

Study on some Polynuclear Metal Complexes with Schiff Base Ligands

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ABSTRACT: Polynuclear macro cyclic complexes with Schiff base ligands are being synthesized easily and with good yield by starting with suitable precursors and allowing them to react with active carbonyl compounds in the presence of metal cations in suitable solvent media. Substituted salicylic acids have been chosen as starting organic ligands having active carbonyl formation. Cobalt(II), nickel(II) and copper(II) complexes of these ligand have been employed as intermediates for metal ion template synthesis of macro cyclic complexes by condensing them with diamines. Series of complexes have been prepared and characterized on the basis of spectral, magnetic and conductivity studies. Condensation with 1, 2-diaminobenzene produces a binuclear series. Synthesis and structural elucidation of bi- and tetra- nuclear Co(II), Ni(II) and Cu(II) complexes with Schiff bases derived from the condensation of 3-acetyl/ benzoyl salicylic acid as carbonyl component and o/p- phenylene diamine as amino component. It is expected that in these complexes the metals ions would be in different-stereochemistry. The complexes have the compositions, $[M_2(L^{1-2})]$ AND $[M_4(L^{3-4})]$ where H_4L^1 is the Schiff base prepared in situ by the condensation of 3-acetyl salicylic acid with ortho-phenylene diamine. H_4L^2 is the Schiff base prepared in situ by the condensation of 3-benzoyl salicylic acid with ortho-phenylene diamine. H_4L^3 is the Schiff the base prepared in situ by the condensation of 3-acetyl salicylic acid with para-phenylene diamine. All the complexes are microcrystalline having high melting points. They are insoluble in common organic solvents. But freshly prepared complexes are soluble in DMF, DMSO and dioxane. The molar conductance values of the complexes in dioxane are negligibly small suggesting them to be non-electrolytes. The complexes are quite stable under normal conditions and can be stored for long. However, they are decomposed with alkalies and acids.

Keyword: 3-acetyl/benzyl salicylic acid as carbonyl component and ortho/para-phenylene diamine as amino component.

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I. INTRODUCTION

Studies on mononuclear complexes have been very extensive but polynuclear complexes reported so far are rare. The most attracting studies on polynuclear complexes are related to magnetic interaction between different centers in oligomeric system. The pioneer works of Sahoo and co-workers on dinuclear, tri nuclear and tetranuclear complexes of Fe (II), Co (II), Ni(II) and Cu (II) have attracted worldwide attention.

Polynuclear high spin nickel (II) complexes have been isolated with a large number of ligands and much attention has been devoted to the study of their magnetic properties with particular emphasis on determining magnetic structural correlations. The magnetic properties are determined by rather complicated interaction between the unpaired electrons in the magnetic orbitals of the metal atoms which are generally indicated as exchange or super exchange interactions and depend on the nature of ligands

and relative orientation of the mononuclear moieties which for the polynuclear complexes. The elucidation and understanding of the exchange interaction between transition metal ions are a severe tests for all the theoretical models used to describe the electronic structure of metal complexes and present fundamental challenges to inorganic and theoretical chemists. Furthermore, the magnetic structural correlations is of considerable practical importance in the design and synthesis of new low – dimensional magnetic systems with specific magnetic properties as well as in all catalytic electron transfer process. Explanation of abnormally low value of magnetic moment of cupric acetate on the basis of anti ferromagnetic super exchange between copper (II) centers in a dimer is well known. The work on polynuclear complexes of copper (II) is more extensive than nickel (II) whereas work on polynuclear complexes of cobalt (II) is relatively rare. The scenario of polynuclear complex ‘vide

supra' have attracted our attention. Consequently the present programme of synthesis and characterization of a series binuclear and tetranuclear Co[II], Ni[II], and Cu[II] complexes with Schiff base ligands derived by condensation of 1,2-, and 1,4 - diaminobenzenes with acetyl/benzoyl salicylic acid have been undertaken.

II. EXPERIMENTAL

The present section is devoted to the experimental procedures adopted for the preparation of Cobalt(II), Nickel(II) and Copper(II)binuclear and tetranuclear complexes with Schiff base ligands and measurement of their physical properties.

The constituent parts of each compound have been estimated by established analytical methods¹ such copper by iodometry, nickel as dimethylglyoximtonickel(II), cobalt as its Oxinate, Carbon, Hydrogen and Nitrogen by semi micro combustion methods² using a MLW-CHN micro analyzer.

All the chemicals used were of Anal R grade, solvents were used as supplied.

Two series of complexes have been prepared and characterized on the basis of spectral, magnetic and conductivity studies.

Infrared spectra in KBr pellets were recorded on a per kin-Elmer 398 spectrophotometer. Reflectance spectra were recorded on a Carry-2390 spectrophotometer. Room temperature magnetic susceptibilities were measured by Guoymethod . Thermo gravimetric analyses were carried out by a metzch - 429, simultaneous recording of TGA and DTA Thermoanalyser at a heating rate of 10⁰c min⁻¹ in air. Around 50-100 mg of the sample was used in each case.

Condensation with 1, 2-diaminobenzene produces a binuclear series whereas 1,4-diaminobenzene give rise to tetra nuclear series.

The synthesis of the complexes may be represented by following two schemes.

Preparation of 3-acetyl salicylic acid (3-ASA) and 3-benzoyl salicylic acid (3-BSA):

3-acetylsalicylic acid (3-ASAS) and 3-benzoyl salicylic acid (3-BSA) were prepared following the method of Duff and Bills².

Attempts were made to prepare the Schiff base by condensing 3-ASA/3-BSA and ortho/para phenyldiamine but could not be achieved. Hence complexes were prepared 'in situ' by taking different quantities of the metal acetates and keeping orth/para phenylenediamine and 3-ASA/3-BSA in stoichiometric ratio 1:2:2. Copper acetate

was an Aldrich reagent but nickel and cobalt acetates were freshly prepared by the action of acetic acid on metal carbonates.

Preparation of binuclear complexes:

1. Preparation of [Cu₂(L¹)]

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g), 3-ASA (0.17 g) and ortho-phenylenediamine (11 g) and an aqueous solution of copper acetate monohydrate (0.200 g) was added. The resultant solution was heated to 60⁰C on a water bath for a while and then refluxed for a period of half an hour, when greenish microcrystalline solids separated. It was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused CaCl₂ and then analyzed.

Element	Found	Calculated
Copper	22.83	22.88
Carbon	51.56	51.88
Nitrogen	5.00	5.04
Hydrogen	2.86	2.88

2. Preparation of [Cu₂(L²)]

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g), 3-BSA (0.24 g) and ortho - phenylenediamine (11 g) and an aqueous solution of copper acetate monohydrate (0.200 g) was added . The resultant solution was heated to 600⁰ C on a water bath for a while and then refluxed for a period of half an hour, when greenish microcrystalline solids separated . It was cooled and filtered , thoroughly washed with hot water and dried in vacuum and over fused CaCl₂ and then analyzed .

Element	Found	Calculated
Copper	18.68	18.71
Carbon	59.92	60.08
Nitrogen	4.02	4.12
Hydrogen	2.92	2.94

3. Preparation of [Ni₂(L¹)]

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g) , 3 -ASA (0.17 g) and ortho phenylenediamine (11 g) and an aqueous solution of nickel acetate monohydrate (0.240 g) was added . The resultant solution was hearted to 60⁰ C on a water bath for a while and then refused for a period of half an hour, when yellowish microcrystalline solids separated. It was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused CaCl₂ and then analyzed.

Element	Found	Calculated
nickel	21.59	21.64
carbon	52.68	52.71
Nitrogen	5.10	5.12
hydrogen	2.91	2.93

4. Preparation of $[Ni_2(L^2)]$

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g) , 3- BSA (0.24 g) and ortho-phenylenediamine(11 g) and an aqueous solution of nickel acetate monohydrate (0.240) was added. The resultant solution was heated 60°C on a

water bath for a while and then refluxed for a period of half an hour, when yellowish microcrystalline solids separated. It was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused $CaCl_2$ and then analyzed.

Element	Found	Calculated
Nickel	17.58	17.61
Carbon	60.80	60.84
Nitrogen	4.15	4.17
Hydrogen	2.97	2.98

5. Preparation of $[Co_2(L^1)]$

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g) and ortho - phenylenediamine (11 g) and an aqueous solution of cobalt acetate monohydrate (0.240 g) was added .The resultant solution was heated to 60°C

on a water bath for a while and then refluxed for a period of half an hour, when red microcrystalline solids separated. It was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused $CaCl_2$ and then analyzed.

Element	Found	Calculated
Cobalt	21.60	21.64
Carbon	52.67	52.71
Nitrogen	5.07	5.12
Hydrogen	2.90	2.93

6. Preparation of $[Co_2(L^2)]$

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g), 3-BSA (0.24 g) and ortho-phenylenediamine (11 g) and an aqueous solution of cobalt acetate monohydrate (0.240 g) was added. The resultant solution was heated to 60°C on a

water bath for a while and then refluxed for a period of half an hour, when pink microcrystalline solids separated. It was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused $CaCl_2$ and then analyzed.

Element	Found	Calculated
Cobalt	17.56	17.61
Carbon	60.79	60.84
Nitrogen	4.12	4.17
Hydrogen	2.95	2.98

7. Preparation of $[Cu_4(L^3)]$

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g),3-ASA (0.17 g) and para-phenylenediamine(11g) and an aqueous solution of copper acetate monohydrate (0.200 g) was added. The resultant solution was heated to

60°C on a water bath for a while and then refluxed for a period of half an hour, when greenish microcrystalline solids separated. It was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused $CaCl_2$ and then analyzed.

Element	Found	Calculated
Copper	23.90	23.92
Carbon	49.68	49.71
Nitrogen	5.26	5.27
Hydrogen	2.99	3.01

8. Preparation of [Cu₄(L⁴)₂]

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g), 3-BSA (0.24) and para-phenylenediamine (11 g) and an aqueous solution of copper acetate monohydrate (0.200 g) was added. The resultant solution was heated to

60°C on a water bath for a while and then refluxed for a period of half an hour, when greenish microcrystalline solids separated. It was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused CaCl₂ and then analyzed

Element	Found	Calculated
Copper	19.37	19.38
Carbon	58.59	58.62
Nitrogen	4.26	4.27
Hydrogen	3.03	3.05

9. Preparation of [Ni₄(L³)₂]

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g), 3-ASA (0.17 g) and para-phenylenediamine (11 g) and an aqueous solution of nickel acetate monohydrate (0.240) was added. The resultant solution was heated to

60°C on a water bath for a while and then refluxed for a period of half an hour, when yellowish microcrystalline solids separated. It was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused CaCl₂ and then analyzed

Element	Found	Calculated
Nickel	22.80	22.82
Carbon	51.00	51.06
Nitrogen	5.41	5.42
Hydrogen	3.07	3.09

10. Preparation of [Ni₄(L⁴)₂]

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g), 3-BSA (0.24 g) and para-phenylenediamine (11 g) and an aqueous solution of nickel acetate monohydrate (0.240 g) was added . The resultant solution was heated to

60°C on a water bath for a while and then refluxed for a period of half an hour, when yellowish microcrystalline solids separated. It was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused CaCl₂ and then analyzed.

Element	Found	Calculated
Nickel	18.24	18.26
Carbon	58.98	59.44
Nitrogen	4.32	4.34
Hydrogen	3.08	3.09

11. Preparation of [Co₄(L³)₂]

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g), 3-ASA (0.17 g) and Phenylenediamine (11 g) and an aqueous solution of cobalt acetate monohydrate (0.240 g) was added. The resultant solution was heated to 60°C on a

water bath for a while and then refluxed for a period of half an hour, when red microcrystalline solids separated. It was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused CaCl₂ and then analyzed.

Element	Found	Calculated
Nickel	22.85	22.82
Carbon	51.01	51.06
Nitrogen	5.37	5.42
Hydrogen	3.05	3.09

12. Preparation of [Co₄(L⁴)₂]

To a mixed solution (water and dioxane) of sodium carbonate (0.106 g) , 3-BSA (0.24 g) and para-phenylenediamine (11 g) and an aqueous solution of cobalt monohydrate (0.240 g) was added . The resultant solution was heated to 60°C

on a water bath for a while and then refluxed for a period of half an hour, when pink microcrystalline solid separated. it was cooled and filtered, thoroughly washed with hot water and dried in vacuum and over fused CaCl₂ and then analyzed.

Element	Found	Calculated
Nickel	18.21	18.26
Carbon	58.95	59.44
Nitrogen	4.37	4.34
Hydrogen	3.05	3.09

III. RESULT AND DISCUSSION

Polynuclear macro cyclic complexes with Schiff base ligands are being synthesized easily and with good yield by starting with suitable precursors and allowing them to react with active carbonyl compounds in the presence of metal cations in suitable solvent media. For the present study, substituted salicylic acids have been chosen as starting organic ligands having active carbonyl formation. Cobalt(II), nickel(II) and copper(II) complexes of these ligand have been employed as intermediates for metal ion template synthesis of macro cyclic complexes by condensing them with diamines.

Two series of complexes have been prepared and characterized on the basis of spectral, magnetic and conductivity studies. Condensation with 1,2-diaminobenzene produces a binuclear series whereas 1,4-diaminobenzene give rise to tetranuclear series. The synthesis of the complexes may be represented by following two schemes.

There are some report^{1,2} of mono and binuclear metal complexes of 3-formyl salicylic acid (3-FSA) and its Schiff bases with alkyl amines and diamines. It is also established in those complexes that the phenolic oxygen acts as a

bridging group while the carboxylate oxygen and mono nitrogen are coordinated to the metal ions. But in case of the complexes of 3-FSA and its Schiff bases with monoamines, the organic constituents remain trans to each other. However, in the complexes of the Schiff bases derived from 3-FSA and diamines such as ethylene diamine with a 4s-configuration with respect to the imino-nitrogen and carboxylate oxygen is formed.

In the above type of complexes the inside coordination site has N₂O₂-chromospheres, where as the outside coordination site has O₄chromophore and because of the hetero coordinating atoms they have different ligand field strengths.

In the present programme synthesis and structural elucidation of two series of bi- and tetra-nuclear Co(II), Ni(II) and Cu(II) complexes with Schiff bases derived from the condensation of 3-acetyl/ benzoyl salicylic acid as carbonyl component and o/p- phenylene diamine as amino component. It is expected that in these complexes the metals ions would be in different-stereochemistry. The characteristic vibrational bands in the i.r. spectra and magnetic moment values have been presented in Table 4.1 and 4.2.

Table 4.1

Characteristic I.R. peaks (cm⁻¹) and magnetic moment values of binuclear cobalt (II), nickel(II) and copper (II) metal chelates of the type [m₂ (L¹⁻²)₂]

Complexes	V _{C=N}	V _{N-N}	V _{M-O}	V _{M-N}	
Co ₂ L ¹	1630	1010	480	435	0.78
CO ₂ L ²	1635	1012	475	430	1.92
Ni ₂ L ¹	1635	1015	485	440	0.6
NI ₂ L ²	1645	1010	480	445	0.7
CU ₂ L ¹	1630	1015	470	435	1.80
CU ₂ L ²	1640	1012	475	430	1.82

TABLE 4.2

Characteristic I.R. peaks (cm⁻¹) and magnetic moment values of binuclear cobalt (II), nickel(II) and copper (II) metal chelates of the type [m₄ (L³⁻⁴)₂]

Complexes	V _{C=N}	V _{N-N}	V _{M-O}	V _{M-N}	
Co ₄ L ³ ₂	1635	1015	475	430	2.0
CO ₄ L ⁴ ₂	1640	1018	470	435	1.9
Ni ₄ L ³ ₂	1645	1012	485	440	0.8
NI ₄ L ⁴ ₂	1630	1015	475	450	0.6
CU ₄ L ³ ₂	1635	1020	480	440	1.78
CU ₄ L ⁴ ₂	1640	1012	480	425	1.76

The complexes have the compositions, [M₂(L¹⁻²)] and [M₂(L¹⁻²)] where H₄L¹ is the Schiff base prepared in situ by the condensation of 3-Acetyl salicylic acid with ortho-phenylene diamine.

H₄L² is the Schiff base prepared in situ by the condensation of 3-benzoyl salicylic acid with ortho-phenylene diamine H₄L³ is the Schiff base prepared in situ by the condensation of 3-Acetyl

salicylic acid with para-phenylene diamine. H_4L^4 is the Schiff base prepared in situ by the condensation of 3-benzoyl salicylic acid with para-phenylene diamine. All the complexes are microcrystalline having high melting points. They are insoluble in common organic solvents. But freshly prepared complexes are soluble in DMF, DMSO and dioxane. The molar conductance values of the complexes in dioxane are negligibly small suggesting them to be non electrolytes. The complexes are quite stable under normal conditions and can be stored for long. However, they are decomposed with alkalis and acids.

Since the Schiff bases could not be isolated, the spectra of the ligand could not be recorded. Hence the spectra of the complexes are compared with spectra of the starting materials and other related compounds. The binuclear as well as the tetranuclear complexes exhibit an identical spectral pattern. On scanning the IR spectra of the complexes no bands in the vicinity of $3300-3100$ and 1690 cm^{-1} due to ν_{N-H} and $\nu_{C=O}$, respectively were observed with the suggestion that condensation has taken place⁴. Instead, a strong band in the region $1630-1645\text{ cm}^{-1}$, attributed to $\nu_{C=N}$ has been observed⁴. This value is comparatively at a higher frequency than the usual $\nu_{C=N}$ value. The shifting of the band to higher frequency region led us to believe that the azomethine group takes part in complexation. The next structurally important band is due to ν_{C-O} of phenolic group which is generally observed at 1320 cm^{-1} . However, the band has undergone a hypsochromic shift indicating the participation of phenolic oxygen in complexation. A carboxylate group may be coordinated to the metal ion either in a unidentate or a bidentate manner. In the present case a pair of bands at 1605 and 1345 cm^{-1} has been observed. The large shift of nearly 200 cm^{-1} is indicative of the monodentate nature of the carboxylate group⁶⁻¹⁰. A moderately strong band at 1012 cm^{-1} corresponding to ν_{N-N} has been observed. The band position is at a lower frequency than those observed for hydrazine complexes.

The low frequency region of the spectra of complexes furnishes some vital information regarding the mode of the coordination of the ligand with the metal centre. The coordination through oxygen and nitrogen is further supported by the appearance of additional bands in the spectra of the complexes in the regions $470-485$ and $425-440\text{ cm}^{-1}$ assignable to ν_{N-N} and ν_{N-O} , respectively¹¹.

Electronic spectra and magnetic properties of complexes

(a) copper(II) complexes

In recent years, the visible spectra of several copper (II) complexes have been interpreted

in terms of ligand field theory. The divalent copper has a d configuration giving rise to a 2D ground state which would be split into two terms under the influence an octahedral field (spin-orbit coupling being ignored). Since the john -Teller effect leads to appropriate tetragonal distortion of copper (II) complexes, they in general, are regarded as distorted octahedral or approximately square planar complexes. where the $^2T_{2g}$ term is placed higher than 2E_g term because the behavior of a d^9 electronic configuration is conveniently described as a d^1 hole configuration.

Thus, if there is no further distortion, we would then expect three transitions whether the symmetry is essentially square planar or distorted octahedral. On this basis, Belford et al have examined the visible absorption spectra of acetyl acetone and ethyl acetyl acetone chelates of copper (II) in solution in several polar and non polar solvents and have divided into three Gaussian components and assigned them by consideration of the field effect to be expected as the solvents . This procedure has also been adopted by other workers .however, graddon has pointed out a band of intermediate intensity ($\epsilon = 500$) in the region of $2.7\text{ }\mu^{-1}$ in the spectra of ethyl aceto acetone complexes of copper (II) and pointed out that the band in the visible region could be resolved into 2 components . Later , Ferguson accepted the assignment of the band at $2.7\text{ }\mu^{-1}$ but pointed out that it was

Incorrect to treat the ligand field as having D_{4h} symmetry which was assumed of , and suggested that D_{2h} or C_{2v} to be a much better approach. This would remove the degeneracy of the doublet level and give rise to 4 transition. Piner and Belford have arrived at a similar conclusion concerning the symmetry of the complex but have questioned the assignment of the higher energy band as a d-d transition. The results of cotton and wilkson the analogous $cu(dmg)_2$ which does have ideal molecular alignment, have apparently resolved the discrepancy . the identification of 4 d-d bands has been possible through the works of basu et al. (3-phenyl acetyl – acetate) copper (II) at liquid nitrogen temperature contain liquid nitrogen temperature contain four partially resolved bands in the visible region which have been ascribed to the required $d \rightarrow d$ transitions end a more intense band at $2.2\text{ }\mu^{-1}$ corresponding to that observed by grad don. At room temperature this band persist but the four former bands are replaced by two broad with maxima at 1.6 and $1.9\text{ }\mu^{-1}$

Gould ana Johnson have reported a broad asymmetric band for hydroxyl amidine complexes of copper (II) which could be divided into two Gaussian components at room temperature. The phosphine oxide complex $[ph_3(po)_4Cu]^{+2}$ is another example of a square planar copper (II) complex.

The spectrum shows a broad band at about 700 m μ .

It appears therefore, that the spectra obtained at room temperature of essentially square-planer copper (II) complexes so far, may be divided empirically into two simple components. Any attempts to resolve the bands further has not been reasonably justified since the transitions expected are of similar energy. Besides, thermal broadening of the bands makes unambiguous assignment further, U.V. and visible spectral studies of several Schiff base complexes of copper(II) believed to be planar, have been carried out in different inert end polar solvents and the bands are located in the region 15,000 to 19,000 cm^{-1} . The crystal spectra of $\text{Cu}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ in which acetate ion acts as a bridging ligand has been reported by Tonnet and coworkers and by Riemann and coworkers. These bands are observed at 11,400; 14,000 and 27,000 cm^{-1} to the transition $d_{x^2-y^2} \rightarrow d_{z^2}$ or d_{xy} and the band at 14,400 cm^{-1} to the transition $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$. The band at 27,000 cm^{-1} is not a d-d transition.

The crystal spectra of alaninate and α -amino butyrate have been studied by Dijkgraaf, Fielding and Eckay and Dey et al. have discussed the crystal spectra of copper phthalocyanine.

Electronic spectra of metal complexes of tetradentate Schiff bases (TSB) such as salicylaldehyde and acetyl acetone imines can act as bidentate chelating agents through their cis oxygen atoms and form bi and tri nuclear

complexes. Mainly through the works of Crubler, Sinn and Harri and Kato et al. prolific information is available on the structures and magnetic behavior of these complexes.

The complexes reported are of two types $[\text{M}(\text{TSB})]\text{MX}_2$ and $[\text{M}(\text{TSB})]_2 \text{MX}_2$ ($\text{X}=\text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{ClO}_4^-$) and encompass a number of transition and mono transition metals. The effects of substituents R and R' on nitrogen and phenyl ring of salicylaldehyde have also constituted the subject matter of study. Amongst the various complexes with the Schiff base, the most widely studied complexes contain copper (II) and Nickel(II) as metal M.

General structures of the bi, tri and tetra nuclear complexes have been suggested on the basis of spectral results. Structurally significant results for some of these complexes are recorded in Table 4.2. The pseudo tetrahedral, tetrachlorocuprate ion, $[\text{CuCl}_4]^{2-}$ shows the ligand field band at 8500 cm^{-1} . The complex, $\text{Cu}(\text{TSB})$ is free from any band in this region. It would be natural to expect that copper (II) ion linked to two halogens and situated in an environment approximating to $[\text{CuCl}_4]^{2-}$ ion would show ligand field bands in vicinity of 8500 cm^{-1} is a matter of fact the complexes, $\text{Cu}(\text{TSB})\text{CuX}_2$ ($\text{X}=\text{Cl}^-, \text{Br}^-$) show a band in the region 8000-12,000 cm^{-1} which is significantly absent in the corresponding bi and tri nuclear complexes containing non transitional elements. Non transitional elements are not expected to show any band in the ligand field region. Thus the electronic spectra of

TABLE-4.2

Ligand field spectra of the binuclear complexes

$\text{Cu}(\text{TSB})\text{CuX}_2 \cdot n\text{H}_2\text{O}$ (fig.101)

R	R'	N	X	SPECTRA IN CM^{-1}	
$-(\text{CH}_2)_2-$	-H	1	CL	18800	10800
$-(\text{CH}_2)_3-$	-H	0	CL	18700	10700
-o Phenylene	-H	1	CL	18300	12000
-o-Phenylene	-H	1	Br	18400	11700
$-\text{CH}_2\text{CH}(\text{CH}_3)_2^-$	-H	0	CL	18200	10900
$-(\text{CH}_2)_3^-$	-H	0	CL	17100	9800
$-(\text{CH}_2)_4^-$	-H	0	CL	17100 14500	9300

Binuclear complexes : The ligand field band for copper (II) complexes is observed at 18,200 cm^{-1} which is in agreement with the band observed for N,N-Salicylidenethylene-diaminato copper (II) and N,N'-Disalicylidene propylene-diaminato copper (II) complexes. This has been assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition. The room temperature magnetic moment is 1.82 BM. The magnetic property and electronic spectra imply that the copper (II) ion in the present complex has square planar stereochemistry

with two types of chromophores namely N_2O_2 and O_4 with almost comparable ligand field strengths

Tetra nuclear Complexes

The reflectance spectra of the copper (II) complexes exhibit two bands in the visible region. The second high-energy band is well in accordance with the band for $\text{CuH}_2\text{FSA-en}$ (where); HFSA-en is Schiff base derived from 3-FSA and ethylene diamine. The position of this practically equal to the band for N,N'-disalicylidene -O-Phenylene

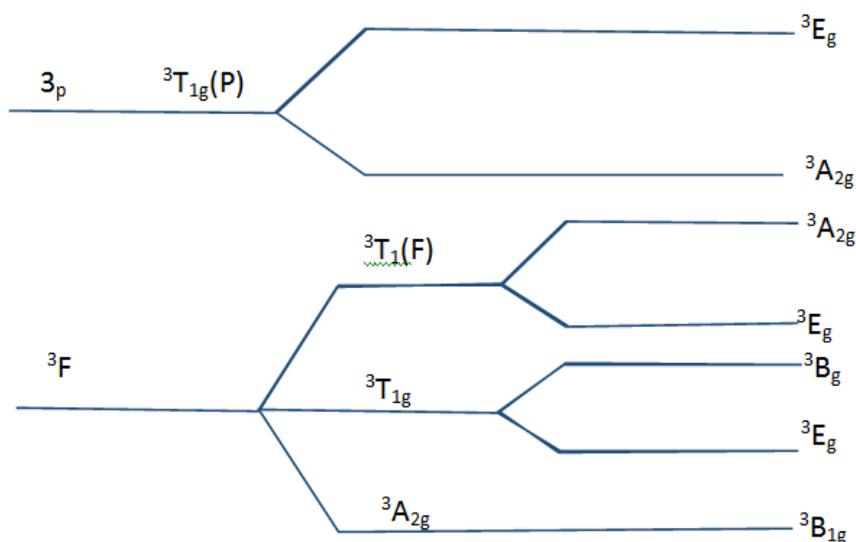
diaminato copper (II) 13,14. Therefore, the second band was tentatively assigned to the inside copper(II) having CuN₂O₂ chromophore¹⁵. Sinn et al,¹⁵ have found that dichloro (N,N'-disalicylidimethylenediaminato copper (II)) has a band at 18,200 cm⁻¹. This fact implies that the coplanarity of the unit

(B) Nickel(II) Complexes

Nickel(II) ion forms complexes with a variety of geometries, hexa coordinated octahedral, penta coordinated trigonal pyramidal and tetra coordinated square planar or rare cases tetrahedral. Nickel(II) ion with d⁸ electronic configuration has ³f ground state and other higher energy level terms ¹D, ³p and ¹S with increasing stereochemistry. It is discussed first followed by discussion on square planar nickel(II) complexes.

Octahedral Nickel (II) Complexes

In a cubic field, ³f ground state of Ni(II) ion is split into three levels, the orbital singlet ³A₂ and the orbital triplets ³T₁ and ³T₂. With an octahedral arrangement of the ligands, the order of energies is, ³A_{2G} < ³T_{2G} < ³T_{1G}. With a tetrahedral arrangement of the ligands, the order of the energies is reversed. The first excited term for free nickel (II) ion is ³P which transforms as ³T_{1g} under cubic symmetry. In a tetragonal field, each T states may further split into two other components. The energy level scheme for nickel (II) ion is shown in fig 4.6. There are, therefore, three spin allowed transitions which may be observed in an octahedral Nickel (II) complex, namely $\nu_1 [^3T_{2G} \rightarrow ^3A_{2G}]$, $\nu_2 [^3T_{1G}(f) \rightarrow ^3A_{2G}]$ and $\nu_3 [^3T_{1G}(p) \rightarrow ^3A_{2G}]$.



Energy level diagram for nickel(II) ion for the triplet states

- free ions
- splitting in octahedral field;
- splitting in tetragonal field (D_{4h} symmetry).

The observed spectra of octahedral Nickel(II) complexes show just the above features. The hexa-aqua nickel(II) ion, [Ni(H₂O)₆]²⁺ shows three spin-allowed bands at 8500 cm⁻¹, 13,500 cm⁻¹ and 25,000 cm⁻¹ respectively and for [Ni(NH₃)₆]²⁺, these are found at 10,700 cm⁻¹ and 28,200 cm⁻¹ respectively.

However, in principle, four triplet-singlet transitions are generally expected in region, 500-300 cm⁻¹. These are to the state ¹E_g(⁶t_{2g}, ¹D), ¹A_{1g}(⁶t_{2g}, ²e_g, ¹G), ¹T_{1g}(⁵t_{2g}, ³e_g, ¹G) and ¹T_{2g}(⁵t_{2g}, ²e_g, ¹G) these transitions, being spin-forbidden as well as Laporte forbidden, are particularly weak and are not generally observed and only the first three spin-

allowed transitions are found in most of the nickel(II) complexes.

The structure of quadricordinated nickel(II) complexes has been the subject of considerable discussion. Controversy has arisen in the assignment of tetrahedral stereochemistry to strictly four coordinate complexes on the basis of paramagnetism. This stereochemistry has been suggested in part by several workers on the basis of Pauling's criterion of bond type which, in the case of quadricordinated nickel(II) complexes, states that paramagnetic complexes are 4s4p³ hybridised and tetrahedral, whereas diamagnetic complexes are 3d4s4p² hybridised and planar. X-ray structural determination of several diamagnetic quadricordinated complexes such as: bis(dithiooxalate)

Ni(II), Ni(II)phthalocyanine, bis(dimethylglyoxime)Ni(II), bis(salicylaldoxime)Ni(II) and bis(salicylaldimine)Ni(II) reveal them to be planar. On the other hand, in the case of a number of quadricordinated

paramagnetic anhydrous nickel (II) complexes of 8- hydroxyquinoline, o-hydroxy acetophenone, anthranilic acid etc . Which have magnetic moment in the range 3.0-3.3 B.M., the Stereochemistry seem to be planar. There is no convincing evidence of any sort that any of these complexes are tetrahedral .It has been pointed out by Ballhausen and coworkers that quadracoordinated planar nickel (II) complex can exist under certain condition , although evidence is at present Lacking in the Form of X- ray structural determination on any four – coordinate paramagnetic nickel (II) complex . These workers have discussed the magnetic and spectral properties of quadracoordinated nickel (II) complexes in the light of the modern ligand field theory and have pointed out that though their Simplified treatment does not correctly predict the absorption spectra of weakly tetragonal nickel (II) complexes, such complexes are more correctly viewed as slightly perturbed octahedral complexes .

Binuclear Complexes:

The reflectance spectra of the nickel (II) Complex shows a single band $18,600\text{ cm}^{-1}$ Which corresponds to the band reported for N, N'-Salicylideneethylenediaaminato nickel (II) .further, the complex is diamagnetic , suggesting a square planar stereochemistry around the metal ion.

Tetra nuclear complexes:

The reflectance spectra of the tetra nuclear nickel (II) complexes have been round to be similar with binuclear complexes indicating square planar environment . The low value of magnetic moment is presumably due to T.I.P. contribution.

(C) Cobalt (II) complexes

The cobalt (II) ion has a d^7 electronic configuration which gives rise to the ground state, 4F with the excited state 4p located above $> 14,500\text{ cm}^{-1}$.Under the influence of an octahedral field the ground state splits into three levels i.e. the orbital triplets $^4T_{1g}$ and $^4t_{2g}$ and the orbital singlet $^4A_{2g}$, the order of energies being $^4T_{1g} < ^4T_{2g} < ^4A_{2g}$; in case of tetrahedral complexes the order or energies being Reversed .The term 4p transforms as $^4T_{1g}$ under an octahedral Symmetry. The above energy level diagram was proposed by Abragam and Pryce⁴³⁰ to inert the optical absorption spectra of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion .The 2G state located just a bit higher than 4p , is also split under the influence of a crystal field . One of the split components i.e. 2E_g state eventually become the ground state at the limit of the strong crystal field. The visible absorption spectra of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions show a band at 8350 cm^{-1} and a band system around $20,000\text{ cm}^{-1}$.The low energy band has been

identified with the transition, $^4T_{2g} \leftarrow ^4T_{1g}$ and the high frequency band with the transition, $^4T_{1g}(\text{P}) \leftarrow ^4T_{1g}$ Ballhausen has shown that the transition corresponding to $^4A_{2g} \leftarrow ^4T_{1g}$ should possess a very small intensity and be placed at $17,000\text{ cm}^{-1}$. Koide⁴³¹ has pointed out that this transition corresponds to a two electron jump and as such be very weak (Oscillator strength 4.8×10^{-6}) while the oscillator's strength value for the transition, $^4T_{2g}(\text{P}) \leftarrow ^4T_{1g}(\text{F})$ is 1.7×10^{-4} .

A large number of six coordinate cobalt(II) complexes are known but it has been difficult to interpret their spectra. Some of the important results have been summarized by Lever. Octahedral cobalt(II) complexes show a band in the region $8000\text{-}10,000\text{ cm}^{-1}$ which has been unequivocally assigned to the transition, $^4T_{2g}(\text{F}) \leftarrow ^4T_{1g}$. The next important band appears in the region $17,000\text{-}22,000\text{ cm}^{-1}$ and arises due to the transition, $^4T_{1g}(\text{P}) \leftarrow ^4T_{1g}$. In most of the cases, it appears as a double peak due to spin-orbit coupling of the $^4T_{1g}(\text{P})$ state. A weak band is found in a few cases in the region $11,000\text{-}17,000\text{ cm}^{-1}$ and has been assigned by several workers to the transition $^4A_{2g} \leftarrow ^4T_{2g}$.

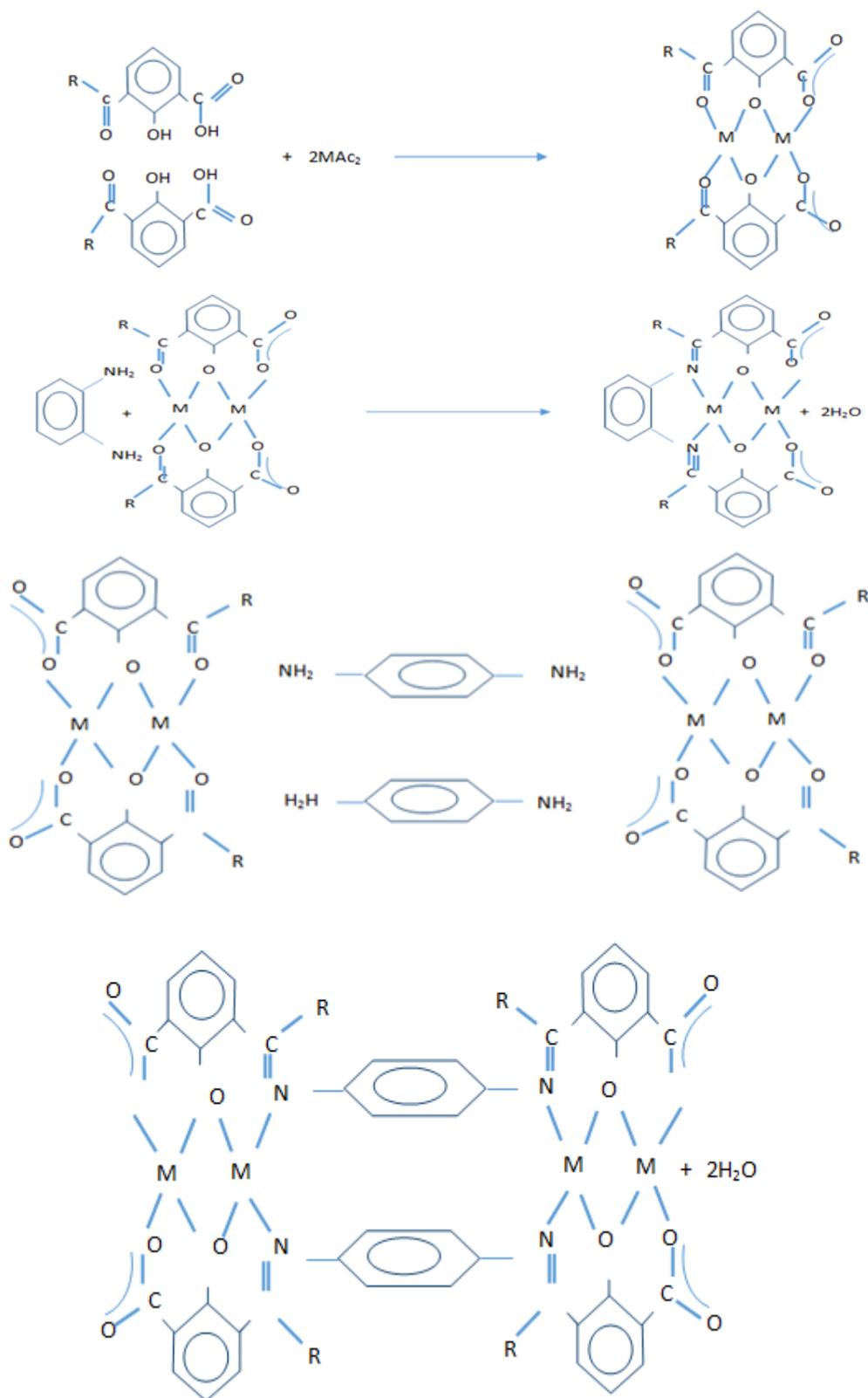
Four coordinated cobalt(II) complexes would be either tetrahedral or planar, in the latter case both spin-free and spin-paired complexes are known. In a tetrahedral case, the ligand field splitting being lower the octahedral case, the transitions are observed at a lower frequency region and the spectra of such complexes have been extensively studied. These workers have also worked out an energy level diagram group theoretically for four coordinated spin-free cobalt(II) ion. However, the spectra have not been satisfactorily explained in term of the energy levels..A number of five coordinated complexes are known. They may be either trigonal bi pyramid or square pyramid, spectra of both types of complexes have been reported and have been discussed on the basis of suitable crystal field energy level diagram. The magnetic moment value and electronic spectra of binuclear and tetra nuclear Co(II) complexes are suggestive of square planar environment with weak antiferromagnetic interaction among metal centers. On the basis of the above discussions, the following structure for Co(II), Ni(II) and Cu(II) binuclear and tetra nuclear metal chelates have been proposed for the tetra nuclear metal complexes. The above structures are also supported by the low value of molar conductance in the range $10\text{-}15\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

Conclusion (structure and bonding)

Two series of complexes have been prepared and characterized on the basis of spectral,

magnetic and conductivity studies. Condensation with 1,2-diaminobenzene produces a binuclear series whereas 1,4-diaminobenzene give rise to

tetranuclear series. The synthesis of the complexes may be represented by following two schemes.



In the present program the synthesis and structural elucidation of bi- and tetra-nuclear Co(II), Ni(II) and Cu(II) complexes with Schiff bases derived from the condensation of 3-acetyl/benzoyl salicylic acid as carbonyl component and o/p-phenylene diamine as amino component. It is expected that in these complexes the metal ions would be in different stereochemistry.

The complexes have the compositions, $[M_2(L^{1-2})]$ and $[M_4(L^{3-4})]$ where H_4L^1 is the Schiff base prepared in situ by the condensation of 3-Acetyl salicylic acid with ortho-phenylene diamine. H_4L^2 is the Schiff base prepared in situ by the condensation of 3-benzoyl salicylic acid with ortho-phenylene diamine. H_4L^3 is the Schiff base prepared in situ by the condensation of 3-Acetyl salicylic acid with para-phenylene diamine. H_4L^4 is the Schiff base prepared in situ by the condensation of 3-benzoyl salicylic acid with para-phenylene diamine. All the complexes are microcrystalline having high melting points. They are insoluble in common organic solvents. But freshly prepared complexes are soluble in DMF, DMSO and dioxane. The molar conductance values of the complexes in dioxane are negligibly small suggesting them to be non electrolytes. The complexes are quite stable under normal conditions and can be stored for long however, they are decomposed with alkalis and acids.

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