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Synthesis-and characterization of some liquid crystal type complexes of Fe, Co, Ni and Cu.

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University of Rajshahi

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TO
MY PARENTS

Synthesis and characterization of some liquid crystal type complexes of Fe, Co, Ni and Cu.

M. Phil Thesis

A Thesis Submitted to the University of Rajshahi for the Degree of Master of Philosophy in Chemistry.

Submitted By

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Roll No. 14
Registration No. 11629
Session : 2000-2001

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I am all the more grateful and obligated to my beloved parents, brothers and sisters who took special care for me, my study and research work.

Sabina Begum

The work reported in the thesis for the M.Phil degree has been carried out directly under my supervision and this work has not been submitted for any other degree.

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This thesis contains original research work carried out by me in the Inorganic Research Laboratory, Rajshahi University and the work has not been submitted for any other degree.

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ABSTRACT

Recently scientists gave special attention to the synthesis of transition metal complexes due to their catalytic, biological mesogenic and paramagnetic properties. Hydrazone ligands and their complexes have pronounced biological as well as mesogenic properties. Considering the above important properties of transition metal hydrazone complexes the present work synthesized and characterized some novel hydrazone complexes of iron(III), nickel(II) and copper(II) having some long chain residue or tailing.

(1) Ethyl-4-benzyloxybenzoate **1** is prepared by the reaction of benzylbromide and ethyl-4-hydroxybenzoate.

(2) The ligand precursor 4-benzyloxybenzoylhydrazine $C_6H_5CH_2OC_6H_4C(O)NHNH_2$, **2** is prepared by the reaction of **1** with three fold excess of hydrazine hydrate.

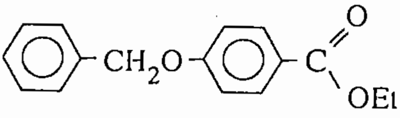
(3) The hydrazone ligands $C_6H_5CH_2OC_6H_4C(O)NHN{=}CHR$ where, R = H, **3** ; CH_3, **4** and $C_6H_5CH_2OC_6H_4C(O)NHN{=}CHC_6H_4X$ where, X = H, **5** ; OCH_3, **6** ; Cl, **7** are prepared by the reaction of 4-benzyloxybenzoylhydrazine with formaldehyde, acetaldehyde, benzaldehyde, p-methoxybenzaldehyde and p-chlorobenzaldehyde respectively.

(4) The copper(II) complexes $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CHR\}_2Cu]$ where, R = H, **8** ; CH_3, **9** and $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CHC_6H_4X\}_2Cu]$ where, X = H, **10** ; OCH_3, **11** ; Cl, **12** are synthesized by the reaction of the ligand precursor 4-benzyloxybenzoylhydrazine with copper(II) monohydrate in presence of formaldehyde, acet-

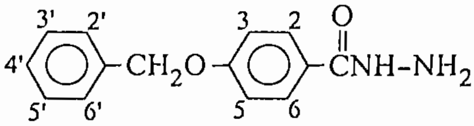
aldehyde, benzaldehyde, p-methoxybenzaldehyde and p-chlorobenzaldehyde respectively. The same complexes **8-12** are also synthesized by the direct reaction of the ligands $C_6H_5CH_2OC_6H_4C(O)NHN{=}CHR$ **3-4** and $C_6H_5CH_2OC_6H_4C(O)NHN{=}CHC_6H_4X$ **5-7** with copper(II) acetate monohydrate.

(5) The iron(III) complexes $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CHR\}_2Fe(H_2O)Cl]$ where, R = H, **13** ; CH_3, **14** ; $CH_3CH{=}CH$, **15** ; C_6H_5, **16** ; $CH_3OC_6H_4$, **17** ; ClC_6H_4, **18** ; $C_6H_5CH{=}CH$, **19** and $C_6H_5CH_2OC_6H_4$, **20** are formed when 4 - benzyloxybenzoylhydrazine **2** and aldehydes (such as formaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde, p-methoxybenzaldehyde, p-chlorobenazaldehyde, cinnamaldehyde and 4-benzyloxybenzaldehyde) are reacted with iron(III) chloride hexahydrate. The carbohydrazone $-C(O)NH{-}N{=}C< \longleftrightarrow -C(OH){=}N{-}N{=}C<$ moiety of the intermediate hydrazone ligands are not coordinated to the metal in keto form, instead they coordinated as a bidentate uninegative ligands via deprotonation through the enol form.

(6) Reaction of 4-benzyloxybenzoylhydrazine **2** and 2-hydroxybenzaldehyde with nickel(II) and copper(II) ions gave the complexes $[\{C_6H_5CH_2OC_6H_4C(O)NHN{=}CHC_6H_4O\}_2M]$, where M = Ni, **21** and Cu, **22** respectively. The reaction of 4-benzyloxybenzoylhydrazine **2** and diacetylmonoxime with nickel(II) and copper(II) ions gave the complexes $[\{C_6H_5CH_2OC_6H_4C(O){=}NN{=}C(CH_3){-}C(CH_3){=}NO\}M]_2$, where, M = Ni, **23** and Cu, **24** respectively.



1



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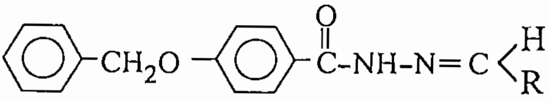
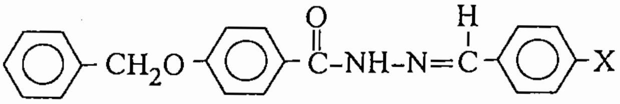
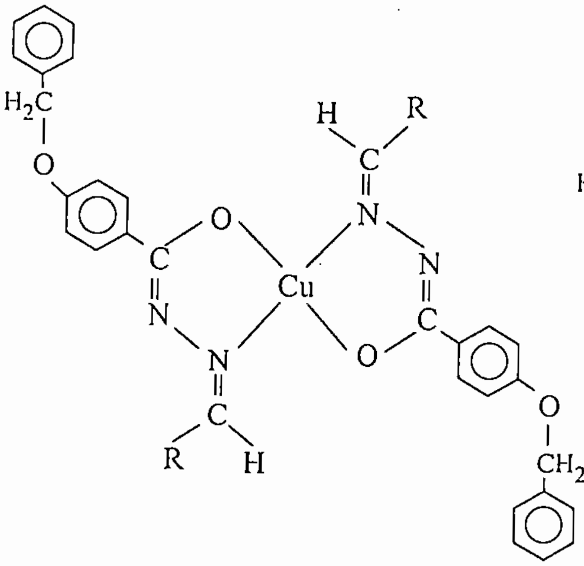


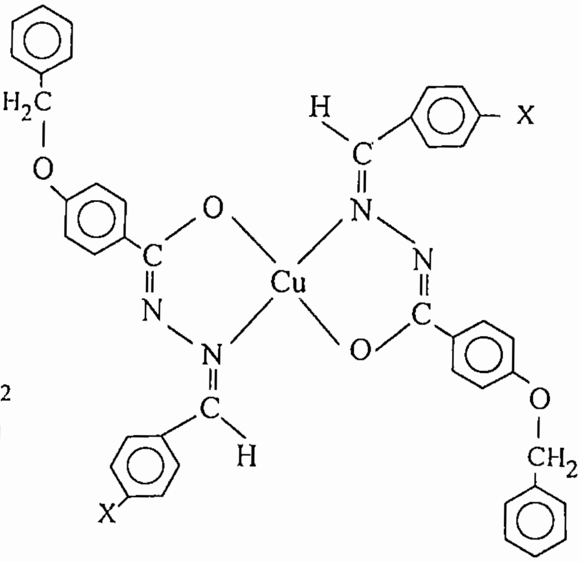
R = H, **3** ; CH_3, **4**



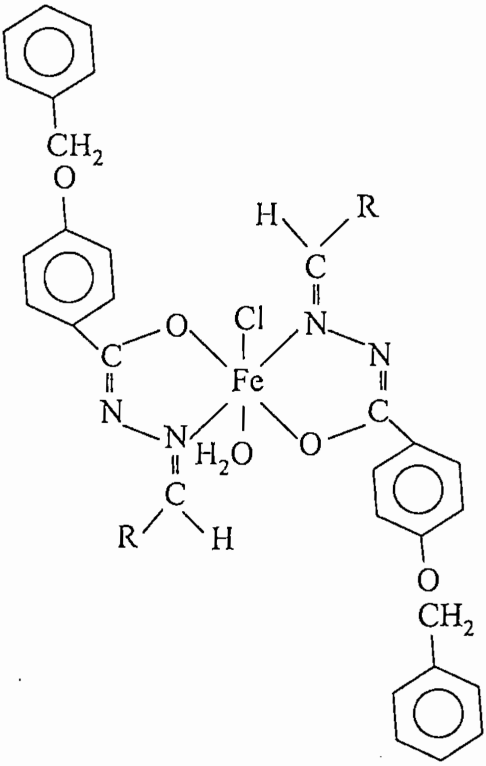
X = H, **5** ; OCH_3, **6** ; Cl, **7**



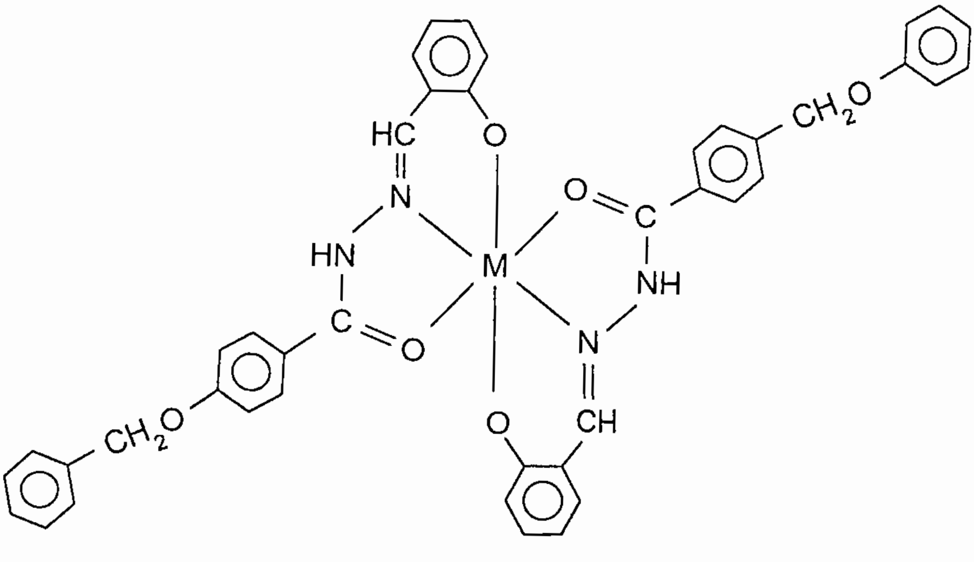
R = H, **8** ; CH_3, **9**



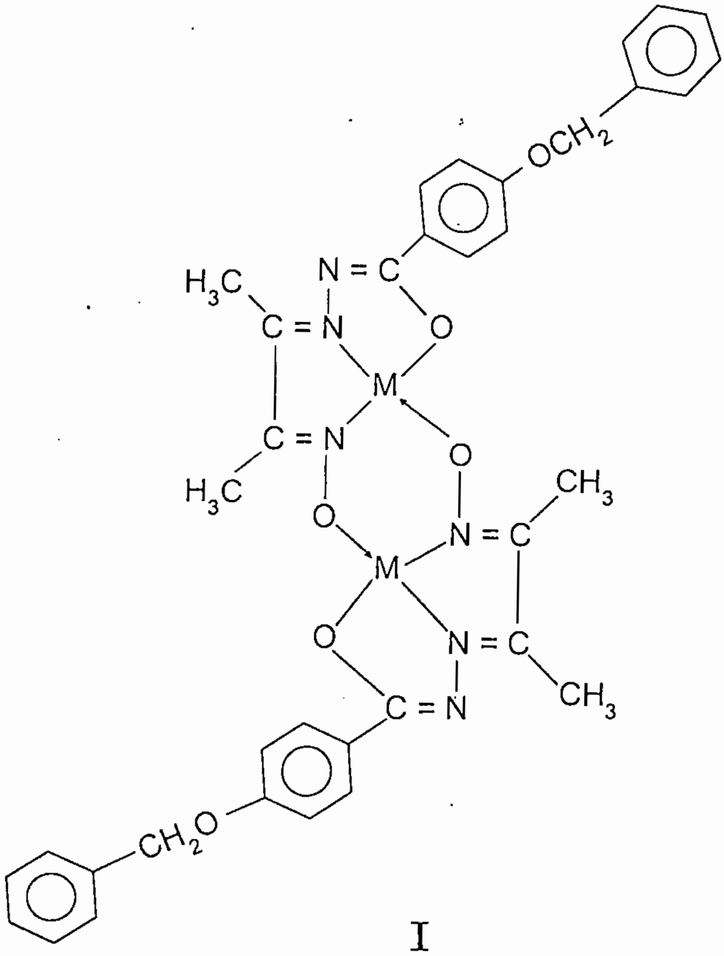
X = H, **10** ; OCH_3, **11** ; Cl, **12**



R = H, **13** ; CH_3, **14** ; $CH_3CH{=}CH$, **15** ; C_6H_5, **16** ; $CH_3OC_6H_4$, **17** ; ClC_6H_4, **18** ; $C_6H_5CH{=}CH$, **19** ; $C_6H_5CH_2OC_6H_4$, **20** ;



M = Ni, **21** ; Cu, **22**



I

M=Ni, **23** ; Cu = **24**

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List of Abbreviations

cm	centimeter
cm^{-1}	per centimeter
Fig.	Figure
i.e.	That is
K	Degree Kelvin
m.p.	Melting point
ml	Milliliter
No.	Number
nm	Nanometer
%	Percent
Λ	Conductance
λ	wave length
χ_g	Mass susceptibility
χ_m	Molar susceptibility
g	Gram
UV	Ultra-violet
IR	Infrared
mmol	Millimole
υ	Absorption maximum

CHAPTER 1

GENERAL INTRODUCTION

1.1 Background of complex compound

Transition metals have the unique tendency to form complexes or coordination compounds [1]. A complex has been defined as a species formed by the association of two or more simpler species capable of independent existance [2]. When one of the simpler species is a metal ion, the resulting entity is konwn as a metal complex. The characteristic feature of such a complex is that the metal atom occupies a central position in it. Thus a metal complex may be defined as a compound containing a central metal ion or atom to which are attached oppositely charged ions and/or neutral molecules whose number usually exceeds the number corresponding to the oxidation number of the metal ion or atom. The ions (usually anions) or neutral molecules, which are coordinated to the central ion in complex compounds, are called ligands or coordinating groups.

In a narrow sense the complex formation may be regarded as reversible association of one or more metal ions and ligand occuring in solution. In the wider sense, every Lewis acid-Lewis base reaction involving essentially the formation of coordinated covalent bond can be called a complex formation reaction.

Coordination compounds have always been a challenge to the inorganic chemist. In the early days of Chemistry they seemed to disagree the unusual rules of valence. Coordination Chemistry, at present, stands as a land mark in the field of scientific advancement embracing most diverse branch of science, engineering and technology. The rapidly developing field of bio-inorganic Chemistry is centered in the presence of coordination compounds in living system [3]. Coordination Chemistry plays an outstanding role in the biological processes that cause interesting changes, i.e., change of oxidation number, change of coordination number, exchange of metals and transfer of charge. This is partly due to an extensive and important involvement of such complexes in bioinorganic Chemistry.

It has now been well established that many of the chemical elements including metal ions control a vast range of biological process. Thus giving a new dimension to the coordination Chemistry.

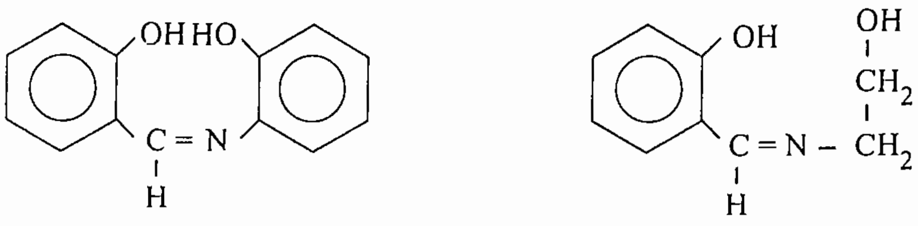
Although Jorgensen (1837-1914) began the extensive studies on the synthesis of complex compounds it was not until 1906 when the recognition of the true nature of the complex began with Alfred Werner (1866-1919) as set out in his classic work Neuere Anschauungen auf dem Gebiete der anorganischen chemie (1905) [4]. For this pioneering work Alfred Werner received the noble prize in 1913. The stereochemical studies of Werner were latter followed by the ideas G.N. Lewis and N.V. Sidgwick, who proposed that a chemical bond required the sharing of an electron pair. This lead to the idea that a neutral molecule with an election pair (Lewis base) can donate these electron to a metal ion or other electron acceptor (Lewis acid).

Although the electron pair donor acceptor concept of Lewis acid-Lewis base interactions for complex formation, it is apparent that the understanding the nature of bonding in metal complexes requires more detailed considerations [5]. At the present time four more or less distinct approaches to the theoretical treatment of the bonding and properties of coordination compounds are recognized. These theories are Valence Bond Theory (VBT) [6,7], The Crystal Field Theory (CFT) [8,9], The Ligand Field Theory (LFT) [10] and The Molecular Orbital Theory (MOT) [11-13].

1.2 Schiff bases ligands

The term 'Schiff base' comes from organic Chemistry which may be represented by the general formula $RCH=NR'$, where R and R' are cycloalkyl, aryl, alkyl or heterocyclic groups which may be rapidly substituted. Shiff bases are formed by the condensation of aldehydes or ketones with amines i.e. condensation between a primary amine and an active carbonyl group and formed the azomethine group (>C=N-) [14]. The Chemistry of Schiff base complexes has attracted a great deal of attension ever since Pfeiffer carried out his pioneering research in the 1930'S [15-18]. Schiff bases act as ligands. Metal chelates of Schiff base have been reviewed by Holm *et al.* [19]. Some of these compounds have analytical applications as colorimetric reagents and as metal indicators in complexometric titrations [20]. Since Schiff bases and their metal chelates are used as analytical reagents [21] for quantitative estimation of metals [22], fluorescence determination of microgram amounts of inorganic ions [23] and detection of many organic compounds present in very minute quantity, Schiff bases have been used as intermediates in the preparation of many organic products. They are used as fungicide and herbicides and appear to be active reagents against the plant enemies. Veil *et al.* [24] reported the action of many Schiff bases on the germination of seeds and found that some of them favour germination. Coloured Schiff bases and their transition metal complexes have been successfully used in dye and pigment industry. Thermally stable polymeric metal chelates of Schiff bases may be fabricated easily to form materials of high mechanical strength are gaining interest. Schiff base complexes have also other momentous physicological properties such as antibiotic activity, anti-inflamatory activity and analgesic activity. The properties of the complex metal ions are often strongly dependent on the ligand structure. And because of a considerable synthetic flexibility of the formation of Schiff base ligands of divers structural type, it is possible to effect certain stereochemical and electronic change and some related properties of the complex metal by using suitable designed Schiff base ligands. The ligand and their metal complexes have acquired wide interest in application to biological system [25-28] in catalyst [28,29]. There are many metallic compounds which have pharmacological effect and used as active ingredients [30].

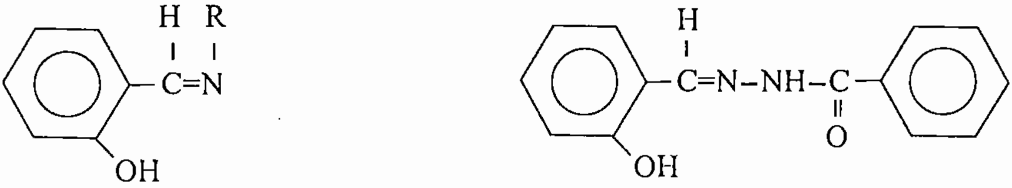
Most of the binuclear complexes have been prepared from tridentate Schiff bases containing ONO or ONS donor atoms; they are derived from the condensation of salicylaldehyde or acetylacetone with o-aminophenols, aminoalcohols, o-amino acids, o-aminothiophenols and aminothiols as in fig 1.1.



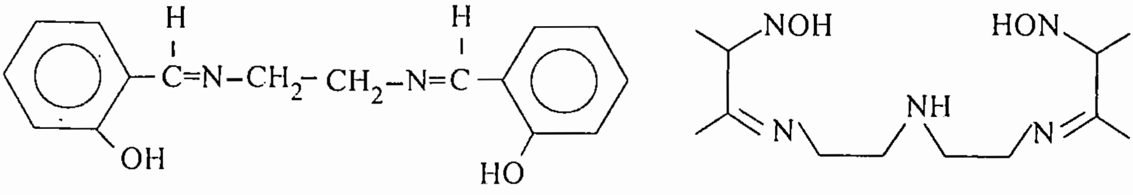
H_2SAP H_2SAE

Fig. 1.1

When these ligands react with metal ions, their tridentate character leads to the polymerization and polynuclear complexes with anomalous magnetic properties. It was presumed that the copper(II) ions of these chelates would have an unusual coordination number of three [31-34]. Some examples of open chain Schiff bases are given in fig.1.2.



Bidentate Tridentate



Tetradentate Pentadentate

Fig. 1.2

1.2.1 Unsymmetrical Schiff base ligand

An unsymmetrical Schiff base ligand as in fig. 1.3, that is very resistant to oxidation and consequently useful for complexing metals in high oxidation states [3].

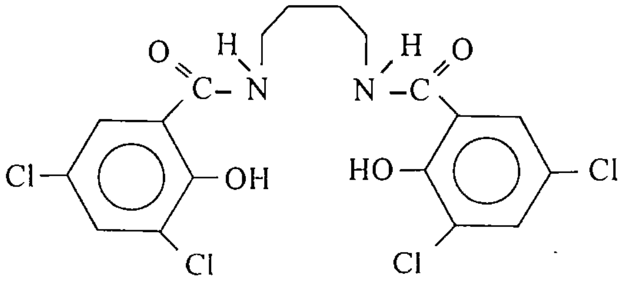


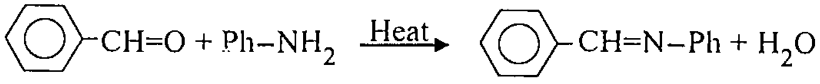
Fig. 1.3

1.2.2 Preparation and mechanism of Schiff base ligands

The Schiff base ligands are formed by the condensation of primary amine and aldehydes or ketones looses the acidic protons and behave as chelating agent (as in eq. 1.1)

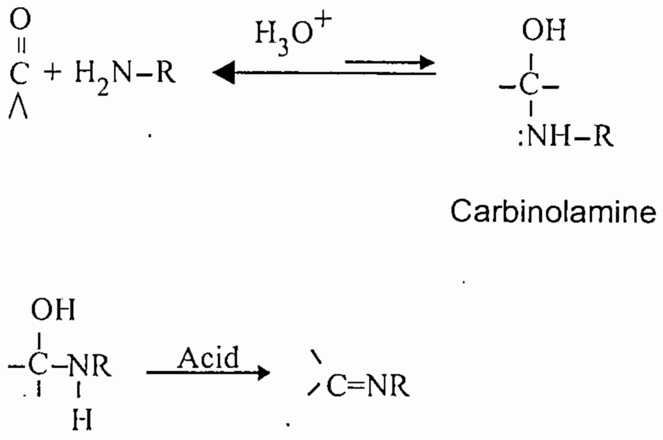
$$R-NH_2 + {>}C{=}O \longrightarrow {>}C{=}N-R \qquad \text{Eq. 1.1}$$

e.g.

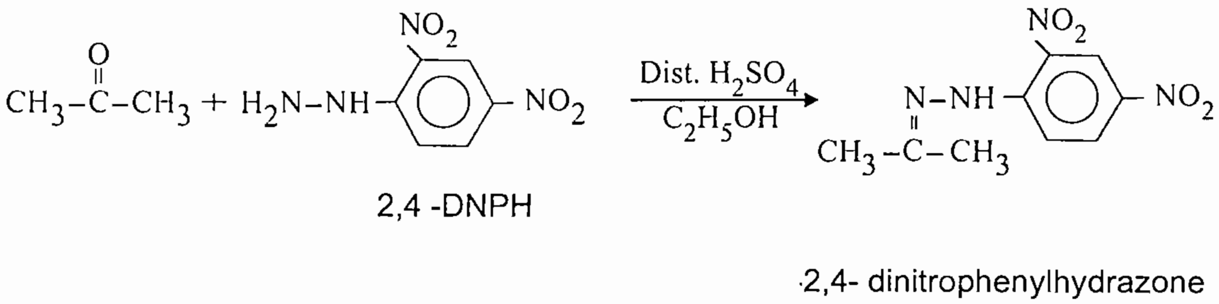


Mechanism :

The mechanism of imine formation (scheme 1.1) begins as a nucleophilc addition to the carbonyl group. In this case, the nucleophile reacts with the aldehydes or ketones to give an unstable addition product called a carbinolamine. A carbinolamine is a compound with an amine group (-NH_2,-NHR or -NR_2) and a hydroxy group of the same carbon (as in scheme 1.1)

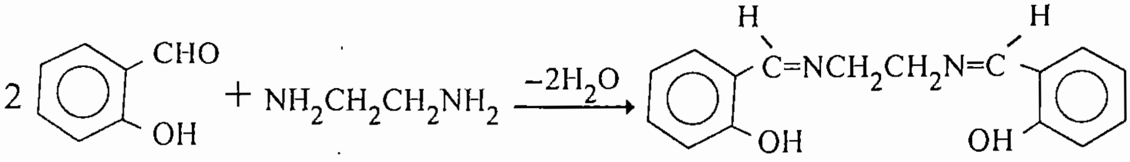


Sheme 1.1



Eq. 1.2

For example, the ligand bis(o-hydroxysalicyladene)ethylenediimine, looses the acidic proton in presence of metal ions to from chelate complexes.



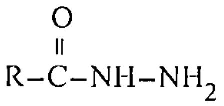
Eq. 1.3

and function as tetradentate ligand containing both oxygen and nitrogen donor atoms as in eq. 1.3.

1.3 Reaction of carbohydrazine or aroylhydrazine with aldehydes or ketones and their complexes

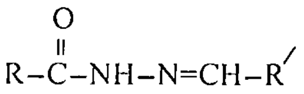
In the recent years there has been a growing interest in the Chemistry of hydrazones, hydrazides or aroylhydrazones owing to their pronounced biological activity and analytical applications [35-37] and form a class of important compounds in medicine and Pharmaceutical field. Besides these ligands have interesting ligational properties due to the presence of several potential coordination sites. They have been widely used as ligands in the preparation of a variety of transition metal complexes and their complexes also showed biological activites and mesogenic properties [38].The biological activities may be responsible for the azomethine linkage and the mesomorphism depends on the chain length of the substituents [39, 40].

Aroyl hydrazines (fig. 1.4) or aroylhydrazones (fig. 1.5) from stable chelates with transition metals [41]. The tuberculostic activity of these compounds has been attributed to the formation of stable chelates with transition metals present in the cell.



$R-\overset{\overset{O}{\parallel}}{C}-NH-NH_2$

Fig. 1.4



$R-\overset{\overset{O}{\parallel}}{C}-NH-N=CH-R'$

Fig. 1.5

(R = alkyl, aryl)

N-alkylidenearoylydrazones (fig. 1.5) can coordinate to a divalent metal ion either enolic from (as in fig. 1.6) or the ketonic form (as in fig. 1.7 and fig. 1.8) [42-45]. The tendency of the ligands (fig. 1.15) to react with Ni(II) in the enolic form to give complex (fig. 1.6) (M=Ni) becomes greater as the conjugating ability of the R group in the hydrazine residue increases [46]. Thus aroyl substituents favour the enolic tautomer of such ligands [47].

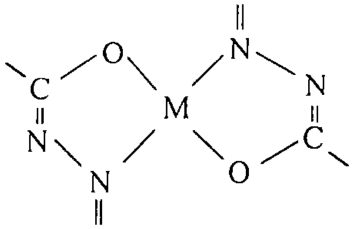


Fig. 1.6

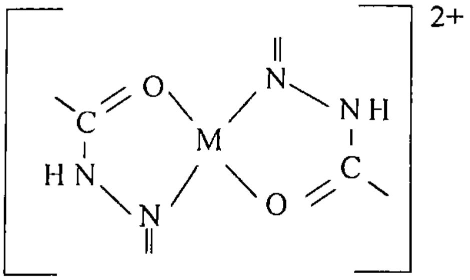


Fig. 1.7

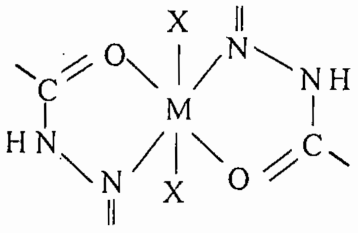
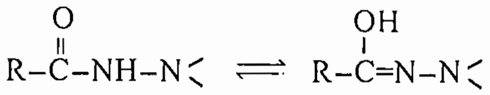


Fig. 1.8



$$R{-}\overset{\overset{O}{\parallel}}{C}{-}NH{-}N\langle \;\rightleftharpoons\; R{-}\overset{\overset{OH}{|}}{C}{=}N{-}N\langle$$

Furthermore, the coordinating ability of the counter ion to the metal determines whether the octahedral or square planar complex is formed [41]. For instance aroylhydrazones react with Ni(II) acetate yielding the corresponding bis(aroylhydrazinato)nickel(II) complex (fig. 1.6) (M=Ni), with the deprotonation of the secondary imino hydrogens, whereas with Ni(II)chloride complexes (fig. 1.8) (M=Ni), however, undergo dehaloprotonation with alcoholic potassium hydroxide to give the square planar neutral complexes.

Thus it seemed that such ligands might be used to form a new family of metal containing liquid crystals with greater thermal stability. And with this view McCabe *et al.* [48, 49] as well as Abser *et al.* [50] have reported the synthesis of a number of square planar aroylhydrazinatonickel(II) complexes; of which the methylidene derivatives were found to be liquid crystalline with wide range of transition temperature and greater thermal stability. However, attempt to introduce alkyl or aralkyl group at the methylidine end of the complexes resulted to non-liquid crystalline material.

Hydrazides or dihydrazides react with metal ion to give the metal complexes as in fig. 1.9, 1.10 (a), 1.10 (b) & 1.10 (c).

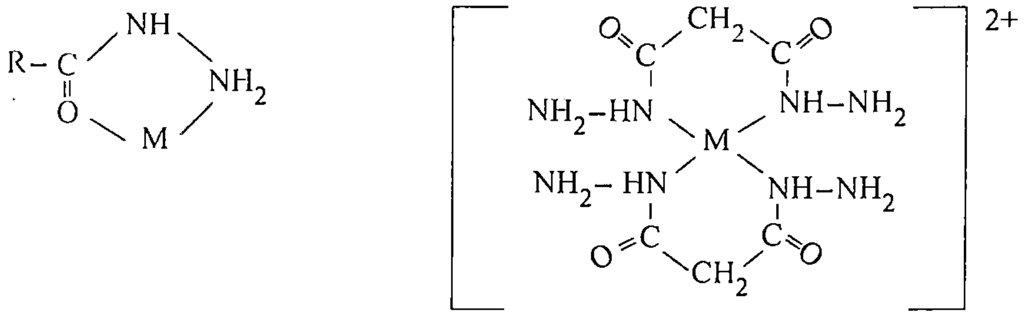


Fig. 1.9

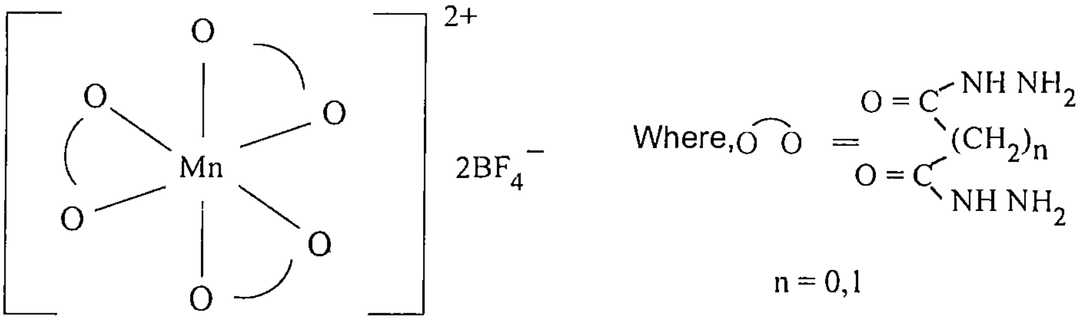


Fig. 1.10 (a)

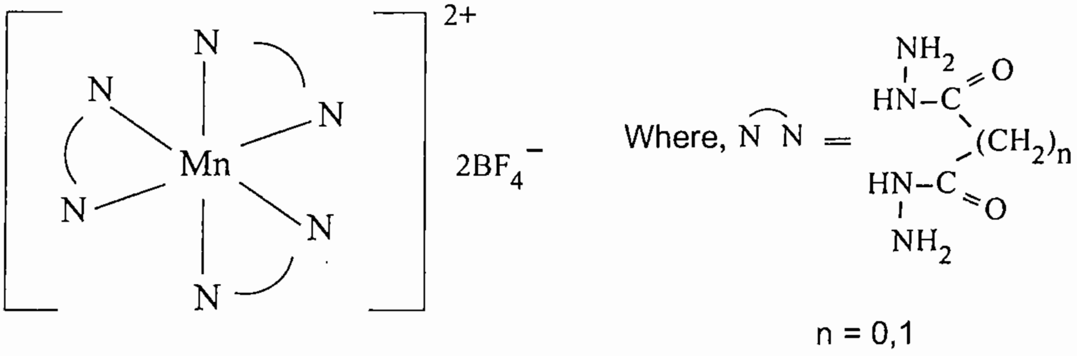


Fig. 1.10 (b)

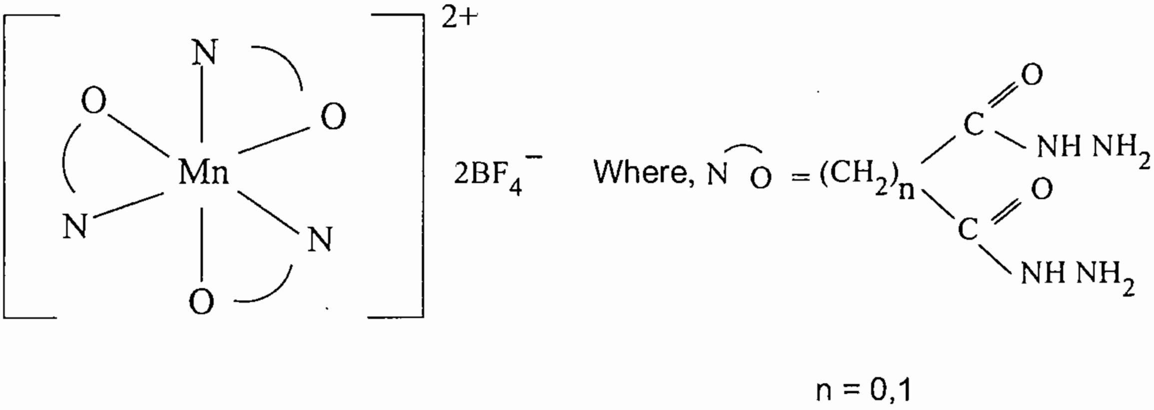
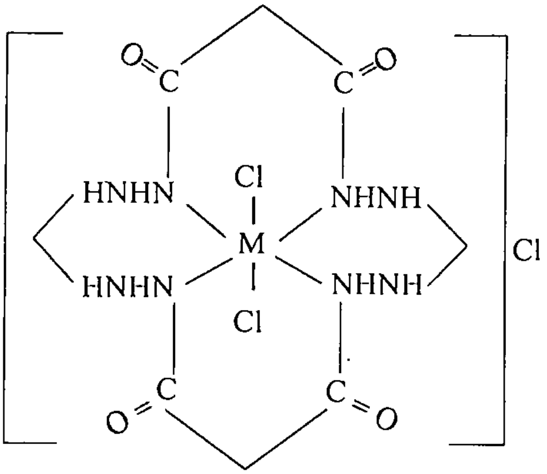


Fig. 1.10 (c)

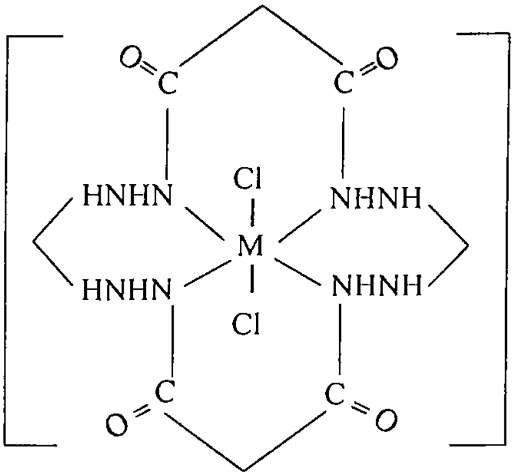
But the same type of complexes react with aldehydes or ketones to give simple Schiff base complexes or macrocyclic complexes depending upon the nature of ligand.

The macrocyclic complexes having the structure (fig. 1.11 and fig. 1.12) were formed by the template condensation of malonodihydrazide and formaldehyde in presence of the corresponding metal chloride [51].



M = Cr(III), Fe(III)

Fig. 1.11



M = Mn(II), Co(II), Ni(II), Cu(II)

Fig. 1.12

Voloshin *et al.* [52] prepared antimony containing oximehydrazonato semiclathro chelate as in fig.1.13(a) by the reaction of diacetylmonoximehydrazone with Fe(II) and $(C_6H_5)_3Sb(OH)_2$. The semiclathrochelate reacts with five fold excess of triethyl orthoformate (TOF) gave the clathrochelate depicted as is fig.1.13(b)

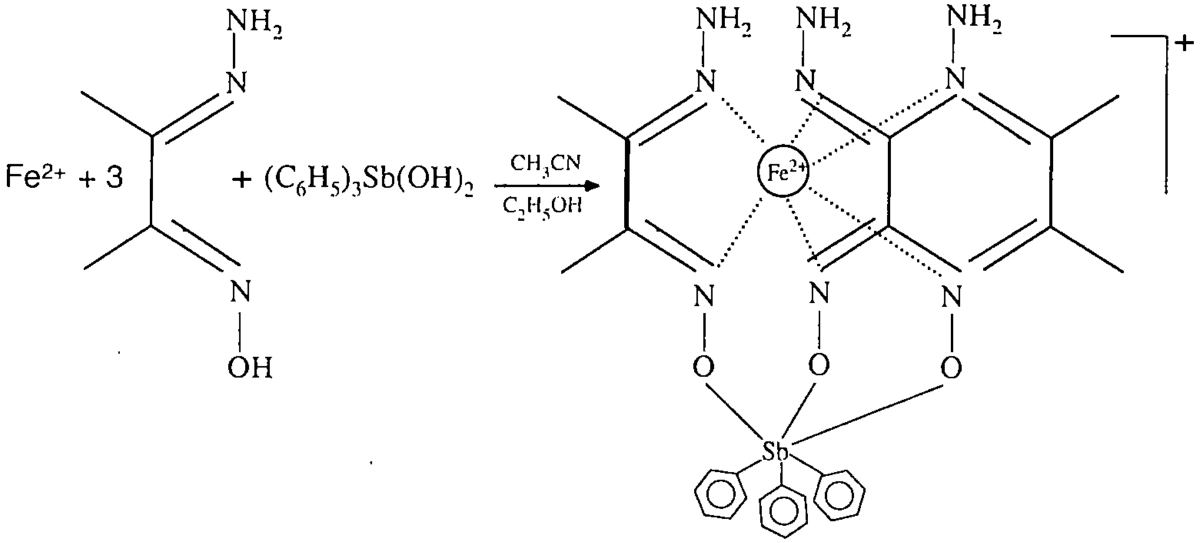


Fig. 1.13 (a)

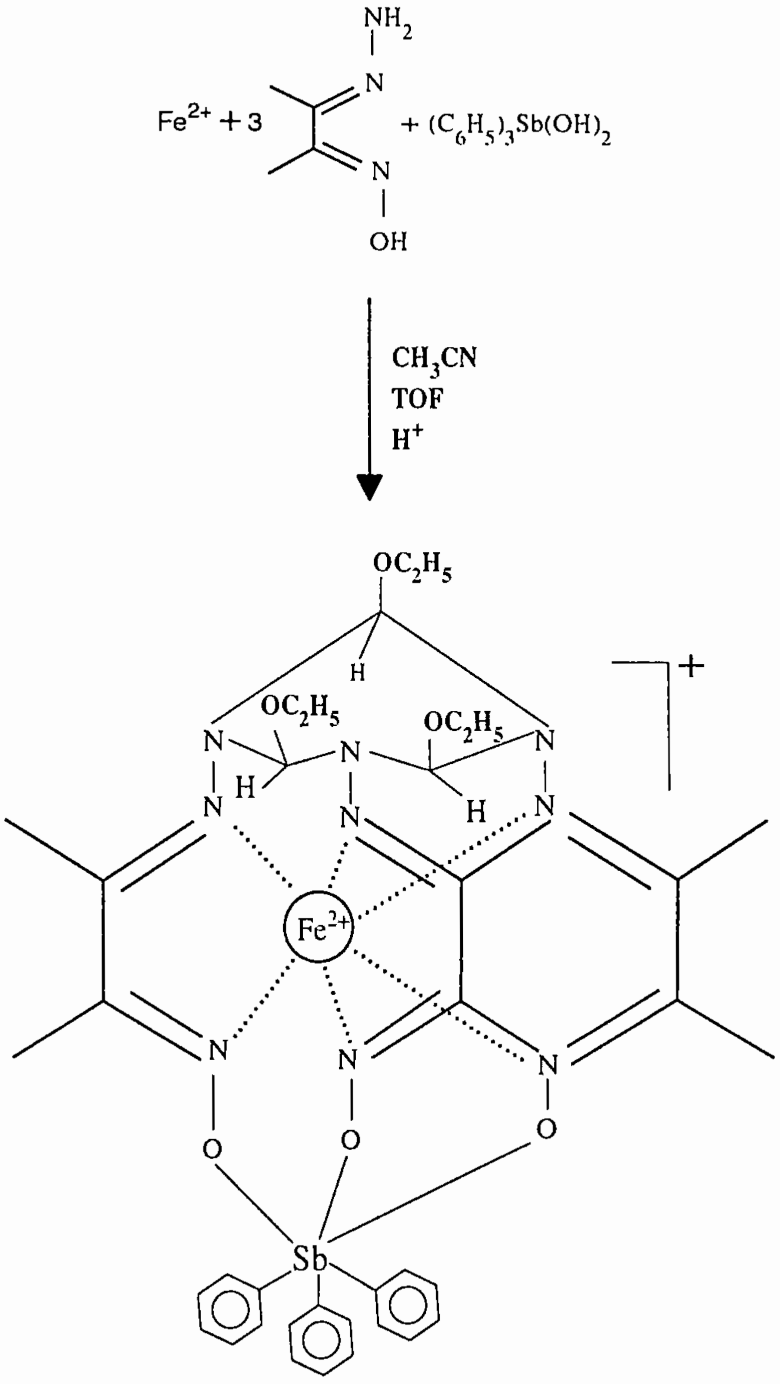

NH2
N
Fe2+ + 3
+ (C6H5)3Sb(OH)2
N
OH
CH3CN
TOF
H+
OC2H5
H
OC2H5
OC2H5
N
N
H
H
+
Fe2+
N
O
Sb

Fig. 1.13 (b)

Ibrahim *et al.* [53] has prepared some hydrazone ligands by mixing furan-2-carboxyldehyde and benzoic p-methyl or p-nitrobenzoic acid hydrazide in absolute ethanol (as in fig.1.14).

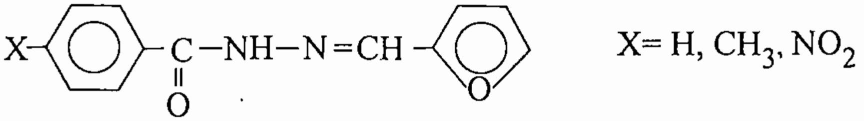
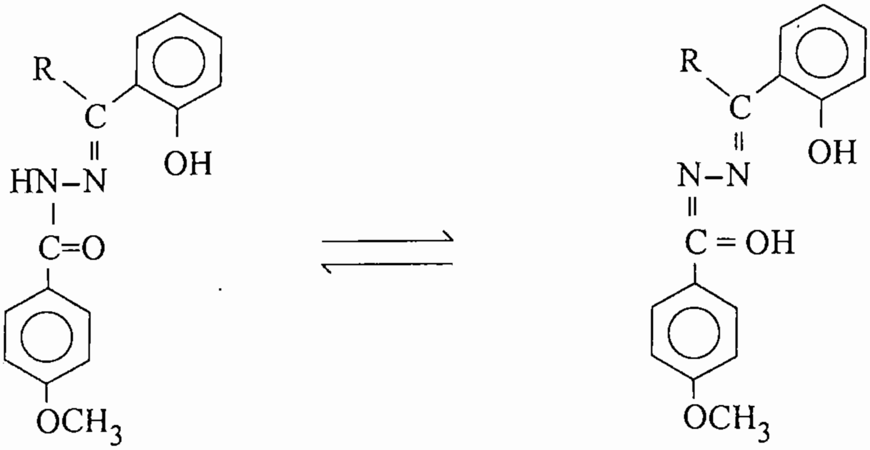


Fig. 1.14

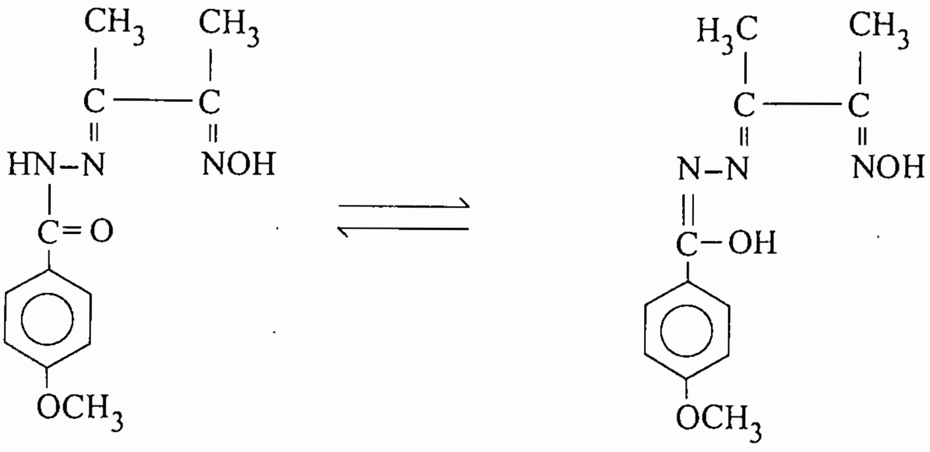
The reaction of salicylaldehyde-4-methoxybenzoylhydrazone, o-hydroxyacetophenone-4-methoxybenzoylhydrazone and diacetylmonoxime hydrazone with Ni(II) have been studied [35].

Salicylaldelyde-4-methoxybenzoylhydrazone [H_2SMBHON] (as in fig.1.15 and diacetylmonoxime-4-methoxybenzoylhydrazone, [H_2DAMMBHON] (as in fig. 1.16) reacts with $NiX_2.xH_2O$ [X=Cl, OAc] to give octahedral [35] and square planar nickel(II) complexes which are [Ni(SMBHON)(H_2O)$_3$], as in fig.1.15 and [Ni(DAMMBHON)H_2O] (as in fig.1.16) respectively.



H_2SMBHON

Fig. 1.15

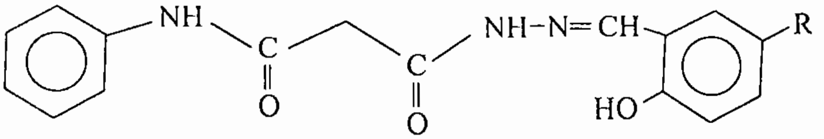


$H_2DAMMBHON$

Fig. 1.16

Metal complexes of aroylhydrazones have been broad application in biological process such as in the treatment of tumour [54, 55], tuberculosis [56], leprosy [57] and mental disorders. These are also known to act as herbacides [58], insecticides [59] and herbicides [60]. The biological activity has been attributed [61] to the complex forming abilities of ligands with metal ions present in the cells. These ligands can act both as neutral and mononegative ligands and favour certain geometries [62] to the complexes. Several new metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with hydrazones derived from benzoic, p-methyl or p-nitro substituted acid hydrazide and furan 2-carboxyaldehyde are reported [63, 64].

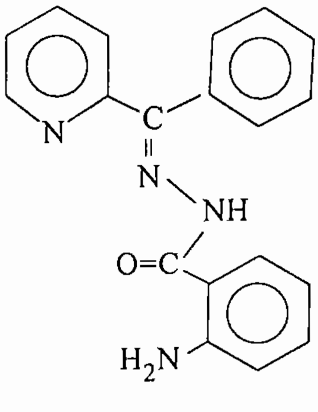
Jahagirder *et al.* [65] synthesized complexes of malonoanilic acid hydrazones with Co(II), Ni(II) and Cu(II). In this case he pointed out that the hydrazone ligand behave in a dibasic tetradentate manner in all the complexes except in the case of Cu(II) complexes where they act as dibasic tridentate ligands with O:N:O donor sequence. The acyl monohydrazones (as in fig.1.17) were synthesized by condensing the hydrazide with corresponding aldehydes in ethanol.



R = H, CH_3, Cl, OCH_3

Fig. 1.17

Dutta *et al.* [66] has been prepared the Schiff base ligands 2-benzoyl pyridine anthraniloyl hydrazone and bis (2-benzoyl pyridine) benzilhydrazone (as in fig. 1.18 and 1.19) by the condensation of anthraniloyl hydrazine and benzildihydrazine respectively with 2-benzoyl pyridine and their compounds of Ni(II), Co(II) and Mn(II).



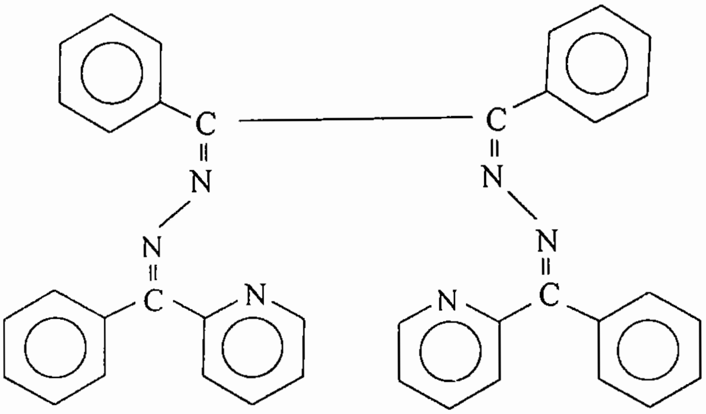


Fig. 1.18

Fig. 1.19

Fe(III) forms octahedral chelate complexes with catechol having amide group [67] as in fig. 1.20(a) and 1.20(b).

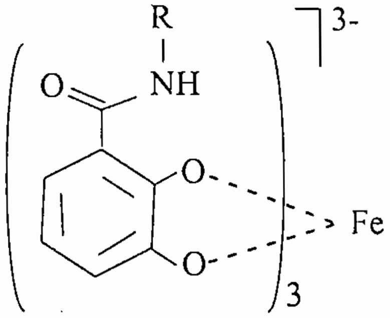


Fig. 1.20(a)

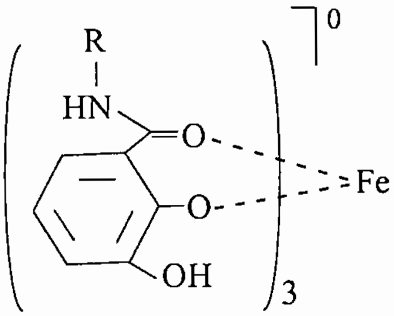
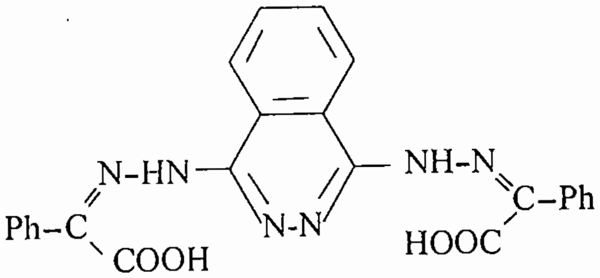


Fig. 1.20(b)

1,4-Dihydrazinophthalazine, and its hydrazone with various aldehydes and ketones, have been tested systematically for their antibacterial and antitumer. Okur *et al.* [68] has synthesized 1,4 bis(α - carboxybenzylidenehydrazino) phthaline (as in fig. 1.21). Rao *et al.* [69] have been synthesized various hydrazides and their Schiff bases by the reaction of 2-acetylpyridine isonicotinoyl hydrazine with aldehydes, one of them is 2-acetylpyridine isonicotinoyl hydrazone (as is fig. 1.22).



1,4 bis (α - carboxybenzylidenehydrazino) phthaline

Fig. 1.21

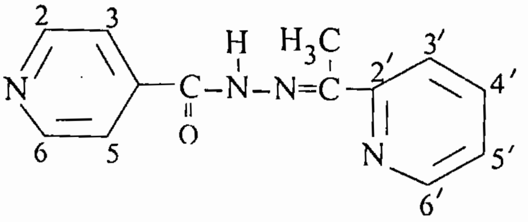


Fig. 1.22

1.4 Liquid crystalline property of Schiff base complexes

Liquid crystals or mesogenic compounds are materials which show liquid crystalline or mesomorphism. This behavior appears under given conditions when phases that do not correspond to an ordered solid or to a disordered liquid or solution are formed. These intermediate phases are called mesophases. Liquid crystals have been defined as 'orientionally ordered' liquids or 'positionally disordered' crystals [70] and combine properties of both the crystalline (optical and electrical anisotropy) and the liquid (molecular mobility and fluidity) states. There are two different ways of taking a crystal to a mesophase, corresponding to two broad families of liquid crystals, namely-

1.4.1 Thermotropic liquid crystals

By heating the crystalline solid or cooling the isotropic liquid : In this case the liquid crystal is termed thermotropic when thermotropic mesophase appears both in the heating and in the cooling process (i.e. When it is thermodynamically stable)it is called enantiotropic. The thermodynamically unstable mesophases which only appear in the cooling process due to histeresis in the crystallization point, are referred to as monotropic.

1.4.2 Lyotropic liquid crystals

By dissolving the compound in an adequate solvent under given concentration and temperature condition : A large number of compounds have been described as thermotropic or lyotropic liquid crystals and some of them exhibit both types of behavior (amphotropic liquid crystals). The thermotropic liquid crystals have gained a relavent place in the field of materials science, whereas lyotropic liquid crystals are fundamental in life science. Both kinds of self - organizing system play an important role in supramolecular Chemistry [71].

In mesogenic materials, the intermolecular forces responsible for the molecular arrangement are essentially the same as those operating in molecular solids. However only certain molecules show liquid crystalline behavior. Mesogenic molecules need to meet a series of structural and electrconic requirement [72] so that a satisfactory packing of molecules is achieved with appropriate interactions between neighbouring molecules. The existance of permanent dipole moments and their magnitude or the anisotropy of the molecular polarizability are determinant in the efficiency of these molecular interactions.

The ubiquitous presence of liquid crystal displays (LCD) has made liquid crystals perhaps the most popular and familiar class of advanced materials in modern life.

In contrast with this popularity, the rather specific character of the field and its absence from the usual academic curricula has kept even its basic principles unknown to most Chemist, unless they have happened to get involved in it at the research level. In recent years, these materials have given rise to important technological innovations. The advanced extend to fields as diverse as eiectrooptiocal displays, temperature sensing divices, high performance polymers, etc. [73]. The logical industrial interest has caused an enormous increment in research on mesogenic compounds.

1.5 Properties of liquid crystalline Schiff base complexes

The first report on covalent liquid crystalline coordination complexes appeared in 1977. Ground *et al.* described the mesomorphic properties of several nickel and palladium dithiolene derivatives [74] (as in fig. 1.23).

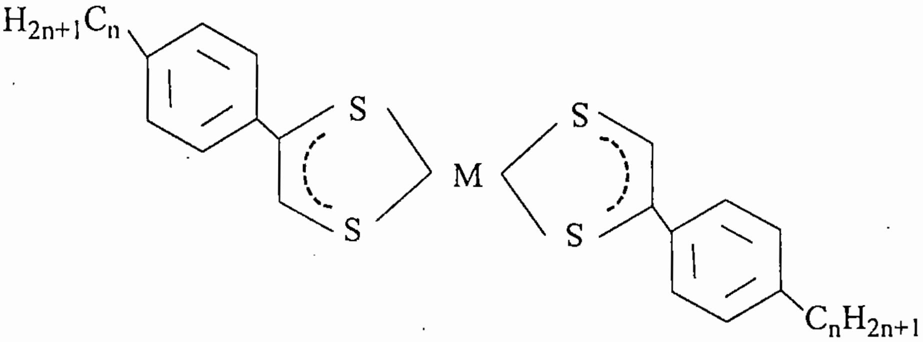


Fig. 1.23

The marked increase in research on metallomesogens gives rise to an important question: why this sudden interest in these materials also in the area of Transition Metal Liquid Crystals (TMLC) [75].

Some potential properties that TMLC offer (high polarizabilities, high birefringence's) have already been found superior to the values met in related organic materials, in spite of the scarcity of studies on physical properties. A property that organic materials cannot offer as easily as TMLC is paramagnetism; the dominance of organic liquid crystals have produced commercial electrooptic displays presently based on electric field (mainly TMLC seen to have some instability in electric field), but it is equally possible to design devices based on magnetic fields, which exert good control on the orientation of paramagnetic TMLC [75]. The complexes represented (as in fig. 1.24) can be obtained by reaction of the corresponding Schiff base with Ni(II) acetate under refluxing in ethanol [75].

The nickel is square planar coordinated as can be inferred form the diamagnetic nature of the complexes and according to the common stereochemistry of this kind of compound.

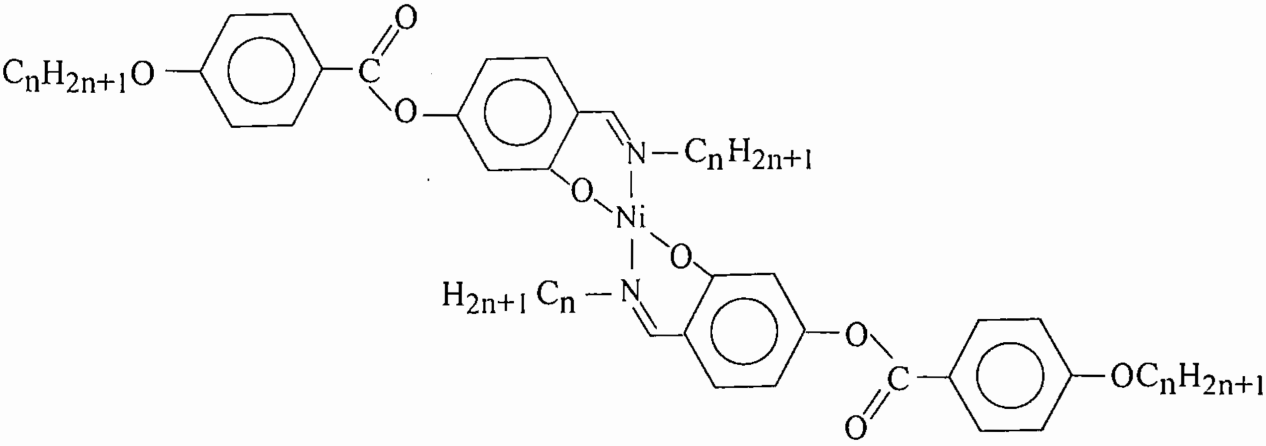


Fig. 1.24

Complexes with n=1,2 display monotropic nematic mesomorphism whereas for n>3 the nematic mesophases are enantiotropic [75] complexes with tetradentate Schiff bases as ligands (as in fig.1.25) give smectic mesomorphism.

Marcos *et al.* [76] synthesized a series of N-alkyl salicylaldimine complexes (as in fig. 1.26) of Ni(II) and Cu(II). Both series were shown to be nimatogenes.

The Schiff bases Cu(II) complexes (as in fig. 1.27) were also shown to be paramagnetic nematogens by Galyametdinol *et al.* [77].

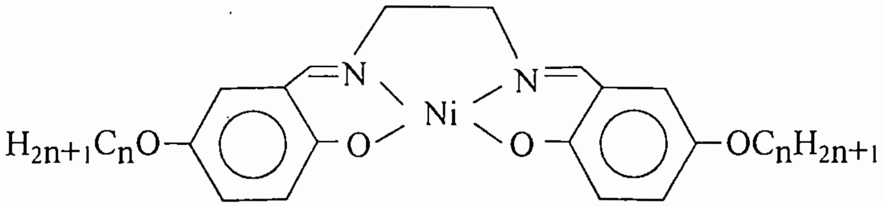
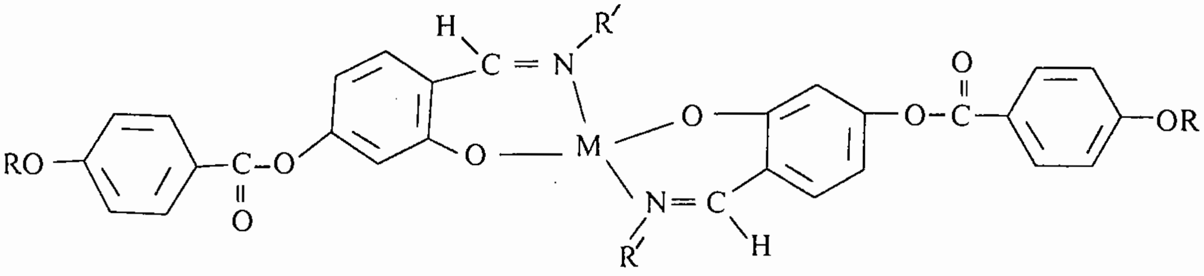


Fig. 1.25



M = Ni, Cu; R = C_nH_{2n+1}

Fig. 1.26

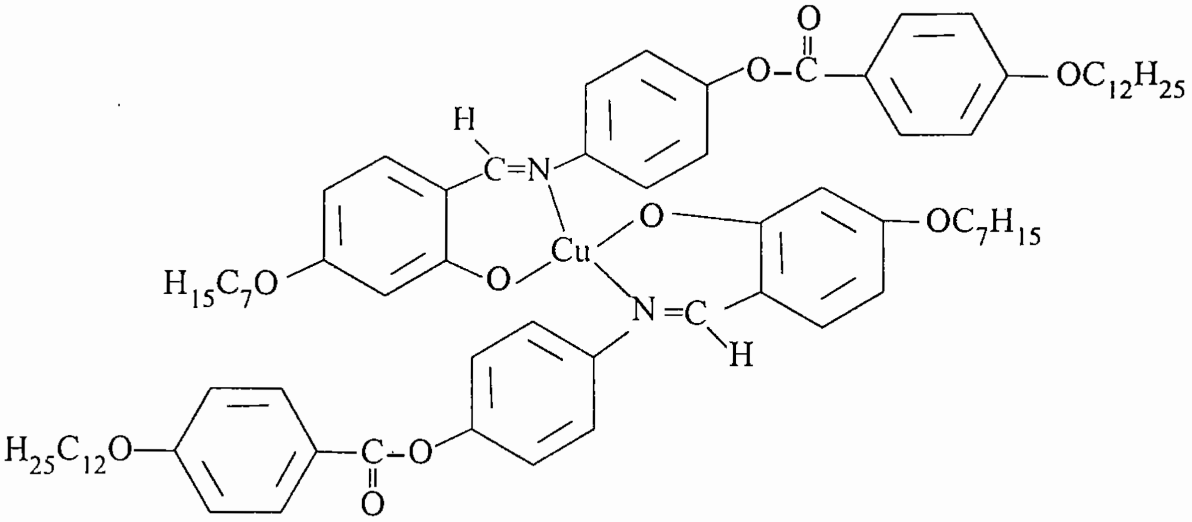


Fig. 1.27

Reaction of salicylaldehyde with different amines gives chelate complexes with first transition series (Fe, Ni, Cu) are known.

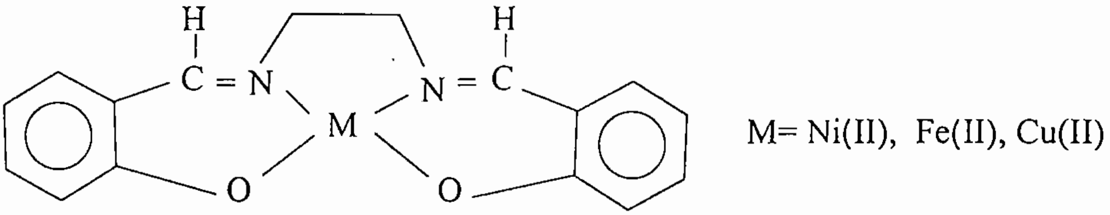


Fig. 1.28

Recently this type of work is extended by introducing long chain substituent in different position of salicylate to prepare liquid crystal types of complexes with various transition metals shown in fig. 1.29, 1.30 & 1.31.

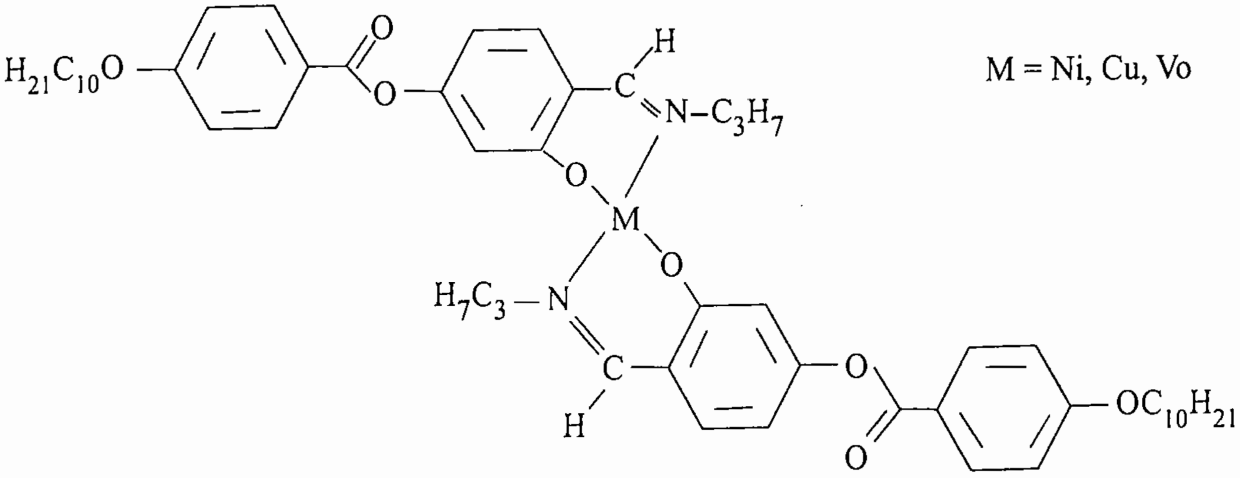


Fig. 1.29

n	m	M
10	1	Ni
10	2	
10	6	
10	10	
6	1	Cu
10	1	
14	1	
14	10	
10	2	
10	6	
10	10	

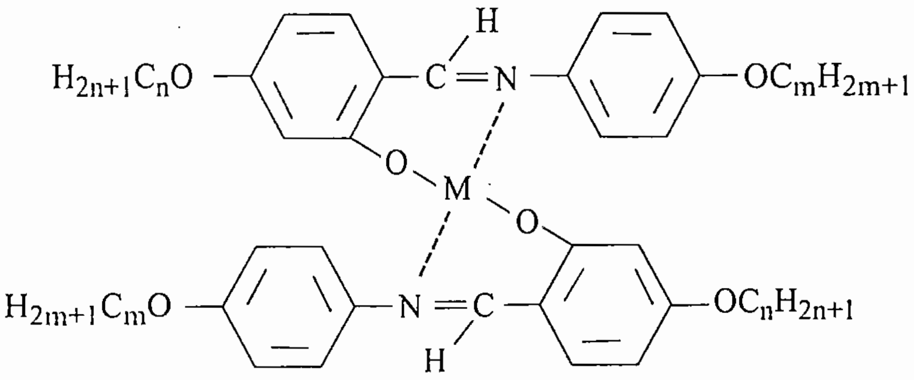


Fig. 1.30

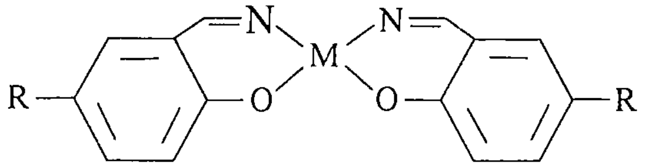


Fig.1.31

The geometrical environment of the iron(III) centre (fig. 1.32) is square pyramidal, similar to that in oxovanadium (IV)Schiff base complexes. Interestingly this complex easily undergoes chemical transformation to form a dinuclear iron(III) complex which also shows mesomorphic behavior [75] (fig. 1.33)

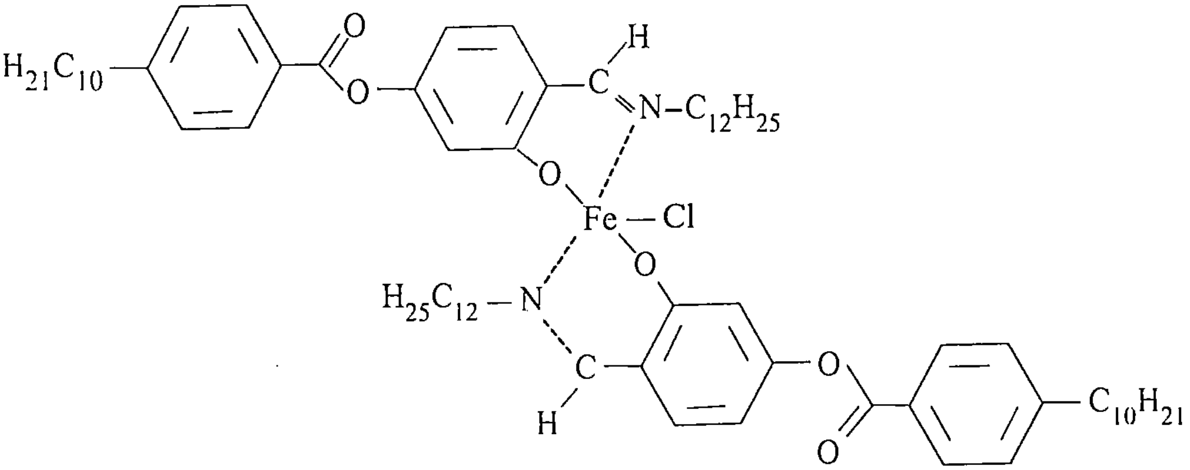


Fig. 1.32

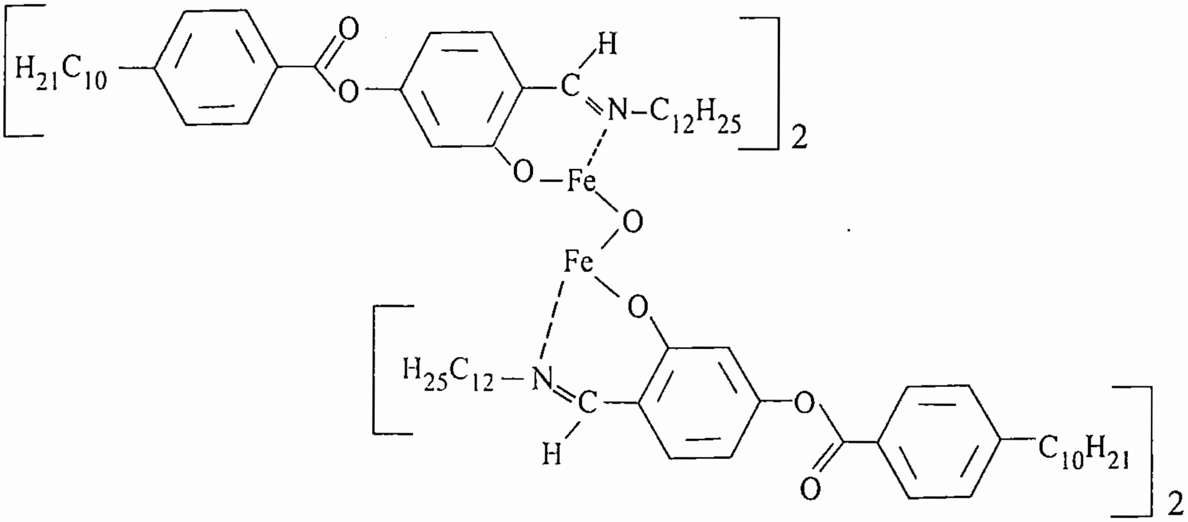


Fig. 1.33

The β -diketones having long chain substituent generally gives square planar β -diketonatocopper(II) complexes showed liquid crystalline properties. Such as,

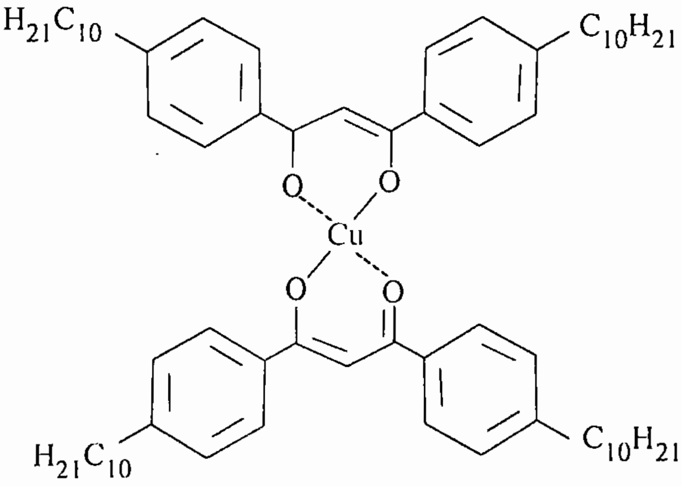
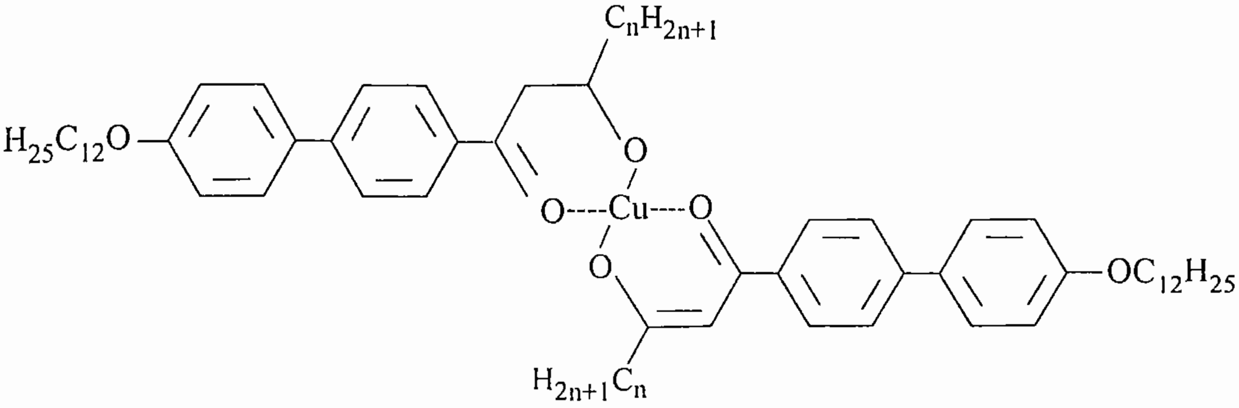
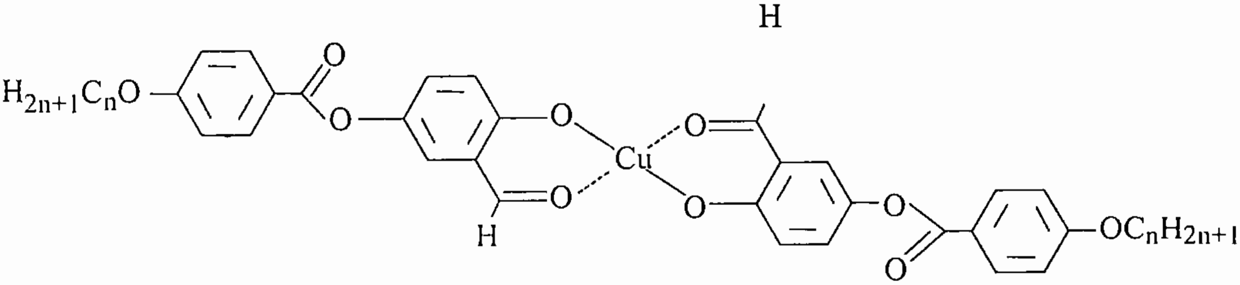


Fig. 1.34



[1-(4-dodecylbiphenyl) - 3 - alkyl propane - 1,3 - dionato]Cu(II) complex

Fig. 1.35



bis [5-(4-alkoxybenzoyloxy) salicylaldehydato]Cu(II) complex.

Fig. 1.36

1.6 Identification of liquid crystals

There are several well recognized techniques for identifying the mesophases, e.g. optical microscopic using a polarizing microscope [78,79], miscibility studies [80], differential scanning calorimetry (DSC) [81], X-ray diffraction. Among these the optical microscopic studies of the textures of different mesophases is probably the most popular and widely used. It is a powerful and economically practical experimental means for classifying the different mesophases particularly when these studies are combined with miscibility studies.

X-ray diffraction analysis gives direct information on the nature of the packing of the molecules in the mesophase while DSC is an excellent method for precise detection of phase transitions which are otherwise difficult to detect.

Miscibility studies, as based on the original investigations, made by Sackmann and Demus [82] can provide valuable confirmation of phase classification. Such studies are based on the experimental observation that for a binary mixture of two mesogens, a continuous region of homogeneous, miscible liquid crystal phase will occur completely across the extremes of the composition range of the phase diagram, only if both phases are of the same type, e. g. both nematic, both S_A, S_c etc.. On the other hand, components exhibiting different mesophase will not be continuously miscible across the whole composition range. Thus miscibility tests with a compound of known mesophase behavior give invaluable information about the type of mesophase formed by the compound in question.

The use of the polarizing optical microscope to study the mesophases is based on the fact that thin films of both crystals and liquid crystals mounted between glass slides and a cover slip are usually birefringence where viewed between crossed polarizes. Only in cases when the long axes of the molecules in the mesophase are arranged orthogonal to the supporting surface (as in the case of mesophases showing homeotropic texture), do the field of view become optically extinct. However, pressure on the cover slip gives immediate strain of flow birefringence in the fluid film, allowing it to be readily distinguished from the isotropic amorphous liquid. In all other cases, the birefringence liquid crystal film exhibit a microscopic texture with optical features which are characteristic of a particular type of mesophase. Thus in combination with the observed fluidity of the phase it allows the worker to identify the phase and to distinguish it from solid crystals and the optically isotropic amorphous liquid. Arrangement of an adjustable hot stage, along with the microscope, allows the transition temperature to be determined by observing the textural changes that occur during heating and cooling cycles. However, the textures of the mesophases are usually influenced by many external factors : the sample thickness boundary surfaces and purity begin some of these. The most commonly observed textures are focal conic, homeotropic, homogeneous, Schilieren and mosaic textures [78,79,80].

1.7 Applications of liquid crystals

The simultaneous possession of liquid like (fluidity) and solid-like (molecular order) character in a single phase makes liquid crystals unique and give rise to so many of their interesting properties and these properties has been exploited to a significant extent in technological applications [83, 84] such as electro-optical devices, direct temperature sensors and in analytical chemistry-particularly in GC / mass spectroscopy.

Applications in medical areas, such as the detection of disorders in the blood circulation and of breast cancer, are as varied as those in non-destructive material testing, e.g. in measurements of stress and tension in components [85]. Because thermometers based on liquid crystals are cheap and toxicologically harmless, and therefore safe to use, they are ideal for the measurement of body temperature or as an 'intelligent egg timer' [86]. In advertising, interesting possibilities arise, e.g. when body heat makes a brand name appear in various colours.

Lyotropic liquid crystals are being discussed as models for biological membranes [87]. The technical applications of liquid crystals were first limited to nematic and cholesteric phases. It was only in 1972 that Kahn first presented a display which used a liquid crystal forming a smectic A phase (88) special smectic phases today promise a new generation of quickly switching displays.

From symmetry considerations, Harvard physicist Meyer in 1974 deduced that smectic C phases of chiral molecules must have ferroelectric properties [89]. Such ferroelectric liquid crystalline phases allow substantially shorter switching times and posses a memory effect. Now a days, the screens of television and computer are making with such ferroelectric liquid crystal [90].

1.8 Aim and objective

Recently scientists gave special attention to the synthesis of transition metal complexes due to their catalytic, biological, mesogenic and paramagnetic properties [75]. Hydrazone ligands and their complexes have pronounced biological [30,40,91] as well as mesogenic properties [74,75]. Complex compounds having long chain residue or tailing may show mesogenic properties. Complex compounds having mesogenic properties as well as paramagnetic properties may overcome the uses of organic liquid crystals to prepare devices in electrooptical displays [75].

Therefore, considering the above importance of hydrazone complex compounds, the aim of the present work is to synthesis and charactarization of some new hydrazone complexes having long chain residue or tailing.

(1) Firstly preparation of some starting materials and ligand precursor, and some hydrazone ligands, such as ethyl- 4-benzyloxybenzoate, 4-benzyloxybenzoylhydrazine, N-(alkalidene/ benzalidene)4-benzyloxybenzoylhydrazone.

(2) Second step is the preparation of some hydrazone complexes by the reaction of the ligand precursor or 4-benzyloxybenzoylhydrazine and some aldehydes (such as formaldehyde, acetaldehyde, butanaldehyde, crotonaldehyde, cinnamaldehyde, benzaldehyde, p-methoxybenzaldehyde, p-chlorobenzaldehyde etc.) with different metal ions such as Fe, Ni, Cu etc.

(3) The synthesized complexes will be characterized by spectroscopic methods (e. g. infrared, UV-Visible, NMR, mass spectra), conductance, magnetic moment measurements and elemental analyses.

(4) If possible, this work will be extended to investigate whether the synthesized complexes possess any mesogenic properties or not.

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CHAPTER 2

METHOD AND MATERIALS

2.1 Physical measurements

2.1.1 Microanalyses (Elemental analysis)

Microanalyses for carbon, hydrogen and nitrogen were performed by using a perkin Elmer 2400 CHN Elemental analyzer at the University College, London, UK.

2.1.2 Estimation of metals

A known weight (say 0.2 g) of the complex was taken into a conical flask. Then concentrated sulfuric acid (2 mL) was added and fumed to dryness. Then concentrated Perchloric acid (2 mL) was added to this and mixture was fumed to dryness where all the complexes are decomposed and converted to the corresponding metal salts. Distilled water (l00 mL) was added to dissolve. The residue and the metal was estimated complexometrically using EDTA and DMG. Excellent agreement of results were found. The presence of chloride was confirmed by *Lassaignes test.*

2.1.3 Infrared spectra

Infrared spectra were recorded with a Shimadzu FTIR-8101 Infrared spectrometer as KBr disc.

2.1.4 Nuclear magnetic resonance spectra

^{1}H NMR spectra were obtained by using JEOl FX 270 MHz, NMR spectrometer from University of Glamorgan, pontypridd, Mid-Glamorgan U.K. Some NMR Spectra were obtained by using ultrashield 500 MHz Bruker spectrospin NMR spectrometer from University College, London, UK.

2.1.5 Mass spectra

Mass spectra were obtained by using a micromass ZAB SE mass spectrometer at the University College London, UK.

2.1.6 Electronic spectra

The UV-Visible spectra were obtained using a UV-160 spectrometer from (200-900) nm and some spectra were obtained from 330 nm to 900 nm (measuring absorbance) by using a SI06 spectrophotometer, WPA.

2.1.7 Conductivity [1,2]

The conductivity cell was normally cleaned several times with water and finally rinsed several times with acetone and allowed to dry in air. Conductivity measurements of the complex were carried out in dimethylsulphoxide, chloroform and dichloromethane. The molar conductivities of the complexes were calculated by using the following formula-

$$\wedge = \left(\frac{1000}{C}\right) \text{ x cell constant x observed conductivity.}$$

Where 'C' represents the concentration of the respective complex in mol/L. Generally 10^{-3}M solutions of the complexes were employed for this purpose. The conductance measurements were made at ambient temperature using type CG 857 No. 71798 SCHOTTGERATE GmbH, Germany, digital conductivity meter and a dip type cell with a polarized electrodes (with a dip type cell having platinized electrodes). The cell was calibrated with 0.01N, 0.001N and 0.0001N KCl solution. The cell constant of the cell is 1.065. The conductance of the pure solvent was also determined. The observed conductivity was obtained by subtracting the conductance of the pure solvent from the observed conductance of the complex solution.

2.1.8 Magnetic moment [3-5]

The Sherwood scientific magnetic susceptibility balance (M.S.B) is the result of collaboration with professor D.F. Evans of Imperial College, London and is designed as a replacement for a traditional Gouy balance system. The Evans method uses the same configuration as the Gouy method but instead of measuring the force which a magnet exerts of the sample, the equal and opposite force which the sample force exerts on a suspended permanent magnet observed.

The following general expression for mass susceptibility χ_g in C.G.S unit may be derived in the same manner for the traditional Gouy method.

$\chi_g = (l/m)\,[C\,(R-R_0) + \chi_{V_{air}}\,A]$ .... (i)

Where, χ_g = Mass susceptibility

R = susceptibility of the tube with sample

R_0 = susceptibility of the empty tube (Normally '-Ve')

l = Length of the tube with sample (in cm)

m = Mass of the sample (in gm)

A = Cross section area of the tube (in cm^2)

$\chi_{V_{air}}$ = Volume susceptibility of the displaced air, for powdered sample the air correction term may be ignored

C = constant of proportionality which is related to the calibration constant of a given balance by the following formula-

$C = C_{bal}/10^9$ ....(ii)

From (i) and (ii)

$\chi_g = C_{bal} \times l \times (R-R_0) \Big/ 10^9 \times m$ .... (iii)

Now, C_{bal} = Calibration constant = $C_{tube} \Big/ R-R_0$

$= (1766.842) \Big/ [\,2830 - (-17)\,]$

$= 2.086$ .... (iv)

From (iii) and (iv) we get

$\chi_g = 2.086 \times l \times (R-R_0) \Big/ 10^9 \times m$ .... (v)

The molar susceptibility, χ_m is the product of χ_g and the molecular weight of the substance. For compounds containing a paramagnetic ion χ_m will be less than the susceptibility per gram of the paramagnetic ion, χ_m^{corr} because of the diamagnetic contribution of the groups or ligand present. Since magnetic moments are additive, χ_m can be obtained from the χ_m by the addition of appropriate corrections.

For paramagnetic metal ions, it is customary to obtain the effective magnetic moments μ_{eff}, in Bohr magnetons (BM). μ_{eff} and χ_m^{corr} are related by the following expression.

$$(\mu_{eff})^2 = 3kT.\ \chi_m^{corr} / NB^2$$

Where, N = Avogadro's number

B = Bohr magneton

k = Boltzmannn constant

T = Absolute temperature

Hence, $\mu_{eff} = 2.828\sqrt{\chi_m^{corr}.T}$ .... (vi)

Magnetic moment was calculated by using the above equation. The temperature was recorded from a thermometer situated in the laboratory. Diamagnetic correction were made using pascal's [5] constant.

Hydrogen (H)	- 2.93
Carbon (C)	- 6.00
Nitrogen (open chain)	- 5.55
Nitrogen (Ring)	- 4.61
Oxygen (O)	- 4.60

For transition metal ions, the moments calculated on spin only basis is often are excellent agreement with the theory of course many of the transition group elements form covalent bonds. When this occurs, the magnetism is greatly modified. In fact, the deviation of susceptibility from normal has been used to determine the possible covalency of bonds and the configuration of the complex molecules. Magnetic measurements reveal the fundamental magnetic properties of coordination compounds. On the basis of magnetic moment measurements of complexes (either paramagnetic or diamagnetic) a possible electronic configuration can be assigned, which gives the clear information of the geometries of the complexes as well as it gives some insight to their bondings. Paramagnetic substances are characterized by the '+ve' values of the magnetic moment. The ions of the first transition group starting with Sc(III) ions and ending with Zn(II) ion have progressively zero to ten electrons in the 3rd shell. The first and the last numbers are diamagnetic but all other is possessing the intermediate number of electrons, are paramagnetic. It might be supposed that these ions would alternatively be paramagnetic and diamagnetic depending upon whether they posses an odd or even number of electrons.

Pairing or unpairing of electrons depends upon the strength of the crystal field. The greater the crystal field strength, the greater tendency of the electrons to become paired. If it is not so sufficient, then the 'Hund's rule is obayed. The configuration with maximum number of unpaired electrons is of high spin type and with minimum number of unpaired electors is of low spin type. As for an example, d^8, Ni(II) ion in presence of octahedral field is of the high spin type shows paramagnetism corresponding to the two unpaired electrons. But in presence of square planar field it becomes low spin type and is diamagnetic.

From the measurement of magnetic moment one can find the number of unpaired electrons present in the system and the possible configuration and also the structure.

2.1.9 Melting point measurement

Melting point of the ligands and the complexes were obtained with an electrothemal melting point apparatus model no. AZ 6512.

2.2 Thin layer chromatography [6]

Thin layer chromatography (TLC) is a technique much used for qualitative analysis. It can also be used for small- scale preparative work. The sample to be examined is applied to a thin layer adsorbent (usually very finely divided silica) coated on glass plate. The plate is developed in a jar containing a solvent, which is allowed to rise up through the adsorbent layer. Components of a mixture, if they are not colored, are rendered visible by a techniques. In preparative work, the components of the mixture are separately scraped from the plate together with the adsorbent and are isolated by extraction from the adsorbent.

R_f values, a useful but not always reproducible index of comparison of TLC behavior may be calculated as follows

$$R_f(A) = d_A / d_s$$

Where, d_A is the distance traveled by component A and d_s is the distance traveled by the solvent. If all the material has traveled virtually to the top of the plate, the experiment should be repeated using a less polar eluting solvent. If the material has moved little or no distance up the plate a more polar solvent is required.

2.3 Purification of solvents [6]

2.3(i) Ethanol

A dry round bottomed flask (2L) was fitted with a double surface condenser and calcium chloride drying tube. Clean dry magnesium turnings (5.0 g) and iodine (0.50 g) was placed in the flask, followed by the addition of 75 mL ethanol. The mixture was refluxed until the magnesium was converted into ethoxide. Then 900 mL of ethanol was added and the mixture was refluxed for one hour. After cooling, the ethanol was distilled off directly into a vessel in which it was collected, by reassembling the condenser for downward distillation via a asphalt head adapter. Then the ethanol was stored over type 4A molecular sieves.

2.3(ii) Methanol

Anhydrous methanol was obtained by distillation of methanol with magnesium turnings as exactly the same procedure for ethanol and stored over type 4A molecular sieves.

2.3(iii) Dichloromethane

The commercial grade of dichloromethane was purified by washing with 5% sodium carbonate solution, followed by water, dried over anhydrous calcium chloride and then distilled. The fraction of boiling point (40^0 C - 41^0 C) was collected and stored over type 4A molecular sieves.

2.3(iv) Chloroform

The commercial product contains upto 1% of ethyl alcohol, which is added as a stabilizer. The alcohol was removed by shaking the chloroform, five or six times, with about half of its volume of water, then dried over anhydrous calcium chloride for at least 24 hours, distilled and stored over type 4A molecular sieves.

2.3(v) Acetone

The acetone was refluxed with successive quantities of potassium permanganate until the violet color persisted. It was then dried with anhydrous potassium carbonate, filtered from the desiccant and distilled. Then acetone was stored over type 4A molecular sieves. Precaution was taken to exclude moisture, i.e., a calcium chloride guard tube was used.

2.3(vi) Water

Water was purified by distillation from Potassium permanganate.

2.4 Name of chemicals used and suppliers

Name of chemicals	Suppliers
Acetone	BDH Chemicals (England)
Acetaldehyde	BDH Chemicals (England)
Anhydrous potassium carbonate	Aldrich Chemical Co.
Benzyl bromide	Aldrich Chemical Co.
Benzaldehyde	Aldrich Chemical Co.
4-bromobenzaldehyde	Aldrich Chemical Co.
Chloroform	E.Merck (Germany)
Crotonaldehyde	Aldrich Chemical Co.
Cinnamaldehyde	Aldrich Chemical Co.
4-Chlorobenzaldehyde	Aldrich Chemical Co.
Conc. ammonia solution	Aldrich Chemical Co.
Conc. sulfuric acid	Aldrich Chemical Co.
Cupric acetate monohydrate	E. Merck (Germany)
Dichloromethane	BDH Chemicals Ltd. (England)
Dimethylglyoxime	Aldrich Chemical Co.
Diacetylmonoxime	Aldrich Chemical Co.
Dimethylsulphoxide	BDH Chemicals Ltd. (England)
4-ethylbenzaldehyde	Aldrich Chemical Co.
Ethyl-p-hydroxybenzoate	Aldrich Chemical Co.
Ethanol	Kerro Co.Ltd. (Bangladesh)
Formaldehyde	J.T. Baker Chemical Co.
Ferric trichloride hexahydrate	E. Merck (Germany)
Hydrazinehydrate	BDH Chemicals Co. (England)
4-hydroxybenzaldehyde	BDH Chemicals Co. (England)
Methanol	BDH Chemicals Co. (England)
Petroleum ether (40^0C - 60^0C)	BDH Chemicals Co.Ltd. (England)
Potassium permanganate	BDH Chemicals Co.Ltd. (England)
Silica gel	E. Merck (Germany)

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CHAPTER 3

EXPERIMENTAL

3.1 Preparation of ligand precursor and ligands [1,2]

(i) Preparation of ethyl-4-benzyloxybenzoate $C_6H_5CH_2OC_6H_4COOC_2H_5$ *1*

A mixture of ethyl-4-hydroxybenzoate (16.6 g, 100 mmol), benzyl bromide (17.28 g, 101 mmol) and anhydrous potassium carbonate (25.08 g, 182 mmol) in acetone (200 mL) was refluxed for 96 hours. The solvent was removed in a vacuum line and the solid mass was treated with water (150 mL). The product was extracted with dichloromethane (4 x 30 mL) and left for overnight to give a colourless crystal which was filtered off and washed with petroleum ether to remove any traces of starting materials and dried in a vacuum desiccator over anhydrous calcium chloride. The product ethyl-4-benzyloxybenzoate was free from starting materials (checked by TLC).

Melting Point : 32^0C

Yield : 70%, 17.9 g

(ii) Preparation of 4-benzyloxybenzoylhydrazine $C_6H_5CH_2OC_6H_4CONHNH_2$ **2**

A mixture of ethyl-4-benzyloxybenzoate (5.09 g, 19.5 mmol) and hydrazine hydrate (2.93 g, 58.5 mmol) in ethanol (25 mL) was refluxed for 72 hours. A silky white precipitate was formed after cooling the reaction mixture to room temperature. The product was filtered off, washed with excess water and finally washed with petroleum ether. The product was recrystallized from hot ethanol and the purity was checked by TLC.

Melting Point : 95^0C

Yield : 80% , 3.80 g

(iii) Preparation of N-methylidene(4-benzyloxy)benzoylhydrazone

$C_6H_5CH_2OC_6H_4C(O)NHN=CH_2$ **3**

To the ethanolic solution of 4-benzyloxybenzoylhydrazine (1.0 g, 4.13 mmol in 50 mL) an aqueous solution of formaldehyde (0.33 g, 4.13 mmol) was added and the reaction mixture was refluxed for 2 hours. The volume of the mixture was reduced to one fourth in a vacuum line. The white precipipate was washed with petroleum ether and recrystallized from chloroform to give compound **3**.

Melting Point : 160^{0}C

Yield : 60%, 0.63 g

(iv) Preparation of N- ethylidene(4-benzyloxy)benzoylhydrazone

$C_6H_5CH_2OC_6H_4C(O)NHN=CHCH_3$ **4**

To the ethanolic solution of 4-benzyloxybenzoylhydrazine (0.48 g, 2 mmol) acetaldehyde (0.09 g, 2 mmol) was added and the reaction mixture was refluxed for about 2 hours. A white precipitate was formed after reducing the volume of the reaction mixture to one fourth in a vacuum line and washed with petroleum ether(40^{0}C-60^{0}C). The precipitate was recrystallized from chloroform.

Melting Point : 165^{0}C

Yield : 65% , 0.35 g

(v) Preparation of N-benzylidene(4-benzyloxy)benzoylhydrazone

$C_6H_5CH_2OC_6H_4C(O)NHN{=}CHC_6H_5$ **5**

A mixture of ethanolic solution of 4-benzyloxybenzoylhydrazine (0.56 g, 2.31 mmol) and a solution of benzaldehyde (0.25 g, 2.31 mmol) was refluxed for about 2 hours. A white precipitate was formed which was washed with petroleum ether (40^0C-60^0C) and recrystallized from chloroform.

Melting Point : 185^0C

Yield : 75%, 0.53 g

(vi) Preparation of N-(p-methoxybenzylidene)(4-benzyloxy)benzoylhydrazone

$C_6H_5CH_2OC_6H_4C(O)NHN{=}CHC_6H_4OCH_3$ **6**

An ethanolic solution of 4-benzyloxybenzoylhydrazine (0.38 g, 1.57 mmol) was added to the solution of 4-methoxybenzaldehyde (0.21 g, 1.57 mmol) and the reaction mixture was refluxed for 2 hours. A white precipitate was formed which was washed with petroleum ether and recrystalized from chloroform.

Melting point : 190^0C

Yield : 70%, 0.38 g

(vii) Preparation of N-(p-chlorobenzylidene)(4-benzyloxy)benzoylhydrazone

$C_6H_5CH_2OC_6H_4C(O)NHN=CHC_6H_4Cl$ **7**

A mixture of 4-benzyloxybenzoylhydrazine (0.48 g, 2 mmol) and p-chlorobenzaldehyde (0.28 g, 2 mmol) in ethanol was refluxed for 2 hours. The volume of the mixture was reduced to one fourth in a vacuum line. A white precipitate was formed which was washed with petroleum ether and recrystallized from chloroform.

Melting Point : 185°C

Yield : 65%, 0.47 g

3.2 Synthesis of copper complexes

(A) Reaction of 4-benzyloxybenzoylhydrazine with coppper(II) acetate in presence of some aldehydes : Synthesis of complexes **8-12**

(i) Synthesis of bis[N-methylidene(4-benzyloxy)benzoylhydrazinato]Cu(II), ***8***

To the ethanolic solution of 4-benzyloxybenzoylhydrazine (0.24 g, 1 mmol in 25 mL) an aqueous formaldehyde solution (0.08 g, 1 mmol, 37% w/w) was added and the mixture was refluxed for half an hour. A solution of copper(II) acetate monohydrate (0.10 g, 0.50 mmol in 5 mL ethanol) was added to the above mixture and further refluxed for another hour under nitrogen to give a brick red precipitate which was filtered off and washed with ethanol, hot methanol and recrystallized from chloroform under nitrogen atmosphere.

Melting point : 170^{0}C (d)

Yield : 69%, 1.96 g

(ii) Synthesis of bis[N-ethylidene(4-benzyloxy)benzoylhydrazinato]Cu(II), ***9***

A mixture of 4-benzyloxybenzoylhydrazine (0.25 g, 1.03 mmol) and acetaldehyde (0.05 g, 1.03 mmol) in ethanol (25mL) was refluxed for about half an hour. Then a solution of cupric acetate monohydrate (0.10 g, 0.52 mmol in 5 mL ethanol) was added to the above reaction mixture and reflux was continued for further one hour to give a gray precipitate, which was collected by filtration and washed thoroughly with ethanol, water and finally by hot methanol. Recrystallization from chloroform gave complex as gray microcrystalline solid.

Melting point : 180^{0}C

Yield : 71%, 2.21 g

(iii) Synthesis of bis[N-benzylidene(4-benzyloxy)benzoylhydrazinato]Cu(II), ***10***

A mixture of 4-benzyloxybenzoylhydrazine (0.25 g, 1.03 mmol) and benzaldehyde (0.11 g, 1.03 mmol) in ethanol (25 mL) was refluxed for half an hour after which a solution of cupric acetate monohydrate (0.10 g, 0.52 mmol in 5 mL ethanol) was added to the reaction mixture and reflux was continued for further one hour to give a brick red precipitate. The product was filtered off, washed thoroughly with ethanol, water and finally with hot methanol.

Melting Point : 240^{0}C

Yield : 40%, 0.75 g

(iv) Synthesis of bis [N-(p-methoxybenzylidene)(4-benzyloxy)benzoylhydrazinato]Cu(II), ***11***

To the ethanolic solution of 4-benzyloxybenzoylhydrazine (0. 30 g, 1.23 mmol in 25 mL) p-methoxybenzaldehyde (0.17 g, 1.23 mmol, 37% w/w) was added and the mixture was refluxed for half an hour. A solution of copper(II) acetate monohydrate (0.12 g, 0.62 mmol in 5 mL ethanol) was added to the above mixture and further refluxed for another hour to give a brick red precipitate which was filtered off and washed with ethanol, hot methanol and recrystallized from chloroform under nitrogen atmosphere.

Melting point : 245^0C (d)

Yield : 75%, 0.20 g

*(v) Synthesis of bis[N-(p-chlorobenzylidene)(4-benzyloxy)benzoylhydrazinato] Cu(II), **12***

A mixture of 4-benzyloxybenzoylhydrazine (0.40 g, 1.65 mmol) and p-chlorobenzaldehyde (0.23 g, 1.65 mmol) in ethanol (25 mL) was refluxed for half an hour after which a solution of cupric acetate monohydrate (0.16 g, 0.83 mmol in 5 mL ethanol) was added to the reaction mixture and reflux was continued for further one hour to give a brown precipitate. The product was filtered off, washed thoroughly with ethanol, water and finally with hot methanol.

Melting point : 250^0C

Yield : 70%, 0.25 g

(B) Preparation of copper complexes **8-12** from corresponding ligands $C_6H_5CH_2OC_6H_4C(O)NHN{=}CHR$, where R = H, CH_3, C_6H_5, $C_6H_4OCH_3$ and C_6H_4Cl **3-7** respectively.

(i) Synthesis of bis[N-methylidene(4-benzyloxy)benzoylhydrazinato] Cu(II), ***8***

To the ethanolic solution of N-methylidene(4-benzyloxy)benzoylhydrazone (0.51 g, 2 mmol) a solution of cupric acetate monohydrate (0.20 g, 1 mmol) was added and the mixture was refluxed for one hour. A brick red precipitate was formed which was filtered off, washed with ethanol, hot methanol and recrystallized from chloroform.

Melting Point : 170^0C

Yield : 69%

Same procedure was applied for the preparation of complexes **9-12** using corresponding ligands $C_6H_5CH_2OC_6H_4C(O)NHN{=}CHR$, where R = CH_3, **9** and $C_6H_5CH_2OC_6H_4C(O)NHN{=}CHC_6H_4X$, where X = H, **10** ; OCH_3 , **11** ; Cl, **12** respectively.

(C) Reaction of 4-benzyloxybenzoylhydrazine ***2*** *with copper(II) acetate*

A mixture of 4-benzyloxybenzoylhydrazine (0.25 g, 1.03 mmol) and copper(II) acetate monohydrate (0.103 g, 0.5 mmol) in ethanol (25 mL) was refluxed for half an hour. A deep off white precipitate was obtained. Reaction of off precipitate with formaldehyde, acetaldehyde etc. in stoicheometric ratio does not from any copper complex.

3.3 Synthesis of iron complexes

Reaction of 4-benzyloxybenzoylhydrazine with ferric chloride in presence of some aldehydes : Synthesis of complexes **13-20**

(i) Reaction of 4-benzyloxybenzoylhydrazine with ferric chloride in presence of formaldehyde : Synthesis of $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CH_2\}_2Fe(H_2O)Cl]$, ***13***

To the hot ethanolic solution of 4-benzyloxybenzoylhydrazine (0.24 g, 1.0 mmol) an aqueous solution of formaldehyde (0.08 g, 1.0 mmol, 37%) was added and the reaction mixture was refluxed for an one hour. Then ethanolic solution of ferric chloride hexahydrate (0.14 g, 0.5 mmol) was added to the above mixture. The mixture was refluxed for 2 hours. The yellow coloured precipitate was filtered off and washed with hot ethanol and dried over calcium chloride. The compound was soluble in dimethylsulfoxide, dimethylformamide but insoluble in acetone, chloroform and dichloromethane.

Melting Point : 215^{0}C (d)

Yield : 60%, 0.18 g

(ii) Reaction of 4-benzyloxybenzoylhydrazine with ferric chloride in presence of acetaldehyde : Synthesis of $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CHCH_3\}_2Fe(H_2O)Cl]$, ***14***

4-benzyloxybenzoylhydrazine (0.48 g, 2 mmol) was dissolved in ethanol by heat. An ethanolic solution of acetaldehyde (0.09 g, 2 mmol) was added to the above solution and was refluxed. The mixture became turbid after an one hour. Then ferric chloride hexahydrate (0.27 g, 1 mmol) solution was added to the above mixture and refluxing was continued for further 2 hours. Orange - cream precipitate was obtained which was filtered off, washed with hot ethanol and dried over calcium chloride. The compound was soluble in dimethylsulfoxide, dimethylformamide but insoluble in acetone, ethanol, dichloromethane and chloroform.

Melting point : 262^{0}C

Yield : 70%, 1.38 g

(iii) Reaction of 4-benzyloxybenzoylhydrazine with crotonaldehyde and ferric chloride : Synthesis of $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CHCH{=}CHCH_3\}_2Fe(H_2O)Cl]$, **15**

Ethanolic crotonaldehyde (0.35 g, 4.99 mmol) solution was added to the hot ethanolic solution of 4-benzyloxybenzoylhydrazine (1.21 g, 4.99 mmol) and the mixture was refluxed for an one hour. To the above mixture ferric chloride hexahydrate (0.67 g, 2.50 mmol) solution was added and the resulting mixture was refluxed for further 2 hours with constant stirring. The colour of the precipitate turned from white to orange red which was filtered off, washed with ethanol and finally washed with hot ethanol. The compound was soluble in dimethylsulfoxide, dimethylformamide but insoluble in acetone, ethanol, dichloromethane and chloroform.

Melting point : 276^{0}C

Yield : 55%, 0.96 g

(iv) Reaction of 4-benzyloxybenzoylhydrazine with ferric chloride in presence of benzaldehyde : Synthesis of $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CHC_6H_5\}_2Fe(H_2O)Cl]$, **16**

4-benzyloxybenzoylhydrazine (0.55 g, 2.27 mmol) solution was prepared in ethanol by heat and benzaldehyde solution (0.24 g, 2.27 mmol) in the same solvent was added to the above solution and refluxed for an one hour. Then ferric chloride hexahydrate solution (0.31 g, 1.14 mmol) was added and the resulting mixture was further refluxed for 2 hours. Orange precipitate was obtained which was filtered off, washed with ethanol and finally washed with hot ethanol. The compound was soluble in dimethylsulfoxide and dimethylformamide.

Melting point : 220^0C

Yield : 69%, 0.60 g

(v) Reaction of 4-benzyloxybenzoylhydrazine with p-methoxybenzaldehyde and ferric chloride : Synthesis of $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CHC_6H_4OCH_3\}_2Fe(H_2O)Cl]$, **17**

Ethanolic p-methoxybenzaldehyde (0.22 g, 1.65 mmol) solution was added to the hot ethanolic solution of 4-benzyloxybenzoylhydrazine (0.40 g, 1.65 mmol) and the mixture was refluxed for an one hour. To the above mixture ferric chloride hexahydrate (0.22 g, 0.83 mmol) solution was added and the resulting mixture was refluxed for 2 hours with constant stirring. Light orange colour precipitate was formed which was filtered off, washed with ethanol and finally washed with hot ethanol. The compound was soluble in dimethylsulfoxide and dimethylformamide.

Melting point : 230^0C

Yield : 71%, 0.49 g

(vi) Reaction of 4-benzyloxybenzoylhydrazine with ferric chloride in presence of p-chlorobenzaldehyde : Synthesis of $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CHC_6H_4Cl\}_2 Fe(H_2O)Cl]$, **18**

4-benzyloxybenzoylhydrazine (0.45 g, 1.86 mmol) was dissolved in ethanol by heat. An ethanolic solution of p-chlorobenzaldehyde (0.26 g, 1.86 mmol) was added to the above solution and was refluxed for an one hour. Then ferric chloride hexahydrate (0.25 g, 0.93 mmol) solution was added to the above mixture and reflux was continued for 2 hours. The product was filtered off, washed with hot ethanol and dried over calcium chloride. The compound was soluble in dimethylsulfoxide, dimethylformamide but insoluble in acetone, ethanol, dichloromethane, and chloroform.

Melting point : 250^0C

Yield : 67%, 0.52 g

(vii) Reaction of 4-benzyloxybenzoylhydrazine with ferric chloride in presence of cinnamaldehyde : Synthesis of $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CHCH{=}CHC_6H_5\}_2Fe(H_2O)Cl]$, **19**

An ethanolic solution of cinnamaldehyde (0.73 g, 5.52 mmol) was added to the hot ethanolic solution of 4-benzyloxybenzoylhydrazine (1.34 g, 5.52 mmol). The resulting mixture was refluxed for an one hour with constant stirring. To the above clear solution ferric chloride hexahydrate (0.75 g, 2.76 mmol) was added and the reflux was continued for 2 hours. A light pink coloured precipitate was obtained which was filtered off, washed with hot ethanol and dried over calcium chloride. The compound was soluble in dimethylsulfoxide and dimethylformamide.

Melting point : 245^0C

Yield : 73%, 1.65 g.

(viii) Reaction of 4-benzyloxybenzoylhydrazine with ferric chloride in presence of 4-benzyloxybenzaldehyde : Synthesis of $[\{C_6H_5CH_2OC_6H_4C(O)NN{=}CHC_6H_4OCH_2C_6H_5\}_2Fe(H_2O)Cl]$, **20**

To the hot ethanolic solution of 4-benzyloxybenzoylhydrazine (0.50 g, 2.07 mmol) 4-benzyloxybenzaldehyde (0.44 g, 2.07 mmol) was added and the reaction mixture was refluxed for an one hour. Then ethanolic solution of ferric chloride hexahydrate (0.28 g, 1.04 mmol) was added to the above mixture. The resulting mixture was further refluxed for 2 hours. The orange coloured precipitate was filtered off, washed with hot ethanol and dried over calcium chloride. The compound was soluble in dimethylsulfoxide, dimethylformamide but insoluble in acetone, chloroform and dichloromethane.

Melting Point : 235^{0}C

Yield : 60%, 0.18 g

(ix) Attempted reaction

Reaction of 4-benzyloxybenzoylhydrazine with ferric chloride in presence of butyraldehyde

To the hot ethanolic solution of 4-benzyloxybenzoylhydrazine (0.50 g, 2.10 mmol) butyraldehyde (0.15 g, 2.10 mmol) was added and the reaction mixture was refluxed for an one hour. Ethanolic solution of ferric chloride hexahydrate (0.28 g, 1 mmol) was added to the above mixture and refluxing was continued for 5 hours. No colour change observed. When volume reduced, some off white precipitate, may be the hydrazone ligand not iron complexes (qualitative).

3.4 Reaction of 4-benzyloxybenzoylhydrazine with Ni(II) and Cu(II) ions in presence of 2-hydroxybenzaldehyde and diacetylmonoxime.

(i) Reaction of 4-benzyloxybenzoylhydrazine and 2-hydroxybenzaldehyde with M(II) ions, where, M = Ni, Cu : *Synthesis of complexes* ***21,22***

A mixture of 4-benzyloxybenzoylhydrazine (0.24 g, 1 mmol in 20 mL ethanol) and 2-hydroxybenzaldehyde (0.12 g, 1 mmol in 10 mL ethanol) was refluxed for an hour. An ethanolic solution of nickel(II) acetate tetrahydrate (0.12 g, 0.5 mmol) was added to the above mixture and reflux was continued for further 2 hours. A greenish yellow precipitate was formed which was filtered off, washed with hot ethanol, dried over calcium chloride and collected as **21.** The compound was soluble in dimethylformamide but insoluble in chloroform,dichloromethane and acetone.

Melting point : > 250^{0}C

Yield : 60%, 0.22 g

Same procedure was applied for the preparation of complex **22** using copper(II) acetate dihydrate.

(ii) Reaction of 4-benzyloxybenzoylhydrazine and diacetylmonoxime with M(II) ions, where, M = Ni, Cu : *Synthesis of complexes* ***23,24***

To the ethanolic solution of 4- benzyloxybenzoylhydrazine (0.24 g, 1mmol in 20 mL) diacetylmonoxime (0.10 g, 1 mmol in 25 mL ethanol) was added and refluxed for an one hour. To the above mixture nickel(II) acetate tetrahydrate (0.12 g, 0.5 mmol in 5 mL ethanol) was added and reflux was continued for further 2 hours. A reddish brown precipitate was formed which was filtered, washed with hot ethanol, dried over calcium chloride and collected as **23**. The compound was soluble in dimethylformamide but insoluble in chloroform, dichloromethane and acetone.

Melting point : > 250^{0}C

Yield : 70%, 0.26 g

Same procedure was applied for the preparation of complex **24** using copper(II) acetate dihydrate.

The same complexes **23** and **24** were also formed if the reactions were carried out in (1: 1: 1) molar ratio instead of (2:2:1) ratio of the ligand precursor, diacetylmonoxime and M(II) ions.

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CHAPTER 4

RESULTS AND DISCUSSION

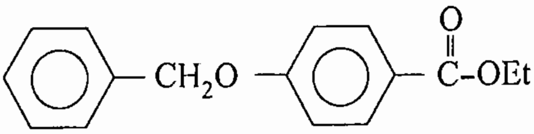
4.1 Preparation of ligand precursor and ligands

(i) Preparation of ethyl-4-benzyloxybenzoate

The reaction of ethyl-4-hydroxybenzoate with benzyl bromide gave ethyl-4-benzyloxybenzoate as described in section 3.1. This ligand was previously prepared in this laboratory [1].

The IR spectral data (Table 1) of compound **1** showed a strong absorption band at 1692 cm^{-1} is suggested for the stretching frequency of ν(C=O) moiety of ester group. The bands at 1605 cm^{-1} & 1578 cm^{-1} are suggested for the aromatic, ν(C=C) stretching frequencies. The peaks at 1174 cm^{-1} and 1100 cm^{-1} may be assigned to the ν(C=O) absorption.

This infrared spectral bands are consistent with the literature [1] values of compound **1**



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*(ii) Preparation of ligand precursor **2** and ligands **3-7***

Reaction of ethyl-4-benzyloxybenzoate with three fold excess of hydrazine hydrate gave compound **2** as described in section 3.1. The IR spectral data (Table 1) of the ligand precursor **2** showed two ν(N-H) bands at 3290 cm^{-1} & 3190 cm^{-1} and a

ν(C=O) band at 1640 cm^{-1}. The ligands **3-7** showed a ν(N-H) band at (3175-3190) cm^{-1} region for the -C(O)NH- moiety. These ligands also showed two absorption's at (1635-1650) cm^{-1} and (1620-1630) cm^{-1} regions suggested for the ν(C=O) and ν(C=N) bands respectively and indicated that condensation have taken place between the -NH$_2$ and CO moieties of the ligand precursor with different aldehydes.

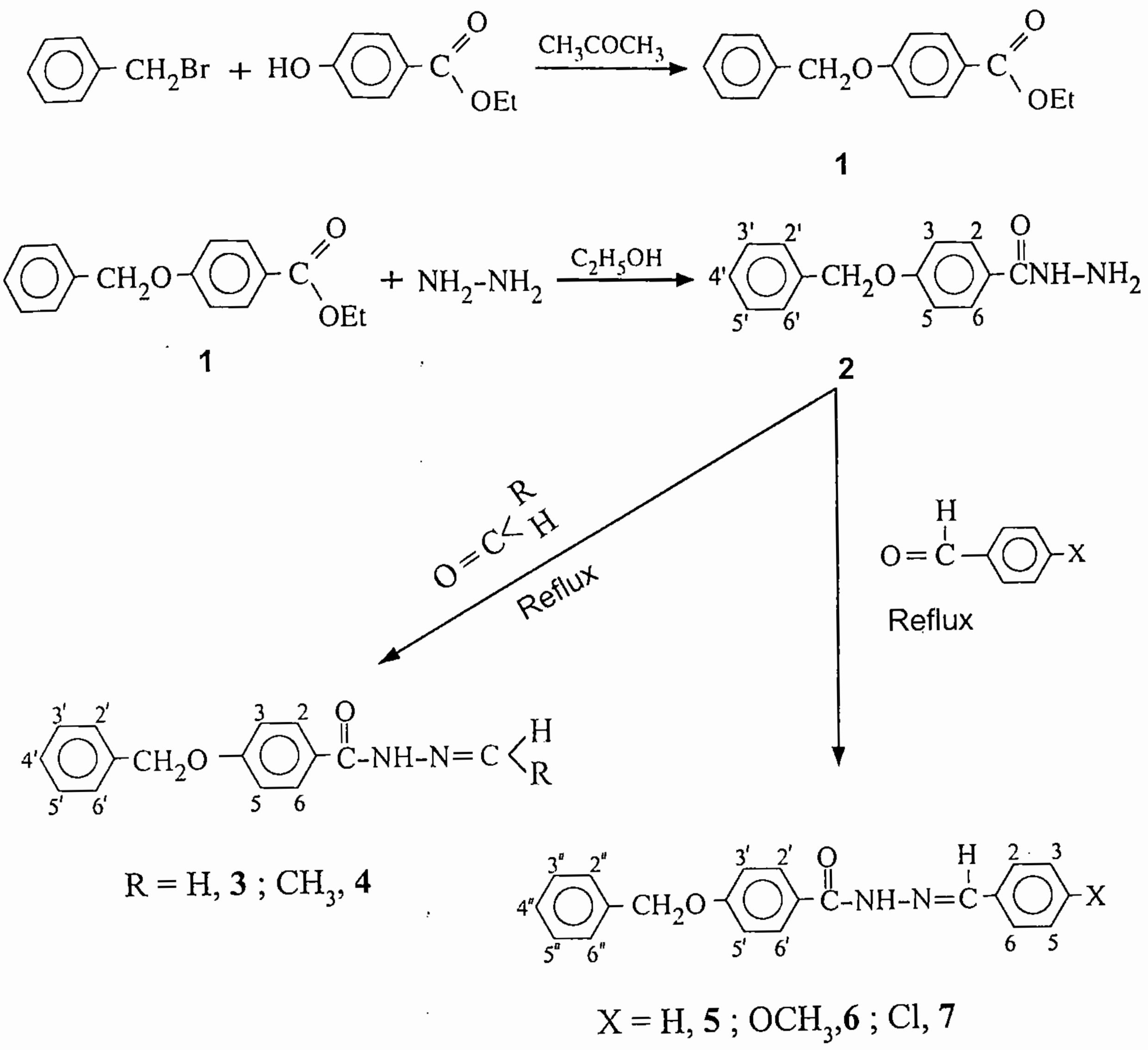
In the ^{1}H NMR spectral data (Table 2) of the ligand precursor **2** have a broad singlet at δ 4.10 for NH$_2$ protons which is absent in the ligands **3-7** suggested that condensation have taken place between NH$_2$ moiety of the ligand precursor **2** and aldehydic group of O=CHR and O=CHC$_6$H$_4$X. The condensation was confirmed by the appearance of a new signal for =CHR protons in the ligands. The ligand precursor **2** showed a singlet at δ 7.4 for the -C(O)NH- protons. The signal is deshielded in the ligands. The signals for other protons in the ligands are slightly shifted or remained unchanged.

Table 1: Infrared spectral data and some physical properties of the ligands **1- 7**

No.	Compound	Yield (%)	M. P. (^0C)	IR in cm^{-1}(as KBr disc)		
				ν(N-H)	ν(C=O)	ν(C=N) / ν(C=N- N=C)
1	$C_{16}H_{16}O_3$	70	32		1692	
2	$C_{14}H_{14}N_2O_2$	80	95	3290 3190	1640	
3	$C_{15}H_{14}N_2O_2$	60	160	3185	1636	1625
4	$C_{16}H_{16}N_2O_2$	65	165	3186	1635	1620
5	$C_{21}H_{18}N_2O_2$	75	185	3180	1645	1628
6	$C_{22}H_{20}N_2O_3$	70	190	3175	1640	1630
7	$C_{21}H_{17}N_2O_2Cl$	65	185	3190	1650	1630

Table 2 : ^{1}H NMR data of the ligands **2-4**
(in $CDCl_3$ and TMS as internal standard).

No.	Chemical Shift (δ)
2	4.10 (bs, 2H, NH_2) 5.15 (s, 2H, CH_2O), 7.00 (d, 2H, H-3, 5, J= 9.0 Hz), 7.32-7.44 (m, 5H, H-2', 3', 4', 5', 6'), 7.54 (s, CONH), 7.72 (d, 2H, H-2, 6, J = 9.0 Hz).
3	5.15 (s, 2H,CH_2O), 6.77 (d,1H, =CHR, J = 11.0 Hz), 6.98 (d, 2H, H-3,5, J=9.0 Hz), 7.32-7.44 (m, 5H, H-2', 3', 4', 5', 6'), 7.52 (d, 2H, H-2, 6,J = 9.0 Hz), 7.58 (d, IH, =CR, R = H, J = 11 Hz) 7.76 (s, CONH).
4	2.40 (d, 3H, CH_3, J = 6.6 Hz), 5.15 (s, 2H, CH_2O), 6.90 (q, IH, =CH-, J= 6.6 Hz), 6.97(d, 2H, H-3, 5, J = 9.0 Hz), 7.32-7.43 (m, 5H, H-2', 4', 5',6'), 7.51 (d, 2H, H-2, 6, J = 9.0 Hz), 7.77 (s, CONH).



Scheme 1 : Synthesis of ligands **1-7**

4.2 Synthesis of copper complexes 8-12

The complexes $[(C_6H_5CH_2OC_6H_4C(O)NN{=}CHR)_2Cu]$ where, R = H, **8** ; CH_3, **9** and $[(C_6H_5CH_2OC_6H_4C(O)NN{=}CHC_6H_4X)_2Cu]$ where, X = H, **10** ; OCH_3, **11** ; Cl, **12** were formed by the reaction of the ligand precursor 4-benzyloxybenzoylhydrazine **2** with copper(II) acetate in the presence of formaldehyde, acetaldehyde, benzaldehyde, 4-methoxybenzaldehyde, 4-chlorobenzaldehyde respectively (scheme 2). The same complexes **8-12** were also formed by the direct reaction of the ligands $C_6H_5CH_2OC_6H_4C(O)NHN{=}CHR$, where, R = H, **3** ; CH_3, **4** and $C_6H_5CH_2OC_6H_4C(O)NHN{=}CHC_6H_4X$, where, X = H, **5** ; OCH_3, **6** ; Cl, **7** with copper(II) acetate (scheme 3). The recation of the ligand precursor **2** with copper(II) acetate only gave a deep off white complex, may be carbohydrazido complex, which on further treatment with aldehydes did not form hydrazinato complexes **8-12.** This indicates that the complexation proceed through the ligand formation not the template condensation. The elemental analyses (Table 3) of the complexes are consistent with the proposed formula. The conductance measurement value reveals that the compexes **8-12** are non-electrolytic in nature [2]. The infrared spectra of the complexes **8-12** showed a strong band at (1604 -1608) cm^{-1} for the ν(C=N-N=C<) moiety. The absence of ν(N-H) band of the carbohydrazone moiety, -C(O)NH-N=C< indicated the unequivocal evidence of the formation of chelate complexes (C-O-M), via the enol form [3,4]. Due to the complexation the ν(C=N) bands are shifted to the lower field ~ 20 cm^{-1}. The complex formation have also been assigned by the presence of ν(M-N) and ν(M-O) bands at (550-565) cm^{-1} and (500-515) cm^{-1} regions respectively [5].

In the UV-Visible spectral data (Table 4) of the complexes **8-12** a single broad band is observed at (500-550) nm region which is assigned to the $^2E_g \rightarrow {}^3T_{2g}$ transition characteristics of square planar geometry [6,7] of Cu(II).

The complexes showed magnetic moment of 1.95-2.15 B.M (Table 5) corresponding to one unpaired electron of square planar Cu(II) configuration [8].

The mass spectral data (Table 4) of the complexes **8-12** showed molecular ion (M^+) peak at 569, 597, 721, 781 and 789 respectively. The complexes showed other (m/z) peaks, Such as 211 for $C_6H_5CH_2OC_6H_4CO^+$,91(100%)base peak for $C_6H_5CH_2^+$, 77 for $C_6H_5^+$, 65 for $C_5H_5^+$ which are consistent with the proposed formula.

Due to the paramagnetic field of the complexes **8-12** ^1H NMR spectra were not obtained.

Table 3 : Analytical data and molar conductance of the compounds **8-12**

No.	Compound Colour	Yield (%)	M.P. (^0C)	Found (Cal)%				Molar Conductance ($Ohm^{-1}cm^2mol^{-1}$) in DMSO
				C	H	N	M	
8	$C_{30}H_{26}N_4O_4Cu$ Brick red	69	170 (d)	63.06 (63.21)	4.57 (4.59)	9.80 (9.83)	11.00 (11.15)	00
9	$C_{32}H_{30}N_4O_4Cu$ Brown	71	180	64.00 (64.26)	5.00 (5.05)	9.40 (9.36)	10.40 (10.62)	00
10	$C_{42}H_{34}N_4O_4Cu$ Brick red	40	240	69.50 (69.84)	4.72 (4.74)	7.70 (7.75)	7.70 (7.80)	08
11	$C_{44}H_{38}N_4O_6Cu$ Brick red	75	245	67.15 (67.55)	4.86 (4.89)	7.12 (7.16)	8.00 (8.12)	05
12	$C_{42}H_{32}N_4O_4Cl_2Cu$ Brown	70	250	63.45 (63.75)	4.05 (4.07)	7.10 (7.08)	7.80 (8.03)	10

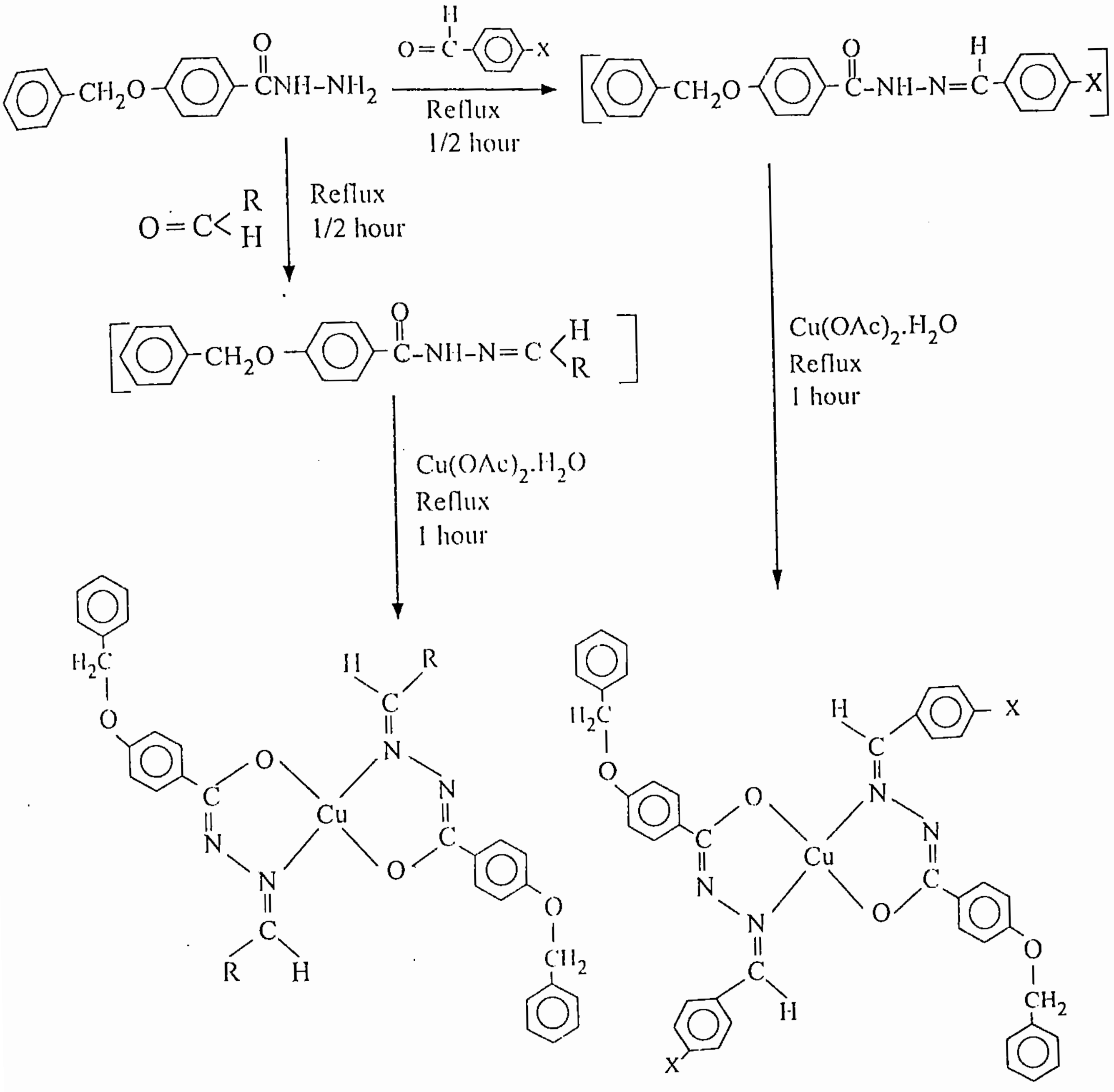
d = decomposition temperature

Table 4 : Infrared, UV- visible and mass spectral data of compounds **8 -12**

No.	IR in cm^{-1} (as KBr disc)			UV-visible d-d transition	Mass spectra (EI at 70 eV)
	ν(C=N)/ ν(C=N-N=C)	ν(M-N)	ν(M-O)	λ_{max} (nm)	(m/z)
8	1608	555	510	550	569(M^+), 211, 91(100%), 77, 65, 63
9	1606	550	500	540	597(M^+), 211, 91 (100%), 77, 65, 63, 15
10	1605	560	505	510	721(M^+), 211, 91 (100%), 77, 65, 63
11	1604	558	512	520	781(M^+), 211, 91 (100%), 77, 65, 63, 29
12	1607	565	515	500	789(Cl^{35}) (M^+), 211, 91 (100%), 77, 65, 63

Table 5 : Magnetic moment data of the compounds **8-12 ; T = 300 K**

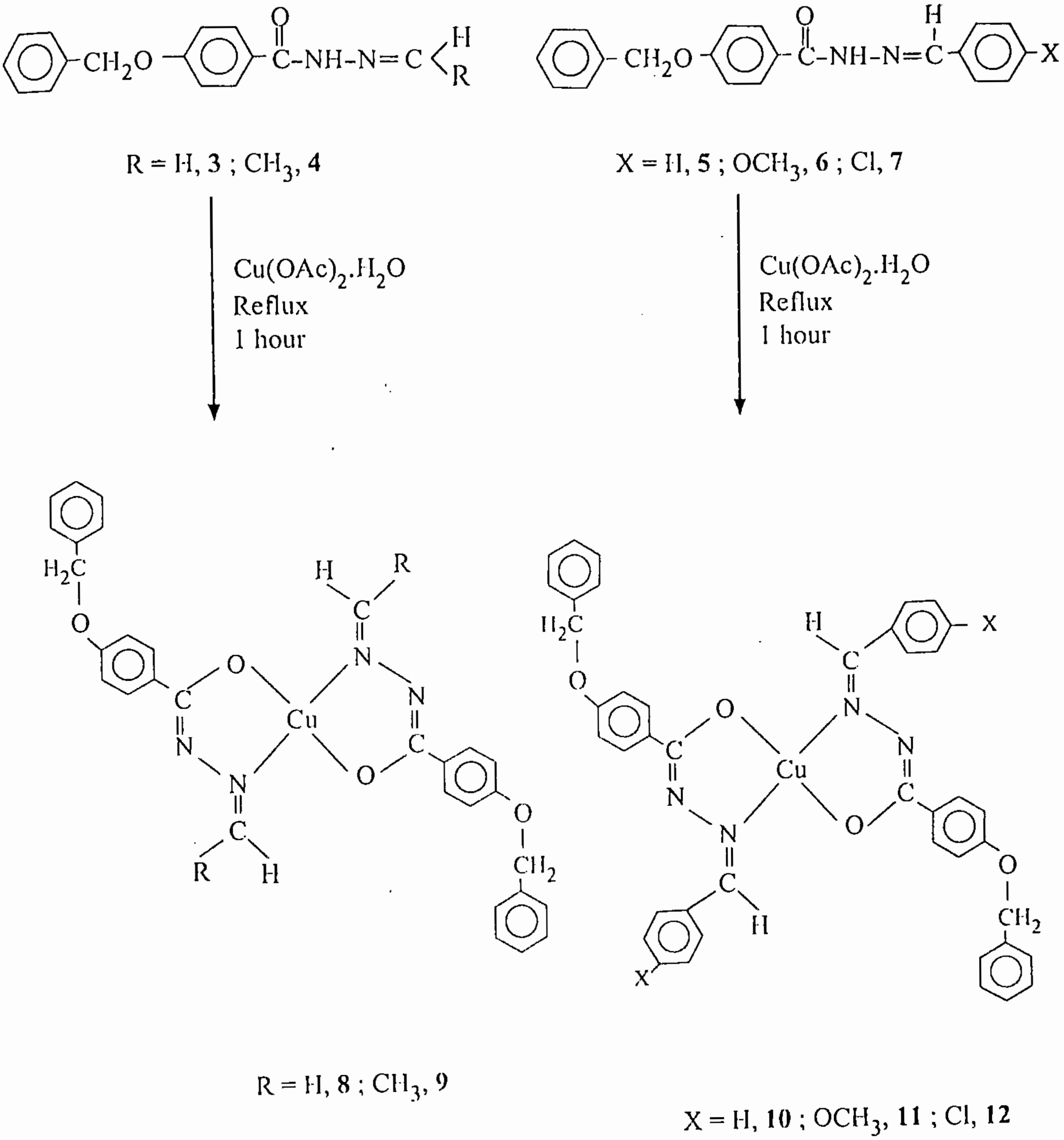
No.	Compounds	Length of the sample, l in cm	Weight of the sample, m in gm	Susceptibility of the empty tube, R_0	Susceptibility of the sample with tube, R	Mass susceptibility, $\chi_g \times 10^{-6}$ C.G.S unit	Molecular weight of the sample, M	Molar Susceptibility, $\chi_m \times 10^{-3}$ C.G.S. unit	Diamagnetic correction of the compound, $\chi_m \times 10^{-6}$ C.G.S. unit	$\chi_m^{corr} \times 10^{-3}$ C.G.S. unit	μ_{eff} in B.M
8	$C_{30}H_{26}N_4O_4Cu$	2.3	0.03	- 57	- 43	2.238	569.54	1.275	- 292.98	1.567	1.95
9	$C_{32}H_{30}N_4O_4Cu$	2.2	0.029	- 66	- 51	2.373	597.54	1.418	- 316.7	1.734	2.05
10	$C_{42}H_{34}N_4O_4Cu$	2.0	0.036	- 78	- 63	1.738	721.54	1.254	- 388.42	1.642	2.0
11	$C_{44}H_{38}N_4O_6Cu$	1.8	0.038	- 73	- 55	1.779	781.54	1.390	- 421.34	1.812	2.10
12	$C_{42}H_{32}N_4O_4Cl_2Cu$	2.1	0.034	- 65	- 50	1.933	789.54	1.526	- 382.56	1.908	2.15



R = H, **8** ; CH_3, **9**

X = H, **10** ; OCH_3, **11** ; Cl, **12**

Scheme 2 : Synthesis of complexes **8–12** from ligand precursor and aldehydes.



R = H, **3** ; CH_3, **4**

X = H, **5** ; OCH_3, **6** ; Cl, **7**

R = H, **8** ; CH_3, **9**

X = H, **10** ; OCH_3, **11** ; Cl, **12**

Scheme 3 : Synthesis of complexes **8-12** from the corresponding ligands **3-7**.

4.3 Synthesis of iron complexes

Reaction of 4-benzyloxybenzoylhydrazine with iron(III) chloride in presence of some aldehydes : Synthesis of complexes **13-20**

Reaction of 4-benzyloxybenzoylhydrazine with iron(III) chloride in presence of formaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde, p-methoxybenzaldehyde, p-chlorobenzaldehyde, cinnamaldehyde and 4-benzyloxybenzaldehyde gave the complexes **13-20** respectively as described in section 3.3. The carbohydrazone $(-\overset{O}{\overset{\|}{C}}-NH-N=C< \longleftrightarrow -\overset{OH}{\overset{|}{C}}=N-N=C<)$ moiety of the intermediate ligand 4-benzyloxybenzoylhydrazone, is not coordinated to the metal in ketonic form, instead it acts as a bidentate uninegative ligand via deprotonation through the enol form to give a five membered ring (through O, N atoms) to the central metal atom. The complexes are octahedral in nature and four equatorial sites are occupied by two ligands (through O, N atoms) and the rest two sites are occupied by a chloride ion and a water molecule. The elemental analyses (Table 5) of the complexes are consistent with the proposed formula. The conductivity measurement values indicated that the complexes are non-electrolytic in nature [2].

The infrared spectral data (Table 7) of the complexes showed a strong band at 1610-1601 cm^{-1} for the ν(C=N-N=C) moieties. The absence of the amide ν(N-H) and ν(C=O) bands of the carbohydrazone -C(O)-NH-N=C< moiety in the complexes indicated the unequivocal evidence for the formation of complexes through the oxygen atom by loosing the NH proton via the enol form. A band at 510-495 cm^{-1} region represent the ν(M-O) stretching. The absence of $\nu(NH_2)$ bands in the complexes indicated that condensation have taken place between the $-NH_2$ moiety of **2** and corresponding aldehydes to give intermediate ligand, (the νNH_2 bands at 3290, 3190 cm^{-1} for **2**). A band at 552-530 cm^{-1} region suggested for the ν(M-N) stretching of the coordinated imine nitrogen atom. The complexes showed a broad band at 3425-3414 cm^{-1} represent the coordinated water molecule.

The UV-visible spectral data (Table 7) of the complexes showed three broad absorption bands at 246-258 nm, 300-343 nm and 360-400 nm. The bands at 300-343 nm for the π-π^* transition. The bands at 360-400 nm region may be the ligand to metal charge transfer transition [9]. Generally trivalent iron ions have greater tendency to charge transfer bands in the near UV region with strong low-energy wings in the visible region that obscure the very weak spin forbidden d-d bands [8].

The magnetic moment of the complexes (Table 9) are 5.7-6.2 B.M, correspond to high spin five unpaired electrons of d^5- configurations of octahedral geometry. Generally magnetically iron(III) complexes are high spin in nearly all of their complexes, except those with strong ligands and possesses the spin only value of 5.9 B.M. because the ground state (derived from the 5S state of the free ion) has no orbital angular momentum and there is no effective mechanism for introducing any by complying with excited states [8].

The mass spectral data (Table 8) of the complexes (in positive ion FAB method) gave the molecular ion peaks (M^+) at 615 for **13**, 643 for **14**, 767 for **16** respectively. The complexes **13**, **14** and **16** also showed peaks (m/z) at 613 for $(M-2H)^+$, $(M-2Me)^+$ and $(M-2Ph)^+$ respectively. The complexes **13**, **14** and **16** showed base peak (m/z) at 138, 137 and 91 respectively with other peaks. The molecular ion peaks and their fragments are consistent with the proposed formula of the complexes.

From the Elemental analyses, Infrared, UV-visible, Mass spectral studies with other physical properties the proposed structure of the complexes are octahedral in nature.

The complexes did not show any liquid crystalline behavior instead they decomposed after the melting temperature as seen by using polarized microscope with the hot stage melting point apparatus.

Table 6 : Analytical data and molar conductance of the compounds **13-20**

No.	Compound Colour	Yield (%)	M.P. (^{0}C)	Found (Cal)%				Molar Conductance (Ohm^{-1}cm^{2}mol^{-1}) in DMSO
				C	H	N	M	
13	$C_{30}H_{28}N_4O_5FeCl$ Yellow	60	215 (d)	58.40 (58.50)	4.60 (4.58)	9.02 (9.10)	9.04 (9.07)	5.00
14	$C_{32}H_{32}N_4O_5FeCl$ Orange-cream	70	262 (d)	59.58 (59.69)	4.97 (5.00)	8.75 (8.70)	8.60 (8.67)	3.50
15	$C_{36}H_{36}N_4O_5FeCl$ Orange-red	55	276	62.12 (62.50)	5.20 (5.21)	8.00 (8.05)	7.97 (8.02)	4.00
16	$C_{42}H_{36}N_4O_5FeCl$ Orange	69	220	65.55 (65.68)	4.68 (4.72)	7.20 (7.29)	7.25 (7.27)	1.00
17	$C_{44}H_{40}N_4O_7FeCl$ Light orange	71	230	63.55 (63.82)	4.86 (4.87)	6.70 (6.77)	6.70 (6.74)	2.00
18	$C_{42}H_{34}N_4O_5FeCl_3$ Light orange	67	250	60.00 (60.27)	4.05 (4.09)	6.62 (6.69)	6.61 (6.67)	5.00
19	$C_{46}H_{40}N_4O_5FeCl$ Light pink	73	245	67.00 (67.37)	4.90 (4.92)	6.80 (6.83)	6.75 (6.81)	00
20	$C_{56}H_{48}N_4O_7FeCl$ Orange	60	235	68.40 (68.61)	4.90 (4.93)	5.70 (5.72)	5.67 (5.70)	2.50

Table 7 : Infrared and UV-Visible spectral data of the complexes **13–20**

No.	IR in cm^{-1} (as KBr disc)				UV-Visible
	$\nu(H_2O)$	ν(C=N–N=C)	ν(M–N)	ν(M–O)	λ_{max}(nm)
13	3425	1601	545	509	300, 343, 362
14	3414	1607	550	510	257, 300, 360
15	3421	1606	552	510	310, 395
16	3425	1604	534	499 (460)	320, 400
17	3420	1605	532	499	310, 392
18	3422	1607	535	498	308, 400
19	3418	1604	535	500	246, 300, 379
20	3420	1610	530	495	246, 300,342

Table 8 : Mass spectral data of the complexes **13,14** and **16** in positive ion FAB method

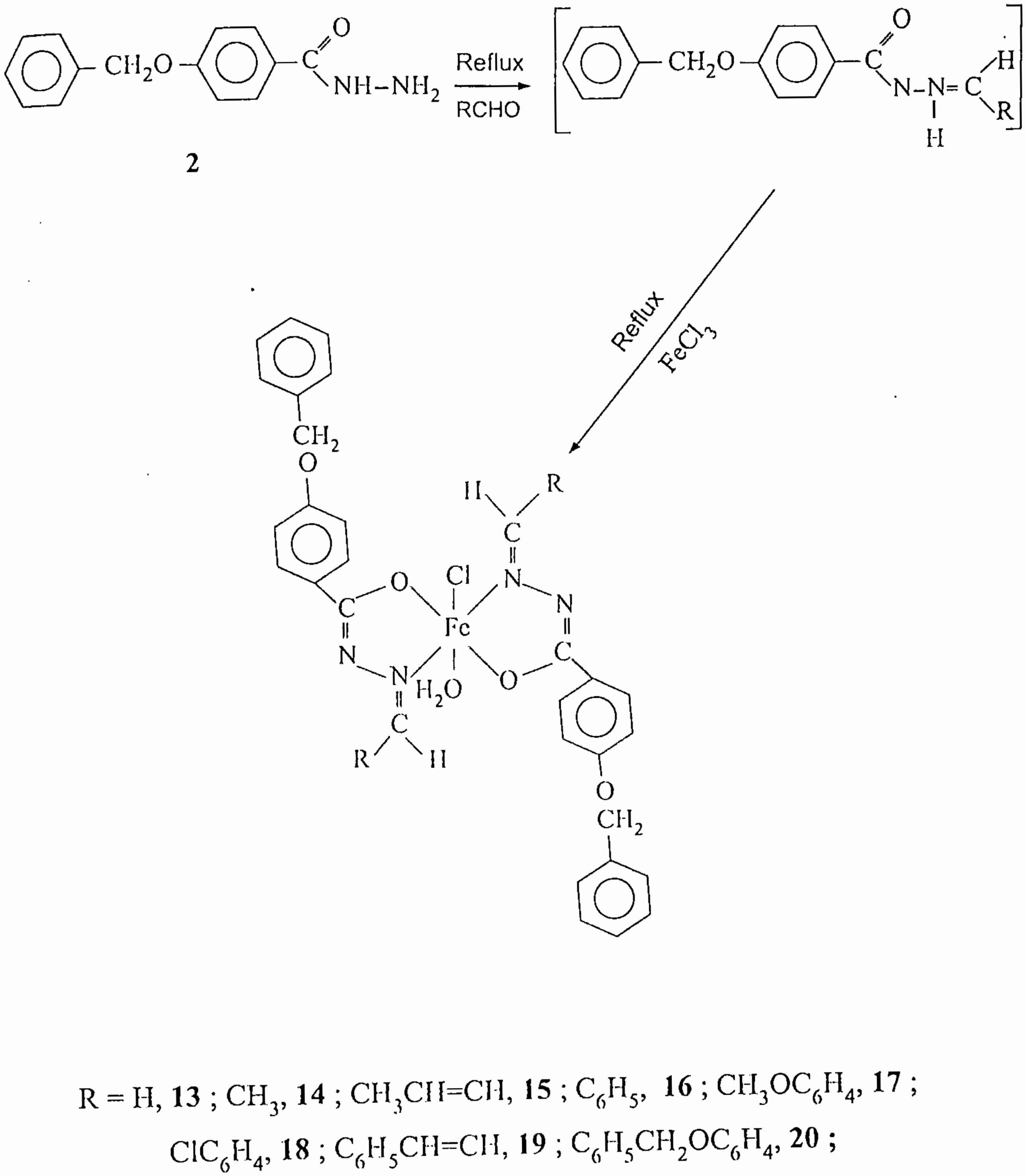
13. 615(M^+), 613$(M-2H)^+$, 460$(M-2H-C_6H_5C_6H_4)^+$, 307 $(M-2H-2C_6H_5C_6H_4)^+$, 211$(C_6H_5CH_2OC_6H_4CO)^+$, 138(100%) $(O{=}C{=}N{-}N{=}CH{-}CH{=}N{=}C{=}O)^+$.

14. 643(M^+), 613$(M-2CH_3)^+$, 460$(M-2CH_3-C_6H_5C_6H_4)^+$, 307$(M-2CH_3-2C_6H_5C_6H_4)^+$, 211$(C_6H_5CH_2OC_6H_4CO)^+$, 137(100%) $(O{=}C{=}N{-}N{=}CH{-}C{=}N{-}N{=}C{=}O)^+$, 91$(C_6H_5CH_2)^+$, 77 $(C_6H_5)^+$.

16. 767(M^+), 751,613$(M-2C_6H_5)^+$, 460, 211$(C_6H_5CH_2OC_6H_4CO)^+$, 91(100%) $(C_6H_5CH_2)^+$, 77 $(C_6H_5)^+$.

Table 9 : Magnetic moment data of the compounds **13-20** ; **T = 300 K**

No.	Compounds	Length of the sample, l in cm	Weight of the sample, m in gm	Susceptibility of the empty tube, R_0	Susceptibility of the sample with tube, R	Mass susceptibility, $\chi_g \times 10^{-6}$ C.G.S unit	Molecular weight of the sample, M	Molar Susceptibility, $\chi_m \times 10^{-3}$ C.G.S. unit	Diamagnetic correction of the compound, $\chi_m \times 10^{-6}$ C.G.S. unit	$\chi_m^{corr} \times 10^{-3}$ C.G.S. unit	μ_{eff} in B.M
13	$C_{30}H_{28}N_4O_5FeCl$	2.9	0.031	- 36	78	22.246	615.34	13.689	- 303.4	13.991	5.82
14	$C_{32}H_{32}N_4O_5FeCl$	2.3	0.027	- 52	67	17.591	643.34	11.318	- 327.16	11.645	5.97
15	$C_{36}H_{36}N_4O_5FeCl$	3.0	0.032	- 48	51	19.361	695.34	13.462	- 362.88	13.825	5.78
16	$C_{42}H_{36}N_4O_5FeCl$	2.3	0.027	- 45	61	18.836	767.34	14.453	- 398.88	14.851	6.0
17	$C_{44}H_{40}N_4O_7FeCl$	2.5	0.034	- 50	69	17.946	827.34	14.847	- 431.8	15.278	6.08
18	$C_{42}H_{34}N_4O_5FeCl_3$	2.4	0.03	- 39	72	18.524	836.34	15.492	- 393.02	15.886	6.20
19	$C_{46}H_{40}N_4O_5FeCl$	2.3	0.033	- 46	63	15.847	819.34	12.984	- 434.6	13.418	5.70
20	$C_{56}H_{48}N_4O_7FeCl$	2.2	0.038	- 38	75	13.647	979.34	13.366	- 527.24	13.893	5.80



R = H, **13** ; CH_3, **14** ; $CH_3CH{=}CH$, **15** ; C_6H_5, **16** ; $CH_3OC_6H_4$, **17** ; ClC_6H_4, **18** ; $C_6H_5CH{=}CH$, **19** ; $C_6H_5CH_2OC_6H_4$, **20** ;

Scheme 4 : Synthetic route of complexes **13–20**

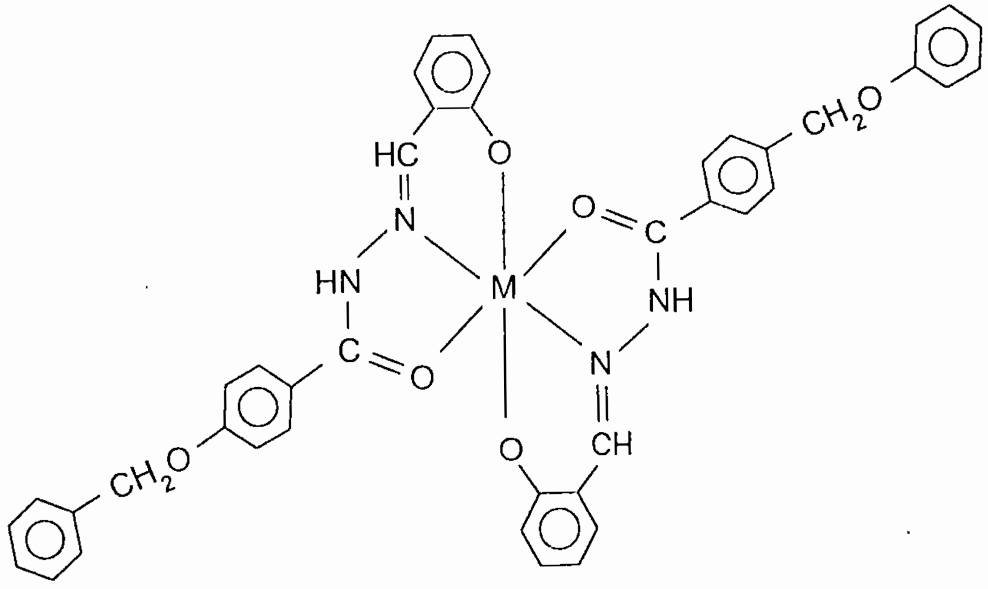
4.4 Reaction of 4-benzyloxybenzoylhydrazine with Ni(II) and Cu(II) ions in presence of 2-hydroxybenzaldehyde and diacetylmonoxime.

(i) Reaction of 4-benzyloxybenzoylhydrazine and 2-hydroxybenzaldehyde with M(II) ions, where, M = Ni, Cu : *Synthesis of complexes **21,22***

Reaction of 4-benzyloxybenzoylhydrazine and 2- hydroxybenzaldehyde with nickel(II) and copper(II) ions gave the complexes **21, 22** respectively as described section 3.4 (i). The intermediate ligand (either I or II)

$$\underset{\mathrm{I}}{C_6H_5CH_2OC_6H_4C(O)NHN{=}CHC_6H_4OH} \longleftrightarrow \underset{\mathrm{II}}{C_6H_5CH_2OC_6H_4C(OH){=}NN{=}CHC_6H_4OH}$$

has three coordination sites. The ligand was coordinated to matal ion through the oxygen atom of the amide moiety (-NHC=O) and by deprotonating the phenolic proton to give the chelate complexes **21,22** as in fig. 1.37.



M = Ni, **21** ; Cu, **22**

Fig. 1.37

The elemental analysis of the complexes are consistent with the proposed formula. The complexes are non-electrolytic in nature [2].

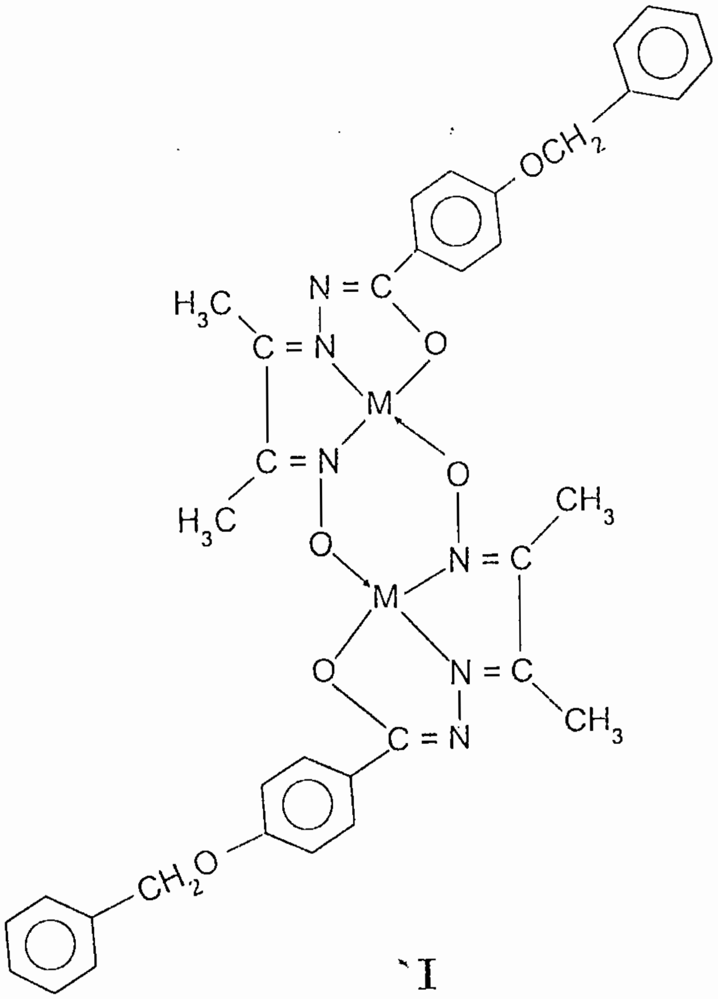
The infrared spectral data (Table 11) of the complexes **21, 22** showed a band at 3185-3192 cm^{-1} for the $\nu(NH)$ stretching and a strong band at 1620-1624 cm^{-1} for the coordinated $\nu(C{=}O)$ stretching of carbohydrazone -C(O)NH-N=C< moiety. Due to coordination the $\nu(C{=}O)$ decreases ~ 20 cm^{-1} as compared to the ligand precursor. The complexes showed a strong band at 1604-1608 cm^{-1} for the $\nu(C{=}N)$ of carbohydrazone -C(O)NH-N=C< moiety, gives an unequivocal evidence of coordination between $-NH_2$ and -CHO moieties of the ligand precursor and aldehydes. The successive coordination of the intermediate ligand I to the metal through nitrogen atom, may be confirmed by the appearence of a band at 594-550 cm^{-1} for the $\nu(M{-}N)$ stretching. A band at 500 - 515 cm^{-1} for the $\nu(M{-}O)$ stretching indicated that coordination have taken place through oxygen atorm by deprotonation of phenolic -OH moiety.

The magnetic moment of the complex **21** is 2.87 B.M. correspond to two unpaired electrons of octahedral Ni(II) d^8 - configuration. The complex **22** showed magnetic moment of 2.0 B.M. correspond to one unpaired electron of octahedral Cu(II) d^9-configuration.

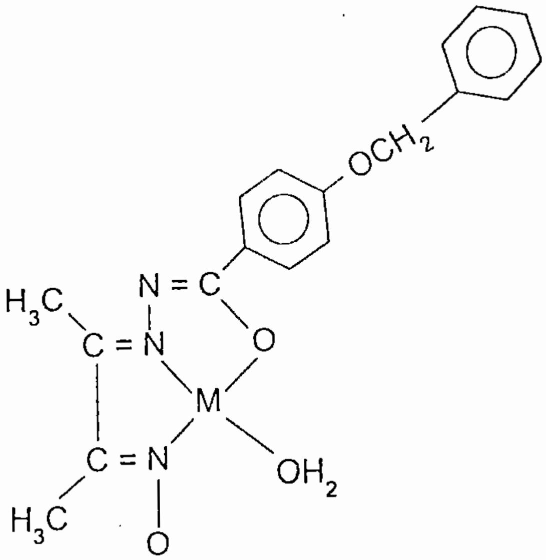
The elemental analysis, infrared, UV-visible, magnetic moment measurement and conductance data are consistent with the proposed octahedral structure of the complexes.

(ii) Reaction of 4-benzyloxybenzoylhydrazine and diacetylmonoxime with M(II) ions, where, M = Ni, Cu : *Synthesis of complexes **23,24***

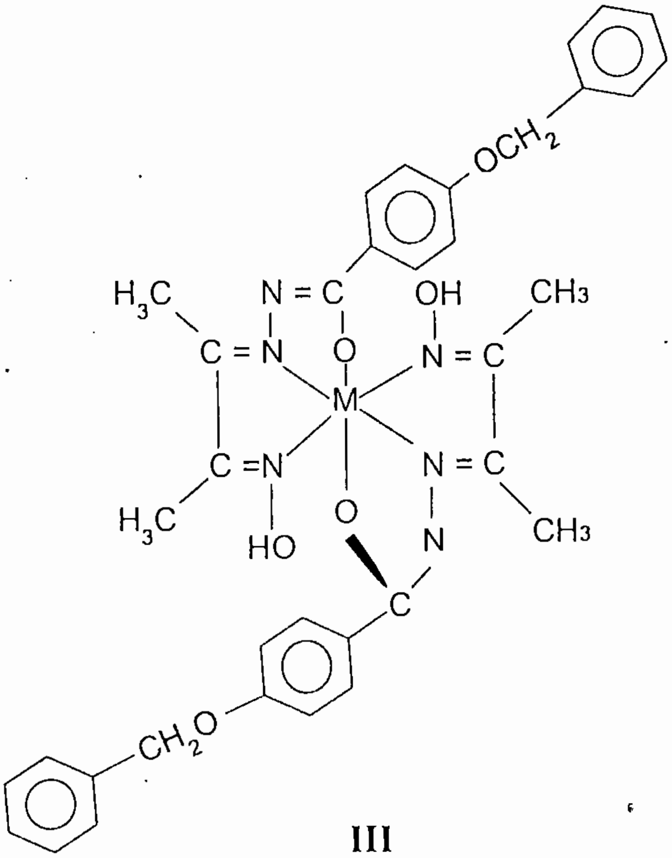
The Reaction of 4-benzyloxybenzoylhydrazine and diacetylmonoxime with Ni(II) and Cu(II) ions gave the complexes **23, 24** respectively as described in section 3.4(ii). The intermediate ligand $C_6H_5CH_2OC_6H_4C(O)\text{-}NHN{=}C(CH_3)\text{-}C(CH_3){=}NONH$ behave as a tridentate ligand and coordinates to the metal by loosing two protons from oxime and amide moiety.



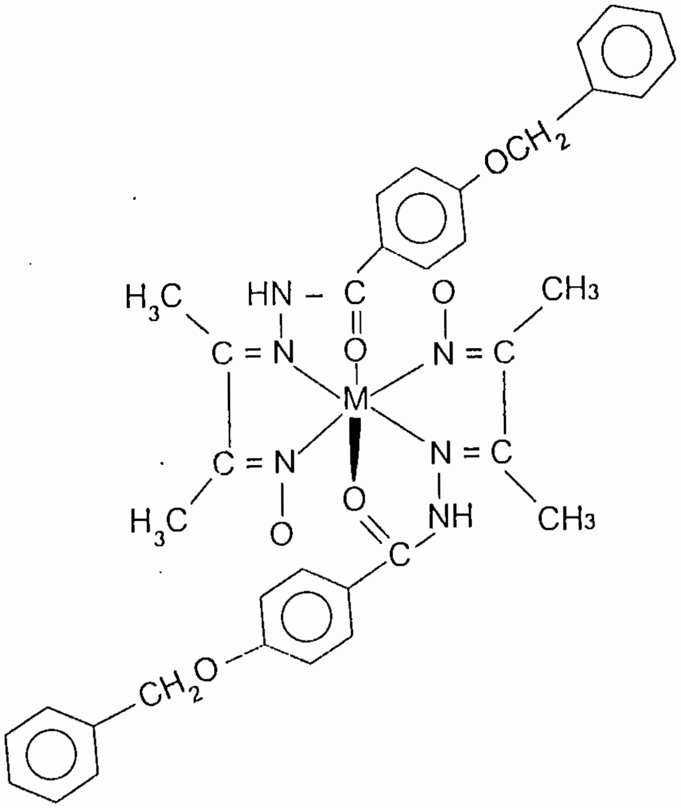
I



II


OCH2
H3C
N = C
OH
CH3
C = N
O
N = C
M
C =N
N = C
O
H3C
N
CH3
HO
C
CH2O

III


OCH2
H3C
HN – C
O
CH3
C = N
O
N = C
M
C = N
N = C
H3C
O
NH
CH3
O
C
CH2O

IV

There are four probable structures of complexes **23, 24.** Different evidences showed that the complexes are dimeric in nature (structure I). Half unit are unique. Deprotonated oxygen atom of oxime moiety of one half molecule is coordinated to the metal of other half of the molecule. The metal estimations are consistent with the dimeric molecule i.e. half unit are unique. The conductance data reveals that the complexes are non- electrolytic in nature [2].

The infrared spectral data (Table 11) of the complexes showed two strong absorption bands at 1600-1610 cm^{-1} region for the different ν(C=N) moieties, for ν(>C=NO), ν(>C=N-N) moieties. The absence of ν(C=O) and ν(N-H) bands in the complexes indicated that coordination have taken place by deprotonation of amidic oxygen atom via enol form. There is no clear band for ν(O-H) of oxime moiety or coordinated water molecule. The complexes showed two bands at 575-633 cm^{-1} and 512-530 cm^{-1} regions for the ν(M-N) and ν(M-O) stretching respectively. The infrared spcetral data of the complexes **23, 24** are consistent with the structure I.

The magnetic moment of the complexe **23** is negative, indicated the square planar symmetry of Ni(II) d^8 - configuration. The magnetic moment of Cu(II) complex is 1.9 B.M. consistent with the square planar symmetry.

The magnetic moment data are consistent with structure I and II, both are square planar. But in the infrared spectra there is no clear bands for the coordinated water molecule. Therefore, the proposed structure is I for the complexes **23** and **24**. The actual structure could be confirmed by crystallographic study.

Table 10 : Analytical data and molar conductance of the compounds **21-24**

No.	Compound Colour	Yield (%)	M.P. (^{0}C)	Found (Cal) %				Molar Conductance (Ohm^{-1}cm^{2}mol^{-1}) in DMSO
				C	H	N	M	
21	$C_{42}H_{34}N_4O_6Ni$ Greenish yellow	60	>250	67.00 (67.30)	4.51 (4.54)	12.72 (12.80)	7.70 (7.83)	10.0
22	$C_{42}H_{34}N_4O_6Cu$ Green	55	>250	65.50 (66.90)	3.49 (4.51)	7.38 (7.43)	8.15 (8.43)	8.00
23	$C_{36}H_{34}N_6O_6Ni_2$ Reddish brown	70	>250	56.20 (56.60)	4.43 (4.45)	10.96 (11.00)	15.09 (15.36)	2.50
24	$C_{36}H_{34}N_6O_6Cu_2$ Olive green	60	>250	55.40 (55.90)	4.38 (4.40)	10.83 (10.86)	16.02 (16.42)	5.00

Table 11 : Infrared spectral data of the complexes **21–24**

No.	IR in cm^{-1} (as KBr disc)				
	ν(N–H)	ν(C=O)	ν(C=N)/ ν(C=N–N=C)	ν(M–N)	ν(M–O)
21	3192	1624	1604	594	515
22	3185	1620	1608	550	500
23	-	-	1610 1600	575	530
24	-	-	1605 1600	633	512

Table 12 : Magnetic moment data of the compounds **21-24** ; **T = 300 K**

No.	Compounds	Length of the sample, l in cm	Weight of the sample, m in gm	Susceptibility of the empty tube, R_0	Susceptibility of the sample with tube, R	Mass susceptibility, $\chi_g \times 10^{-6}$ C.G.S unit	Molecular weight of the sample, M	Molar Susceptibility, $\chi_m \times 10^{-3}$ C.G.S. unit	Diamagnetic correction of the compound, $\chi_m \times 10^{-6}$ C.G.S. unit	$\chi_m^{corr} \times 10^{-3}$ C.G.S. unit	μ_{eff} in B.M
21	$C_{42}H_{34}N_4O_6Ni$	3.2	0.03	- 71	- 53	4.005	748.69	2.999	- 397.62	3.396	2.87
22	$C_{42}H_{34}N_4O_6Cu$	2.4	0.039	- 58	- 45	1.669	753.54	1.258	- 397.62	1.655	2.0
23	$C_{36}H_{34}N_6O_6Ni_2$	2.1	0.032	- 35	- 50	- 2.053	763.38	- 1.568	- 370.88	- 1.938	Dia
24	$C_{36}H_{34}N_6O_6Cu_2$	2.0	0.035	- 69	- 57	1.430	773.08	1.106	- 370.88	1.476	1.90

Suggestion for further work :

In the present work the reactions were carried out by using the ligand precursor 4-benzyloxybenzoylhydrazine with different metal ions in presence of some aldehydes. If the benzyl moiety of the ligand precursor is replaced by a long chain alkyl moiety (such as octyl, decyl, dodecyl, hexadecyl groups) then the ligand precursor will be 4-alkoxybenzoylhydrazine. If we will be used the ligand precursor 4-alkoxybenzoylhydrazine with different metal ions such as iron then the synthesized complexes may possesses liquid crystalline behavior.

The synthesis of complexes by using cobalt ion is undone in the present work. Therefore, the suggestion for the future work is to synthesis of the cobalt complexes by using 4-benzyloxybenzoylhydrazine and 4-alkoxybenzoylhydrazine ligand precursors.

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