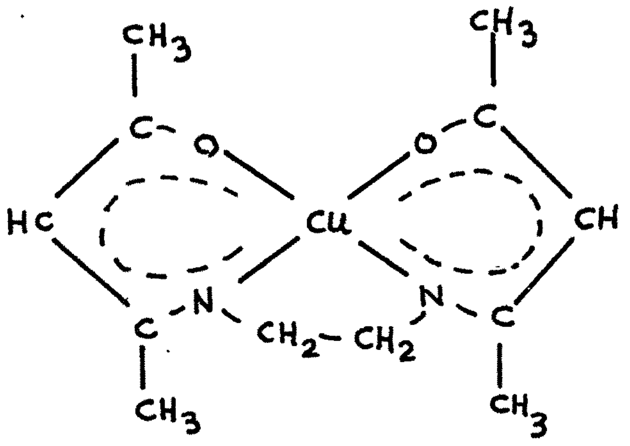
CHAPTER V

Mixed ligand complexes containing β-dicarbonyls and their reactions with monoamines, diamines and N-hydroxyalkylamine

Metal complexes of Schiff base have occupied a central role in the development of coordination chemistry. Transition metal complexes with Schiff base as ligands have been amongst the most widely studied coordination compounds. 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 donar 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 for over a hundred years. Schiff was the first to discover the exceedingly important synthetic technique of preparing salicylaldimine complexes by reaction of the preformed metal salicylaldehyde complexes with primary amines.[1,2]

After a lapse of nearly 50 years, the systematic synthetic study of Schiff base complexes was started by Pfeiffer[3] and coworkers in 1931. In the same year Dubsky and Sokol[4] isolated N-N' ethylene bis(salicylideneaminato) Cu(II) and Ni(II). The first complex of a β-ketoamine was prepared in 1889 by Combes[5] who isolated the remarkably stable copper complex.



Mixed ligand complexes of the type [LnLL'] where Ln = lanthanones, L' = bis(salen) and L' = β-diketone have been synthesised by Dutta.[6] Poddar has carried out[7] reactions of N-N' ethylene bis(salicylideneaminato)Co(II) with acetylacetone, propionylacetone and benzoylacetone. Mixed ligand complexes [COLL'], where L = N,N'-ethylene bis(salicylideneaminato) and its methyl derivatives and L' = β-diketone, salicylaldehyde or ω-nitroacetophenonate have also been prepared.[8] The preparation, physical properties and chemical reactions of Schiff bases have been reviewed by Layer.[9] Various aspects of their chelating characteristics have been described in the work edited by Dwyer and Mellor.[10] Two excellent reviews of Schiff base complexes appeared in 1960[11] and 1966.[12] The first of these stressed 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, as well as some aspects of behaviour of such complexes in solution has also been published.[13] Few more review articles[14] concerning this general area have appeared in the last few years. Sacconi and coworkers[15] reported normal and mixed ligand chelates of vanadyl(V) with salicylaldehyde and Schiff base derived from ring substituted salicylaldehyde and N-substituted ethylenediamines. Mixed ligand complexes of Cu(II) derived from salicylaldehyde or 2-hydroxyacetophenone or acetylacetone and their Schiff base with N-substituted ethylenediamine have also been reported by Chakravorty et al.[16,17]

Reactions of amines on mixed ligand complexes of the type [MLL'] where M = Cu(II) or Ni(II); LH = salicylaldehyde or 2-hydroxy-1-naphthaldehyde; L'H = 2-hydroxyacetophenone and methyl derivatives are known to yield the mixed Schiff base complexes, both the coordinated aldehyde and ketone forming the Schiff base.[18,19] Coordinated β-diketones are, however, known[20] to be resistant to reaction with amines. It was, therefore, thought to be of interest to study the reaction of amines on mixed ligand complexes containing β-diketones. In the present work mixed ligand complexes of the type [MLL'] where M = Cu(II) or Ni(II); LH = salicylaldehyde and L'H = acetylacetone (AcAc) or benzoylacetone(BA) or dibenzoylmethane(DBM) have been synthesised. Such compounds have been treated with ammonia and amines.

Similarities between chemistries of salicylaldehyde and 2-hydroxyacetophenone complexes are to be expected from the common O-O donor atom set of each ligand system and the presence of conjugated six membered chelate rings in each group of complexes. The present study was, therefore, also extended, to prepare mixed ligand complexes [MLL'] where M = Cu(II); LH = 2-hydroxyacetophenone or 2-hydroxy-3-methylacetophenone and L'H = acetylacetone. The above mixed ligand complexes have also been treated with primary amines and diamines.

Experimental :

Materials used :

2-Hydroxyacetophenone and 2-hydroxy-3-methylacetophenone were prepared by Fries migration of phenyl acetate using anhydrous aluminium chloride without solvent. 2-Hydroxyacetophenone and 2-hydroxy-3-methylacetophenone were purified by distillation under reduced pressure. Copper acetate and nickel acetate salts (BDH) were used. Ethanol and chloroform were analar grade reagents. Other ligands used were of pure grade, Acetylacetone (BDH), benzoylacetone (Fluka), dibenzoylmethane (K.Light), salicylaldehyde (Fluka).

Preparation of ternary metal complexes and their Schiff bases :

1. M(II) salicylaldehyde or 2-hydroxyacetophenone and β-diketone.

The above complex was prepared by adding salicylaldehyde and diketone to metal ion solution in alcoholic medium in 1:1:1 ratio. The reaction was carried out at 0°C. After mixing, the pH was raised by dilute ammonia upto ~5.5. The mixture was stirred well. The solid that separated out was filtered, washed with water and finally with 50% alcohol. The compound was recrystallised from chloroform and analysed.

2. Preparation of amine Schiff base complex :

M(II) salicylideneaminato or 2-hydroxyacetophenoniminato or 2-hydroxy-3-methylacetophenoniminato and β-diketone.

The above complexes can be prepared by two methods :

(a) Here the preformed mixed complex I was treated with excess of ammonia, in alcoholic medium and warmed on a water bath with constant stirring for about half an hour. The solid that separated was filtered, washed with water and finally with 50% alcohol. The compound was recrystallised from chloroform and analysed.

(b) To the metal acetate solution an excess of ammonia was added till the hydroxide formed dissolved resulting in the formation of metal amine complex. To this was added an alcoholic solution of the two ligands such that the metal and the two ligands were in 1:1:1 ratio. The mixture was stirred well and the solid that separated was filtered, washed with water and finally with 50% alcohol. The compound was recrystallised from chloroform and analysed. (In case of 2-hydroxyacetophenone and methyl derivatives it required longer refluxing).

(3) Preparation of N-alkylamine compounds :

The compounds were prepared by amine exchange method. The preformed mixed complex I or the amine Schiff base complex II was treated with very dilute amines (methyl or ethyl) ∽0.05M (3-5 ml.) and refluxed for some time. The solids obtained were filtered, washed with water and finally with 50% alcohol. The compounds were recrystallised from chloroform and analysed.

4. Preparation of diamine Schiff base complexes :

(a) N,N'-ethylene (salicylideneaminato-acetylacetoniminato) Cu(II).

(b) N,N'-ethylene (1-(2-hydroxyphenyl)ethylideneaminato-acetylacetoniminato)Cu(II).

The above complexes could be prepared directly or by amine exchange method. The preformed mixed complex I or the amine Schiff base complex II were treated with ethylenediamine or propylenediamine. It was refluxed on a water bath for half an hour. Longer refluxing was required in case of propylenediamine. The solid was filtered, washed with water and finally with 50% alcohol. The compounds were recrystallised from chloroform and analysed.

(c) N,N'-ethylene(salicylideneaminato-acetylacetoniminato) M(II). (direct method)

To a mixture of the metal ion solution, salicylaldehyde and diketone (alcoholic medium), was added ethylenediamine, such that the metal, two ligands and ethylenediamine were in 1:1:1:1 ratio. This was refluxed on a water bath for about an hour with stirring. The resulting compounds were filtered, washed with water and finally with 50% alcohol. In case of Cu(II) complexes longer refluxing has to be avoided because it leads to some kind of disproportionation. The solids obtained were filtered, washed with water and finally with 50% alcohol. The compounds were recrystallised from chloroform and analysed.

In order to characterise and determine the structures of the complexes obtained, the following studies were undertaken :

1. Analysis :

The compounds were analysed for metal, carbon, hydrogen and nitrogen. Nickel was estimated gravimetrically as nickel dimethylglyoximate, after decomposing the complexes in nitric acid. Cu, C, H, N were estimated as detailed in previous chapter.

2. TLC analysis :

TLC analysis were done on a silica gel G(Sichem) using chloroform + ether (1:3) mixture as solvent.

3. Magnetic measurements :

Magnetic measurements were carried out at room temperature ∽30°C, using Guoy balance, has detailed in previous chapter.

4. Conductance :

Conductivity measurements were done in chloroform solutions of the complexes, using Toshniwal Conductivity Bridge type C101/01A. It is observed that all the complexes obtained are insoluble in water and soluble in chloroform. They are found to be non-conducting.

5. Spectrophotometric measurements :

(a) Visible spectral measurements :

The visible spectra of the compounds were studied in chloroform solutions on a DU-2 Beckman Spectrophotometer at room temperature (∽30°C) using 1 cm quartz cell in the range of 300 nm to 1000 nm. The absorbance was noted at different wavelengths and optical density was plotted against the wavelengths. The peaks obtained are shown in the graphs.

(b) Infra-Red measurements :

Discs were made by preparing an intimate mixture of about 1 mg. of solid sample and approximately 100 mg. of carefully dried KBr. IR spectra were obtained in the range 4000 - 625 cm^{-1} on a Perkin Elmer model 427 IR grating spectrophotometer. Characteristic bands obtained are as follows :

Compound	Characteristic bands cm^{-1}		
1. (Salicylaldihydato-acetylacetonato)Cu(II)	∽3080w	∽3020w	∽2920w
	∽1610s	∽1600s	∽1580s
	∽1550s	∽1530s	∽1460s
	∽1435s	∽1415s	∽1360s
	∽1340s	∽1270s	∽1240m
	∽1210s	∽1190s	∽1150s

~1120w ~1020s ~935s
~900s ~850m ~780s
~765m ~730s ~680m
~660s ~650s.

2. (Salicylaldihydato-benzoyl-acetonato)Cu(II)

~3090w ~3020w ~2910w
~1605s ~1600s ~1580s
~1545s ~1535s ~1460s
~1435s ~1420s ~1360s
~1335s ~1280s ~1240m
~1200s ~1190s ~1140s
~1110s ~1020s ~940s
~900s ~840m ~780s
~770m ~740s ~690m.

3. (salicylaldihydato-2-hydroxy-acetophenonato)Cu(II)

~2950w ~2900m ~2850s
~2790s ~1620s ~1520s
~1425s ~1300s ~1250m
~1180m ~1155s ~1130s
~1030m ~900s ~750m
~730m ~660m ~590w
~530w.

4. (salicylideneaminato-acetyl-acetonato)Cu(II)

~3300s ~3010w ~2930w
~2880w ~2780w ~1600w
~1580s ~1550m ~1520-1540s
~1470s ~1450s ~1440m
~1350s ~1330s ~1270s
~1240s ~1200w ~1180s
~1160m ~1150s ~1120s
~1020s ~940s ~900s
~860w ~850w ~820s
~780s ~740s ~730w
~680s ~670s ~650s.

5. (Salicylideneaminato-benzoyl-acetonato)Cu(II)

~3300s ~3000w ~2920w
~2880w ~2780w ~1605s
~1590s ~1550w ~1520s
~1485m ~1460s ~1445s
~1420w ~1380m ~1340s

	∼1310s	∼1290s	∼1260s
	∼1225s	∼1180s	∼1145s
	∼1115s	∼1090w	∼1060w
	∼1025m	∼1000m	∼955m
	∼940s	∼890s	∼850s
	∼815s	∼750s	∼700s
	∼690w	∼680w	∼670w.
6. (Salicylideneaminato-dibenzoylmethanato)Cu(II)	∼3300s	∼3000w	∼2920w
	∼2880w	∼2780w	∼1625s
	∼1590s	∼1540w	∼1525s
	∼1460s	∼1400s	∼1340s
	∼1310s	∼1250m	∼1230s
	∼1180s	∼1140s	∼1115s
	∼1065s	∼1020s	∼930s
	∼885s	∼810s	∼745s
	∼705s	∼680m.	
7. [1-(2-hydroxyphenyl)ethylideneaminato-acetylacetonato]Cu(II)	∼3300s	∼2860s	∼1600s
	∼1525s	∼1460s	∼1440m
	∼1410s	∼1350m	∼1325m
	∼1280s	∼1270m	∼1250m
	∼1210s	∼1180m	∼1135s
	∼1125m	∼1110s	∼1060m
	∼1020s	∼980s	∼930s
	∼900s	∼890s	∼840s
	∼825m	∼805s	∼760m
	∼740s	∼690s	∼660m.
8. (N-Methyl-salicylideneaminato-acetylacetonato)Cu(II)	∼3060w	∼2960w	∼2900w
	∼2780w	∼1600s	∼1575s
	∼1545w	∼1510s	∼1485w
	∼1470m	∼1450s	∼1410s
	∼1335m	∼1310s	∼1275m
	∼1195s	∼1150s	∼1110m
	∼1070w	∼1030w	∼1010s
	∼1000w	∼960w	∼910s
	∼850s	∼800s	∼755s
	∼740w	∼710s	∼690m.

9. (N-Methyl-salicylideneaminato-benzoylacetonato)Cu(II)

∽3050w ∽2960w ∽2900w
∽1600s ∽1570s ∽1540m
∽1515s ∽1460w ∽1450s
∽1420w ∽1390s ∽1350s
∽1330m ∽1320w ∽1220w
∽1200s ∽1145s ∽1115s
∽1065m ∽1030m ∽1010s
∽955s ∽910s ∽840s
∽805m ∽745s ∽725s
∽710m.

10. (N-Methyl-salicylideneaminato-dibenzoylmethanato)Cu(II)

∽3060w ∽2960w ∽2900w
∽1600s ∽1580s ∽1540s
∽1520s ∽1470m ∽1455s
∽1415w ∽1395s ∽1355s
∽1330s ∽1320m ∽1210w
∽1190s ∽1150s ∽1120s
∽1070m ∽1030m ∽1000s
∽960s ∽910s ∽850s
∽800m ∽750s ∽720s
∽700m.

11. [N-Methyl-1-(2-hydroxyphenyl)ethylideneaminato,acetylacetonato]Cu(II)

∽3040m ∽3000m ∽2900s
∽2775m ∽1600s ∽1530s
∽1460s ∽1440s ∽1390m
∽1360m ∽1290m ∽1270m
∽1250m ∽1210m ∽1180m
∽1140m ∽1025m ∽1000s
∽960s ∽900s ∽840s
∽790s ∽750s ∽730m
∽710m ∽650m.

12. (N-Ethyl-salicylideneaminato-acetylacetonato)Cu(II)

∽3050m ∽3000m ∽2900s
∽1600s ∽1570s ∽1515s
∽1455s ∽1405s ∽1370w
∽1345w ∽1330s ∽1280s
∽1215s ∽1180w ∽1145s
∽1085w ∽1050w ∽1025m
∽1000w ∽970w ∽930w
∽890s ∽845s ∽795w

	∼750s	∼710s.	
13. (N-Ethyl-salicylideneaminato-benzoylacetonato)Cu(II)	∼3060w	∼2900w	∼2790w
	∼1600w	∼1535w	∼1520w
	∼1450s	∼1400s	∼1380w
	∼1345w	∼1330s	∼1250w
	∼1200s	∼1140s	∼1120m
	∼1085s	∼1040w	∼1025s
	∼980s	∼925s	∼885s
	∼845s	∼795s	∼755s
	∼740w.		
14. (N-Ethyl-salicylideneaminato-dibenzoylmethanato)Cu(II)	∼3050w	∼2900w	∼2890w
	∼1600s	∼1540s	∼1460s
	∼1400s	∼1380w	∼1340w
	∼1330w	∼1315s	∼1230s
	∼1200m	∼1145s	∼1120w
	∼1090w	∼1070s	∼1020s
	∼980w	∼945w	∼930m
	∼885s	∼850m	∼790m
	∼740s	∼710s	∼680m.
15. [N-Ethyl,1-(2-hydroxyphenyl)ethylideneaminato-acetylacetonato]Cu(II)	∼3050m	∼3020m	∼2950s
	∼1600s	∼1525s	∼1440s
	∼1390s	∼1360s	∼1340s
	∼1325s	∼1290m	∼1235s
	∼1220s	∼1190m	∼1140s
	∼1120s	∼1100s	∼1040s
	∼1025s	∼1000s	∼960s
	∼920s	∼885s	∼875s
	∼855m	∼840s	∼815s
	∼740s	∼655s.	
16. N,N'-ethylene(salicylidene-aminato-acetylacetoniminato)Cu(II)	∼3080w	∼3050w	∼3020w
	∼2960w	∼2920w	∼1600s
	∼1540w	∼1530s	∼1470s
	∼1450s	∼1430m	∼1390s
	∼1350s	∼1335s	∼1305m
	∼1240m	∼1190s	∼1140s
	∼1125s	∼1085s	∼1050s

	~1025s	~980s	~950s
	~930m	~905s	~850s
	~785m	~750s	~740w
	~730s	~645m	~630w.
17. N,N'-ethylene[1-(2-hydroxyphenyl)ethylideneaminato, acetylacetoniminato]Cu(II)	~3050w	~3025w	~3000w
	~2940w	~2900w	~1600s
	~1530s	~1475s	~1450s
	~1425s	~1390s	~1350s
	~1340s	~1300s	~1250w
	~1240s	~1220m	~1200s
	~1140s	~1130s	~1070s
	~1060s	~1030s	~980s
	~960s	~940s	~910s
	~890w	~860s	~850m
	~790m	~750s	~745m
	~740s	~650w	~625m.
18. N,N'-ethylene(salicylideneaminato,acetylacetoniminato) Ni(II)	~3070w	~3020w	~2940w
	~1600s	~1535s	~1465m
	~1450s	~1385s	~1350s
	~1330s	~1320m	~1250m
	~1240s	~1220m	~1200s
	~1150w	~1140s	~1125s
	~1085s	~1025s	~990m
	~970m	~950s	~905s
	~850s	~800m	~750s
	~730s	~665s	~625s.
19. N,N'-Propylene(salicylideneaminato,acetylacetoniminato) Cu(II)	~3080w	~3020w	~2960w
	~2920w	~1600s	~1535s
	~1470s	~1445s	~1390s
	~1345s	~1310s	~1230w
	~1190s	~1150s	~1125s
	~1115w	~1090w	~1030s
	~1010s	~980s	~970w
	~900s	~850s	~790m
	~750s	~740s	~705w.

20. N,N'-Propylene[1-(2-hydroxyphenyl)ethylideneaminato, acetylacetoniminato]Cu(II)	∼3040w	∼3000w	∼2940w
	∼2830w	∼1600m	∼1500w
	∼1460m	∼1420m	∼1320m
	∼1300m	∼1260w	∼1250s
	∼1230m	∼1205s	∼1170s
	∼1140m	∼1055s	∼1040w
	∼1030s	∼1010w	∼950s
	∼925s	∼905s	∼870s
	∼840s	∼800s	∼760m
	∼730m	∼610w.	
21. [N-Hydroxyethyl,1-(2-hydroxyphenyl)ethylideneaminato]Cu(II).H_2O	∼3500b	∼3080w	∼3020w
	∼2940w	∼2920w	∼2890w
	∼2840w	∼1600s	∼1540s
	∼1450m	∼1440s	∼1415s
	∼1380s	∼1330s	∼1250w
	∼1235s	∼1180m	∼1140m
	∼1080s	∼1060m	∼1030m
	∼1010m	∼980s	∼935s
	∼890s	∼860s	∼830m
	∼780w	∼740s	∼720m
	∼700m	∼650w	∼620m
	∼570m	∼560m.	
22. [N-Hydroxyethyl-salicylideneaminato]Cu(II).H_2O	∼3500b	∼3040w	∼3010w
	∼2980m	∼2920m	∼2860w
	∼1600s	∼1540s	∼1480s
	∼1460s	∼1430m	∼1400s
	∼1360s	∼1330s	∼1210s
	∼1150s	∼1130s	∼1070s
	∼1050s	∼1030s	∼975m
	∼950s	∼930m	∼890s
	∼870s	∼855s	∼810m
	∼760s	∼750s	∼640m
	∼590m.		
23. [N-Hydroxyethyl-salicylideneaminato,benzoylacetonato]Ni(II)	∼3500b	∼2980w	∼2900w
	∼1600s	∼1570s	∼1510s
	∼1460s	∼1410s	∼1340w

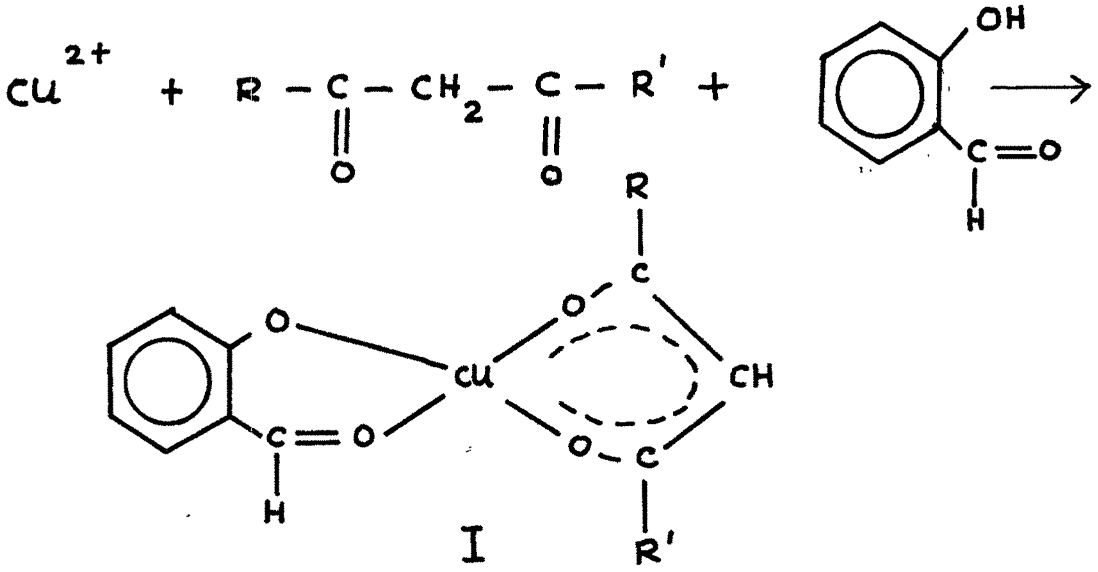
∽1305s ∽1270w ∽1220s
∽1190s ∽1150m ∽1120s
∽1070s ∽1025s ∽1000w
∽950m ∽930m ∽890m
∽850s ∽750s ∽735m
∽710s ∽690m.

Results and Discussion :

The analysis of the compounds agree with the expected composition.

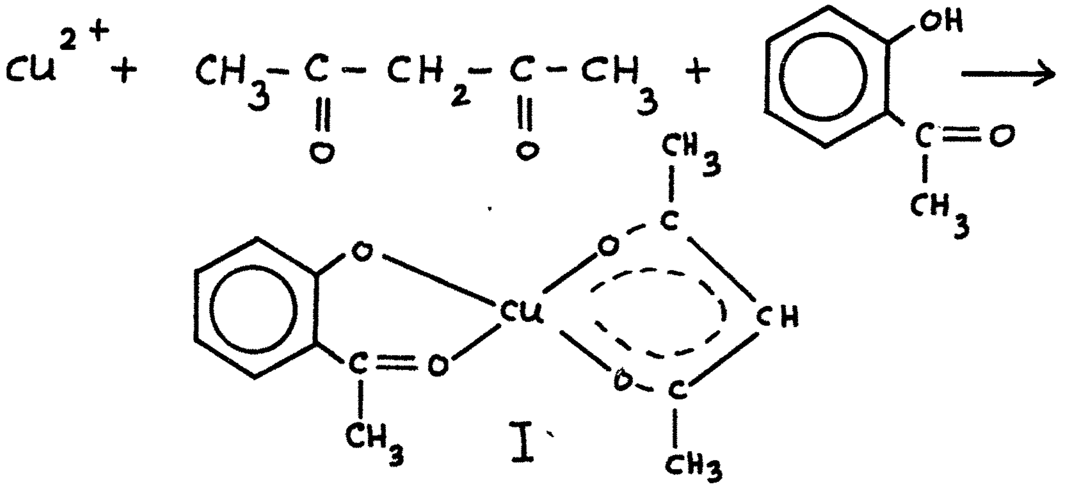
It is observed that all mixed ligand complexes are insoluble in water and soluble in organic solvents. They are found to be non-conducting indicating non-electrolyte nature. TLC of all the complexes show only one dot indicating that the compounds are pure single compounds, MAL, where A and L are the two ligands and not mixtures. In case of mixtures ($MA_2 + ML_2$) two dots are obtained for the same solvents.

Cu(II) on being treated with equimolar amounts of salicylaldehyde or 2-hydroxyketone and β-diketone, results in the formation of mixed ligand complex.

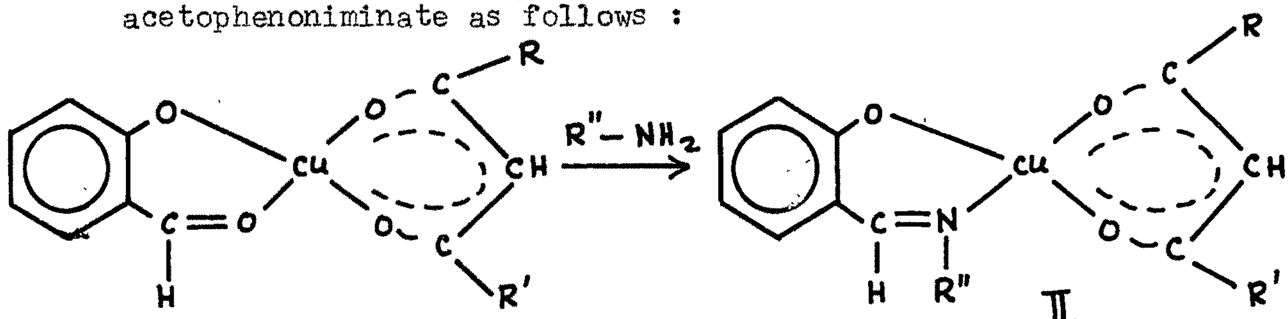


I

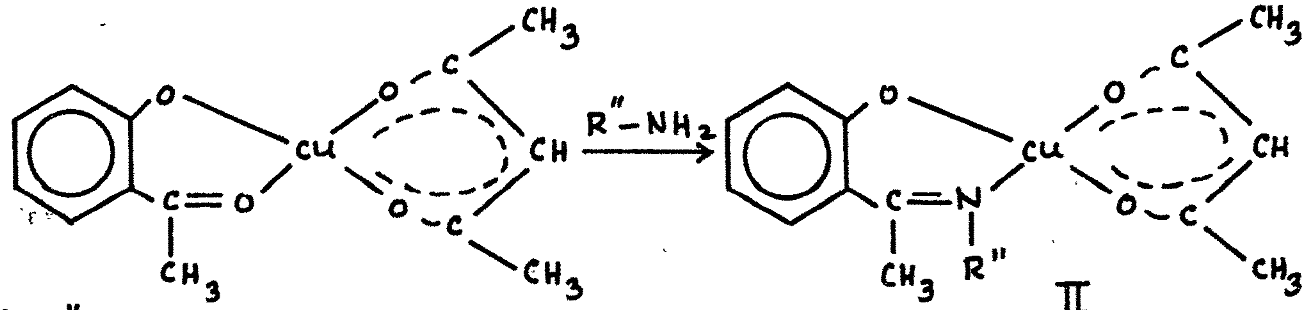
(i) $R = R' = CH_3$; (ii) $R = CH_3$; $R' = C_6H_5$.


I

The compound I on being treated with excess of ammonia or N-alkylamine, results in the formation of mixed ligand complex which contains one equivalent of β-diketone and another equivalent of salicylideneaminate or 2-hydroxyacetophenoniminate or N-alkyl salicylideneaminate or N-alkyl acetophenoniminate as follows :

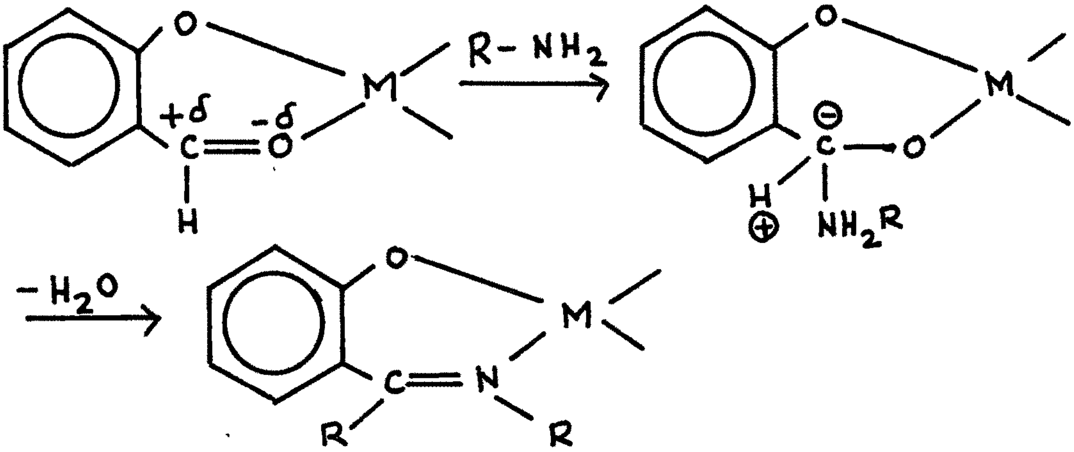

II

(i) $R = R' = CH_3$ (ii) $R = CH_3$; $R' = C_6H_5$ (iii) $R'' = H$, CH_3 or C_2H_5.


II

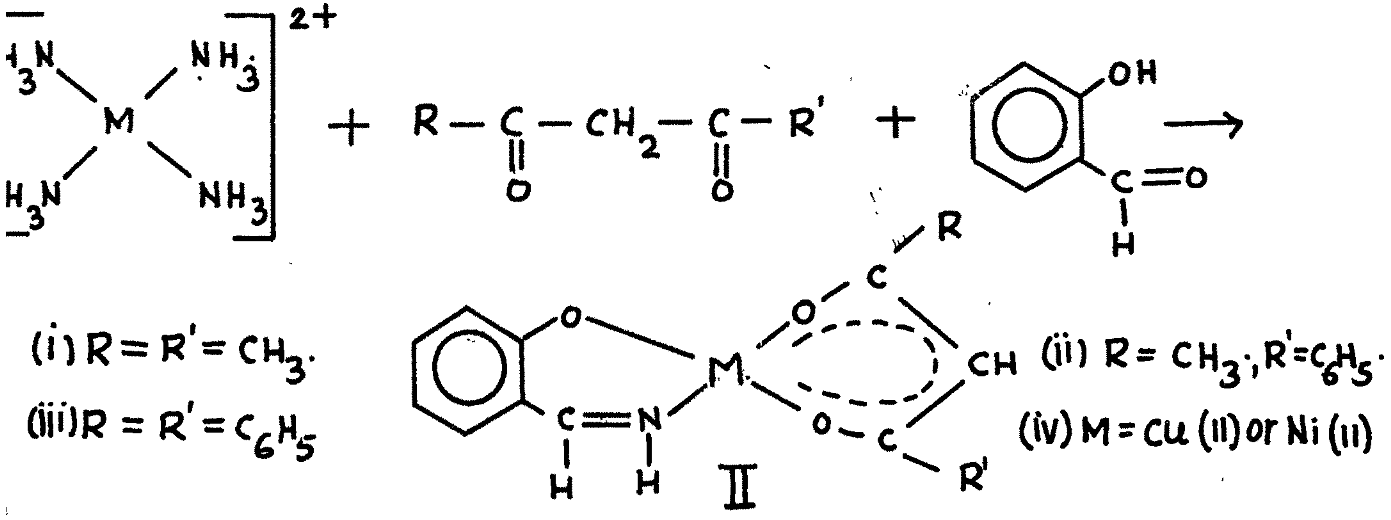
(i) $R'' = H$, CH_3 or C_2H_5.

Here the coordinated aldehyde or acetophenone undergoes reaction with primary amines to form Schiff base. Schiff base formation involves nucleophilic attack by the basic nitrogen compound on carbonyl carbon. Polarisation of carbonyl group on coordination to a positive metal ion will result in the carbonyl carbon becoming more susceptible to nucleophilic attack by the lone pair of the amines.[21] The polarisation of the carbonyl group is presumably enhanced by the metal ion thereby promoting nucleophilic attack. The condensation is well facilitated in the present complexes because salicylaldehyde forms a strong chelate ring. The reaction may be represented as follows :



The diketone, however, remains unaffected because coordinated diketones have very little tendency to undergo Schiff base formation.[20] It is a well known phenomenon that when β-diketone gets coordinated with a metal ion it forms a five atom π net work. This has π electron delocalised over it which gives it a pseudo aromatic character. As a result of this the reactivity of the carbonyl group is very much reduced.

Compound II could also be prepared by adding a mixture of the two ligands to the metal amine solution keeping all the three components in 1:1:1 ratio. Here the Schiff base formation of salicylaldehyde or acetophenone is facilitated due to the template effect.[21] Here the coordination sphere of the metal ion acts as a "template" and induces ammines, aldehyde or ketone molecules to orient in a manner that is suitable for condensation and complex formation. Reaction could be shown to take place as follows :



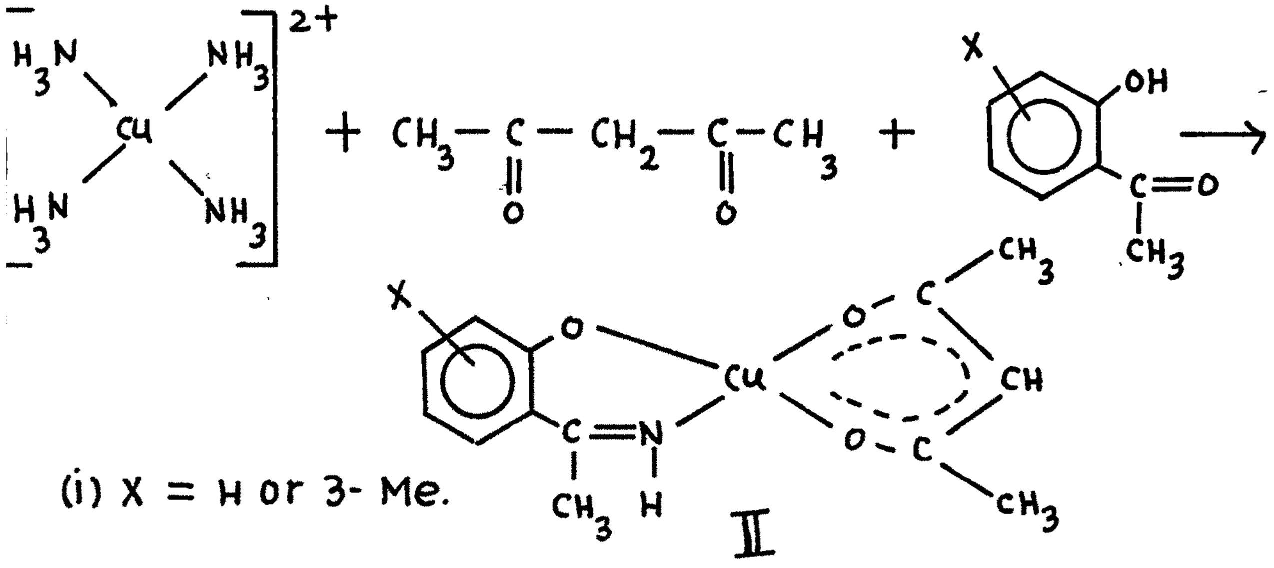
(i) $R = R' = CH_3$.

(ii) $R = CH_3$; $R' = C_6H_5$.

(iii) $R = R' = C_6H_5$

(iv) M = Cu (II) or Ni (II)

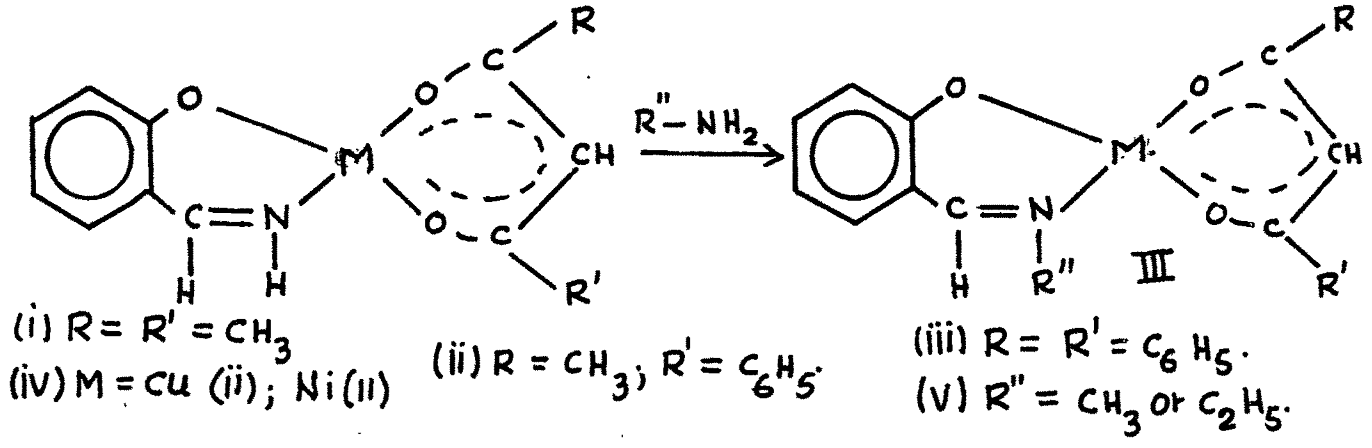
II

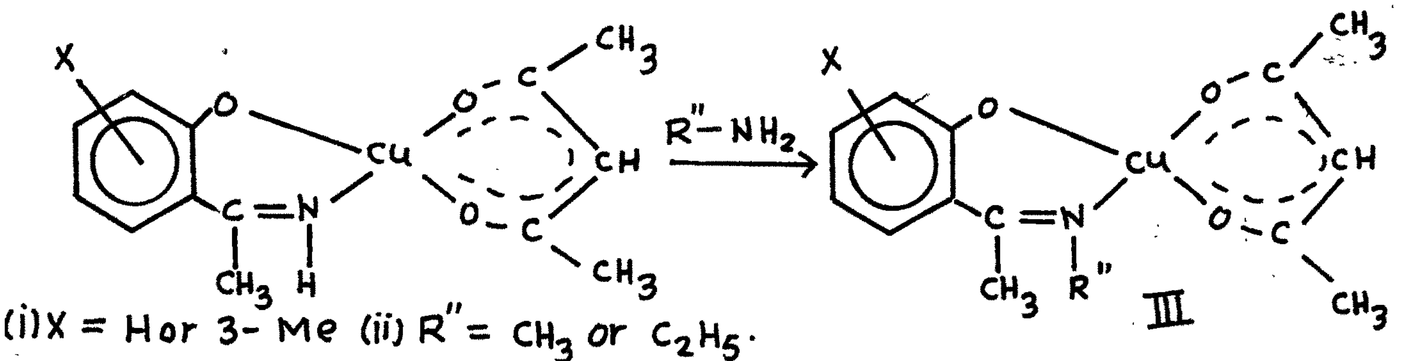


(i) X = H or 3- Me.

II

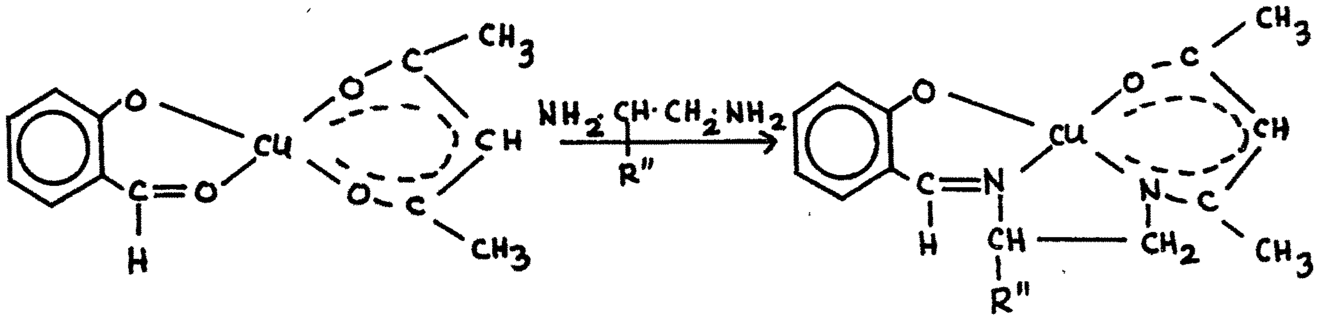
Compound III could be prepared by amine exchange with compound II -





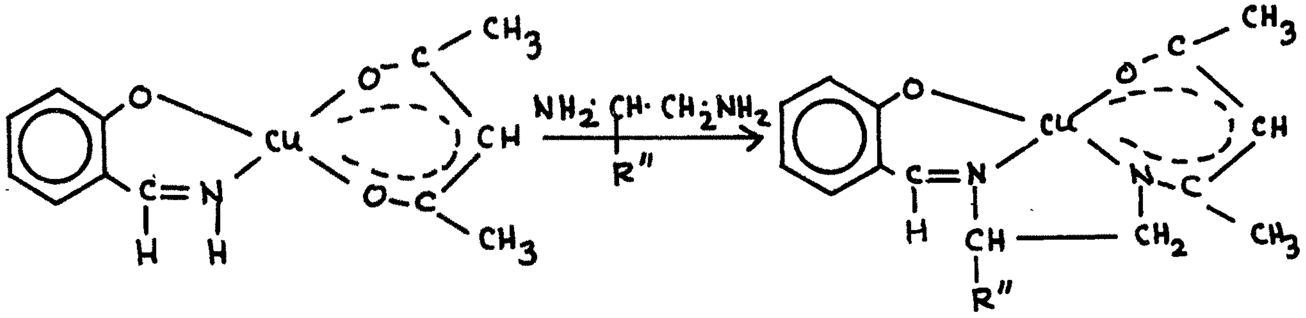
The reaction proceeds by a nucleophilic attack of the exchanging amine on the electron deficient carbon of the polarised imine. A more basic amine which is more nucleophilic replaces a less basic amine from the Schiff base. Alkylamines are more basic than ammonia and hence can replace it easily from the imine Schiff base complexes. The reaction is, however, also concentration dependent. A higher concentration of less basic amine may replace the more basic amine from the Schiff base.[22,23]

The Cu(II) mixed complex I or the imine Schiff base complex II was treated with diamines (ethylideneamine or propylenediamine). As in previous cases it was thought that the diamine part would condense only with salicylaldehyde or acetophenone. The other end would remain free or coordinate at fifth position. The analysis of the compounds is, however, in agreement with the formula where diamine is condensed at one end with salicylaldehyde or acetophenone and at the other end with diketone. The reaction can be shown as follows :



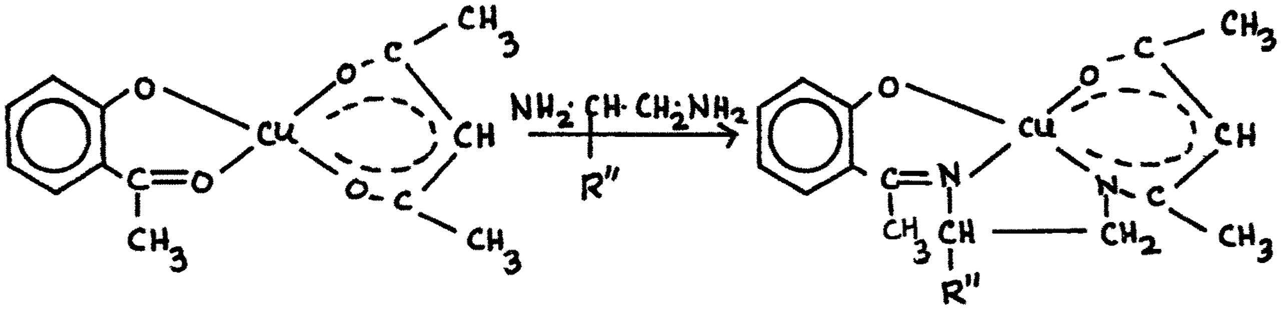
(i) $R'' = H$ or CH_3.

IV



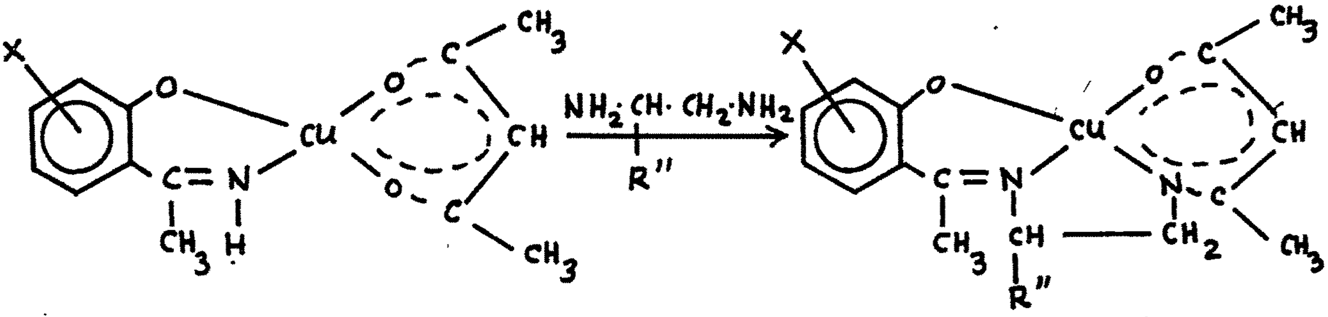
(i) $R'' = H$ or CH_3.

IV



(i) $R'' = H$ or CH_3.

IV



IV

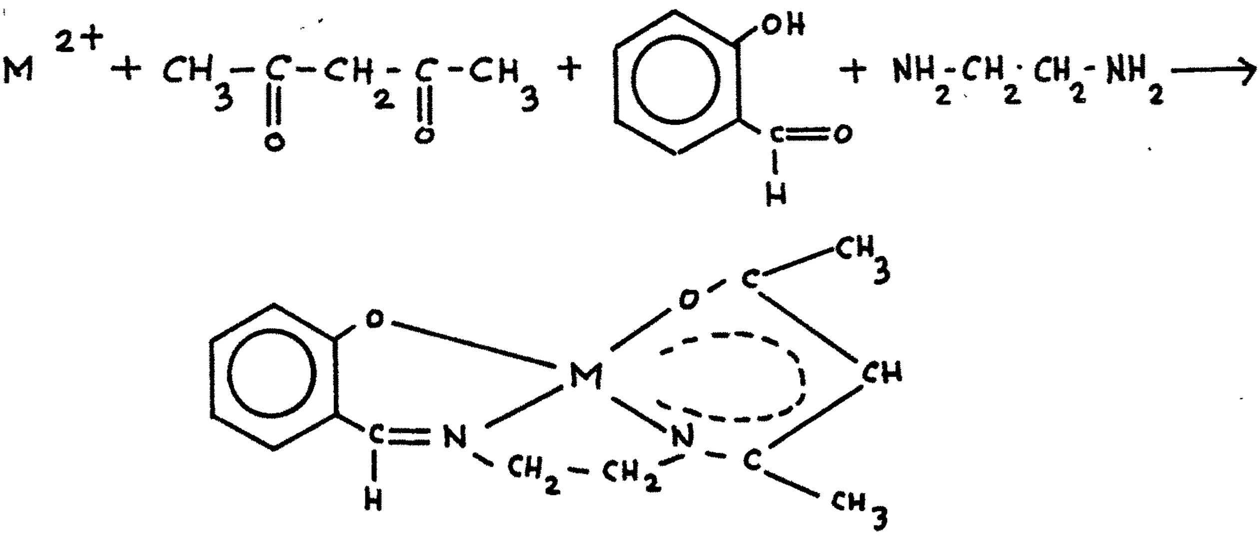
(i) X = H or 3- Me. (ii) R'' = H or CH_3.

The mechanism of the reaction of the diamine is same as in case of alkylamine. It undergoes condensation with the coordinated β-diketone also. This is because the diamines are strong bases. Further on condensation of one of the $-NH_2$ group of the diamine with salicylaldehyde, the other end comes close to the diketone and hence chances of collision are more, resulting in condensation with $C=O$ of the diketone. The above compound could also be prepared by addition of salicylaldehyde, acetylacetone and metal to an equivalent quantity of ethylenediamine. The method was adopted for the preparation of N-N'-ethylene(salicylideneaminato,acetylacetoniminato)Ni(II). The mechanism could be explained on the basis of template effect.

In case of benzoylacetone and dibenzoylmethane the reaction of diamine on compound I or compound II did not give compound with definite proportion.

Cu(II) complex of Schiff base of acetylacetone has been prepared earlier by mixing Cu(II), acetylacetone and ethylenediamine in 1:2:1 ratio respectively.[24] The complex

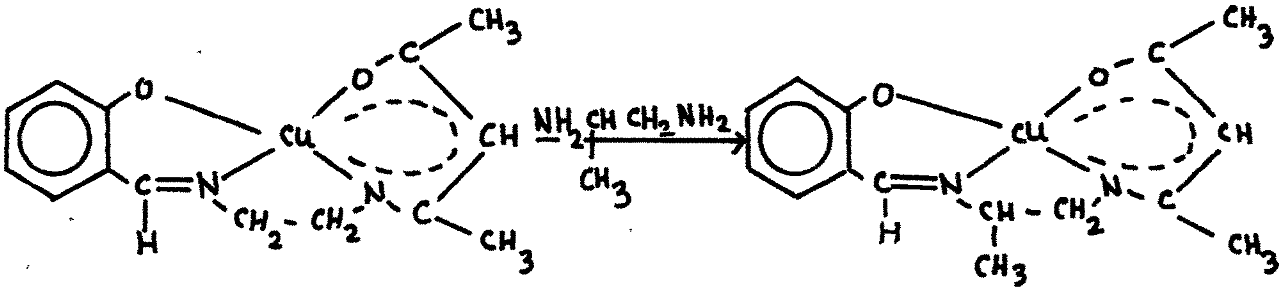
N-N'-ethylene(salicylideneaminato,acetylacetoniminato) Ni(II) has been prepared similarly and the reaction can be shown as follows :



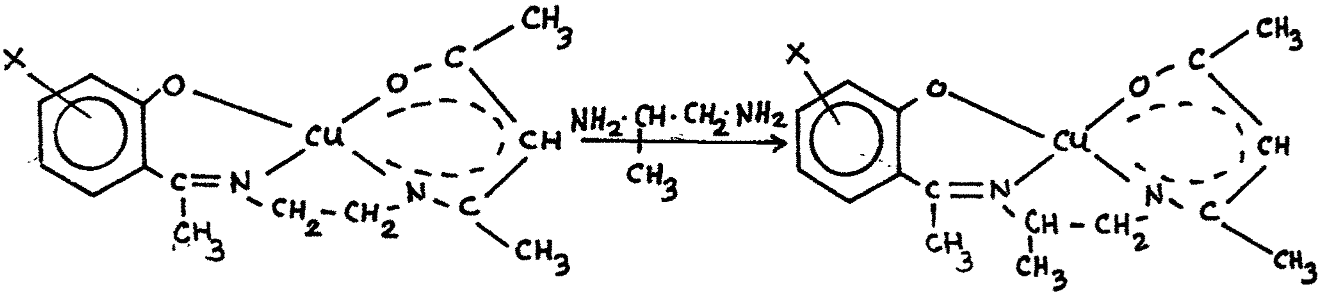
(i) M = Cu(II) or Ni(II)   V

The fact that acetylacetone in compound I does not undergo condensation with ammonia or primary amines can be explained by considering that, ammonia is a weaker base compared to the diamine.

It is interesting to see that when the ethylenediamine Schiff base complex (IV) is treated with propylenediamine, the compound slowly changes to give the propylenediamine Schiff base complex. The reaction can be shown as follows :



VI



VI

(i) X = H or 3-Me.

Spectral and Magnetic properties of complexes :

The Cu(II) complexes are paramagnetic having magnetic moment corresponding to one unpaired electron (~1.9 B.M.). This rules out the probability of metal-metal interaction and polymerisation.

The visible spectra show a broad band at ~560 nm (en and pn compounds) and ~650 nm (amine and mixed complexes). This broad band is a combination of $^2B_{1g} \rightarrow {}^2A_{1g}$; $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_{1g}$; transitions,[25] corresponding to D_{4h} symmetry, most probably square planar in these cases.

Ni(II) square planar complexes are expected to be diamagnetic. The present Ni(II) complexes, however, exhibit paramagnetism. Paramagnetism could be attributed to oxygen bridging in these complexes,[26,27,28] leading to distorted octahedral structure.

The visible spectra of Ni(II) complexes in chloroform exhibit shoulders at ~550 nm. There is no band beyond ~600 nm proving it to be a square planar structure in solution. This may be because polymerisation breaks in solution.

In IR spectra of all compounds bands in the region

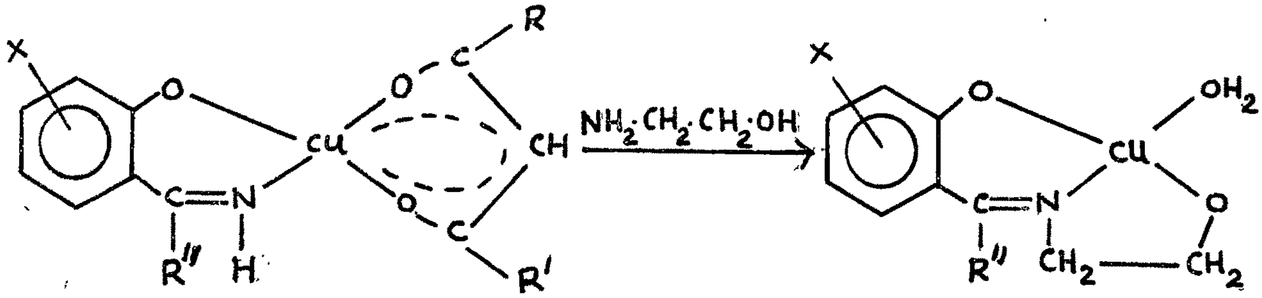
$\sim$3400 cm^{-1} is absent indicating that the O-H hydrogen of the aldehyde or ketone or the Schiff base gets dissociated after complexation. In compound I the band $\sim$1625 cm^{-1} corresponds to aldehyde or acetophenone C=O and a band $\sim$1580 cm^{-1} corresponds to $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ of acetylacetone in which there is delocalisation of π electrons. In the spectra of compound II the band at $\sim$1625 cm^{-1} disappears and a band at $\sim$1600 cm^{-1} corresponding to C=N stretch appears. The band corresponding to ketonic $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ at $\sim$1580 cm^{-1} is retained indicating that only salicylaldehyde undergoes condensation. There is also a band at $\sim$3300 cm^{-1} corresponding to N-H stretching frequency. This band is, however, absent in the N-alkylamine compounds and ethylenediamine and propylenediamine compounds. The absence of N-H stretching frequency in the diamine compounds shows that both NH_2 ends undergo condensation. The band at $\sim$1580 cm^{-1} corresponding to $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ ketonic stretch disappears and there is appearance of a band at $\sim$1540 cm^{-1} corresponding to $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ stretch, due to condensation of acetylacetone with ethylenediamine.

Reactions of mixed ligand complexes with N-hydroxyalkylamine:

Metal analysis, elemental analysis and TLC analysis have proved that the present compounds are mixed ligand complexes. However, in order to study the mixed ligand nature of the present complexes, they have been treated with monoethanolamine.

Such reactions have been carried out earlier in our laboratory[29] on bis salicylideneaminato Cu(II) and Ni(II). It has been observed that in Cu(II) complexes one of the salicylaldehyde molecules forms a tridentate ligand with monoethanolamine and occupies three positions around the Cu(II) ion; the fourth being coordinated with water. The other salicylaldehyde is removed. In case of Ni(II) complexes, however, both the salicylaldehyde molecules undergo condensation with monoethanolamine.

In the present case of Cu(II) mixed Schiff base complexes, the aldehyde or the acetophenone part reacts with monoethanolamine to form a tridentate ligand and gets bound to copper, the fourth being occupied by a water molecule. The β-diketone part is, however, removed. The reaction can be shown as follows :



VII

(i) $R = R' = CH_3$

(ii) $R = CH_3$; $R' = C_6H_5$

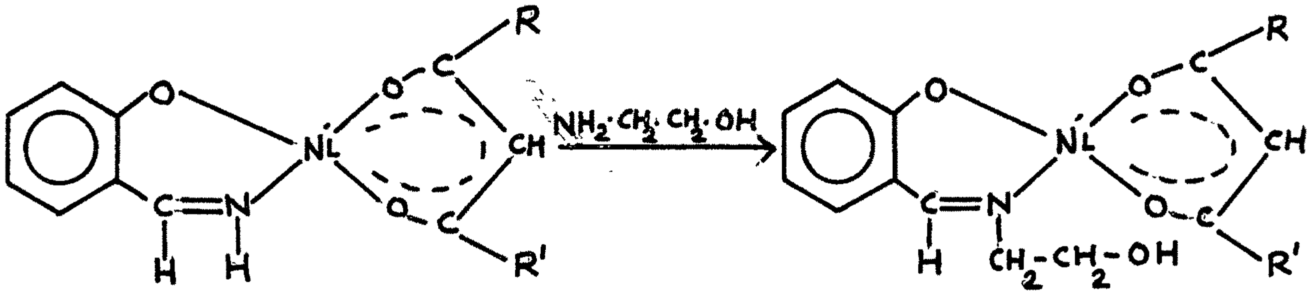
(iii) $R = R' = C_6H_5$.

(iv) $R''' = H$ or CH_3

(V) X = H or 3-Me.

Similar monomeric complexes of tridentate ligand with solvent molecule occupying fourth position has been observed earlier.[30-35] Chakravorty and coworkers[36] have also observed that mixed ligand complexes of Cu(II) containing salicylaldehyde and N-N-diethyl ethylenediamine Schiff base of salicylaldehyde reacts with acid to remove the salicylaldehyde part and results in the complex of tridentate Schiff base with water at fourth position. The H^+ ion attacks the phenolic -O of one salicylaldehyde reforming -OH and salicylaldehyde is detached from the complex. A similar mechanism could be thought to be operating in these complexes, which causes the rupture of the diketone.

In case of Ni(II) complexes, also, the salicylaldehyde condenses with monoethanolamine to form tridentate ligand. However, the β-diketone part is also retained though it does not undergo condensation, with monoethanolamine. Thus all the four equatorial positions around Ni(II) remain occupied. The -OH group of the N-hydroxy ethylene salicylideneamine remains uncoordinated, because the Schiff base with C=N bond cannot occupy positions in two different planes.[37,38] The reaction can be shows as follows :



VII

(i) $R = CH_3$; $R' = C_6H_5$ (ii) $R = R' = C_6H_5$

The reason why the diketone is removed in case of Cu(II) and retained in case of Ni(II) may be due to the difference in the stereochemistry of Cu(II) and Ni(II) complexes.

TLC analysis have shown the compounds to be pure.

The results of metal and elemental analysis agree with the suggested structures. The complexes obtained are insoluble in water and soluble in organic solvents. They are found to be non-conducting indicating non-electrolyte nature.

The Cu(II) compounds exhibit a broad band $\sim$600 nm. They are paramagnetic having magnetic moment corresponding to one unpaired electron. The Ni(II) complexes are paramagnetic. It is due to the weak coordination of the -OH group of the Schiff base with vacant fifth and sixth positions around the metal ion in other complex molecules. This results in polymerisation and formation of distorted octahedral structure in solid state and accounts for paramagnetism.

The visible spectra of Ni(II) in chloroform exhibits shoulders at $\sim$550 nm. There is no band beyond $\sim$600 nm proving it to be a square planar structure in solution. This may be because polymerisation breaks in solution.

The IR spectra of compound VI exhibits a broad band in the region 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 O-H out of plane deformation mode. This indicates the presence of coordinated water. The compound also exhibits normal paramagnetism expected for one unpaired electron.

The IR spectra of compound VII exhibits a band $\sim$3400cm^{-1} corresponding to -OH stretching frequency. This shows that the -OH of the bridging ethanolamine has weak coordination and hence the H^{+} does not get dissociated. Besides, the compounds also exhibit bands in the region $\sim$1600 cm^{-1} and $\sim$1580 cm^{-1}

corresponding to $\mathrm{C{=}N}$ and $\mathrm{C}\overset{\cdots\cdots}{\text{——}}\mathrm{O}$ of diketone, respectively; indicating thereby that the diketone is retained.

Table V-1 : Analytical data, electronic spectral band and magnetic moments of Cu(II) ternary complexes.

No.	Name of the complex	Analytical data %								λ max	μ_{eff}
		Calculated				Found					
		Cu	C	H	N	Cu	C	H	N	in nm	in B.M.
1	(Salicylaldehydato,acetylacetonato)Cu(II)	22.40	50.78	4.23	-	22.40	50.45	4.03	-	650	1.90
2	(Salicylaldehydato,benzoylacetonato)Cu(II)	18.39	59.00	4.05	-	18.47	58.79	3.89	-	650	1.90
3	(2-Hydroxyacetophenonato,acetylacetonato)Cu(II)	21.36	52.43	4.70	-	21.57	51.92	4.68	-	660	1.96

Table V-2 : Analytical data, electronic spectral band and magnetic moments of Cu(II) and Ni(II) ternary Schiff base complexes.

No.	Name of the complex	Analytical data %									
		Calculated				Found				λmax	μ_{eff}
		M	C	H	N	M	C	H	N	in nm	in B.M.
1	(Salicylideneaminato,acetyl-acetonato)Cu(II)	22.48	-	-	4.95	22.43	-	-	4.96	660	1.78
1a	(Salicylideneaminato,acetyl-acetonato)Cu(II)	22.48	-	-	4.95	22.50	-	-	4.94	660	1.76
2	(Salicylideneaminato, benzoylacetonato)Cu(II)	18.44	-	-	4.06	18.59	-	-	4.12	630	1.94
2a	(Salicylideneaminato, benzoylacetonato)Cu(II)	18.44	-	-	4.06	18.36	-	-	4.13	630	1.87
3	(Salicylideneaminato, benzoylacetonato)Ni(II)	17.28	-	-	4.12	17.09	-	-	4.08	550	2.59
4	(Salicylideneaminato,di-benzoylmethanato)Cu(II)	15.63	-	-	3.44	15.49	-	-	3.56	640	1.88
5	(Salicylideneaminato,di-benzoylmethanato)Ni(II)	14.61	-	-	3.48	14.53	-	-	3.24	550	2.57

contd....

6	[1-(2-Hydroxy-phenyl) ethylideneaminato,acetyl-acetonato] Cu(II)	21.43	-	-	4.72	21.43	-	-	4.61	630	1.87
6a	[1-(2-Hydroxy-phenyl) ethylideneaminato,acetyl-acetonato] Cu(II)	21.43	-	*	4.72	21.37	-	-	4.58	630	1.90
7	[1-(2-Hydroxy-m-tolyl) ethylideneaminato,acetyl-acetonato] Cu(II)	20.40	-	-	4.49	20.31	-	-	4.42	660	1.91

a = from mixed complex.

Table V-3 : Analytical data, electronic spectral band, and magnetic moments of Cu(II) and Ni(II) N-alkylamine Schiff base ternary complexes.

No.	Name of the complex	Analytical data %									
		Calculated				Found				λmax	μ_{eff}
		M	C	H	N	M	C	H	N	in nm	in B.M.
1a	(N-Methylsalicylideneaminato,acetylacetonato)Cu(II)	21.43	-	-	4.72	21.32	-	-	4.52	650	1.76
1a'	(N-Methylsalicylideneaminato,acetylacetonato)Cu(II)	21.43	-	-	4.72	21.52	-	-	4.54	650	1.70
2a	(N-Ethylsalicylideneaminato,acetylacetonato)Cu(II)	20.46	-	-	4.51	20.25	-	-	4.24	640	1.80
2a'	(N-Ethylsalicylideneaminato,acetylacetonato)Cu(II)	20.46	-	-	4.51	20.15	-	-	4.33	640	1.75
3a	(N-Methylsalicylideneaminato,benzoylacetonato) Cu(II)	17.71	-	-	3.90	17.54	-	-	3.81	630	1.93
3a'	(N-Methylsalicylideneaminato,benzoylacetonato) Cu(II)	17.71	-	-	3.90	17.61	-	-	3.83	630	1.87
4a	(N-Ethylsalicylideneaminato,benzoylacetonato) Cu(II)	16.44	-	-	3.62	16.33	-	-	3.54	640	1.87

contd..

4a'	(N-Ethylsalicylideneaminato, benzoylacetonato) Cu(II)	16.44	-	-	3.62	16.59	-	-	3.57	640	1.88
5a'	(N-Methylsalicylideneaminato, benzoylacetonato) Ni(II)	16.59	-	-	3.96	16.67	-	-	3.73	560	3.10
6a'	(N-Ethylsalicylideneaminato, benzoylacetonato) Ni(II)	15.38	-	-	3.67	15.55	-	-	3.75	560	2.92
7a'	(N-Methylsalicylideneaminato, dibenzoylmethanato) Cu(II)	15.11	-	-	3.33	15.03	-	-	3.16	650	1.89
8a'	(N-Ethylsalicylideneaminato, dibenzoylmethanato) Cu(II)	14.17	-	-	3.12	14.36	-	-	3.09	650	1.89
9a'	(N-Methylsalicylideneaminato, dibenzoylmethanato) Ni(II)	14.12	-	-	3.37	14.26	-	-	3.46	540	3.13
10a'	(N-Ethylsalicylideneaminato, dibenzoylmethanato) Ni(II)	13.23	-	-	3.16	13.12	-	-	3.28	560	2.91
11a	[N-Methyl-1-(2-hydroxyphenyl)ethylideneaminato, acetylacetonato] Cu(II)	20.46	-	-	4.50	20.51	-	-	4.46	640	1.88
11a'	[N-Methyl-1-(2-hydroxyphenyl)ethylideneaminato, acetylacetonato] Cu(II)	20.46	-	-	4.50	20.73	-	-	4.39	640	1.90

contd...

12a	[N-Ethyl-1-(2-hydroxyphenyl)ethylideneaminato, acetylacetonato]Cu(II)	19.58	-	-	4.31	19.38	-	-	4.26	630	1.86
12a'	[N-Ethyl-1-(2-hydroxyphenyl)ethylideneaminato, acetylacetonato]Cu(II)	19.58	-	-	4.31	19.43	-	-	4.40	630	1.89
13a'	[N-Methyl-1-(2-hydroxy-m-tolyl)ethylideneaminato, acetylacetonato]Cu(II)	19.52	-	-	4.30	19.36	-	-	4.25	640	1.92
14a'	[N-Ethyl-1-(2-hydroxy-m-tolyl)ethylideneaminato, acetylacetonato]Cu(II)	18.72	-	-	4.12	18.83	-	-	4.06	630	1.89

a = from mixed complex

a' = imine exchange

Table V-4 : Analytical data, electronic spectral band and magnetic moments of Cu(II) and Ni(II) ternary diamine Schiff base complexes.

No.	Name of the complex	Analytical data %									
		Calculated				Found				λ max	μ_{eff}
		M	C	H	N	M	C	H	N	in nm	in B.M.
1a	N,N'-ethylene(salicylideneaminato,acetylacetoniminato)Cu(II)	20.73	-	-	9.13	20.45	-	-	8.83	560	1.80
1a'	N,N'-ethylene(salicylideneaminato,acetylacetoniminato)Cu(II)	20.73	-	-	9.13	20.44	-	-	8.69	560	1.82
1a'''	N,N'-ethylene(salicylideneaminato,acetylacetoniminato)Cu(II)	20.73	-	-	9.13	20.65	-	-	8.75	560	1.79
2a'''	N,N-ethylene(salicylideneaminato,acetylacetoniminato)Ni(II)	19.45	-	-	9.28	19.26	-	-	8.93	550	diamagnetic
3a	N,N-propylene(salicylideneaminato,acetylacetoniminato)Cu(II)	19.83	-	-	8.74	19.54	-	-	8.43	570	1.98
3a'	N,N-propylene(salicylideneaminato,acetylacetoniminato)Cu(II)	19.82	-	-	8.74	19.58	-	-	8.39	570	1.95
3a"	N,N'-propylene(salicylideneaminato,acetylacetoniminato)Cu(II)	19.83	-	-	8.74	19.62	-	-	8.34	570	1.89

contd...

4a	N,N'-ethylene[1-(2-hydroxy-phenyl)ethylideneaminato,acetylacetoniminato] Cu(II)	19.76	-	-	8.71	19.59	-	-	8.58	560	1.82
4a'	N,N'-ethylene[1-(2-hydroxy-phenyl)ethylideneaminato,acetylacetoniminato] Cu(II)	19.76	-	-	8.71	19.61	-	-	8.63	560	1.82
5a'	N,N'-ethylene[1-(2-hydroxy-m-tolyl)ethylideneaminato,acetylacetoniminato] Cu(II)	18.89	-	-	8.32	18.96	-	-	8.13	560	1.83
6a	N,N'-propylene[1-(2-hydroxy-phenyl)ethylideneaminato,acetylacetoniminato] Cu(II)	18.94	-	-	8.34	18.78	-	-	8.29	560	1.91
6a'	N,N'-propylene[1-(2-hydroxy-phenyl)ethylideneaminato,acetylacetoniminato] Cu(II)	18.94	-	-	8.34	18.81	-	-	8.19	560	1.94
6a"	N,N'-propylene[1-(2-hydroxy-phenyl)ethylideneaminato,acetylacetoniminato] Cu(II)	18.94	-	-	8.34	18.71	-	-	8.21	560	1.89

contd...

7a'	N,N'-propylene[1-(2-hydroxy-m-tolyl)ethylideneaminato,acetylacetoniminato]Cu(II)	18.13	-	-	7.98	18.26	-	-	7.83	560	1.89
7a"	N,N'-propylene[1-(2-hydroxy-m-tolyl)ethylideneaminato,acetylacetoniminato]Cu(II)	18.13	-	-	7.98	18.08	-	-	7.78	560	1.86

a = from mixed complex ; a' = imine exchange ; a" = en to pn exchange and

a"' = compound formed in equimolar ratio.

Table V-5 : Analytical data, electronic spectral band and magnetic moment of binary and mixed hydroxy alkylamine Schiff base complexes of Cu(II) and Ni(II).

No.	Name of the complex	Analytical data %								λmax	μ_{eff}
		Calculated				Found					
		M	C	H	N	M	C	H	N	in nm	in B.M.
1	(N-Hydroxyethyl-salicylideneaminato)Cu(II).H_2O	25.88	39.29	4.49	5.72	25.57	39.15	4.25	5.85	600	1.75
2	[N-Hydroxyethyl-1-(2-hydroxy-phenyl)ethylideneaminato] Cu(II).H_2O	24.48	41.77	5.02	5.39	24.37	41.52	4.95	5.08	620	1.72
3	[N-Hydroxyethyl-1-(2-hydroxy-m-tolyl)ethylideneaminato] Cu(II).H_2O	23.15	-	-	5.09	23.48	-	-	5.40	620	1.70
4	(N-Hydroxyethyl-salicylideneaminato,benzoylacetonato)Ni(II).	15.30	-	-	3.65	14.98	-	-	3.42	560	2.89
5	(N-Hydroxyethyl-salicylideneaminato,dibenzoylmethanato)Ni(II)	13.17	-	-	3.14	13.54	-	-	3.41	550	2.91

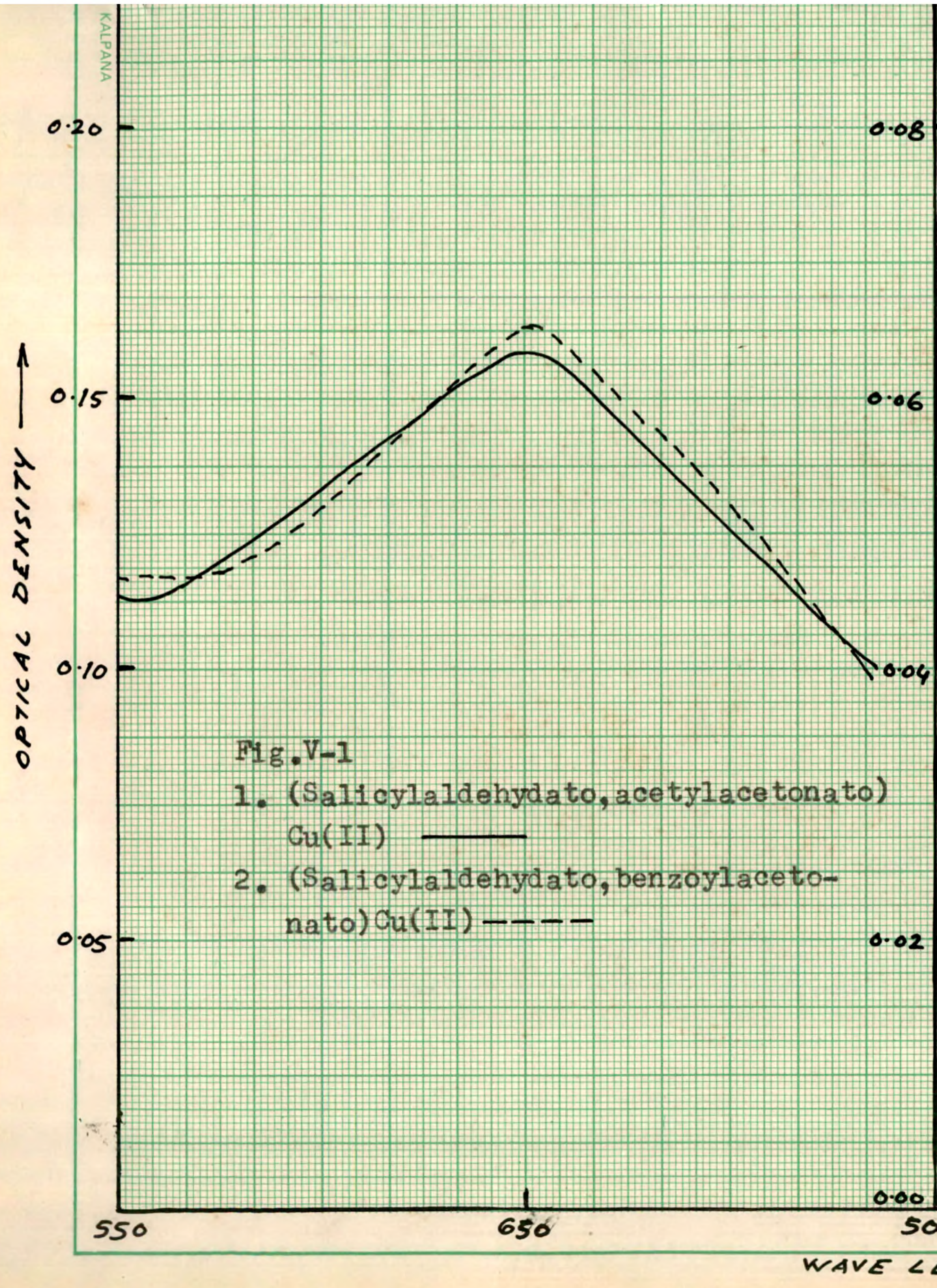


Fig.V-1

1. (Salicylaldehydato,acetylacetonato)Cu(II) ————

2. (Salicylaldehydato,benzoylacetonato)Cu(II) - - - -

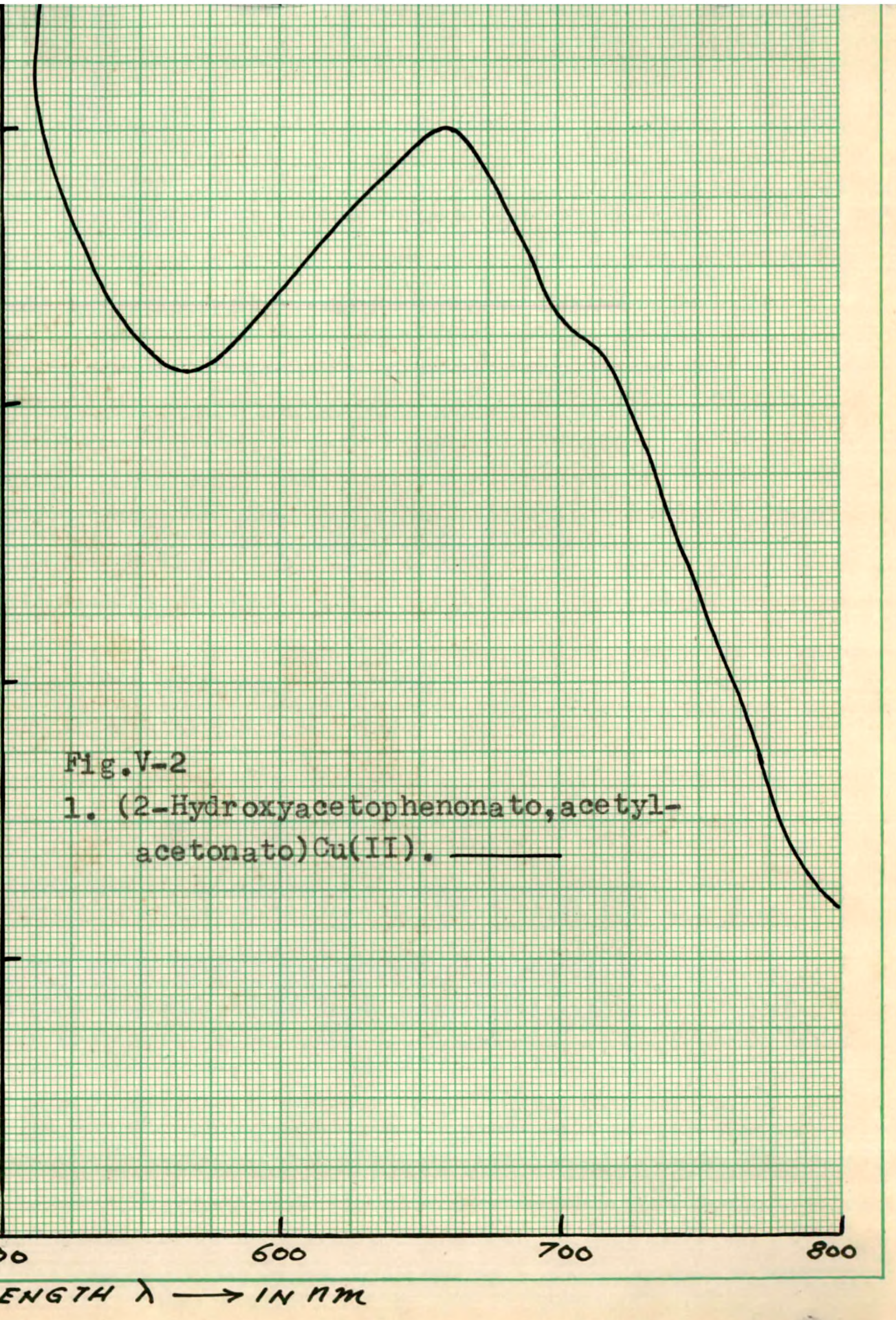


Fig.V-2

1. (2-Hydroxyacetophenonato,acetylacetonato)Cu(II). ————

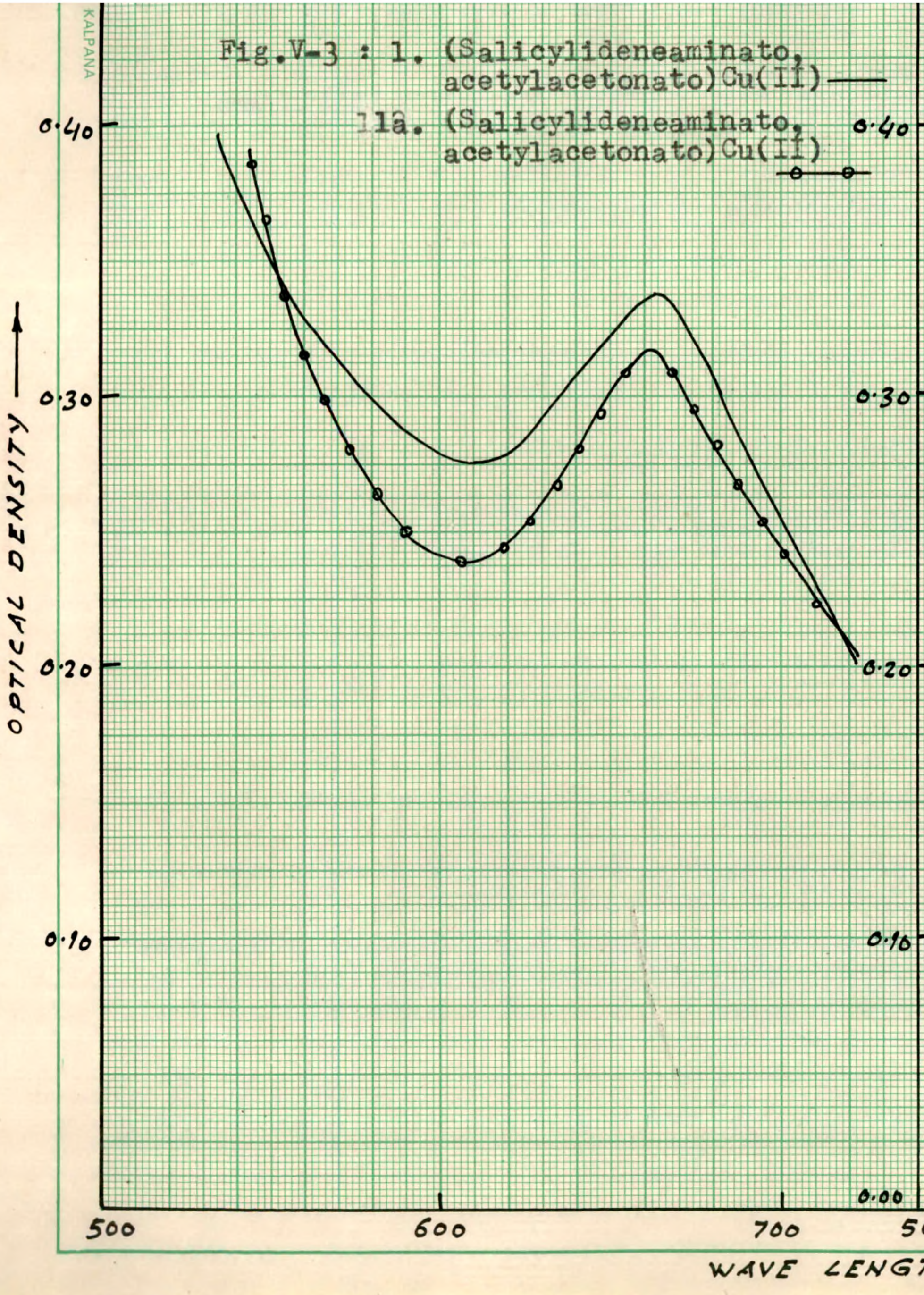


Fig.V-3 : 1. (Salicylideneaminato, acetylacetonato)Cu(II) ——

1a. (Salicylideneaminato, acetylacetonato)Cu(II) —o—o—

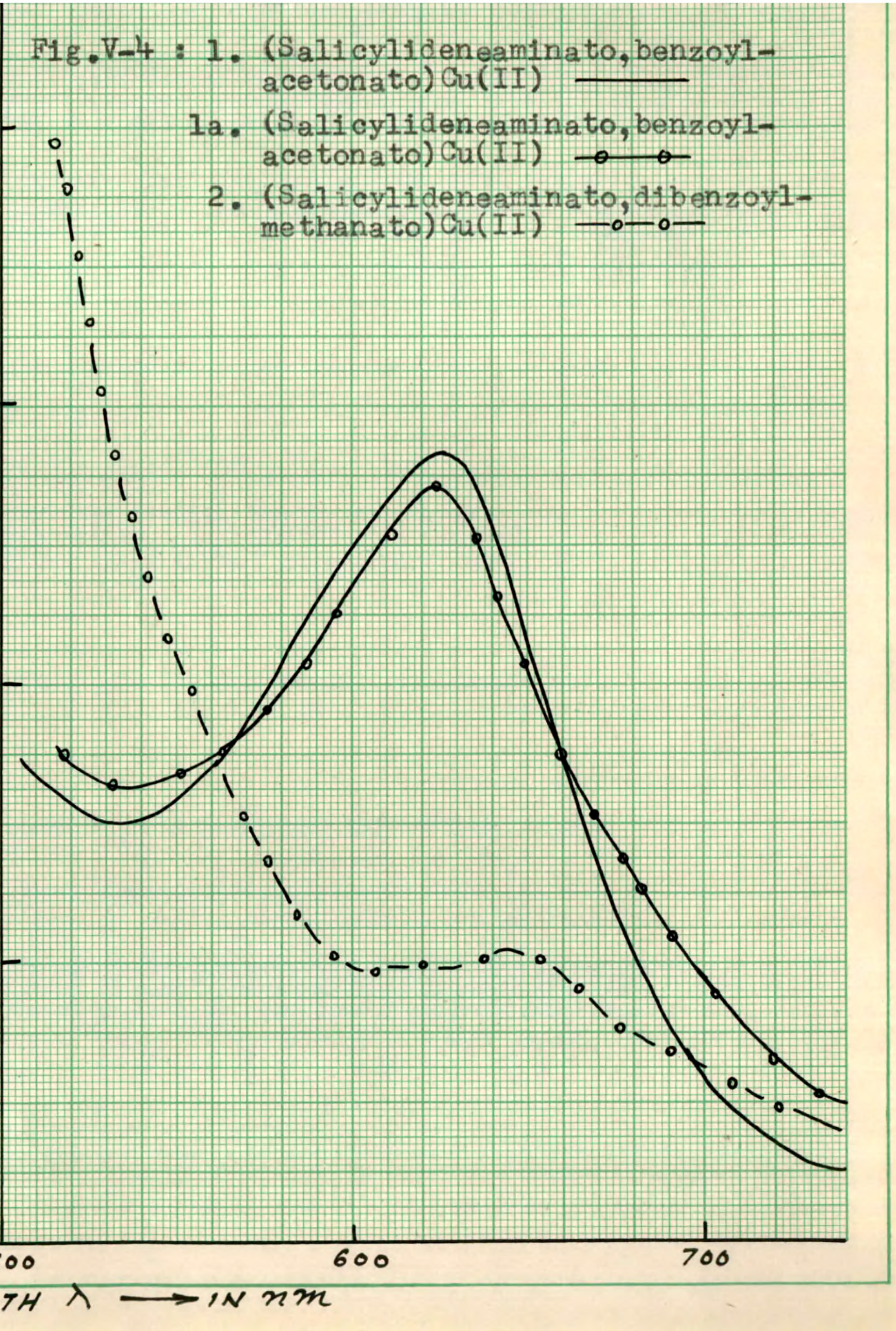


Fig.V-4 : 1. (Salicylideneaminato,benzoylacetonato)Cu(II) ——

1a. (Salicylideneaminato,benzoylacetonato)Cu(II) —o—o—

2. (Salicylideneaminato,dibenzoylmethanato)Cu(II) —o—o—

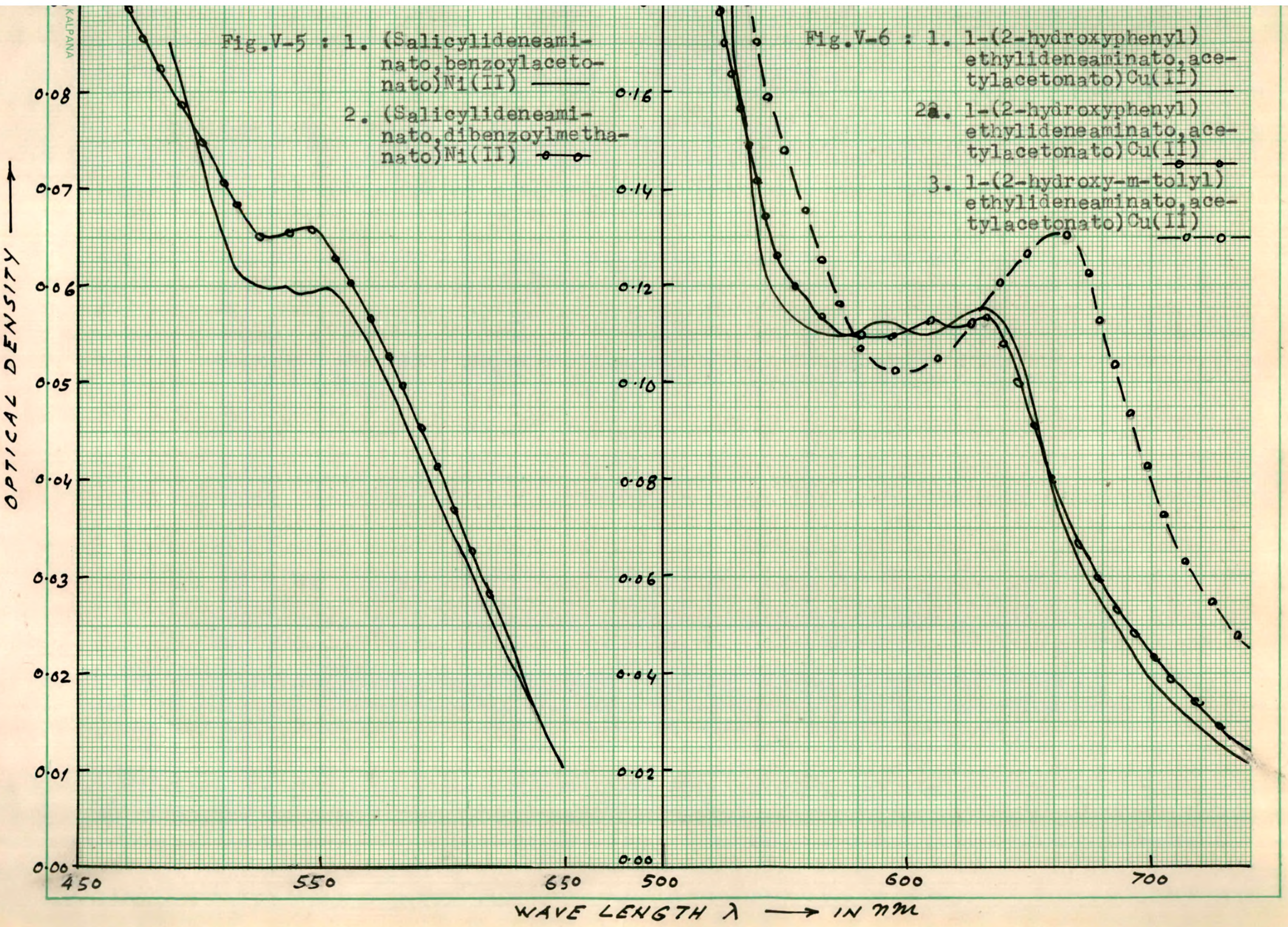


Fig.V-5 : 1. (Salicylideneaminato,benzoylacetonato)Ni(II) ——
2. (Salicylideneaminato,dibenzoylmethanato)Ni(II) —o—o—

Fig.V-6 : 1. 1-(2-hydroxyphenyl)ethylideneaminato,acetylacetonato)Cu(II) ——
2. 1-(2-hydroxyphenyl)ethylideneaminato,acetylacetonato)Cu(II) —o—o—
3. 1-(2-hydroxy-m-tolyl)ethylideneaminato,acetylacetonato)Cu(II) -o-o-

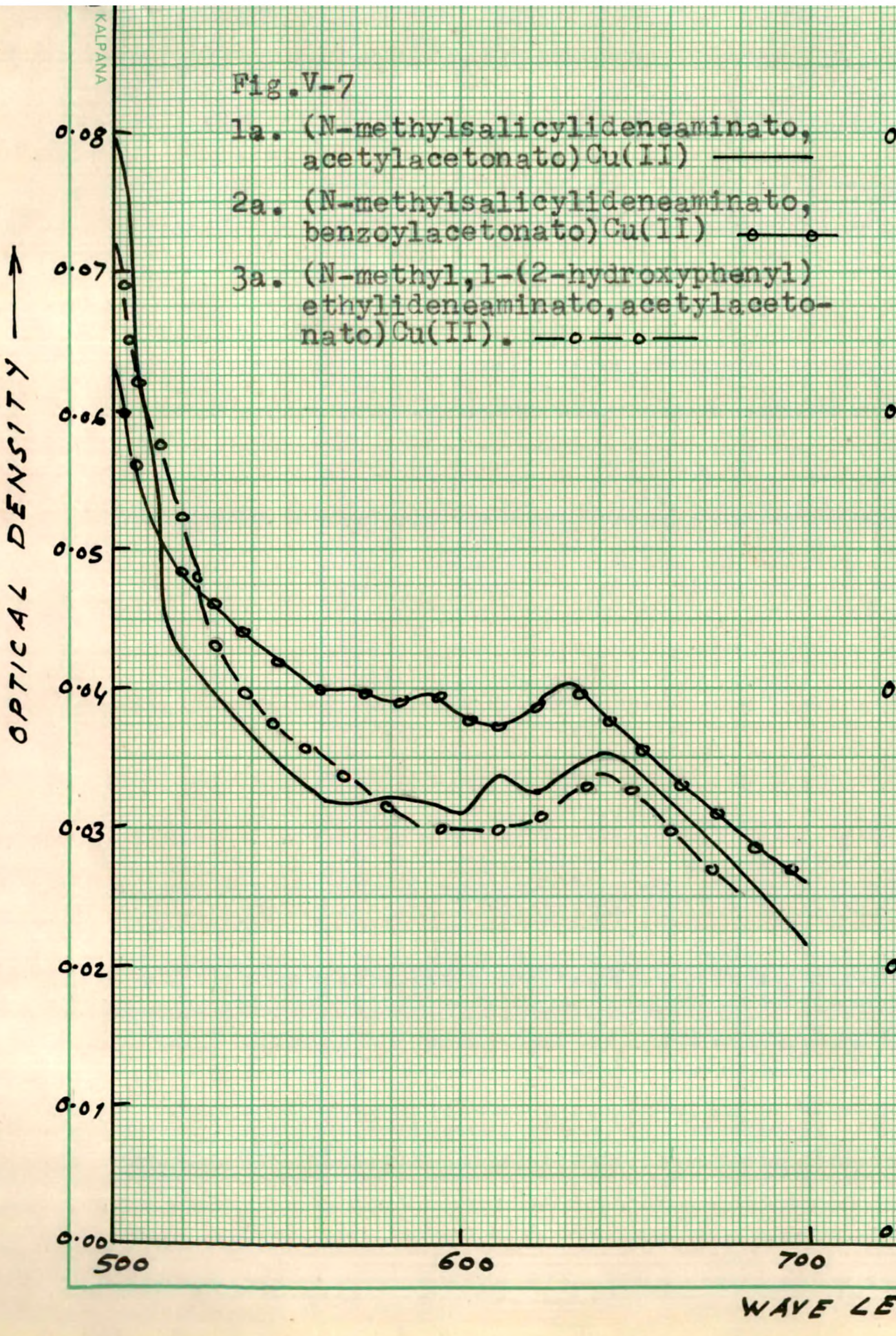


Fig.V-7

1a. (N-methylsalicylideneaminato, acetylacetonato)Cu(II) ———

2a. (N-methylsalicylideneaminato, benzoylacetonato)Cu(II) —o—o—

3a. (N-methyl,1-(2-hydroxyphenyl) ethylideneaminato,acetylacetonato)Cu(II). —o— o —

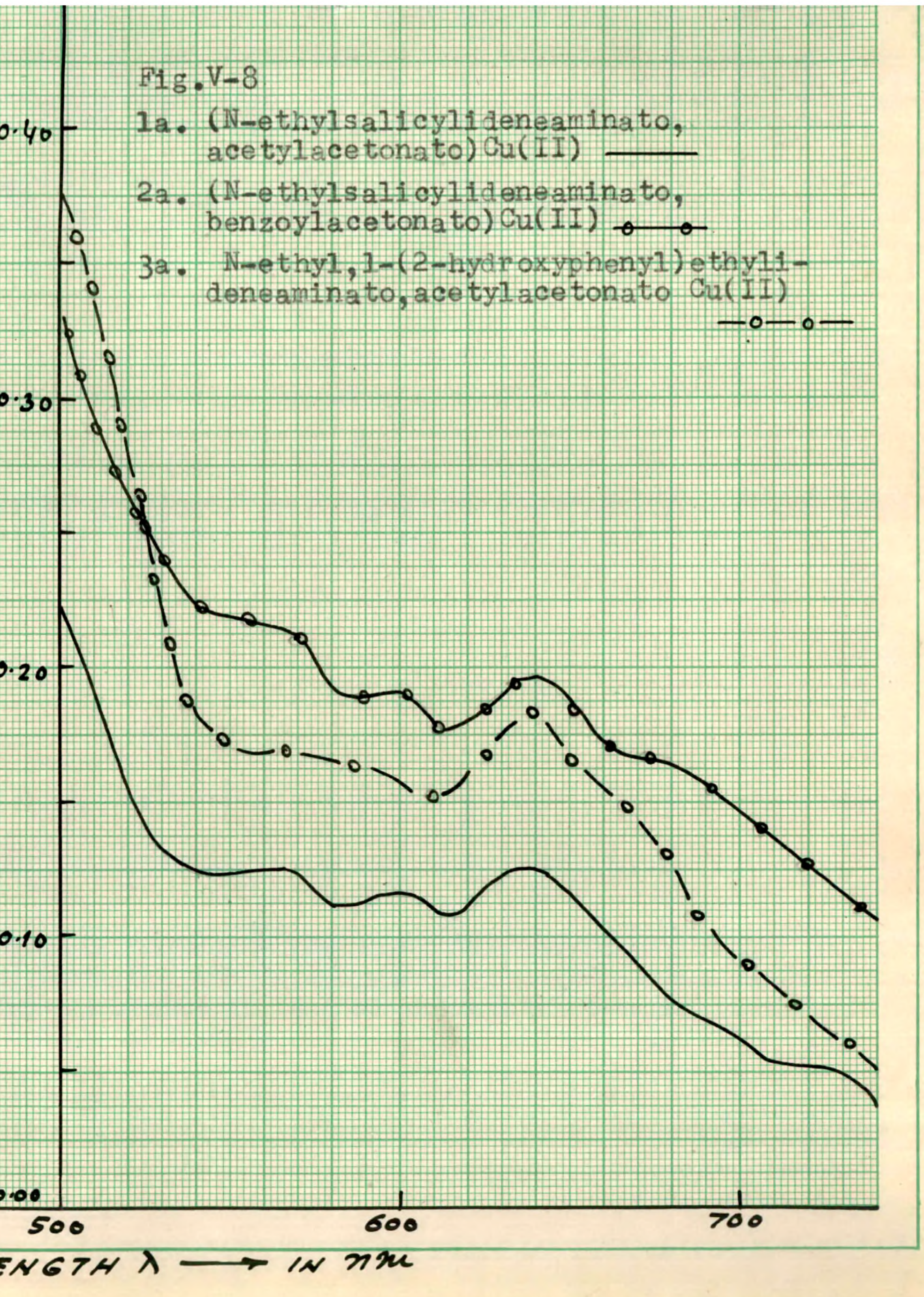


Fig.V-8

1a. (N-ethylsalicylideneaminato, acetylacetonato)Cu(II) ———

2a. (N-ethylsalicylideneaminato, benzoylacetonato)Cu(II) —o—o—

3a. N-ethyl,1-(2-hydroxyphenyl)ethylideneaminato,acetylacetonato Cu(II) —o—o—

Fig.V-9

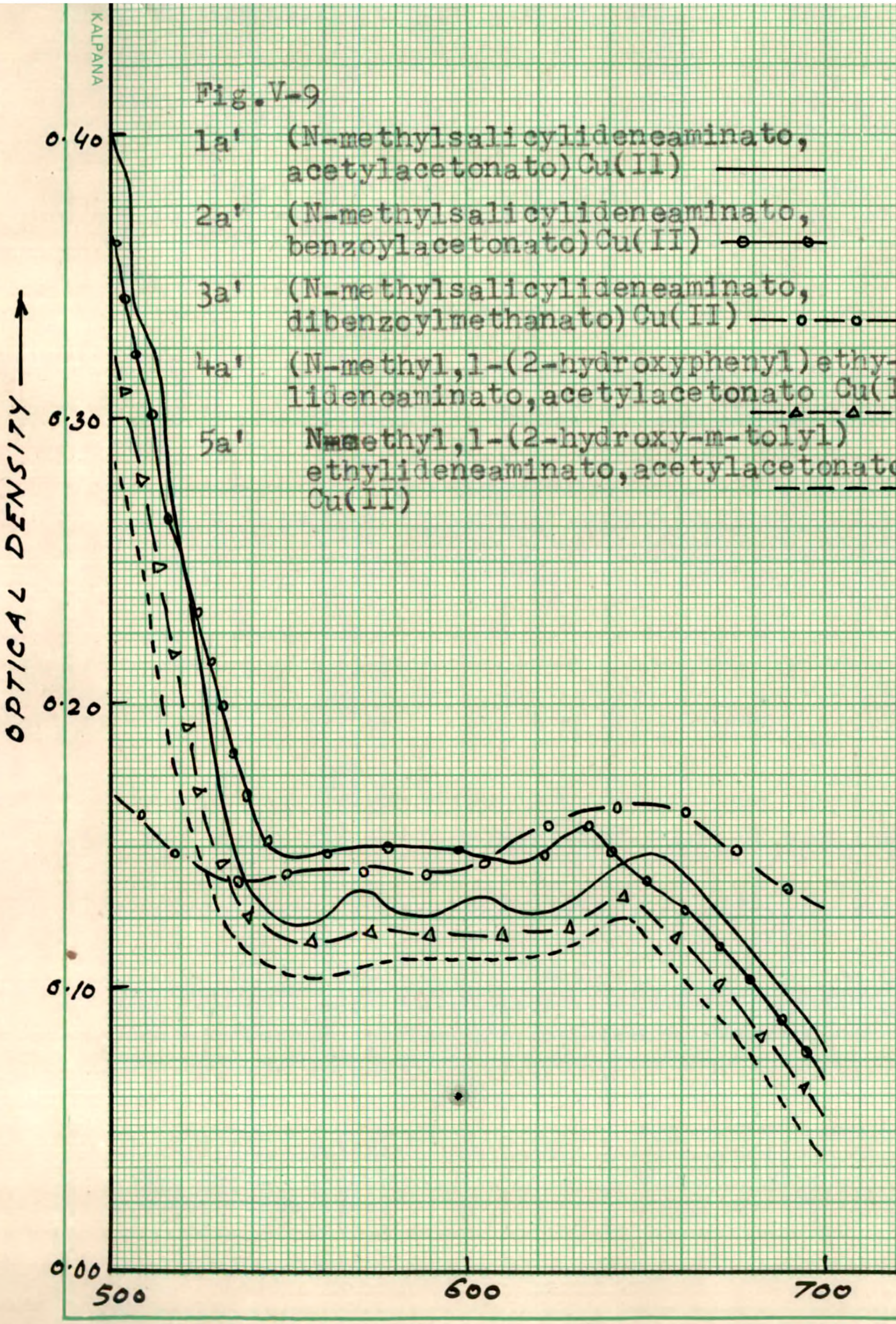
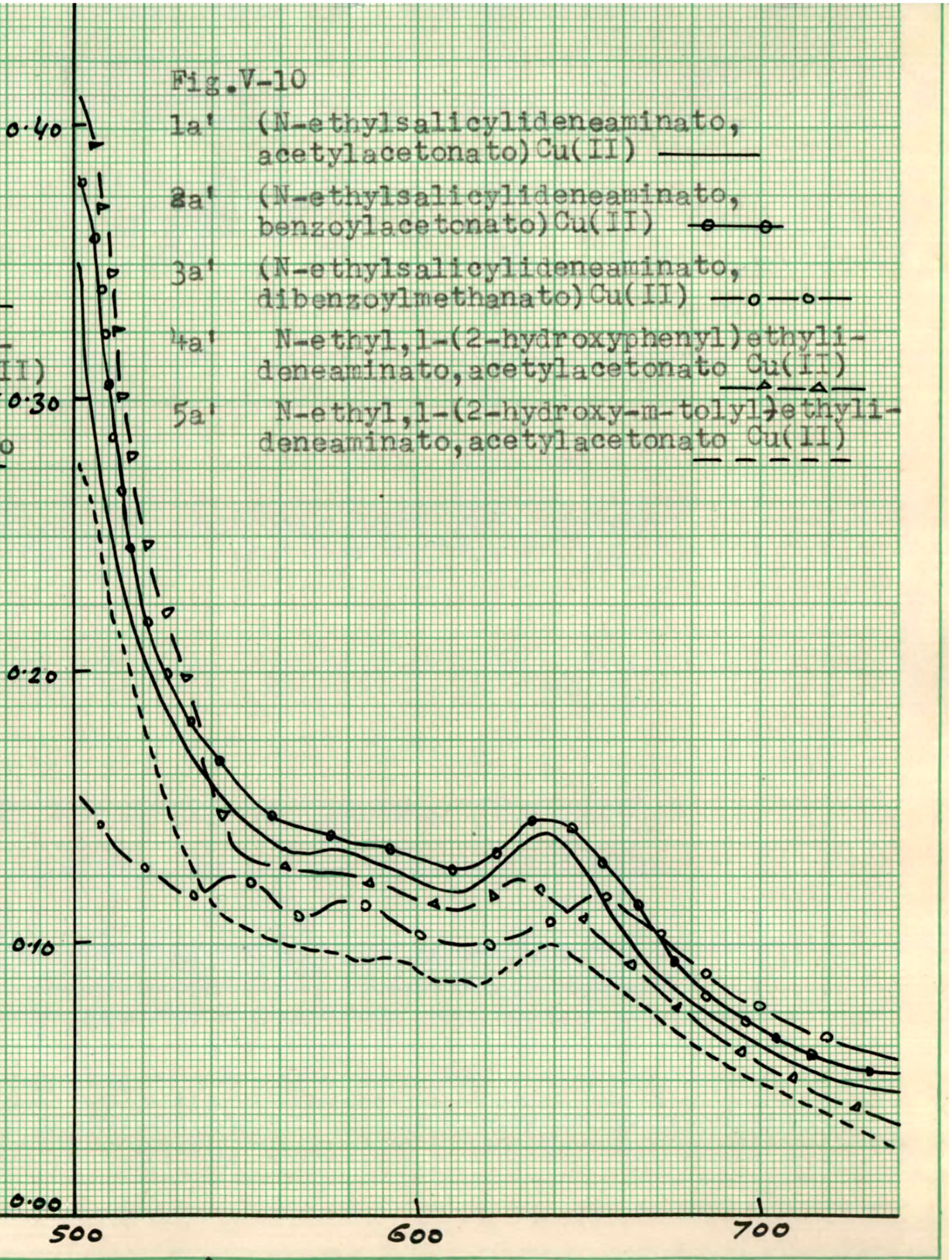


Fig.V-10



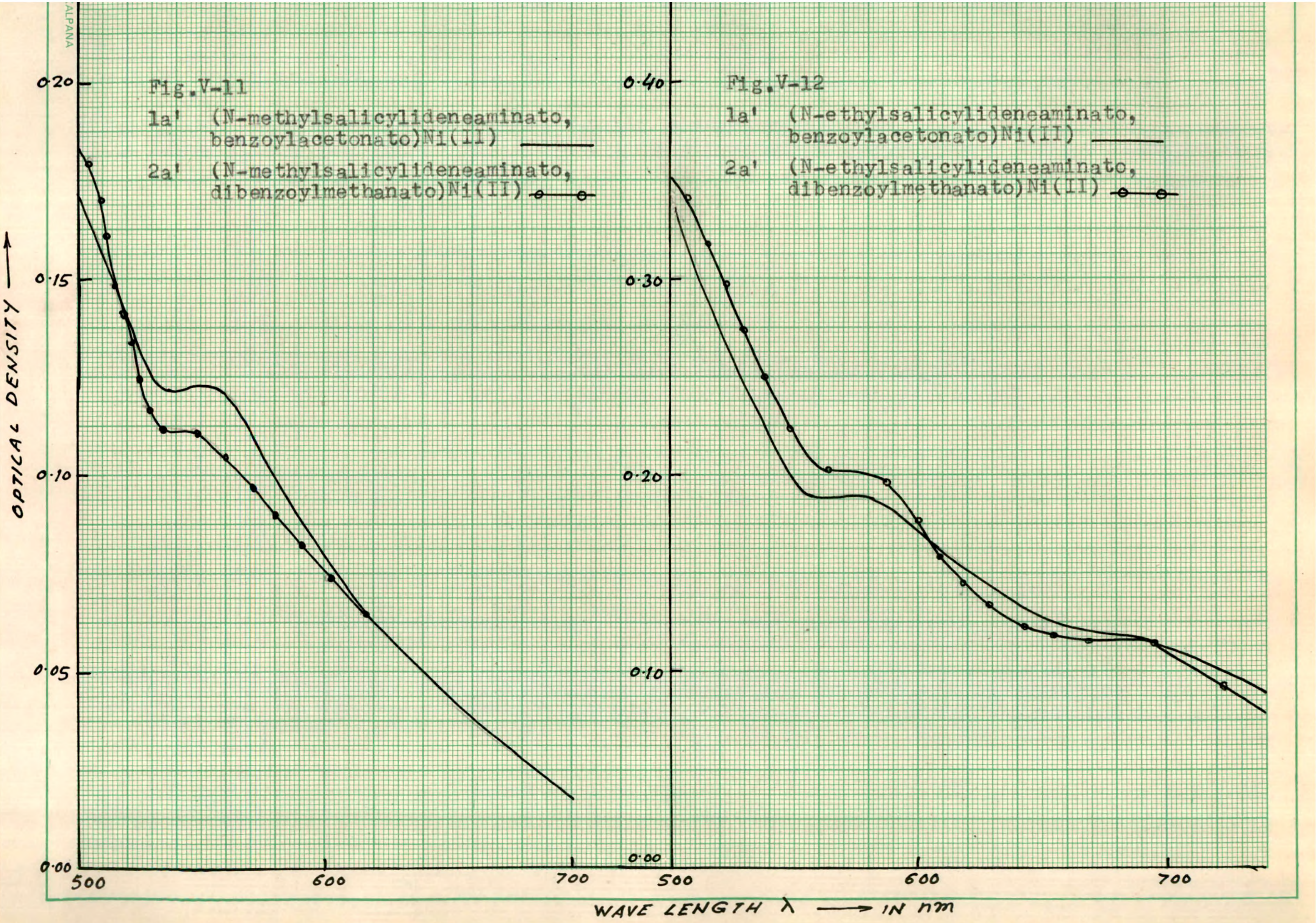


Fig.V-11

Fig.V-12

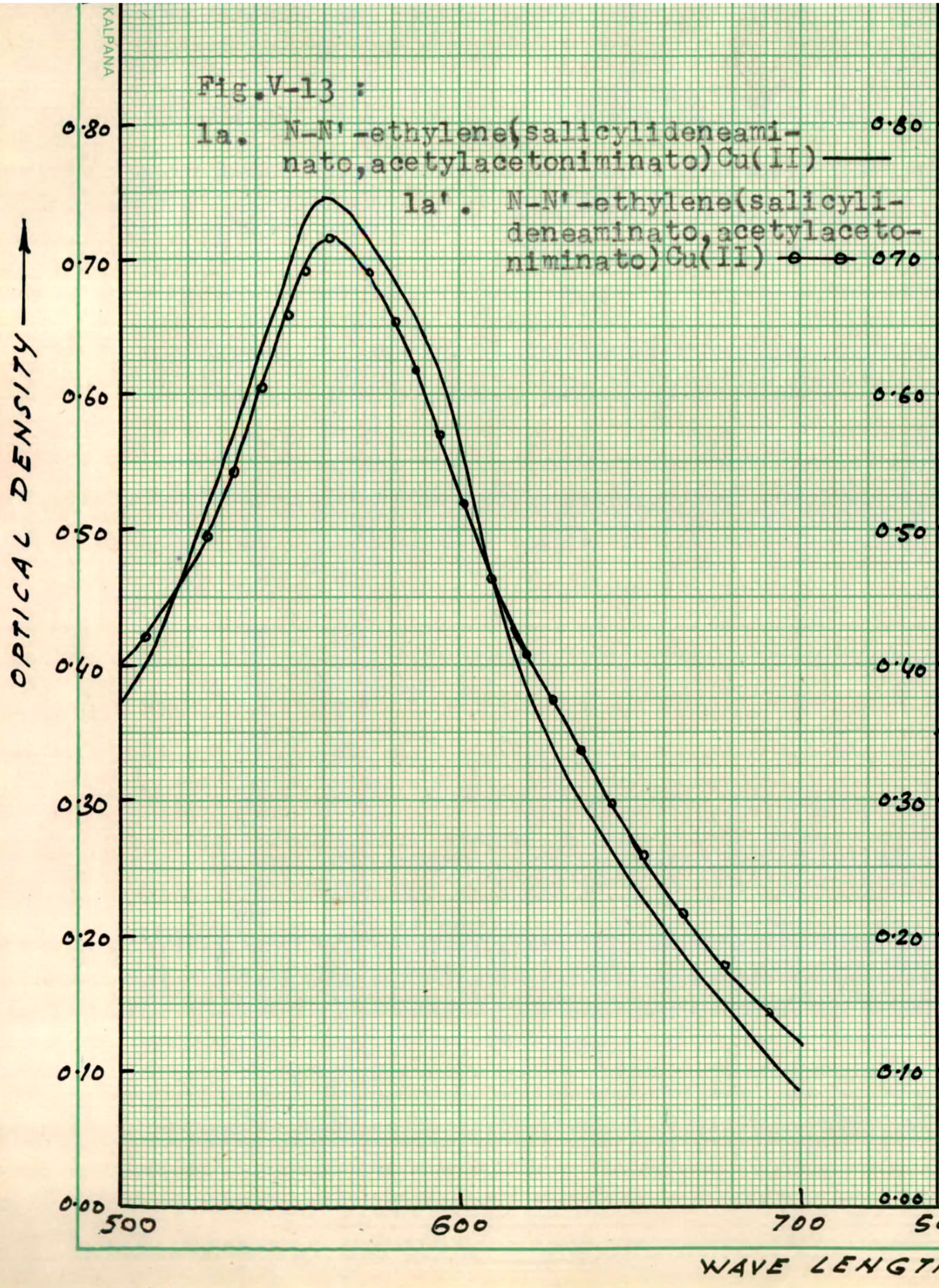


Fig.V-13 :

1a. N-N'-ethylene(salicylideneaminato,acetylacetoniminato)Cu(II) ——

1a'. N-N'-ethylene(salicylideneaminato,acetylacetoniminato)Cu(II) —o—o—

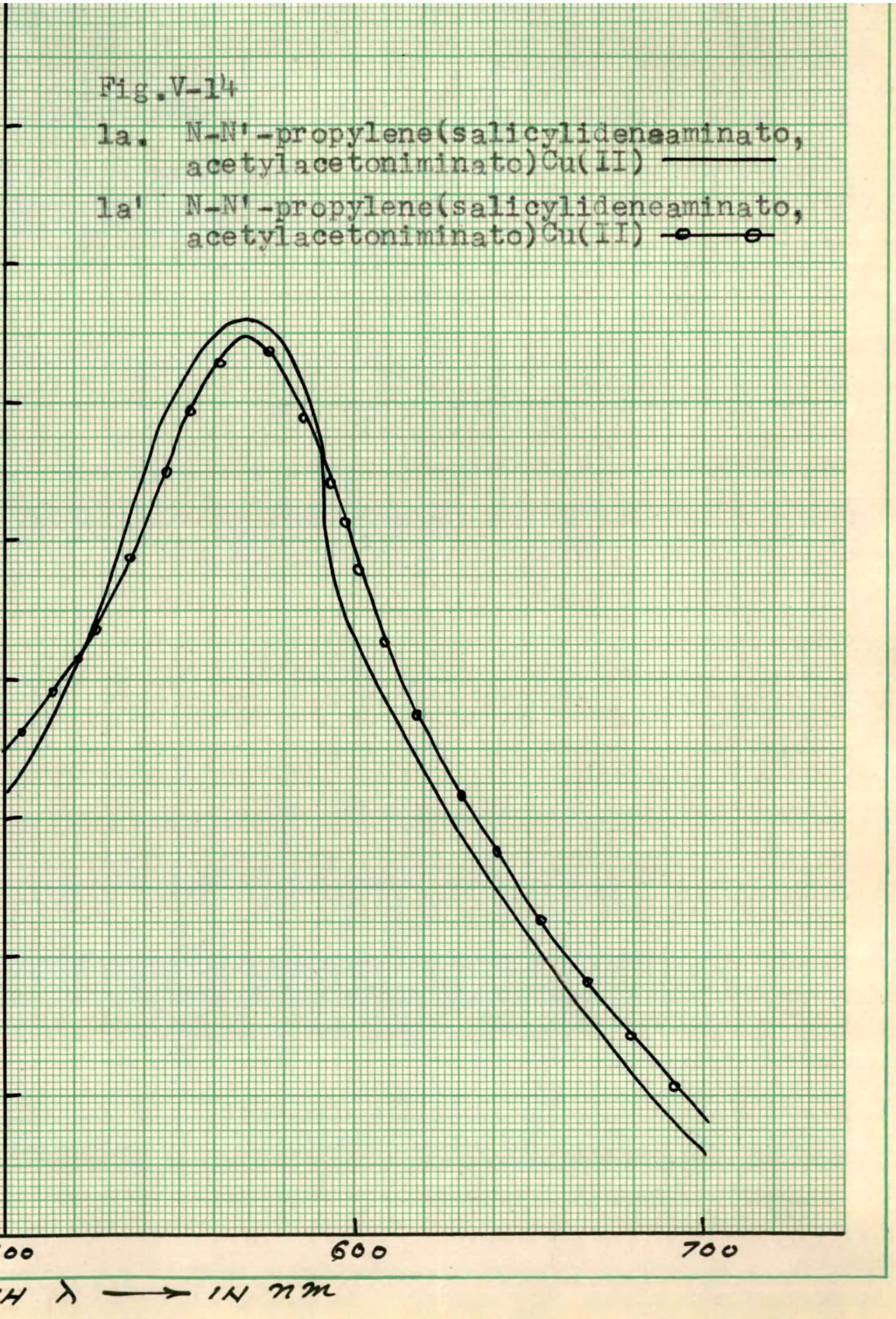


Fig.V-14

1a. N-N'-propylene(salicylideneaminato,acetylacetoniminato)Cu(II) ——

1a' N-N'-propylene(salicylideneaminato,acetylacetoniminato)Cu(II) —o—o—

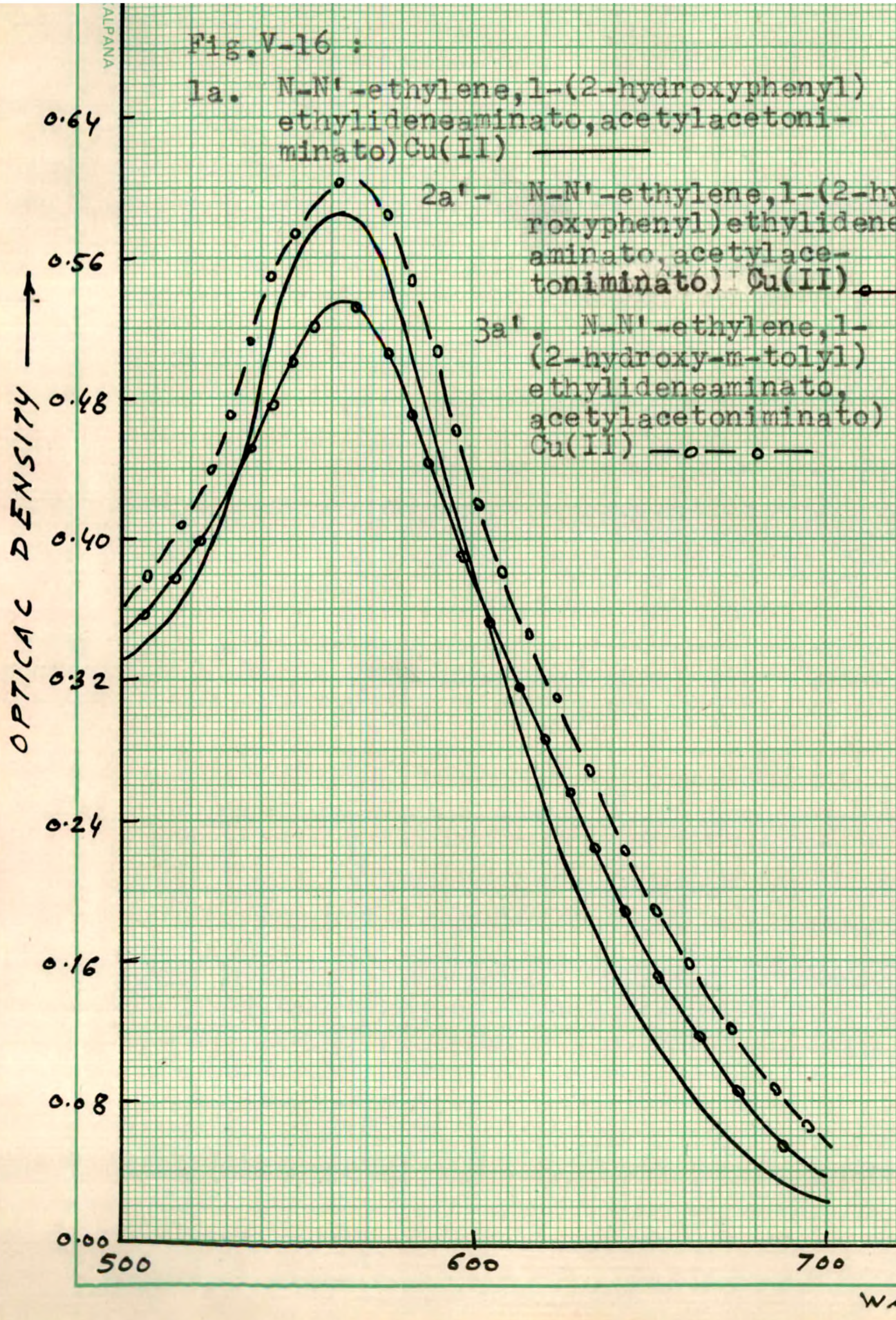


Fig. V-16 :

1a. N-N'-ethylene,1-(2-hydroxyphenyl) ethylideneaminato,acetylacetoniminato)Cu(II) ———

2a'- N-N'-ethylene,1-(2-hydroxyphenyl)ethylideneaminato,acetylacetoniminato) Cu(II) —o—o—

3a'. N-N'-ethylene,1-(2-hydroxy-m-tolyl) ethylideneaminato, acetylacetoniminato) Cu(II) —o— o—

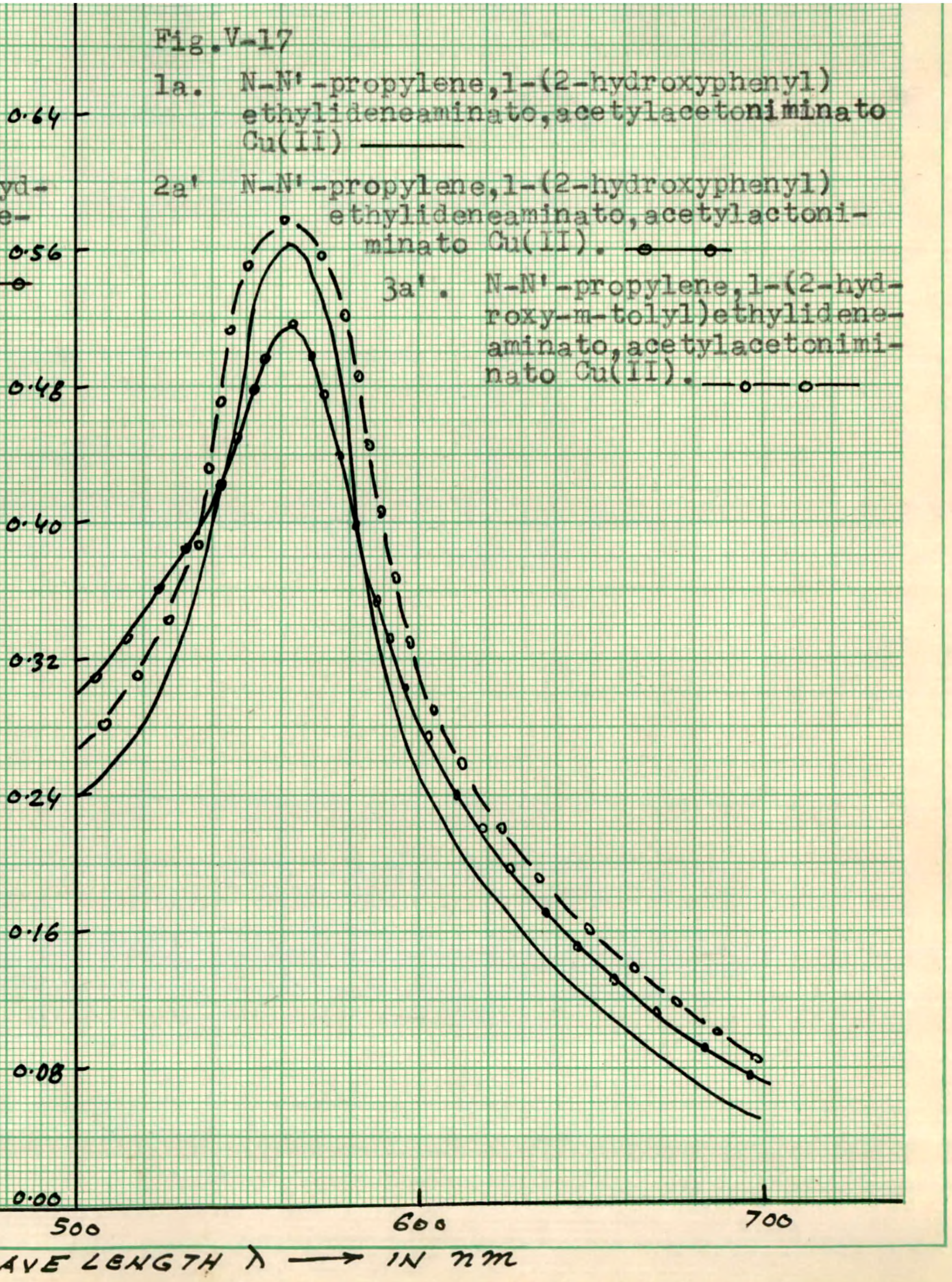


Fig. V-17

1a. N-N'-propylene,1-(2-hydroxyphenyl) ethylideneaminato,acetylacetoniminato Cu(II) ———

2a' N-N'-propylene,1-(2-hydroxyphenyl) ethylideneaminato,acetylactoniminato Cu(II). —o—o—

3a'. N-N'-propylene,1-(2-hydroxy-m-tolyl)ethylideneaminato,acetylacetoniminato Cu(II). —o—o—

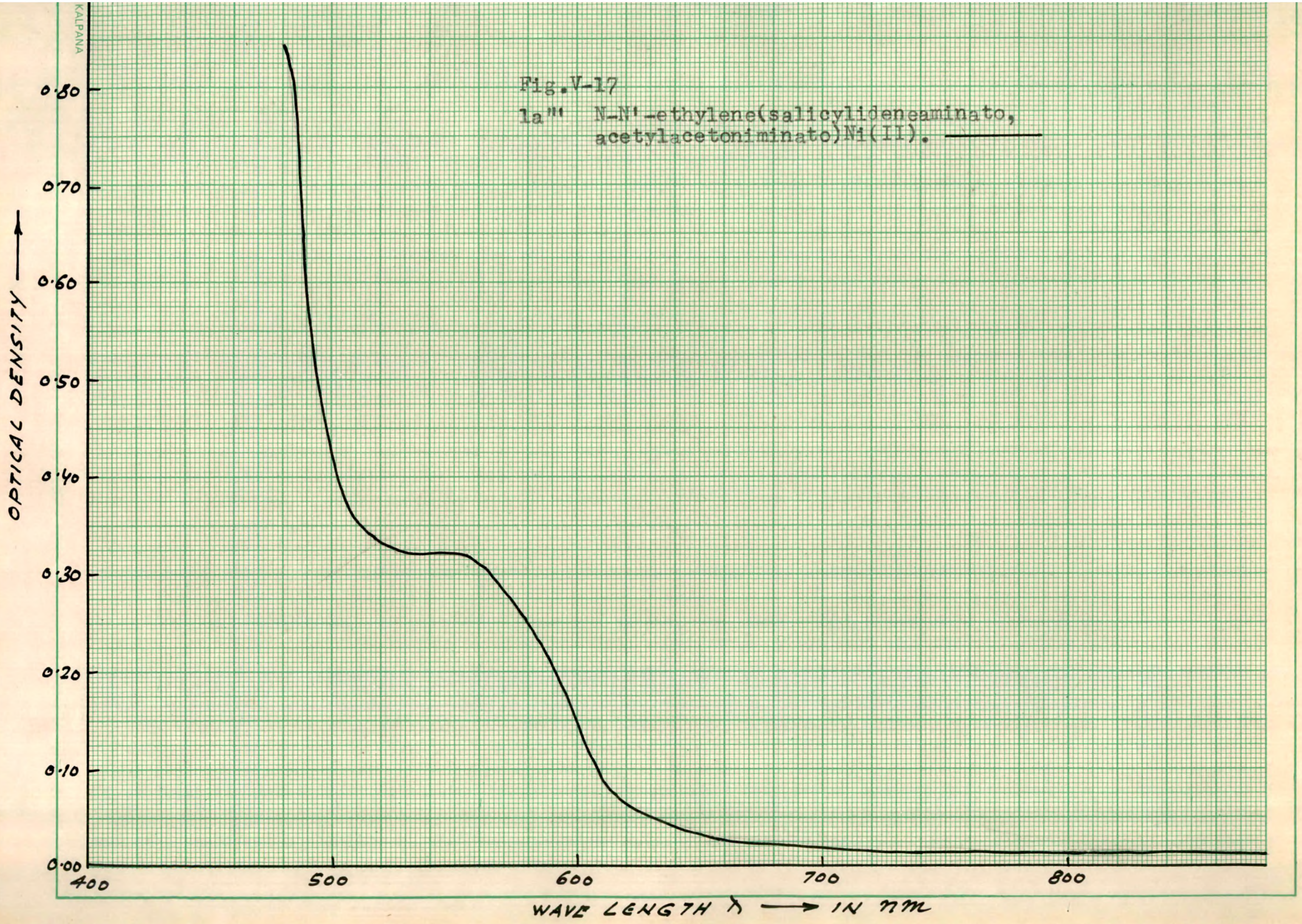


Fig.V-17

1a''' N-N'-ethylene(salicylideneaminato,
acetylacetoniminato)Ni(II). ——

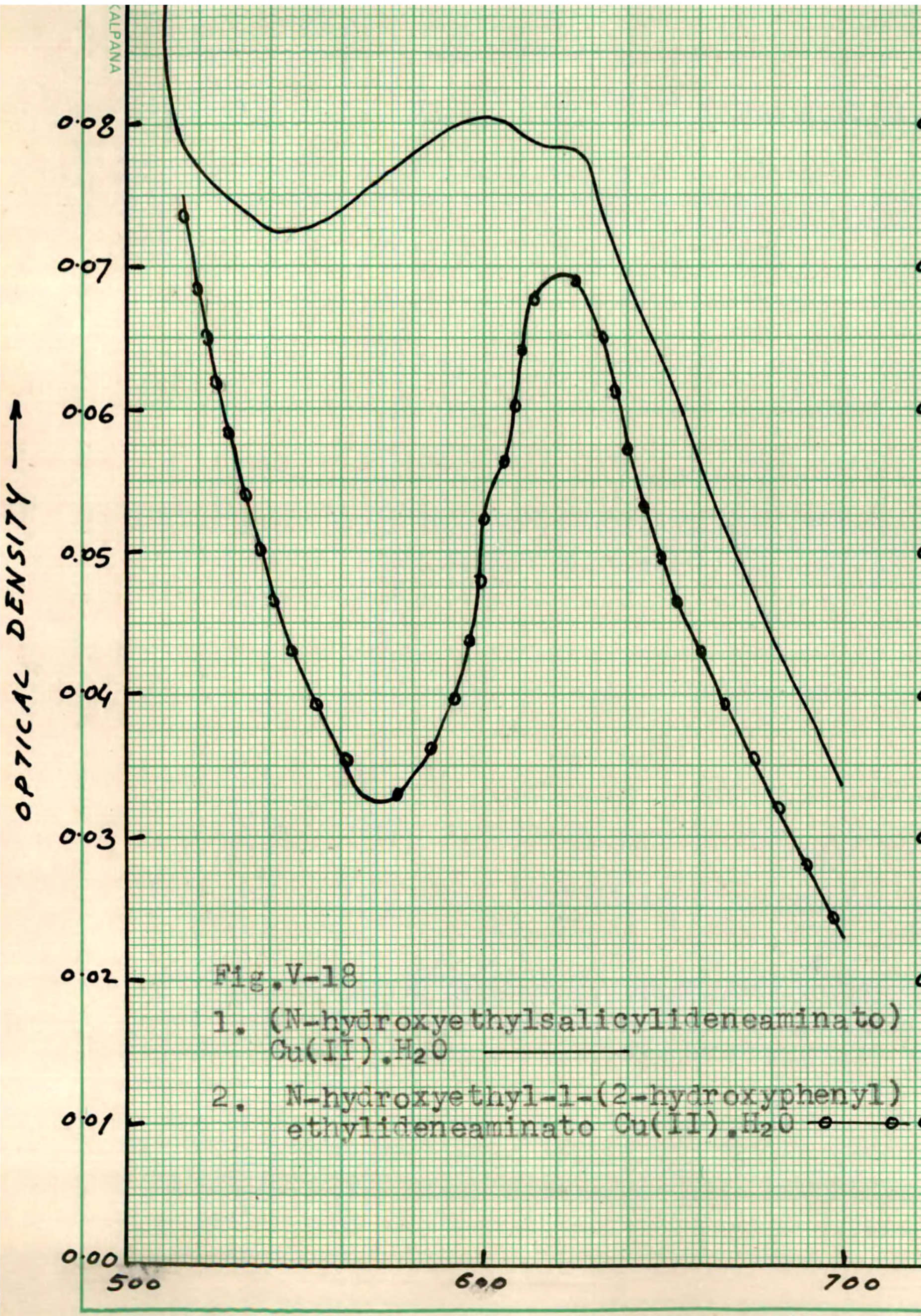


Fig.V-18

1. (N-hydroxyethylsalicylideneaminato) Cu(II).H_2O ———

2. N-hydroxyethyl-1-(2-hydroxyphenyl) ethylideneaminato Cu(II).H_2O —o——o—

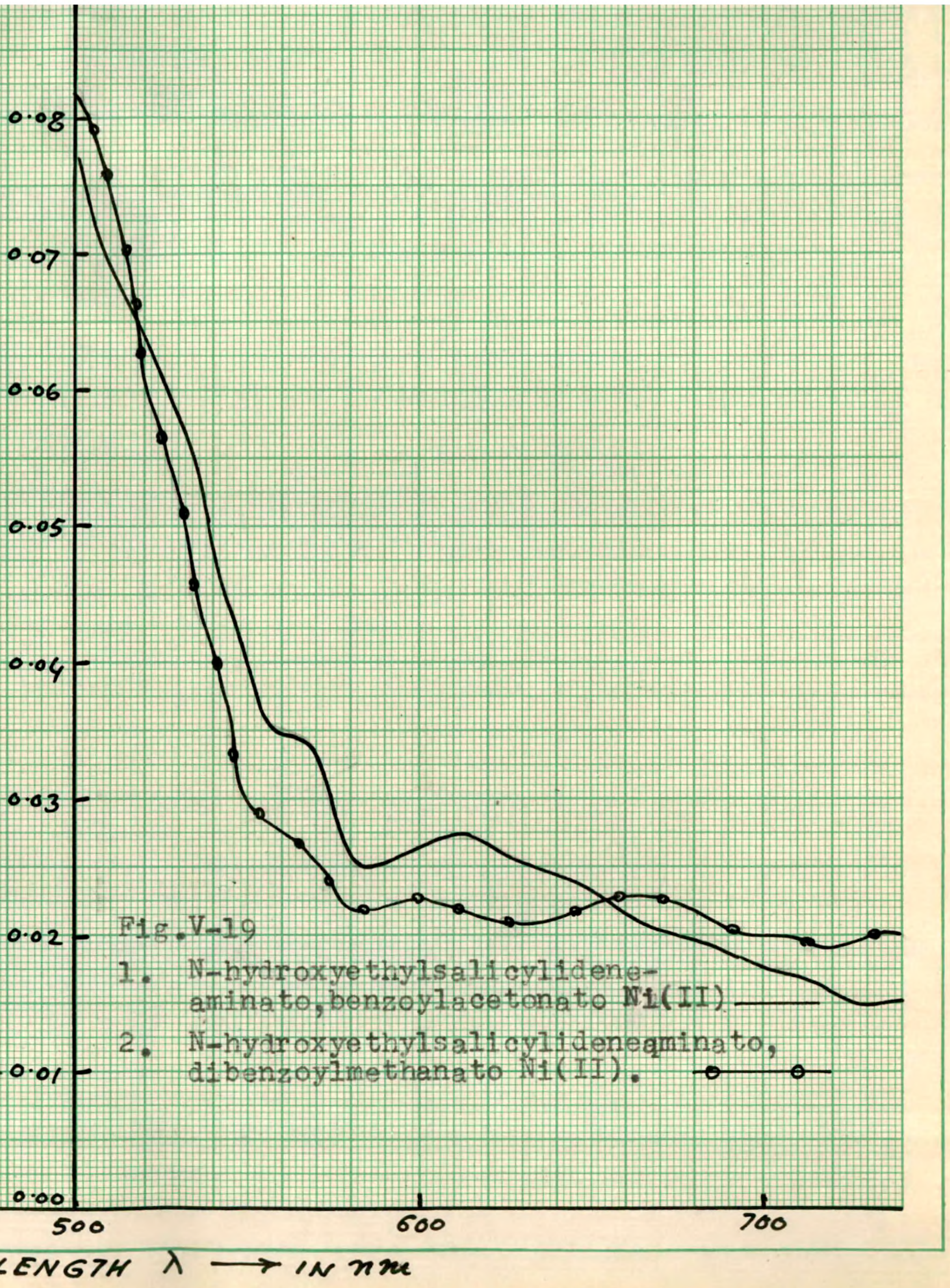


Fig.V-19

1. N-hydroxyethylsalicylideneaminato,benzoylacetonato Ni(II) ———

2. N-hydroxyethylsalicylideneaminato, dibenzoylmethanato Ni(II). —o——o—

References :

1. Schiff,H, Ann., 131, 118 (1864).
2. Schiff,H. Ann., 150, 193 (1869).
3. Pfeiffer,P., Buchholz,E., and Bayer,O., J.Pract.Chem., 129, 163 (1931).
4. Dubsky,J.V., and Sokol,A., Collection, Czech.Chem.Comm., 3, 548 (1931).
5. Combes,A., Compt.Rend., 108, 1252 (1899).
6. Dutt,N.K., J.Inorg.Nucl.Chem., 30(10), 2779 (1968).
7. Poddar,S.N., J.Inorg.Nucl.Chem., 31(2), 565 (1969).
8. Cummins,D., J.Chem.Soc., (Dalton), 13, 1359 (1973).
9. Layer,R.W., Chem.Rev., 63, 489 (1963).
10. Dwyer,F.R., and Mellor,D.P. (Eds.), "Chelating agents and metal chelates", Academic Press N.Y., (1964).
11. West,B.O., Rev.Pure.Appl.Chem.(Australia), 10, 207 (1960).
12. Holm,R.H., Everett,G.W., and Chakravorty,A., Prog.Inorg. Chem., 7, 83 (1966).
13. West,B.O., "The chemistry of coordination compounds of Schiff base", in "New pathways in inorganic chemistry" (Eds.), Ebsworth,E.A.B., Maddock,A.G., and Sharpe,A.G., Cambridge Univ.Press, (1968).
14. Yamada,S., Coord.Chem.Rev., 1, 415 (1966).
15. Sacconi,L., and Campigli,U., Inorg.Chem., 5, 606 (1966).
16. Balundgi,R.H., and Chakravorty,A., Inorg.Chem., 12, 981(1973).
17. Balundgi,R.H., and Chakravorty,A., Inorg.Nucl.Chem.Letters, 9(2), 167 (1973).
18. Thaker,B.T., and Bhattacharya,P.K., J.Inorg.Nucl.Chem., 37, 615 (1975).

19. Mohankumar,V.B., and Bhattacharya,P.K., Ind.J.Chem., (communicated).
20. Ebsworth,E.A.V., Maddock,A.G., and Sharpe,A.G., "New pathways in inorganic chemistry", (Cambridge),307 (1968).
21. Lindoy,L.F., Q.Rev., 25, 379 (1971).
22. Verter,H.S., and Frost,A.E., J.Am.Chem.Soc., 82,85 (1960).
23. Olsgwski,E.J., and Martin,D.F., J.Inorg.Nucl.Chem., 27, 345 (1965).
24. Martell,A.E., and Calvin,M., "Chemistry of the metal chelate compounds", Prentice Hall Inc., 424 (1966).
25. Ballhausen,C.J., "Introduction to ligand field theory" (McGraw Hill Book Comp., Inc.N.Y.), 268 (1962).
26. Graddon,D.P., and Mockler,G.M., Aust.J.Chem., 20,21 (1967).
27. Donini,J.C., Hollebone,B.P., and Lever,A.B.P., J.Am.Chem. Soc., 93, 24, 6455 (1971).
28. Sacconi,L., Paoletti,P., and Cini,R., J.Am.Chem.Soc., 80, 3583 (1958).
29. Kohli,R.K., Mohankumar,V.B., Thaker,B.T., and Bhattacharya, P.K., Bull.Chem.Soc.Japan, (accepted).
30. Holm,R.H., "Inorganic biochemistry", Eicchorn,G.L., Elsevier Scheitific Publishing Comp.,N.Y., 1140 (1973).
31. Kubo,M., Kuroda,Y., Kishita,M., and Muto,Y., Aust.J.Chem., 16, 7 (1963).
32. Barclay,F.A., and Hoskins,B.F., J.Chem.Soc., 1979 (1965).
33. Hetfield,W.E., and Bunger,F.L., Inorg.Chem., 5, 1161 (1966).
34. Verter,H.S., and Frost,A.E., J.Am.Chem.Soc., 82, 85 (1960).
35. Kishita,M., Nakahara,A., and Kubo,M., Aust.J.Chem., 17, 810 (1964).

36. Balundgi,R.H., and Chakravorty,A., Inorg.Chem., 12, 981 (1973).

37. Cotton,F.A., "Progress in inorganic chemistry", Vol.7, Edited by Cotton. (Interscience Publishers, N.Y.), 108, 193 (1966).

38. Carlin,R.L, "Transition metal chemistry", Vol. 4, N.Y., 289 (1968).