SUMMARY

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Mixed ligand complexes are known to provide models for metalloenzymes [1, 2] and several other biological processes involving metal ions. Also they have importance as intermediates in catalytic processes [3]. Both enzymatic and catalytic activities are function of the stability of the mixed ligand complex [2, 3] (enzyme - metal - substrate or reactant and metal catalyst) which in turn depends mainly on the nature of the two ligands with which the metal binds [2, 4].

Some of the important observations regarding the stability of the ternary complexes are the astatistical stabilization of ternary complexes involving π bonding ligands due to metal $\longrightarrow$ ligand π interaction [4, 5] and discriminating behaviour of [MA] complexes, where A = hetero aromatic N - base, towards N-N, N-O^- and O^--O^- coordinating ligands [2, 4, 6, 7].

The stability of the ternary complex was observed to increase with increase in $M \longrightarrow A$ π bonding [4, 5]. This has been explained on the basis of the increase in π acid character of the metal in [MA] due to $M \longrightarrow A$ π bonding. This depletes the electron density over the metal ion and thus reduces the electronic repulsion between the metal $d\pi$ electrons and the electrons of the secondary ligand, thus facilitating the coordination of L with [MA] than with free metal ion.

The release of repulsion in ternary complexes compared to the binary complexes is more in case where L is O^--O^- coordinating ligand because of lone pairs of electrons over both O^-. It is less where L is N-O^- with lone pair of electrons over only O^- and is the least when L is N-N coordi-

nating ligand with no lone pair of electrons. Hence, $\Delta \log K$ follow the order [Cu A (O⁻O⁻)] > [Cu A (N-O⁻)] > [Cu A (N-N)] [8,10]. In other words [Cu A] prefers to coordinate with O⁻O⁻ coordinating ligand than to coordinate with N-O⁻ containing ligand which is further prefered over N-N coordinating ligand.

The effect of noninteracting substituents over the ligands was also seen. Initial reports include comparison between the series of tertiary diimines as primary ligands [11] and catechol derivatives [12, 13] and some amino acids [14] as secondary ligands. General observation was that the electron withdrawing substituents over the primary ligand increases the stablity of the ternary complex whereas electron releasing substituents decrease it. The effect was reverse when the substituents were on the secondary ligands.

In both the above cases metal to primary ligand π-interaction plays a significant role in stabilizing or destabilizing the ternary complexes. It was, therefore, thought of interest to consider the effect of π-bonding secondary ligands as well as the effect of substituents on both the ligands, on the stability of the ternary complexes [Cu A L], their spectral properties and thier reactions.

A general introduction to the subject in the beginning covers broad survey of literature regarding important milestones in the research in related areas and motivation for the present work.

In the second chapter systematic study of the potentiometric determination of the stability constants of the ternary complexes [Cu A L] has been described and the results disucssed in terms of the electronic characteristics of the two ligands. The ligands considered are , A = bis (2-pyridyl) amine (A^1) and 5-nitro-1, 10-phenanthroline (A^2).

and L = salicylaldehyde (HL^1), 5-bromosalicylaldehyde (HL^2), 5-nitro-salicylaldehyde (HL^3), 2-hydroxy naphthaldehyde (HL^4), and 2-hydroxy aceto phenone (HL^5),

aceto acetanilide (HL^6), acetoacet-o-toluedide (HL^7), aceto acet-o-anisidide (HL^8), benzoyl acetanilide (HL^9), salicyl amide (HL^{10}), salicylanilide (HL^{11}) and 5-bromo salicylamide (HL^{12}).

The third chapter deals with the synthesis and characterization of the above ternary complexes.

The reactions of the aldehyde containing ternary complexes with aromatic diamines (1, 2- , 1, 3- and 1, 4-phenylene diamine, opd, mpd and ppd, respectively) resulted in the formation of binuclear complexes. This has been described in the fourth chapter. Spectral and magnetic properties of these binuclear complexes have been discussed.

Stablity constants of ternary complexes -

Stability constants of the ternary complexes were determined by carrying out potentiometric titration in 50% (v/v) aq. dioxane medium at 30°C and processing the titration data on computer using the programme SCOGS [15]. Both, stepwise (eq. 1) and simultaneous (eq. 2) formation of the complexes was considered.

$$Cu + A \longrightarrow [Cu\ A] \quad \text{and} \quad [CuA] + L \rightleftharpoons [Cu\ A\ L] \qquad (1)$$

$$Cu + A + L \rightleftharpoons [Cu\ A\ L] \qquad (2)$$

In the later case simultaneous formation of all the species AH^+, A, LH L^-, [CuA] , [CuA_2] , [CuL] , [CuL_2] and [CuAL] was considered. The stability constants of the complexes obtained by both the methods are in close agreement indicating stepwise formation. The protonation constants of the ligands and the formation constants of the binary metal - ligand complexes were determined under similar conditions for use in computer calculation of $\log K^{M}_{MAL}$ values and to calculate the values of $\Delta \log K$.

$$(\Delta \log K = \log K^{M}_{MAL} - \log K^{M}_{MA} - \log K^{M}_{ML})$$

A comparison of $\Delta \log K$ values within the series of primary and secondary ligands used in the present study and the ligands reported earlier reveal that the basicity as well as the π - acidity of the tertiary diimines has a significant influence on the stability of the ternary complexes. Coordination of a tertiary diimine with a metal ion having filled d orbitals results in the delocalization of metal electrons over the tertiary diimine molecule thereby decreasing the effective electron density over the metal ion. Hence , electron density over [MA] is almost equal to that in [$M(H_2O)_6^{n+}$] , which results in less nagative $\Delta \log K$ values. In terms of electron repulsion concept , in [ML] complexes when L coordinates with M there is a repulsion between the metal dπ electrons and the ligand electrons. However , in [MAL] complexes L coordinates with [MA] where metal is already bound with a strong π acceptor ligand like tertiary diimine. The effective electron density over the metal ion in [MA] is less and hence the incoming ligand L has to face less repulsion from the metal d electrons. This release of repulsion in ternary [MAL] complexes compared to that in binary complexes [ML] results in higher stability of [MAL] than [ML] .

As the stabilizing effect of heteroaromatic N-bases is because of $M \rightarrow A$ π bonding, greater extent of $M \rightarrow A$ π interaction should result in greater stabilization of the ternary complexes. When electron withdrawing - NO_2 group is substituted over 1, 10-phenanthroline, it should result in greater drift of electron density from metal to A and hence one would expect greater stabilization of ternary complexes with 5-N-phen than with o-phen. For similar reasons coordination of bis(2-pyridyl) amine having an electron releasing $>$NH group can be expected to have weaker π bonding than 2,2'-bipyridyl and hence should result in less stabilization of ternary complexes.

However, the order of stabilization is observed to be reversed in ternary complexes of o-hydroxy aromatic aldehydes. This can be explained in terms of $M \rightarrow L$ π bonding. In o-hydroxy aromatic aldehydes $M \rightarrow L$ π bonding is possible and hence their tendency to combine with metal already bound to a stronger π-acceptor ligand (as in MA) is reduced, thus resulting in lower Δ log K. In β-ketoanilides and salicylamide derivatives the presence of amine N plays an important role. It is supposed that electron releasing effect of the amide or anilide N is strong enough to prevent the molecule from behaving as a π-acceptor ligand. Thus $M \rightarrow L$ π interaction is lowered down to a negligible level, L acting only as a σ-bonding ligand and hence normally expected stability order is observed in ternary complexes with heretoaromatic N-bases.

The electronic characters of the secondary ligands also have considerable influence on the ternary complexes.

In case of π bonding secondary ligands like salicylaldehyde, electron withdrawing substituents make the ligand stronger π acceptor and hence stabilize the ternary complex as compared to the binary [ML] complex. Electron withdrawing bromo- or nitro-groups in 5-bromo salicylaldehyde and 5-nitro salicylaldehyde decrease the electron density over O^- and hence destabilize the complex as compared to [Cu A salicylaldehydate]. In case of 2-hydroxy naphthaldehyde, again the other phenyl ring acts as an electron withdrawing substituent and destabilizes the ternary complex whereas electron releasing - CH_3 group at α-carbon atom in 2-hydroxy acetophenone increases the basicity of the ligand thereby increasing the repulsion between metal $d\pi$ electrons and lone pair of electrons over the ligand in binary complex and thus stabilizes the ternary complex as compared to the corresponding complex of salicylaldehyde.

Complexes of the amide or anilide ligands (L^6 to L^{12}) provide examples of non - π bonding ligands. As indicated by the IR spectra of the solid complexes of these ligands, the coordination sites are enolate O^- and the amide O. Amide N, although not taking part in coordination, influences the electron density over the coordinating atoms and the overall electronic characters of the ligands and hence the stability of the complexes. Electron releasing effect of the - NHR prevents the anilide ligand from behaving as a π acceptor (difference from β-diketones or salicylaldehyde). In contrast to the salicylaldehyde complexes, electron withdrawing substituents over the anilide ligands are observed to stabilize the ternary complexes. Similarly, [CuA salicylanilide] complexes with electron withdrawing phenyl group are observed to have higher $\Delta \log K$ values than [CuA salicylamide] complexes. This is considered to be a combined effect of the two substituents.

Electronic spectra of the complexes are consistant with the above observations. The positions of the d-d transitions in the ternary complexes have been observed to be blue shifted compared to the positions in binary [ML] complexes. The order of $\Delta \bar{\nu}$ values in various complexes is in agreement with the Δ log K values.

Isolation of Ternary Complexes in Solid State :

Study of the ternary complexes in solid state is important in the sense that it provides a proof for the formation of the complexes under particular condition supporting their existence in solutions under similar conditions. It also enables one to carryout the studies which are not possible or which are difficult to be carried out in aq ueous solutions.

The complexes [Cu A L]. ClO_4 where A = A^1 or A^2 and L = L^1 - L^{12} , have been isolated in solid state and characterized by elemental analyses. Conductance and magnetic measurements are consistant with the formula [Cu A L]. ClO_4.

IR spectra of the complexes exhibit the features of ionic perchlorate and of both the primary and secondary ligands with the expected shifts in the band positions due to coordination with the metal ion. IR spectra of the complexes of amides and anilides (L^6 - L^{12}) exhibit distinct ν_{N-H}. This confirms that O^- of the enolate form and amide O are the coordinating sites and amide N is not getting deprotonated.

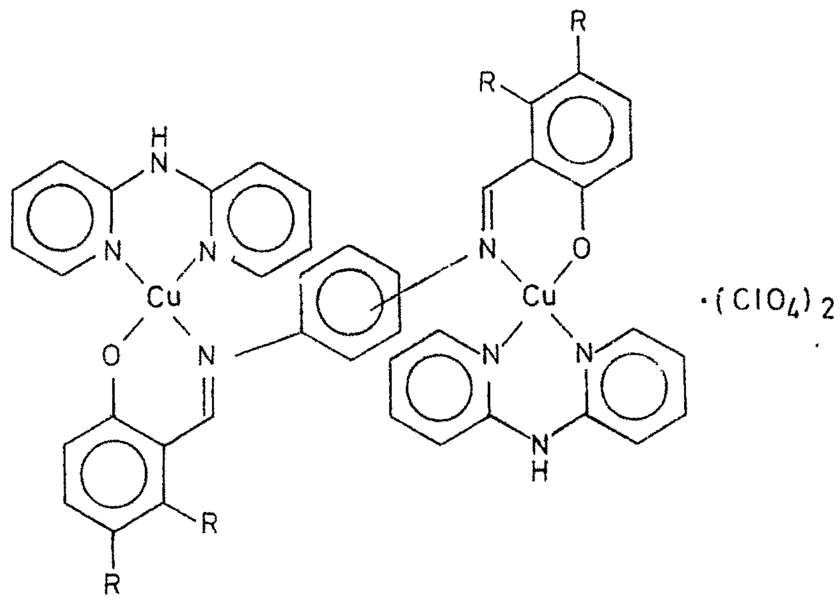
Electronic spectra of the complexes in both solid state and in aq. dioxane solutions are similar indicating that the geometry around the metal ion is same in both cases.

Binuclear Schiff base Complexes :-

Coordination of aldehydes with metal ions facilitates Schiff base formation because of the drift of electron density from aldehyde to the metal. In ternary complexes, presence of π bonding primary ligand results in greater drift of electron density from the secondary ligand to the metal and hence it can be expected that Schiff base formation will be still easier in case of ternary complexes than in binary complexes. With this point of view reactions of aromatic diamines were carried out over some ternary aldehyde containing complexes, which resulted in the formation of binuclear Schiff base complexes with the general structures as in fig. 1.

The complexes were charactarized by elemental analyses, conductance, electronic and IR spectral studies. Magnetic measurements of these complexes indicated intramolecular antiferromagnetic interaction between two paramagnetic copper centres. ESR spectral studies have also been carried out over representative compounds, which exhibit $\Delta M_s = 2$ and $S \longrightarrow T$ transitions supporting the antiferromagnetic exchange. The intramolecular nature of the interaction has been considered by comparison with the magnetic properties of parent ternary complexes. The room temperature magnetic moment values of ppd and opd Schiff base complexes have been observed to be less than their mpd analogues. In order to explain this a σ and π exchange mechanism has been suggested.

Figure 1



R = R = H   or   RR = $-(CH{=}CH)_2-$

R = R = H   when   dpa   is   replaced by bipy or phen.

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