

CHAPTER - IV

PREPARATION OF MIXED LIGAND COMPLEXES AND THEIR REACTIONS WITH AMMONIA

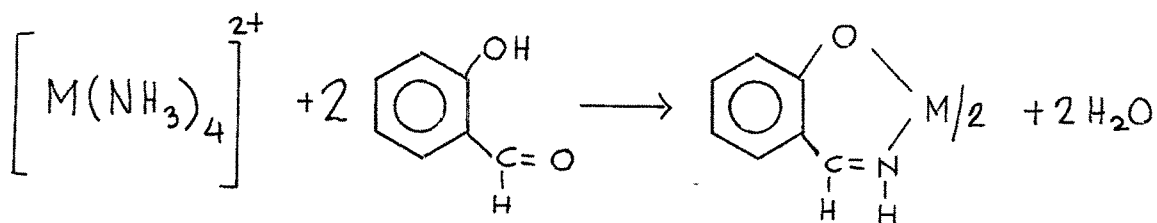
Besides π interaction affecting the formation constants of ternary complexes MAL, there are also other non-statistical factors which govern the formation of mixed-ligand complexes. These factors, other than **statistical**, are, increased polarisation of the metal ions in the fields of ligands of more than one type, charge neutralisation with decreased solvation and asymmetry of ligand field.

Margerum and coworkers^{1,2} studied the formation constants of some mixed-ligand complexes, to study the above various factors affecting the values of mixed-ligand formation constants. They used the spectrophotometric method to work out the values of $K_{Ni.L.X}$, where L = EDTA, NTA, EDPA, Tetren or diene and X = NH_3 , oxalate, glycinate or ethylenediamine. They considered the contribution of the electrostatic effects, chelation and the number of type of groups bound, to calculate the free energy change in the formation of mixed-ligand complex.

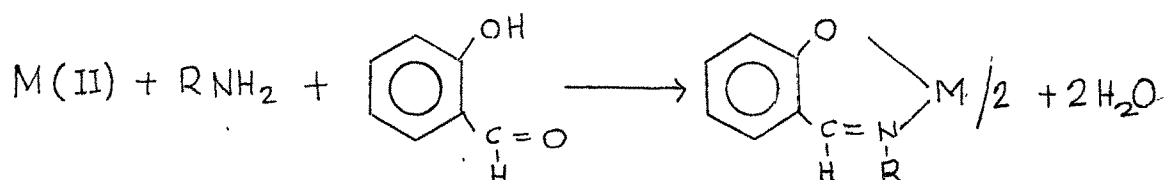
Hydrogen bonding between the two ligands, as in binary $\text{Ni}(\text{dimethylglyoxime})_2$ complex, may exist in ternary complex also. It was suggested by Perrin and coworkers³ that the addition of en or histamine to 1:1 copper serine or salicylic acid complex is favoured by electrostatic interaction between the amine hydrogens of these bases and the carboxyl or hydroxyl oxygen of serine or salicylic acid.

The polarisation effect has been discussed⁴ in cases of mixed complexes containing monodentate ligands. Spiro and Hume⁵ observed that in Hg^{2+} mixed halide complexes, the reproportionation constant $\log K$ was more than 6.0. It has been suggested that water stabilizes the polar mixed-ligand complex more, relative to non-polar binary complexes.

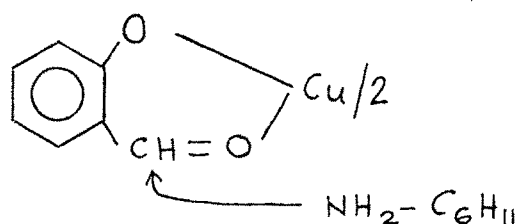
Metal complexes of Schiff bases have occupied a central role in the development of coordination chemistry. Transition metal complexes with Schiff base as ligands have been among the most widely studied coordination compounds. Besides the method suggested by Schiff⁴⁸ and later developed by Pfeiffer⁶ (as detailed in Chapter-II, Page 33), Schiff base complexes can also be prepared by the reaction of metal ammine complex with aldehydes or ketones. This method has been widely used for the synthesis of planar quadridentate complexes. A very interesting series of cationic complexes, containing macrocyclic ligands have been prepared by Curtis and coworkers⁷⁻⁹ 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, a compound containing an active carbonyl group and the ammine together 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 (salicylaldehydato) Cu(II) with cyclobexylamine has established the first order rate dependence of Schiff base complex formation on both copper complex and amine¹⁰. 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:



In the above two methods the presence of metal ion is supposed to promote the formation of metal Schiff base complex due to template effect as termed by Busch¹¹. "Metal template 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."¹² Two types of template effects can regulate the formation of Schiff base insitu. Firstly, the metal

ion can bring the carbonyl group and the amine 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 directed kinetic template 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 template effect. Leüssing and coworkers have, however, considered the reaction to proceed in two steps as detailed in Chapter-II (P.34).

Sacconi and coworkers¹³ reported normal and mixed ligand chelates of vanadyl (V) with salicylaldehyde and N-substituted ethylenediamines. Mixed-ligands complexes of Cu(II) derived from salicylaldehyde or 2-hydroxy-acetophenone or acetylacetone and their Schiff bases with N-substituted ethylenediamine have been reported by Chakravorty et al.^{14,15} Mixed-ligand complexes (CoLL'), where L = N,N' ethylene bis(salicylideneaminate) and its methyl derivatives and L' = β -diketones, salicylaldehyde or α -nitroacetophenone have also been prepared.¹⁶ The preparation, physical properties and chemical reactions of Schiff bases have been reviewed by Layer¹⁷. Various aspects of their chelating tendencies have been described in the work edited by Dwyer and Mellor.¹⁸ Two excellent reviews on Schiff base complexes have appeared in 1960¹⁹ and 1966²⁰. The first of these stressed the chemistry of inner complexes whereas the latter dealt in detail with the chemistry of the complexes of salicylideneamine and ketoamine and closely related ligands. A text concerned primarily with stereochemistry of Schiff base complexes in solution has also been published²¹. More review articles¹⁰ concerning this general area have appeared in last few years. Schiff base metal

complexes as ligands have also been reviewed in terms of the mode of bridging, types of complexes, antiferromagnetic interaction of binuclear and trinuclear complexes, structures, stereochemistry etc. by Sinn²² et al. Hatfield²³ has given another excellent review on the copper complexes resulting from different donor atoms and physical characteristic of such complexes. Chakravorty²⁴ and coworkers reported a new class of mixed-ligand complexes of bivalent nickel. Only evidence of formation of mixed ligand complexes of differently substituted bis (salicylideneamine) Ni(II) in solution, have been shown on the basis of NMR studies by Chakravorty and Holm²⁵. Such complexes, however, have not been isolated in solid state.

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 complexes MAL alongwith some MA₂ and ML₂. However, these MA₂ and ML₂ complexes are trans in nature and are nonpolar²³, 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 MA₂ or ML₂ and the resulting complex is only MAL. Complexes of the type MLL', where M = Cu(II) or Ni(II) and L = Salicylaldehyde and L' = 2-hydroxy, 2-hydroxy-4-methyl and 2-hydroxy-5-methyl benzophenones, 2-hydroxy-acetophenone or acetylacetone have been reported from our laboratory²⁶⁻²⁸.

Mixed-ligand complexes (MAL), where M = Cu(II) and Ni(II), A = Salicylaldehyde or 2-hydroxy-1-naphthaldehyde and L = 2-hydroxy-1-naphthaldehyde or 2-acetyl-1-naphthol, have, however, not been reported earlier. Such complexes have been isolated and characterized

in the present investigation. In Schiff base complexes, similarities between salicylaldehyde and 2-hydroxy-1-naphthaldehyde or 2-acetyl-1-naphthaldehyde complexes, are expected from the common O-N donor atom set of each ligand systems and the presence of conjugated six-member chelate ring in each group of complexes. The present study was, therefore, also extended to prepare mixed-Schiff base complexes of Cu(II) or Ni(II) with above ligands by treating them with ammonia.

Experimental:

Material Used:

Salicylaldehyde and 2-hydroxy-1-naphthaldehyde (Fluka, Germany) were used. Nickel nitrate, cupric chloride and copper acetate used were of BDH make. Ethanol and chloroform were Analar grade reagents. 2-acetyl-1-naphthol (or 1-hydroxy-2-acetylnaphthalene) was prepared by taking α -naphthol (40g), anhydrous $ZnCl_2$ (40g) and 20 ml. dry nitrobenzene into a flat bottom flask. To this 24 g of acetyl chloride was slowly added while stirring. The mixture was stirred for three hours and allowed to stand 48 hours. A mixture of isomers 4-hydroxy-1-acetylnaphthalene and 1-hydroxy-2-acetyl naphthalene were obtained, from which the latter was removed by the treatment with benzene in which the former is practically insoluble. This was then recrystallized from alcohol. M.P. = $102^\circ C$.

Synthesis of Mixed-ligand Complexes (Salicylaldehydato, 2-hydroxy-1-naphthaldehydato or 2-acetyl-1-naphthaldehydato) Cu(II) or Ni(II).

These complexes were obtained in cold condition by adding equimolar alcoholic solution of the metal and the two ligands. To a 0.5M salicylaldehyde (25 ml.) and 0.5M 2-hydroxy-1-naphthaldehyde

or 2-acetyl-1-naphthol (25 ml.) was added 0.5 M copper acetate or nickel nitrate solution (25 ml.). The reaction mixture was stirred well, when green and yellowish green complexes for Cu(II) and Ni(II) respectively, separated out. It was filtered, washed successively with water and ethanol and air dried. The solid was recrystallized from ethanol and analysed.

Synthesis of Mixed Imine Schiff base Complexes:

These complexes were prepared by two methods:

1. Reaction of ammonia with preformed mixed ligand complexes of Cu(II) and Ni(II). (Salicylaldiminato, 2-hydroxy-1-naphthalldiminato) Cu(II) or Ni(II), (Salicyldiminato, 2-acetyl-1-naphtholdiminato) Cu(II) or Ni(II), were prepared by refluxing, above preformed mixed-ligand complexes of Cu(II) or Ni(II) with excess of ammonia in alcoholic medium. After refluxing the reaction mixture for about an hour, well defined, red coloured solid Ni(II) complexes or dark green crystalline Cu(II) complexes separated out. The complexes (2-hydroxy-1-naphthalldiminato-2-acetyl-1-naphtholdiminato) Cu(II) or Ni(II), were also prepared in the same way. The complex compounds were washed with water and finally with 50% alcohol. The compounds were recrystallised from chloroform and analysed.

2. Template Method:

To copper chloride or nickel nitrate solution an excess of ammonia was added until the hydroxide formed, dissolved resulting in ^{the} formation of metal ammine complex. To this was added one equivalent each of alcoholic solution of salicylaldehyde and 2-hydroxy-1-naphthaldehyde or 2-acetyl-1-naphthol. The compound obtained was filtered, washed with water and ethanol and dried. These mixed-ligand

imine Schiff base complexes were same as complexes obtained by method (1).

The compounds were analysed for metal and nitrogen. Carbon and hydrogen analyses have also been carried out in some cases. Metals were estimated as detailed in earlier chapter. Nitrogen analyses were carried out using Duma's method, while carbon and hydrogen analyses were carried out using Collman carbon-hydrogen analyser. The results have been presented in table IV, (1).

TLC Analysis:

TLC analyses of all the complexes have been done on silicagel-G (Sichem.), using a mixture of chloroform-ether (6:4) as a solvent. The solvent was selected after several trials. TLC was also run for the mixture of MA_2 and ML_2 using the same solvent.

Magnetic Measurement:

Magnetic susceptibilities were determined at room temperature (28°C) using Gouy balance. The magnetic moment values have been shown in table IV, (1).

Conductance Measurements:

The mixed-ligand and imine Schiff base complexes were found to be soluble in chloroform and conductivity of the solutions were measured using Toshniwal conductivity Bridge type CLO/01A.

Spectrophotometric Measurements:

The visible spectra of all the complexes were studied in chloroform solution, on a DU2 Beckman spectrophotometer at room

temperature (30°C), using 1 cm. quartz cell in the range of 300-1000 nm. The plots of optical density against wavelength have been shown in the graph.

Infra-red spectral studies:

The ir spectra of the compounds were recorded in nujol in the range 4000-625 cm^{-1} on a Perkin Elmer Model 427. Characteristic bands are represented below:

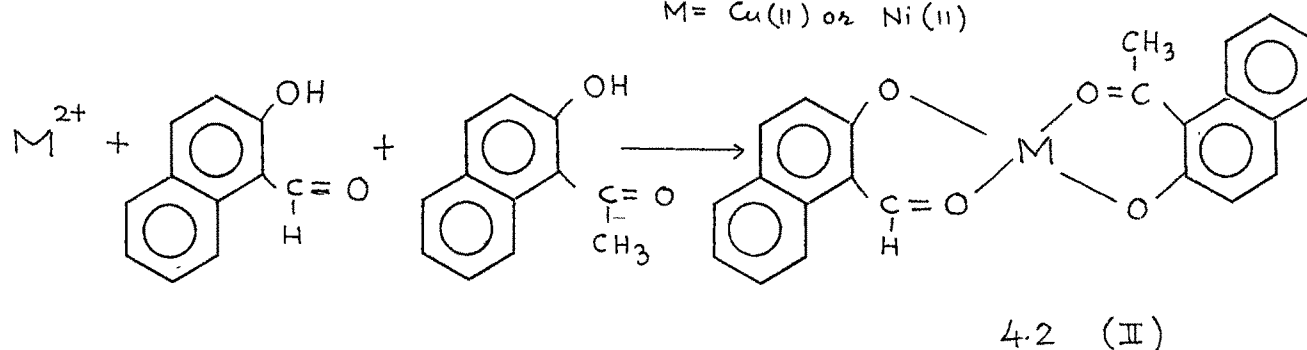
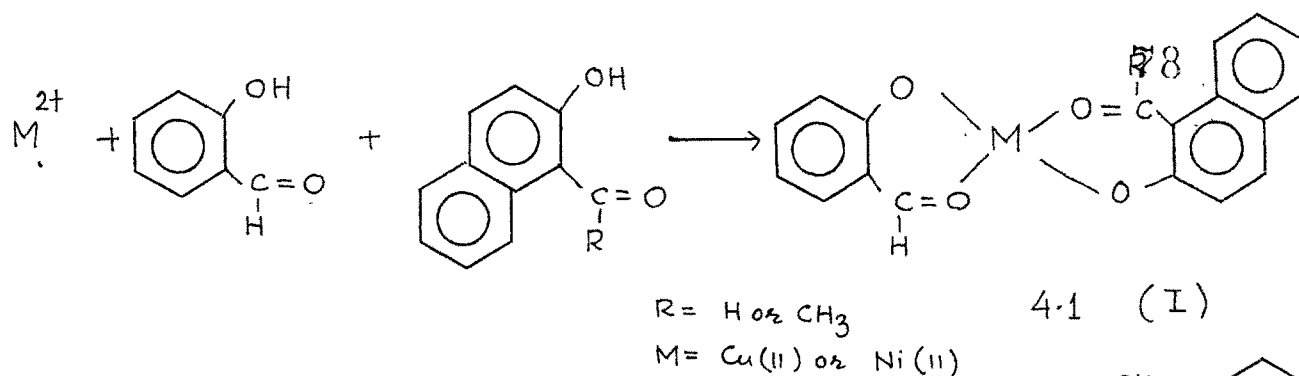
<u>Compound</u>	<u>Characteristic bands cm^{-1}</u>		
1. (Salicylaldehydato-2-hydroxy-1-naphthaldehydato) Ni(II).	3000 _s 1550 _s 1380 _s 1280 _m 1140 _s 1080 _w 900 _m 780 _s	2860 _s 1500 _m 1360 _s 1200 _s 1120 _w 1050 _s 860 _m	1630 _s 1450 _s 1300 _m 1180 _m 1100 _s 975 _s 810 _w
2. (2-hydroxy-1-naphthaldehydato, 2-acetyl-1-naphthaldehydato) Cu(II).	3000 _s 1535 _s 1410 _w 1310 _w 1190 _s 1020 _m 760 _s	2860 _s 1500 _w 1380 _s 1300 _m 1150 _w 860 _w 750 _s	1625 _s 1450 _s 1365 _s 1250 _s 1130 _w 820 _s
3. (2-hydroxy-1-naphthalaldiminato, 2-acetyl-1-naphthalaldiminato) Cu(II).	3250 _{vs} 1550 _s 1320 _w 1180 _s 1000 _w 820 _s	2980-2860 _b 1480 _s 1260 _w 1110 _m 920 _s 750 _s	1600 _s 1400 _s 1200 _m 1040 _m 830 _s 700 _s

4. (Salicylaldiminato-2-hydroxy-1-naphthaldiminato)Cu(II).	3300 _{vs}	2980-2860 _b	1600 _s
	1550 _s	1510 _w	1465 _s
	1380 _s	1350 _s	1300 _w
	1285 _w	1210 _s	1165 _s
	1140 _s	1120 _w	1090 _s
	1065 _w	1040 _s	970 _s
	900 _w	860 _w	820 _m
	780 _s .		
5. (Salicylaldiminato-2-acetyl-1-naphtholdiminato)Cu(II).	3285 _{vs}	3000-2880 _b	1600 _{vs}
	1560 _s	1500 _m	1480 _s
	1400 _w	1320 _m	1260 _m
	1180 _s	1120 _w	1030 _s
	970 _w	910 _s	880 _s
	830 _s	800 _s	750 _s
	700 _s .		
6. (2-hydroxy-1-naphthaldiminato-2-acetyl-1-naphtholdiminato)Cu(II).	3280 _{vs}	2980-2860 _b	1600 _s
	1540 _s	1520 _m	1460 _s
	1425 _s	1400 _s	1375 _s
	1340 _s	1300 _w	1275 _s
	1250 _s	1200 _s	1090 _s
	990 _s	860 _w	820 _w
	800 _s	750 _s .	

Results and Discussion:

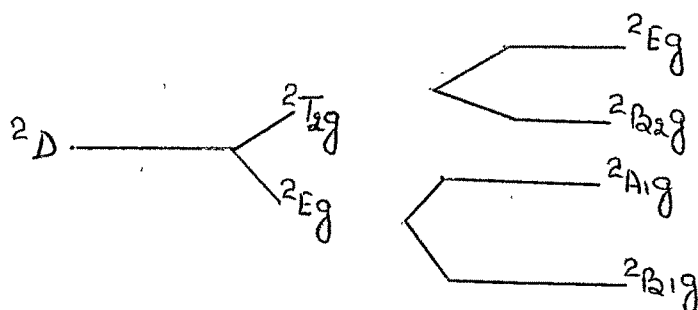
The analysis of the compounds, agree with the expected composition. The molar conductance of all the complexes in chloroform show them to be non-electrolytes. TLC of all the complexes show only one dot indicating that the compounds are pure single compounds (MAL) and not the mixtures. In case of artificial mixtures ($MA_2 + ML_2$) two dots are obtained for the same solvents.

The mixed-ligand complexes are formed by the following reaction:



Copper (II) has the electronic configuration $(\text{Ar}) 3d^9$ with one unpaired 'e'. It gives rise to only one free ion term $2D$. A lot of work on Cu(II) complexes has been surveyed in review articles that have appeared recently^{29,30}. It has been pointed out that the stereochemistry is expected to have little effect on the magnetic moment of Cu(II) ion, which should be some what above the spin only value of 1.73 B.M. Ray and Sen³¹ divided the four coordinate copper(II) complexes into two groups. With value of μ_{eff} equal to 1.72-1.82 and 1.90 - 2.2 B.M., respectively. They attributed to the former group a planar dsp^2 structure and to the latter a tetrahedral sp^3 or planar sp^2d structure. Figgis and Harris³² showed that magnetic moments of octahedral copper(II) complexes with $\Delta \approx 20,000 \text{ cm}^{-1}$ and $\lambda = -850 \text{ cm}^{-1}$ are about 1.90 B.M. Tetrahedral distortion leading to square-pyramidal complex would change the moment little from the value of octahedral complexes. They have shown that the moments for planar complexes would normally be lower (1.80 - 1.90 B.M.) than for octehedral systems. For a regular tetrahedral

arrangement, the ground state, 2T_2 is split by spin-orbit interaction leading to a system in which the moment is dependent upon temperature, being of the order of 2.20 B.M. at room temperature, but falling to 1.90 B.M. at 100°K . However, distortion from tetrahedral symmetry leads to a decrease in temperature dependence and reduces the room temperature moment to the range for octahedral complexes. Sacconi et al^{33,34} showed that complexes of bis (N-alkyl salicylideneaminate)Cu(II) had a square planar structure. The bis (salicylideneamine)Cu(II) complexes are found to have trans planar structure. X-ray crystal structure data on these complexes have been summarized by Hatfield and Whyman²³. Although no X-ray crystal studies have been attempted by us for the present complexes, it may be assumed that these complexes might possess planar configuration too, like bisketonc or bis aldehydic complexes. Since Jahn Teller distortion^{35,36} brings additional stability in Cu^{2+} octahedral complexes, the two spectral states 2E_g and $^2T_{2g}$ undergo further splitting into two components each, as shown below :



Therefore in a square planar configuration three transitions should be possible, corresponding to $^2B_{1g} - ^2A_{1g}$, $^2B_{1g} - ^2B_{2g}$ and $^2B_{1g} - ^2E_g$. These bands are closely spaced and in some cases may overlap each other, giving rise to a broad band.

The magnetic moment of the mixed-ligand complexes of Cu(II) are in the range of 1.9 to 2.0 B.M. as expected for square-planar geometry. In the visible absorption spectra of Cu(II) complexes, there is a broad band at ~ 670 nm as expected for square planar structure. This band, as pointed earlier, may be combination of three transitions.

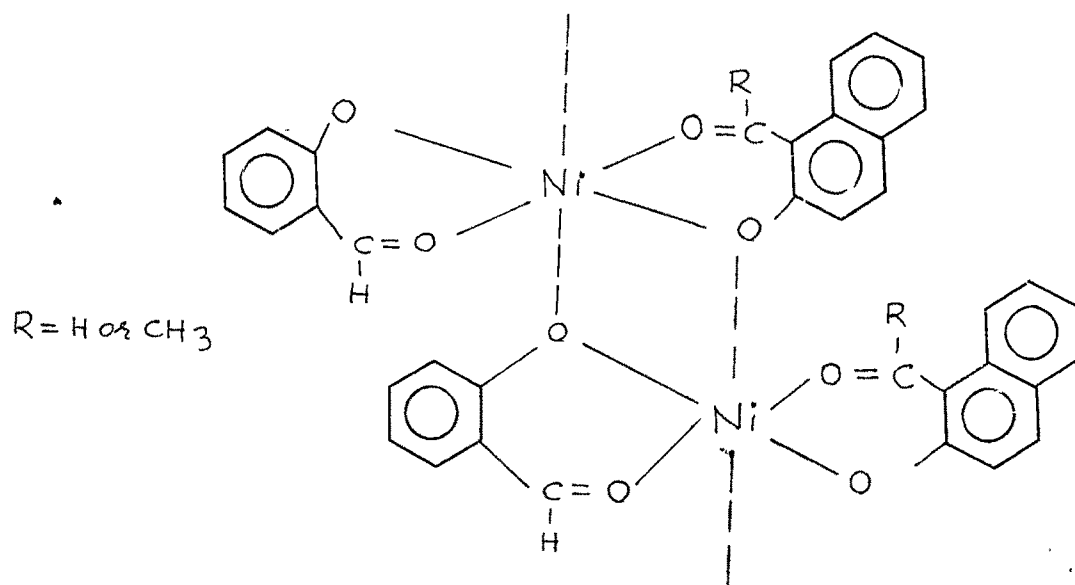
Nickel (II) Complexes:

Nickel (II) complexes are known to have six coordinated octahedral configuration, five coordinated square-pyramidal or trigonal bipyramidal structure or four coordinated square or tetrahedral configurations. These configurations are in most cases only approximately regular and complexes of one configuration can often easily be converted to another configuration. This structural lability implies that there is small energy difference between stereochemical forms. Many instances of structural isomerism are known and in a few cases two isomers have been found together in one crystalline unit cell. Several excellent articles on the chemistry of nickel (II) complexes have been published earlier³⁷⁻³⁹.

The nickel (II) ion has, the electronic configuration (Ar) $3d^8$ which gives rise to the free ion terms 3F , 1D , 3P , 1G , 1S . The triplet term 3F_4 represents the electronic ground state of the free ion and triplet terms derived from this, usually represent the ground state of nickel (II) compounds. The electronic ground state of a regular planar nickel (II) complex may be either a spin singlet, $^1A_{1g}$ or a spin triplet, $^3A_{2g}$. The relative stabilities of the $^1A_{1g}$ and $^3A_{2g}$ states is determined by the energy separation of the $dx^2 - y^2$

orbitals. Thus with a sufficiently weak field a square planar complex could be paramagnetic⁴⁰. Generally all known square planar complexes of nickel (II) are diamagnetic.

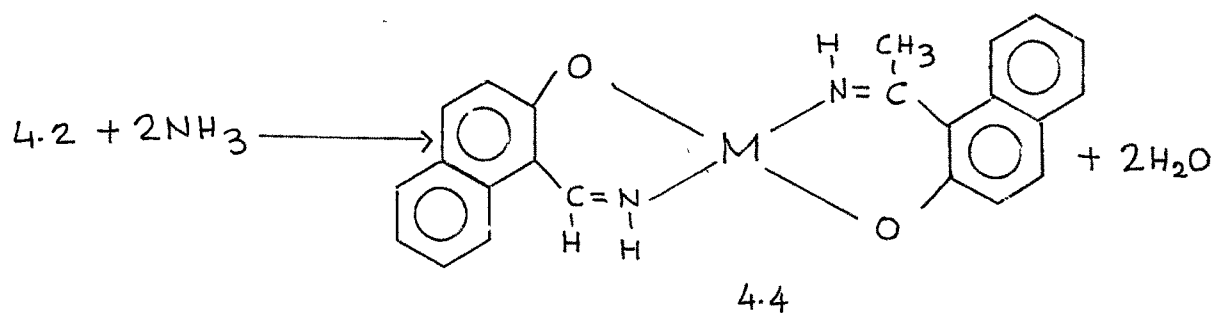
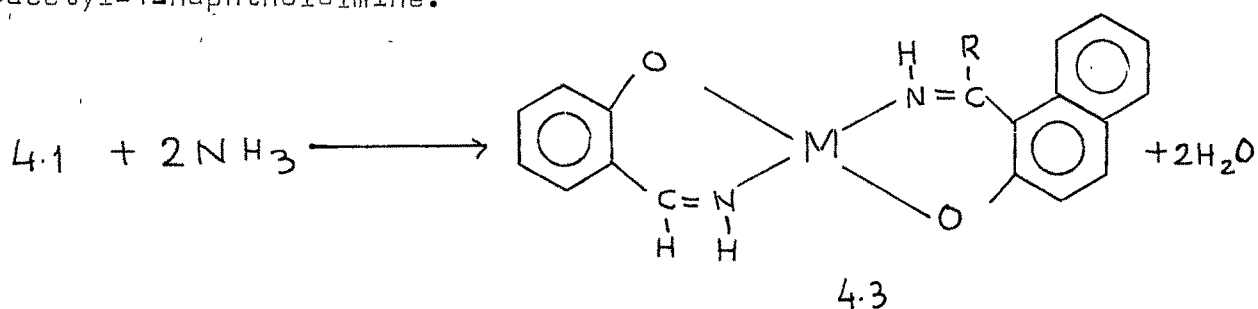
The present Ni(II) complexes, however, exhibit paramagnetism. The values of μ_{eff} for the solid green compounds of Ni(II) complexes (salicylaldehydato-2-hydroxy-1-naphthaldehydato or 2-acetyl-1-naphthaldehydato) Ni(II) and (2-hydroxy-1-naphthaldehydato-2-acetyl-1-naphthaldehydato) Ni(II) are found 3.0 B.M., typical for Ni(II) in the high spin configuration in an octahedral environment. This can be explained, to be due to, the polymerization leading to distorted octahedral structure.



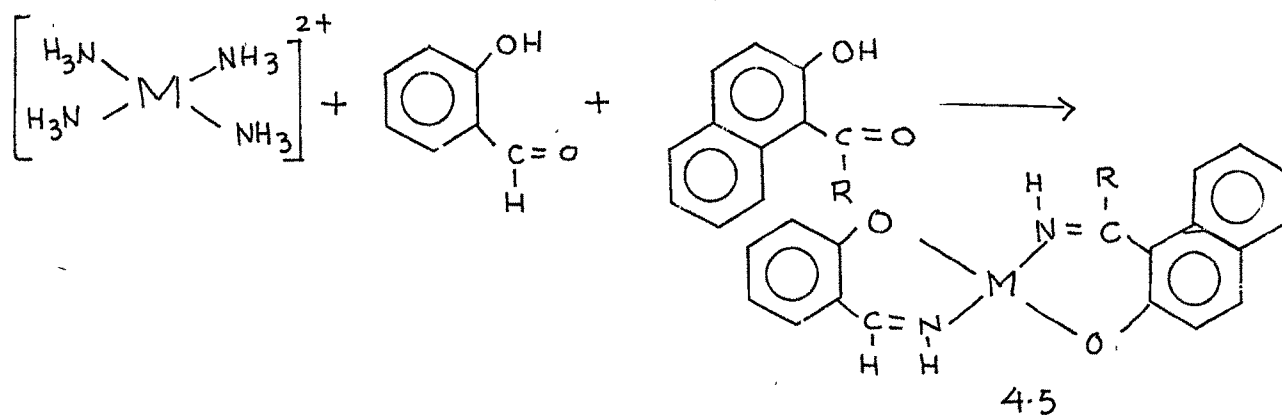
The green colour of the present complexes is not exceptional⁴¹, though the four coordinate complexes of Ni(II) are usually orange or red. The visible spectral study in chloroform show a broad band at 620 nm. In solution the polymerization breaks and spectra correspond to square planar geometry. Square planar configuration of nickel can be distinguished from octahedral or tetrahedral derivatives by the fact, that no electronic transitions occur below

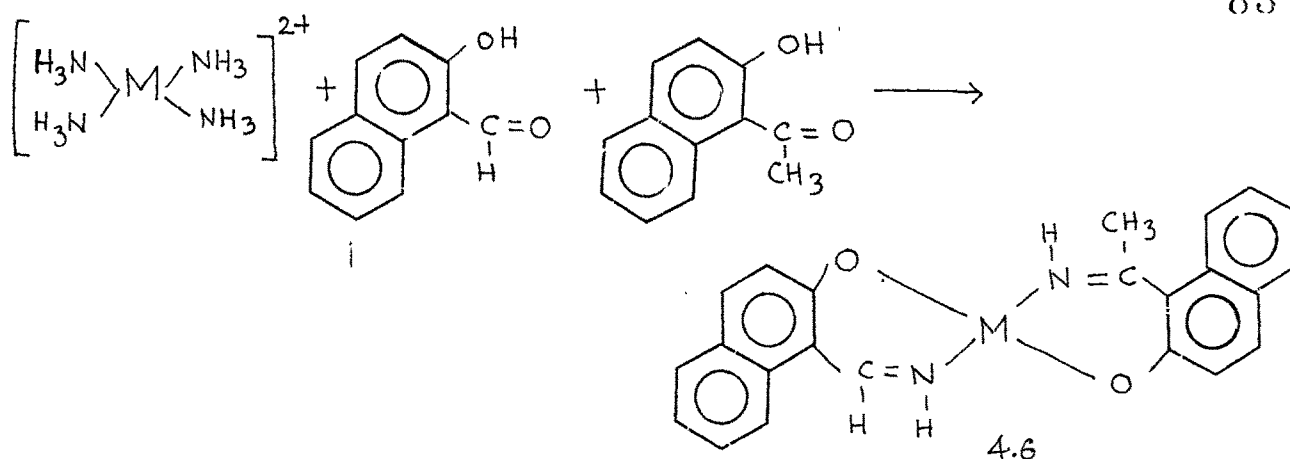
$10,000\text{ cm}^{-1}$. This situation arises as a consequence of a large crystal field splitting in a square complex.

The above mixed ligand complexes on treatment with ammonia form the mixed imine Schiff base complexes. Here metal is linked with one salicylaldehyde and another 2-hydroxy-1-naphthaldehyde or 2-acetyl-1-naphthaldehyde.



Mixed imine Schiff base complexes were also formed by treating solution of Cu(II) or Ni(II) in excess of ammonia, with one equivalent each of salicylaldehyde and 2-hydroxy-1-naphthaldehyde and (or) 2-acetyl-1-naphthol. The reaction can be represented as under :





In the mixed imine Schiff base complexes, one salicylaldehyde and another 2-hydroxy-1-naphthaldehyde and (or) 2-acetyl-1-naphthol-dimine, molecules are disposed in a square-planar way around the central metal ion. This is supported by the magnetic moment values of Copper (II) complexes ~ 1.85 B.M., corresponding to spin - only value of one unpaired electron. The paramagnetism corresponding to one unpaired 'e' exhibited by the compounds indicate the absence of Cu-Cu⁴² interactions and this rules out the possibility of polymerization.

The visible spectra of these mixed imine Schiff base complexes in solution exhibited a broad band at 560 nm, indicating the square planar structure for Cu(II) mixed imine Schiff base complexes.

The imine Schiff base complexes of Ni(II) obtained by reacting (salicylaldehyde and 2-hydroxy-1-naphthaldehyde or 2-acetyl-1-naphtholdehyde) Ni(II) with ammonia show paramagnetism. The magnetic moment value of these complexes is ~ 1.02 B.M. On recrystallisation from chloroform, the compound becomes almost diamagnetic. This shows that the compounds are initially polymeric, resulting in the distorted octahedral structure with paramagnetism. Since the Schiff base is formed from polymeric compounds (MAL), partial polymerization.

may continue even after Schiff base complex formation. Such observations have been made earlier^{43,44}. The lowering in the paramagnetism of the present Schiff base complexes on recrystallization from chloroform is because of the formation of monomeric diamagnetic square-planar molecules. The Ni(II) imine Schiff base complexes obtained by 'template method' are diamagnetic as expected for square planar geometry.

The visible absorption spectra of both diamagnetic and partial paramagnetic complexes show shoulders at λ 550 nm. This shows that compounds are square-planar in structure and polymerization breaks in solution. The formation of Schiff base complex shifts the bands in the visible range to lower wave-length indicating the formation of stronger M-N bond³⁵. The square-planar complexes show no absorption beyond 600 nm and thus can be distinguished from octahedral structure.

The bands in the ir spectra of the complexes correspond to stretching and bending modes of salicylaldehyde or salicylalimine, 2-hydroxy-1-naphthaldehyde or 2-hydroxy-1-naphthalimine moiety. The spectra show no band in the range $3,400\text{ cm}^{-1}$ indicating that O-H hydrogen of aldehydic or ketonic or Schiff base ligand is dissociated after complexation. In the compounds I and II, two sharp bands appear between $3,000\text{--}2,900\text{ cm}^{-1}$ due to asymmetric and symmetric stretch of C - H. In the same compounds the band at $1,625\text{ cm}^{-1}$ corresponds to aldehydic and ketonic - C=O. This band, however, disappears and a new band $1,600\text{ cm}^{-1}$ appears in the imine Schiff base complexes due to formation of - C = N bond. It is also observed that there is lowering in C = N frequency, compared to that of free Schiff base, due to the coordination of azomethine nitrogen in metal Schiff base complexes^{46,47}.

In mixed imine complexes a sharp band appears at $\sim 3300 \text{ cm}^{-1}$ corresponding to =NH stretching frequency. The C-O stretching band of phenolic group is observed in the region 1300 cm^{-1} . The band in the range 900 cm^{-1} and below may be due to out of plane bending vibration of the C-H bond. M-O and M-N bands occur at lower frequency and hence could not be observed. The band corresponding to C = O, C = N and N-H stretching frequencies show small splitting into two or slight broadening, because there are two types of ligands with C = O, C = N and N - H groups in the mixed-ligand complexes.

Table IV-1 : Analytical data, electronic spectral band and magnetic moments of mixed ligand and mixed imine Schiff base complexes of Cu(II) and Ni(II).

No.	Name of the complex	Calculated				Analytical data%				N	λ_{max} in nm.	μ_{eff} in B.M.
		M	C	H	N	M	C	H	N			
1.	(Salicylaldehydato - 2-hydroxy-1-naphthaldehydato) Cu(II).	17.86	60.72	3.37	-	17.60	61.01	3.09	-	-	650	1.90
2.	(Salicylaldehydato - 2-acetyl-1-naphthaldehydato) Cu(II).	17.18	61.66	3.78	-	16.80	61.81	4.02	-	-	630	1.92
3.	(2-hydroxy-1-naphthaldehydato-2-acetyl-1-naphthaldehydato) Cu(II).	15.13	-	-	-	15.01	-	-	-	-	620	1.86
4.	(Salicylaldehydato - 2-hydroxy-1-naphthaldehydato) Ni(II).	17.72	-	-	-	17.60	-	-	-	-	610	2.98
5.	(Salicylaldehydato - 2-acetyl-1-naphthaldehydato) Ni(II).	16.08	-	-	-	16.20	-	-	-	-	600	3.00
6.	(2-hydroxy-1-naphthaldehydato-2-acetyl-1-naphthaldehydato) Ni(II).	14.14	-	-	-	14.28	-	-	-	-	615	2.92
7.	(Salicylaldiminato-2-hydroxy-1-naphthaldiminato) Cu(II).	17.97	-	-	7.91	17.78	-	-	7.29	-	530 550	1.83
8.	(Salicylaldiminato-2-acetyl-1-naphthaloldiminato) Cu(II).	17.28	62.03	4.35	7.61	17.18	61.69	4.27	7.81	-	560	1.88

Contd....

No.	Name of the complex	Analytical data %							λ_{max} in nm.	μ_{eff} in B.M.	
		M	Calculated		Found						
			C	H	N	M	C	H	N		
9.	(2-hydroxy-1-naphthal-diminato-2-acetyl-1-naphtholdiminato) Cu(II).	15.21	-	-	6.70	15.34	-	-	6.50	555	1.81
10.	(Salicylaldiminato-2-hydroxy-1-naphthal-diminato) Ni(II).	16.83	61.94	4.01	8.02	16.28	62.37	4.40	7.56	550	Diamagnetic (a).
11.	(Salicylaldiminato-2-hydroxy-1-naphthal-diminato) Ni(II).	16.83	-	-	8.02	16.39	-	-	7.60	550	1.43
12.	(Salicylaldiminato-2-acetyl-1-naphtholdiminato) Ni(II).	16.18	62.86	4.41	7.71	16.10	62.45	4.27	7.57	550	1.40
13.	(2-hydroxy-1-naphthal-diminato-2-acetyl-1-naphtholdiminato) Ni(II).	14.22	-	-	6.78	14.10	-	-	6.88	540	1.23

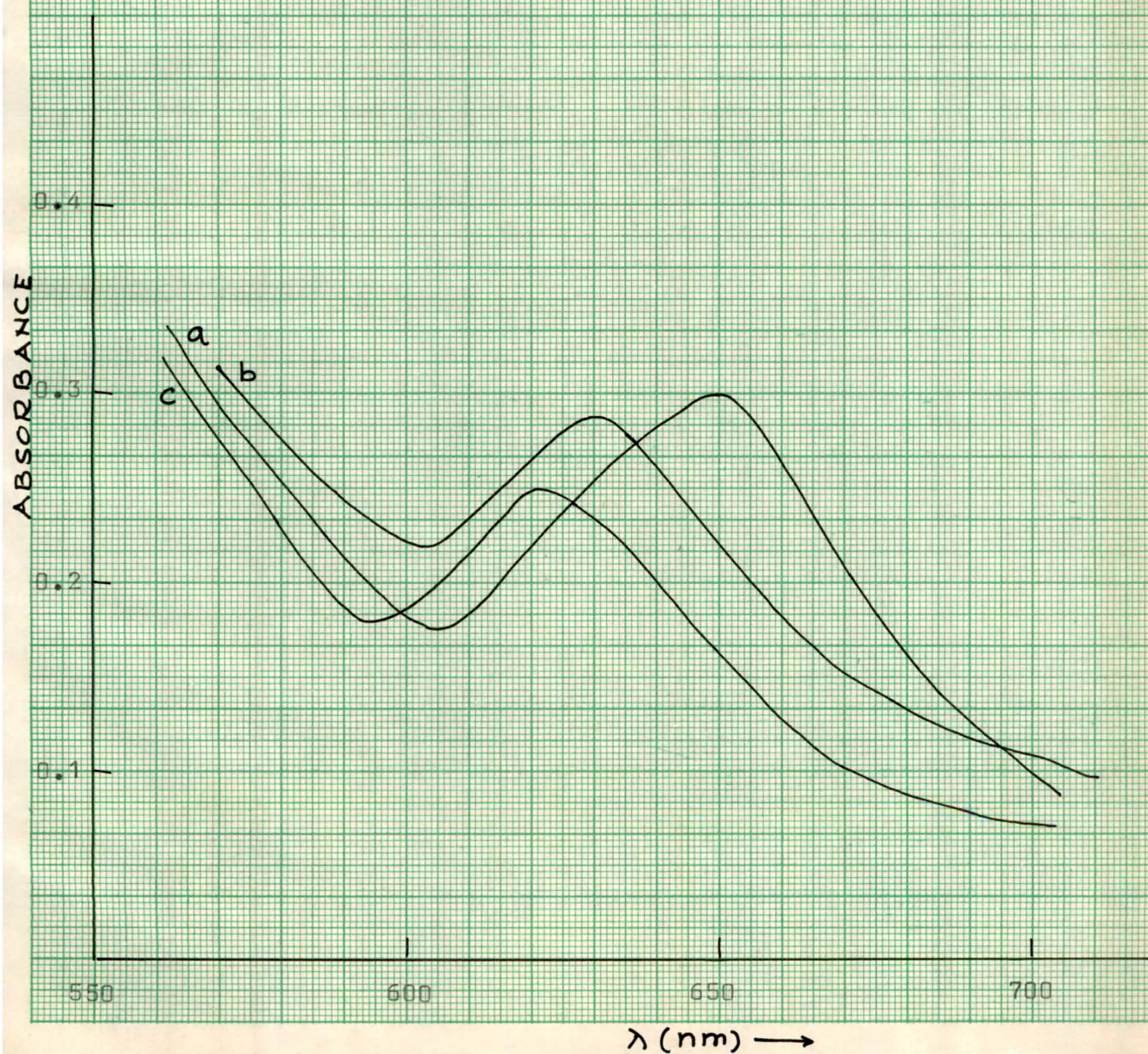
(a) Compound from metal ammine complex.

Visible Spectra of

a = (Salicylaldehydato-2-hydroxy-1-naphthaldehydato) Cu(II).

b = (Salicylaldehydato-2-acetyl-1-naphtholdehydato) Cu(II).

c = (2-hydroxy-1-naphthaldehydato-2-acetyl-1-naphtholdehydato) Cu(II).

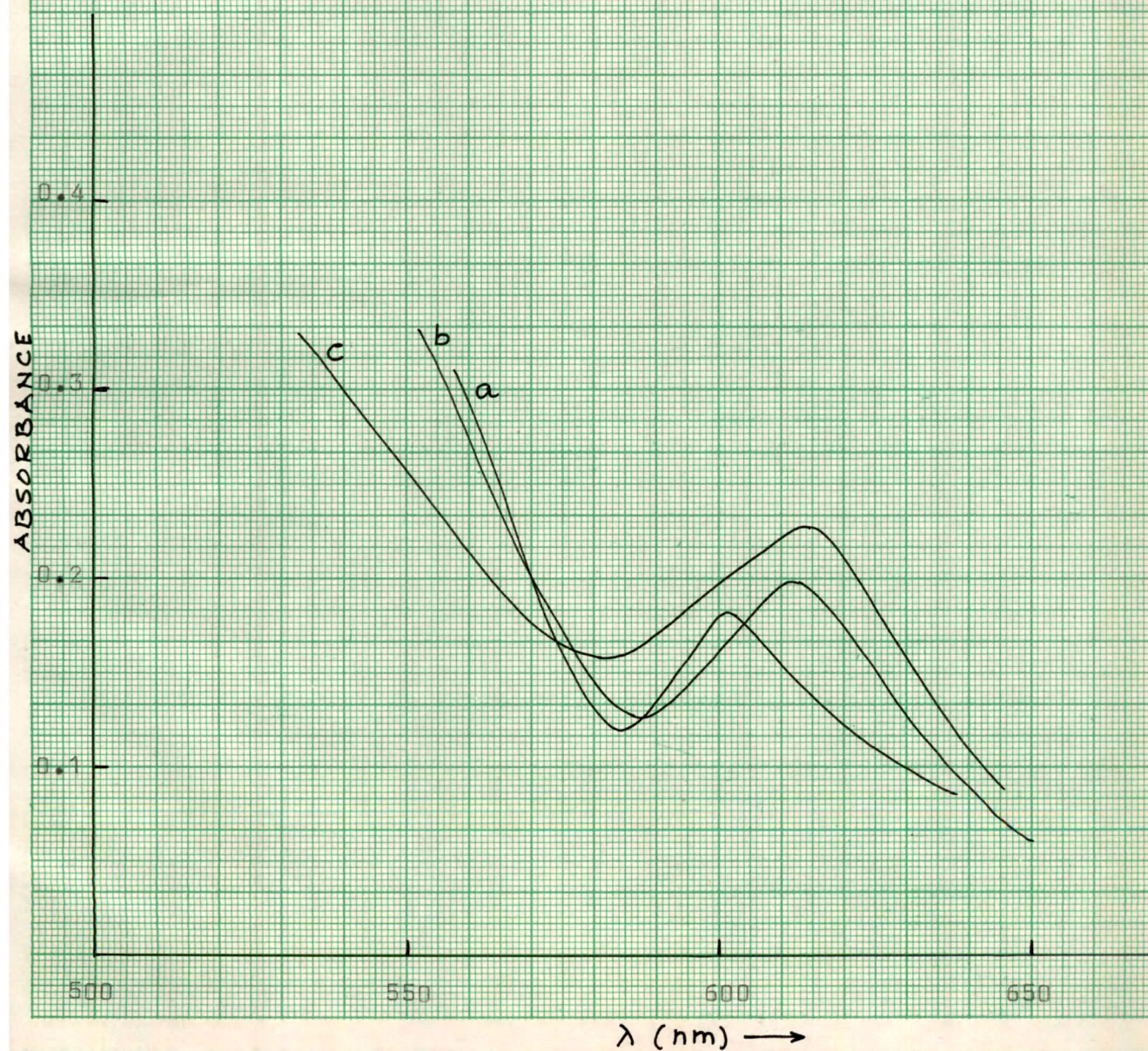


Visible Spectra of

a = (Salicylaldehydato-2-hydroxy-1-naphthaldehydato) Ni(II).

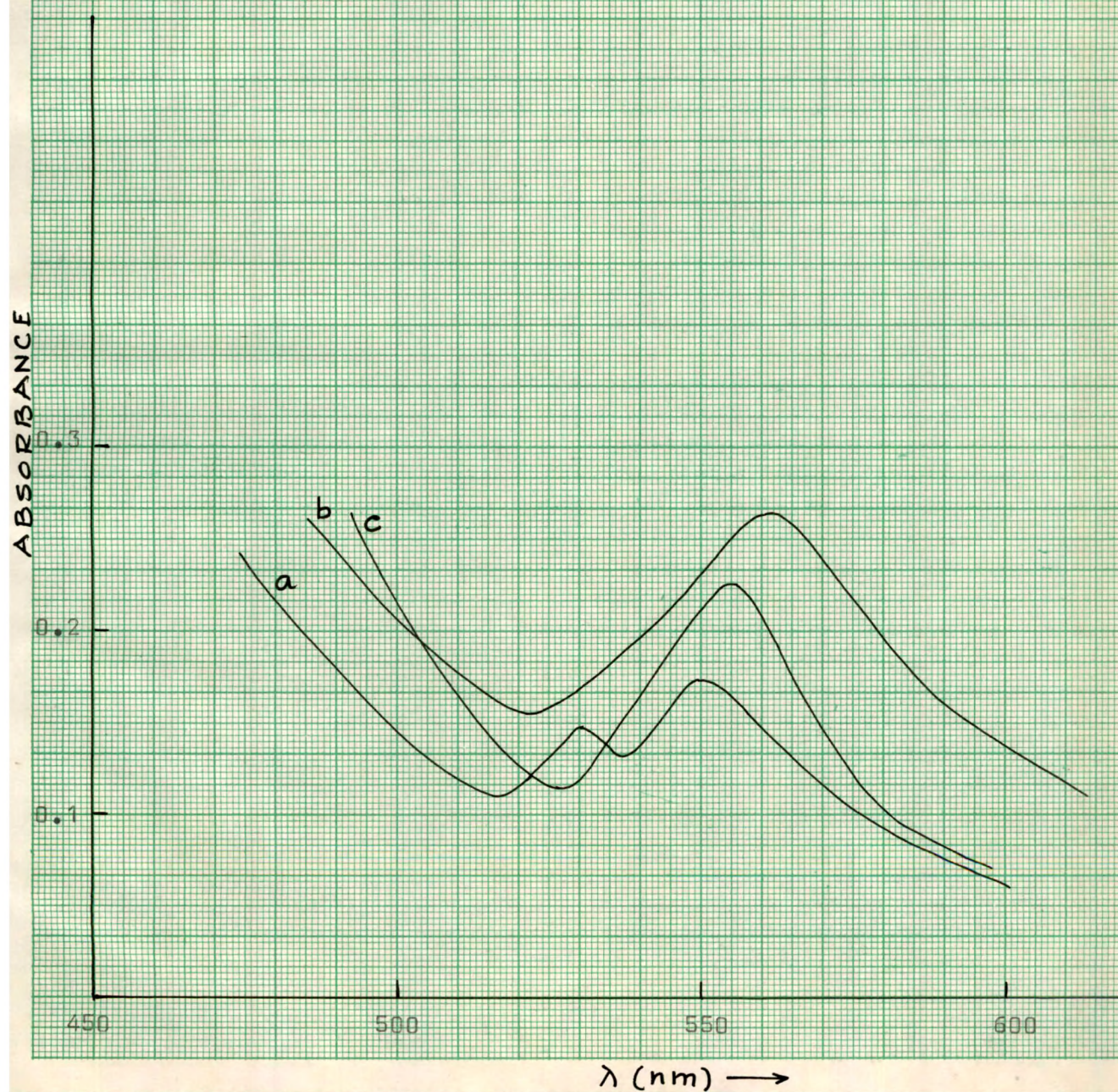
b = (Salicylaldehydato-2-acetyl-1-naphtholdehydro) Ni(II).

c = (2-hydroxy-1-naphthaldehydato-2-acetyl-1-naphtholdehydro) Ni(II).



Visible Spectra

- a = (Salicylaldiminato-2-hydroxy-1-naphthalaldiminato) Cu(II).
b = (Salicylaldiminato-2-acetyl-1-naphthalaldiminato) Cu(II).
c = (2-hydroxy-1-naphthalaldiminato-2-acetyl-1-naphthalaldiminato) Cu(II).

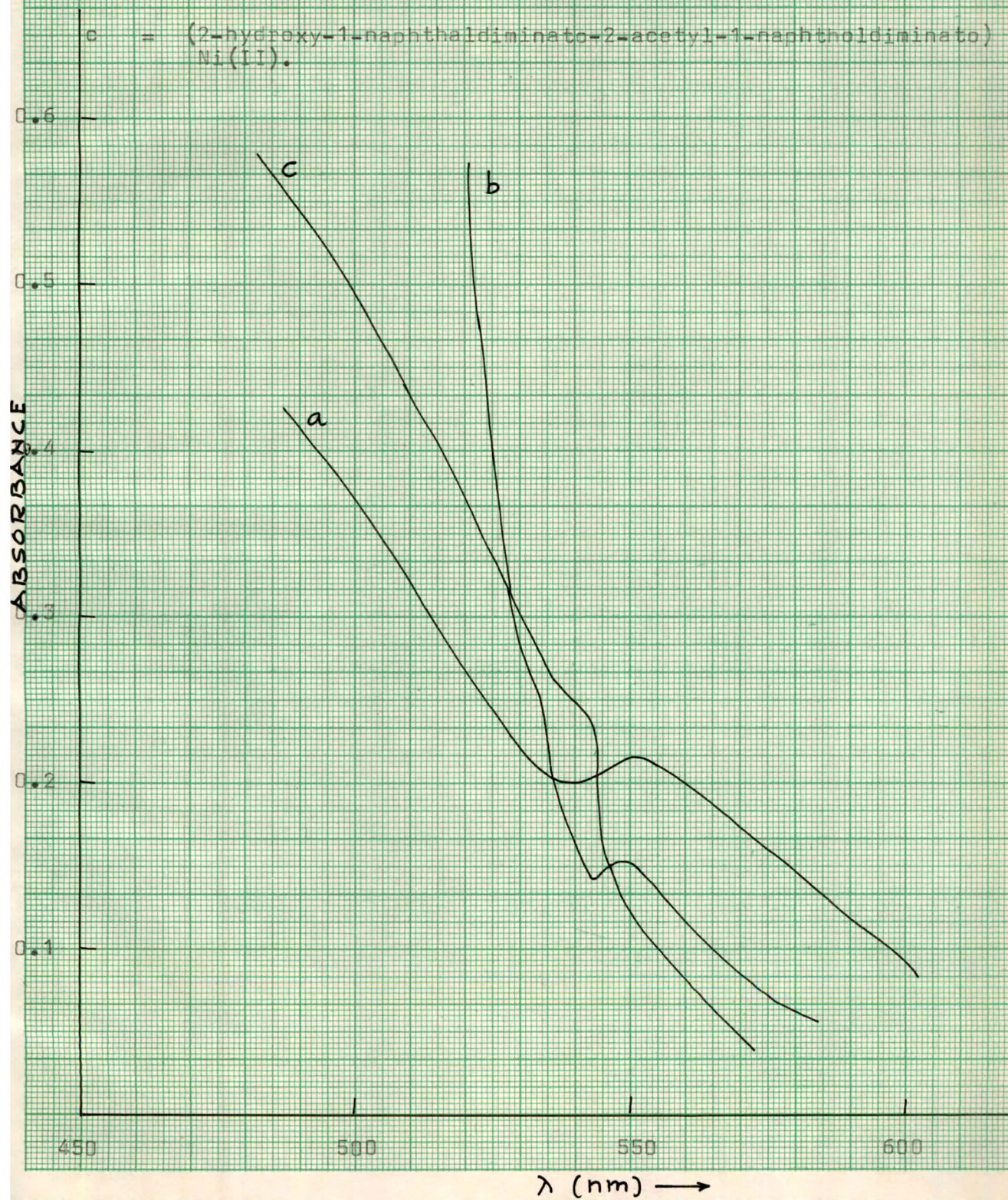


Visible Spectra of

a = (Salicylaldiminato-2-hydroxy-1-naphthalaliminato) Ni(II).

b = (Salicylaldiminato-2-acetyl-1-naphtholdiminato) Ni(II).

c = (2-hydroxy-1-naphthalaliminato-2-acetyl-1-naphtholdiminato) Ni(II).



REFERENCES

1. H.Havor, B.J.Billoo and D.W.Margerum, J.Am.Chem.Soc.93, 4173 (1971).
2. N.R.Jackobs and D.W.Margerum, Inorg.Chem.6, 2038 (1967).
3. D.D.Perrin and V.S.Sharma, J.Inorg.Nucl.Chem.28, 1271 (1966).
4. Y.Marcus and I.Elizer, J.Phys.Chem.66, 1661 (1962).
5. T.G.Spiro and D.N.Hume, J.Am.Chem.Soc.83, 4305 (1961).
6. P.Pfeiffer, E.Buchholz and O.Bayer, J.Pract.Chem. 129, 163 (1931), P.Pfeiffer, ibid, 149, 217 (1937).
7. N.F.Curtis, J.Chem.Soc.4409 (1960), 4109, 4115 (1963).
8. M.M.Blight and N.F.Curtis, J.Chem.Soc.1204 (1962).
9. D.A.House and N.F.Curtis, J.Am.Chem.Soc.86, 223, 1331 (1964).
10. S.Yamada, Coord.Chem.Rev.1, 415 (1966).
11. D.H.Bush, Adv.Chem.37, 1 (1963).
12. J.Burgers, D.N.Hague, R.D.W.Kemitt and A.MoAuley, "Inorganic Reaction Mechanisms", Vol.1, p.260 (1971).
13. L.Sacconi and U.Camigli, Inorg.Chem.5, 606 (1966).
14. R.H.Balundgi and A.Chakravorty, Inorg.Chem.12, 981 (1973).
15. R.H.Balundgi and A.Chakravorty, Inorg.Nucl.Chem.letters, 9(2), 167 (1973).
16. D.Cummins, J.Chem.Soc.(Dalton) 13, 1359 (1973).
17. R.W.Layer, Chem.Rev.63, 489 (1963).
18. F.R.Dwyer and D.P.Mellor (Eds), "Chelating agents and Metal-Chelates" Academic Press N.Y.(1964).
19. B.O.West, Rev.Pure.Appl.Chem.(Australia), 10, 207 (1960).
20. R.H.Holm, G.W.Everett and A.Chakravorty, Prog.Inorg.Chem.7, 83 (1966).

21. B.O.West, "The Chemistry of Coordination compounds of Schiff bases" in "New Pathways in Inorganic Chemistry (Eds), E.A.B.Ebsworth, A.G. Maddock and A.G.Sharpe, Cambridge Univ.Press (1968).
22. E.Sinn. and C.Melville, Coord.Chem.Rev.4 (4), 391 (1969).
23. W.E.Hatfield and R.Whyman, "Transition-Metal-Chemistry", 5, 47 (1969).
24. T.S.Kanan and A.Chakravorty, Inorg.Nucl.Chem.letters, 6, 903 (1970).
25. A.Chakravorty and R.H.Holm, J.Am.Chem.Soc.86, 3999(1964).
26. B.T.Thakar and P.K.Bhattacharya, J.Inorg.Nucl.Chem.37, 615 (1975).
27. U.Doraswamy and P.K.Bhattacharya, J.Inorg.Nucl.Chem.37, 1665 (1975).
28. V.B.Mohan Kumar and P.K.Bhattacharya, Indian.J.Chem. 15A, 132 (1977).
29. E.L.Mutterties and R.A.Schunn, Quart.Rev.(London) 20, 245 (1966).
30. B.N.Figgis and J.Lewis, J.Prog.Inorg.Chem.6, 37 (1964).
31. P.Ray and D.N.Sen, J.Indian, Chem.Soc. 25, 473 (1948).
32. B.N.Figgis and C.M.Harris, J.Chem.Soc. 855 (1959).
33. L.Sacconi, M.Ciampolini, F.Maggio and F.P.Cavasiono, J.Inorg.Nucl.Chem. 19, 73 (1961).
34. L.Sacconi, P.Paoletti and G.ReDel, J.Am.Chem.Soc.79, 4062 (1957).
35. H.S.French, M.Z.Magge and E.Sheffield, J.Am.Chem.Soc.64, 1924 (1942).
36. H.A.Jahn and E.Tellor, Proc.Roy.Soc.A161, 220 (1937).

37. R.S.Nyholm, Chem.Rev.53, 263 (1953).
38. J.R.Miller, "Advances in Inorg.Chem. and Radio Chemistry"
Volume IV (H.J.Emeleus, A.G.Sharpe Eds) Academic Press,
Newyork p.133 (1962).
39. L.Sacconi, Transition Metal Chemistry, 4, 199 (1968).
40. F.A.Cotton and G.Wilkinson, "Advanced Inorganic Chemistry",
Interscience publishers p.885 (1962).
41. A.B.P.Lever, "Inorganic Electronic Spectroscopy", Elsevier,
Publishing company, Newyork, p.343 (1960).
42. F.A.Cotton and G.Wilkinson, "Advanced Inorganic Chemistry",
Interscience publishers, John Wiley and Sons, p.755 (1962).
43. D.P.Graddon and G.M.Mockler, Aust.J.Chem.21,907 (1968).
44. M.W.Blackmore, R.W.Cattrall and R.J.Magee, Inorg.Nucl.Chem.
lett. 4, 305 (1968).
45. R.S.Drago "Physical Methods in Inorganic Chemistry"
(Reinhold Newyork) p.179 (1968).
46. S.N.Poddar and N.S.Das Indian, J.Chem.12, 1105 (1974).
47. D.H.Busch and J.C.Bailer, J.Am.Chem.Soc. 78, 1137 (1956).
48. H.Schiff Ann., 150, 193 (1869), 131, 118 (1864).