow a similar pattern as those of the amino alcohol complexes studied by Alner and co-workers except the 3-amino propionic acid complex which gives a higher value of log $\beta_2$ than the corresponding 3-amino propan-1-ol complex. This could be due to proximity effect, a possible explanation being quasi-chelation which would provide the extra stability for the 3-amino propionic acid complex (I-A-7). Apart from this, there is no evidence of chelation in case of any of the other ligands. The quantity $\log K_1/K_2$ is on the average smaller for the amino acid complexes than it is for the amine and amino alcohol complexes. This may be due to the added electrostatic bonding which could be present in the amino acid complexes but not in the uncharged ligands. In general, it was found that introduction of carboxylate ion tends to decrease the stability of the complexes in solution in comparison
with the amine complexes.

Because of biological importance Lenz and Martell studied Ag(I) complexes of some sulphur containing amino acids. The results indicate the formation of 1:1 complexes in every case. It appears that co-ordination of Ag(I) occurs by monodentate binding by the ligands through the unshared pair of electrons of the amino nitrogen atom. Further chelation through either the S or a carboxylate oxygen is sterically hindered. Since Ag(I) has affinity for NO₃⁻ in solution the structure of the complex in the electrolyte medium employed has been represented as in I-A-8.

With penicillamine however, the first buffer region corresponds to the formation of a 1:1 protonated complex with the ligand which functions as a monodentate ligand co-ordinating through the mercapto group. This structure (I-A-9) is assigned because of the large difference between the formation constant for the S-substituted sulfur acids where complexation is through N and
Another interesting class of amine compounds are aromatic amines. Britton and co-workers\textsuperscript{42} and Bjerrum\textsuperscript{48} studied anilines along with other aromatic amines in Ag(I) complexation equilibria. Britton and co-workers reported that although with aniline results are in favour of complexation, the stability is much less than any other members of the amines they investigated. Notable investigations have been made by Armeanu and Luca\textsuperscript{33}, Golumbic\textsuperscript{86} and Fyfe\textsuperscript{59} with a series of anilines of which ortho NO\textsubscript{2}C\textsubscript{6}H\textsubscript{4}NH\textsubscript{2} does not form Ag(I) complexes. Evidently the results showed that a substitution in NH\textsubscript{2} by an aryl radical diminishes the stability. Still the observed trend in the formation constants of AgB\textsuperscript{+} and Ag\textsubscript{2}B\textsuperscript{++} appears to be most consistent with the amino N-atom and the second with the aromatic nucleus. The stability is, however, increased by introduction of a CH\textsubscript{3}-group in the aromatic nucleus but it is diminished by substitution of Cl, NO\textsubscript{2} and I on the nucleus. The diminished stability with o-toluidine and dimethyl o-toluidine supports the hypothesis that the lower basicity of o-toluidine is caused by steric hindrance. Although the formation of bis-amine complexes was the general trend, presence of mono-amines and sometimes tris-amines has also been detected.
Many more studies on the equilibria of Ag(I) and various nitrogen-containing ligands (both aliphatic and aromatic) can be seen from the works cited in the ref. 87-105. These include various amines, nitriles, substituted amino alcohols, amino acids - both simple and substituted, amino polycarboxylic acids - simple and substituted and various complex amines and polyamines. Detailed discussions of these are, however, not included here due to their lack of proper relevance as well as for want of space.

Heterocyclic compounds having nitrogen atoms in the ring created a lot of interest in this field practically since the beginning of investigations made with argentation equilibria in general. The mostly investigated compounds are pyridines and substituted pyridines. The work of Koch and Britton and co-workers revealed the formation of AgPy$_2^+$ as the only species in solution. Yosburgh and Cogswell, however, reported the stability constant values of AgPy$^+$ as well as AgPy$_2^+$ and compared the values with those of amines. Prior to that Larsson studied the formation of Ag(I) complexes with pyridine, 2,4,6 trimethyl pyridine and quinoline along with some aliphatic amines. Later on Bruühlman and Verhoek and Fyfe made systematic investigations with some pyridines,
Bjerrum pointed out that pyridine and its homologues have a relatively high affinity for Ag(I) and fall into the same group of NH₃ and primary amines. The bases have a spatial configuration which is far more favourable to co-ordination with a metal ion than the more space-consuming secondary and tertiary amines.

Resonance stabilisation in terms of dative dπ-bonding by the metal ion for some bis(pyridine)silver (I) complexes has been suggested by Murmann and Basolo. Minor deviations from the linear plots can be explained in terms of the π-donor or acceptor properties of the substituents on the ligand. The investigation was made with a number of 3- and 4-substituted pyridines and nicotine derivatives.

Peard and Pflaum reported relative stabilities of some Ag(I)-pyridines, quinolines and bidentate polynuclear amines like bipyridyl, biquinoline and o-phenanthroline in acetonitrile and ethanol media. The magnitude of the amine interaction depends on the basicity and structural behaviour of the particular ligand, whereas the solvent ion interaction depends on the nature and availability of the dipole of solvent molecule. Overall stability is influenced by both. Results
showed that the co-ordination compounds of polynuclear amines are more stable than the compounds of mononuclear ligands.

The effect of solvent on the stabilities of Ag(I) pyridine and substituted pyridine complexes has also been studied by Popa, Luca and Magaru\textsuperscript{110,111}. For each of the Ag(I)-pyridine complexes studied, the dependence of the instability constant on the proportion of the organic solvent in the solution is non-linear as indicated by the Born theory\textsuperscript{112} of electrolytic solvation of acids and bases applied to these complexes by Turian. This non-linearity is attributed to an inequality between the effect of solvent on the Ag\textsuperscript{+} activity and that on the corresponding complex ion activity. However, the mode of variation of pK with solvent composition is different for the two studies\textsuperscript{110,111}. Further works with pyridines, substituted pyridines and related heterocycles have been done by Sun and Brewer\textsuperscript{113} and others\textsuperscript{114-119}.

Thermodynamic data available\textsuperscript{120-124} for the formation of pyridine complexes in aqueous solution refer to the formation of $[\text{Ag(Py)}_n]^+$, where $n = 1$ or 2. It is noteworthy that the addition of a second pyridine molecule involves a stepwise enthalpy change of $-6.51 \text{ Kcal/mole}$ which is greater than that for the addition of the first pyridine molecule.
(ΔH = -4.83 Kcal/mole). This trend is not common in the stepwise formation of transition metal complexes, where the enthalpies of stepwise addition are either equal or are successively reduced. The entropy changes which accompany the formation of bis(pyridine) Ag(I) complexes in aqueous solution are also negative. Similar studies with 6-methyl 2-aminomethyl pyridine has been done by Fernelius and co-workers\textsuperscript{125} and with bipyridyl by Cabani and co-workers\textsuperscript{126,127}.

Another interesting class of heterocyclic ligand is imidazoles and related compounds. Detailed investigation of argentation equilibria with these ligands is still lacking. Gold and Gregor\textsuperscript{128} proposed co-ordination of the pyrrole nitrogen (N\textsuperscript{1} atom - I-A-10) but Bauman et al\textsuperscript{129} suggested co-ordination through the pyridine nitrogen (N\textsuperscript{3} atom). Nakatsuji et al\textsuperscript{130} by M-0 calculation supported the suggestion of Bauman et al. All the works\textsuperscript{62,128-130}, however, suggested the existence of 1:1 and 1:2 Ag(I)-complexes in solution with imidazole (Imdz) and various alkyl substituted imidazoles.
Bauman and Wang\textsuperscript{129} also reported the stepwise thermodynamic parameters like $\Delta H_n$, $\Delta G_n$ and $\Delta S_n$ (for $n = 1$ and 2) for the argentation equilibria with imidazoles. It was noted that substitution of a methyl group in the 4-position has virtually no effect on the thermodynamic values. Other works in the field with related ligands include that with pyrazine (1,4-diazine) reported by Schmidt and Trimble\textsuperscript{131} and with metrazole and its derivatives (I-A-11) reported by Popov and Holm\textsuperscript{132}. The latter workers showed that complexes having general formula $\text{Me}_2\text{Ag}^+$ were all more or less equally unstable with $pK_a$ values $\sim 2.14$ when the ligands (Met) were either metrazole or its substituted products.

The class of ligands not containing any donor atom like N, O, S etc. includes unsaturated compounds having an
ethylenic linkage. The inherent interest lying with this class of ligands is their ability to form co-ordination compounds of comparatively low stability, which easily undergo several interesting secondary reactions. Metals having filled d-orbitals like Ag(I) are highly attractive for the study of this class.

Lucas and co-workers, by means of distribution measurements studied a series of Ag(I) complexes with some mono-olefins, diolefins and the unsaturated oxygenated compounds. Complex ions of three types have been observed viz., combination of one Ag(I) with one unsaturated molecule (Un), AgUn+, two Ag(I) with one Un, Ag₂Un²⁺ and one Ag(I) with two Un, AgUn₂⁺. The structure of the complexes have been discussed by these workers.

In 1952, Lucas et al reported the results of other similar studies viz., with butenes, ethylene and propene. With ethylene and propene results indicated 1:1 complex formation and stability values were more or less same for the two olefins. No significant amount of bis-olefin complexes was formed by either of the hydrocarbons in the concentration range
studied but there was evidence for disilver complexes at high concentration of Ag(I). The variation of the stability constants with the isomeric butenes was provisionally interpreted in terms of steric effects. The ligands gave information on the effect of stereoisomerism and position isomerism on the stability of Ag(I) complexes. Lucas et al subsequently studied the relative nucleophilic character of 24 polycyclic hydrocarbons by measuring argentation equilibrium constant with the hydrocarbons in solution.

Andrews, Keefer and co-workers also made some interesting investigations in the same field. With various aromatic hydrocarbons \( \text{Ar} \), two water soluble species \( \text{AgAr}^+ \) and \( \text{Ag}_2\text{Ar}^{2+} \) were obtained. The relative magnitudes of the argentation constants for a variety of mono and disubstituted benzene derivatives have been discussed in terms of Hammett's \( \rho-\sigma \) substituent constants and the structures of the Ag(I)-aromatic complexes have been discussed.

Argentation constant for a large number of polyalkyl benzenes have also been obtained by Ogimachi, Andrews and Keefer. The stabilities appeared to be controlled by opposing electronic and steric effects of alkyl substituents on the aromatic nucleus. The assumption that the unfavourable steric
effects are minimised when Ag(I) is co-ordinated with the aromatic nucleus from a position above and between two unsaturated ring carbon is in accord with the data. The results of studies of the effects of temperature changes on the magnitudes of the argentation constants indicate that as steric effects of alkyl substituents become more pronounced the entropy losses accompanying the interaction become larger. The other investigations done by the same group of workers in the field include the studies with toluene\textsuperscript{142}, unsaturated alcohols and acids\textsuperscript{143}, halosubstituted aliphatic and aromatic hydrocarbons\textsuperscript{144}, stilbenes and styrenes\textsuperscript{145}. Some similar investigations have also been done by others\textsuperscript{146-153}.

Fueno et al\textsuperscript{150-153} presented a theoretical interpretation of the observed substituent effect\textsuperscript{151}. For olefinic compounds\textsuperscript{152} available data indicate the importance of electronic, steric and structural strain effects of the alkyl groups on the relative stabilities of complexes. The investigations reported that equilibrium obeys Hammett relation provided the sigma meta values are used for the polar groups. The ease of complexation of an ethylenic bond appears to be governed by the inductive effect.

Complexation of Ag(I) with ligands containing the donor atom of Gr. VIB has been scantily investigated. One
ligand of this class which has been widely studied is thiourea. Fyfe\textsuperscript{154} reported the electrometric determination of stability of Ag(I) complex with the ligand. Prior to that Morgan and Burstall\textsuperscript{155} prepared a series of complexes with 1 to 4 moles of thiourea per Ag(I). On the addition of the ligand to AgNO\textsubscript{3}, the precipitate first formed dissolves when the molar ratio of ligand : Ag(I) is about 3:1. The resultant complex, which the author claimed to be of 3 co-ordinated Ag(I), is very stable, even stabler than NH\textsubscript{3} complexes and the observation is in good agreement with the results of overlap calculations made by Fyfe\textsuperscript{156}. The structure of the complex has been discussed by Fyfe\textsuperscript{154} and Sutton et al\textsuperscript{157} basing on the configuration of S-atom. Complexes of similar type have also been reported by Pawelka\textsuperscript{38}.

Toropova and Kirillova\textsuperscript{158} showed that the enthalpy of formation of the Ag(I)-thiourea complex found by temperature dependence of stability constant is much less negative than that found by direct calorimetric measurements by Yatsimirskii and Astasheva\textsuperscript{159}. The thermodynamic characteristics of thiosemicarbazide complexes of Ag(I) are not greatly different from those of the analogous thiourea complexes. In thiourea complex the central atom is bonded through the S-atom\textsuperscript{160} and the thiosemicarbazide complexes have similar structure.
The hydrazine N-atom of thiosemicarbazide does not take part in bonding.

With 2-aminoethyl 2'-hydroxy ethylsulphide (I-A-12a), ΔG value for the stepwise addition of the second molecule of ligand is less negative than that for the first molecule. This irregular behaviour of the ligand is thought by Lotz et al. to be due to the formation of a cyclic dimeric complex having the structure shown in I-A-12b. This type of dimeric complex is formed in preference to a 5-membered monomeric chelate ring involving both N and S atoms, because of the undue strain in the latter. Addition of a second molecule of ligand to each Ag(I) would cause the ring to open (presumably at the S-atom) to give the usual type of 1:2 complex

\[ [\text{Ag}(\text{H}_2\text{N},\text{CH}_2,\text{CH}_2,\text{SCH}_2,\text{CH}_2\text{OH})]^+ \]
Some other works$^{161-178}$ have reported studies with a few more S-ligands, with ligands where O is expected to be the donor atom as well as with ligands having P or As as donor atoms. Detailed discussions of the results with these ligands are irrelevant for the present study.

The review would point out to the enormous interest shown by chemists in the study of argentation equilibria during the last few decades. The picture gets brightened with the advent of the results of study of argentation equilibria with some non-classical type of compounds having some biological importance viz., gelatin$^{179}$, riboflavin$^{180}$ and above all D.N.A.$^{181}$ This prompted the present investigator to undertake an investigation of the argentation equilibria with some new, important as well as interesting heterocyclic compounds viz., pyrazole and some of its substituted products. The results obtained during the present study will be reported and discussed in subsequent sections, before which a brief statement of the importance of the ligands used will be presented in the next section.
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SECTION B

INTRODUCTION TO THE PRESENT WORK
Heterocyclic compounds are drawing the increasing attention of chemists because of the facts that there is a steady stream of discovery of new heterocyclic substances playing important roles in metabolism of all living cells and also due to the increasing availability of intermediates suitable for the large scale production of heterocyclic substances, many of which are finding important non-biological uses in industries e.g. in dyes, plastics, resins and rubber.

Of the several interesting classes of heterocyclic compounds, a typical class comprises diazoles, which are five membered heterocyclic ring compounds containing two nitrogen atoms. Imidazole (1,3 diazole) (1-B-1a) is an important member
of this class and this is present in a number of natural and synthetic compounds which possess marked physiological activity. Imidazole itself is almost inactive and is relatively non-toxic\(^1\). 4(5) methyl imidazole is more toxic\(^2\) and is reported to possess a slight hypertensive action\(^3\). 4-5 dimethyl imidazole, imidazole-4-aldehyde, 4-chloro-imidazole, 4-aminomethyl and N-substituted 4-aminomethyl imidazoles cause vaso constriction and increase blood-pressure\(^4\).

Imidazoles of the type shown in I-B-1b are reported to have some antimalarial activity\(^5\). 1-Decyl-2-methyl imidazole is said to be a typical anesthetic\(^6\). N-aryl substitution also seems to induce anesthetic action\(^7\). 2-thio-4-aminomethyl imidazole is reported to possess some insulin-like activity in diabetics\(^8\). The study of the above compounds and other derivatives of imidazole indicates that the extent of physiological effects are largely controlled by the nature of the substituents.
which are present in the ring.

Histamine, 4(5)-(β-amino ethyl)imidazole is probably the most active among imidazoles. The best natural source of histamine is ergot where it is probably formed by enzymatic decarboxylation of histidine. Histamine stimulates smooth muscle and exerts a profound effect on the mammalian circulatory system. It is a strong gastric stimulant, causing increased gastric secretion. It also increases blood sugar content. Release of histamine or 'histamine-like' substances is believed to be responsible for certain allergic manifestations in the human body like bronchial asthma and urticarial eruptions.

L-Histadine, a naturally occurring amino acid, is also another important compound of the series and it is considered an essential amino acid excepting for human being. Haemoglobin has a very high L-histidine content and the hydrolysate from red-blood corpuscles is a good source of L-histidine. L-Histidine plays an important role in the behaviour of haemoglobin.

Another important diazole is pyrazole, the 1,2 diazole (1-B-2a), the interest in the study of which arose as a result
of early discovery of antipyrine\textsuperscript{17} (1-B-2b), a compound introduced into medicine in 1884 and widely used as an antipyretic and analgesic.

\begin{align*}
\text{HC} & \text{-} \text{C} \text{-} \text{CH} \\
\text{H} & \text{-} \text{C} \text{-} \text{N} \text{-} \text{N} \\
\text{H} & \text{-} \text{N} \\
\end{align*}

(a)

\begin{align*}
\text{HC} & \text{-} \text{C} \text{-} \text{CH}_3 \\
\text{H} & \text{-} \text{C} \text{-} \text{N} \text{-} \text{N} \text{-} \text{CH}_3 \\
\text{O} & \text{-} \text{C}_6 \text{H}_5 \\
\end{align*}

(b)

(I-B-2)

Pyrazole ring system was first synthesised by Knorr\textsuperscript{18,19}. Since many drugs and dyes contain the pyrazole nucleus, this group of compounds has been widely studied and the field continues to be of active interest even to this day, although antipyrine and related medicinals are no longer in common use.

The potential biological importance of the diazoles are also evident from some other investigations on physiological and chemotherapeutic activities of imidazoles and pyrazoles\textsuperscript{20-23}. Primarily this imposed an intense interest on the extensive investigations of imidazole both in the synthetic and structural field\textsuperscript{24} and as well as on the studies of various
The investigations on the association of the imidazole (Imdz) with metal ions have been made by several workers. Of various metal ions, Cu (II) and Cd (II) have been mostly investigated. While studying the association equilibria of Cd (II) with Imdz Tanford and Wagner attempted to verify if in the combination of metals with serum albumin the principal binding sites are imidazole groups of the protein molecule. Gurd and Goodman made a similar verification with Zn (II). Tanford and Wagner obtained 4-consecutive constants log K for such reaction and the value of log K was identical with the intrinsic association constants obtained for the combination of Cd (II) with Imdz groups of bovine albumin. The results also showed the similarity between Imdz and NH3 in their affinity towards Cd. The thermodynamic data ΔH for the binding of first imidazole molecule was found to be -5 kcal/mole.

The interactions of Cu (II) and Cd (II) with imidazole and 1-methyl imidazole have been studied polarographically by Li and co-workers. The indication for the existence of highest order complex Cd(Imdz)2+ and Cu(Imdz)2+ were obtained with enough certainty in both the cases. The values of ΔH and ΔS for Cd + 4 Imdz ⇌ Cd(Imdz)2+ have been reported (-10.8 Kcal/mole
and -2.2 cal deg^{-1}mole^{-1} respectively). The solvent effect on complex formation has been found to be negligible. The result indicated that the binding site of imidazole is the pyridine N rather than the pyrrole N.

Edsall and co-workers\textsuperscript{27} studied the interaction of imidazole with Cu (II) and Zn (II) by pH-measurements and calculated the successive formation constants of the complexes and found that the maximum co-ordination number for these ions were four. An approximate estimate of the thermodynamic parameters for the complexation process has also been made.

Martin and Edsall\textsuperscript{28} also studied the reaction of imidazole with Mn (II) and Co (II) ions which form weak complexes giving 1:1, 1:2 complexes for Mn (II) and 1:1 to 1:4 complexes for Co (II). Their results have been supplemented by the works of Lal and Mathur\textsuperscript{29} who got comparable formation constants.

Mickel and Andrews\textsuperscript{30} studied the complexation reactions between imidazole and Cu (II) and Ni (II) ions. James and Williams\textsuperscript{31} reported the formation of cuprous and cupric complexes with imidazole. The maximum co-ordination numbers
were reported as 2 and 4 for Cu (I) and Cu (II) respectively. Hawkins and Perrin in a similar investigation determined the stability of Cu (I) and Cu (II) complexes of imidazole and benzimidazole. Holmes and Jones studied the chelating ability of 3-2'-amino ethyl pyrazole, 4-amino methyl imidazole and related ligands towards Cu (II), Ni (II) and Co (II). The first ligand forms only 1:1 complexes with all the three metal ions, while the others form bis complexes with Cu (II) and tris complexes with Ni (II) and Co (II). Chakraborty and Cotton also determined the stability constants and structures of Cu (II), Ni (II) and Zn (II) complexes of imidazole and with some of its derivatives such as histidine, histamine etc.

Edsall et al studied the interactions of Cu (II) and Zn (II) with 4-methyl and 2,4 dimethyl imidazoles by pH titration method. The number of bound ligands approached an upper limit of 4, which was the same as the case with unsubstituted imidazole. Bauman and Wang reported the thermodynamic data of the complexation reactions of the imidazoles with Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Ag$^+$ using calorimetric procedure.

By polarographic and pH measurements methods, Li and others, calculated the successive formation constants of the Ni (II)-imidazole system and found that the maximum number of
imidazole molecules associated with a Ni (II) ion was six and this would suggest an octahedral stereochemistry of the complex formed. Barium and calcium ions were shown to have little tendency to enter into complex formation.\(^39\)

In addition to the complexes of Cu (II) with 1, 2, 3 or 4 moles of imidazoles, the existence of penta and hexa imidazole complexes of Cu (II) in solution has been suggested by Sjöberg\(^40\) from e.m.f. measurements. Using the polarographic and potentiometric methods Jensen\(^41\) reported the consecutive complexity constant of the reaction:

\[
Cd(\text{Imdz})_{j-1}^{2+} \text{(aq)} + \text{Imdz} \rightarrow Cd(\text{Imdz})_j^{2+} \text{(aq)}
\]

and the maximum value of \(j\) was found to be six.

High values for the formation constant of the complexes \(\text{Hg}(C_3H_4N_2)_{2+}^{2+}\) (log \(K = 16.7\)) have been reported by Brooks and Davidson\(^43\), who suggested that the insoluble precipitate of \(\text{Hg}(C_3H_3N_2)\text{ClO}_4\cdot H_2O\) at pH > 4 consisted of linear polymers (I-B-3)
while Gold and Gregor\textsuperscript{44} and Dutta and Grzybowski\textsuperscript{45} determined the formation constants of Ag (I) imidazole. Stabilities of Ag (I) complexes with various C-substituted and N-substituted imidazoles have been determined by Nakatsuji et al\textsuperscript{46}.

By direct proton magnetic resonance study of the Co (II) complexes with imidazole Bartolini et al\textsuperscript{47} found that in water-acetone mixture the dominant species was Co(Imdz\textsubscript{6})\textsuperscript{2+}.

Wang and Li\textsuperscript{48} also similarly studied the Zn (II)-imidazole system and reported the stability constants of complexes in DMSO. The thermodynamic aspects of the complexation with imidazole have been studied by Skelinskaya and Karapet Yant\textsuperscript{42}. Such varied works on imidazoles should create much interests in exploring the similar reactions of the isomeric compounds pyrazoles.

A recent review by Trofimenko\textsuperscript{49} on complexes of pyrazole stimulated further interest in the studies of this interesting diazole, a thorough knowledge about which is still wanting.

The attention of the co-ordination chemists have been largely directed in recent years to the elucidation of properties, stabilities and structures of the metallic complexes of
pyrazoles as well as the nature of bonds involved in the formation of these complexes.

The pyrazole nucleus (I-B-4a) is thermally and hydrolytically very stable. As a ligand, it co-ordinates to metals and metalloids through the N$_2$ atom as do 1-alkyl pyrazoles; when deprotonated pyrazole becomes the pyrazolide ion (I-B-4b), which can co-ordinate through both nitrogen atoms as an exobidentate (the term 'bidentate' alone all too frequently implies 'chelate'). Trofimenko proposed calling a chelating bidentate ligand 'endobidentate' and a bidentate which cannot form a chelate but binds two separate metals or metalloids an 'exobidentate' ligand) ligand of C$_{2v}$ symmetry. The nucleophilicity may be varied through appropriate ring substitution. Despite these attractive features and the vigorous development of pyrazole chemistry in general, the co-ordination chemistry...
of pyrazole and its derivatives received very little attention until the last decade.

Most of the important compounds in which a pyrazole ring is $N$-bonded to a metal or metalloid, fall into the following four categories.

1. Complexes involving a simple, pyridine-like coordination of pyrazole or a substituted pyrazole through the $N^2$ atom.

2. Compounds in which pyrazolide ion acting as 1,2-dihapto exobidentate ligand bridges two identical metals or metalloids.

3. Asymmetric chelates containing the metal bound to one pyrazole nitrogen and to some other bonding site in a substituent attached to the pyrazole ring. These bidentate ligands may be neutral or uninegative.

4. Compounds involving geminal poly(1-pyrazolyl) compounds as ligands. These ligands are neutral or uninegative and they range from bidentate to tetradaentate.

The simplest and most thoroughly studied type of pyrazole complexes are $M(Pz)_nX_m$, where $M$ is the metal, $Pz$ is a 2-
monohaptopyrazole ligand, X is the counter ion and m is the valency of the metal, n, its co-ordination number. The complexes are produced readily by reaction of the metal salts with pyrazole or substituted pyrazoles in neutral or slightly acid media, since formation of pyrazolide polymers e.g. \([M(Pz')_2]^n\) predominates under basic conditions. For a bivalent metal ion \(M^{2+}\), the reactions are represented by

\[
MX_2 + m \text{Pz} \quad \rightarrow \quad m(Pz)m X_2 \quad \ldots \quad (1)
\]

\[
MX_2 + 2(Pz')^- \quad \rightarrow \quad [M(Pz')]_2^n + 2X^- \quad \ldots \quad (2)
\]

where \((Pz')^-\) denotes 1,2-dihaptopyrazolide ion. The number of pyrazoles co-ordinated to the metal ion depends on a number of factors, e.g.

(1) Co-ordinating ability of the counter ion—maximum co-ordination of pyrazole is found with non-coordinating anion, \(\text{NO}_3^-'\), \(\text{BF}_4^-\) or \(\text{ClO}_4^-\) in comparison to halides\(^{54-59}\).

(2) Nature of the metal ion e.g. Cu (II) forms only tetra co-ordinate complexes\(^{54,60-63}\).

(3) Substitution on the pyrazole ring.

In the area of the co-ordination compounds of simple pyrazole and its derived products, comparatively more informations are available on the synthetic and structural aspects of
the complexes with various transitional and non-transitional metals \(^{54-75}\) and diverse organometallic species \(^{76-83}\). In comparison to the above considerable attention is still lacking so as to ascertain the behaviour of these ligands in solution with metal ions.

Complex formation between pyrazole and various metal ions in solution have been investigated polarographically. With Cd (II), formation of \([\text{Cd}(\text{Pz})_n]^{2+}\) (Pz being the molecule of pyrazole) complexes was suggested with \(n = 1, 2\) and but not 4 even at high pyrazole concentrations \(^{84}\). In a comparative study of pyrazole and 3,5-dimethyl pyrazole complexes with Cd (II), only three complex species were detected for each \(^{85,86}\). Complex formation between Pb (II) and pyrazole and between Ni (II) and Co (II) and 3,5-dimethyl pyrazole were studied. Stability constants were determined for the reversibly reduced Pb (II) complexes and the irreversibly reduced complexes of Ni (II) as well as complexes of the substituted ligand \(^{87}\).

With Zn (II) and pyrazole three weak complex species were detected while Cu (II) formed primarily the 'bis' co-ordinated species. Ni (II) gave evidence for the formation of all possible complexes up to \(\text{Ni}(\text{Pz})_6^{2+}\). With Mn (II) only mono- and bis-co-ordinated ions were stable, while Fe (II) and Co (II) showed existence of complex ions up to \(\text{M}(\text{Pz})_4^{2+}\).
Association equilibria of pyrazole with protons, Ni (II) and Cu (II) have been studied as a function of ionic strength and the first stability constants for the Ni (II) and Cu (II) complexes were also determined potentiometrically. Little work has, however, been done on the determination of thermodynamic parameters on the complexation reaction with pyrazoles. Andrews and Romary reported $\Delta H_n, \Delta S_n$ and $\Delta G_n$ values for only $[\text{Gd(Pz)}_n]^{2+}$ with $n = 1, 2$ and 3.

With such a trend of affairs the present investigator undertook the study of the solution equilibria of pyrazoles and some of its substituted products systematically.

A survey of literature provides no such systematic approach to the study the complexation of pyrazoles or its derived products with silver (I). Buchner in 1889 reported the formation of the insoluble silver pyrazolide $\text{Ag(Pz')}$ which he simply denoted as silver salt. The structure of the compound has not yet been established, but it is probably polymeric as in (I-B-5). Buchner also reported the silver salts of 4-bromo-, 4-iodo- and 4-nitro-pyrazoles. These compounds are remarkably insensitive to light and have also been used for the purpose of organic synthesis. Recently a report
on the preparation of the complexes of the type $L_2AgNO_3$ and $L_2(HgCl_2)_3$ has been made with $L = 3(5)$-methyl pyrazole.

The equilibria of pyrazoles as well as some of its derivatives with silver (I) ions in solution has, therefore, been studied systematically using potentiometric methods. Both stability constants determination and thermodynamic parameters determination have been undertaken for the complete study in order to get a clear picture about the above reactions. Determination of various factors controlling the reactions, location of probable bonding site between the metal ion and the ligands as well as search for speciality of the ligands under investigation among the class to which they belong have been attempted. In the following sections the observations made will be reported. At first the results of
the association equilibria with protons and various pyrazoles (under the experimental conditions) will be reported and discussed and these will be followed by the results and discussions of similar studies on silver (I)-pyrazole complexes in the subsequent section.
SECTION C

ASSOCIATION EQUILIBRIA OF PYRAZOLE AND SOME METHYL SUBSTITUTED PYRAZOLEs WITH PROTON
Diazoles represent ring systems with excess of \( \pi \)-electrons. The present investigation is based on the electronic structures and the basicities of these class of compounds. Similar studies with imidazole (I-C-1a) and its various substituted products have been successfully carried out by various workers\(^{37,44,46}\). Although pyrazole (I-C-1b) is isomeric with imidazole, little work has been done on the studies of association equilibria of pyrazoles with protons.

(a) \[ \text{imidazole} \]

(b) \[ \text{pyrazole} \]
In the present investigation pH-titration technique has been resorted to for the determination of acid dissociation constants of the quaternised pyrazoles at 25°C. Pyrazole, 3(5)-methyl-, 3,5-dimethyl- and 3,4,5-trimethyl pyrazoles have been taken up for the study. A 20% aqueous-ethanol medium was chosen for all the systems. The values of the acid dissociation constants of the quaternised pyrazoles revealed the influence of the substituents on the affinity of the ligands towards hydrogen ion. An attempt has also been made to account for the differences in the basic behaviour of the isomeric diazoles in the light of structural differences of active atoms. The proton-ligand association constant values helped to work out a correlation between the basigenic properties of the ligands and the stabilities of Ag(I) complexes of different pyrazoles.
Experimental

Materials:

Preparation of the ligands:

Pyrazole (Pz) was obtained from Koch Light Lab. (England) and was further purified by repeated crystallization from absolute alcohol.

3(5)-methyl pyrazole (MPz) was prepared according to the method of Snyder et al. by decarboxylating 3-methyl pyrazole 5-carboxylic acid with powdered copper oxide. The latter was prepared as described in literature. The product was purified by fractional distillation (b.p. 204°/73 mm).

Preparation of 3-methyl pyrazole-5-carboxylic acid:

A freshly prepared sodium ethoxide, prepared by adding 11.0 gms. of metallic sodium to the requisite amount of dry ethanol, was added dropwise to a mixture of 73 gms. of diethyl oxalate and 29 gm. acetone over a period of 2-3 hours with constant stirring. The yellow precipitate formed (sodium salt of acetopyruvic ester) was stirred for one hour more and then filtered under suction.
To 5.6 gm of KOH in 75 ml water, 18 gms of sodium salt of acetopyruvic ester were added slowly with stirring and the mixture was allowed to stand for about half an hour, when all of the Na-salt dissolved. To the solution, 12.5 gms of hydrazine sulfate, \((\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{SO}_4)\) were added with constant stirring. A yellow granular mass was obtained. This was filtered, dissolved in hot water containing a little active charcoal and then filtered hot. White shining crystals of 3-methyl pyrazole 5-carboxylic acid were obtained.

**Preparation of 3(5)-methyl pyrazole:**

About 20-25 gms of dry 3 methyl pyrazole 5-carboxylic acid was intimately mixed with about 0.25 gms of powdered copper oxide and the mixture was transferred to a claisen flask with a modified side-arm. The receiving flask was loosely placed over the side-arm. The mixture was heated gently in a free flame. After a small forerun at 95-100°C, the temperature rose steadily to ~ 204° and methyl pyrazole distilled at that temperature and was collected.

3,5-Dimethyl (Dmpz) and 3,4,5-trimethyl pyrazoles (Tmpz) were prepared by condensing acetyl acetone and methyl acetyl acetone respectively with hydrazine hydrate.\(^{97,98}\)
About 0.5 moles of acetyl acetone or methyl acetyl acetone was taken in a beaker, cooled to -5°C. To this about 0.5 moles of previously cooled hydrazine hydrate was added dropwise with stirring. White crystalline product obtained was filtered, washed with cold water, dried in air and purified by repeated crystallisation from absolute alcohol (m.p. 107° for Dmpz and 136° for Tmpz).

Measurements:

Potentiometric measurements were carried out in 20% ethanol-water media at an ionic strength of 0.1 M maintained with AnalaR grade KNO₃. Nitric acid was used for studying the association equilibria of the pyrazoles with proton.

Glass electrode potentiometric technique followed by graphical analysis of the data obtained therefrom was resorted to for the determination of acid dissociation constants of quaternised pyrazoles. All the pH measurements were made with a precision pH meter equipped with a combination glass-calomel electrode in a thermostated cell, the temperature of which was maintained at 25°C ± 0.1°C throughout all the measurements. At the beginning of each experiment, sufficient time was allowed so that all the experimental solutions could attain the proper
temperature. Each of the pH values was taken twice and the same was not recorded until the values were identical.

All the solutions were made with double distilled air-free conductivity water. Other chemicals used were of analytically pure grade.

pH-titration was carried out in the 100 ml capacity cell made of Jena glass, the contents of which were stirred with a magnetic stirrer and the temperature recorded with a thermometer suspended in the solution. The titre was added from a microburette fitted with a fine jet at the delivery tip. The pH meter was standardised before any titration at the experimental temperature with two different buffer solutions, the phthalate and the borate buffers.

Phthalate buffer: M/20 potassium hydrogen phthalate solution, pH = 4.00 at 15°C.
Temperature co-efficient = $\frac{1}{2} \left( \frac{t - 15}{10} \right)^2$, t being any temperature between 20° and 60°C.

Borate buffer: M/20 sodium borate solution. pH = 9.27 at 15°C.
Temperature co-efficient = 0.0085 (t - 15) where t is any temperature between 0° and 60°C.
5 ml of nitric acid in 20% ethanol-water medium with an ionic strength of 0.1M (with \( \text{KNO}_3 \)) was taken and diluted with a solution of \( \text{KNO}_3 \) in the same solvent to an initial volume of 30 ml so that the mixture may attain low pH values. To this, small volume of the titre (either pyrazole solutions, prepared in 20% aqueous ethanol having sufficient \( \text{KNO}_3 \) to maintain ionic strength of 0.1M or the solvent alone having the same ionic strength) was added in steps. The solution was stirred each time and after allowing sufficient time to attain the temperature of the bath, the pH value was recorded.

Since pH readings of most glass electrodes are not perfect, values of pH of nitric acid solutions of different known concentrations prepared in the same solvent and having same ionic strength were measured and a graph of \(- \log C_\text{H}^+ \) vs. pH was plotted. Hydrogen ion concentrations corresponding to any pH value were obtained from this graph (calibration curve).

**Method of calculation:**

Pyrazoles are weakly basic in nature. In acid solution they are present as quaternised salts. The acid dissociation constants \( K_a \) of the quaternary pyrazole ions undergoing the
dissociation,

\[ \text{HL}^+ \rightleftharpoons H^+ + L \]

is given by \( K_a = \frac{[H^+]}{[L]}/[\text{HL}^+] \), (where L represent the respective substituted or unsubstituted neutral monodentate pyrazole molecules) and were determined following the method of Musgrave and Humburg Jr. by performing the following two titrations:

In the first, an acid solution was titrated with 20% ethanol-water solution of the respective pyrazole and in the second, an identical acid solution was titrated with the solvent alone. In every case, the ionic strength was maintained constant at 0.1M throughout the titrations using KNO₃. The difference in hydrogen ion concentrations at any identical point in the two titrations gave the concentration of the quaternised pyrazoles at that point. Knowing the total pyrazole concentration and concentration of quaternised pyrazole, the concentration of free pyrazole could be determined. If \( [\text{HL}^+] \) denotes concentration of respective quaternised pyrazole, \( C_L \) " total concentration of pyrazole, \( [L] \) " concentration of free pyrazole, and \( [H^+] \) " concentration of hydrogen ion obtained from pH readings.

and as at any point in dual titrations,

\[ [L] = C_L - [\text{HL}^+] \]
the rearrangement of the $K_a$ in the above expression leads to,

$$\frac{C_L}{[L]} = \frac{[HL^+] + [L]}{[L]} = \frac{[H^+]}{K_a} + 1$$

So plots of $C_L/[L]$ vs $[H^+]$ represent a linear curve and provide a slope of $1/K_a$. 
Results and Discussion

The data pertinent to the determination of acid dissociation constants $K_a$ of the quaternised byrazoles $LH^+$ at 25°C in 20% ethanol-water medium at 0.1M ionic strength maintained with $KNO_3$ have been shown in Table I-C-1 and I-C-2. Figure I-C-1 represents the calibration curve from which the hydrogen ion concentrations corresponding to any pH value were obtained. Figures I-C-2a and I-C-2b are the corresponding plots of $C_L/[L]$ vs. $[H^+]$ for the data of pyrazole and substituted pyrazoles given in the Table I-C-2. The results of the above plots have been recorded as $pK_a$ along with the estimated probable error in the Table I-C-3.

The slightly lower $pK_a$ values of some of the pyrazoles in the Table I-C-3 than those reported earlier $^{50,89,100}$ are probably due to the increase of the dielectric constant of the experimental medium.

Introduction of methyl substituents in steps to the pyrazole ring gradually increases the base strength of the
**Table I-C-1**

Titration data for determining acid dissociation constants of pyrazole and substituted pyrazoles.

Initial acid concentration = $9.4 \times 10^{-5}$ M. Initial volume = 30 ml. 
\( \mu = 0.1 \) M. Temp. = 25°C. Medium - 20% aqueous ethanol

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<thead>
<tr>
<th>Volume of the reagent (ml.)</th>
<th>Recorded pH values</th>
</tr>
</thead>
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<td>With solvent added</td>
<td>With 0.3003M</td>
</tr>
<tr>
<td>With 0.2878M pyrazole</td>
<td>With 0.2104M</td>
</tr>
<tr>
<td>With 0.1951M pyrazole</td>
<td>With 0.1951M</td>
</tr>
<tr>
<td>With 0.3003M 3(5)-methyl pyrazole</td>
<td>With 0.2104M 3,5-dimethyl pyrazole</td>
</tr>
<tr>
<td>With 0.1951M 3,4,5-trimethyl pyrazole</td>
<td>With 0.1951M 3,4,5-trimethyl pyrazole</td>
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</table>
Fig. I-C-1: Calibration Curve:

Plot of $-\log C_H^+$ vs. pH in the pH range 2-6.
Table I-C-2

Relevant data (obtained from table I-C-1) used for determining acid dissociation constants of pyrazole and substituted pyrazoles.

Initial volume = 30 ml. \( \mu = 0.1 \text{M} \), Temperature = 25°C

Medium = 20% ethanol-water

Pyrazole (concentration: 0.2878M)

<table>
<thead>
<tr>
<th>Volume of reagent added (ml)</th>
<th>( [H^+] \text{ with solvent added} ) (M)</th>
<th>( [H^+] \text{ with reagent added} ) (M)</th>
<th>( [HL^+] ) (M)</th>
<th>( C_L ) (M)</th>
<th>( [L] ) (M)</th>
<th>( C_L/[L] )</th>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.25</td>
<td>( 8.736 )</td>
<td>( 5.722 \times 10^{-5} )</td>
<td>( 3.014 \times 10^{-5} )</td>
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<tr>
<td>2.00</td>
<td>( 7.898 )</td>
<td>( 1.608 )</td>
<td>( 6.290 )</td>
<td>( 1.799 \times 10^{-2} )</td>
<td>( 1.793 \times 10^{-2} )</td>
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<td>( 7.195 )</td>
<td>( 7.190 )</td>
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Table I-C-2 (Contd.)

3(5)-Methyl pyrazole (concentration : 0.3003 M )

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<td>0.00</td>
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<td>-</td>
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</table>
Plot of $\frac{C_{L}[L]}{[L]}$ vs $[H^+]$ for determination of $K_a$ of pyrazoles at 25°C.

Pyrazole: - - -

3(5) Methyl pyrazoles: - - -
Table I-C-2 (Contd.)

3,5-Dimethyl pyrazole (concentration: 0.2104 M)

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*3,4,5-Trimethyl pyrazole (concentration: 0.1951 M)*
**FIG. 1-3-2h**

Ilots of $\frac{C_l}{[l]}$ vs. $[H]$ for determination of $K_b$ of pyrazoles at 25°C.

- 3,5 dimethyl pyrazole
- 3,4,5 trimethyl pyrazole
Table I-C-5

Acid dissociation constants of the quaternary pyrazoles

Medium: 20% ethanol-water, Temperature: 25°C
Ionic Strength - 0.1M (KNO₃)

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<th>No.</th>
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<td>1.</td>
<td>Pyrazole</td>
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</tr>
<tr>
<td>2.</td>
<td>3(5)-Methyl pyrazole</td>
<td>2.68 ± 0.03</td>
</tr>
<tr>
<td>3.</td>
<td>3,5-Dimethyl pyrazole</td>
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</tr>
<tr>
<td>4.</td>
<td>3,4,5-Trimethyl pyrazole</td>
<td>4.08 ± 0.01</td>
</tr>
</tbody>
</table>

molecules, the order of pKₐ values being

Pz < Mpz < Dmpz < Tmpz

Alkyl groups acting as electron-repelling groups usually give rise to an increased electron density at the basic nitrogen atom and hence an increased basicity results. Since this is a phenomenon of inductive transmission, the effect decreases with increase in distance of the substituted methyl group from the
basic nitrogen atom. Thus slight increase in basicity of 3(5)-methyl pyrazole over pyrazole indicates that it is 5-substituted rather than 3-substituted. 3,5-Dimethyl pyrazole, on the other hand, has both the positions adjacent to the nitrogen substituted with methyl groups and as such shows an appreciable increase in pKa value. Introduction of an extra-methyl group in the 4-position in 3,4,5-trimethyl pyrazole has an effect not of much significance.

There has been much controversy regarding which N-atom is the basic one. With imidazole, an isomer of pyrazole, Edsall et al.\textsuperscript{35} and Gold et al.\textsuperscript{44} considered pyrrole-nitrogen atom as the basic nitrogen atom, while Baumann et al.\textsuperscript{37} and Li et al.\textsuperscript{26} believed the pyridine-nitrogen as the basic nitrogen atom. Orgel and co-workers\textsuperscript{99} and latter Nakatsuji and co-workers\textsuperscript{46} calculated the electron distributions in various heterocyclic compounds including diazoles by applying molecular orbital method and discussed the effect of chemical environments on the $\pi$-electron distribution in them. According to Orgel et al.\textsuperscript{99} the electron densities and mobile bond order for the diazoles are shown in the figures below (I-C-2). The results of Nakatsuji and co-workers on imidazole differ from
those of Orgel and co-workers as is evident from Table I-C-4.

Table I-C-4

Molecular diagram of imidazole derivatives, calculated by simple LCAO method and determination of N-atom as donor (According to the work of Nakatsuji et al)

<table>
<thead>
<tr>
<th>Ligands</th>
<th>1-Position</th>
<th>3-Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole</td>
<td>0.549</td>
<td>-0.277</td>
</tr>
<tr>
<td>2-Ethyl Imidazole</td>
<td>0.421</td>
<td>-0.336</td>
</tr>
<tr>
<td>2,4-Diethyl Imidazole</td>
<td>0.475</td>
<td>-0.392</td>
</tr>
<tr>
<td>4-Methyl Imidazole</td>
<td>0.479</td>
<td>-0.414</td>
</tr>
<tr>
<td>N-Methyl Imidazole</td>
<td>0.963</td>
<td>-0.506</td>
</tr>
</tbody>
</table>
Thus the fact that the nitrogen atoms at the 1- and 3-positions in imidazoles are assigned with the positive and negative charges respectively indicates that the pyridine-nitrogen atom acts as a basic nitrogen in the case of 1:3 diazoles. In analogy to the above and also following the work of Orgel et al.\textsuperscript{99}, it may be presumed that the pyridine-nitrogen atom acts as the basic nitrogen in the case of pyrazoles also.

Table I-C-5 illustrates \( pK_a \) values of some other heterocyclic bases. It includes some six-membered heterocyclic compounds where the nitrogen atom in the heterocaromatic ring attracts electrons from the \( \pi \)-double layer. They are generally known as \( \pi \)-deficient N-heterocaromatics. Pyridine is a typical example. Its weakness in basicity than the aliphatic tertiary amine \( \text{Et}_3\text{N} \) is found to be characteristic of bases in which the nitrogen atom is multiply bonded. This is due to the fact that as the nitrogen atom becomes progressively more multiply bonded its lone-pair of electrons is accommodated in an orbital that has progressively more s character; they are thus drawn closer to the nitrogen nucleus and held more tightly by it, thereby becoming less available for forming a bond with proton with a consequent decline in basicity of the compound. Introduction of a second nitrogen into pyridine ring greatly reduces the basicity. Though a small loss of basic strength upon the introduction of a second nitrogen is seen in saturated compounds
Table I-C-5

Acid-dissociation constants of some heterocyclic bases

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Bases</th>
<th>pKₐ</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ammonia</td>
<td>9.30</td>
<td>104, 105</td>
</tr>
<tr>
<td>2.</td>
<td>Hydrazine</td>
<td>8.50</td>
<td>103</td>
</tr>
<tr>
<td>3.</td>
<td>Pyridine</td>
<td>5.45</td>
<td>107, 108</td>
</tr>
<tr>
<td>4.</td>
<td>Pyridazine</td>
<td>2.33</td>
<td>109</td>
</tr>
<tr>
<td>5.</td>
<td>Pyrimidin</td>
<td>1.30</td>
<td>109</td>
</tr>
<tr>
<td>6.</td>
<td>Pyrazine</td>
<td>0.60</td>
<td>109</td>
</tr>
<tr>
<td>7.</td>
<td>Pyrrole</td>
<td>0.40</td>
<td>110</td>
</tr>
<tr>
<td>8.</td>
<td>Imidazole</td>
<td>7.33</td>
<td>46</td>
</tr>
<tr>
<td>9.</td>
<td>2-Methyl imidazole</td>
<td>8.13</td>
<td>46</td>
</tr>
<tr>
<td>10.</td>
<td>2-ethyl imidazole</td>
<td>8.02</td>
<td>46</td>
</tr>
<tr>
<td>11.</td>
<td>2,4-Dimethyl imidazole</td>
<td>8.57</td>
<td>46</td>
</tr>
</tbody>
</table>

like ammonia and hydrazine, this loss is appreciable in the present class of compounds because of several factors involved. In the first, the second nitrogen is electron-attracting and hence base-weakening. Then again, in some cases there are possibilities of the formation of exactly equivalent dipolar...
structures in the non-ionised molecule (I-C-3) and these may strengthen the resonance of this species at the expense of the ion. The basic strength of pyridine remarkably increases, however on insertion of an amino group where it permits more resonance in the cation than in the neutral molecule as in the case of 4-amino pyridine. This principle of additional ionic resonance\(^{109}\) is found to be responsible for the enhanced basic strength of many other heterocyclic bases.

N-heteroaromatics with at least one five-membered ring, contain the nitrogen atom in an electron-releasing setting (=CH-NH-CH=). Pyrrole is a typical example of such a system. The nitrogen atom in such a ring in pyrrole adds its lone-pair of electrons to the four electrons furnished by the two double bonds and thus makes an aromatic sextet. These are thus the cases of ring systems in which the carbon atoms have an excess of \(\pi\)-electrons.

The weakness of pyrrole is because of the fact that the lone-pair of electrons is not free to anchor a hydrogen ion as it is involved in maintaining the aromatic sextet (I-C-4). Looked from another angle, the effect is ascribable
to a base-weakening resonance in which the nitrogen of the non-ionised molecule become positive and somewhat quaternary as in aniline.

The insertion of a second nitrogen in a \( \pi \)-excessive heteroaromatic ring generally points to an effect which sharply in contrast with what has been shown in the cases of six-membered \( \pi \)-deficient heteroaromatics. Insertion of another nitrogen atom in pyrrole ring (as is the case with diazoles) is base-strengthening. The insertion of a doubly-bound nitrogen atom into the ring of pyrrole might be expected to have a base-weakening (inductive) effect on the singly bound nitrogen. The doubly bound nitrogen should be the more basic of the two. The additional base-strengthening effect of the second nitrogen must be due to the additional ionic resonance possible in the cations (e.g. between I-C-5c and I-C-5d and also between I-C-5e
and I-C-5f) of the diazoles as compared with their neutral molecules. The resonance arises from the equivalence of both nitrogen atoms in the cation as in I-C-5c and I-C-5d. From this, a base-weakening effect must be subtracted in those compounds which have adjacent nitrogen atoms (cf. pyrazole and imidazole), owing to hydrogen bonding of the non-ionised molecules (I-C-6a and I-C-6b).

The base-strengthening effect is not so marked in pyrazole as in imidazole. It appears from the above discussion that the lower basicity of pyrazole compared to that of imidazole is primarily because of the fact that in pyrazole the two nitrogens
are adjacent and hence much closer to each other, while in imidazole they are much apart from each other. This difference in the relative positions of the two nitrogen atoms in pyrazole and imidazole results in rather different environment for association through intermolecular hydrogen-bonding. The presence of two adjacent nitrogens in pyrazole suggests \textsuperscript{112,113} that association may involve a cyclic, hydrogen-bonded dimer resulting in a fairly stable six-membered ring (I-C-6a), while the case of imidazole is different. Though there is positive evidence\textsuperscript{112,114} of association through unsubstituted -NH- groups in imidazole the hydrogen-bonding here, instead of involving 5 or 6-membered structures, are of unsymmetrical zig-zag nature (the exact configuration being still unknown) and comparatively less stable (cf. I-C-6b). Thus the contribution of base-weakening effect by hydrogen-bonding is more
in the case of pyrazole than in imidazole. A similar type of hydrogen-bonding is present in ring substituted pyrazoles also (I-C-7). These may perhaps be cited as reasonings, though of a qualitative nature, for the increased basicity of imidazoles over their isomeric species, pyrazoles.
SECTION D

ASSOCIATION EQUILIBRIA OF PYRAZOLE AND SOME METHYL-SUBSTITUTED PYRAZOLEs AND SILVER (I) ION.
An early observation of Schmidt revealed that pyrazole produces colourations with certain transition metal ions. Recently some information has been gathered on the preparative and structural aspects of metal-pyrazole complexes with various metal ions, both transitional and non-transitional. The first quantitative information regarding the complexation of pyrazoles with cadmium was, however, given by Andrews and Romary and later by Grow using polarographic methods. Grow and Westwood subsequently reported the results of their polarographic studies of complexation reactions of pyrazole with some other transition metal ions. To these, an interesting potentiometric investigation by Musgrave and Hum-burg Jr. has been added on the association equilibria with
protons, Ni (II) and Cu (II). Though pyrazole is weakly basic in nature, the behaviour of these metal ions in presence and in absence of the ligand as outlined in the above works, is in strong support of its good complexing ability with the metal ions.

Although sufficient quantitative information\textsuperscript{25-48} has been gathered on the complexing ability of the isomeric imidazoles with many metal ions in solution, the chemistry of pyrazoles and its derivatives in solution, specially its association equilibria with various metal ions, received very little attention until the last decade. The present investigator, was, therefore, interested to study some aspects of the ligands in solution. A survey of literature does not provide any report on the study of the silver (I)-pyrazole complexes. We have, therefore, studied the potentiometric behaviour of silver (I) ions in presence and in absence of pyrazole as the ligand. Such a study gave sufficiently clear indication regarding complex formation and allowed to make quantitative assessment of the composition and the stability constants of these complexes. The stability data have been further utilised in computing different thermodynamic parameters of the complexation reactions in solution for the Ag (I)-pyrazole complexes. The present section reports the results of the above study.
The work has further been extended to the study of silver (I) complexes in solution with some methyl substituted pyrazoles, viz. 3(5)-methyl, 3,5-dimethyl, 3,4,5-trimethyl pyrazoles (I-D-1). The effect of methyl substitution of the pyrazole ring on the stabilities of the silver (I) complexes has been studied and an attempt has been made to correlate the evaluated acid dissociation constants i.e. pK\textsubscript{a} values of the quaternary pyrazoles (vide Section I-C) with the first step and overall stability constants of the silver (I) complexes of all the pyrazoles studied.

A comparative study on the ligational behaviour of pyrazole as well as of substituted pyrazoles and isomeric imidazoles towards silver (I), based on the results of the present study and those of the similar studies on Ag (I)-imidazoles\textsuperscript{44,46} has also been made. Both the stability constant values as well as the values for the thermodynamic parameters for both Ag (I)-pyrazoles and Ag (I)-imidazoles\textsuperscript{37} have been considered for the above mentioned comparative study.
Material:

Pyrazole was obtained from Koch Light Lab. (England) which was further purified by repeated crystallisation from absolute alcohol. 3(5)-Methyl-, 3,5-dimethyl- and 3,4,5-trimethyl pyrazoles have been prepared by the methods described in Section I-C. Silver was weighed as nitrate and the working solution was standardised with standard KCl. All the solutions were prepared in doubly distilled air-free conductivity water. A solution of A.R. grade KNO₃ (1.0 M) was used to maintain the required ionic strength of the solutions. All the solutions used in the potentiometric measurements contained, in addition to pyrazole or substituted pyrazole, a silver ion concentration of 0.5 mM and 0.1 M KNO₃ in 20% ethanol-media. The respective pyrazole concentration was varied from 0.01 M to 0.1 M. The silver electrode used was a pure silver wire cleansed with dilute nitric acid and then washed with water.

Measurements:

For recording the e.m.f. of different mixtures, a 'Leeds and Northrup' K₃ type Universal potentiometer bridge (reading upto 0.5 mV) in conjunction with a thermostated cell was used, and the current detecting device was a Scalamp Pye
Galvanometer. SCE in conjunction with KNO₃-agar salt-bridge was used as the reference electrode.

Temperature of 25 ± 0.1°C, 30 ± 0.1°C and 35 ± 0.1°C were maintained in all the measurements, care being taken that no measurements were made until proper temperature equilibrium has become established. Each of the e.m.f. values was taken twice and the same was not recorded until the repeated values differed by not more than ± 0.5 mV.

**Method of Calculation:**

The overall stability constant \( \beta_n \) (the activity quotient or the so-called thermodynamic equilibrium constant) for the reaction (i), is related to the stepwise stability constants \( K_n \) for the reaction (2):

\[
M + nL \rightleftharpoons ML_n \rightleftharpoons ML_{n-1} + L \rightleftharpoons ML_{n-2} + L + L \rightleftharpoons \cdots \rightleftharpoons ML_1 + nL \rightleftharpoons ML_0 + \cdots \rightleftharpoons ... \rightleftharpoons M + nL
\]

by the relation:

\[
\beta_n = \frac{\prod_{n=0}^{n} K_n}{n}
\]

The composition and the overall stability constants of various silver (I)-pyrazoles complexes have been determined potentiometrically using Leden's method.
The following cells were set up for the purpose.

Cell 1. \(-\text{SCE} // \ 0.5\text{mM AgNO}_3 / \text{Ag}^+\)  
(in 20% ethanol)

Cell 2. \(-\text{SCE} // \ 0.5\text{mM AgNO}_3 / \text{Ag}^+\)  
\(+\text{xml 0.5M respective pyrazoles} \in 20\% \text{ ethanol}\)

The e.m.f. of the cell of type 1, when there is no ligand present, is given by,

\[ E_1 = E' + \frac{RT}{nF} \ln [M] \]

where \([M]\) is the metal ion concentration. In the above equation \(E'\) includes the potential of the calomel electrode, the liquid junction potential and the correction term for activity co-efficients in mixed solvents.

When varied but sufficient amounts of the respective ligands are added, some of the metal ions are involved in the complex formation and a new potential (say \(E_2\)) will be set up. Thus in the case of the cell of type 2, containing varied amount of the ligand (since all the other factors were kept constant in measuring the e.m.f.), the e.m.f. is given by

\[ E_2 = E' + \frac{RT}{nF} \ln [M] \]
where \([M]\) is the corresponding free metal ion concentration.

Hence,

\[
\Delta E = E_1 - E_2 = \frac{RT}{nF} \ln \frac{[M]}{[C_M]}
\]

The quantity \([C_M]/[M]\) is the degree of the complex formation, so that,

\[
[C_M]/[M] = \text{Antilog} \left( \frac{nF}{2.303 RT} \Delta E \right)
\]

Now a series of \(F_0[X]\) functions for each system dependent on the free ligand concentration \([X]\) of the respective pyrazole ligand were derived from the shift of potentials of the metal ions over a wide range of ligand concentrations and the function may be defined as:

\[
\text{Antilog} \left( \frac{nF}{2.303 RT} \Delta E \right) = F_0[X] = \sum_{j=0}^{j=n} \beta_j [X]^j
\]

The initial term \(\beta_0\) is the stability constant of the 'zero' th complex, which by definition has the value unity and \(\beta_j\) terms refer to the consecutive overall stability constant of the \(j\)th complex. The consecutive overall stability constant
values were determined by graphical extrapolation procedure devised by Lederi, using the formula,

\[ F_j \{X\} = \left\{ F_{j-1}\{X\} - \beta_{j-1} \right\}/[X] \]

A series of \( F_j \{X\} \) values corresponding to \( F_0 \{X\} \) values were obtained and plots of \( F_j \{X\} \) vs. \([X]\) where \( j = 1, 2 \) etc. were made until the final function \( F_N \{X\} \) independent of \([X]\) i.e. \( F_N \{X\} = \beta_N \) was obtained. The values of \( \beta_j \) were the \( F_j \{X\} \) values obtained from the graphs at \([X] = 0\).

Different thermodynamic functions viz., the values of the changes in free energy (\( \Delta F \)), enthalpy (\( \Delta H \)) and entropy (\( \Delta S \)) of complex formation have been determined at 30°. The expression,

\[ \Delta F = -RT \ln \beta \]

relating stability constant \( \beta \) to the free energy change of the reaction was employed for evaluating the value of \( \Delta F \).

The value of \( \Delta H \) was determined with the help of an isobar equation\(^{119}\).
\[
\frac{d \ln \beta}{dT} = \frac{\Delta H}{RT}
\]
or
\[
\frac{d \log \beta}{d(1/T)} = \frac{\Delta H}{4.57}
\]

The values of \(\Delta H\) were calculated graphically. The value of \(\log \beta\) obtained at different temperatures were plotted as a function of \((1/T)\). The gradient of this line at the point corresponding to \(30^\circ\) was equated with \(-\Delta H/4.57\).

The entropy change \((\Delta S)\) of the reaction was calculated from the equation,

\[
\Delta S = \frac{(\Delta H - \Delta F)}{T}.
\]
Results and Discussion

The shift in potentials of the cells containing metal ions [silver (I)] with increasing ligand (viz. Pyrazole, 3(5)-Methyl-, 3,5-dimethyl- and 3,4,5-trimethyl pyrazoles) concentrations strongly favours the complex formation and the values have been recorded in Tables I-D-1(a) to I-D-1(d).

The various $F_j[X]$ functions obtained from the shift in potential and used in calculation of stability constants for the respective silver (I)-pyrazole systems have been presented in Table I-D-2(a) to I-D-2(d).

Owing to the relatively large excess of the ligand used, the free ligand concentration was justifiably assumed to approximate closely to the total ligand concentration. Figures I-D-1(a) to I-D-1(d) and I-D-2(a) to I-D-2(d) show the plots of the $F_1[X]$ and $F_2[X]$ respectively vs. ligand concentration $[X]$ for the respective systems. Extrapolation of these curves at $[X] = 0$ give the values for the formation constants $\beta_1$ and $\beta_2$ for each system which are presented as $\log \beta_j$ along with the estimated probable error in Table I-D-3.
Table I-D-1(a)

Effect of varying ligand concentration on the shift in potentials ($\Delta \theta$) at different temperatures.

\[ 0.005 \text{ M } \text{AgNO}_3 = 5.0 \text{ ml}, \quad 1.0 \text{ M } \text{KNO}_3 = 5.0 \text{ ml}, \quad 0.5 \text{ M ligand in } \text{ethanol} = x \text{ ml}, \quad \text{Ethanol} = (10-x) \text{ ml}, \quad \text{Water} = 30 \text{ ml}. \]

Ligand : Pyrazole

<table>
<thead>
<tr>
<th>0.5 M ligand in ethanol (ml)</th>
<th>E.M.F. (volts) at 25°C</th>
<th>30°C</th>
<th>35°C</th>
<th>Shift in potentials ($\Delta \theta$) (volts) at 25°C</th>
<th>30°C</th>
<th>35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>0.0</td>
<td>0.35675</td>
<td>0.35410</td>
<td>0.34905</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
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<td>0.31725</td>
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<td>0.31505</td>
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<td>0.03400</td>
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<td>0.08205</td>
<td>0.05950</td>
</tr>
<tr>
<td>3.0</td>
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<td>0.27400</td>
<td>0.27205</td>
<td>0.08540</td>
<td>0.08010</td>
<td>0.07700</td>
</tr>
<tr>
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<td>0.26120</td>
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<td>0.10365</td>
<td>0.10085</td>
</tr>
<tr>
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<td>0.24120</td>
<td>0.23915</td>
<td>0.12015</td>
<td>0.11290</td>
<td>0.10990</td>
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<tr>
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<td>0.12100</td>
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<td>0.22250</td>
<td>0.22840</td>
<td>0.22375</td>
<td>0.13425</td>
<td>0.13770</td>
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<tr>
<td>Ligand: 3(5)-Methyl pyrazole</td>
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<tr>
<td>-----------------------------</td>
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<table>
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<td>0.24615</td>
<td>0.11430</td>
<td>-</td>
<td>0.10290</td>
</tr>
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<td>0.23925</td>
<td>0.12100</td>
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<td>0.13130</td>
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<td>-</td>
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<td>-</td>
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### Table I-D-2(a)

Relevant $F_1[X]$ and other data used in calculation of stability constants for silver(I)-pyrazole and substituted pyrazole systems at 25°, 30° and 35°C.

(Ionic strength: 0.1 M KNO₃)

**Ligand: Pyrazole**

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Plots of $F_1(x)$ vs. $[x]$ for silver(I) ions in pyrazole solutions at 25°C, 30°C, & 35°C.
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Table I-D-2(b)

Ligand: 3(5)-Methyl pyrazole
Plots of $F_1[X]$ vs. $[X]$ for Silver(I) ions in solutions (at 25°, 30°, 35° C) of 3(5)-methyl pyrazole.

FIG. I-D-1(b)
FIG. I-D-2a: Plots of $F_2[X]$ vs. $[X]$ for Silver(I) ions in pyrazole solutions at 25°, 30° and 35°C.

FIG. I-D-2b: Plots of $F_2[X]$ vs. $[X]$ for Silver(I) ions in 3(45) methyl pyrazole solutions at 25°, 30° and 35°C.
Table I-D-2(c)

Ligand: 3,5-Dimethyl pyrazole

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FIG. I-D-1c.
Plots of $F_1[X]$ vs. $[X]$ for Silver-(I)ons in 3,5 dimethyl pyrazole solutions at 25°, 30° & 35°C.
Table I-D-2(d)

Ligand: 3,4,5-Trimethyl pyrazole

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<td>0.2625</td>
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<td>0.0945</td>
<td>1.87</td>
<td>2.69</td>
<td>3.55</td>
<td>6.34</td>
<td>1.887</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
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<td>0.0228</td>
<td>0.0561</td>
<td>0.0945</td>
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<td>2.69</td>
<td>3.55</td>
<td>6.34</td>
<td>1.887</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.02</td>
<td>0.0228</td>
<td>0.0561</td>
<td>0.0945</td>
<td>1.87</td>
<td>2.69</td>
<td>3.55</td>
<td>6.34</td>
<td>1.887</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
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<td>0.0561</td>
<td>0.0945</td>
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<td>2.69</td>
<td>3.55</td>
<td>6.34</td>
<td>1.887</td>
<td>-</td>
</tr>
<tr>
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<td>0.0945</td>
<td>1.87</td>
<td>2.69</td>
<td>3.55</td>
<td>6.34</td>
<td>1.887</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>0.02</td>
<td>0.0228</td>
<td>0.0561</td>
<td>0.0945</td>
<td>1.87</td>
<td>2.69</td>
<td>3.55</td>
<td>6.34</td>
<td>1.887</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>0.02</td>
<td>0.0228</td>
<td>0.0561</td>
<td>0.0945</td>
<td>1.87</td>
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<td>1.87</td>
<td>2.69</td>
<td>3.55</td>
<td>6.34</td>
<td>1.887</td>
<td>-</td>
</tr>
</tbody>
</table>
Flots of $F_1[X]$ vs. $[X]$ for Silver(II)ions in 2,4,5 trimethyl pyrazole solutions at $25^\circ$, $30^\circ$, and $35^\circ$. 

FIG. I-D-14.
FIG. I-D-2c: Plots of $F_2(x)\times 10^5$ vs. $[x]$ for Silver(I) ions in 3,5 dimethyl pyrazole solutions at 25, 30, 35°C.

FIG. I-D-2d: Plots of $F_3(x)\times 10^{-5}$ vs. $[x]$ for Silver(I) ions in 3,4,5 trimethyl pyrazole solutions at 25, 30, 35°C.
Table I-D-3

Stability constants of Silver (I)-pyrazole complexes at different temperatures.

Medium: 20% Ethanol-Water, $\mu = 0.1$ M KNO$_3$

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Composition of the complex (Metal:Ligand)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1:1</td>
<td>1:2</td>
<td>1:1</td>
<td>1:2</td>
</tr>
<tr>
<td></td>
<td>Stability constants log $\beta_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stability constants log $\beta_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25°C</td>
<td>30°C</td>
<td>35°C</td>
<td>25°C</td>
<td>30°C</td>
</tr>
<tr>
<td>Pyrazole</td>
<td>2.05</td>
<td>1.90</td>
<td>1.80</td>
<td>4.44</td>
<td>4.31</td>
</tr>
<tr>
<td></td>
<td>± 0.08</td>
<td>± 0.05</td>
<td>± 0.07</td>
<td>± 0.012</td>
<td>± 0.007</td>
</tr>
<tr>
<td>3(5)-Methyl pyrazole</td>
<td>2.41</td>
<td>2.33</td>
<td>2.13</td>
<td>4.80</td>
<td>4.61</td>
</tr>
<tr>
<td></td>
<td>± 0.03</td>
<td>± 0.03</td>
<td>± 0.03</td>
<td>± 0.007</td>
<td>± 0.007</td>
</tr>
<tr>
<td>3,5-Dimethyl pyrazole</td>
<td>3.09</td>
<td>2.96</td>
<td>2.93</td>
<td>5.54</td>
<td>5.38</td>
</tr>
<tr>
<td></td>
<td>± 0.04</td>
<td>± 0.05</td>
<td>± 0.04</td>
<td>± 0.005</td>
<td>± 0.008</td>
</tr>
<tr>
<td>3,4,5-Trimethyl pyrazole</td>
<td>3.86</td>
<td>3.74</td>
<td>3.46</td>
<td>5.90</td>
<td>5.81</td>
</tr>
<tr>
<td></td>
<td>± 0.02</td>
<td>± 0.02</td>
<td>± 0.04</td>
<td>± 0.007</td>
<td>± 0.007</td>
</tr>
</tbody>
</table>
For all the complexes of silver (I)-pyrazoles, the values of various thermodynamic functions viz., $\Delta F$, $\Delta H$ and $\Delta S$ at 30° were evaluated and have been recorded in Table I-D-4. Although the precision of $\Delta F$ is within $\pm 0.07$ Kcal/mole, the precision of the values of $\Delta H$ is within $\pm 1$ Kcal/mole which is due to methodical defects.

The value of $\Delta H$ was determined graphically. Different values of log $\beta$ obtained at different temperatures were plotted as a function of $(1/T)$ and the gradient at the point corresponding to 30°C (Fig. I-D-3(a) and I-D-3(b)) was equated with $-\Delta H/4.57$. The value of $\Delta F$ and $\Delta S$ were obtained with the help of standard relations.

From the stability constant data, the values of $\lambda_j$, the degree of formation of the $j$th complex may be calculated over the whole ligand concentration range. The degree of formation of the $j$th complex is given by,

$$
\lambda_j = \frac{[MX_j]}{c_M} = \frac{[MX_j]}{[MI] + [MX] + [MX_2] + \ldots} \\
\sum_0^N \beta_j [X]^j = \frac{\beta_j [X]^j}{\sum \beta_j [X]^j} = \frac{\beta_j [X]^j}{F_0 [X]}
$$
Plots of log $\beta_1$ vs. $(1/T)$ for evaluating $\Delta H_1$ values at 20°C of the complexation reaction in solution of Silver(I) with various pyrazoles.

(1) pyrazole, (2) 3-(3)methyl pyrazole,
(3) 3,5 dimethyl pyrazole, (4) 3,4,5 trimethyl pyrazole.

FIG. I-D-3a.
FIG. 1-D-3b: Plots of \( \log \beta_a \) vs. \((1/T)\) for evaluating \( \Delta H_a \) values at 20°C of the complexation reaction in solution of Silver(I) with various pyrazoles.

(1) pyrazole, (2) 3,5-methyl pyrazole, (3) 3,5-dimethyl pyrazole, (4) 3,4,5-trimethyl pyrazole.

(153x425) \( \log \beta_a \) vs. \((1/T)\) for evaluating \( \Delta H_a \) values at 20°C of the complexation reaction in solution of Silver(I) with various pyrazoles.

(1) pyrazole, (2) 3,5-methyl pyrazole, (3) 3,5-dimethyl pyrazole, (4) 3,4,5-trimethyl pyrazole.
**Table I-D-4**

Thermodynamic functions of the complexation reactions of Ag(I) with pyrazoles in solution at 30°C. (Medium 20% Ethanol-Water, $\mu = 0.1$M KNO$_3$)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Composition of the complex (Metal:Ligand)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>l:1</td>
</tr>
<tr>
<td></td>
<td>l:2</td>
</tr>
<tr>
<td></td>
<td>$\Delta H$ (Kcal/mole)</td>
</tr>
<tr>
<td>Pyrazole</td>
<td>9.14</td>
</tr>
<tr>
<td>3,5-Dimethyl pyrazole</td>
<td>9.14</td>
</tr>
<tr>
<td>3,4,5-Trimethyl pyrazole</td>
<td>12.57</td>
</tr>
</tbody>
</table>
A graph of $\xi_j$ vs. $\log [X]$ for each species in the respective Ag (I)-substituted pyrazole system gives the family of the distribution curves in the specified concentration range. Figure I-D-4(a) to I-D-4(d) illustrates such typical families of distribution curves for the respective Ag (I)-substituted pyrazole systems (at 25°C for only one set of data). Rest of the data represents almost similar distribution and hence repetition has been avoided.

The plots of $F_2[X]$ vs. $[X]$ for all the ligands showed horizontal lines which indicate that two complexes are formed with silver and substituted pyrazoles. Since most stable silver complexes have linear structures with co-ordination number 2,37,44,46,105,107,108 and the present work provides two stability constant values, for each complex system, we may correlate our observation by assuming the formation of two complex species viz. $\text{AgL}^+$ and $\text{AgL}_2^+$ in solution to be in compatible with the following equilibrium,

$$\text{Ag}^+ + L \rightleftharpoons \frac{k_1}{[\text{AgL}^+]} \text{AgL}^+ \quad \text{and} \quad \text{AgL}^+ + L \rightleftharpoons \frac{k_2}{[\text{AgL}_2^+]} \text{AgL}_2^+$$

The consecutive formation constants are given by,

$$K_1 = \frac{[\text{AgL}^+]}{[\text{Ag}^+] [L]} \quad \text{and} \quad K_2 = \frac{[\text{AgL}_2^+]}{[\text{AgL}^+] [L]}$$
Figure I-D-4a.

Distribution of complex species as a function of ligand concentration in the Silver(I)-pyrazole system at 25°C.
FIG. I-D-4b.

Distribution of complex species as a function of ligand concentration in the Silver(I)-3\(\beta\) methyl pyrazole system at 25°C.
FIG. I-D-4c.
Distribution of complex species as a function of ligand concentration in the Silver(I)-3,5 dimethylpyrazole system at 25°C.
FIG. 1-D-4d.

Distribution of complex species as a function of ligand concentration in the Silver(I)-3,4,5 trimethylpyrazole system at 25°C.
so that \( \beta_1 = k_1 \) and \( \beta_2 = k_1 k_2 \)

[where \( l \) represents one molecule of each of the unidentate neutral pyrazole ligands].

This view is supported by the earlier works in similar field vi\( s.\), the complexation of silver (I) with ammonia and imidazole.

The stabilities of both 1:1 and 1:2 complex species decrease with increase in temperatures suggesting thereby that the dissociation of the complexes formed in solution increases with the rise of temperature. With ligands like ammonia\(^\text{105}\), imidazole\(^\text{44}\), substituted imidazoles\(^\text{37,46}\), the magnitude of the second formation constants \( K_2 \) of the complexes of silver (I) have been found to be higher than those of the first, suggesting the predominance of the 2:1 species over the 1:1 variety. But in the present cases, the particular trend is not always observed, although the difference between the two formation constants is not much pronounced. This is evidenced by the data presented in Table I-D-5. The table further shows that although the values in stability constants have differences among the systems, there is a close similarity in the values of \( \log K_1 \approx \log K_2 \)

The discussions made in the earlier section pointed towards the fact that in the diazoles, out of the two nitrogen
Co-ordination of ammonia and some diazoles towards silver (I) along with their acid dissociation constants at 25°C.

<table>
<thead>
<tr>
<th>Ligands</th>
<th>pK_a</th>
<th>Stability constants of silver complexes</th>
<th>log K_1~log K_2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>log β_1</td>
<td>log β_2</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>9.28</td>
<td>3.24</td>
<td>7.05</td>
<td>0.57</td>
</tr>
<tr>
<td>Imidazole</td>
<td>7.33</td>
<td>3.08</td>
<td>6.95</td>
<td>0.79</td>
</tr>
<tr>
<td>2-Methyl imidazole</td>
<td>8.13</td>
<td>3.11</td>
<td>6.98</td>
<td>0.76</td>
</tr>
<tr>
<td>2,4-Dimethyl imidazole</td>
<td>8.57</td>
<td>3.44</td>
<td>7.50</td>
<td>0.62</td>
</tr>
<tr>
<td>Pyrazole</td>
<td>2.36</td>
<td>2.05</td>
<td>4.44</td>
<td>0.34</td>
</tr>
<tr>
<td>3(5)-Methyl pyrazole</td>
<td>2.68</td>
<td>2.41</td>
<td>4.80</td>
<td>0.02</td>
</tr>
<tr>
<td>3,5-Dimethyl pyrazole</td>
<td>3.68</td>
<td>3.09</td>
<td>5.54</td>
<td>0.64</td>
</tr>
<tr>
<td>3,4,5-Trimethyl pyrazole</td>
<td>4.08</td>
<td>3.86</td>
<td>5.90</td>
<td>1.82</td>
</tr>
</tbody>
</table>
atoms, the pyridine nitrogen atom acts as the basic nitrogen and hence the donor atom. This explains the increase in the values of the formation constants of the metal complexes with methyl substituted imidazole ligands having increasing negative charges at the 3-position. In analogy to the above, it may be presumed that co-ordination through pyridine nitrogen is also effective in the cases of pyrazole and the methyl substituted pyrazoles studied, during the present investigation.

This is further evidenced by the X-ray crystallographic studies on the metallic complexes of pyrazoles by Reimann and co-workers. With \([\text{Ni}(\text{Pz})_4\text{Cl}_2]\) and \([\text{Ni}(\text{Pz})_4\text{Br}_2]\), compounds, the pyrazole rings are coplanar and the direction of the Ni-N bond makes an angle of 2° with the plane of the pyrazole ring (I-D-2a). Co-ordination through the pyrrole nitrogen would have been resulted in the formation of a
quaternary nitrogen and the bond angle would have been half the tetrahedral angle i.e. 54° which was not found to be the case. Moreover, the results indicated the formation of H-bonding with the co-ordinated Cl or Br atoms and pyrrole H-atom (I-D-2b).

The substitution of an alkyl group in the heterocyclic ring usually gives rise to a base strengthening effect of the molecule, particularly while they are in α- or γ-position. Introduction of electron repelling CH₃-groups in steps to the pyrazole ring gradually increases the electron density of the pyridine nitrogen atom producing increased basicity of the molecules and this makes it reasonable that the value of the formation constant increases with the increasing negative charge on the pyridine nitrogen. Thus the affinity of pyrazole and its methyl derivatives for silver (I) parallels its affinity towards hydrogen ion. Similar trend was also observed in the silver (I) complexes as well as in cadmium (II) complexes of imidazoles but not in their copper (II) complexes.

The observed trend in the stability constant values of silver (I)-pyrazoles, viz.,

\[
[Ag(3\text{MeP}_2)_2]^+ < [Ag(Dmp)_2]^+ < [Ag(Tmp)_2]^+
\]
can thus be well understood. With 3(5)-methyl pyrazole, the log $\beta_j$ values increase slightly from the corresponding values of pyrazole. The 3-substituted product always co-exists with its 5-substituted tautomer and since the increased basicity of 3(5)-methyl pyrazole over pyrazole is a result of inductive transmission, the effect of which decreases with increase in distance, it is highly probable that during complexation with silver (I), the co-ordinating species is the 5-methyl rather than 3-methyl pyrazole. 3,5-Dimethyl pyrazole with both positions adjacent to the nitrogens substituted with methyl groups is endowed with no such choice and consequently there is an appreciable increase in log $\beta_j$ values. Introduction of an extra methyl group in the 4-position in 3,4,5-trimethyl pyrazole has an effect of not much significance. Figure I-D-5, illustrates a graphical relation between the basicities of the ligands with their ability to undergo complexation with silver (I). Fairly good linear relationship between log $\beta_j$ and $pK_a$ was obtained as expected.

The values of the formation constants of the complexes of silver (I) with imidazoles and pyrazoles (table I-D-5) reflect the much weaker donor nature of both the ligands. This is probably caused by the lower basicity of the ligands in comparison to other N-donor ligands which is discussed in Section I-C.
FIG. I-D-5.: Graphical relation between $pK_a$ of the quaternary pyrazoles and the $\log\beta_1$ values of their Silver(I)-complexes. (A- pyrazole, B- 3(5) methylpyrazole, C- 3,5 dimethylpyrazole and D- 3,4,5-trimethylpyrazole.)
Further, the reasons which are operative in lowering the basicities of pyrazoles in comparison to those of imidazoles, are believed to control the co-ordinating ability of the ligands, and hence the weaker donor capability of pyrazole and substituted pyrazoles towards Ag (I) than those of the corresponding imidazoles is reflected in the results of the present study.

Table I-D-4 gives the values of different thermodynamic functions favouring complex formation between silver (I) with pyrazole and substituted pyrazoles. Different values obtained give an estimation of the effect of the substituents on the thermodynamic parameters of the above complexation reactions $\Delta H_2$, $\Delta F_2$ and $\Delta S_2$ show a regular change in their respective values from pyrazole to 3,4,5-trimethyl pyrazole. All the values favour a gradual increasing tendency in donor capability of the pyrazole ligands from pyrazole to 3,4,5-trimethyl pyrazole. Thus the trend in stability of Ag (I)-pyrazoles explained on the basis of increasing basic character of the diazoles gets further evidence from the thermodynamic behaviour of the complexation reactions between silver (I) and the ligands. Although the $\Delta H_1$, $\Delta F_1$ and $\Delta S_1$ values show some irregularity, the order of the respective thermodynamic parameters have been
### Table I-D-6

Thermodynamic data for the formation of Ag(I) complexes in solution

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Medium</th>
<th>Temperature &amp; Method</th>
<th>( \Delta H_f ) ((n = 1))</th>
<th>( \Delta F_f ) ((n = 1))</th>
<th>( \Delta S_f ) ((n = 1))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrazole</td>
<td>0.1 M KNO(_3) ((2\times \text{aq.} \cdot \text{H}_2\text{O}))</td>
<td>30°C Temp. dependence of St. constants</td>
<td>-9.14</td>
<td>-5.98</td>
<td>-10.43</td>
<td>Present investigation</td>
</tr>
<tr>
<td>Imidazole</td>
<td>1.0 M KNO(_3) ((\text{aq}))</td>
<td>Cal.</td>
<td>-7.3</td>
<td>-9.4</td>
<td>-21</td>
<td>37</td>
</tr>
<tr>
<td>Ammonia</td>
<td>( \mu = 0 ) ((\text{corr.}))</td>
<td>25°C Cal.</td>
<td>-13.40</td>
<td>-9.85</td>
<td>-11.9</td>
<td>124</td>
</tr>
</tbody>
</table>
found to be the same. The corresponding thermodynamic parameters for the 1:2 complexation reaction, although changes gradually, the difference in the values of two consecutive members is not very sharp.

Table I-D-6 gives the values of different thermodynamic function favouring complex formation between Ag (I)-NH₃, Ag (I)-imidazole along with Ag (I)-pyrazole for comparison. The values with all the ligands are of the same order, although the calorimetrically determined values of Ag (I)-NH₃ and Ag (I)-imidazole can be more relied upon.

One interesting observation is worth mentioning here. In all the pyrazole studied, the \( \Delta H_1 \) and \( \Delta H_2 \) are practically equal while in the cases of other ligands like NH₃, imidazole etc., the value of \( \Delta H_2 \) is about twice that of \( \Delta H_1 \). Hence, some other reactions of opposing character which diminish the values of \( \Delta H_2 \) may be expected to be operative. As discussed earlier, the present ligands prefer to exist as hydrogen-bonded dimers and co-ordination with silver (I) results in breaking up of two H-bonds per molecule of complexes formed. This probably causes a lowering in the values of \( \Delta H_2 \) to the extent as observed experimentally. Values in \( \Delta S_2 \) also favour this idea.
In view of the weakly basic nature of the pyrazole molecules, these ligands would not form strong complexes. It is possible, however, that during complexation with silver (I) ions, metal ligand π-bonding may occur, to some extent, as has been pointed out by Crow and Westwood. They reported that with most of the transition metals, the possibilities of strong complexations are very much poor with pyrazoles as ligands. But with metals having a high proportions of filled d-shells it is possible for metal-ligand π-bonding to occur.
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