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CHAPTER V

Mixed-Ligand Complexes of Copper(II) with Salicylaldimine and 2-hydroxyacetophenonimine as Primary Ligands and β-ketoanilides or Salicylamide derivatives as Secondary Ligands

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Metal complexes of schiff bases have occupied a central role in the development of coordination chemistry. In general, the azomethine group $>C=N$ which is the functional group of the schiff base, is aided in forming a stable complex by another donor group such as a phenolic -OH. The formation of a chelate ring seems essential for the production of stable complexes, with ligands containing $>C=N$ group.

Metal complexes derived from schiff bases have been known over a hundred years. Schiff was the first to discover the exceedingly important synthetic technique of preparing salicylaldimine complexes by reaction of preformed metal-salicylaldehyde complexes with primary amines.[157,158]

After a lapse of nearly fifty years, the systematic synthetic study of schiff base complexes was started by Pfeiffer and coworkers[159] in 1931. In the same year Dubsky and Sokol[160] isolated N-N'-ethylene-bis-(salicylideneaminato)Cu(II) and Ni(II).

The preparation, physical properties and chemical reactions of schiff bases have been reviewed by Layer.[161] Various aspects of the chelating characteristics have been described in the work edited by Dwyer and Mellor.[162] Two excellent reviews of schiff base complexes appeared in 1960[163] and 1966.[164] The first of these stressed on the chemistry of inner complexes whereas the latter dealt in detail with the chemistry of salicylideneamine and β-ketoamine and closely related ligands. A text concerned primarily with stereochemistry of schiff base complexes in solution has also been published.[165] Another review article concerning this general area has also appeared.[166] The influence of metal ions on schiff base stabilities and on their rates of formation and transamination has been thoroughly discussed by Leussing.[167]

Schiff base complexes can also be prepared by reactions in which the schiff base is formed in the presence of metal ion. The coordination of the carbonyl group to the positive metal ion is supposed to result in polarization of the C=O bond. The oxygen atom becomes more electronegative and pulls the electrons from the carbon atom. Thus, the carbon atom becomes more susceptible to nucleophilic attack by the amine and schiff base formation is facilitated. The mechanistic course of the reaction is, a rapid nucleophilic attack of the carbonyl carbon by the amine, first yielding an intermediate carbinolamine complex, followed by the dehydration of the carbinolamine to yield the schiff base complex.[167]

Further, the presence of metal ion is supposed to promote the formation of schiff base complex due to template effect as termed by Busch.[168] Metal template reactions may be defined as reactions involving ligands which require or get significantly enhanced by particular geometrical orientation imposed by coordination to a metal.[169] The metal ion can bring the carbonyl group and the amine group in close vicinity by the formation of mixed-ligand complex. This is called sterically directed kinetic template effect. Further, the metal ion is useful to remove the schiff base from an equilibrium by forming the complex and thus favours the forward reaction leading to the formation of more of the schiff base. This is termed thermodynamic template effect.

Leussing and coworkers,[170-173] from kinetic and equilibrium studies of schiff base formation, have established that Pb(II), Cd(II), Mn(II), Mg(II) and Zn(II) were kinetically active, while Co(II), Ni(II) and Cu(II) with partially filled d orbitals were kinetically inactive. This was explained to be due to the rigid metal-ligand geometries imposed in the case of Cu(II), Ni(II) and Co(II) complexes due to the crystal field stabilization energy of the 3d orbitals. In the case of Zn(II), Pb(II), Cd(II), Mn(II) and Mg(II), however, there is no crystal field stabilization and hence the metal ligand bonds are less rigid. This facilitates the reaction of the amine and the aldehyde in the mixed-ligand complex leading to easy formation of the schiff base. Thus, the requirement of the catalysing metal ion is that it should form a ternary complex with the two reactants but should impose a minimum steric requirement on them. Leussing and coworkers[171,172] prefered to term the role of the metal ion as promnastic effect (match maker) rather than template effect.

Mixed-ligand complexes of the type [LnLL'], where Ln = lanthanones, L = bis(salen) and L' = β-diketonates have been synthesized by Dutta.[174] Mixed-ligand complexes of Cu(II) derived from salicylaldehyde or 2-hydroxyacetophenone or acetylacetone and their schiff bases have also been reported by Balundgi and Chakravorty.[175,176]

Bhattacharya and coworkers[136,177-189] synthesized mixed schiff base complexes of the type [MLL'], where M = Cu(II) or Ni(II), L and L' are a pair of the following ligands salicylaldehydimine, 2-hydroxy-1-naphthaldimine, 2-hydroxyacetophenonimine, 2-hydroxypropiophenonimine and 2-hydroxybenzophenonimine, by treating metal amine complexes with equivalent amounts of the aldehydes or ketones. Bromination and nitration reactions were also carried out on these mixed schiff base complexes.[182,190] Amine exchange with monoamines and diamines were also carried out, latter resulting in the formation of a new unsymmetrical tetradentate schiff base with (en) condensed with two different carbonyl group at the two ends. Demetallation reactions were also carried out on some of these mixed schiff base complexes to isolate the free unsymmetrical tetradentate schiff bases.[186,189] Mixed-ligand schiff base complexes of the type [CuLL'] where L = salicylaldimine and L' = β-ketoimine have also been prepared.[131-133,191]

In the present work mixed-ligand complexes of the type [CuLL'], where LH = acetoacetanilide, acetoacet-o-toluidide, acetoacet-o-anisidide, benzoatoacetanilide, salicylamide or salicylanilide and L'H = salicylaldimine or 2-hydroxyacetophenonimine have been synthesized. These complexes were synthesized specially to see whether they differ from [Cu.dipyridyl.L] complexes in ligand field spectral properties and show that the crystal field in the mixed-ligand complex is average of the fields in the binary complexes $[CuL_2]$ and $[CuL'_2]$. Amine exchange reactions have also been carried out on these complexes.

EXPERIMENTAL

Material used :

2-hydroxyacetophenone was prepared by Fries migration of phenylacetate using anhydrous aluminium chloride without solvent and was purified by distillation under reduced pressure. Salicylaldehyde (Fluka) and other chemicals were same as detailed in earlier chapters.

1. Preparation of mixed-imine schiff base complex (I) :

To an aqueous solution of copper acetate (0.001M, 25 ml), in excess ammonia, was added an alcoholic solution of the two ligands, in equimolar ratio. The mixture was stirred well and the solid that separated was filtered, washed with water and 50% alcohol. The compound was recrystallised from chloroform and analysed. (In case where 2-hydroxyacetophenone was one of the ligands, the preparation of the complex required refluxing for ∼20 minutes).

2. Preparation of N-alkylamine complex (II) :

The compounds were prepared by amine exchange method. The preformed mixed-imine schiff base complex (I) was treated with very dilute solutions of amine (methyl or ethyl) 0.05M (3-5 ml) and was refluxed for about 30 minutes. The solids obtained were filtered, washed with water and finally with 50% alcohol. The compounds were recrystallised from chloroform and analysed.

3. Preparation of tridentate schiff base complex (III) :

Complex (I) was refluxed on water bath with an ethanolic solution of ethanolamine. The solid that separated on adding water to the reaction mixture was filtered, washed with water and 50% ethanol and recrystallised from ethanol and analysed.

The elemental analyses, TLC analyses, magnetic measurements, molar conductance determination and visible and infrared spectral studies of all the isolated schiff base complexes were carried out as detailed in Chapter IV.

Table V 1 : Analytical data and magnetic moments of mixed-ligand complexes [CuLL']

Name of the complex	Analyses % *				μ eff in B.M.
	Cu	N	C	H	
[Salicylideneaminato, acetoacetanilidato Cu(II)]	17.50 (17.67)	7.76 (7.79)	- -	- -	1.88
[Salicylideneaminato, acetoacet-o-toluididato Cu(II)]	16.67 (17.01)	8.10 (7.50)	55.27 (55.45)	4.52 (4.62)	1.91
[Salicylideneaminato, acetoacet-o-anisididato Cu(II)]	16.00 (16.31)	7.50 (7.19)	- -	- -	1.95
[Salicylideneaminato, benzoatoacetanilidato Cu(II)]	14.95 (15.07)	6.26 (6.64)	62.17 (62.63)	4.64 (4.27)	1.95
[Salicylideneaminato, salicylamidato Cu(II)]	19.50 (19.88)	9.16 (8.76)	- -	- -	1.80
[Salicylideneaminato, salicylanilidato Cu(II)]	15.89 (16.06)	7.18 (7.08)	- -	- -	1.91
[2-hydroxyacetophenonaminato, acetoacetanilidato Cu(II)]	16.96 (17.01)	7.55 (7.50)	57.83 (57.37)	4.82 (4.95)	1.86
[2-hydroxyacetophenonaminato, acetoacet-o-toluididato Cu(II)]	16.51 (16.40)	7.14 (7.23)	- -	- -	1.83

cont...

[2-hydroxyacetophenonaminato, acetoacet-o-anisididato Cu(II)]	15.60 (15.75)	7.17 (6.94)	57.00 (56.50)	5.44 (4.96)	1.74
[2-hydroxyacetophenonaminato, benzoatoacetanilidato Cu(II)]	14.15 (14.59)	5.98 (6.43)	63.08 (63.37)	4.83 (4.59)	1.98
[2-hydroxyacetophenonaminato, salicylamidato Cu(II)]	18.75 (19.05)	8.28 (8.39)	- -	- -	1.89
[2-hydroxyacetophenonaminato, salicylanilidato Cu(II)]	15.40 (15.51)	6.65 (6.84)	- -	- -	1.99
[N-methylsalicylideneaminato, acetoacetanilidato Cu(II)]	16.67 (17.01)	7.12 (7.50)	-	-	1.91
[N-methylsalicylideneaminato, acetoacet-o-toluididato Cu(II)]	16.52 (16.39)	7.00 (7.23)	- -	- -	1.97
[N-methylsalicylideneaminato, acetoacet-o-anisididato Cu(II)]	15.52 (15.75)	7.23 (6.94)	- -	- -	1.86
[N-methylsalicylideneaminato, benzoatoacetanilidato Cu(II)]	14.35 (14.59)	6.13 (6.43)	62.13 (63.37)	4.76 (4.59)	2.04
[N-methylsalicylideneaminato, salicylamidato Cu(II)]	18.70 (19.05)	8.85 (8.39)	- -	- -	2.02
[N-methylsalicylideneaminato, salicylanilidato Cu(II)]	15.25 (15.51)	7.15 (6.84)	- -	- -	1.93

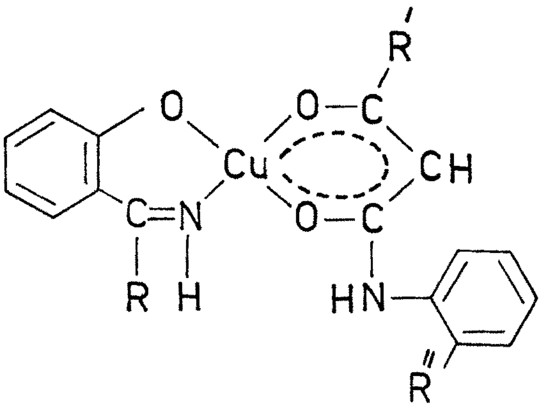
cont....

[N-ethylsalicylideneaminato, acetoacetanilidato Cu(II)]	16.12 (16.35)	6.72 (7.21)	- -	- -	1.98
[N-ethylsalicylideneaminato, acetoacet-o-toluididato Cu(II)]	15.59 (15.82)	7.70 (6.97)	59.62 (59.65)	5.47 (5.90)	1.92
[N-ethylsalicylideneaminato, acetoacet-o-anisididato Cu(II)]	15.48 (15.22)	6.97 (6.71)	- -	- -	1.80
[N-ethylsalicylideneaminato, benzoatoacetanilidato Cu(II)]	14.00 (14.13)	6.09 (6.23)	63.60 (64.07)	5.08 (4.89)	1.85
[N-ethylsalicylideneaminato, salicylamidato Cu(II)]	18.10 (18.28)	8.04 (8.06)	- -	- -	1.89
[N-ethylsalicylideneaminato, salicylanilidato Cu(II)]	14.65 (15.00)	7.16 (6.61)	- -	- -	1.97
[N-hydroxyethylsalicylideneaminato, monoaquo Cu(II)]	25.57 (25.88)	5.85 (5.72)	39.15 (39.29)	4.25 (4.49)	1.75
[N-hydroxyethyl-2-hydroxyacetophenonaminato monoaquo Cu(II)]	24.37 (24.48)	5.08 (5.39)	41.52 (41.77)	4.95 (5.02)	1.72

* Calculated values are given in parentheses

RESULTS AND DISCUSSION

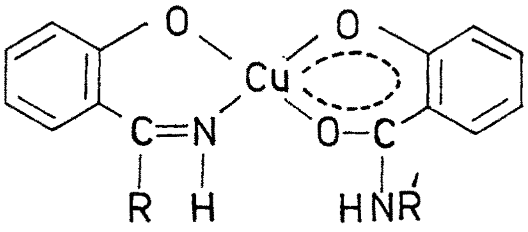
TLC analysis of these complexes show a single dot confirming their purity. The results of elemental analyses agree well with the proposed structures of the complexes (I).



R $= H$ or CH_3

R' $= CH_3$ or C_6H_5

R" $= H$ or CH_3 or OCH_3



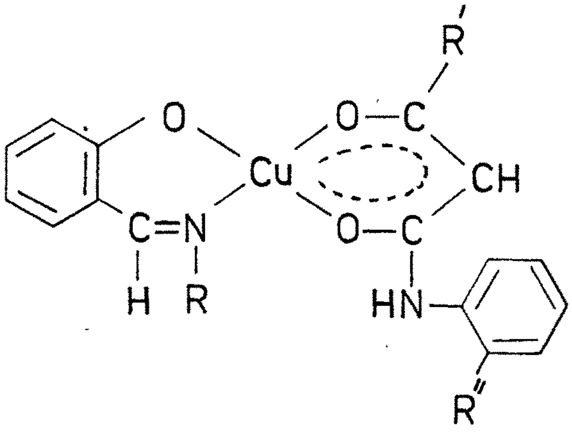
R $= H$ or CH_3

R' $= H$ or C_6H_5

They are found to be nonconducting indicating their non-electrolytic nature.

It is seen that salicylaldehyde or 2-hydroxyacetophenone part undergoes schiff base formation. The β-ketoanilides and salicylamide derivatives remain unaffected, like β-diketones.[165] This may be because the carbonyl group is not very active and keto character is reduced due to pseudoaromaticity.

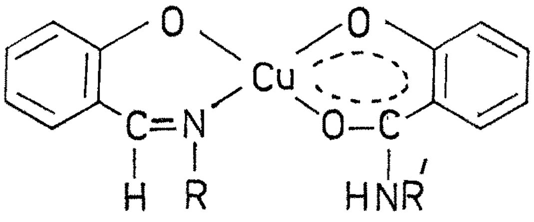
The compound (I) on being treated with excess of N-alkylamine, results in the formation of mixed-ligand complex (II) which contains one equivalent of β-ketoanilide or salicylamide derivative and another equivalent of N-alkylsalicylideneaminato as follows :



R = CH_3 or C_2H_5

R' = CH_3 or C_6H_5

R'' = H or CH_3 or OCH_3



R = CH_3 or C_2H_5

R' = H or C_6H_5

The reaction proceeds by a nucleophilic attack of the exchanging amine on the electron deficient carbon of the polarised imine. A more basic amine, and hence a more nucleophilic amine, replaces a less basic amine from the schiff base. Alkylamines are more basic than ammonia and hence can replace it easily from the imine schiff base complexes. The reaction is, however, concentration dependent also. A higher concentration of less basic amine may replace the more basic amine from the schiff base.[192,193]

Spectral and magnetic properties :

All the Cu(II) complexes are paramagnetic having magnetic moment corresponding to one unpaired electron. This rules out the possibility of metal-metal interaction and polymerisation.

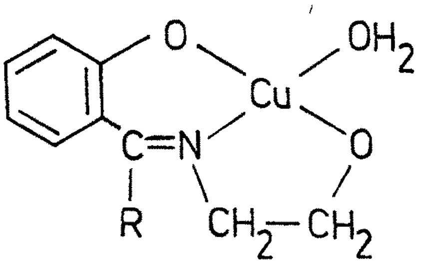
The visible spectra show a broad band around 16 000 cm^{-1}. This broad band is a combination of $^2A_{1g} \longleftarrow {}^2B_{1g}$, $^2B_{2g} \longleftarrow {}^2B_{1g}$ and $^2E_{1g} \longleftarrow {}^2B_{1g}$ transitions[156] corresponding to D_{4h} symmetry. The maxima in the visible spectral bands of Bis-salicylaldiminato, Bis-2-hydroxyacetophenoniminato, Bis-acetoacetanilidato and Bis-salicylamidato complexes of Cu(II) occur at 17 000 cm^{-1}, 17 860 cm^{-1}, 13 500 cm^{-1} and 12 900 cm^{-1}, respectively. Thus, it can be seen that in the mixed-ligand complexes, $[CuLL']$, the maxima in the spectral band at $\sim$ 16 000 cm^{-1} is intermediate between $[CuL_2]$ and $[CuL'_2]$. As expected, in the absence of any other stabilizing factor in the ternary complex, the two ligands create an average field of that in $[CuL_2]$ and $[CuL'_2]$.

In the I.R. spectra of all the compounds, the absence of bands in the region $\sim$3400 cm^{-1} indicate that the -OH of aldehyde or ketone gets dissociated after complexation. In compounds (II) a band at $\sim$1560 cm^{-1} corresponds to $\nu_{C=O}$ of the secondary ligand and shows that it does not undergo schiff base formation. Another band at $\sim$1625 cm^{-1} is assigned to $\nu_{C=N}$ stretching frequency. There is also a band at $\sim$3300 cm^{-1} corresponding to ν_{N-H} of the amide/anilide group.

Reaction of mixed-ligand complexes with ethanolamine :

The mixed-ligand complexes were further treated with monoethanol amine. Such reactions have been carried out earlier in our laboratory on various mixed schiff base complexes.[131-133,136,184-190]

In the present case of Cu(II) mixed schiff base complexes, the aldehyde or the ketone part reacts with monoethanolamine to form a tridentate ligand and gets bound to Copper(II). The second ligand is knocked out, and the fourth coordination position is occupied by a water molecule. The resulting compound (III) can be represented as follows :



R = H or CH_3

Similar monomeric complexes of tridentate ligand with solvent molecule occupying fourth coordination site have been prepared earlier.[176,192,194-198]

TLC study shows that these complexes (III) are pure. The elemental analyses correspond to the suggested structure. They are found to be nonconducting indicating non-electrolytic nature. Visible spectra show a broad band around 16 600 cm^{-1}. The compounds are paramagnetic corresponding to one unpaired electron. This shows the absence of binuclear species.

The I.R. spectra exhibit a broad band around $\sim 3400\ cm^{-1}$ corresponding to -OH stretching frequency, confirming the presence of water. There is also a band at $\sim 800\ cm^{-1}$ corresponding to the -OH out of plane deformation mode. This indicates that the water molecule is coordinated.