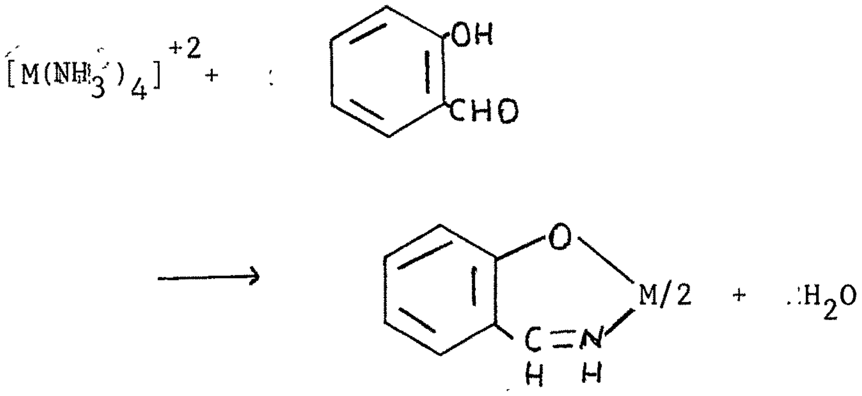
CHAPTER-II

MIXED SCHIFF BASE COMPLEXES USING NH_3 AS PRIMARY AMINE

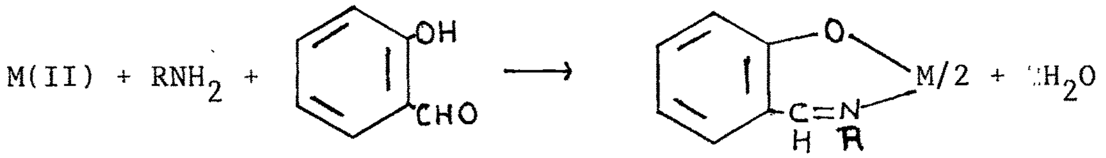
CHAPTER - 2

MIXED SCHIFF BASE COMPLEXES USING NH_3 AS PRIMARY AMINE

Metal complexes of Schiff bases have occupied a central role in the development of coordination chemistry. Transition metal complexes with Schiff bases as ligands have been among the most widely studied coordination compounds. Besides the method suggested by Schiff and later developed by Pfeiffer, Schiff base complexes can also be prepared by the reaction of metal amine complex with aldehydes or ketones. A very interesting series of cationic complexes, containing macrocyclic ligands have been prepared by Curtis and coworkers[3-5] by adopting this method. This can be represented as under :



The third method of preparation of the Schiff base complex is by mixing the metal salt solution with a compound containing an active carbonyl group and the amine and refluxing the mixture to get the complex. This is illustrated as under :



The mechanistic course of the reaction reveals that the Schiff base formation must be taking place by rapid nucleophilic attack of the carbonyl carbon by the ammine. The study of the reaction of bis (salicylaldehydeto) Cu(II) with cyclohexylamine has established the first order rate dependant of Schiff base complex formation on both copper and amine[6]. The rate was much faster than between salicylaldehyde and amine alone. This suggests strongly that the reaction involved a direct attack by the ammine on the carbon atom of a coordinated carbonyl group, than requiring complete dissociation of a salicylaldehyde anion from the copper as a first step as shown in the Figure.2.01 .

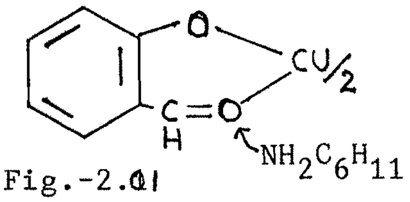


Fig.-2.01

In the above two methods the presence of metal ion is supposed to promote the formation of metal Schiff base complex due to templete effect as termed by Bush[6]. Metal templete reactions can be defined as reactions involving ligands which require or can be significantly enhanced by a particular geometrical orientation imposed by coordination to a metal[7]. Two types of templete effects can regulate the formation of Schiff base. Firstly, the metal ion can bring the carbonyl group and the amino group in the close vicinity by the formation of mixed ligand complex. This facilitates the interaction of the carbonyl group with amines and more Schiff base is formed. This is called sterically direct kinetic templete effect. Secondly, the metal ion may also be useful to remove the Schiff base from an equilibrium by forming a complex and thus favours the forward reaction, leading to the formation of more Schiff base. This is termed as thermodynamic templete effect.

The addition of two aromatic aldehydes or ketones and their Schiff bases with close coordinating tendencies to a metal ion should result in the formation of complex MAL along with some MA_2 and ML_2. However, these MA_2 and ML_2 complexes are trans in nature and are nonpolar[8]. Whereas, the mixed ligand complex is polar and is stabilized by the polar solvents. Thus it can be expected that the formation of mixed ligand complex is favoured over the formation of MA_2 or ML_2 and the resulting complex is only MAL. Complexes of the type MAL', where M = Cu(II), Ni(II), Zn(II) and L = salicylaldehyde and L' = 2-hydroxy 4-methoxy Benzophenone, 2-hydroxy Acetophenone have been reported in the literature[9-11].

Mixed Schiff base complexes (MAL) where M = Cu(II), Ni(II), and Zn(II), A = 7-aldimine 8-hydroxy quinoline and L = salicyladimine, or 0-hydroxy Acetophenomine or 2,4-dihydroxy Acetophenomine or 0-hydroxy 4-methoxy Acetophenomine or 2-hydroxy 1-Naphthaldimine, or 0-hydroxy Acetonaphthomine or 2-amino 5-chloro Benzophenomine have however not been reported earlier. Such complexes have been isolated and characterized in the present investigation. In Schiff base complexes, similarities between salicylaldimine and 2-hydroxy 1-Naphthaldimine or 7-Aldimine 8-Hydroxy quinoline complexes, are expected from the common 0-N donor group and the presence of conjugated six member chelate ring in each group of complexes. The present study is also extended to prepare mixed Schiff base complexes of Cu(II), Ni(II) or Zn(II) with above ligands by treating them with Ammonia.

EXPERIMENTAL

Material used :

7-Formyl 8-hydroxy quinoline was prepared in our laboratory, Salicylaldehyde, 2-hydroxy Acetophenone, 2,4-dihydroxy Acetophenone, 2-hydroxy 4-methoxy Acetophenone, 2-hydroxy 1-Naphthaldehyde, 2-hydroxy Acetonaphthone, 2-Amino 5-chloro Benzophenone were of BDH make. Ethanol, Benzene, Ether, Chloroform, DMF were Analar grade.

Preparation of 7-formyl 8-hydroxy quinoline

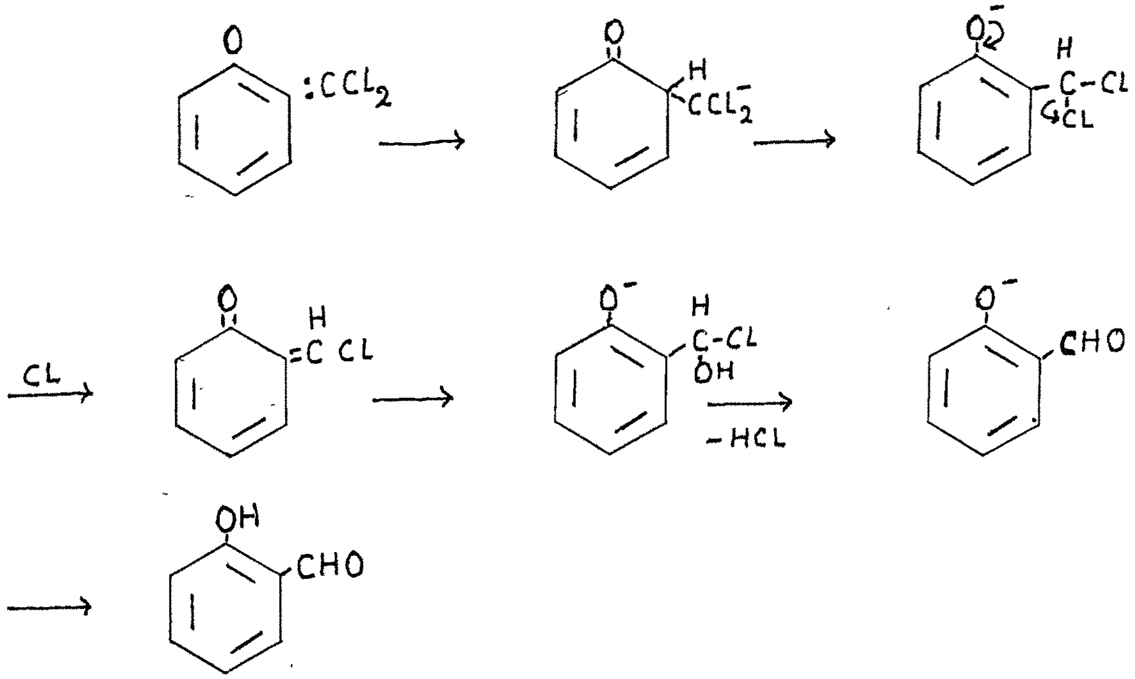
Riemen - Tiemen Reaction

The Riemen-Tiemen reaction involved electrophilic substitution on the highly reactive phenoxide ring. The electrophilic reagent is dichlorocarbene, CCl_2, generated from chloroform by the action of base. Although electrically neutral dichlorocarbene contains a carbon atom with only a sextet of electrons and hence is strongly electrophilic.

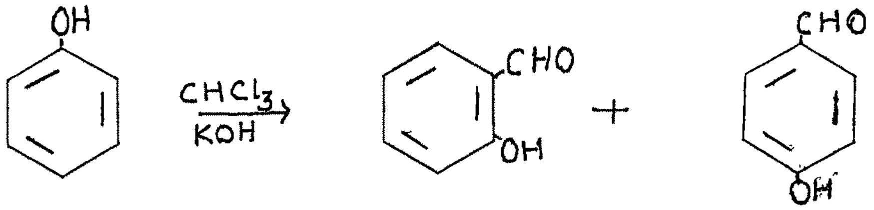
A dichlorocarbene is initially formed as follows:-

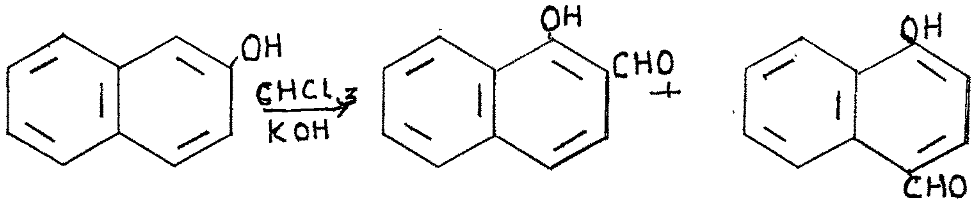
$$CHCl_3 + OH^- \rightleftharpoons CCl_3^\ominus + H_2O$$
$$CCl_3^\ominus \longrightarrow :CCl_2 + Cl^\ominus$$

The sequence of reactions involved in the mechanism is shown below :

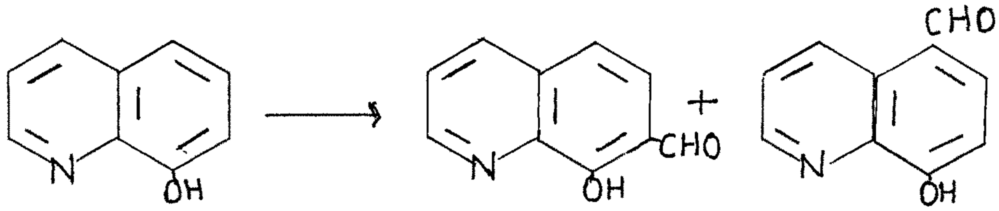


This is a method for synthesis of phenolic aldehydes.





The entering group generally enters the ortho position. The conversion of β-naphthol to 2-hydroxy naphthaldehyde is 38-48 %.



A systematic investigation of the Reimen-Tiemen reaction described in this communication, where in the influence of the nature and position of substituents has been studied revealed that when chloroform or carbon tetrachloride is mixed with alcohol (1:3) the yield of the aldehyde is increased. When Riemen-Tiemen reaction is applied to o-Coumaric acid, the entrant aldehyde group attacks the para-position only. Similar results are obtained also with 8-hydroxy quinoline where para derivative is formed (30 %) to greater extent than the ortho (16 %)[12].

A mixture of 8-hydroxy quinoline (15 gm), chloroform (14 ml), alcohol (60 ml) and sodium hydroxide solution (16.5 gm in 28 ml water) was heated at 100°C for 16 hrs. Alcohol and the excess of chloroform were driven off. The solution was made just acidic with hydrochloric acid when brick-red precipitate separated which was washed first with ether to remove the unchanged 8-hydroxy quinoline and then with chloroform. The chloroform solution furnished the 7-Aldehydo 8-hydroxy quinoline. This was crystallished from chloroform in reddish microcrystalline form. The yield is 3 gms. The M.p. is 263°C and it is insoluble in water cold ethanol, acetone, carbon tetrachloride and benzene but easily soluble in chloroform, pyridine, quinoline, DMF hot ethanol and acetic acid. It gives a greenish yellow coloration with ferric chloride. Its elemental analysis correspond to the structural formula Fig.-2.02.

Molecular formula	(Found)	C	H	N
$C_{10}H_7O_2N$	Calculated	(67.15)	(4.12)	(8.15)
		67.05	4.03	8.09

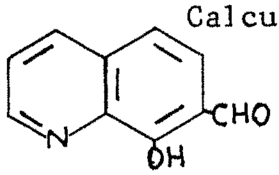


Fig.-2.02

Synthesis of Mixed Ligand Complexes : [Fig. 2.1 to 2.3]

Mixed Schiff base complexes were prepared by treating solution of Cu(II), Ni(II) or Zn(II) in excess of ammonia with one equivalent each of 7-formyl 8-hydroxy quinoline (0.5 M) in chloroform (50 ml) or ethanol and salicylaldehyde or hydroxy ketones or 2-hydroxy naphthaldehyde or 2-Amino 5-chloro Benzophenone (0.5 M) in chloroform (50 ml) or in ethanol. The mixture was refluxed for 3-4 hrs. then cooled filtered dried in vacuum at room temperature.

Physical measurements

The isolated mixed Schiff base complexes were analysed for metal contents using complexometric titration with EDTA. Elemental analysis for C, H and N was done by microanalysis Table-2.1.

The purity of complexes was checked by TLC technique using silica gel (Si-chem) with chloroform ether (5:3) mixture as adsorbent and UV light as visualising agent.

The molar conductances of the complexes were measured in DMF with a Toshniwal Conductivity bridge. The magnetic subsceptibility was measured using Guoy's balance at room temperature. The I.R. spectral data were recorded in KBr on Perkin - Elmer 427 grating spectrophotometer and electronic spectra in DMF on Beckman spectrophotometer.

IR bands are shown in Table. 2.2.

Results and Discussion

The analytical data Table 2.1 shows that the composition of the complex is MAL'. $2H_2O$ where M = Cu(II) or Ni(II) Zn(II) and A = 7-Aldimine 8-hydroxyquinoline and L' = Salicylaldimine or O-hydroxy acetophenomine or 2,4-dihydroxy acetophenomine or - 2 hydroxy 4 methoxyacetophenomine or - 2 hydroxy acetonaphthomine or 2-Amino 5-chloro Benzomine or 2-hydroxy naphthaldimine. The chloroform solutions of complexes showed very poor molar conductivity (6.2 to 8.5 ohm^{-1} cm^{2} mol^{-1}) indicating the complexes to be neutral.

The electronic spectra of Cu(II) complexes showed a broad absorption maximum at 17100 cm^{-1} corresponding to $^2B_{1g} \longrightarrow {}^2A_{1g}$ transition, characteristics of distorted octahedral geometry[10]. This is supported by magnetic measurements. The magnetic moment values at 300 K for Cu(II) complexes were found to be in the range of 1.82 - 1.92 B.M. suggesting the central Cu^{2+} retains its d^9 configuration and Cu(II) chelates are magnetically dilute. These values are also consistent with the copper ions being in non-generate ground state.

The molecular models in which one ligand group attains 'gauche' conformation and Van der Waals volumes of the group comprising the unsymmetrical Schiff bases are taken into account, indicate increased strain in the formation of complexes leading to distorted structure formation.

The Cu(II) 1:1 ML^{2+} or MA^{2+} chelate appears to possess discriminating qualities towards other ligand A or L species to preferably coordinate to oxygen and azomethine nitrogen is found to be more general. It is observed that the reaction is slow if M = 7-aldiminato 8 hydroxy quinoline species are reacted with other ligand but reverse reaction is faster. The slower reaction must be due to steric hinderance and also may be due to less stable M - 7 aldiminato 8-hydroxyquinoline chelate moiety. The reduction of the charges by ML or MA formation suggests that enthalpy and entropy effects favours the formation of ternary chelates, coordination of 7-aldiminato 8-hydroxyquinoline takes place through the azomethine nitrogen and hydroxy oxygen atoms and an additional chelate ring is formed with the Copper(II) ion at common vertex. In these compounds the M-N and M-O bonds are covalent in nature and are extensively delocalised over both the metal and the ligand orbitals. This may have some effect on the mechanism of the reaction mentioned above.

In metal 7-formalidine 8-hydroxyquinoline species the azomethine group is susceptible to both resonance and field effects brought about by heterocyclic ring in the ligand molecule, this will have an adverse effet on further chelate formation by ligand and hence the second reaction path is favoured.

The field effects created by the phenyl group also reduces the electronic charge on the phenolic oxygen but to a lesser extent. At the same time the mutual co-planarity of the phenyl group with the chelate ring facilitates resonance interaction and ensuring charge accumulation on the oxygen atom strengthens the Cu-O bond.

It is known that Cu(II) ion has a tendency towards oxygen or nitrogen to attain a coordination number greater than four. Incorporation of electron attracting substituents lower the stability while at the same time increases their strength as Lewis acid thus enhancing their affinity for axial ligation. Consequently more stable compounds are obtained.

The electronic spectra of Ni(II) complexes in chloroform showed three bands at 8500, 15500 and 25500 cm^{-1} which are assigned to

$$^{3}A_{2g} \longrightarrow {}^{3}T_{2g} \quad F(\nu_1)$$

$$^{3}A_{2g} \longrightarrow {}^{3}T_{1g} \quad F(\nu_2)$$

$$^{3}A_{2g} \longrightarrow {}^{3}T_{1g} \quad P(\nu_3)$$

transitions respectively, indicating a pseudo octahedral environment around the Ni(II) ions[11]. This is also supported by magnetic measurements[12,13]. The magnetic measurement values at 300 K were found to be in the range of 3.20 to 3.28 B.M. The slightly higher values for Ni(II) complexes than the spin only value may be due to orbital contribution. The reaction path followed during the formation of Ni(II) complexes is same as the Cu(II) complex formation. Zn(II) is found to be diamagnetic in nature.

The IR spectra of the complexes is a plethore of bands appears stemming from the chemical entities present in the chelates. Bond formation is revealed by absorptions in the specific regions of the spectra and disappearance of certain bands that are observed in spectra of free ligands. The bands are distinguished in those due to the ligands and in those emanating from the metal complexes.

The spectra of the free Schiff base ligands exhibited two bands at $\sim$1600 and $\sim$1690 cm^{-1} due to $>C = N$ and $>C = C$ frequencies respectively[14]. These bands show shift to lower wave numbers in the I.R. of metal complexes indicating the involvement of nitrogen of azomethine group in the metal complex formation. The coordinated nature of water molecule is confirmed by a broad band in the region 3300 - 3400 cm^{-1} due to stretching mode and a band $\sim$800 cm^{-1} due to rocking mode in the Cu(II), Ni(II) and Zn(II) complexes. The new bands observed in the Far I.R. spectra of the metal complexes at $\sim$ 460 and $\sim$380 cm^{-1} are due to ν M-O and νM-N respectively[14,15].

MIXED SCHIFF BASE COMPLEXES USING AMMONIA

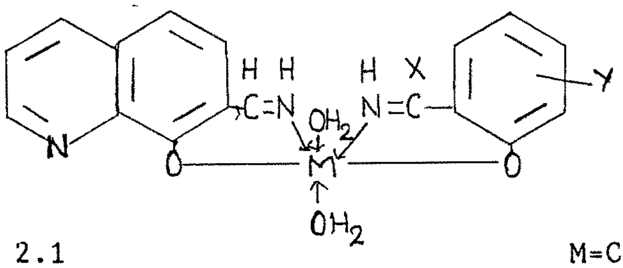


Fig. 2.1

M=Cu(II), Ni(II), Zn(II)

X=H, CH_3

Y=H, 4-OH, 4-OCH_3

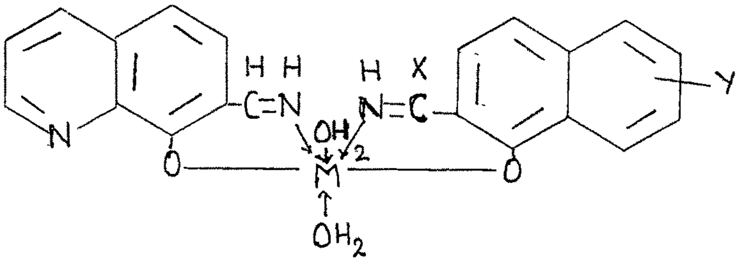


Fig. 2.2

M=Cu(II), Ni(II), Zn(II)

X=H, CH_3

Y=H

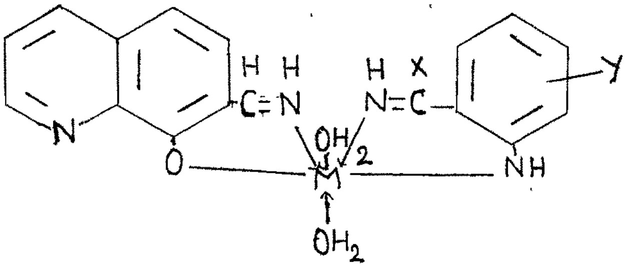


Fig. 2.3

M=Cu(II), Ni(II), Zn(II)

X=C_6H_5

Y=5-Cl

Name of the Mixed Schiff base Complexes using Ammonia as Primary Amine.

MSB (1) (7-Aldiminato 8-Hydroxyquinoline Salicylaldiminato) Ni(II).

(7-Aldiminato 8-hydroxyquinoline Salicylaldiminato) Cu(II).

(7-Aldiminato 8-hydroxyquinoline Salicylaldiminato) Zn(II).

MSB (2) (7-Aldiminato 8-hydroxyquinoline O-hydroxy Acetophenominato) Ni(II).

(7-Aldiminato 8-hydroxyquinoline O-hydroxy Acetophenominato) Cu(II).

(7-Aldiminato 8-hydroxyquinoline O-hydroxy Acetophenominato) Zn(II).

MSB (3) (7-Aldiminato 8-hydroxyquinoline 2,4-dihydroxy Acetophenominato) Ni(II).

(7-Aldiminato 8-hydroxyquinoline 2,4-dihydroxy Acetophenominato) Cu(II).

(7-Aldiminato 8-hydroxyquinoline 2,4-dihydroxy Acetophenominato) Zn(II).

MSB (4) (7-Aldiminato 8-hydroxyquinoline 0-hydroxy-4-methoxy Acetophenominato) Ni(II).

(7-Aldiminato 8-hydroxyquinoline 0-hydroxy-4-methoxy Acetophenominato) Cu(II).

(7-Aldiminato 8-hydroxyquinoline 0-hydroxy-4-methoxy Acetophenominato) Zn(II).

MSB (5) (7-Aldiminato 8-hydroxyquinoline 2-hydroxy naphthaldiminato) Ni(II).

(7-Aldiminato 8-hydroxyquinoline 2-hydroxy naphthaldiminato) Cu(II).

(7-Aldiminato 8-hydroxyquinoline 2-hydroxy naphthaldiminato) Zn(II).

MSB (6) (7-Aldiminato 8-hydroxyquinoline 0-hydroxy Acetonaphthominato) Ni(II).

(7-Aldiminato 8-hydroxyquinoline 0-hydroxy Acetonaphthominato) Cu(II).

(7-Aldiminato 8-hydroxyquinoline 0-hydroxy Acetonaphthominato) Zn(II).

MSB (7) (7-Aldiminato 8-hydroxyquinoline 2-Amino 5-chloro Benzophenaminato) Ni(II).

(7-Aldiminato 8-hydroxyquinoline 2-Amino 5-chloro Benzophenaminato) Cu(II).

(7-Aldiminato 8-hydroxyquinoline 2-Amino 5-chloro Benzophenaminato) Zn(II).

Table - 2.1

Mixed SB Complexes using Ammonia as Pri. Amine

		Type of Compounds	Calculated(Found)				μeff B.M.
			C%	N%	H%	M%	
		Fig. 2.1 X=H, Y=H					
MSB 1.	a	$[C_{17}H_{13}O_2N_3 \cdot 2H_2O]Ni$	52.98 (53.01)	10.90 (10.50)	4.40 (4.50)	15.06 (15.10)	3.02
	b	$[C_{17}H_{13}O_2N_3 \cdot 2H_2O]Cu$	52.24 (52.20)	10.75 (10.80)	4.35 (4.30)	16.16 (16.20)	1.85
	c	$[C_{17}H_{13}O_2N_3 2H_2O]Zn$	52.04 (52.08)	10.70 (10.72)	4.33 (4.30)	16.58 (16.61)	-
		2.1, X=CH_3, Y=H					
MSB 2.	a	$[C_{18}H_{15}O_2N_3 \cdot 2H_2O]Ni$	54.13 (54.20)	10.52 (10.50)	4.76 (4.80)	14.53 (14.50)	3.04
	b	$[C_{18}H_{15}O_2N_3 \cdot 2H_2O]Cu$	53.39 (53.40)	10.38 (10.41)	4.69 (4.70)	15.69 (15.70)	1.84
	c	$[C_{18}H_{15}O_2N_3 2H_2O]Zn$	53.20 (53.25)	10.34 (10.30)	4.67 (4.70)	16.00 (16.20)	-
		2.1 X=CH_3, Y=4-OH					
MSB 3	a	$[C_{18}H_{15}O_3N_3 \cdot 2H_2O]Ni$	52.04 (52.08)	10.12 (10.20)	4.57 (4.61)	13.97 (14.01)	3.04

cont...

Table cont...

	b	$[C_{18}H_{15}O_3N_3\cdot 2H_2O]Cu$	51.36 (51.50)	9.98 (10.02)	4.51 (4.50)	15.10 (15.00)	1.89
	c	$[C_{18}H_{15}O_3N_3\cdot 2H_2O]Zn$	51.18 (51.20)	9.95 (10.06)	4.50 (4.62)	15.40 (15.50)	-
MSB 4.	Fig. 2.1 $X=CH_3$, $Y=4\text{-}OCH_3$						
	a	$[C_{19}H_{17}O_3N_3\cdot 2H_2O]Ni$	53.14 (53.20)	9.79 (10.01)	4.89 (4.85)	13.51 (13.50)	3.12
	b	$[C_{19}H_{17}O_3N_3\cdot 2H_2O]Cu$	52.47 (52.50)	9.66 (10.02)	4.87 (5.02)	14.61 (14.50)	1.94
	c	$[C_{19}H_{17}O_3N_3\cdot 2H_2O]Zn$	52.29 (52.30)	9.63 (10.06)	4.81 (4.92)	14.90 (15.02)	-
MSB5.	Fig. 2.2 $X=H$, $Y=H$						
	a	$[C_{21}H_{15}O_2N_3\cdot 2H_2O]Ni$	57.93 (58.01)	9.65 (9.72)	4.36 (4.40)	13.33 (13.50)	3.06
	b	$[C_{21}H_{15}O_2N_3\cdot 2H_2O]Cu$	57.20 (57.35)	9.53 (9.58)	4.31 (4.38)	14.41 (14.52)	2.02
	c	$[C_{21}H_{15}O_2N_3\cdot 2H_2O]Zn$	57.01 (57.10)	9.50 (9.60)	4.29 (4.32)	14.70 (14.82)	-

cont...

Table cont...

MSB 6.		Fig. 2.2 $X=CH_3$, $Y=H$					
	a	$[C_{22}H_{17}O_2N_3\cdot 2H_2O]Ni$	58.79 (58.82)	9.35 (9.40)	4.67 (4.52)	12.91 (13.00)	3.05
	b	$[C_{22}H_{17}O_2N_3\cdot 2H_2O]Cu$	58.00 (58.12)	9.24 (9.32)	4.62 (4.72)	13.97 (14.00)	2.03
	c	$[C_{22}H_{17}O_2N_3\cdot 2H_2O]Zn$	57.89 (58.06)	9.21 (9.30)	4.60 (4.75)	14.25 (14.30)	-
		Fig. 2.3 $X=C_6H_5$, $Y=5-Cl$					
MSB 7.	a	$[C_{23}H_{17}ON_4Cl.2H_2O]Ni$	53.95 (53.60)	10.94 (11.12)	4.30 (4.35)	11.33 (11.36)	3.04
	b	$[C_{23}H_{17}ON_4Cl.2H_2O]Cu$	53.38 (53.42)	10.83 (11.02)	4.25 (4.32)	12.28 (12.32)	1.98
	c	$[C_{23}H_{17}ON_4Cl.2H_2O]Zn$	53.23 (53.34)	10.80 (11.06)	4.24 (4.30)	12.53 (12.56)	-

Table - 2.4

I.R. Characteristics frequencies of
Mixed Schiff base Complexes cm^{-1}

1.	MSB_1-Cu	MSB_1-Ni	MSB_1-Zn
	3300(w)	3350(w)	3345(w)
	1600(s)	1600(s)	1600(s)
	1570(vs)	1570(vs)	1570(vs)
	1410(m)	1415(m)	1410(m)
	1325(s)	1330(s)	1320(s)
	1160(s)	1150(m)	1160(s)
	1130(m)	1125(s)	1120(s)
	1108(s)	1110(m)	1110(m)
	810(m)	820(m)	800(s)
	470(m)	460(s)	475(m)
	375(d)	395(s)	380(s)

2.	MSB_2-Cu	MSB_2-Ni	MSB_2-Zn
	3310(w)	3350(w)	3340(w)
	1600(s)	1600(s)	1600(m)
	1570(s)	1570(vs)	1570(m)
	1410(m)	1410(m)	1410(s)
	1320(s)	1320(s)	1325(s)
	1160(s)	1155(m)	1150(m)
	1140(m)	1140(s)	1135(s)
	1105(s)	1110(s)	1108(s)
	805(s)	800(m)	805(m)
	475(m)	470(s)	470(s)
	380(s)	390(m)	385(s)

W = Wide
m = medium
vs = very strong
s = strong

Table cont...

3.	MSB$_3$-Cu	MSB$_3$-Ni	MSB$_3$-Zn
	3310 (w)	3300 (w)	3320 (w)
	3200 (s)	3180 (s)	3190 (s)
	1600 (s)	1600 (s)	1590 (s)
	1570 (vs)	1570 (m)	1570 (m)
	1410 (s)	1415 (m)	1410 (s)
	1320 (m)	1310 (s)	1315 (m)
	1170 (s)	1170 (s)	1175 (s)
	1130 (m)	1130 (m)	1135 (m)
	815 (s)	820 (s)	815 (s)
	465 (m)	470 (m)	475 (s)
	380 (s)	385 (s)	390 (m)

4.	MSB$_4$-Cu	MSB$_4$-Ni	MSB$_4$-Zn
	3300 (w)	3260 (w)	3270 (w)
	1600 (s)	1600 (s)	1585 (s)
	1570 (vs)	1570 (vs)	1570 (m)
	1420 (s)	1425 (s)	1420 (s)
	1310 (m)	1315 (s)	1310 (m)
	1240 (s)	1240 (m)	1235 (s)
	1170 (s)	1175 (s)	1175 (s)
	1135 (m)	1130 (m)	1130 (m)
	1040 (s)	1045 (s)	1040 (s)
	825 (s)	815 (s)	820 (m)
	455 (m)	450 (m)	475 (s)
	370 (s)	385 (s)	390 (s)

cont....

Table cont...

5.	MSB_5-Cu	MSB_5-Ni	MSB_5-Zn
	3300 (w)	3280 (w)	3280 (w)
	1600 (s)	1600 (s)	1600 (s)
	1570 (m)	1570 (vs)	1570 (vs)
	1410 (m)	1425 (m)	1410 (m)
	1330 (s)	1320 (s)	1325 (s)
	1160 (m)	1170 (m)	1170 (s)
	1140 (s)	1130 (s)	1130 (m)
	1110 (vs)	1108 (m)	1105 (s)
	810 (m)	815 (s)	810 (m)
	460 (s)	470 (m)	475 (m)
	375 (s)	385 (s)	380 (s)

6.	MSB_6-Cu	MSB_6-Ni	MSB_6-Zn
	3310 (w)	3290 (w)	3290 (w)
	1600 (s)	1600 (s)	1600 (m)
	1570 (vs)	1570 (vs)	1570 (m)
	1420 (m)	1410 (s)	1415 (s)
	1320 (s)	1320 (s)	1325 (s)
	1160 (m)	1160 (m)	1160 (s)
	1135 (s)	1130 (s)	1130 (s)
	1108 (s)	1110 (s)	1108 (m)
	815 (m)	810 (m)	815 (s)
	475 (s)	470 (s)	475 (s)
	380 (s)	395 (m)	390 (m)

cont....

Table cont...

7.	MSB$_7$-Cu	MSB$_7$-Ni	MSB$_7$-Zn
	3320(s)	3330(s)	3320(s)
	3210(w)	3200(w)	3200(w)
	1600(s)	1600(s)	1600(s)
	1570(vs)	1570(m)	1570(m)
	1510(m)	1510(m)	1515(m)
	1415(m)	1410(s)	1410(s)
	1320(m)	1315(s)	1315(s)
	1250(s)	1245(m)	1235(m)
	1160(s)	1165(m)	1160(s)
	1140(s)	1135(s)	1140(s)
	1105(m)	1110(s)	1108(s)
	790(s)	785(s)	800(s)
	680(m)	685(m)	665(m)
	460(s)	470(s)	470(s)
	390(s)	395(s)	390(s)

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