METAL COMPLEXES OF SCHIFF BASES DERIVED FROM ARYLHYDRAZONES OF 1,3-DIKETONES

THESIS SUBMITTED TO THE
FACULTY OF SCIENCE, UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY

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MARCH 2005

DECLARATION

I hereby declare that the thesis bound herewith is an authentic record of the research work carried out by me under the supervision of Dr. K. Krishnankutty, Professor of Chemistry, University of Calicut, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry of the University of Calicut, and further that, no part thereof has been presented before for any other Degree.

Sayudevi

Sayudevi P.

CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of the research work carried out by **Smt. P. Sayudevi**, under my supervision in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry of the University of Calicut, and further that no part thereof has been presented before for any other Degree.

Dr. K. Krishnankutty
(Supervising Teacher)

Acknowledgement

I cannot express in words the role of my supervising teacher and guide Dr.K.Krishnankutty, Professor, Department of Chemistry, University of Calicut in the preparation and fulfilment of this Thesis. I express my indebtedness to him for the inspiration, timely suggestions and healthy criticism I have received from him during the entire period of this project.

I am grateful to Dr. K.K. Aravindakshan, Head of the Department of Chemistry, University of Calicut and Dr. T.D. Radhakrishnan Nair, Dr. M.P. Kannan, former Heads of the Department for providing necessary facilities. I sincerely appreciate the whole hearted co-operation and help extended by the teaching and non teaching staff, Department of Chemistry, University of Calicut.

I express my thanks to RSIC, CDRI, Lucknow, RSIC, IIT, Mumbai, RSIC, IIT, Madras and University of Cochin for providing the spectral analysis.

I am extremely thankful to my friends and fellow research scholars at Calicut University for their help especially to Muhammed Basheer Ummathur, Babu Joseph, John V.D., Mathew Paul Ukken, Smt. Malini P.T. and Smt. Preeji.

I express my sincere thanks to the management and principal, N.S.S. College, Manjeri for deputing me for the research work and also to UGC for providing me teacher fellowship under FIP. I would like to express my gratitude to teaching and non teaching staff and students of N.S.S. College, Manjeri for their timely help I have obtained.

My sincere thanks to M/s Microtech Computer Centre, Chenakkal and Beena Commercial Institute, Chenakkal for their job in processing of the manuscript.

Sayudevi P.

PREFACE

Aryldiazonium salts react with 1,3-diketones to form 1,2,3-triketone-2-arylhydrazones. However reaction of heteroaryl-diazonium salts with 1,3-diketones lead to 2-heteroarylazo-1,3-diketones rather than the hydrazone tautomeric form. The term "Arylhydrazones of 1,3-diketones" in the title of the thesis has been used in a wide sense to include both the tautomeric forms. Arylhydrazones of certain 1,3-diketones in which the diketo function is directly attached to olefinic groups have been synthesised and characterised. These unsaturated 1,3-diketones are the major active chemical constituents present in the traditional Indian medicinal plant turmeric (*Curcuma longa*). Typical metal complexes of these ligand systems have been studied from a structural context. That arylhydazones of various 1,3-diketones serves as the starting material for the synthesis of novel polydentate ligand systems has been demonstrated. Thus condensation of 1,2,3-triketone-2-aryl hydrazones with various aliphatic and aromatic diamines resulted schiff bases having interesting ligand properties.

The break-up of the thesis is as follows:

Chapter 1 is general introduction which highlight briefly the importance of metal coordination in 1,3-diketones and their arylazo derivatives and schiff bases. Structure and tautomeric behaviour of various arylazo-1,3-diketones have been discussed. The use of 1,2,3-triketone-2-arylhydrazones in the design and synthesis of polydentate ligand systems having wide applications in many fields particularly in bioinorganic studies have been included. Salient aspects of the present investigation have been interspersed at appropriate places.

Chapter 2 is mainly on arylazo derivatives of 1,3-diketones and their metal complexes. A preliminary investigation on structure and tautomeric nature of phenylazo- and thiazolylazo derivatives of 1,3-diketones such as acetylacetone and unsaturated 1,3-diketones such as curcuminoids have been discussed in **section 1** in order to facilitate interpretation of more complex ligand systems discussed in subsequent chapters. The metal complexes (ML_2), discussed in this chapter are hydrazonates in which the intramolecularly hydrogen bonded hydrazono nitrogen and one of the carbonyl group of the ligand formed the six membered metal chelate ring. The importance of ir, nmr and mass spectral data in structural elucidation of these types of compounds have been illuminated.

In **section 2**, synthesis and chracterisation of schiff base ligands derived from the unsaturated 1,3-diketone, dicinnamoyl-methane, and their typical metal complexes are included.

The schiff base condensation of the bidentate arylhydrazones of 1,3-diketones with both aromatic and aliphatic diamines yielded a series of polydentate ligand systems. The results are discussed in **chapter 3.** For convenience the chapter is divided into two sections.

The condensation of the arylhydrazones with aliphatic diamines, 1,2-diaminoethane, 1,3-diaminopropane and 1,6-diamino hexane resulted in the formation of polydentate diimine ligands. The compounds formed [ML] type complexes with various divalent transition metal ions. Ir, nmr and mass spectral data revealed that the ligands behave as $N_4(O_2)$ donor. Details of their synthesis and characterisation are provided in **section 1**.

In the case of the aromatic diamines, 1,2-and 1,3-diaminobenzene, only one of the amino group reacted with the carbonyl groups of the phenylhydrazone. Thus a new series of schiff bases containing only nitrogen donors have been synthesised and characterised in **section 2**. These tetradentate N_4 donors form stable 1:1 metal complexes with various transition metal ions. However 1,4-diaminobenzene condensed with two molecules of the

arylhydrazones to from the schiff bases which function as N_4 donor ligands.

In **chapter 4** metal complexes of Schiff bases derived from the arylazo-2, 4-pentanediones with 2-aminophenol and 2-amino-thiophenol are considered. 2-Aminophenol and 2-aminothiophenol react with the 3-arylazo-2,4-pentanediones resulted in the formation of certain new tridentate schiff base ligands. The structure and tautomeric nature of these compounds and their metal complexes have been established on the basis of their ir, nmr, esr and mass spectral data. However spectral and analytical data revealed that two molecules of 2-aminophenol condensed with the two carbonyl groups of 3-thiazolylazoderivative of 2,4-pentanedione which resulted in the formation of an N_2O_2 tetradentate ligand. Synthesis and characterisation of transition metal complexes of the compound are also discussed.

Finally **references** are given in the order cited.

Nomenclature and Abbreviations

Although many of the arylazo derivatives of the 1,3-diketones considered in this Thesis exist entirely in the hydrazone form, azo names have also been freely used wherever necessary to ease nomenclature and to conform to literature usage. In the case of the unsaturated 1,3-diketones, their systematic names and trivial names to conform with their structure are given. For naming polydentate ligand systems, rather than pollysyllabic systematic names, their simpler trivial names and suitable abbreviations have been used for better readability. Names along with abbreviations of the ligand systems studied in this investigation are given below.

Hdhd	dicinnamoylmethane
Hphd	cinnamoylacetylmethane
Hdpd	cinnamoylbenzoylmethane
Hpad	phenylazodiphenylheptadienedione
Haph	phenylazophenylhexenedione
Hpap	phenylazodiphenylpentenedione
Htad	thiazolylazodiphenylheptadienedione
Htah	thiazolylazophenylhexenedione
Htap	thiazolylazodiphenylpentenedione
H_2bde	bis(dicinnamoylmethane)ethylenediimine
H_2dca	dicinnamoylmethaneorthoaminophenol

H_2bpe	bis(phenylhydrazonoacetylacetone)ethylenediimine
H_2bpp	bis(phenylhydrazonoacetylacetone)propanediimine
H_2bph	bis(phenylhydrazonoacetylacetone)hexanediimine
H_2bte	bis(2-thiazolylazoacetylacetone)ethylenediimine
H_2btp	bis(2-thiazolylazoacetylacetone)propanediimine
H_2bth	bis(2-thiazolylazoacetylacetone)hexanediimine
H_2bbe	bis(2-benzothiazolylazoacetylacetone)ethylenediimine
Htop	thiazolylazoacetylacetoneorthophenylenediimine
Hmp	thiazolylazoacetylacetonemetaphenylenediimine
H_2tpp	thiazolylazoacetylacetoneparaphenylenediimine
H_2paa	phenylazoacetylacetoneaminophenol
H_2pat	phenylazoacetylacetoneaminothiophenol
H_2tap	thiazolylazoacetylacetoneaminophenol
H_2tat	thiazolylazoacetylacetoneaminothiophenol

Other important abbreviations used in the thesis are:

Ar	aryl group
BM	Bohr Magneton
FAB	Fast atom bombardment
h	hour
Hz	Hertz
L	Deprotonated ligand
M	Central metal ion in a metal complex
M.P.	Melting point

OAc	Acetate group
Ph	Phenyl group
tlc	thin layer chromatography
μ_{eff}	effective magnetic moment in Bohr magnetons.

The infrared bands are given cm^{-1}.

Chemical shifts in ^1H nmr spectra are expressed as δ values (ppm downfield from tetramethylsilane, (TMS). While reporting mass spectral data, P^+ represents the parent ion (molecular ion). In the case of metal complexes, the m/z of P^+ correspond to the most abundant isotope of the concerned metal atoms.

CONTENTS

CHAPTER 3
METAL COMPLEXES OF SCHIFF BASE LIGANDS DERIVED FROM 3-ARYLAZO-2,4-PENTANEDIONE WITH DIAMINES

Section 1
Metal complexes of multidentate schiff base ligands derived from 3-(arylazo)-2,4-pentanediones with aliphatic diamines

A. Synthesis and characterisation of Schiff base ligands and their metal complexes derived from phenylazoacetylacetone with aliphatic diamines

Experimental

Results and discussion

B. Synthesis and characterisation of Schiff base ligands and their metal complexes derived from thiazolylazoacetylacetone and benzothiazolylazoacetylacetone with aliphatic diamines

Experimental

Results and discussion

Section 2
Metal complexes of multidentate Schiff base ligands derived from thiazolylazoacetylacetone and aromatic diamines

A. Synthesis and characterisation of thiazolylazoacetylacetone *ortho*-phenylenediimine and its metal complexes

CHAPTER 1

GENERAL INTRODUCTION

CHAPTER 1

GENERAL INTRODUCTION

Alfred Werner's coordination theory has been a welcome renaissance in inorganic chemistry. The basic tenets of Werner's celebrated theory have not been discarded still now, but only been refined and extended greatly. New synthetic strategies and development of highly efficient spectral and diffraction techniques for structural investigations together with great theoretical advances have made coordination chemistry a self consistent field in modern scientific studies.

In the later half of the twentieth century, there developed, due to hectic and systematic research, new fields based on the fundamental concepts of coordination chemistry, such as organometallic, bioinorganic, medicinal inorganic, environmental and metalloenzyme chemistry in tune with the challenges of life posed by the period.

The importance of coordination compound in chemical analysis, catalysis, metal winning, the technology of dyes and pigments, etc. have been well established and studies in these areas still constitute a major research activity in coordination chemistry.[1] However in recent years studies on coordination compounds have

been further stimulated mainly by revealing the role of various metal ions in numerous vital biological reactions responsible for life.[2-4] Further developing coordination compounds of biologically important metal ions with new ligand systems, that can function as model compounds in the study of various biological activities have gained much importance.[5,6] Thus synthesis and characterisation of new compounds containing donor[7,8] sites similar to biological ligand systems and studies on their metal complexes, have considerable significance. The present investigation is also an attempt in this direction.

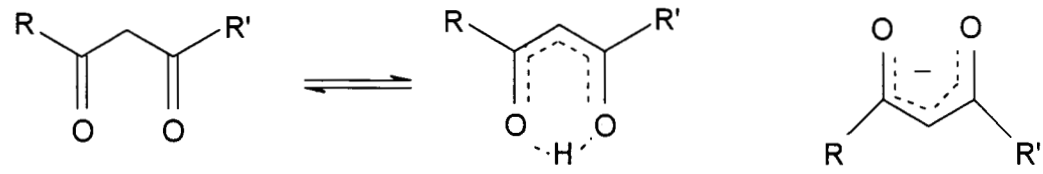
The properties, structure and application of metal complexes are dependant both on the nature of the metal ion and on the ligands. These aspects of coordination chemistry have been thoroughly discussed in the form of various theories particularly based on the Ligand Field theory (LFT) and Molecular Orbital Theory (MOT).[9] The various factors affecting the formation, stability, structure and reactivity of metal complexes are also well established. No attempt is made here to discuss these aspects since these are well documented in the general literature. However it is to be pointed out that the variation in metal ion is considerable, on the other hand variation in ligands is virtually limitless, thanks to the ingenious works of synthetic organic chemists.

Although ligand systems based on organic molecules are limitless, literature reveals that ligands based on certain important structural types as azo, azomethine, hydrazone, di- and polyketones, etc. have proliferated much during recent years. This trend is evident from the use of β-dicarbonyl compounds such as β-diketones, β-ketoesters, β-ketoanilides, etc. in the design and synthesis of numerous ligand systems having tremendous applications in diverse fields of chemical science. **The present study is also aimed at in developing new ligand systems from these types of compounds, particularly β-diketones.**

The β-diketones are important in several respects for coordination chemists. The β-diketones constitute the best known example of proton transfer and hydrogen bonding which are two important aspects of the chemistry that governs the behaviour and structure of many molecules both simple and complex starting from water to DNA. In this respects, perhaps, the most important features of β-diketones and their derivatives are their ability to exhibit keto-enol tautomerism and to form complexes with almost all metal and metalloid elements in the periodic table. Since the present study is based on suitable derivatisation of 1,3-diketones such as acetylacetone, a brief mention on the tautomerism and complexation behaviour of β-diketones and allied derivatives is given below.

Tautomerism of β-diketones

The 1,3-diketones are a group of compounds in which a methylene group or a substituted methylene group is interposed between two alkyl and/or aryl groups as in structure **1**.



R = R' = alkyl / aryl

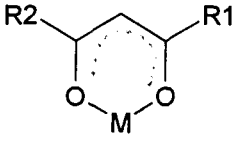
1 **2** **3**

Since the hydrogen of the methylene group is activated by the adjacent carbonyl groups, a conjungate system can arise by a prototropic shift leading to keto **1** and enol **2** tautomeric forms. The amount of enol is dependent on a variety of factors such as solvents,[10-15] temperature[16] substituents at 1-,2- and 3-positions[17-25] and the presence of other species that are capable of hydrogen bonding[26-29]. In general, bulky alkyl substitutes on 2-carbon lead to decreased amount of enol tautomer, while Cl, Br, CN, $COOCH_3$, SCH_3, etc groups lead to almost 100% enol from. No enolisation is possible if both the hydrogen atoms of α-carbon atom are substituted.

The methinic protons in the keto form and the hydroxyl proton in the enol form are acidic. The removal of this hydrogen generates

the 1,3-diketonate anion **3**, which is the source of a broad class of coordination compounds referred to as metal 1,3 diketonates.

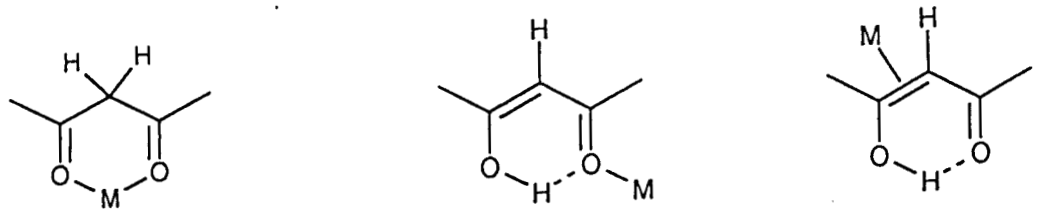
The coordinating ability of 1,3-diketones was recognised as early as in 1887 when Combes[30] reported the synthesis of beryllium acetylacetonate. This was followed by the pioneering work of Werner[31], Morgan[32] and Sidgwick[33] who confirmed the bifunctional chelating character of these ligands. Being powerful chelating agents, the diketonate anions form complexes with virtually all the transition and main group[34-39] metals. 1,3-Diketones can bond to metal ion in different ways. Some of the well established bonding modes of this versatile ligand systems are summarized in figure 1. Among these the most common is the one which contains a quasi aromatic six membered C_3O_2M ring system as in structure **4**.



4

Several review articles, monographs and books[34,36], are available on 1,3-diketones and their diverse types of inorganic derivatives, and therefore no attempt is made here to discuss such details. However since the present study is mainly based on arylazo derivatives of 1,3-

i) Neutral molecule



ii) Mono anion

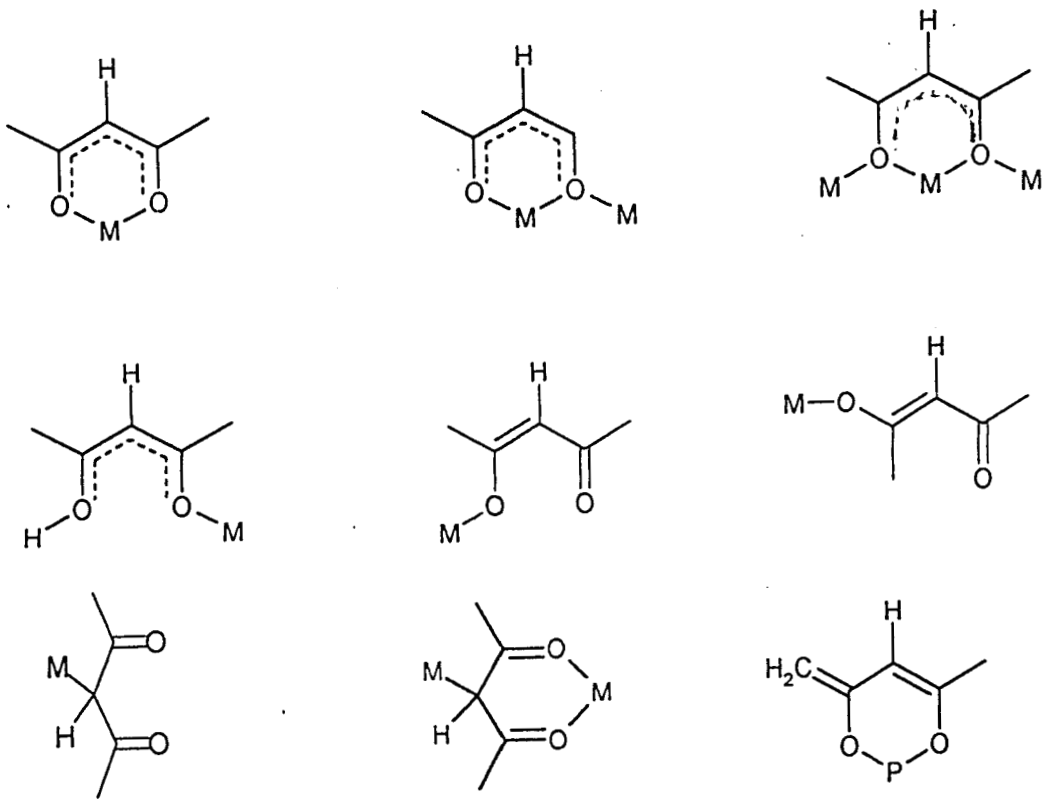


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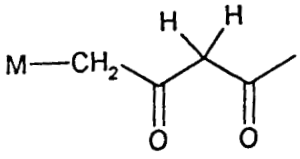
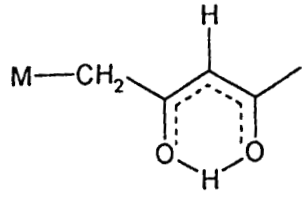
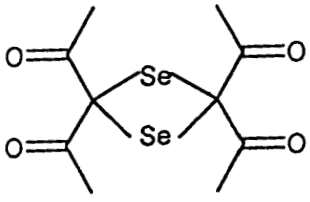
Fig. 1. Different bonding modes of β-diketones.

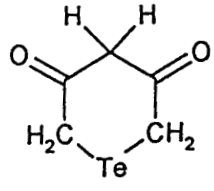


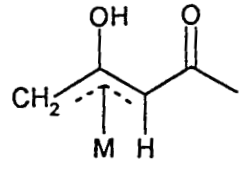
and

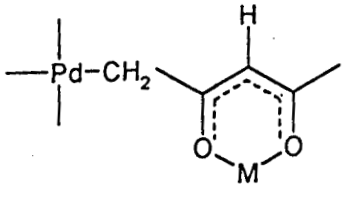


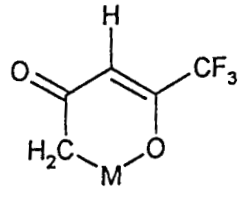
iii) Dianion

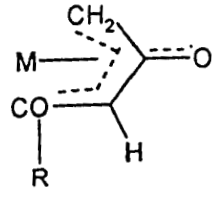


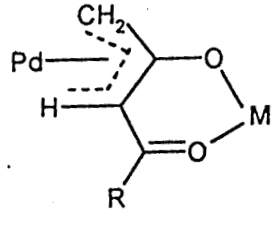












diketones, some of the salient features of the chemistry of 1,3-diketones pertinent to the investigation are briefly discussed below.

Reactivity of 1,3-diketones and metal 1,3-diketonates

Traditionally the study of coordination compounds has centred on the behaviour of the metal ions rather than on the attached ligands. It has always been obvious that the properties of ligands could be modified by coordination to metals. Metal coordination plays important roles in many biological processes. Metal ions can influence the ligand reaction in various ways. In a simple sense a metal ion can cause polarisation of the ligand by virtue of an electron withdrawing effect. This phenomenon can result in increased acidity of the ligand either directly or through conjugation to another part of the ligand. The two important types of reactions of 1,3-diketones and metal 1,3-diketonates[40,41] are (i) the electrophilic substitution at the 2-carbon atom of 1,3-diketone moiety and (ii) nucleophilic attack of an amine at the carbonyl function.

In the present study these two reactions are used to develop several new polydentate ligand systems. The electrophilic substitution reaction resulted in the formation of 2-arylazoderivatives of the 1,3-diketones and the reaction with amines yielded multidentate schiff base ligand systems. Therefore certain structural features of these two types of ligand systems and their coordination

behaviour which are related to the present investigation are outlined below.

Arylazo derivatives of 1,3-diketones

In general, a compound containing the group >C-NH_2 and one other centre of unsaturation, is diazotisable using nitrous acid.[45] Though majority of the diazonium ions are derived from aromatic carbocyclic amines, many heteroarylamines[43,44] also undergo diazotization leading to great variation in diazotisability, and in properties and structure of the diazo compounds. A dominant characteristic property of aryldiazonium ion is its behaviour as a powerful electrophile, effecting substitution in compounds having one or more of the necessary nucleophilic centres.[45,46,47] In its reaction with a nucleophile, usually a proton is ejected and an arylazo group becomes attached at the position of displacement as shown below,

$$Ar\ N_2^+ \xrightarrow{H-Y} Ar - N = N - Y + H^+,$$

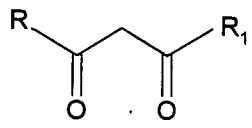
where H–Y is known as the coupling component.

An azo group can become attached to a carbon atom only when that atom is in a region of high electron density produced by polarization effects in the molecule. Diazo compounds react with a large number of coupling components to form azo derivatives. These

coupling components include aromatic hydroxy compounds, aromatic amines, substances containing reactive methylene groups and even hydrocarbons. As a result the possible permutations in azo-coupling reaction run into millions, and thousands of commercial azo dyes have been prepared in this way.[45,46]

Majority of the coupling components are derived from aromatic hydroxy compounds and amines.[45] However, there are several aliphatic compounds that are able to couple with aryldiazonium ion.[45] Nearly all such compounds may be regarded as methane derivatives, bearing one or more ionisable or resonating substituents which bestow upon the coupling carbon site sufficient electron density to allow substitution by the diazonium ion.[48,49] Coupling components of these types are often classed as compounds containing reactive methylene or methine groups. The number of such azo compounds known is large, and new examples are frequently reported. Victor Mayer[50-52] as early as in 1875 recognized these types of compounds and termed them as 'mixed azo' compounds.

Typical 1,3-dicarbonyles that are able to couple with aryldiazonium ion include the following types (**5**).



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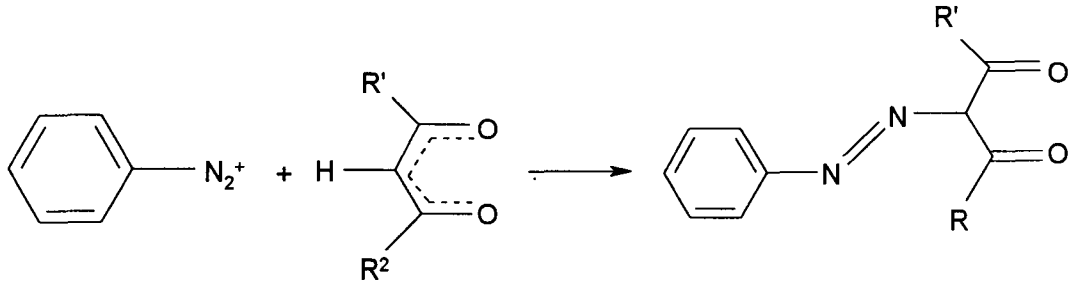
R	R_1	Type of compounds
alkyl / aryl	alkyl / aryl	1,3-diketone
alkyl	alkoxy/aryloxy	β-ketoesters
alkyl	OH	β-ketoacids
alkyl / aryl	NHPh	β-ketoanilides

The realization and proof that diazo coupling reaction is an electrophilic substitution reaction was established in the 1950's by Zollinger and his coworkers[46,53] in tune with the mechanism of electrophilic substitution elucidated by Ingold[47] and his coworkers during the 1930's. The reactivity of the active C–H bonds of 1,3-diketones and metal 1,3-diketonates has aroused wide interest. The active methylinic carbon in these compounds can act as nucleophilic centre. This property of 1,3-diketones has been demonstrated in their reaction with aryldiazonium salts.[45,54,55]

The coupling of diazo compounds with active methylinic compounds such as β-dicarbonyls, that can exhibit keto $\rightleftharpoons$ enol tautomerism result in a large and diverse group of products.

Hundreds of active methylinic compounds have been used as coupling components and many of these diazo-coupled products and their metal complexes serve as technically important dyes and pigments. For instance, the typical yellow dye, Hansa yellows are prepared by coupling of aryldiazonium salts with 1,3-dicarbonyl compounds[56-58] such as β-ketoanilides.

In general in the diazo coupling reaction between an aryldiazonium ion[59] and an active methylene compound such as 1,3-diketone, usually a proton is ejected and an areneazo group becomes covalently attached to it. The reaction without considering the exact tautomeric form can be represented as below (Scheme **1**):



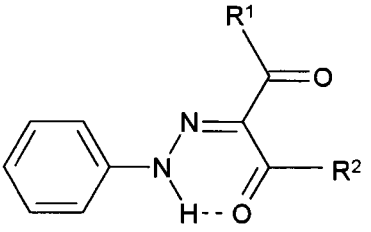
Scheme 1

In general the product can be termed as 2-arylazo-1,3-diketones.

Tautomerism of 2-arylazo-1,3-diketones

Tautomerism of these mixed azo compounds has evoked considerable interest and controversy in the past.[60-64] In fact much

of the early works on these compounds were directed towards settling different view points. The introduction of an areneazo group at the 2-position of the 1,3-diketones raises the possibility of azo-hydrazone tautomerism, apart from the keto-enol tautomerism of the diketo group. Thus, at least the following structures **6-9** can be distinguished even in simple 2-phenylazo-1,3-diketones.



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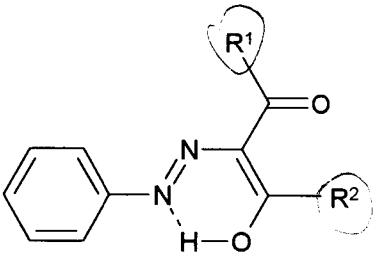

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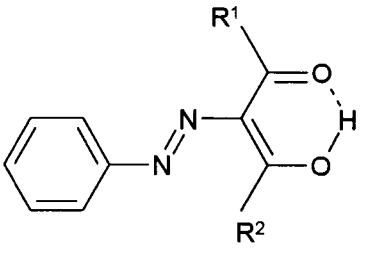

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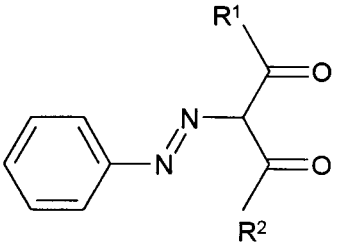


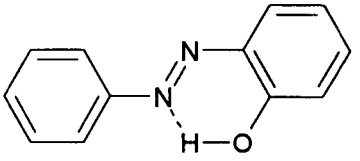
9

In unsymmetrical 1,3-diketones, (when R' and R^2 are different), the number of possible structures may further increase. When hydrogen bonding groups such as OH, SH, COOH or NH_2 are present in the phenyl ring, the tautomeric behaviour of the compounds may

become still complicated. Similarly the electronic effects of R groups also have influence on the resulting structure.

The tautomeric behaviour of arylazo-1,3-diketones is comparable to that of the well studied tautomerism of *ortho* hydroxydiarylazo compounds. Various studies employing several techniques including theoretical calculations have helped to build up a coherent picture in determining the predominant form in a wide variety of diarylazo compounds.

Thus, it has been shown that phenylazoderivatives of phenols exist entirely in the internally hydrogen bonded azo-enol form, **10**. The corresponding derivatives of napthalenols and anthracenols exist predominantly or entirely in the internally hydrogen-bonded quinone-hydrazone form, **11**. Studies in the case of heterocyclic azo compounds such as 1-(2-pyridylazo)-2-napthalenol, and 1-(2-thiazolylazo)-2-napththalenol have shown their occurrence in the azophenol form, **12**.



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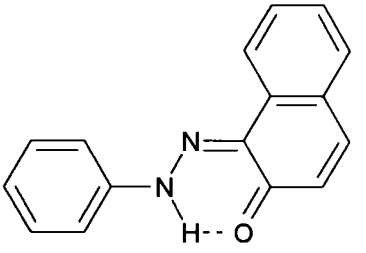

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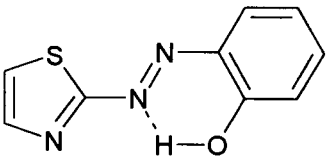

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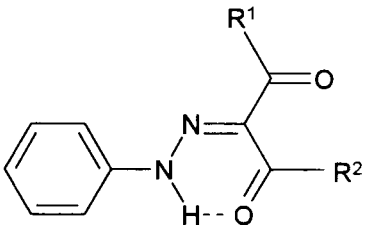


13

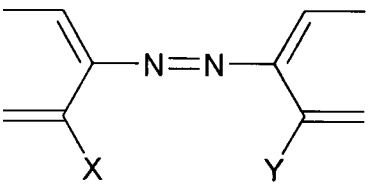
Phenylazo derivatives of 1,3-dicarbonyl compounds such as acetyl acetone, benzoylacetone, dibenzoylmethane, thenoyltrifluro-acetone, methylacetoacetate and acetoacetanilide have been shown to exist entirely in the intramolecularly hydrogen-bonded hydrazo-keto form, **13**, rather than in any other tautomeric form. Bulk of the information in this regard comes from electronic, ir, nmr and mass spectral data. These compounds are therefore systematically named as 1,2,3-triketone-2-arylhydrazones.[64,65] However, heteroarylazo derivatives of 1,3-diketones have been shown to exist predominantly in the azo-enol form, based on both experimental and theoretical basis. Thus the 2-pyridylazo-, 2-thiazolylazo-1,3-diketones exist in the azo-enol form **12** rather than in the keto-hydrazone form.

Metal complexes of 2-arylazo-1,3-diketones

The net result of coupling aryldiazonium ion with 1,3-diketones is the introduction of a potential donor site (azo/hydrazone) into the bidentate 1,3-diketone. Thus at least three donor sites are present in 2-arylazo-1,3-diketones. In the

intramoelcularly H-bonded form of these compounds steric factors prevent the participation of all the three donor groups simultaneously to the same metal ion.[65]

The donor property of azo groups is weak and its ability to coordinate with metals was originally inferred from the observation that azobenzene having *ortho*-hydroxy or *ortho*-amio group form metal complexes, whereas those having OH or NH_2 groups *meta* or *para* to the azo linkage do not. Stable metal complexes cannot result from the donor strength of the azo group alone. Important metallizable azo dyes are therefore characterized by additional metal binding groups at suitable positions with respect to the azo linkage, as in fig. 2.

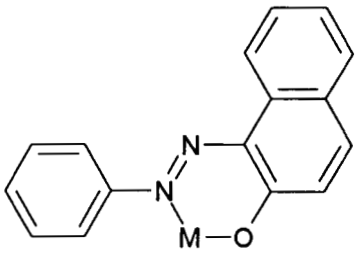


X	Y
H	OH / NH_2 / COOH / SH
OH	OH / NH_2 / COOH / SH
NH_2	OH / NH_2 / OOH / SH
COOH	OH / NH_2 / COOH / SH

Fig. 2.

These structures can form stable five or six-membered chelate ring with the metal ion as given for instance in the case of phenylazo-

2-naphthol **14**. In the case of heteroarylazo compounds, the hetero atom can also involve in bonding with the metal as in **15**.



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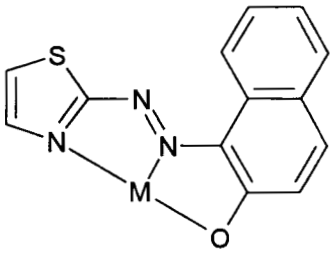
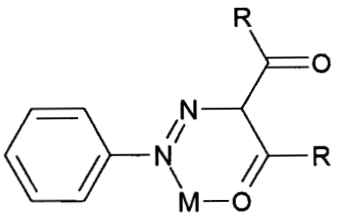


15

The nature of coordination of arylazo-1,3-dicarbonyls is comparable to that of diarylazodyes. The keto groups of these arylazo-1,3-diketones which are at *alpha* position with respect to the azo group, may be regarded as equivalent to *ortho* position of *ortho*-hydroxy diarylazo compounds. Therefore 2-arylazo-1,3-diketones can form stable chelate complexes with metal ions as in structure **16** and numerous such complexes have been reported.[65-72]

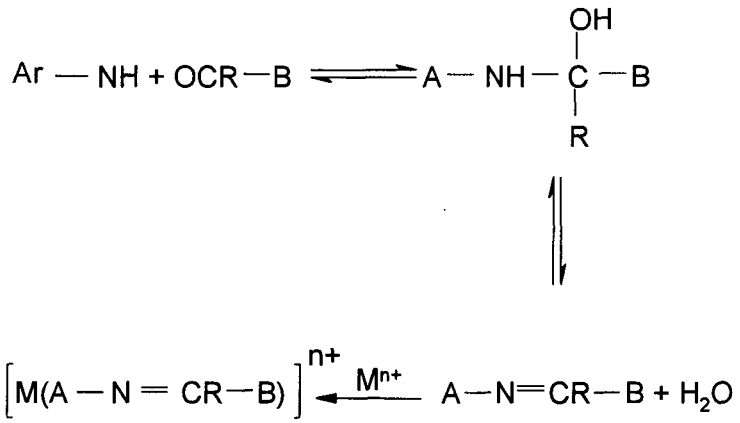


16

Schiff bases derived from 1,3-diketones

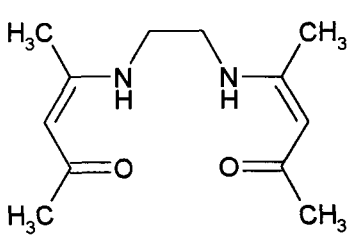
The reactivity of the carbonyl functions of 1,3-diketones and metal 1,3-diketonates towards amino compounds has been utilised in the synthesis of a large number of multidentate and macrocylic ligands. These ligand systems have evoked considerable interest because of their utility as model compounds in bioinorganic studies.[73-75]

The formation of imine or Schiff base metal complexes can be effected very readily through reaction of the amine with the carbonyl compound in presence of metal ion. Nucleophilic attack of the amine on the carbonyl group is enhanced by polarisation of the carbonyl group by coordination of the oxygen atom to the metal ion. Furthermore, the reaction is reversible unless steps are taken to dehydrate the intermediate hydroxy amine, and coordination of the product imine is an important factor in promoting the reaction by suitable metal ions. The initial reactions of these types were used to produce copper(II) complexes of salicylaldimines, where additional coordination support is provided by the phenolate oxygen atom. Several bi- and tridentate ligand systems have been prepared by this method.[76-80]



Scheme 2

Tetradentate Schiff bases with N_2O_2 donor sets have been widely studied for their ability to coordinate with metal ions. The properties of these complexes are determined by the electronic nature of the ligand as well as by its conformational behaviour.[76,81-86] Synthesis of such quadridentate imine chelate usually requires the combination of two equivalents of dicarbonyl compounds and a diamine.[87-93] The Schiff bases that have been most widely studied are derivatives of acetylacetone, salicylaldehyde, and hydroxy methylene compounds whose prototypes with ethylenediamine are shown below **17, 18, 19**.



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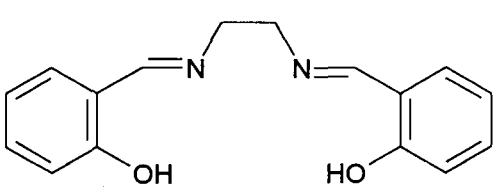

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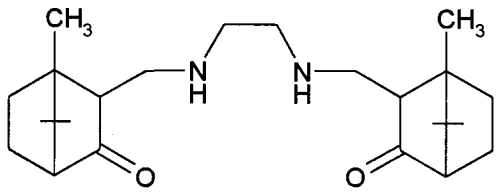


19

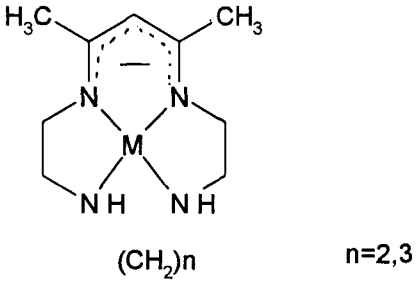
Higher multidentate chelating agents have also received considerable attention in view of their wide range of possible structural variations. Lions[75,94] has suggested synthetic guidelines for the design of numerous such potential ligands. **The use of arylhydrazones of 1,3-diketones in the design and synthesis of new multidentate chelating agents have been demonstrated in this investigation.**

Synthetic macrocyclic chelates

Synthetic ring complexes which mimic the behaviour of more complicated natural macrocyclic ring systems (such as those containing porphyrin or corrin rings) are known and at present the study of such compounds is receiving much attention. Although the results obtained so far do not always closely parallel those in nature, a knowledge of the chemistry is being built up and the biochemical role of metal ions in the natural systems is beginning to be better understood.

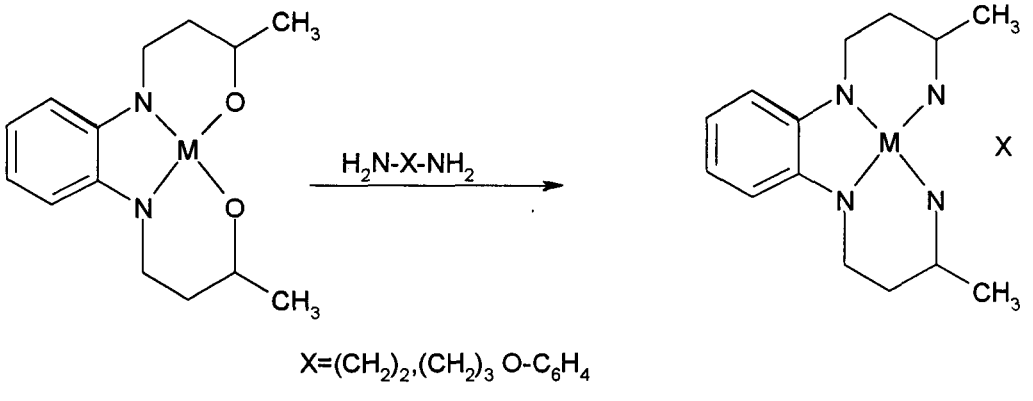
The Schiff base condensation between a dicarbonyl compound and a di-(or poly-) amine to yield an imine linkage has formed the basis of many successful polyaza macrocylic ligand synthesis.[94-101]

1,3-Dicarbonyl compounds form 1,3-diimine macrocycles, which are usually isolated with the deprotonated dienylato (1-) chelate ring as in the case of **20** formed from tetraimines and 2,4-pentanedione.



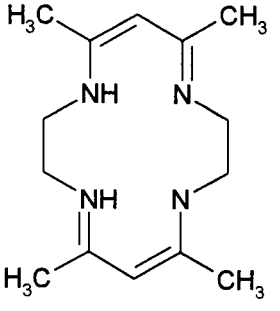
20

The reactivity of oxygen is enhanced with 1,2-diamino benzene, and benzo- and dibenzo macrocylic complexes are readily prepared.[102] For aliphatic diamines the reactivity is sufficiently enhanced by a variety of substituents (eg., acetyl, bromo, diazophenyl, etc.) at the 2-position of the 1,3-dicarbonyl compounds (scheme **3**).

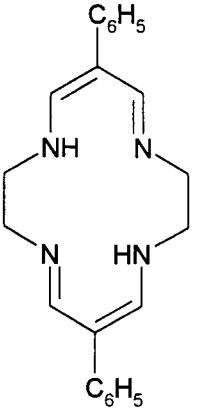


Scheme 3

A number of macrocycles (eg., **21** and **22**) have been prepared in the absence of metal ions.[102]



21



22

Binucleating ligands

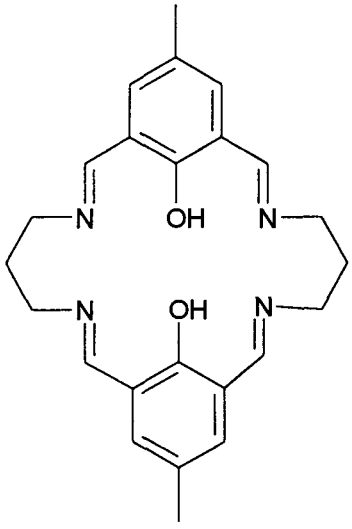
There are many metalloproteins or metalloenzymes that possess functional centres to hold two metal atoms close together, less than 10A° apart, and often less than 5A° apart. The metal atoms often share a bridging ligand or ligands, and the pairing of metal may be homobimetallic or heterobimetallic. The desire to understand the nature of metal binding sites in metalloenzymes has led to the use of bimetallic complexes of binucleating ligands as speculative models for the metal environment.[103]

The term binucleating ligand, introduced by Robson[104] in 1970, was defined as "polydentate chelating ligands capable of simultaneously binding two metal ions". The definition was later

refined to present macrocyclic binucleating ligands as macrocyclic ligands capable of securing two metal ions in close proximity.[105]

Complexes of binucleating ligands fall into two general classes[106] (i) complexes in which the metals share at least one donor atom in species containing adjacent sites in which the central donor atoms(s) provide bridge (bridging donor sets), (ii) complexes in which donor atoms are not shared and so isolated donor sets exist.

The ligands of the first type are collectively known as compartmental ligands.[102] This class of ligands are predominantly Schiff bases derived from 2,6-disubstituted, phenols and thiophenols, 1,3,5-triketones and 3-ketophenols. Typical examples in this category[108-117] are structures **23, 24** and **25**.



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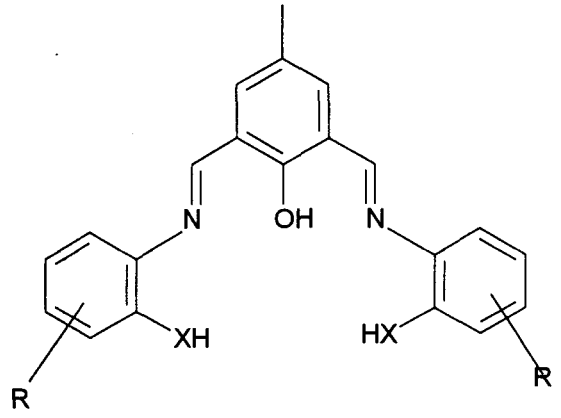
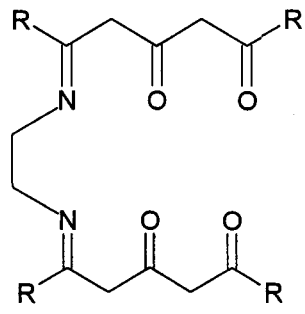


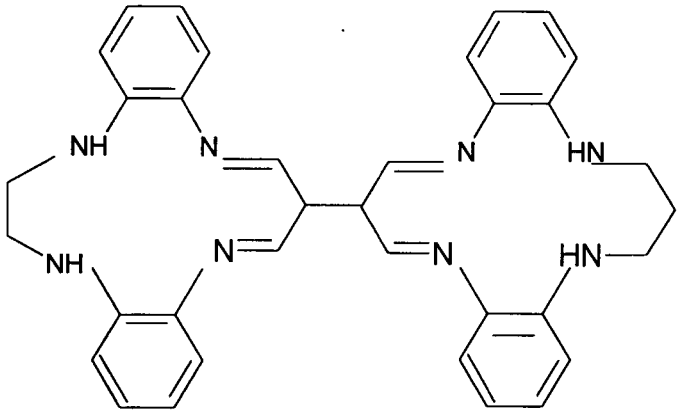
24



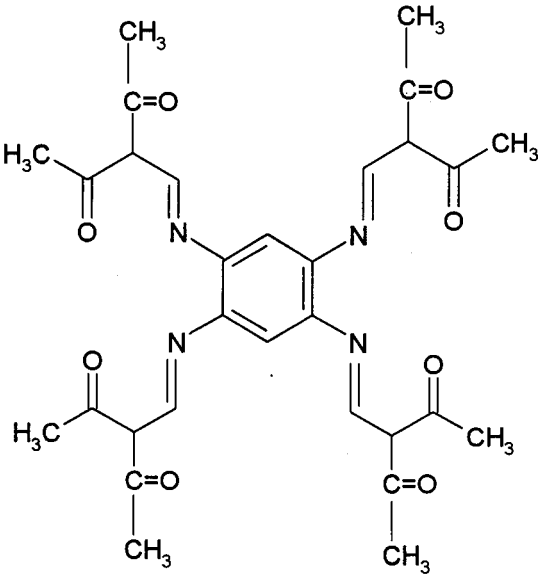
25

Ligands in which isolated donor sets separated by aromatic or other bridging function constitute an important group of polydentate and macrocyclic binucleating ligands. A large variety of ligand types exists in this category.

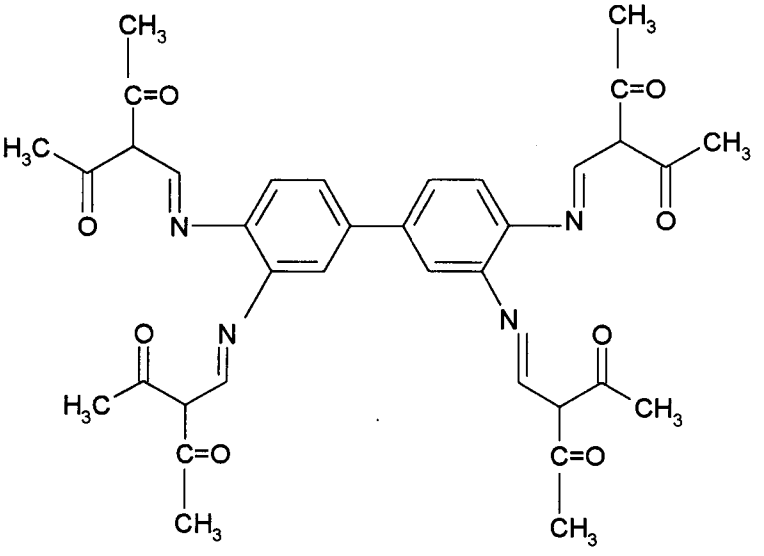
The class of linked-closed compartmental compounds has been designed to investigate the transmission of electronic effects through conjugated bridge ligand systems. The tetrazo macrocyle **26** is a typical example.[118] Small antiferromagnetic exchange interactions have been detected in the complexes of the linked-open compartmental ligand, **27** whereas no exchange was found for **28** where through conjugation is broken at the biphenyl link.[119] The imidazole bridged[120-122] binucleating complex, **29** the 1,4-dihydrazonophthalazine bridged[123] **30**, and the pyrazine bridged[124] ligand **31** are some of the binucleating systems that show interesting properties.


NH
N
N
HN
NH
N
N
HN

26


CH3
C=O
H3C
O
N
N
CH3
C=O
CH3
O
N
N
O
H3C
C=O
CH3
O
CH3
C=O
CH3

27



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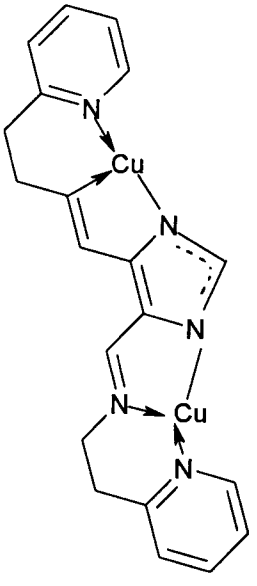

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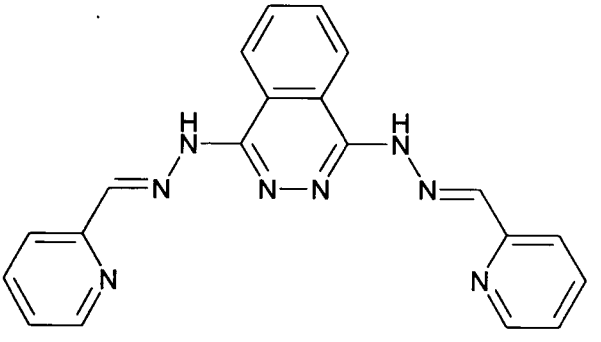

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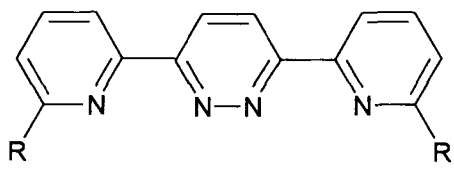


31

It may be noted that the reaction of suitably substituted dicarbonyl compounds and diamines is an important synthetic route[125-128] for designing and preparing a wide variety of polydentate and macrocyclic ligands and chelates. **In the present work a new series of polydentate and binucleating ligand systems, containing the isolated donor sets based on 2-arylhydrazones of 1,3-diketones have been investigated with particular reference to the structural aspects of the ligands, and of the ligand moieties in metal complexes.**

MATERIALS, INSTRUMENTS AND METHODS

Materials

Chemicals used for synthesis in this investigation were of C.P. grade. For analytical purposes 'AnalaR' grade chemicals were employed. Commercial solvents were distilled and used for synthesis.

The metal salts used for synthesis of metal complexes were cobalt(II)acetate tetrahydrate, nickel(II)acetate tetrahydrate, copper(II) acetate monohydrate and zinc(II) acetate dihydrate.

Only analytically pure compounds are reported in this Thesis. The complexes reported here in are stable and have good keeping qualities. Compounds for recording spectra were recrystallised from proper solvents several times till chromatographically pure (tlc-silica gel).

Instruments

Instruments used in this investigation are:

1. 8101 Schimadzu – FTIR spectrometer.
2. Varian 300 nmr spectrometer.
3. Jeol SX-102 (FAB) mass spectrometer.
4. Heraeus CHN–O–rapid analyser.

5. Gouy type magnetic balance.
6. Varian E112 ESR spectrometer.
7. Toshniwal Conductivity bridge.
8. Systronic pH meter.

Methods

Elemental analysis: Metal complexes were analysed by standard methods[183] after decomposing them with concentrated sulphuric-nitric acid mixture. Carbon, hydrogen and nitrogen percentages reported are by microanalysis carried out at RSIC, Central Drug Research Institute, Lucknow.

Infrared spectra of compounds were recorded from discs with potassium bromide in the region 4000-400 cm^{-1}. Bands were calibrated using the nearest polystyrene bands.

^{1}H nmr spectra were recorded using $CDCl_3$ and DMSO solution using TMS as reference.

The FAB **mass spectra** were recorded at room temperature using Argon (6 KV, 10 mA) as the FAB gas and *m*-nitrobenzyl alcohol (NBA) as the matrix. The probable matrix peaks are located at m/z 136, 137, 154, 289, 307.

ESR spectra (X-band) of copper complexes were recorded at 77K in glassy state between 8.5 – 9.5 GHz and calibrated with diphenyl picrylhydrazil (DPPH) free radical for which g = 2.0036.

Magnetic susceptibility[184] was determined at room temperature (28 ± 2°C) using $Hg[Co(NCS)_4]$ as the standard.

Molar conductance[185] of the complexes were determined in dmf at 28 ± 2°C, using solutions of about 10^{-3} M.

Molecular weights of compounds reported were determined by Rast's[186] method using naphthalene/camphor as medium.

CHAPTER 2

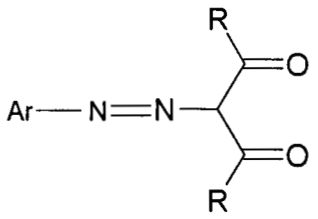
ARYLAZODERIVATIVES OF 1,3-DIKETONES AND THEIR METAL COMPLEXES

CHAPTER 2

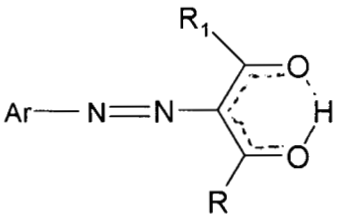
ARYLAZO DERIVATIVES OF 1,3-DIKETONES AND THEIR METAL COMPLEXES

The most important structural aspect of arylazo derivatives of active methylene compounds such as 1,3-diketones is their possible azo-hydrazone tautomerism. The tautomerism of these 'mixed azo' compounds has evoked considerable interest and controversy in the past.[60-64] Investigations on the tautomerism of azo compounds have started as early as in 1884, when Zincke and Bindewald[129] suggested that a mobile equilibrium of azo and hydrazone forms exists between certain hydroxy diarylazo compounds. Extensive research followed, which is still continuing. Evidence for the presence of tautomerism, in both solid and in solution of such compounds has been provided by many techniques[130-138] such as electronic, ir, nmr, mass and fluorescence spectra. Many studies on the quantitative aspects of these phenomena also exist.[139-143]

In principle at least the following tautomeric structures **1-4** are possible for these type of compounds.



1



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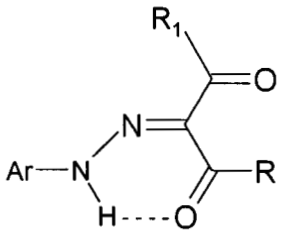

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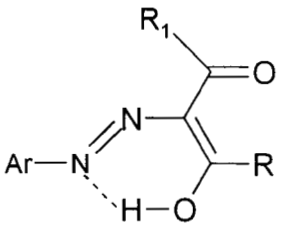

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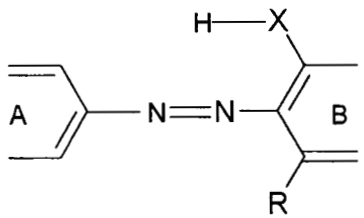
The percentage of the azo and hydrazone forms depends on several factors but principally on the relative thermodynamic stabilities of the azo **5** and hydrazone **6** tautomers.



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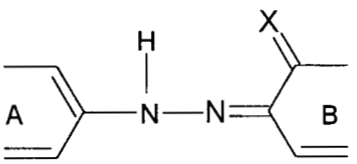
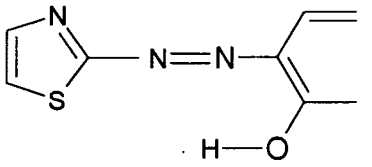


6

If stabilities of two forms are similar both the tautomers are generally observed. When one tautomer is more stable than the other the compound will exist entirely in the stabler form. For instance when A and B are phenyl rings, the bond energy of the azo form is calculated as about 108 kjmol^{-1} (when X = O) less than the hydrazone form. Thus the hydrazone form appears to be more stable than the azo form. However in aromatic systems resonance stabilisation energy must also be considered. Thus in the azo form, when A and B are phenyl groups the two phenyl rings each contribute 150.5 kJ mol^{-1} as resonance stabilization energy. In the hydrazone form, the aromaticity of one of the phenyl ring is decreased and about 134 kJ mol^{-1} is lost.[144] Taking into account both effects, the azo tautomer is more stable than the hydrazone tautomer by about 26 kjmol^{-1}. Thus most phenyl azo phenols exist entirely in the azo form.

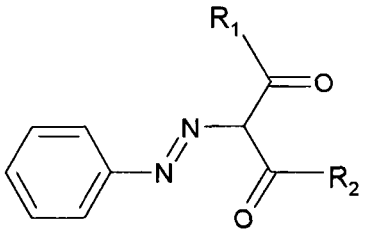
Extending the same argument it can be seen that when A is phenyl and B is naphthyl groups the resonance stabilisation energy is insufficient to offset the greater bond energy stability of the hydrazone form and consequently such systems exist predominantly in the hydrazone form. This has been clearly demonstrated in the case of phenylazonaphthalenols and phenylazoanthracenols. Such compounds exist totally in the hydrazone form, a fact also confirmed from Hückel molecular orbital calculation.[139]

Azo compounds containing heterocyclic ring such as thiazolyl, pyridyl, etc. have lower resonance stabilisation energy compared to their carbocyclic analogues[145-147] consequently these compounds exist predominantly in the azo form **7**.



7

Compared to diarylazo compounds, the situation is entirely different in the case of diazo coupled products derived from aryldiazonium ion and active methylene compounds such as 1,3-diketones. Victor Mayer[50] was the first to report the coupling of a diazonium salt with active methylene compounds. Even during that time the question regarding the structure of the reaction product arose. In fact there is only negligible difference in resonance stabilisation energy between the azo **8** and hydrazone **9** forms of these 2-arylazo-1,3-dicarbonyls. Therefore, the hydrazone tautomer[148-157] with its greater bond energy stabilisation is expected to be more stable. In recent years various investigators[60-72] have presented uv, ir, nmr and mass spectral data of arylazo derivatives of 1,3-dicarbonyl compounds to corroborate this view.



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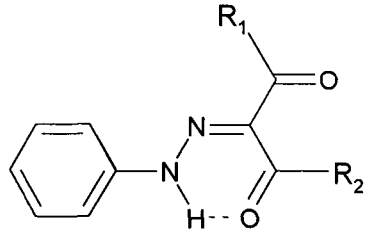
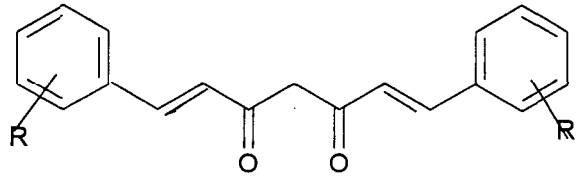


9

Based on spectral and X-ray crystallographic data[158-163] it has been well demonstrated that heteroarylazo derivative of 1,3-diketones such as 2-thiazolylazo-1,3-diketones, 2-benzothiazolylazo-1,3-diketones and 2-pyrydylazo-1,3-diketones exist predominantly in the azo-enol form rather than the keto-hydrazone form. Thus it can be concluded that the nature of the tautomeric forms of arylazoderivatives of 1,3-dicarbonyls depends both on the arylazo group and the coupling component. Most of the reported studies on arylazo derivatives of 1,3-diketones are based on 1,3-diketones in which the diketo function is directly linked to alkyl or aryl groups. No report appeared on arylazo derivatives of 1,3-diketones in which the diketo group is linked to alkenyl function. Such unsaturated 1,3-diketones constitute the active chemical species present in several traditional medicinal plants. For instance the major physiologically important compounds present in the herbaceous Indian medicinal plant turmeric (*Curcuma longa*) are the yellow coloured curcuminoids. Structurally they are typical 1,3-diketones of the general structure **10**. Chemical and biochemical aspects of

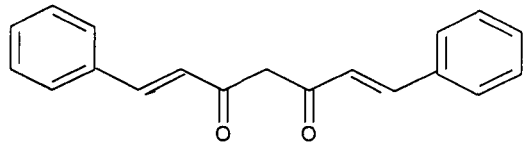
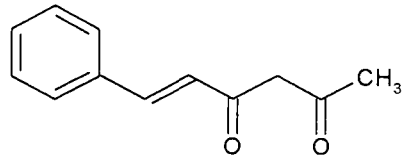
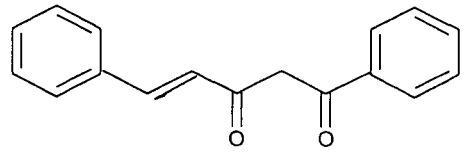
these type of compounds have received considerable attention in recent years.[163,169]



10

In the present investigation arylazo derivative of some of these unsaturated β-diketones and their typical complexes were synthesised and characterised.

The unsaturated 1,3-diketones considered in this study are given below.

	Systematic name	**Structure**
1	1,7-Diphenyl-1,6-heptadiene-3,5-dione, Dicinnamoylmethane (**Hdhd**)	
2	6-Phenyl-5-hexene-2,4-dione, Cinnamoylacetylmethane (**Hphd**)	
3	1,5-Diphenyl-4-pentene-1,3-dione, Cinnamoylbenzoylmethane (**Hdpd**)	

Synthesis and characterisation of phenylazo and thiazolylazo derivatives of these unsaturated 1,3-diketones and their metal complexes are discussed in section 1.

The unsaturated 1,3-diketone, dicinnamoylmethane, Hdhd, on condensation with ethylenediamine and 2-aminophenol yielded two new Schiff base ligands. In **section 2** synthesis and characterisation of these Schiff bases and their metal complexes are considered.

SECTION 1

SYNTHESIS AND CHARACTERISATION OF PHENYLAZO- AND THIAZOLYLAZO DERIVATIVES OF UNSATURATED 1,3-DIKETONES AND THEIR METAL COMPLEXES

A. Synthesis and characterisation of phenylazo derivatives of the unsaturated 1,3-diketones and their metal complexes

Experimental

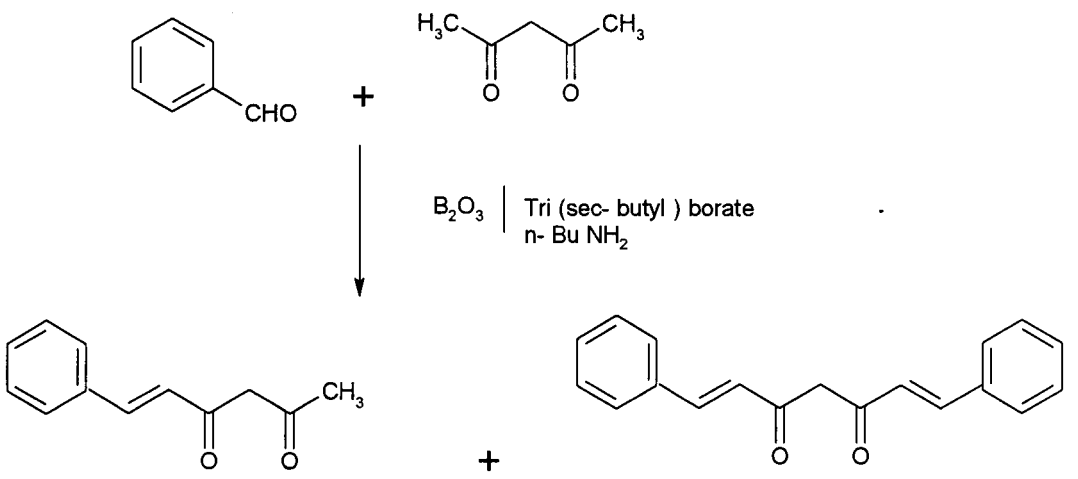
Synthesis of the unsaturated 1,3-diketones

1. Synthesis of 1,7-diphenyl-1,6-heptadiene-3,5-dione, Hdhd

The **Hdhd** was synthesised through the condensation of benzaldehyde with acetylacetone (2,4-pentanedione) in the presence of boric oxide and tri(sec-butyl) borate using n-butylamine as the condensing agent.[164] The reaction leads to the formation of **Hdhd** as the major product along with small amounts of 6-phenyl-5-hexene-2,4-dione (Scheme 1). Separation of pure **Hdhd** was achieved through column chromatography. A typical procedure for the synthesis and purification of **Hdhd** is outlined below.

To the product obtained by shaking acetylacetone (0.5 g, 0.005 mol) with boric oxide (0.25 g, 0.0035 mol) for ~ 1 h, a solution of benzaldehyde (0.01 mol) in dry ethyl acetate (5 mL) and tri (sec-butyl) borate (4.6 g, 0.02 mol) were added. The reaction mixture was stirred

continuously and n-butylamine (0.1 mL) was added dropwise during 40 min. Stirring was continued for an additional period of ~ 4 h and the solution was set aside overnight. Hot(~ 60°C) hydrochloric acid (0.4 M, 7.5 mL) was then added and the mixture again stirred for ~ 1 h before extraction with ethyl acetate. The combined extracts were evaporated and the residual paste was stirred with dil. HCl (10%, 10 mL) for ~ 1 h. The solid product separated was collected, washed with water and dried in vacuum.



Scheme 1

When an ethanolic or benzene solution of the product obtained above subjected to tlc (silica gel) revealed the presence of two compounds. Both the compounds were quantitatively separated by column chromatography as detailed below.

The crude product was dissolved in minimum quantity of dry ethyl acetate and placed over the column (2 x 100 cm) densely

packed with silica gel (mesh 60-120) and eluted with a 1:5 v/v acetone-chloroform mixture at a uniform flow rate of 1 mL per min. As the elution proceeds, two bands were developed in the column, a pale yellow lower band and an yellow to orange red upper band. The lower region was collected as 10 mL aliquots in separate tubes and in each case the homogeneity was established by tlc. The combined eluates on evaporation gave the 6-phenyl-5-hexene-2,4-dione (~ 10%).

The elution was then continued using a 2:1 v/v mixture of chloroform and acetone to recover the orange-yellow band retained in the upper portion of the column. The eluates were collected in aliquots of 10 mL in separate tubes, checked by tlc, and the combined extracts on removing the solvent in vacuum yielded **Hdhd** (~ 75%). All the compounds isolated were recrystallised from hot benzene to give spectroscopically pure material. The compound melts at 160°C (literature[164] value 158°C). The ir spectrum of the compound is exactly similar to the reported spectrum.[164]

2. Synthesis of 6-phenyl-5-hexene-2,4-dione, Hphd

Small quantities (5-10%) of 6-phenyl-5-hexene-2,4-dione were found during the synthesis of **Hdhd** through the condensation of acetylacetone with aromatic aldehydes. However, when the condensation reaction was carried out at ice-cold temperature, the

monocondensation product, 6-phenyl-5-hexene-2,4-dione was formed in good yield and separated using column chromatography. A typical procedure is outlined below.

The product formed by mixing acetylacetone (0.075 mol, 7.5 g) and boric oxide (0.055 mol, 3.75 g) was suspended in dry ethyl acetate (50 mL) containing tri (sec-butyl) borate (0.1 mol, 23 g). To this mixture, kept at ~ 0°C, a solution of the aromatic aldehyde (0.025 mol) in dry ethylacetate (15 mL) and n-butyl amine (0.5 mL) were added dropwise during 90 min with constant stirring. The stirring was continued for an additional period of ~2 h and the solution was set aside overnight. The reaction mixture was then stirred for ~ 1 h with hot (~ 50°C) hydrochloric acid (0.4 M, 20 mL) and extracted repeatedly with ethylacetate. The combined extracts were concentrated in vacuum and subjected to chromatographic separation to get the 6-phenyl-5-hexene-2,4-dione as outlined below.

The concentrated extracts were uniformly applied on the top of a silica gel (mesh 60-120). Column (2 x 100 cms) and then eluted with a 5:1 v/v mixture of chloroform-acetone at a uniform flow rate of 2 mL per min. When the void volume has been run out, the yellow band comes down and the eluates were collected in aliquots of 10 mL in separate tubes and each samples were spotted on a tlc (silica gel) plate to ensure the presence of only a single component in the eluate.

The yellow band developed in the lower region was recovered by successive elution and combined eluates on evaporation yielded **Hphd**. The elution was then repeated by using a 2:1 v/v mixture of chloroform and acetone to recover the orange yellow band retained in the upper portion of the column. The eluates were collected in aliquots of 10 mL in separate tubes, checked by tlc and the combined extracts on removing the solvent in vacuum yielded **Hdhd** (15-25%). The isolated **Hphd** was recrystallised from hot benzene to get chromatographically (tlc) pure material. The compound melts at 124°C (literature[164] value 124°C). The ir spectrum of the compound was identical with the reported spectrum.[164]

3. Synthesis of 1,5-diphenyl-4-pentane-1,3-dione, Hdpd

The compound was synthesised by the condensation of benzaldehyde and benzoylacetone.[165] The reaction was carried out in presence of tri(sec-butyl)borate, B_2O_3 and n-butyl amine.

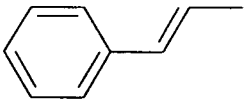
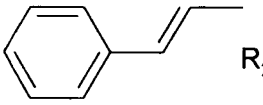
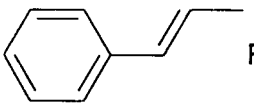
Benzoylacetone (0.005 mol) mixed with boric oxide (0.005 mol) and 5 mL dry ethyl acetate was stirred well for ~ 1 h. The stirring was further continued for ~ 1 h with the slow addition of a solution of the benzaldehyde (0.0025 mol) in 5 mL dry ethylacetate, followed by tri(sec-butyl) borate (0.01 mol) and 0.5 mL of n-butylamine. After stirring for an additional period of ~ 3 h the solution was set aside overnight. Hot (~ 60°C) hydrochloric acid (0.4 M, 75 mL) was then

added to the reaction mixture and again stirred for ~ 1 h before extraction with ethylacetate. The washed extracts were combined, concentrated and the residual paste obtained was stirred with hydrochloric acid (2 M, 10 mL). The separated solid product was collected, washed with water, ethanol and dried under reduced pressure. The compounds were recrystallised from hot benzene to get chromatographically (tlc) pure material. The observed m.p. of the compound 158°C agree well with the literature[165] value of 158°C. The identity of the compound was further confirmed from a comparison of the ir spectrum of the compound with that of the reported spectrum.

The phenylazo derivatives of unsaturated 1,3-diketones were synthesised by coupling benezene diazonium salt with the unsaturated 1,3-diketones. The systematic name of the compounds along with a suitable abbreviation are provided in table 1.

TABLE 1

Analytical and physical data of Hpad, Hpah, Hpap

	Compound / Systematic name	Yield %	M.P. °C	Elemental analysis % Found/(Calcd.)		
				C	H	N
1	$R_1 = R_2 =$  1,7-diphenylhepta-1,6-diene-4-phenyl azo-3,5-dione, (phenylazodiphenyl heptadienedione) **Hpad**	70	160	77.80 (78.90)	5.00 (5.26)	6.94 (7.36)
2	$R_1 =$  $R_2 = CH_3$ 6-Phenyl-5-hexene-3-phenylazo-2,4-dione (phenylazophenyl hexenedione), **Hpah**	72	125	72.65 (73.97)	5.4 (5.48)	9.02 (9.58)
3	$R_1 =$  $R_2 = C_6H_5$ 1,5-diphenyl-4-pentene-2-phenylazo-1,3-dione (phenylazodiphenyl pentenedione) **Hpap**	75	144	77.86 (77.96)	4.94 (5.08)	7.23 (7.90)

1. Synthesis of phenylazo derivative of 1,7-diphenyl-1,6-heptadiene-3,5-dione Hpad

The compound was synthesised by the coupling of benzene diazonium salt with **Hdhd**. Benzene diazonium salt was prepared as reported[166] by the following method. Aniline (1 mL, 0.01 mol) dissolved in HCl[162] (8 mL, 50% HCl) was cooled below 0°C in an ice-salt bath. To this an ice cold solution of sodium nitrite (0.8 g in 2 mL H_2O) was added slowly with stirring. After destroying the excess nitrous acid present in the resulting solution with urea, it was added drop by drop to a solution of the **Hdhd** (0.01 mol, 2.76 g in 20 mL methanol) kept below 0°C with constant stirring. The pH of the solution was maintained around 6, using sodium acetate. The precipitated compound was filtered, washed with water and recrystallised from methanol to get chromatographically pure (tlc) compound.

Synthesis of metal complexes

Nickel(II) and copper(II) complexes of the compounds were prepared by the following general method. To a refluxing ethanolic solution of the compound (0.01 mol, 20 mL) concentrated aqueous solution of the metal acetate (0.01 mol) was added, refluxed for ~ 2 h and the volume was reduced, cooled to room temperature and the

precipitated complex was filtered, washed with excess water and then with methanol and dried in vacuum.

2. Synthesis of phenylazoderivative of 6-phenyl-5-hexene-2,4-dione, Phenylazophenylhexenedione, Hpah

The compound was synthesised by the coupling of benzene diaoznium salt with **Hphd**. Aniline was diazotised as reported.[166] Excess nitrous acid present in the diazonium salt solution was destroyed by adding urea to it. The diazonium salt solution (0.01 mol) was added drop by drop to a stirred solution of **Hphd** (0.01 mol, 1.88 g, 20 mL ethanol) kept below 0°C. Sodium acetate was added to keep the pH of the mixture in the range 6-7. After fifteen minutes the precipitated compound was filtered, washed with water and recrystallised twice from methanol to get chromatographically pure (tlc) compound.

Synthesis of metal complexes

Nickel(II) and copper(II) complexes were prepared by the following method.

A concentrated aqueous solution of the metal(II) acetate (0.01 mol) was added to an ethanolic solution of the ligand (0.01 mol) and the mixture was refluxed on a boiling water bath for ~ 2 h. The precipitate formed on cooling to room temperature was filtered,

washed with water then with methanol and dried in vacuum desicator.

3. Synthesis of phenylazo derivative of 1,5-diphenyl-4-pentene-1,3-dione, Phenylazodiphenylpentenedione, Hpap

The compound was synthesised by the coupling of benzenediazonium salt with **Hdpd** as follows. Aniline was diazotised as reported.[166] After destroying the excess of nitrous acid with urea, the diazonium salt solution (0.01 mol) was added drop by drop to an ethanolic solution of the **Hdpd** (0.01 mol, 2.5 g in 20 mL ethanol). The pH of the solution was maintained ~ 6 using an ice cold solution of sodium acetate. The precipitated compound was filtered, washed with water and recrystallised from methanol to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

Nickel(II) and copper(II) complexes of the compounds were prepared by the following general method. A mixture of the ligand (0.01 mol, 20 mL ethanol) and metal acetate (0.01 mol) in ethanol refluxed on a water bath for ~ 3 h. The volume was reduced and cooled to room temperature. The precipitated complex was filtered, washed with water and then with methanol and dried in vacuum.

Results and discussion

Characterisation of the Hpad, Hpah and Hpap

The elemental analytical data and other physical details of the chromatographically pure (tlc) compounds are given in table 1.

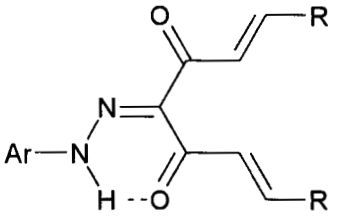
The analytical data clearly showed that the diazo-coupling reaction has occurred in the 1:1 ratio. The products are crystalline and soluble in common organic solvents. The ir, nmr and mass spectral data are discussed below with a view to establish the nature of the tautomeric form of the compounds. The systematic names given in table 1 are based on the structure arrived at from the spectral data of the compounds.

Infrared spectra

Infrared spectroscopy has been one of the most efficient tool in establishing the structure and nature of tautomerism of different types of 1,3-diketones.[167,168] This is mainly because of the fact that assignment of carbonyl groups in different electronic environment are possible by careful examination of the carbonyl stretching frequency. The carbonyl stretching frequency is strongly influenced by the electronic environment of the groups attached to it. The normal acetyl carbonyl gives stretching band usually at ~ 1720 cm^{-1}. The carbonyl stretching frequency of benzoyl carbonyl is lower than

that of CH_3CO group. Hydrogen bonding decrease the νCO. A further shift to lower value can be observed when C=O is in conjugation with C=C, C=N, etc. Electron withdrawing groups such as fluorine shifts the νCO to higher frequency. Thus the position of νCO can provide valuable information regarding the structure of the compound.

In 1,3-diketones the introduction of an arylazo group at 2-position leads to several tautomeric forms. Of these, in the case of **Hpad**, the following structures needs serious consideration.



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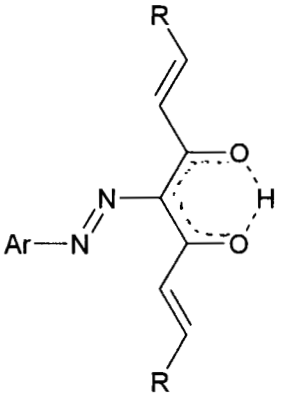

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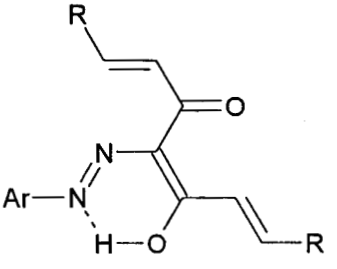


13

Distinguishing functional groups present in these structures are:

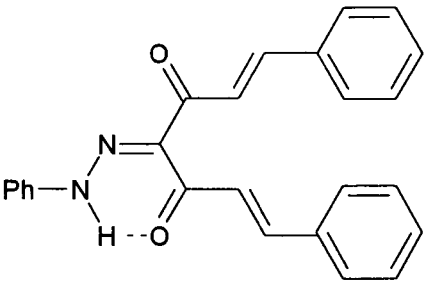
In structure **11**: Free conjugated carbonyl, hydrogen bonded conjugated carbonyl and N–H...O=C group.

In structure **12**: Intramolecularly hydrogen bonded enolised conjugated carbonyl and O...H..O group.

In structure **13**: Free conjugated carbonyl, enolised conjugated carbonyl and O–H...N group.

Ir spectral data do provide a distinction to be made between these structures. The ir spectrum of **Hpad** in the region 1600-2000 cm^{-1} is chracterised by the presence of three strong bands at 1709, 1651 and 1603 cm^{-1}. From a comparison of the reported[169-174] spectra of arylazo derivatives of acetylacetone these bands can be assigned respectively to free cinnamoyl carbonyl, H-bonded cinnamoyl carbonyl and C=N stretchings of structure **11**. The νC=C of aryl groups are observed in the range 1580-1600 cm^{-1}. A medium intensity band appeared at 1540 cm^{-1} is due to NH deformation vibration. A prominent band present at 1280 cm^{-1} can be assigned to νC-N. That the compound exists in the intramoelcularly H-bonded form is clearly evident from the broad band appeared in the region 2500-3500 cm^{-1}. Thus the ir data strongly support structure **14** of

the compound. The ir spectrum of the compound is given in figure 1.



14

The most important functional difference between **Hpad** and **Hpah** is the presence of an acetyl carbonyl in the latter compound instead of a cinnamoyl carbonyl. Thus the ir spectrum of the latter should exhibit peaks due to the stretching of free conjugated acetyl carbonyl at ~ 1675 cm^{-1}. However the band can shift to lower wave number when the acetyl carbonyl is involved in strong intramolecular hydrogen bonding as has been well established in the case of phenylazo derivatives of acetylacetone.[167,168]

The ir spectrum of **Hpah** in the 1600-1800 cm^{-1} region displayed strong peaks at 1705, 1628 and 1610 cm^{-1} and several medium intensity bands in the range 1590-1605 cm^{-1}. The band at 1705 cm^{-1} can confidently be assigned to the stretching of the cinnamoyl carbonyl as has been done in the case of **Hpad**. Since no other band assignable to free or conjugated acetyl carbonyl (~ 1675

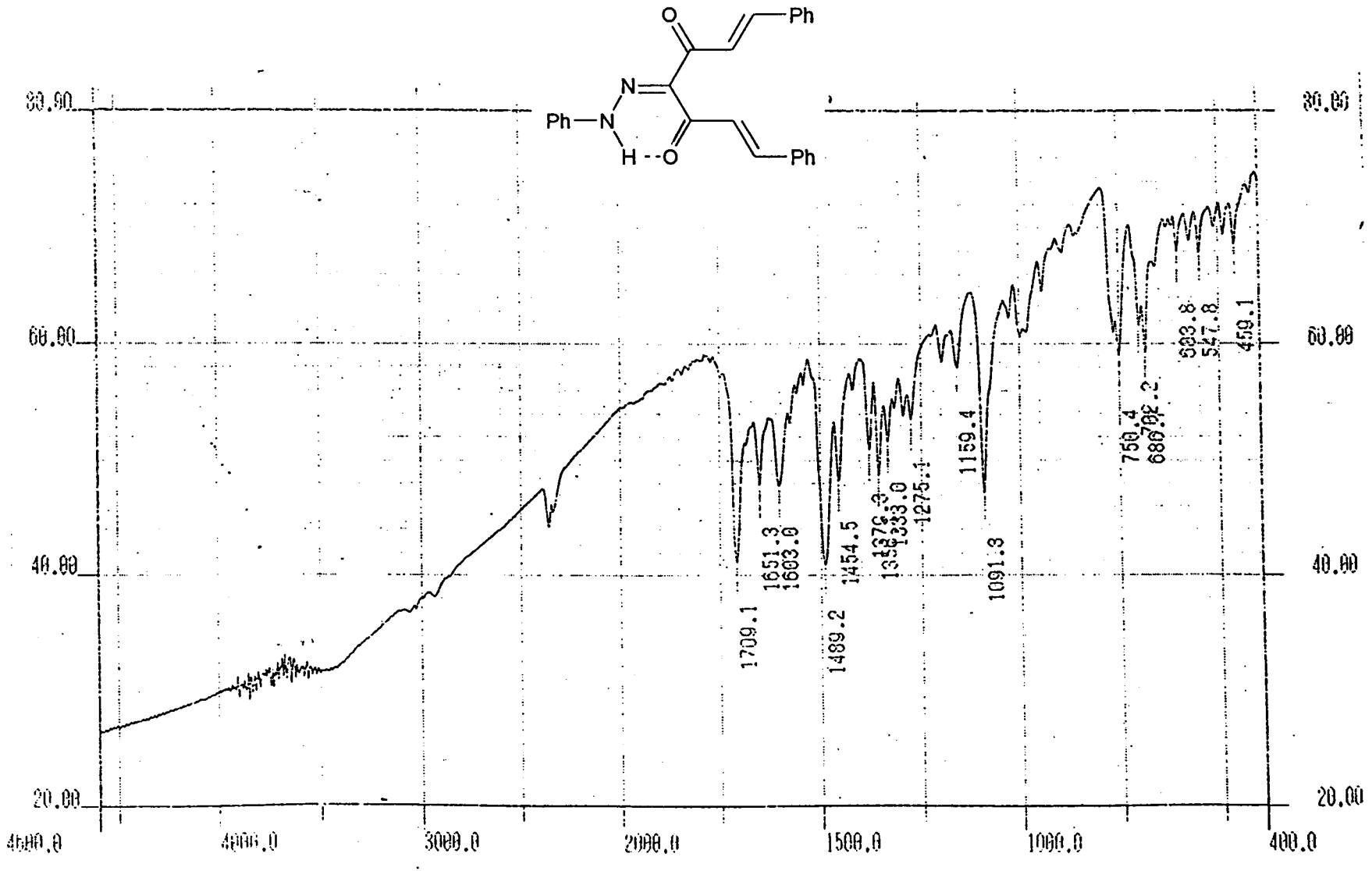
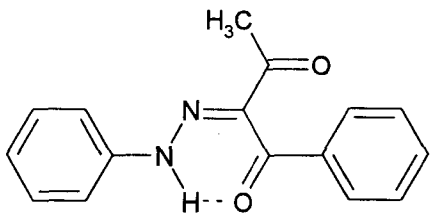


Fig. 1. Ir spectrum of Hpad

cm^{-1}) is observed in the spectrum, the band at 1628 cm^{-1} is due to a conjugated and intramolecularly H-bonded acetyl carbonyl similar to the spectrum of phenylazobenzoylacetone which exist as in structure **15**. The 1610 cm^{-1} band can be assigned to a νC=N vibration. The NH deformation band appeared at 1515 cm^{-1} and νC-N at 1275 cm^{-1}. Thus it appears that the conjugated acetyl carbonyl is involved in hydrogen bonding with the hydrazone NH as in structure **16**. That strong intramolecular hydrogen bonding exist in the compound is clearly indicated from the presence of a broad band in the 2500-3500 cm^{-1} region of the spectrum.



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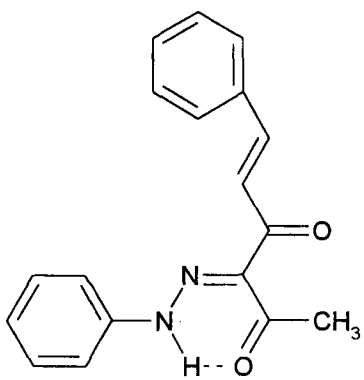
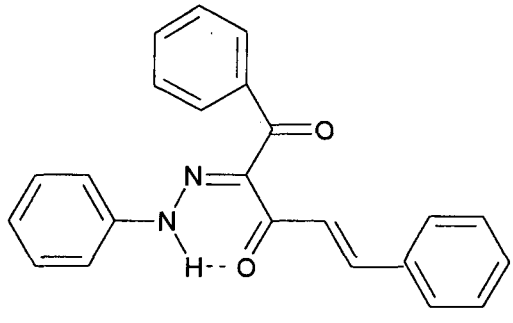


16

The most important feature of the spectrum of **Hpap** is the absence of any peak assignable to free cinnamoyl carbonyl. The spectrum consists of two strong bands at 1652 cm^{-1} and 1668 cm^{-1} and a medium intensity band at 1612 cm^{-1}. The conjugated benzoyl carbonyl of phenylazobenzoylacetone show stretching band[159-163] at ~ 1650 cm^{-1}. Therefore the 1652 cm^{-1} band can be assigned as due to νC=O of benzoyl carbonyl. Since band assignable to free cinnamoyl carbonyl at ~ 1700 cm^{-1} is not observed in the spectrum the band at 1668 cm^{-1} can originate only from strong intramolecularly hydrogen bonded cinnamoyl function as in structure **17**. The band at 1621 cm^{-1} can be assigned to νC=N. The presence of strong N–H...O=C hydrogen bonding is evident from the appearance of a broad band in the 2500-3500 cm^{-1} region.



17

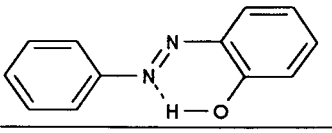
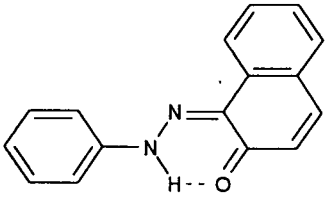
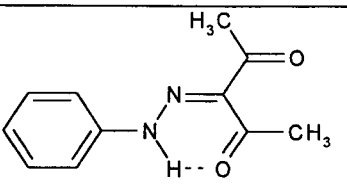
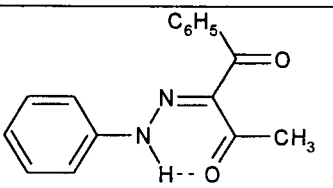
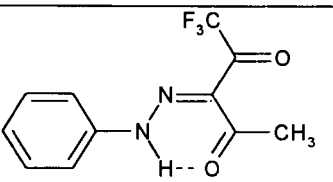
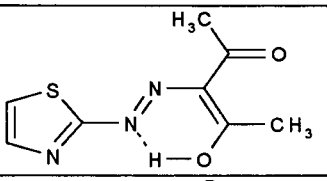
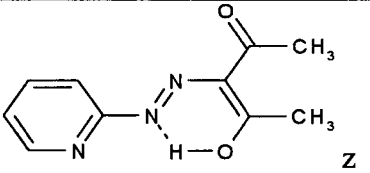
Nmr spectra

Nmr spectra has been very valuable in studies of tautomerism, but when the tautomer in question contains NH and OH protons it is

frequently difficult to assign unambiguously a given acidic proton resonance to particular functional group. The acidic proton signals observed for a number of arylazo derivatives that can exhibit azo-hydrazone tautomerism are listed in table 2.

TABLE 2

Acidic proton signals of azo-hydrazone tautomers

	Compound	δ (ppm)
1		12.6
2		15.6
3		14.74
4		14.70
5		15.10
6		13.20
7		13.12

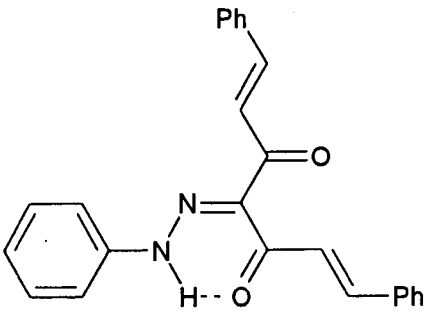
In general the hydrazone NH resonance comes ~ 3-4 ppm lower than the azo-hydrazone resonance.[145-147,175]

The ^1H nmr spectrum of the phenylazo derivatives of the unsaturated 1,3-diketone is charactarised by the presence of a low field one proton signal at ~ 16.5 ppm. Considering the position, the signal can arise only as due to N–H...O=C group rather than O–H...N. The alkenyl group(s) and aryl groups show signals at positions as expected of structures **14, 16, 17**. The integrated intensities of all the signals agree well with the structure **14, 16, 17** of the compound. The ^1H nmr spectral data of **Hpad**, **Hpaph** and **Hpap** are given in table 3. The ^1H nmr spectrum of **Hpad** is given in figure 2.

TABLE 3

Characteristic ^1H nmr spectral data of Hpad, Hpah, Hpap

Compound	Chemical shift δ ppm			
	NH	alkenyl	aryl	alkyl
Hpad	16.52	8.22 (2H) 7.98 (2H)	6.80 - 7.80	--
Hpah	16.46	7.90 (1H) 7.58 (1H)	6.80 - 7.50	2.58 (3H)
Hpap	16.32	7.98 (1H) 7.97 (1H)	6.50 - 7.58	—



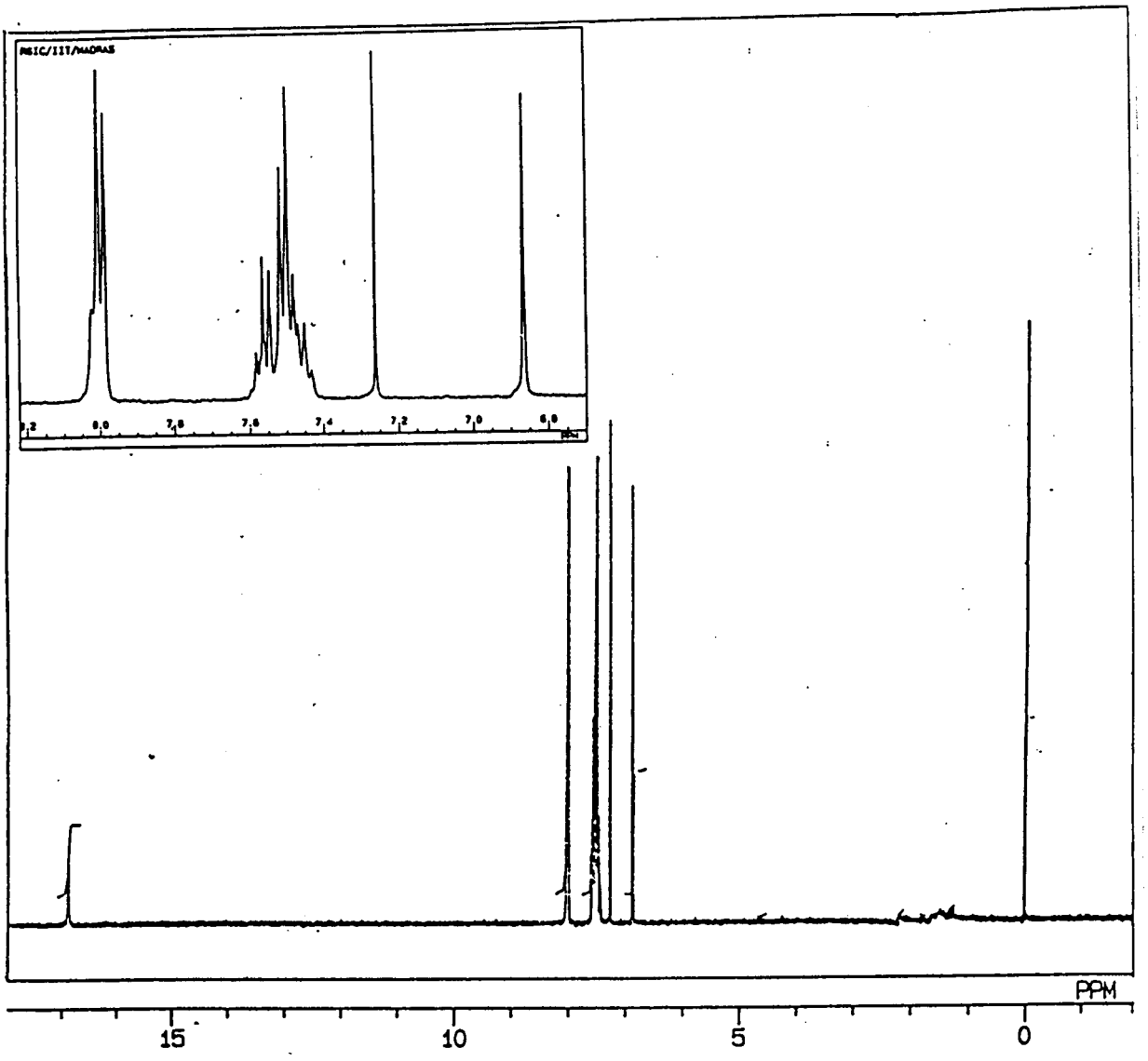


Fig. 2. ^{1}H nmr spectrum of Hpad.

Mass spectra

Arylazo derivatives of the 1,3-diketones exist in solid state and in solution predominantly as hydrazones as evidenced by the ir[167,168] and nmr spectral data.[145-147] Djerassi[176] *et al.* have reported that no tautomerisation occurs in electron bombardment so that mass spectra of the compounds could reflect the true state of the molecules in gaseous states. Mass spectrometry have been used extensively to study the keto-enol and azo-hydrazone tautomerism.[176,178]

The mass spectra of **Hpad** is given in figure 3. The most prominent peak in the spectrum at m/z 381 correspond to the $(P+1)^+$ peak of the compound. Several mass spectral studies[177,179] confirmed that elimination of N_2 from the molecular ion is a characteristic feature of the mass spectra of the azo tautomer of azo compound that can exhibit azo-hydrazone tautomerism. Since no such peak has been observed in this case it is logical to assume that the compound exists in the hydrazone form. The formation of other important peaks can be explained by the elimination of PhNH, Ph, PhC_2H_2, etc. from the molecular ion or subsequent fragments. Thus all the available evidences suggest the hydrazone structure **14, 16, 17** of the compounds.

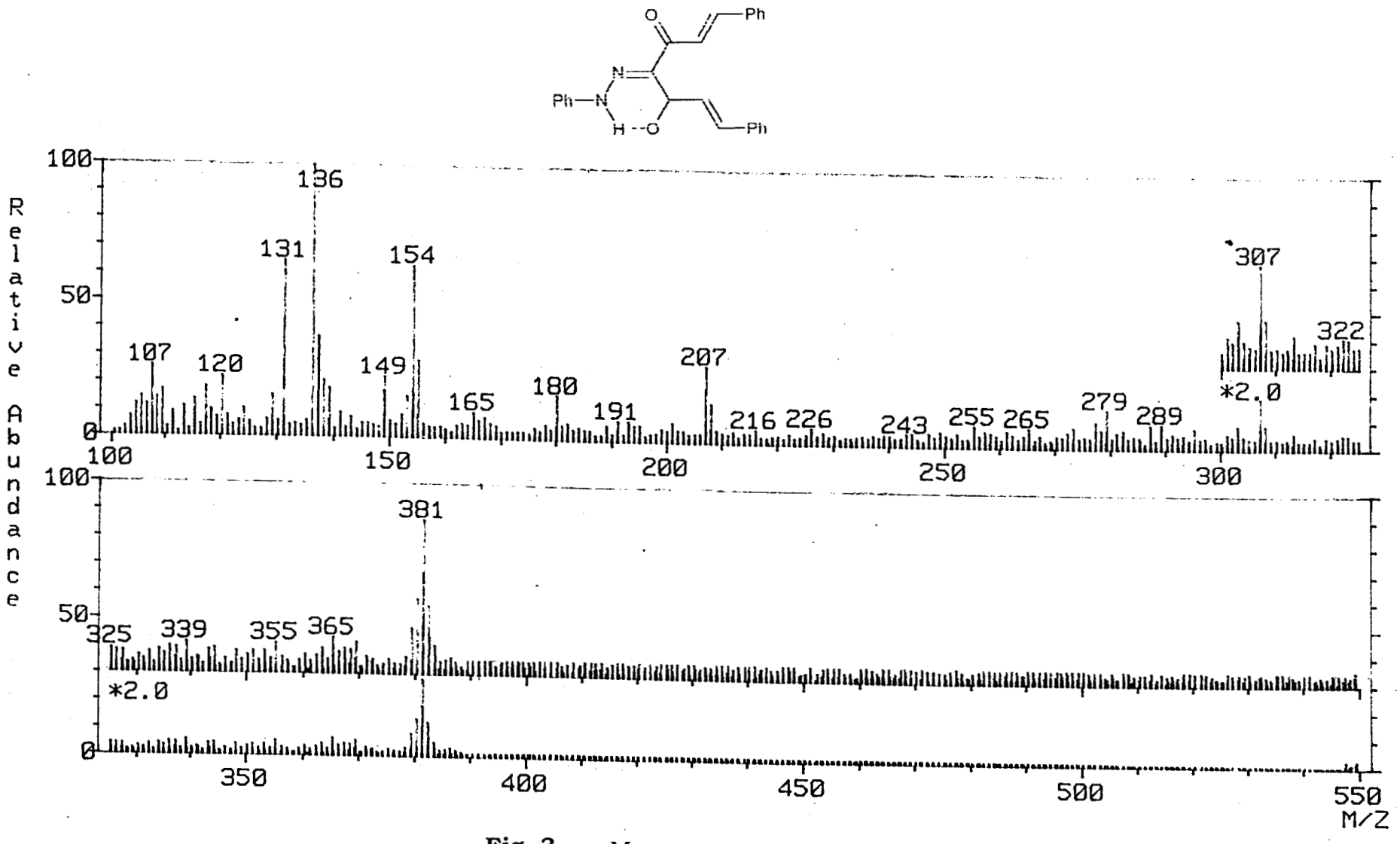


Fig. 3. Mass spectrum of Hpad.

Characterisation of metal complexes

The phenylhydrazones of the unsaturated 1,3-diketones formed stable crystalline complexes with copper(II) and nickel(II). The C, H, N and metal percentages determined are given in table 4. The data suggests $[ML_2]$ stoichiometry of the complexes. All the complexes are non-conducting in dmf solution. The copper(II) complexes showed paramagnetic moment in the range 1.75-1.80 BM. The ir, nmr and mass spectral data of the complexes are discussed below.

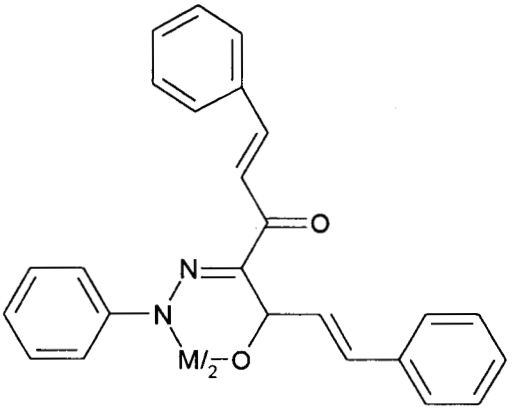
TABLE 4

Analytical and physical data of complexes of Hpad and Hpap

	Complex	Yield %	M.P. °C	Elemental analysis % Found / (Calcd.)			
				C	H	N	M
1	$[Cu(pad)_2]$	70	> 300	73.06 (73.03)	4.32 (4.62)	6.41 (6.81)	7.00 (7.73)
2	$[Cu(pah)_2]$	65	> 300	65.98 (66.92)	4.62 (4.64)	8.44 (8.67)	9.64 (9.84)
3	$[Cu(pap)_2]$	60	> 300	70.96 (71.73)	4.22 (4.41)	7.04 (7.27)	8.00 (8.25)
4	$[Ni(pad)_2]$	65	> 300	73.06 (73.46)	4.32 (4.65)	6.41 (6.85)	7.00 (7.19)
5	$[Ni(pah_2]$	70	> 300	66.98 (67.42)	4.23 (4.68)	8.45 (8.74)	9.00 (9.05)
6	$[Ni(pap)_2]$	75	> 300	72.00 (72.18)	4.21 (4.44)	7.10 (7.32)	7.55 (7.67)

Infrared spectra

In the ir spectra of the complexes of **Hpad**, the band at 1709 cm^{-1} of the ligand due to the cinnamoyl carbonyl remained almost unaffected indicating that this carbonyl is not involved in complexation. However, in the spectra of all the complexes, the band due to the hydrogen bonded cinnamoyl carbonyl at 1651 cm^{-1} disappeared and instead a new strong band appeared at ~ 1550 cm^{-1} assignable to the stretching of metal bonded carbonyl group. The broad free ligand band in the 2500-3500 cm^{-1} cleared up indicating the replacement of the chelated proton by metal ion. Thus it appears that the metal ion is bonded to one of the cinnamoyl oxygen and hydrazo nitrogen with the formation of a six-membered chelate ring as in structure **18**. Two additional band appeared at ~ 420 and ~ 530 cm^{-1} in the spectra of complexes can be due to νM–O and νM–N vibrations.



18

Important ir bands and their probable assignments are given in table 5.

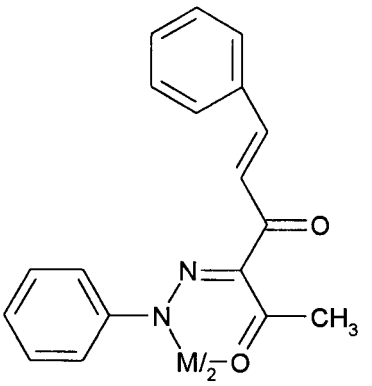
TABLE 5

Characteristic ir spectral data (cm^{-1}) of Hpad, Hpah, Hpap and their metal complexes

Compound	free C=O	chelated C=O	C=N	C=C	C–N	M–N	M–O
Hpad	1709	1651	1603	1598, 1592 1588, 1580	1280	--	--
[Cu(pad)$_2$]	1707	1558	1605	1595, 1590 1585, 1582	1268	528	422
[Ni(pad)$_2$]	1708	1560	1608	1592, 1588 1585, 1580	1266	525	418
Hpah	1705	1628	1610	1600, 1595 1588, 1585	1278	--	--
[Cu(pah)$_2$]	1710	1552	1612	1602, 1598 1593, 1586	1258	518	428
[Ni(pah)$_2$]	1768	1558	1614	1600, 1596 1595, 1588	1282	530	420
Hpap	1656	1668	1612	1600, 1596 1595, 1588	1282	--	--
[Cu(pap)$_2$]	1652	1562	1605	1598, 1592 1588, 1585	1272	526	418
[Ni(pap)$_2$]	1655	1568	1602	1595, 1590 1586, 1580	1268	522	422

In the ir spectra of metal complexes of **Hpah**, the free ligand band at 1628 cm^{-1} due to hydrogen bonded acetyl carbnonyl is absent and instead a new band appeared at ~ 1550 cm^{-1}. This indicates that the metal ion is involved in bonding with the acetyl carbonyl oxygen. The cinnamoyl carbonyl band (1705 cm^{-1}) only marginally shifted in the spectra of complexes suggests its non-

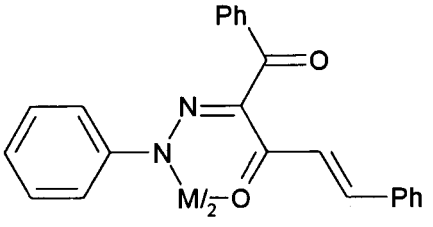
involvement in compelxation. The broad free ligand band in the 2500-35000 cm^{-1} due to the hydrogen bonded structure **16** also disappeared indicating the replacement of the NH proton by metal ions. Several medium intensity bands appeared in the region due to various νC-H vibrations. Further the presence of new medium intensity band at ~ 425 and ~ 550 cm^{-1} assignable to νM–O and νM–N in the spectra of complexes, supported structure **19**. Characteristic ir bands of the complexes are given in table 5.



19

In the ir spectra of the metal complexes of **Hpap** the benzoyl carbonyl band of the free ligand at 1656 cm^{-1} showed only marginal shift. However the band at 1668 cm^{-1} due to the intramolecularly hydrogen bonded cinnamoyl carbonyl disappeared and a new band appeared at ~ 1560 cm^{-1} due to metal bonded cinnamoyl carbonyl. That the NH proton has been replaced by metal ion is evident from the disappearance of the broad free ligand band in the region 2500-3500 cm^{-1} due to N–H...O=C hydrogen bond. Important bands and

their assignments are given in table 5. Thus the spectral data supports structure **20** of the complexes.



20

Nmr spectral data

In the ^1H nmr spectra of the diamagnetic nickel(II) complex, the low field signal due to the intramolecularly H-bonded NH proton disappeared. This supports the replacement of the hydrazone proton by metal ion as in structures **18-20**. Integrated intensities of all other protons agree well with the structure. The spectrum of **[Ni(pad)$_2$]** is given in figure 4.

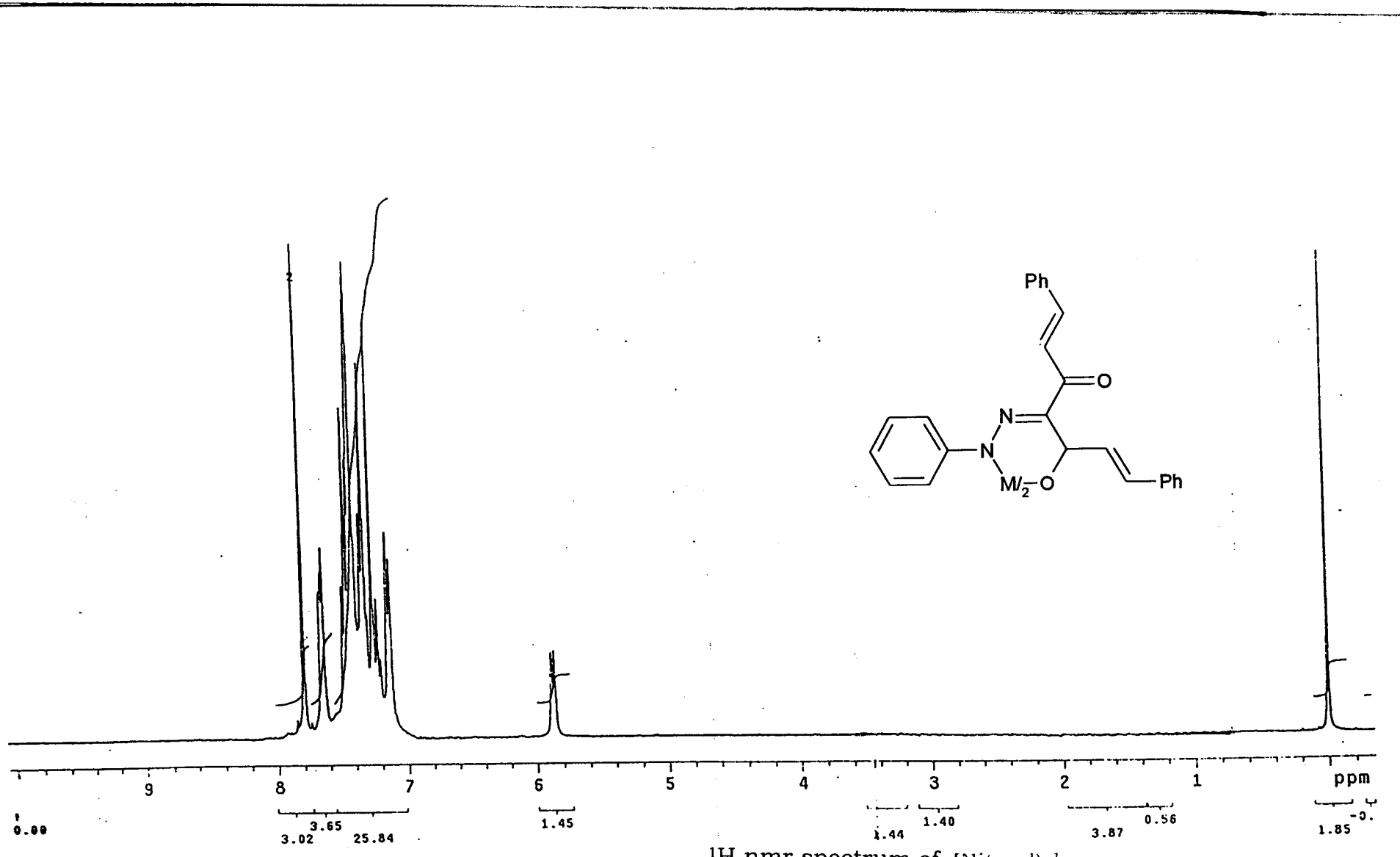


Fig. 4. ^{1}H nmr spectrum of $[Ni(pad)_2]$

B. Synthesis and characterisation of thiaolylazo derivatives of the unsaturated 1,3-diketones and their metal complexes

Experimental

Details on the synthesis and characterisation of these compounds and their metal complexes are discussed below. The thiazolylazo derivatives of unsaturated 1,3-diketones were synthesised by coupling thiazolyl diaozonium salt with the unsaturated 1,3-diketones.

1. Synthesis of thiazolylazo derivative of 1,7-diphenyl-1,6-heptadiene-3,5-dione, thiazolylazodiphenylheptadiene dione

The compound was synthesised by coupling diazotised 2-aminothiazole with **Hdhd** by the following method.

2-Aminothiazole was diazotised as reported.[180] The procedural details are given below:

To a solution of 2-aminothiazole (1 g, 0.01 mol) in aqueous suphuric acid (10 N, 15 mL), kept cold below 0°C was added a cold aqueous solution of sodium nitrite (0.7 g, 2 mL) drop by drop with constant stirring. After destroying the excess nitrous acid in the resulting solution with urea, the solution was added drop by drop with stirring to an ice cold (< 5°C) solution of **Hdhd** (2.76 g, 0.01 mol, 20 mL ethanol). Sodium acetate was added to adjust the pH

around 6. Stirring was continued for about half an hour and the precipitated compound was filtered, washed with water and recrystallised twice from hot methanol to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

Nickel(II) and copper(II) complexes of the compound were synthesised as follows.

A concentrated aqueous solution of metal(II) acetate (0.01 mol) was added to 20 mL of hot methanolic solution of the ligand (0.01 mol). The mixture was refluxed on a hot water bath for ~ 3 h. The volume of the solution was then reduced to half and poured into crushed ice with constant stirring. The precipitated complex was filtered, washed with water and dried in vacuum.

2. Synthesis of thiazolylazo derivative of 6-phenyl-5-hexene-2,4-dione, thiazolylazophenylhexenedione, Htah

The compound was synthesised by the diazocoupling of 2-aminothiazole with **Hphd** by the following method.

2-Aminothiazole was diazotised by the reported[180] method. The excess nitrous acid present in the diazonium salt solution was removed using urea. The diazonium salt solution (0.01 mol) kept below 0°C was added drop by drop to an ice cold (< 5°C) solution of

Hphd (1.88 g, 0.01 mol, 20 mL ethanol). Sodium acetate was added to maintain the pH around 6-7. The mixture was stirred for about 15 m and the precipitated compound was filtered, washed several times with small quantities of water and recrystallised twice from hot methanol to get chromatographically pure (tlc) compound.

Synthesis of metal complexes

Nickel(II) and copper(II) complexes of the compound were synthesised as follows.

A concentrated aqueous solution of the metal(II) acetate (0.01 mol) was added to a refluxing solution of the ligand (0.01 mol, 20 mL ethanol) on a boiling water bath. Refluxing was continued for ~ 4 h, precipitated complex was filtered, washed with water and dried in vacuum.

3. Synthesis of thiazolylazo derivative of 1,5-diphenyl-4-pentene-1,3-dione, thiazolylazodiphenylpentenedione, Htap

The compound was synthesised by the diazo coupling reaction of 2-Aminothiazole with **Hdpd** by the following method.

2-Aminothiazol was diazotised as reported.[180] After removing the excess nitrous acid by urea, the cold diazonium salt solution (0.01 mol) was added drop by drop to **Hdpd** (0.01 mol, 2.5 g 20 mL ethanol) kept below 5°C with constant stirring. Sodium acetate was

added to maintain the pH ~ 7. The precipitated compound was filtered, washed with water and recrystallised twice from hot methanol to get chromatographically pure (tlc) compound.

Synthesis of metal complexes

Nickel(II) and copper(II) complexes of the compound were synthesised as follows:

A concentrated aqueous solution of metal(II) acetate (0.01 mol) was added to a hot solution of the ligand (0.01 mol) in 20 mL of ethanol. The mixture was refluxed on a boiling water bath for ~ 3 h. The solution was concentrated to half its original volume and the precipitated complex was filtered, washed with water and dried in vacuum.

Results and discussion

Characterisation of Htad, Htah and Htap

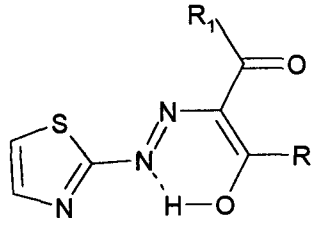
The observed elemental analytical data of the thiazolylazo derivative of **Hdhd**, **Hphd**, **Hdpd** given in table 6 suggest the diazocoupling reaction has occurred in 1:1 ratio. The systematic name along with suitable abbreviations of the compounds are also provided in table 6.

TABLE 6

Analytical and physical data of Htad, Htah, Htap

	Compound / Systematic name	Yield %	M.P. °C	Elemental analysis % Found / (Calcd.)		
				C	H	N
1	1,7-diphenylhepta-1,6-diene-4-thiazolylazo-3,5-dione, (thiazolylazodiphenyl-heptadienedione), **Htad**	70	180	66.20 (68.21)	4.00 (4.39)	10.14 (10.85)
2	6-phenyl-5-hexene-3-thiazolylazo-2,4-dione (thiazolylazophenyl-hexenedione), **Htah**	75	140	59.64 (60.20)	4.00 (4.34)	13.96 (14.04)
3	1,5-diphenyl-4-pentene-2-thiazolylazo-1,3-dione (thiazolylazodiphenyl-pentenedione), **Htap**	70	171	66.14 (66.48)	4.00 (4.15)	11.34 (11.63)

The ir, nmr and mass spectral data of the compounds are in agreement with the structure **21**.

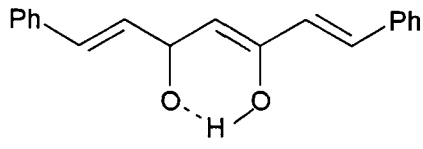


21

Infrared spectra

The ir spectrum of **Htad** in the region 1600-1800 cm^{-1} shows two strong peaks at 1702 and 1620 cm^{-1} and a medium intensity

band at 1605 cm^{-1}. The band at 1702 cm^{-1} can safely be assigned to the stretching of free cinnamoyl carbonyl as has been done in the case of the phenylazoderivative, (**Hpad**). The H-bonded cinnamoyl carbonyl of **Hpad** was observed at 1651 cm^{-1}. No such band is present in the spectrum of **Htad**. It has been well established[168,171] that 1,7-diphenyl-1,6-heptadiene-3,5-dione (the unsaturated β-diketone), **Hdhd** exist entirely in intramolecularly hydrogen bonded enol form **22**.



22

The characteristic carbonyl stretching frequency is at 1620 cm^{-1}. Therefore, the band at 1622 cm^{-1} of **Htad** can be accounted as due to the stretching of the enolised carbonyl. This together with the absence of any band assignable to H-bonded cinnamoyl carbonyl suggest that **Htad** exists in the azo-enol form rather than in the keto-hydrazone form as in the case of the phenylazo derivative. The hydrazone C=N stretching of these types of compound usually appear at above 1610 cm^{-1}, also suggests the enol form. The band at 1605 cm^{-1} is due to the thiazole νC=N.

The ir spectrum of **Htah** also displayed a strong band at 1705 cm^{-1} due to a free cinnamoyl carbonyl and another strong band at 1624 cm^{-1} presumably due to the enolised acetyl carbonyl. The thiazole ring νC=N is observed at 1608 cm^{-1}. In the spectrum of **Htap** two bands appeared at 1652 and 1628 cm^{-1} can be assigned respectively to the free benzoyl carbonyl and enolised cinnamoyl carbonyl of structure **21**.

In the spectra of all the three compounds two medium intensity bands are observed at ~ 1280 and 1450 cm^{-1}. Based on earlier reports these bands can be assigned to C–O–H in plane bending and νN=N respectively.[167-181] In keeping with the presence of strong O–H...N, hydrogen bonding, spectra of the compounds showed an extremely broad band ranging from 2350 to 3500 cm^{-1}.

Nmr spectra

The ^1H nmr spectrum of **Htad** shows a one proton signal at 13.52 ppm. This value is considerably lower than that reported for hydrazone NH...O=C proton of arylazo derivatives of 1,3-diketone that exist in hydrazone form. Since azo-enol protons show signal in the range 10-14 ppm, the signal at 13.52 ppm of **Htad** can be assigned to the intramolecularly hydrogen bonded enol proton. The alkenyl protons are observed in the range 7.9-8.2 ppm and aryl protons in 6.5-7.5 ppm.

Mass spectra

The mass spectrum of **Htah** given in figure 5 show a relatively intense peak at m/z 298 in agreement with the formulation of the compound. Elimination of N_2 from molecular ion is characteristic of the mass spectra of azo compound. The peak at m/z 270 present in the spectrum may be due to the N_2 elimination from the molecular ion thereby supporting the azo structure of the compound. The most intense peak at m/z 131 is due to the cinnamoyl fragment. Similarly fragments due to the elimination of CH_3CO, thiazole group, etc. are typical of the spectrum. Thus all available evidence support the existence of the compound in the azo-enol form rather than the keto-hydrazone form.

Characterisation of metal complexes

The thiazolylazo-1,3-diketones formed stable complexes with copper(II) and nickel(II). The observed analytical data suggest $[ML_2]$ stoichiometry of the complexes (Table 7). The copper(II) complex show magnetic moment in the range 1.75-1.80 BM and nickel(II) complex around 2.85 BM.

In the ir spectra of all the complexes (Table 8) the broad free ligand band in the region 2350-3500 cm^{-1} disappeared indicating that the replacement of the enol proton by metal ion. Several medium intensity bands are present in the region of the spectra due

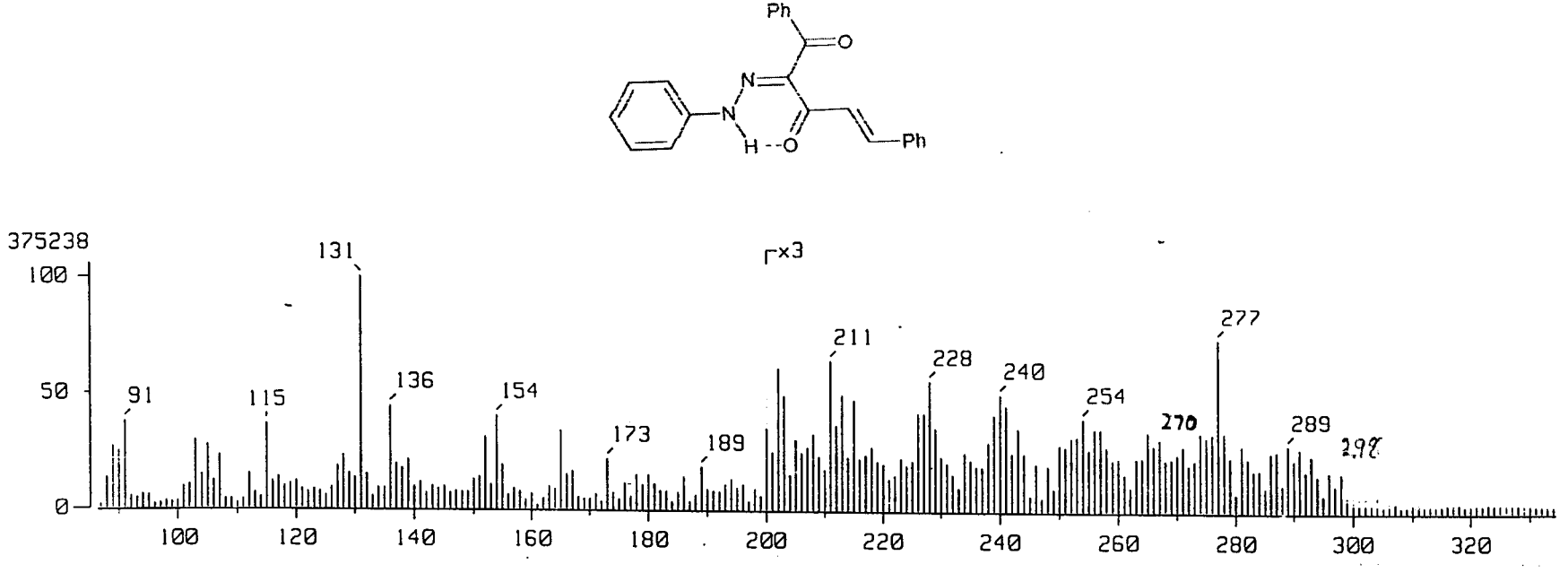


Fig. 5. Mass spectrum of Htah.

to various νC-H vibration. In the spectra of the complexes of **Htad**, the free cinnamoyl band of the ligand is only marginally shifted indicating that this carbonyl is not involved in coordination.

TABLE 7

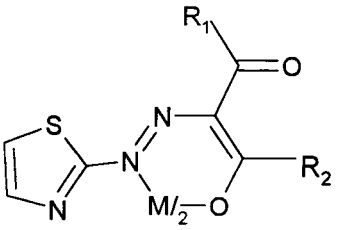
Analytical and physical data of the complexes of Htad, Htah, Htap

	Complex	Yield %	M.P. °C	Elemental analysis % Found / (Calcd.)			
				C	H	N	M
1	**[Cu(tad)$_2$]**	60	> 300	63.00 (63.19)	3.78 (3.82)	9.65 (10.05)	7.00 (7.60)
2	**[Cu(tah)$_2$]**	65	> 300	54.00 (54.48)	3.30 (3.63)	12.55 (12.73)	9.54 (9.63)
3	**[Cu(tap)$_2$]**	70	> 300	60.23 (61.26)	3.44 (3.57)	10.64 (10.72)	7.99 (8.10)
4	**[Ni(tad)$_2$]**	65	> 300	63.14 (63.56)	3.44 (3.85)	10.00 (10.11)	6.99 (7.06)
5	**[Ni(tap)$_2$]**	65	> 300	54.06 (54.98)	3.33 (3.66)	12.23 (12.83)	8.45 (8.96)
6	**[Ni(lap)$_2$]**	70	> 300	61.00 (61.64)	3.46 (3.59)	10.69 (10.72)	7.49 (7.53)

However the band at 1622 cm^{-1} disappeared and instead a new band appeared at ~ 1540 cm^{-1} in the spectra of complexes. This clearly support the involvement of the hydrogen bonded cinnamoyl carbonyl in bonding with the metal ion.

The free cinnamoyl carbonyl band of **Htah** remained unaffected in the spectra of its complexes whereas the acetyl

carbonyl band vanished and a new band appeared at ~ 1550 cm^{-1} due to metal bonded carbonyl. Similarly the spectra of complexes of **Htap** the benzoyl carbonyl band suffered only slight shift while the cinnamoyl carbonyl disappeared and a new band observed at ~ 1560 cm^{-1} assignable to metal bonded carbonyl function.



23

In the spectra of all the complexes, the band at ~ 1450 cm^{-1} due to νN=N of the free ligand shifted appreciably to low wave number (~ 20-30 cm^{-1}) indicating that the azo group is also involved in bonding with the metal. Similarly νC=N of the thiazole ring of the free ligand in the 1600-1610 cm^{-1} also not observed in the spectra of complexes. This may probably due to the participation of the ring nitrogen in bonding with metal. Another characteristic feature of the spectra of all the complexes is absence of the free ligand signal at 1280 cm^{-1} due to C–O–H bending. This undoubtedly support the replacement of the enol proton by metal ion. Further, in spectra of all the complexes two additional band are present at ~ 550 cm^{-1} and one medium intensity band at ~ 420 cm^{-1}. These band can be

assigned to νM-N and νM-O respectively. Thus the ir spectra strongly support structure **23** of the complexes. Characteristic ir bands of the compounds are given in table 8.

TABLE 8

Characteristic ir spectral data (cm^{-1}) of Htad, Htah, Htap and their complexes

Compound	free CO	Chelated CO	C=N	N=N	M–N	M–O
Htad	1702	1622	1605	1455	--	--
$Cu(tad)_2$	1698	1542	1582	1430	518 510	422
$Ni(tad)_2$	1700	1545	1580	1428	522 515	418
Htah	1705	1624	1608	1445	--	--
$Cu(tah)_2$	1698	1555	1578	1420	520 510	428
$Ni(tah)_2$	1702	1552	1582	1418	--	--
Htap	1652	1628	1605	1450	--	425
$Cu(tap)_2$	1650	1562	1580	1425	528 522	--
$Ni(tap)_2$	1648	1560	1582	1422	524 515	430

SECTION 2

SYNTHESIS AND CHARACTERISATION OF METAL COMPLEXES OF SCHIFF'S BASES DERIVED FROM THE DICINNAMOYL METHANE WITH ETHYLENE DIAMINE AND *ORTHO*-AMINOPHENOL

Dicinnamoylmethane on schiff base condensation with ethylenediamine and 2-aminophenol yielded well defined crystalline compounds. These compounds formed stable complexes with nickel(II) and copper(II). The synthetic details and spectral characterisation of these compounds are discussed below.

A. Synthesis and characterisation of bis(dicinnamoylmethane) ethylenediimine and its metal complexes

Experimental

Synthesis of bis(dicinnamoylmethane) ethylenediimine, H_2bde

Dicinnamoylmethane (2.76 g, 0.01 mol) dissolved in 30 ml of methanol and was added to ethylenediamine (0.6 g, 0.01 mol) with stirring. The mixed solution was boiled on a water bath for ~ 3 h and kept overnight. The orange crystalline precipitate formed was filtered and recrystallised from hot methanol to get chromatographically (tlc) pure compound.

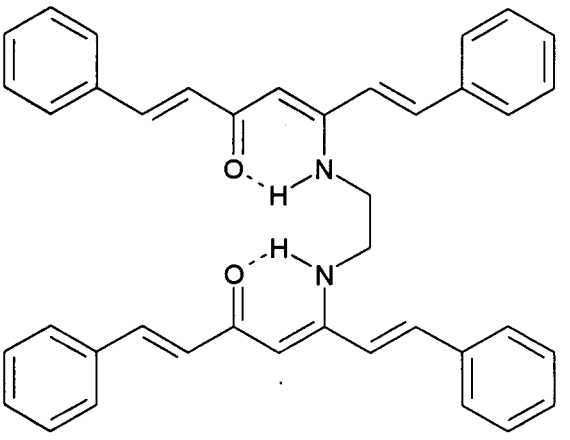
Synthesis of metal complexes

A solution of the metal(II) acetate (0.001 mol) in minimum amount of water was added to the ligand (0.001 mol) dissolved in 20 mL methanol. The mixture was boiled on a waterbath for ~ 4 h and the precipitate formed was filtered, washed thrice with small quantities of water, then with ethanol (10 ml), and dried in vacuum.

Results and discussion

Characterisation of bis(dicinnamoylmethane) ethylenediimine

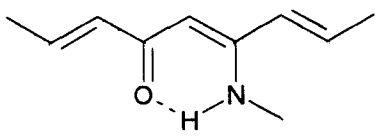
Analytical and physical data of the compound is given in table 9. The data suggest that two molecules of the diketone reacted with one molecule of ethylenediamine. The observed ir, nmr and mass spectral data of the compound are in conformity with structure **24**.



24

The ir spectrum of the compound is characterised by the presence of strong slightly broadened band at 1666 cm^{-1}. The carbonyl band of dicinnamoylmethane is usually observed at 1620 cm^{-1}. The very low value of the carbonyl stretching is due to the strong intramoelcular O...H...O hydrogen bond of the compound. In this compound only one of the carbonyl group is involved in the schiff base formation. Therefore the possibility of such a strong O...H...O hydrogen bonding is prevented and thereby restoring more double bond character to the remaining carbonyl. Hence the cabronyl group not involved in imine formation is expected to show its νC=O band at much higher frequency. Thus the band at 1666 cm^{-1} is not unexpected and can confidently be assigned to νC=O of the cinnamoyl carbonyl of structure **24**.

Cinnamoyl carbonyl usually shows stretching vibration at ~ 1700 cm^{-1}. However extended conjugation and involvement in hydrogen bonding decreases the value. Therefore the νC=O band of the compound at 1666 cm^{-1}, a low value compared to conjugated cinnamoyl carbonyl suggest its involvement in strong intramolecular N–H...O hydrogen bonding as in structure **24**. The most important feature of the spectrum of the compound in the 1600-1650 cm^{-1} region is the absence of any signal assignable to νC=N. This together with the presence of a cabronyl band suggest that the compound exists in the keto-imine form **25** rather than the enol-imine form **26**.



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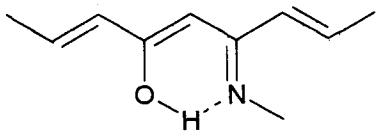


26

This observation leads to the conclusion that N–H...O=C hydrogen bonding is more stable than O–H...N=C hydrogen bonding as has been confirmed in several related compounds.[182]

The strong intramolecular hydrogen bonding present in the compound is clearly indicated from the appearance of a broad band in the range 2700-3600 cm^{-1} with several peaks at 2936, 3076,3308 cm^{-1} assignable to olefinic and aromatic νC-H vibrations (figure 6).

The ^1H nmr spectrum of the compound displayed a two proton singlet at δ 13.60 ppm assignable to the hydrogen bonded imine protons. The CH_2 proton, are observed at δ 3.34 ppm, the olefinic protons at δ 7.98 (2H), 8.01 (2H), the methine proton at 6.86 (2H) and the aryl protons in the range δ 6.8-7.7 ppm in agreement with structure **24** of the compound.

The mass spectrum of the compound showed a relatively intense molecular ion peak at m/z 576. Other prominent peaks are due to the elimination of CO, $NH_2CH_2CH_2NH_2$, tropylium ion, CH≡CH, etc., from the parent ion and subsequent fragments.

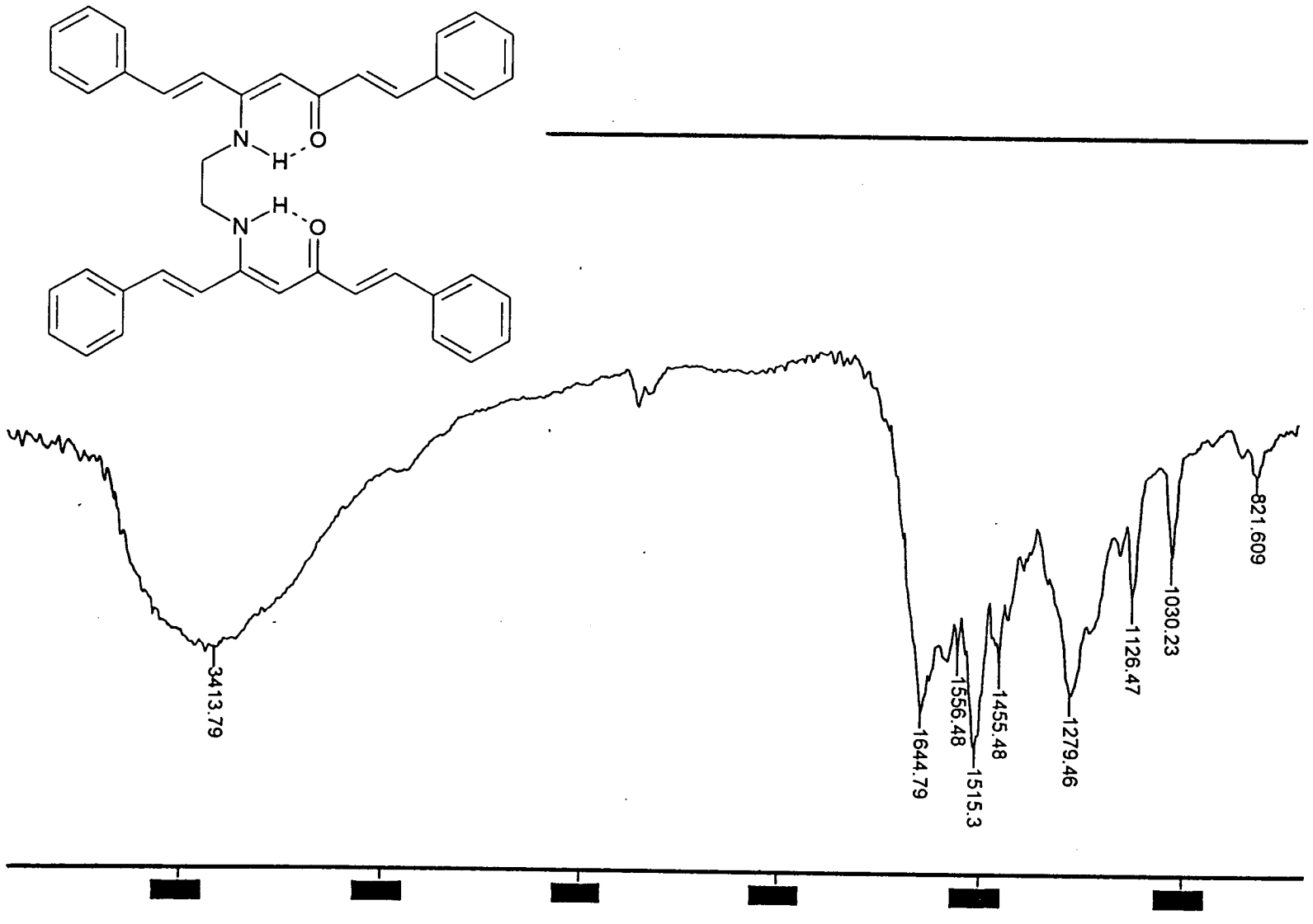


Fig. 6. Ir spectrum of H_2bde

Characterisation of metal complexes

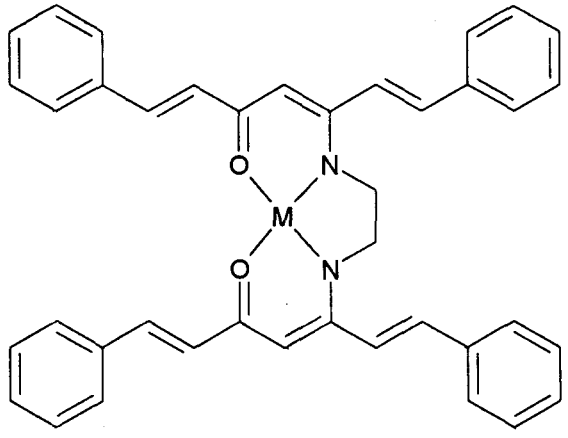
The schiff base formed well defined crystalline complexes with nickel(II) and copper(II) (table 9). This complexes are non-ionic and do not contain the anion of the metal salt used for their preparation.

TABLE 9

Analytical and physical data of H_2bde and it complexes

Compound	M.P. °C	Yield %	Elemental analysis % Found / (calcd.)			
			C	H	N	M
H_2bde	120	70	81.25 (83.33)	6.00 (6.25)	4.14 (4.86)	--
Ni(bde)	> 300	75	74.24 (75.05)	5.12 (5.62)	4.00 (4.37)	9.24 (9.93)
Cu(bde)	> 300	75	74.12 (75.62)	5.10 (5.67)	4.70 (4.41)	9.48 (9.24)

The nickel(II) complex is diamagnetic and the copper(II) complex shows a paramagnetic moment of 1.76 B.M. The elemental analytical data of the complexes suggest their [ML] stoichiometry. The observed ir, nmr and mass spectral data of the complexes are in conformity with structure **27**. The spectral data are discussed below.



27

In the ir spectra of the complexes the band at 1666 cm^{-1} of the free ligand due to hydrogen bonded νC=O disappeared. Instead a new band appeared at ~ 1644 cm^{-1} and no other prominent band present in the 1600-1800 cm^{-1} region. However the spectra of the complexes show a broad band starting from ~ 1550 cm^{-1} and extending up to 1610 cm^{-1} presumably due to the olefinic and aromatic νC=C vibrations. The spectrum of the copper complex is reproduced in figure (fig. 7). For comparison the ligand spectrum is also provided (fig. 6). Further the spectra of the complexes display two new medium intensity bands at ~ 420 and 540 cm^{-1} assignable to νM-O and νM–N of the complexes.

The spectra of the complexes in the 2500-3500 cm^{-1} region reveal the replacement of the hydrogen bonded imine proton by metal ion. Spectra in this region contain several weak and medium

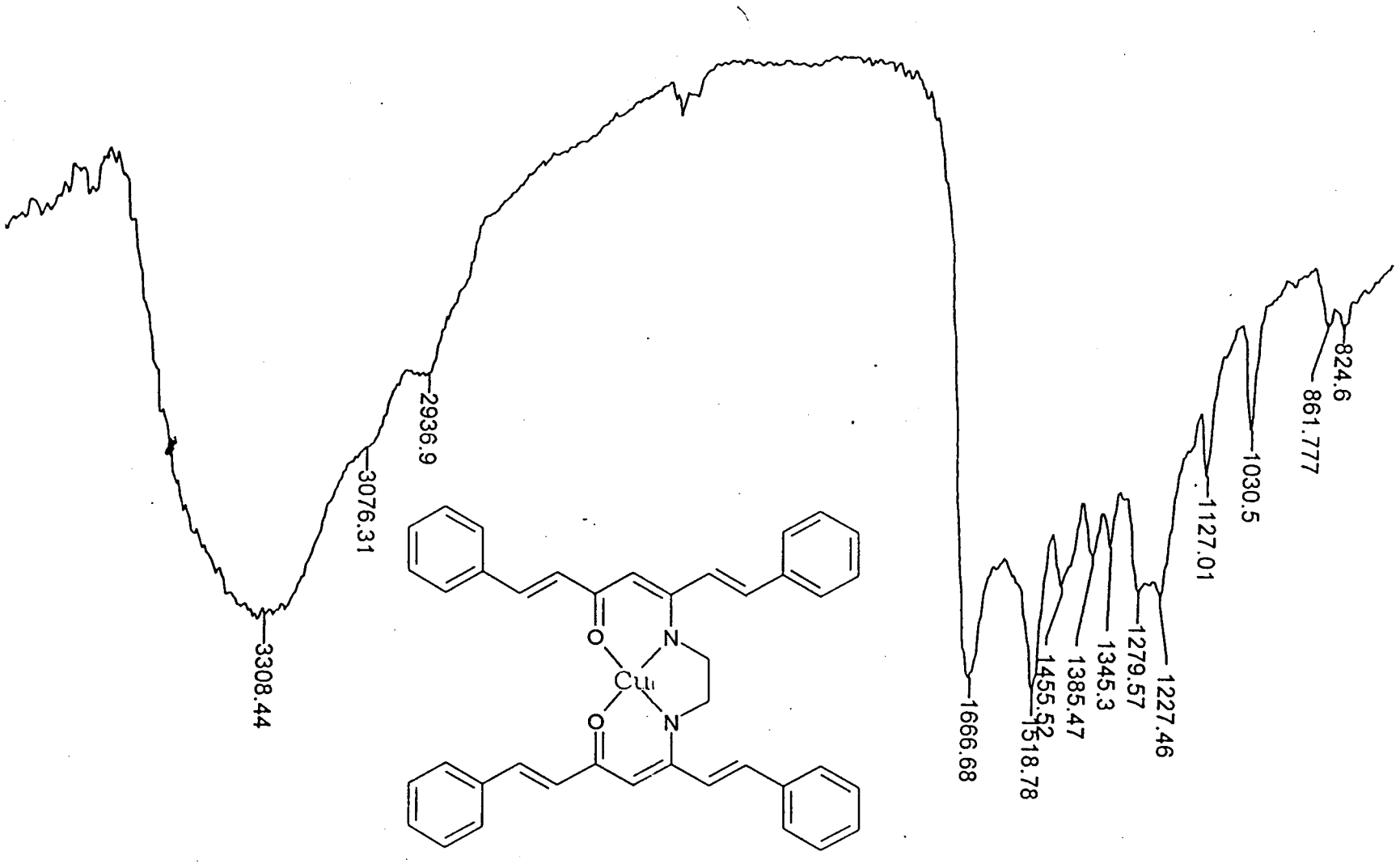


Fig. 7. Ir spectrum of [Cu(bde)$_2$]

intensity band due to various C–H stretching vibrations. Thus the ir spectra fully support the structure proposed of the complexes.

That the hydrogen bonded imine protons of the schiff base replaced by metal ion is clearly indicated in ^1H nmr spectrum of the diamagnetic nickel(II) complex. Thus the NH proton signal of the free ligand disappeared in the spectrum of the complex. The olefinic proton signals are slightly shifted to low values and all other signals show only marginal shift. The integrated intensities of the $(CH_2)_2$ and olefinic protons agree well with the formulation of the complexes.

B. Synthesis and characterisation of dicinnamoylmethane *ortho*-aminophenol and its metal complexes

Experimental

Synthesis of dicinnamoylmethane orthoaminophenol, H_2dca

Dicinnamoylmethane (2.76 g, 0.01 mol) was dissolved in 30 mL of methanol. To this added *ortho*-aminophenol (1.09 g, 0.01 mol) dissolved in ethanol drop by drop with constant stirring. Boiled the mixture on a water bath for ~ 3 h and concentrated to half its original volume. The crystalline precipitate formed was filtered and recrystallised from hot methanol to get chromatographically (tlc) pure compound.

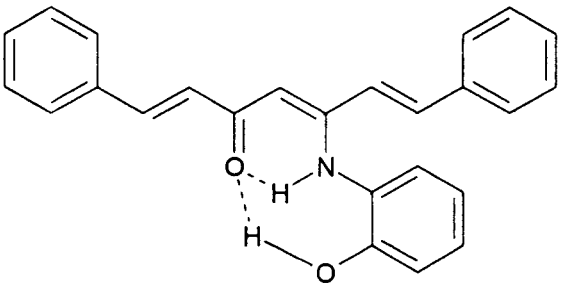
Synthesis of metal complexes

Solution of the metal(II) acetate (0.001 mol) in minimum amount of water was added to the ligand (0.001 mol in 20 mL ethanol). Refluxed the mixture for ~ 4 h on a boiling water bath and the volume reduced to half and the precipitated complex was filtered, washed with water, then with methanol and dried in vacuum.

Results and discussion

Characterisation of dicinnamoylmethane aminophenol

The elemental analytical data (table 10) of the condensation product suggest the formation of a 1:1 compound. This is also supported by the mass spectrum of the compound from the presence of a peak at m/z 368 (fig. 8). This together with the ir and nmr spectral data supports the structure **28** of the compound.



28

Thus the ir spectrum of the compound shows a strong band at 1646 cm^{-1} due to the highly conjugated and strongly hydrogen bonded cinnamoyl carbonyl stretching. The spectrum of the compound in the region 600-1800 cm^{-1} is reproduced in fig. 9 clearly indicate the absence of any band assignable to νC=N vibrations. The spectrum in the 2500-3500 cm^{-1} shows a broad band due to the intramolecular hydrogen bonding possible in the compound.

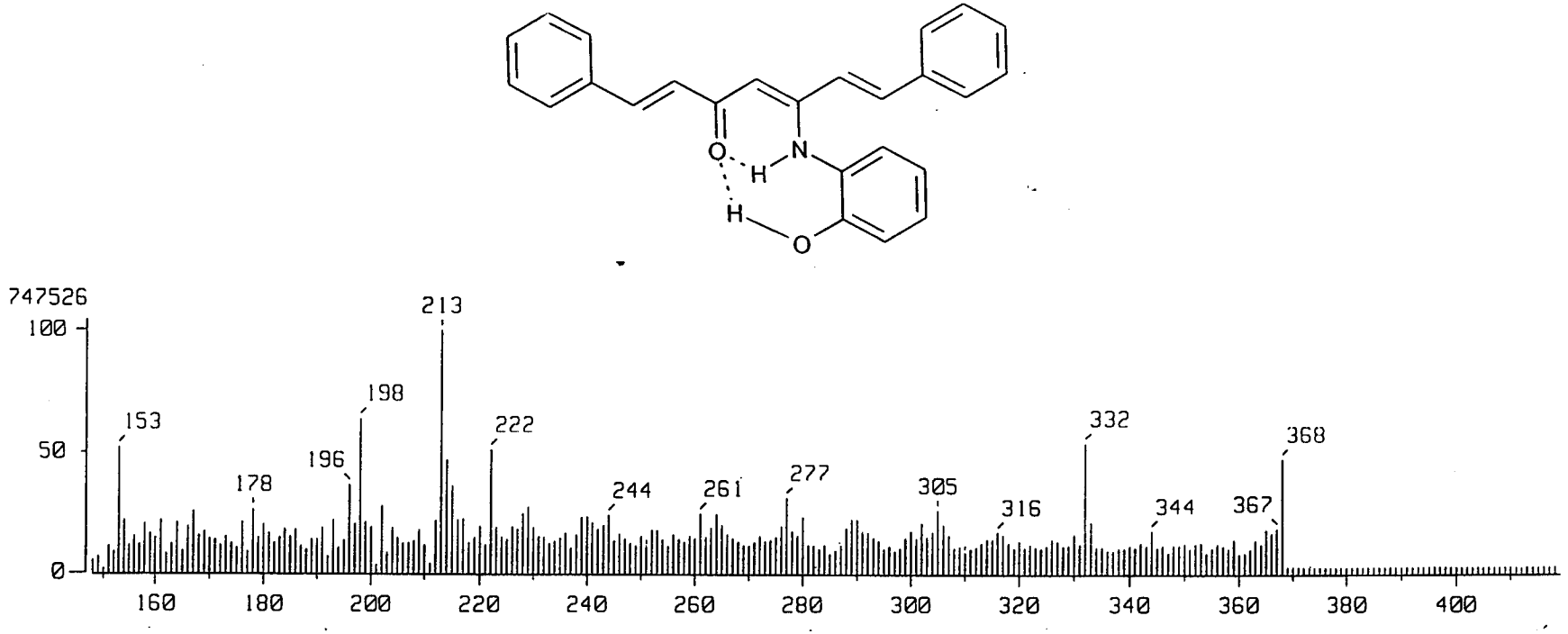


Fig. 8. Mass spectrum of H_2dca

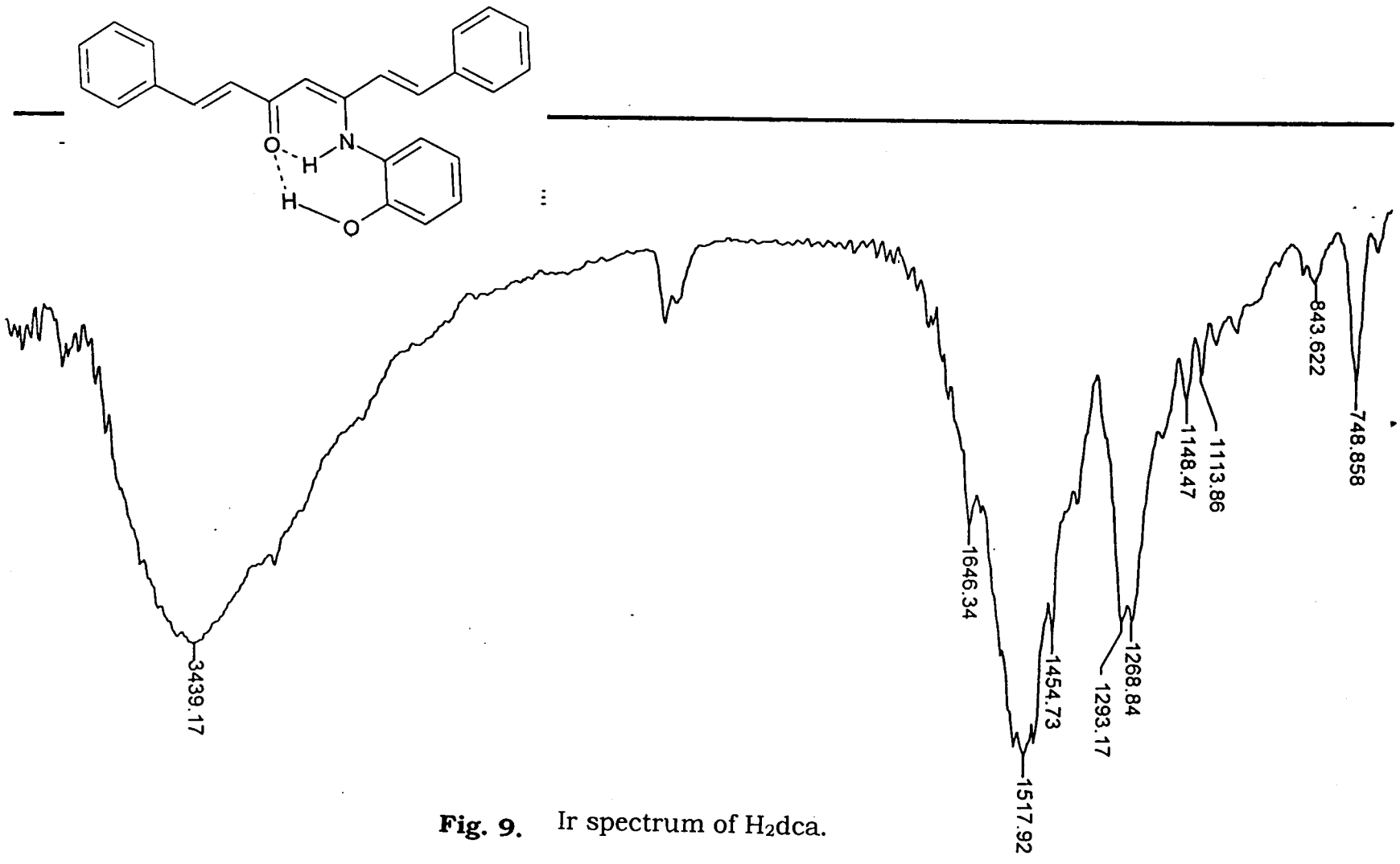


Fig. 9. Ir spectrum of H_2dca.

TABLE 10

Analytical and physical data of Hdca and its complexes

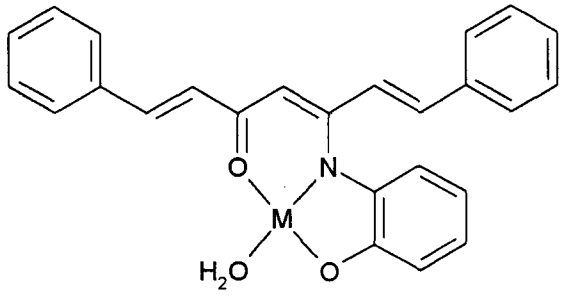
Compound	M.P. °C	Yield %	Elemental analysis % Found / (calcd.)			
			C	H	N	M
H_2dca	135	60	79.21 (81.74)	4.14 (5.72)	2.90 (3.81)	--
[Ni(dca)(H_2O)]	> 300	75	65.46 (67.92)	3.97 (4.75)	2.98 (3.16)	13.00 (13.28)
[Cu(dca)(H_2O)]	> 300	70	65.10 (67.18)	3.99 (4.70)	2.85 (3.13)	13.94 (14.22)

The ^{1}H nmr spectrum show two low field one proton signals at δ 10.8 ppm and δ 13.5 ppm respectively due to the phenolic and imine hydrogen. The olefinic protons are observed at 7.92 and 8.02 ppm and the aryl protons in the range 6.5-7.5 ppm.

Characterisation of metal complexes

Elemental analytical data of the copper(II) and nickel(II) complexes are given in table 10. The values agree with the [ML(OH_2)] stoichiometry of the complexes. The nickel(II) complex is diamagnetic and the copper(II) complex shows a paramagnetic moment of 1.75 B.M. The complexes are neutral as evident from their non-conducting nature in their dmf solutions. The ir, and nmr spectra of the complexes are in conformity with the structure that would result

when the phenolic and imine protons are replaced by metal ion as in structure **29**.



29

In agreement with structure **29** in the ir spectra of the complexes, the band due to νC=O of the ligand shifted appreciably to low values and appeared at ~ 1603 cm^{-1} assignable to metal bonded carbonyl function. Several bands present in the 1550-1600 cm^{-1} region of the spectra (fig. 10) are due to olefinic and aromatic νC=C. Instead of the broad band in the ligand spectrum, the spectra of the complexes in the region 2300-3750 cm^{-1} region show a number of bands arising from νC-H, and vibrations due to coordinated H_2O as expected of the complexes. The low frequency region of the spectra revealed the presence of two new medium intensity bands at ~ 425 and 415, 530 cm^{-1} due to νM–O and νM–N vibrations.

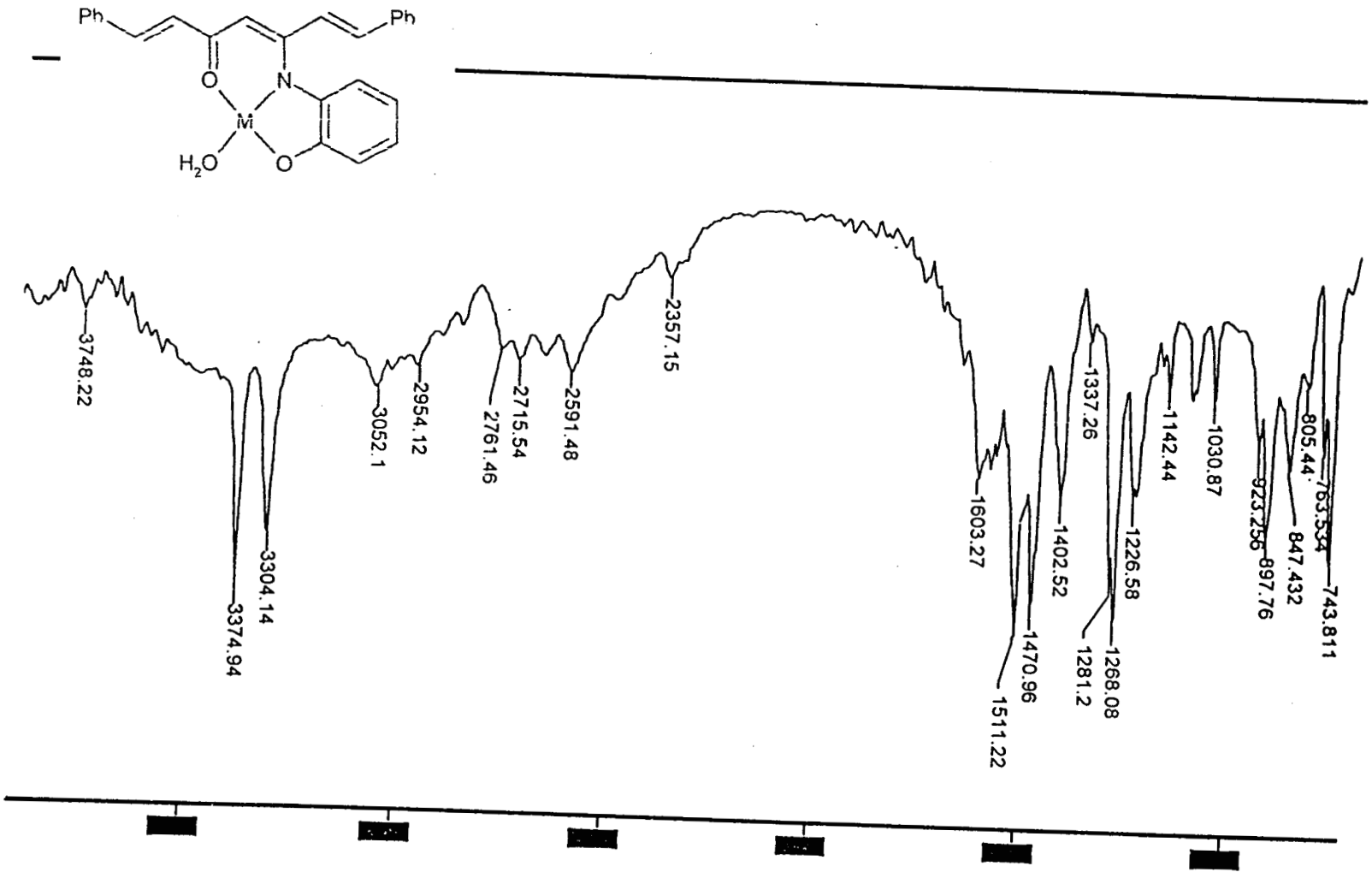


Fig. 10. Ir spectrum of $[Cu(dca)H_2O]$

In the ^{1}H nmr spectrum of the nickel(II) complex the low field signals due to the NH and OH protons disappeared. This clearly indicate the replacement of these protons by metal ion. Further the position and intensities of all other signals totally agree with the structure **29** of the complex.

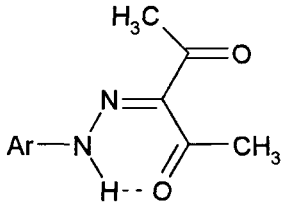
CHAPTER 3

METAL COMPLEXES OF SCHIFF BASE LIGANDS DERIVED FROM 3-ARYLAZO-2,4-PENTANEDIONE WITH DIAMINES

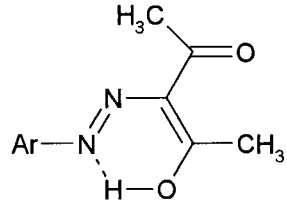
CHAPTER 3

METAL COMPLEXES OF SCHIFF BASE LIGANDS DERIVED FROM 3-ARYLAZO-2,4-PENTANEDIONE WITH DIAMINES

It has been well established that phenylazo derivatives of active methylene compounds such as 2,4-pentanedione (acetylacetone) exist, predominantly in the intramolecularly hydrogen bonded keto-hydrazone tautomeric form **1** rather than the azo-enol form **2**. However heteroarylazo derivatives such as thiazolylazo and benzothiazolylazo-2,4-pentanediones prefer the azo-enol form **2**.



1



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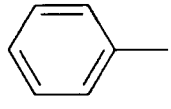
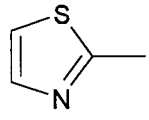
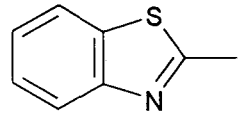






The carbonyl group(s) of these arylazo derivatives of acetyl acetone readily condense with diamines, both aliphatic and aromatic, to yield polydentate schiff base ligand systems. Synthesis and

characterisation of these schiff base and their typical metal complexes are discussed in this chapter. For convenience the chapter is divided into two sections:

Section 1

Metal complexes of multidentate schiff base ligands derived from 3-(arylazo)-2,4-pentanediones with aliphatic diamines.

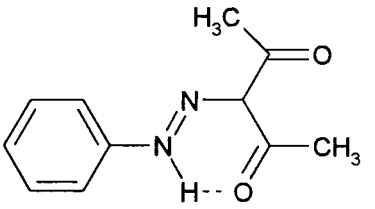
Section 2

Metal complexes of multidentate schiff base ligands derived from thiazolylazoacetylacetone with aromatic diamines.

SECTION 1

METAL COMPLEXES OF MULTIDENTATE SCHIFF BASE LIGANDS DERIVED FROM 3-(ARYLAZO)-2,4-PENTANEDIONES WITH ALIPHATIC DIAMINES

The 3-arylazo-2,4-pentanediones considered in this chapter are given below.



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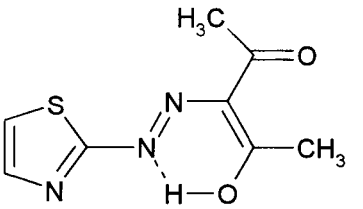

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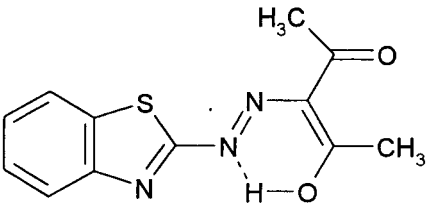

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The diamines used for the Schiff base condensation reactions are 1,2-diamionoethane, 1,3-diaminopropane and 1,6-diaminohexane. Synthetic details of the compounds are given below. Methods adopted for the preparation of their metal complexes are also included.

A. Synthesis and characterisation of Schiff base ligands derived from phenylazoacetylacetone with aliphatic diamines

Experimental

Synthesis of 3-(phenylazo)-2,4-pentanedione

The 3-(phenylazo)-2,4-pentanedione was prepared as follows. Aniline was diazotised as reported.[166] Excess nitrous acid present in the diazonium salt solution was destroyed by adding urea to it. The diazonium salt solution (0.01 mol) kept below 5°C was then added dropwise to a stirred 50% v/v methanol-water solution (20 ml) of acetylacetone (1 g, 0.01 mol). Sodium acetate (~ 3 g) was added to keep the pH of the mixture in the range 6-7. The precipitated product was filtered, washed with water and recrystallised twice from hot methanol to get chromatographically (tlc) pure product. The product was confirmed as 3-phenylazo-2,4-pentanedione from its m.p., mixed m.p. and spectral data.[149]

Synthesis of bis(phenylhydrazonoacetylacetone) diimines

The Schiff bases were synthesised by the condensation of 3-phenylazo-2,4-pentanedione with 1,2-diaminoethane (en), 1,3-diaminopropane (pn) and 1,6-diaminohexane (hn) as follows.

An ethanolic solution of the diamine (0.01 mol, 20 mL) was added to an ethanolic solution of the phenylazoacetylacetone (0.02 mol, 20 mL). The mixed solution was stirred using a magnetic stirrer for ~ 4 h and evaporated at reduced pressure. The crystalline precipitate formed was filtered, and recrystallised from hot methanol to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

The following general method was employed for the preparation of metal complexes of Ni(II), Cu(II) and Zn(II).

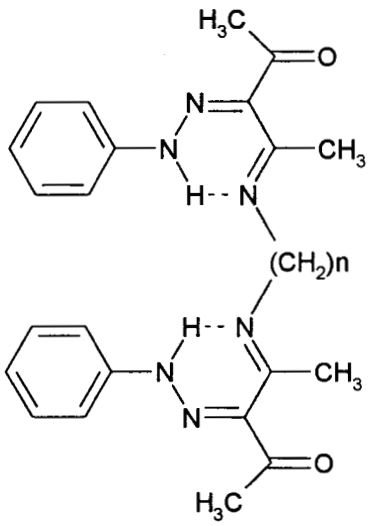
An ethanolic solution of acetates of Ni(II), Cu(II) and Zn(II) (0.01 mol, 20 mL) was added to an ethanolic solution of the ligand (0.01 mol, 20 mL). The mixture was refluxed on a boiling water bath for ~ 3 h and reduced to half of the original volume. The concentrated solution was then added to ice cold water containing 1 g of sodium acetate. The precipitated complex was filtered, washed with water several times and dried in a vacuum desicator.

Results and discussion

Characterisation of bis(phenylhydrazonoacetylacetone) diimines

The condensation reaction of the phenylazoacetylacetone with the diamines yielded well defined crystalline solids soluble in common organic solvents. Elemental analytical data suggested that

one equivalent of the diamine condensed with two equivalents of phenylazoacetylacetone (Table 1). Thus it can be presumed that only one of the carbonyl groups of the phenylhydrazonoacetylacetone was involved in the Schiff base condensation reaction and both the amino groups of the diamine have reacted to form the compounds. The observed ir, ^1H nmr and mass spectral data of the compounds are in conformity with the structure **6**. The spectral data are discussed below.



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Compound	diamine	n
H_2bpe	en	2
H_2bpp	pn	3
H_2bph	hn	6

TABLE 1

Analytical and physical data of H_2bpe, H_2bpp, H_2bph

	Compound*	M.P. °C	Yield %	Elemental analysis % Found/(Calculated)		
				C	H	N
1	4,9-Dimethyl-5,8-diazododeca-4,8-diene-2,11-dione-3,10-diphenylhydrazone Bis(phenylhydrazonoacetyl-acetone)ethylenediimine **H_2bpe**	78	60	66.15 (66.67)	5.83 (6.48)	18.69 (19.44)
2	4,10-Dimethyl-5,9-diazotrideca-4,9-diene-2,12-dione-3,11-diphenylhydrazone Bis(phenylhydrazonoacetyl-acetone)propanediimine, **H_2bpp**	85	75	68.40 (67.26)	5.91 (6.73)	18.02 (18.83)
3	4,13-Dimethyl-5,12-diazohexadeca-4,12-diene-2,15-dione-3,14-diphenylhydrazone Bis(phenylhydrazonoacetyl-acetone)hexanediimine, **H_2bph**	144	82	68.22 (68.86)	6.59 (7.38)	16.74 (17.21)

* The systematic names of the compounds are given followed by a trivial name and a suitable abbreviation.

Infrared Spectra

The ir spectra of the compounds in the 1600-1800 cm^{-1} region showed three strong bands at ~ 1670, ~ 1620 and ~ 1610 cm^{-1}. The band at ~ 1670 cm^{-1} can originate only from a conjugated acetyl carbonyl not involved in hydrogen bonding. Had the acetylcarbonyl been involved in hydrogen bonding the stretching frequency would have been at still lower values.[167,168] From a comparison of the

spectra of the compounds with those of phenylazoacetylacetone, the bands at ~ 1620 and 1610 cm^{-1} can confidently be assigned to the stretching of the C=N functions. The low frequency band ~ 1610 cm^{-1} is due to the hydrogen bonded νC=N. Further in the spectra of all compounds several medium intensity bands appeared in the 1550-1600 cm^{-1} region due to the stretching of various C=C vibrations. A prominent band appeared at ~ 1540 cm^{-1} in the spectra of all the compounds can be assigned to NH deformation vibration.

The X-H stretching region of the compounds clearly indicated the presence of relatively strong intramolecular N–H...N hydrogen bonding. The broad band present in the region 3500-2400 cm^{-1} is due to hydrogen bonded NH groups. Thus the ir spectra strongly support structure **6** of the compounds in which strong intramolecular N–H...N hydrogen bonding exist rather than the possible O...H–N hydrogen bonding. Important ir bands and their probable assignments are given in table 2.

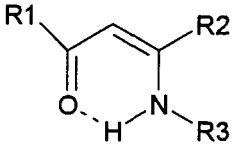
TABLE 2

Characterisitic ir data (cm^{-1}) of H_2bpe, H_2bpp, H_2bph diimines

Compound	νC=O	νC=N	νC=C
H_2bpe	1670	1620 1608	1595 1590
H_2bpp	1675	1622 1616	1598 1592
H_2bph	1668	1628 1612	1592 1588

Nmr spectra

The ketohydrazone tautomer of 2-phenylazoderivatives of 1,3-diketones usually exhibit a signal above δ 15 ppm in their ^1H nmr spectra due to the intramolecularly hydrogen bonded N–H...O proton.[175] In the case of azo-enol tautomer the acidic proton signal due to O–H...N is observed below δ 13 ppm. The same trend is observed also in the case of schiff bases where both the possibilities exist. However the schiff bases of the type considered in this section, presence of N–H...N hydrogen bonding is also possible. Generally in schiff bases N–H...N proton show resonance signal below δ 10 ppm. ^1H nmr studies on schiff base derived from 1,3-diketones and amines indicate that they exist as the ketoamine tautomer **7** rather than the enol-imine **8** or the keto tautomer **9**.



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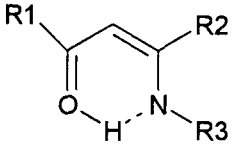

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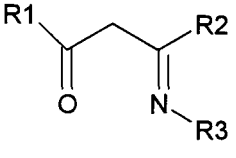


9

In the ^1H nmr spectra of the compounds considered, no signals were observed above 10 ppm assignable to intramolecularly hydrogen bonded N–H...O=C / O–H...N groups of the keto-hydrazone / azo-enol forms typical of arylazo derivatives of acetylacetone. However,

the spectra of all the compounds show a two proton signal at ~ δ 9 ppm. This signal can be safely assigned to the intramolecularly hydrogen bonded N–H...N protons. Further the spectra is devoid of any signal assignable to methylene protons. Another characteristic feature of the spectra is the presence of two six proton singlets at δ 2.20 - 2.70 ppm due to the methyl groups. The integrated intensities of the aryl proton signals suggest that two aryl groups are present in the molecules. Thus the ^{1}H nmr spectra strongly suggest structure **6** of the compounds. The spectral data are brought out in table 3.

TABLE 3

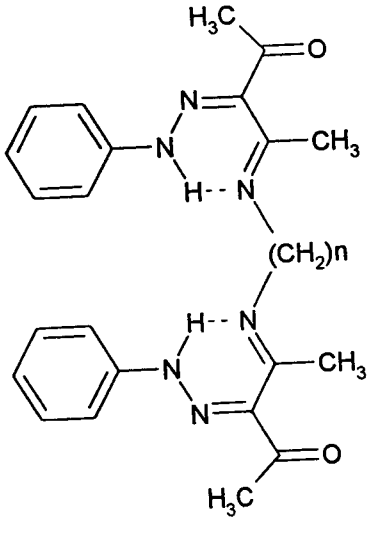
^{1}H nmr spectral data of H_2bpe, H_2bpp, H_2bph

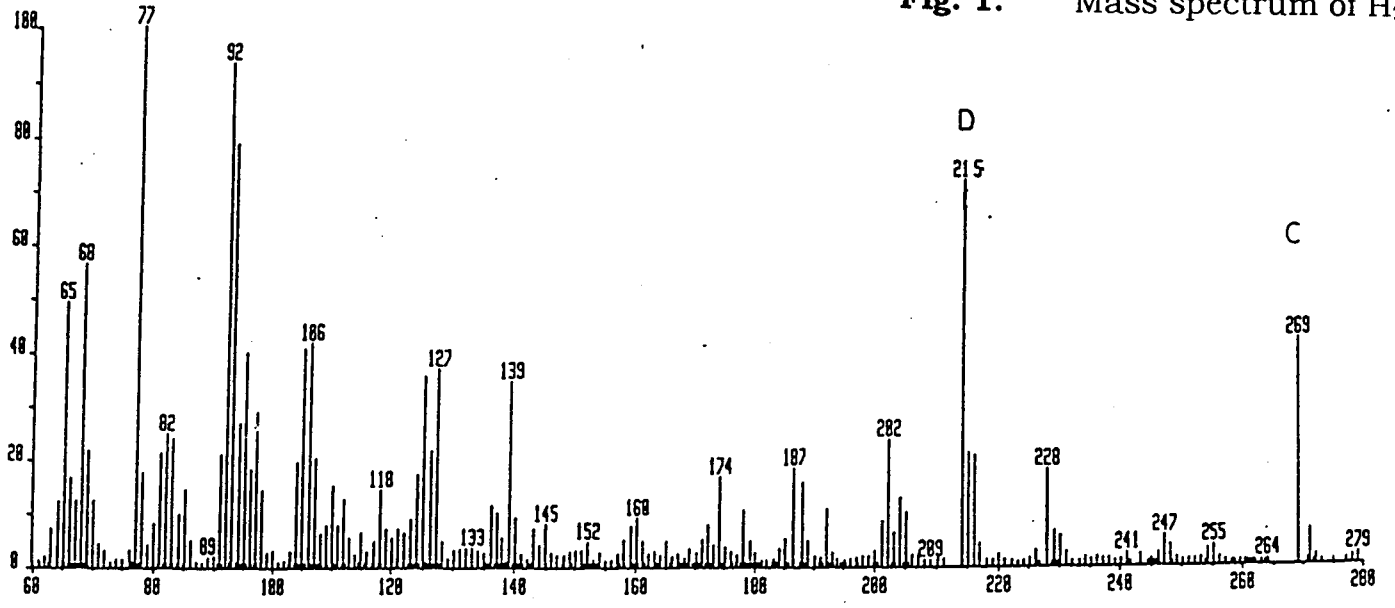
Compound	^{1}H nmr chemical shift (ppm)			
	NH	Aryl	$(CH_2)_n$	CH_3
H_2bpe	9.25 (2H)	6.87-7.35 (10H)	3.85 (4H)	2.44 (6H) 2.65 (6H)
H_2bpp	9.20 (2H)	6.88-7.35 (10H)	3.53 (4H) 3.45 (2H)	2.52 (6H) 2.68 (6H)
H_2bph	9.20 (2H)	6.50-7.35 (10H)	3.38 (4H) 3.12 (8H)	2.50 (6H) 2.70 (6H)

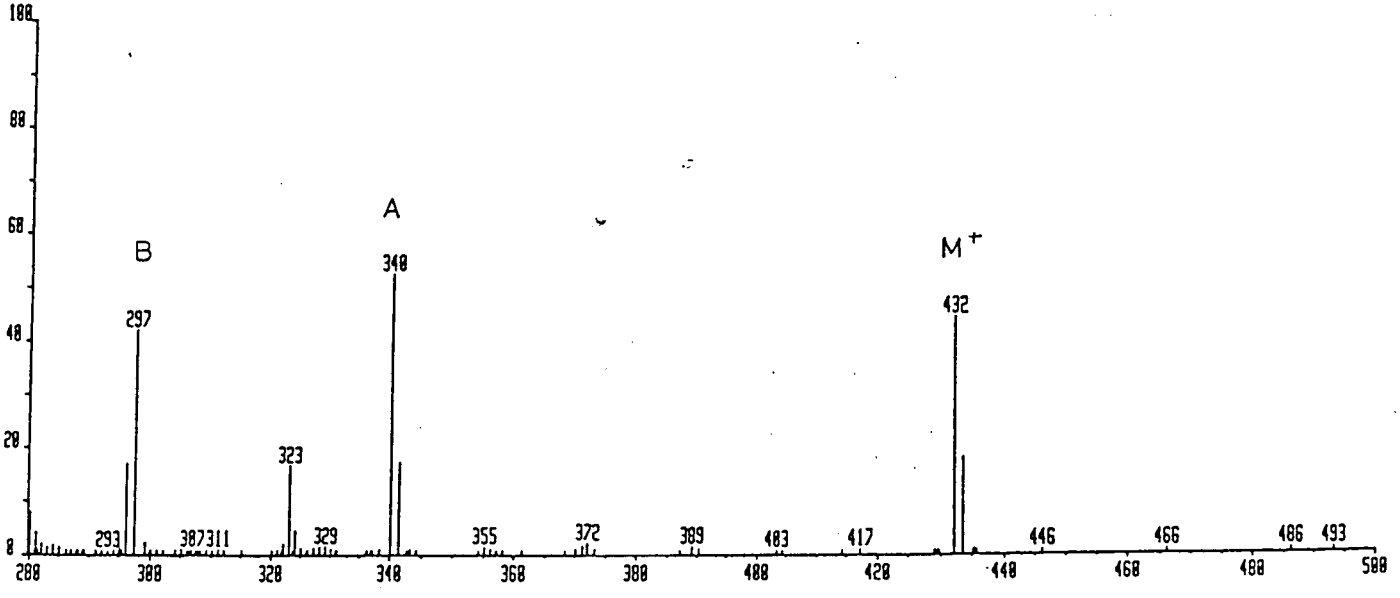
Mass spectra

The mass spectra of all the compounds show molecular ion $P^+/(P+1)^+$ peaks as expected of structure **6**. Peaks due to the elimination of CH_3CO^+, $C_6H_5NH^+$ are observed in all the spectra. Typical spectra are reproduced in figure **1**. The observed peaks can

Fig. 1. Mass spectrum of H_2bpe.



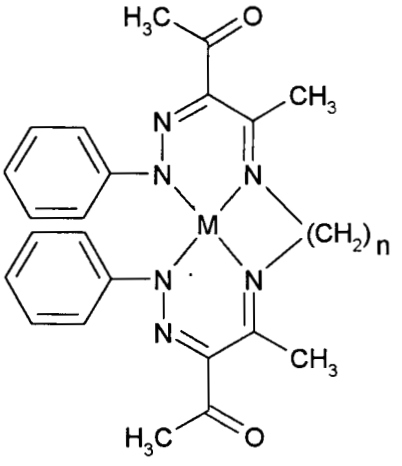




be accounted by considering the elimination of $(C_6H_5NH)^+$, CH_3CO^+, CO, etc. groups from the molecular ion.

Characterisation of metal complexes

All the schiff bases formed well defined complexes with Ni^{2+}, Cu^{2+} and Zn^{2+}. The C, H, N and metal percentages (Tables 4) determined showed [ML] stoichiometry of the complexes. The Cu^{2+} complexes showed normal paramagnetic moment. All the complexes behave as non conducting in dmf (10^{-3} M) solution. The observed ir, ^1H nmr and mass spectral data of the complexes are in conformity with structure **10**. The spectral data are discussed below.



10

TABLE 4

Analytical and physical data of H_2bpe, H_2bpp, H_2bph

Compound	M.P. °C	Elemental analysis % Found / (Calcd.)			
		C	H	N	M
[Ni(bpe)]	250	57.44 (58.93)	5.00 (5.32)	16.94 (17.18)	11.44 (12.00)
[Cu(bpe)]	284	57.60 (58.35)	4.94 (5.26)	16.44 (17.01)	12.21(12.87)
[Zn(bpe)]	218	57.40 (58.13)	4.98 (5.24)	15.90 (16.95)	12.82 (3.20)
[Ni(bpp)]	260	58.44 (59.67)	5.00 (5.57)	16.22 (16.71)	11.00 (11.67)
[Cu(bpp)]	285	58.20 (59.10)	5.00 (5.51)	15.94 (16.55)	12.00 (12.51)
[Zn(bpp)]	200	57.14 (58.09)	5.11 (5.49)	16.11 (16.48)	12.21 (12.83)
[Ni(bph)]	> 300	61.04 (61.68)	5.82 (6.24)	14.44 (15.42)	10.00 (10.77)
[Cu(bph)]	> 300	60.02 (61.14)	5.94 (6.18)	14.97 (15.28)	11.22 (11.56)
[Zn(bph)]	265	58.44 (60.93)	5.94 (6.10)	14.43 (15.23)	11.02 (11.86)

Infrared spectra

The most characteristic feature of the spectra of all the complexes is the presence of a strong band at ~ 1670 cm^{-1}. It is clear that such a band can arise in the complex only from the stretching of a conjugated free acetyl carbonyl group. Thus it appears that acetyl carbonyls of the free ligand is not involved in bonding with the metal ion.

In the spectra of all the complexes the strong bands at ~ 1610 cm^{-1} of the free ligand due to νC=N (imine) shifted to low wave number and appeared as a prominent band in the 1550-1600 cm^{-1}

region. The hydrazone νC=N is only marginally affected in the spectra of complexes. Thus it appears that the imine and one of the hydrazo nitrogens as in structure **10** are involved in bonding with the metal. The replacement of the NH proton by metal ion is clearly indicated from the disappearance of the NH deformation band of the free ligand at ~ 1540 cm^{-1} in the spectra of all the complexes. Further two medium intensity bands not found in the free ligand appeared in the 500-550 cm^{-1} region of the spectra of all the complexes presumably due to νM-N.

The broad free ligand band in the 2500-3500 cm^{-1} region cleared up in the spectra of all the complexes thereby confirming the replacement of the hydrogen bonded NH proton by metal ion. Spectra of the complexes in the region show several bands due to both aliphatic and aromatic C–H stretching vibrations.

Nmr spectra

In the ^1H nmr spectra of the diamagnetic Ni^{2+} complexes, signal due to the NH protons of the free ligand at δ ~ 9 ppm disappeared indicating the replacement of these protons by metal ions. Integrated intensities of all other protons agree well with the 1:1 metal-ligand stoichiometry of the complex.

Mass spectra

Mass spectrum of the nickel(II) complex of **H_2bpe** shows a relatively intense peak corresponding to the molecular ion $[ML]^+$. Other prominent peaks are due to the elimination of CH_3CO, Ar etc. groups from the parent ion. The spectrum is given in figure 2.

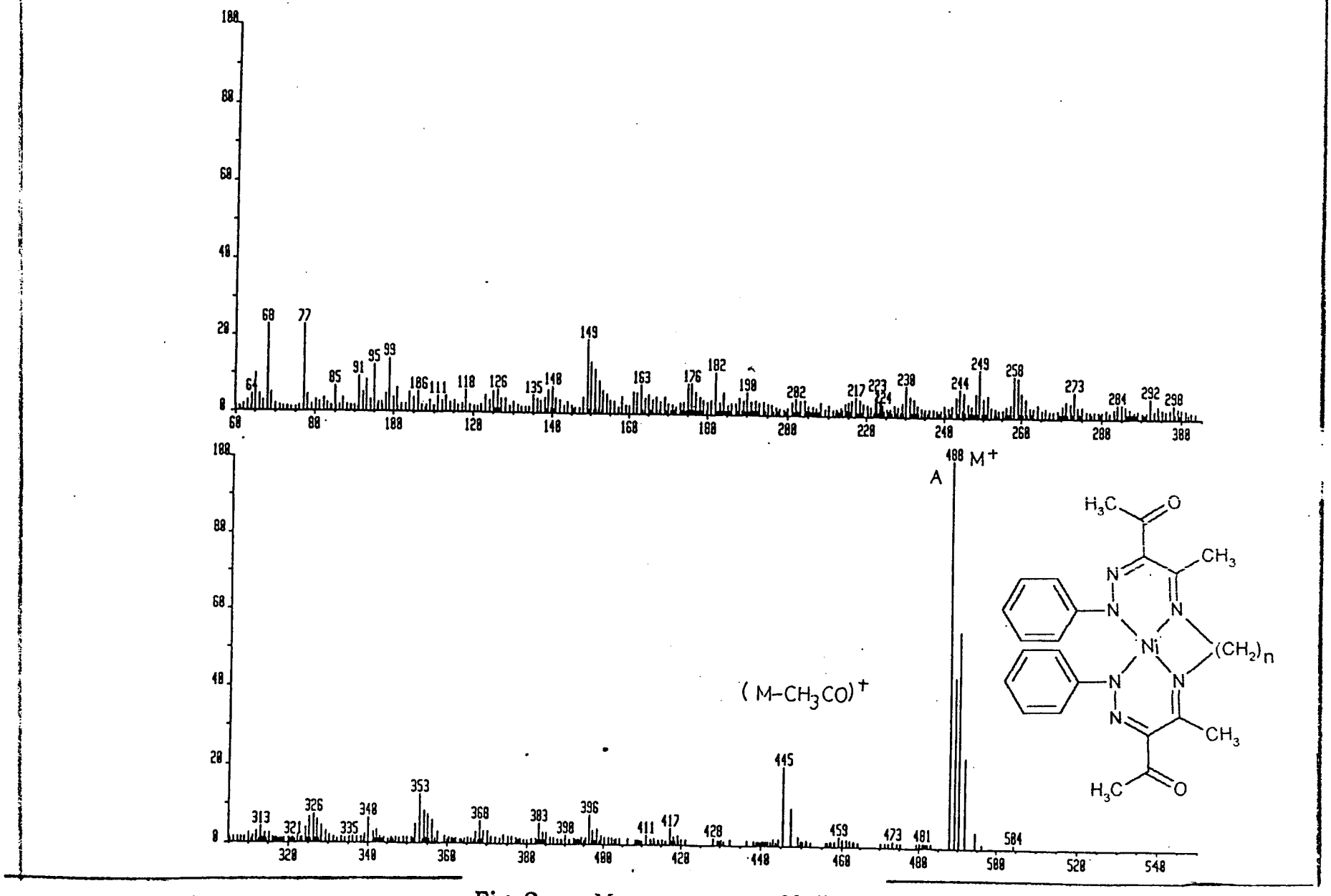


Fig. 2. Mass spectrum of [Nibpe].

B. Synthesis and Characterisation of schiff base ligands derived and their metal complexes from thiazolylazoacetylacetone and benzothiazolylazoacetylacetone with aliphatic diamines

The synthesis and characterisation of Schiff bases obtained from the condensation of thiazolylazo and benzothiazolylazo acetylacetone with 1,2-diaminoethane, 1,3-diaminopropane and 1,6-diaminohexane and their metal complexes are considered are discussed below (Table 5).

Experimental

Synthesis of 3-(2-thiazolylazo)- and 3-(2-benzothiazolylazo)-2,4-pentanediones

The thiazolylazo and benzothiazolylazo derivatives of 2,4-pentanedione were prepared as detailed below.

To a solution of 2-aminothiazole (2 g, 0.02 mol) / 2-aminobenzothiazole (3 g, 0.02 mol) in aqueous sulphuric acid (10 N, 15 mL) kept cold below 0°C was added drop by drop a concentrated aqueous solution of sodium nitrite (1.4 g). After stirring for about 15 minutes, the brown diazonium salt solution (0.02 mol) was added drop by drop to an ethanolic solution of acetylacetone (2 g; 0.02 mol, 20 mL) kept at temperature below 5°C. Sodium acetate (~ 4 g) was added to maintain the pH of the reaction below 7. Stirring was

continued for about 30 minutes. The precipitated product was filtered, washed with cold water and recrystallised from hot methanol. The product was confirmed as 3-(2-thiazolylazo)/ benzothiazolylazo-2,4-pentanedione from its m.p., mixed m.p. and ir spectral data[149] (thiazolylazo-2,4-pentanedione m.p. 116°C, lit.[149] 116°C, benzothiazolylazo-2,4-pentanedione m.p. 192°C, lit.[149] 192°C).

Synthesis of bis(thiazolylazoacetylacetone) bis(benzothiazolyl-azoacetylacetone) diimines

An ethanolic solution of the diamine (1,2-diaminoethane, 1,3-diaminopropane and 1,6-diaminohexane) (0.01 mol in 20 mL) was added to an ethanolic solution of thiazolylazo/benzothiazolylazo acetylacetone (0.01 mol, 20 mL) drop by drop with constant stirring. The mixture was stirred mechanically for ~ 5 h in a closed vessel maintaining the temperature 60-65°C. Evaporated at reduced pressure and the crystalline compound formed was filtered and recrystallised from hot methanol to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

The following method was employed for the preparation of complexes of Ni(II), Cu(II) and Zn(II).

TABLE 5

Analytical and physical data of H_2bte, H_2btp, H_2bth and H_2bbe

	Compound*	M.P. °C	Yield %	Elemental analysis % Found/(Calculated)		
				C	H	N
1	4,9-Dimethyl-5,8-diazododeca-4,8-diene-2,11-dione-3,10-di(2-thiazolylhydrazone) Bis(2-thiazolylhydrazonoacetyl-acetone)ethylenediimine **H_2bte**	85	50	47.88 (48.43)	4.54 (4.90)	24.78 (25.11)
2	4,10-Dimethyl-5,9-diazotrideca-4,9-diene-2,12-dione-3,11-di(2-thiazolylhydrazone) Bis(2-thiazolylhydrazonoacetyl-acetone)propanediimine, **H_2btp**	70	64	49.30 (49.56)	5.06 (5.21)	23.97 (24.34)
3	4,13-Dimethyl-5,12-diazohexadeca-4,12-diene-2,15-dione-3,14- di(2-thiazolyl-hydrazone) Bis(2-thiazolylhydrazonoacetyl-acetone)hexanediimine, **H_2bth**	225	70	52.48 (52.58)	5.44 (5.97)	22.00 (22.31)
4	4,10-Dimethyl-5,8-diazododeca-4,8-diene-2,11-dione-3,10-di(2-benzothiazolylhydrazone) Bis(2-benzothiazolylhydrazono-acetylacetone) ethylenediimine, **H_2bbe**	94	70	57.00 (57.14)	4.44 (4.76)	20.32 (20.51)

* The systematic names of the compounds are given followed by a trivial name and a suitable abbreviation.

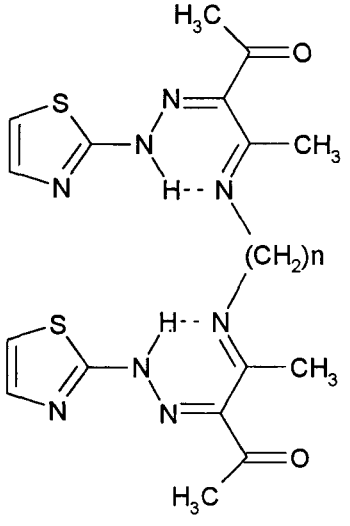
An ethanolic solution of metal acetate (0.01 mol, 20 mL) was added to an ethanolic solution of the ligand (0.01 mol, 20 mL). The mixture was refluxed on a boiling water bath for ~ 2 h and reduced to half the original volume. This solution was kept overnight and added to crushed ice containing ~ 1 g sodium acetate. The solution

was stirred for ~ 15 minutes and the precipitated complex was filtered, washed with excess of water and dried in vacuum desicator.

Results and discussion

Characterisation of bis(thizolylazoacetylacetone bis(benzo-thiazolylazoacetylacetone) diimine

The condensation reaction of 3-(2-thiazolylazo) and (benzothiazolylazo)-2,4-pentanediones, with the diamines yielded stable crystalline products. Analytical and physical data of the compounds are given in table 5. The elemental composition indicate that two moles of thiazolylazo/benzothiazolylazo acetylacetone has condensed with one mole of the diamine. The ir, nmr and mass spectral data of the compounds are consistent with structure **11**. In the case of benzothiazolylazo derivatives, in structure **11** benzothiazole ring instead of thiazole ring).



11

Infrared spectra

The ir spectra of all the compounds are characterised by the presence of a strong band at ~ 1675 cm^{-1} and three medium intensity bands at ~ 1625, 1615 and 1610 cm^{-1}. From a comparison of the spectrum of thiazolylazoacetylacetone, the band at 1675 cm^{-1} can safely be assigned to the free conjugated acetyl carbonyl of structure **11**. Similarly the above low frequency bands can confidently be assigned to the stretching of hydrazone νC=N, imine νC=N and the thiazole νC=N respectively. A medium intensity band appeared at ~ 1535 cm^{-1} assignable to δNH also observed in the spectra of the compounds. In the region 2400-3600 cm^{-1} of the spectra consist of a broad band due to the strong intramolecular hydrogen bonding existing in these compounds. Characteristic ir bands of the compounds are given in table 6.

TABLE 6

Characersitic ir data (cm^{-1}) of H_2bte, H_2btp, H_2bth, H_2bbe

Compound	νC=O	νC=N	νC=C
H_2bte	1680	1620 1615	1590 1585 1580
H_2btp	1672	1622 1612 1608	1593 1588 1580
H_2bth	1665	1625 1615 1608	1598 1590 1585
H_2bbe	1668	1626 1518 1610	1598 1590 1582

Nmr spectra

The ^1H nmr signals of the compounds and their probable assignments are given in table 7. All the compounds have a low field two proton signal at ~ δ 9.5 ppm due to the hydrogen bond N–H...N protons. That the compounds contain two sets of methyl protons is clearly indicated in the spectra. The integrated intensities of the signals agree well with their formulation as in structure **11**.

TABLE 7

^1H nmr spectral data of H_2bte, H_2btp, H_2bth, H_2bbe

Compound	^1H nmr chemical shift (ppm)			
	NH	Aryl	$(CH_2)_n$	CH_3
H_2bte	9.44 (2H)	7.06 2H) 7.26 (2H)	3.86 (4H)	2.26 (6H) 2.47 (6H)
H_2btp	9.63 (2H)	7.26 (2H) 7.06 (2H)	2.67 (2H) 3.80 (4H)	2.26 (6H) 2.47 (6H)
H_2bth	9.58 (2H)	6.80-7.50	3.40 (4H) 3.20 (8H)	2.45 (6H) 2.56 (6H)
H_2bbe	9.44 (2H)	6.90-7.55	3.82 (4H)	2.24 (6H) 2.42 (6H)

Mass spectra

The mass spectra of the thiazolylazo derivatives are presented in figure 3, 4, 5. In all the spectra the highest peak correspond to the molecular ion of the compounds in accordance with their formulation. Elimination of CH_3CO, $CH_3C{\equiv}N$, C_3H_2NS (thiazole),

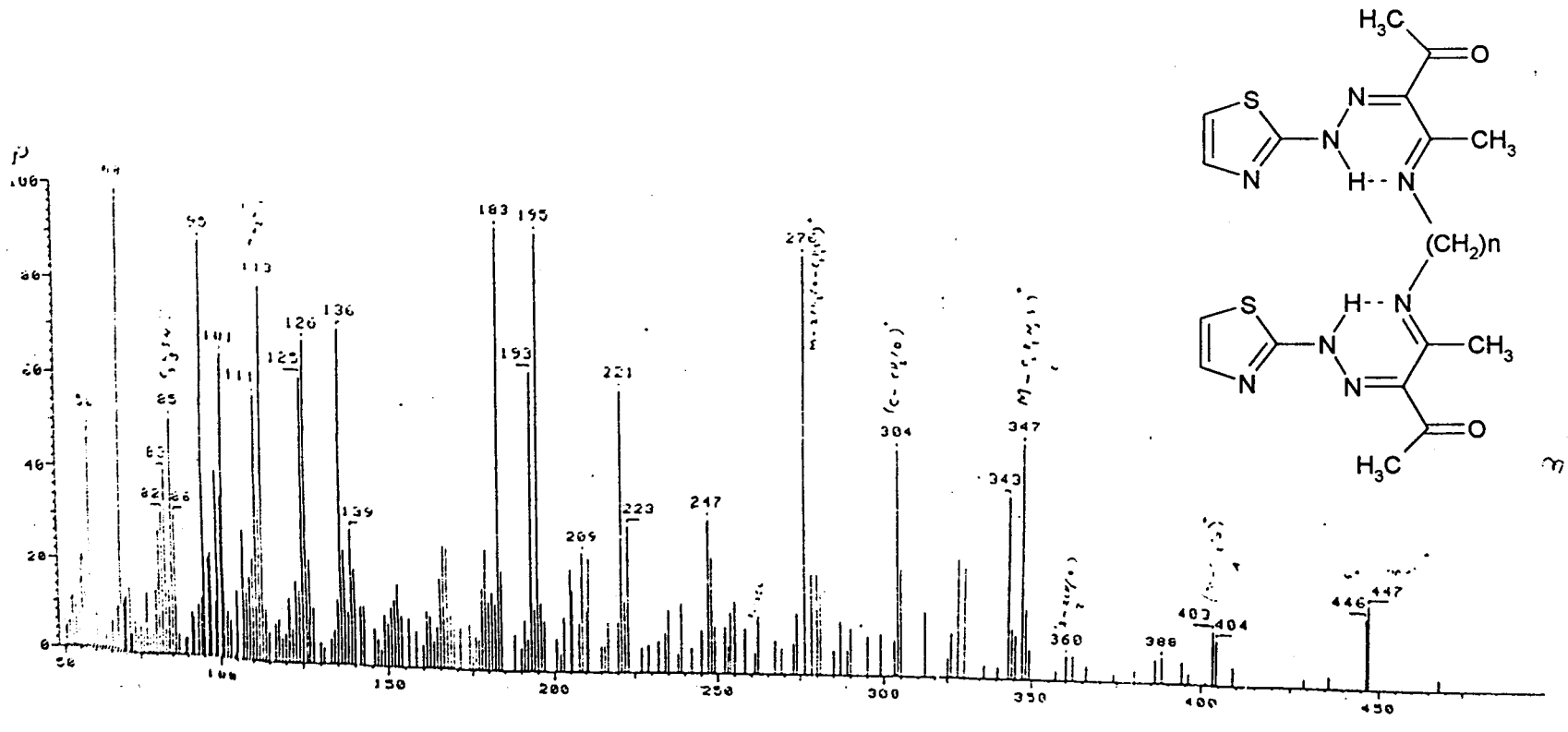


Fig. 3. Mass spectrum of H_2bte.

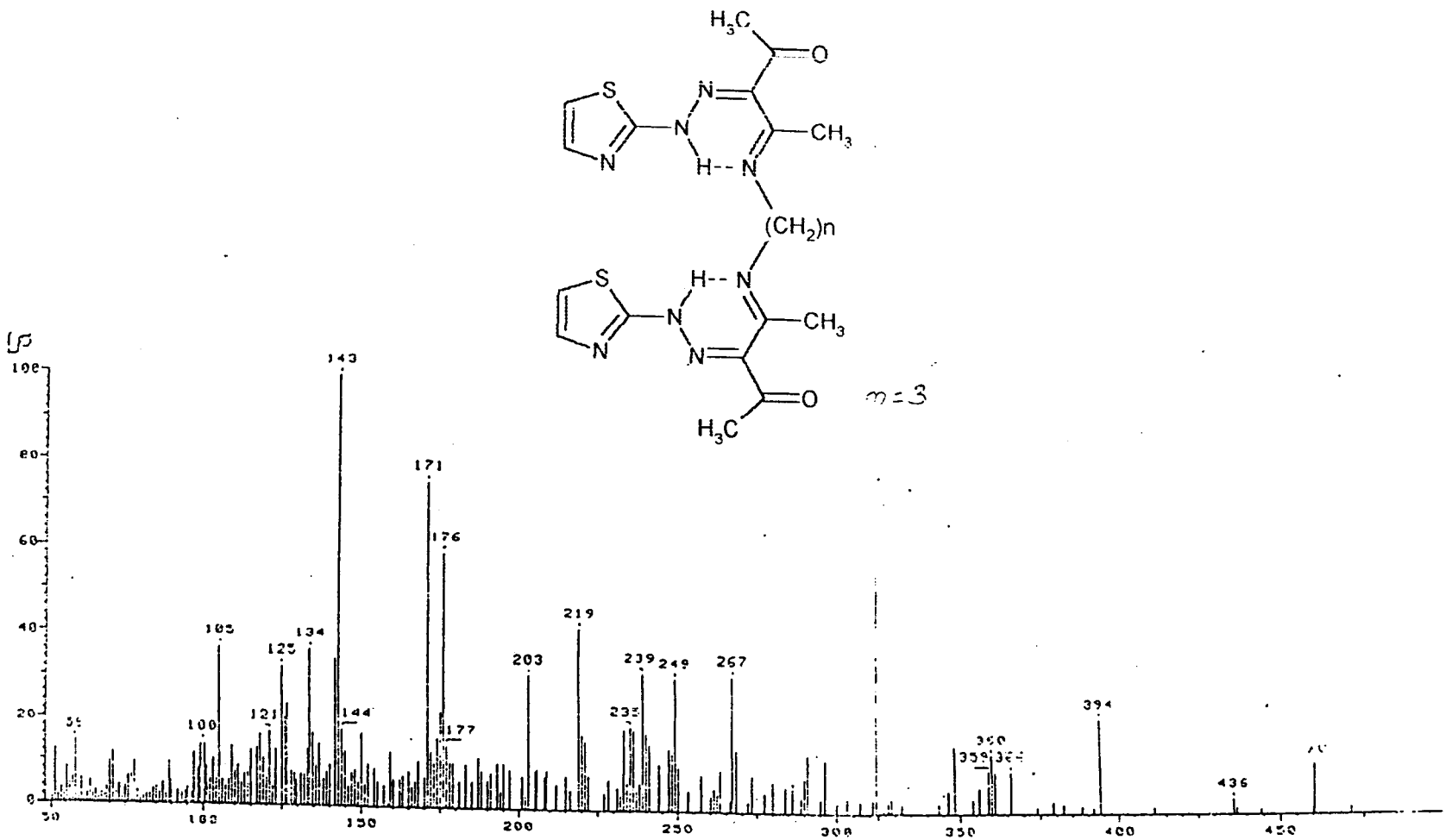


Fig. 4. Mass spectrum of H_2btp.

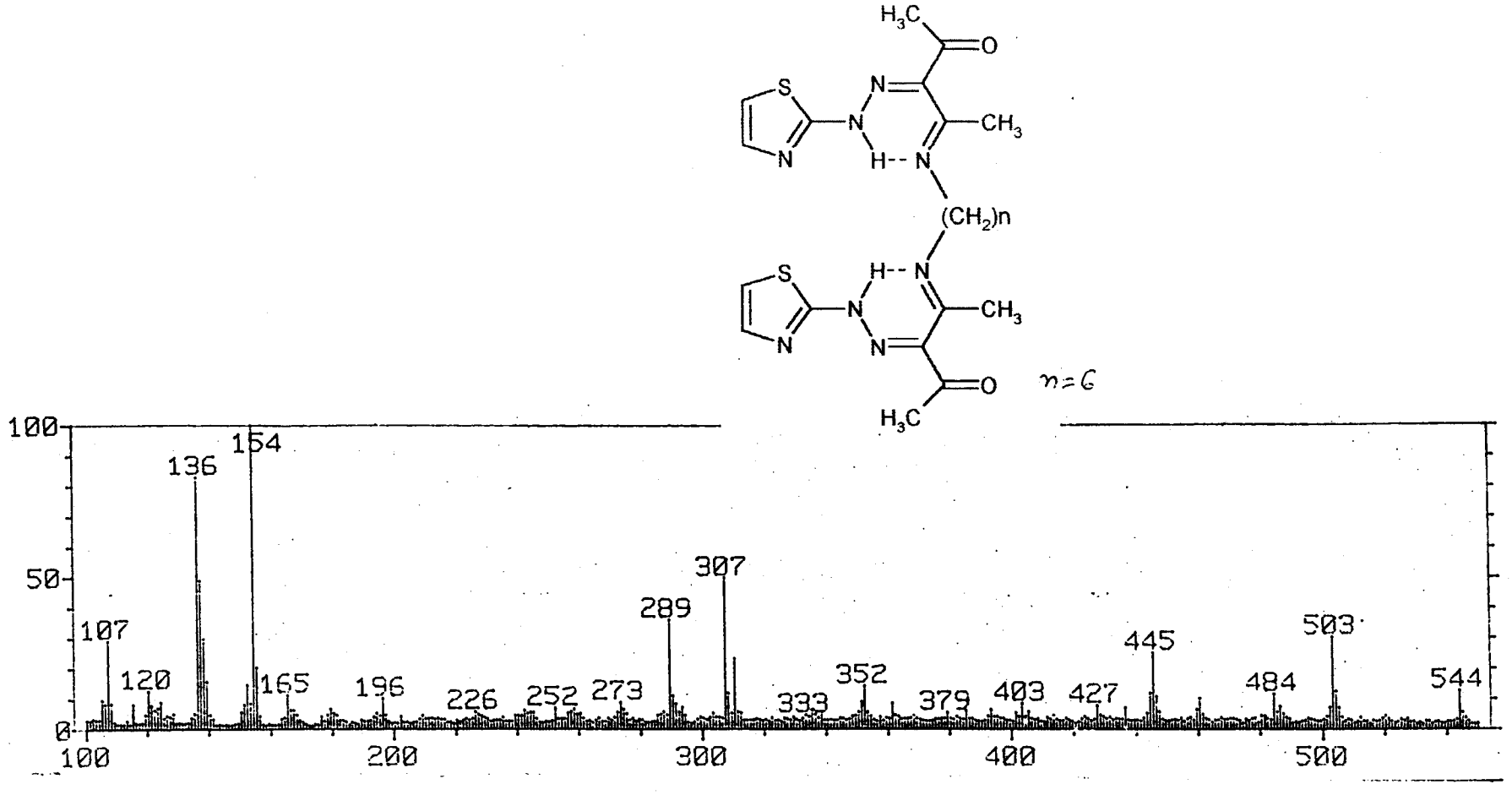


Fig. 5. Mass spectrum of H_2bth.

C_3H_3NSNH, etc. fragments from the molecular ion are also observed in the spectra.

Characterisation of metal complexes

With nickel(II), copper(II) and zinc(II) all the schiff bases formed well defined stable neutral complexes. The observed C, H, N and metal percentages suggest the [ML] stoichiometry of all the complexes. The analytical and physical data of the complexes are given in table 8. The structure and nature of bonding of these complexes are discussed on the basis of their ir, ^1H nmr and mass spectral data.

TABLE 8

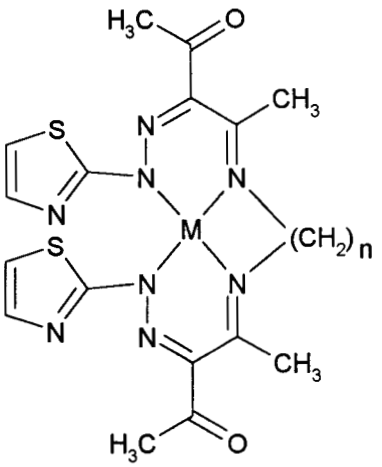
Analytical and physical data of H_2btp, H_2bth, H_2bbe of complexes

Compound	M.P. °C	Elemental analysis % Found / (Calcd.)			
		C	H	N	M
[Ni(bte)]	> 300	42.00 (42.96)	3.14 (3.98)	20.00 (22.28)	11.02 (11.67)
[Cu(bte)]	> 300	41.98 (42.55)	3.24 (3.94)	21.22 (22.06)	12.00 (12.52)
[Zn(bte)]	> 260	41.56 (42.39)	3.41 (3.92)	20.92 (21.98)	12.41 (12.83)
[Ni(btp)]	242	43.84 (44.12)	4.02 (4.25)	20.92 (21.67)	10.94 (11.36)
[Cu(btp)]	> 300	42.41 943.71)	4.01 (4.21)	20.95 (21.47)	11.94 (12.18)
[Zn(btp)]	280	41.98 (43.56)	3.82 (4.20)	21.00 (21.39)	11.94 (2.49)
[Ni(bth)]	242	43.84 (44.12)	4.02 (4.25)	20.92 (21.67)	10.94 (11.36)
[Cu(bth)]	> 300	42.41 (43.71)	4.01 (4.21)	20.95 (21.47)	11.94 (12.18)
[Zn(bth)]	280	41.98 (43.56)	3.82 (4.20)	21.00 (21.39)	11.94 (12.49)
[Ni(bbe)]	> 300	50.21 (51.35	3.44 (3.98)	18.10 (18.58)	9.23 (9.73)
[Cu(bbe)]	260	51.00 (51.76)	3.21 (3.95)	16.98 (18.43)	10.00 (10.45)
[Zn(bbe)]	110	50.94 (51.19)	3.45 (3.93)	18.11 (18.37)	10.12 (10.73)

Infrared spectra

A comparison of the ir spectra of the complexes with that of the ligands (Table 9) revealed that the free acetyl carbonyl of the ligand remained almost unaffected in the spectra of complexes. This indicate that the carbonyl groups are not involved in complexation. However, the νC=N bands of the ligands shifted appreciably to low frequency and appeared at ~ 1610, ~ 1605 and ~ 1600 cm^{-1}. The specific assignments of these bands among the three C=N functions appeared to be difficult because such assignments are possible only with ^{15}N labelling. From the observed position and nature of bands it can be stated that atleast one of the C=N groups is involved in bonding with the metal ion. The possible coordination of a second C=N group (probably the thiazole C=N) with the metal ion also cannot be ruled out.

The broad band of the free ligand in the region 2400-3000 cm^{-1} cleared up in the spectra of all the complexes and instead weak bands due to various νC-H appeared at ~ 2400 and ~ 3000 cm^{-1}. This indicate the replacement of the NH protons by metal ion. Further the band at ~ 1530 cm^{-1} due to NH bending vibration of free ligand also disappeared in the spectra of complexes. The two medium intensity bands observed at ~ 550 cm^{-1} can be assigned to νM-N. Thus the ir spectra strongly support structure **12** of the complexes.



12

Nmr spectra

In the ^1H nmr spectra of the diamagnetic nickel(II) complexes of **H_2bte** and **H_2btp**, the two proton signal at ~ 9.2 ppm due to hydrogen bonded N–H protons are absent. Thus the replacement of these protons by metal ion is confirmed. The position and nature of all other signals (Table 10) agree well with the N_4 coordination of the schiff bases.

TABLE 9

Characteristic ir data (cm^{-1}) of H_2bte, H_2btp, H_2bth, H_2bpe and its complexes

Compound	νC=N	νC=N	νM–N
H_2bte	1680	1625, 1615, 1610	--
[Ni(bte)]	1678	1616, 1608, 1602	548, 532
[Cu(bte)]	1675	1615, 1608, 1600	555, 538
[Zn(bte)]	1675	1615, 1616, 1600	542, 530
H_2btp	1678	1627, 1618, 1610	--
[Ni(btp)]	1672	1610, 1605, 1600	545, 530
[Cu(btp)]	1670	1612, 1608, 1600	550, 535
[Zn(btp)]	1675	1615, 1610, 1605	535, 525
H_2bth	1671	1628, 1618, 1603	--
[Ni(bth)]	1665	1615, 1605, 1600	530, 518
[Cu(bth)]	1668	1612,1608, 1600	538, 512
[Zn(bth)]	1665	1610, 1600, 1598	538, 522
H_2bpe	1668	1630, 1618, 1610	--
[Ni(bpe)]	1662	1618, 1608, 1600	528, 518
[Cu(bpe)]	1665	1615, 1610, 1600	522, 515
[Zn(bbe)]	1600	1620, 1612, 1608	524, 518

TABLE 10

^{1}H nmr spectral data of H_2bte, H_2btp and its complex

Compound	NH	Thiazolyl	$(CH_2)_n$	Methyl
H_2bte	9.24 (2H)	7.065 (2H) 7.269 (2H)	3.86 (4H)	2.26 (6H) 2.47 (6H)
[Ni(bte)]	--	7.26 (2H) 6.69 (2H)	3.60 (4H)	2.51 (6H) 2.49 (6H)
H_2btp	9.43 (2H)	7.26 (2H) 7.06 (2H)	2.67 (2H) 3.80 (4H)	2.26 (6H) 2.47 (6H)
[Ni(btp)]	--	7.18 (2H) 6.69 (2H)	2.57 (2H) 3.62 (4H)	2.26 (6H) 2.48 (6H)

Mass spectra

The mass spectra of the copper(II) and nickel(II) chelates of H_2bte are reproduced in figure 6, 7. The formulation of chelates as in structure **12** is evident from the appearance of intense peak due to the molecular ion. Other important peaks present in the spectra are also in agreement with the structure proposed.

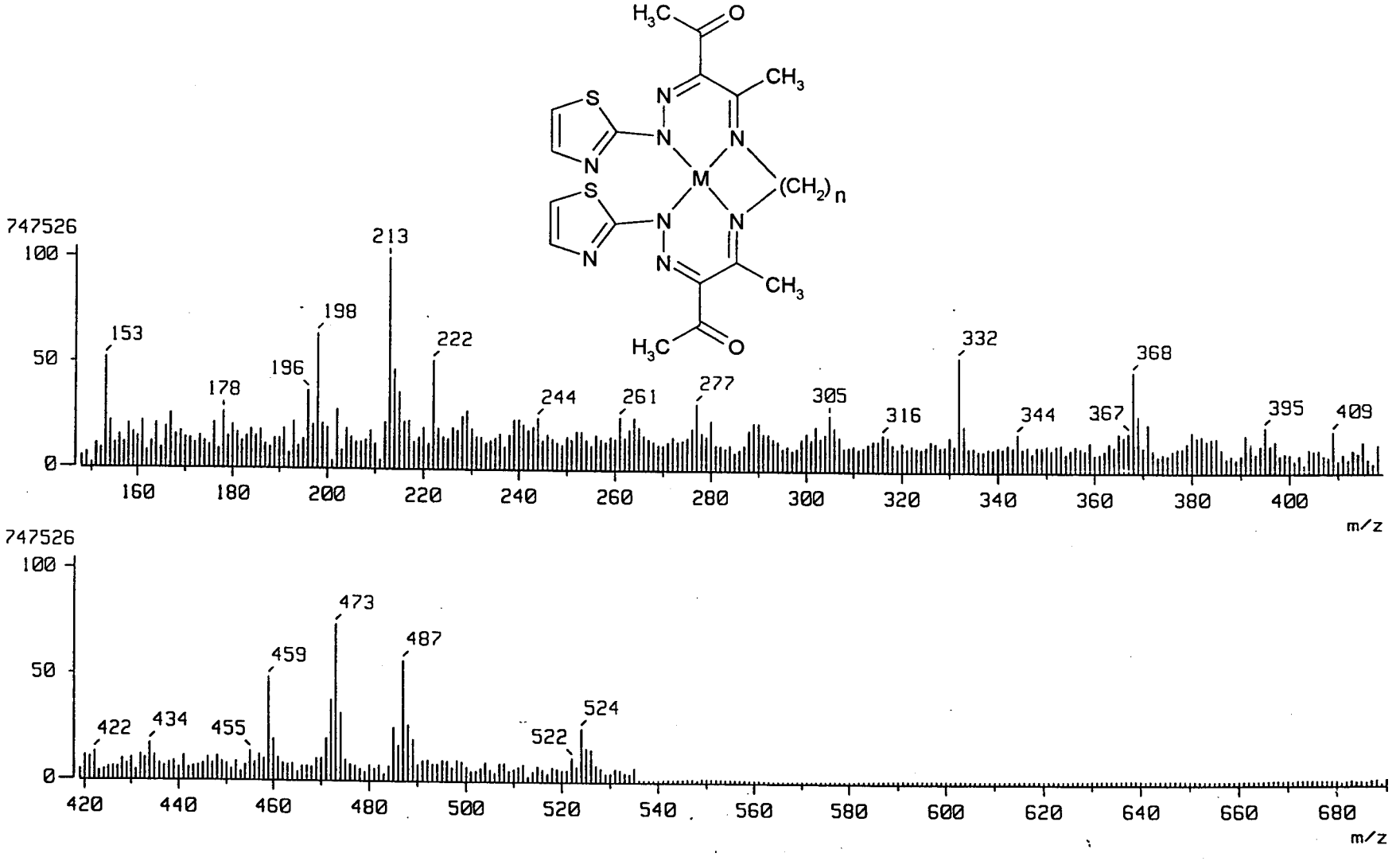


Fig. 6. Mass spectrum of [Cu(btp)]

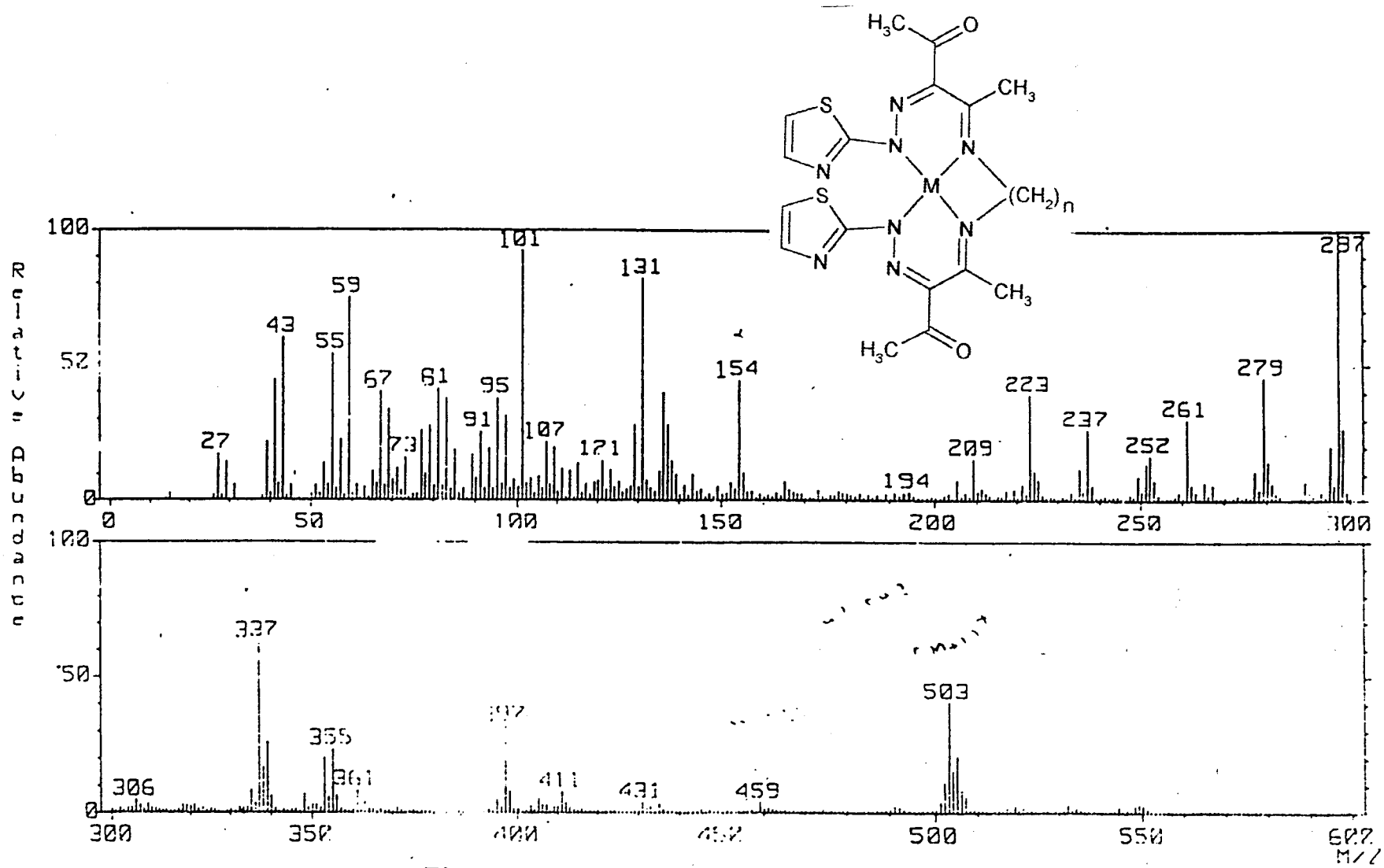


Fig. 7. Mass spectrum of [Ni(bte)]

SECTION 2

METAL COMPLEXES OF MULTIDENTATE SCHIFF BASE LIGANDS DERIVED FROM THIAZOLYLAZOACETYLACETONE WITH AROMATIC DIAMINES

The synthesis and characterisation of schiff bases obtained from the condensation of thiazolylazoacetylacetone with 1,2-, 1,3- and 1,4-diaminobenzenes, are considered in this section. Since the schiff bases formed by the condensation reactions are of different composition and structure, their synthesis and characterisation are discussed separately. Synthesis and characterisation of typical metal complexes of these ligand systems are also included.

A. Synthesis and characterisation of thiazolylazo acetylacetone *ortho*-phenylenediimine, Htop, and its metal complexes

Experimental

Synthesis of Htop

Ortho-phenylenediamine (1.08 g, 0.01 mol) was dissolved in 20 mL of ethanol and added to an ethanolic solution of thiazolylazoacetylacetone (2.11 g, 0.01 mol, 20 mL). The mixture was refluxed for ~ 3 h and kept the solution overnight. The volume was reduced and the precipitated compound was filtered and

recrystallised from hot methanol thrice to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

Co(II), Ni(II), Cu(II) and Zn(II)) complexes of the compound were prepared as given below.

A concentrated aqueous solution of the metal(II) acetate (0,01 mol) was added to a methanolic solution of the ligand (0.01 mol, 20 mL) and the mixture was refluxed on a boiling water bath for about ~ 2 h. The precipitate formed on cooling was filtered, washed with excess water and then with methanol and dried in vacuum.

Results and Discussion

Characterisation Htop

The C, H and N percentages of the condensation products of thiazolylazoacetylacetone with *ortho*-phenylenediamine suggest that one mole of the former reacted with 2 mole of the phenylenediamine (Table 11). Thus it appears that unlike the aliphatic diamines only one of the amino groups of aromatic diamines has involved in the schiff base formation. The ir, nmr and mass spectral data of the compound also support this observation. The spectral data are discussed below.

TABLE 11

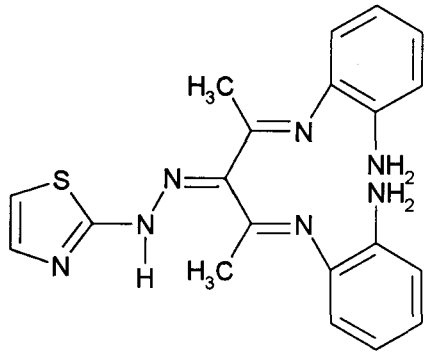
Analytical and physical data of Htop and its metal complexes

Compound	Yield %	M.P. °C	μ_{eff} B.M.	Elemental analysis (%) Found / (Calcd.)			
				C	H	N	M
Htop	65	125		62.04 (61.38)	5.94 (5.37)	25.44 (25.06)	--
[CoHtop(OAc)$_2$]	75	> 300	3.68	49.44 (50.71)	4.44 (4.75)	16.94 (17.25)	10.14 (10.37)
[NiHtop(OAc)$_2$]	85	> 300	3.80	49.64 (50.73)	4.32 (4.75)	17.44 (17.26)	10.49 (10.33)
[CuHtop(OAc)$_2$	85	> 300	1.76	50.67 (50.30)	4.96 (4.71)	16.92 (17.11)	10.96 (11.09)
[ZnHtop(OAc)$_2$]	80	> 300	--	50.25 (50.13)	4.64 (4.70)	16.94 (17.06)	11.54 (11.38)

Infrared Spectra

The most important feature of the ir spectrum of the compound is the absence of any signal assignable to free or hydrogen bonded acetylcarbonyl function. Thus no absorption peak is observed in the ir spectrum of the compound in the 1650-1800 cm^{-1} region where the carbonyl stretching bands of these types of compounds appear. However the spectrum in the regions 1600-1650cm^{-1} displayed three medium intensity bands at 1628, 1615 and 1605cm^{-1} and several bands in the 1550-1600cm^{-1} range. The origin of these bands can only be associated with the stretching of various

C=N and C=C functions. The ir data together with the elemental analytical data strongly favours structure **13** of the compound.



13

The spectrum consist of a considerably broad band in the range 3000-3500 cm^{-1} and several weak but prominent absorption in the 2500-3000 cm^{-1} region. The former broad band indicate the involvement of the NH and NH_2 protons in hydrogen bonding and the latter bands are due to various νC-H vibrations.

A comparison of the spectrum of the compound with the spectra of schiff bases reported in section 1 of the chapter, revealed the presence of several medium intensity bands in the range 1500-1550 cm^{-1} and 1250-1300 cm^{-1}. The former bands are typical of imine ligands containing NH groups due to its inplane bending vibration and the later bands are characteristic of compounds containing C–N groups. The observed values are given in table 12.

TABLE 12

Characteristic ir data (cm^{-1}) of Htop and its metal complexes

Compound	CH_3COO					
	νCO	νCH	νC=N	νNH	νCN	νM–N
Htop	--	--	1625 1615 1605	1535 1520	1290 1282 1275	--
[Co(Htop)$(OAc)_2$]	1632	1312	1622 1608 1562	1530 1510	1282 1268 1252	545 532 528
[Ni(Htop)$(OAc)_2$]	1635	1308	1620 1600 1568	1522 1508	1280 1265 1248	543 530 525
[Cu(Htop)$(OAc)_2$]	1638	1315	1620 1602 1570	1532 1505	1288 1270 1245	540 522 518
[Zn(Htop)$(OAc)_2$]	1625	1308	1628 1610 1575	1530 1502	1292 1272 1255	530 521 519

Nmr spectra

The ^1H nmr spectrum of the compound shows a low field one proton signal at δ 8.02 ppm. This signal cannot be assigned to an intramolecularly hydrogen boned N–H...O= or O–H...N= group, since the former usually appears in the region δ >15 ppm and the latter in the 10-14 ppm range. However, considering the broad nature of the signal it can be associated with the weakly hydrogen boned hydrazone NH of structure **13**. Similarly the slightly broadened two proton signals in the range 4.60 - 4.75 ppm may probably from the

resonance of the two aryl NH_2 groups of the structure. The integrated intensities of the two three proton signals at δ 2.56 and 2.62 ppm due to the methyl protons agree well with the formulation of the compound. The aryl protons are observed in the region 6.69-7.75 ppm.

Mass Spectrum

The mass spectrum of the compounds is given in fig. 8. The most intense peak (other than the matrix peaks) is at m/z 391 corresponds to the molecular ion of structure **13**. Peaks due to the elimination of $C_3H_3N_3S$, $C_6H_5NH_2$ etc. are also observed in the spectrum.

Characterisation of metal complexes of Htop

The elemental analytical data of the Co(II), Ni(II), Cu(II) and Zn(II) complexes of Htop are given in table 11 along with other physical data. The observed C, H, N and M percentage support the values calculated on the basis of $[M(Htop)(OAc)_2]$ composition of the complexes. The complexes are non-conducting in dmf. The Zn(II) complex is diamagnetic and all others show normal paramagnetic moment expected of octahedral coordination. The ir, nmr and mass spectral data of the complexes are discussed with a view to determine the nature of bonding.

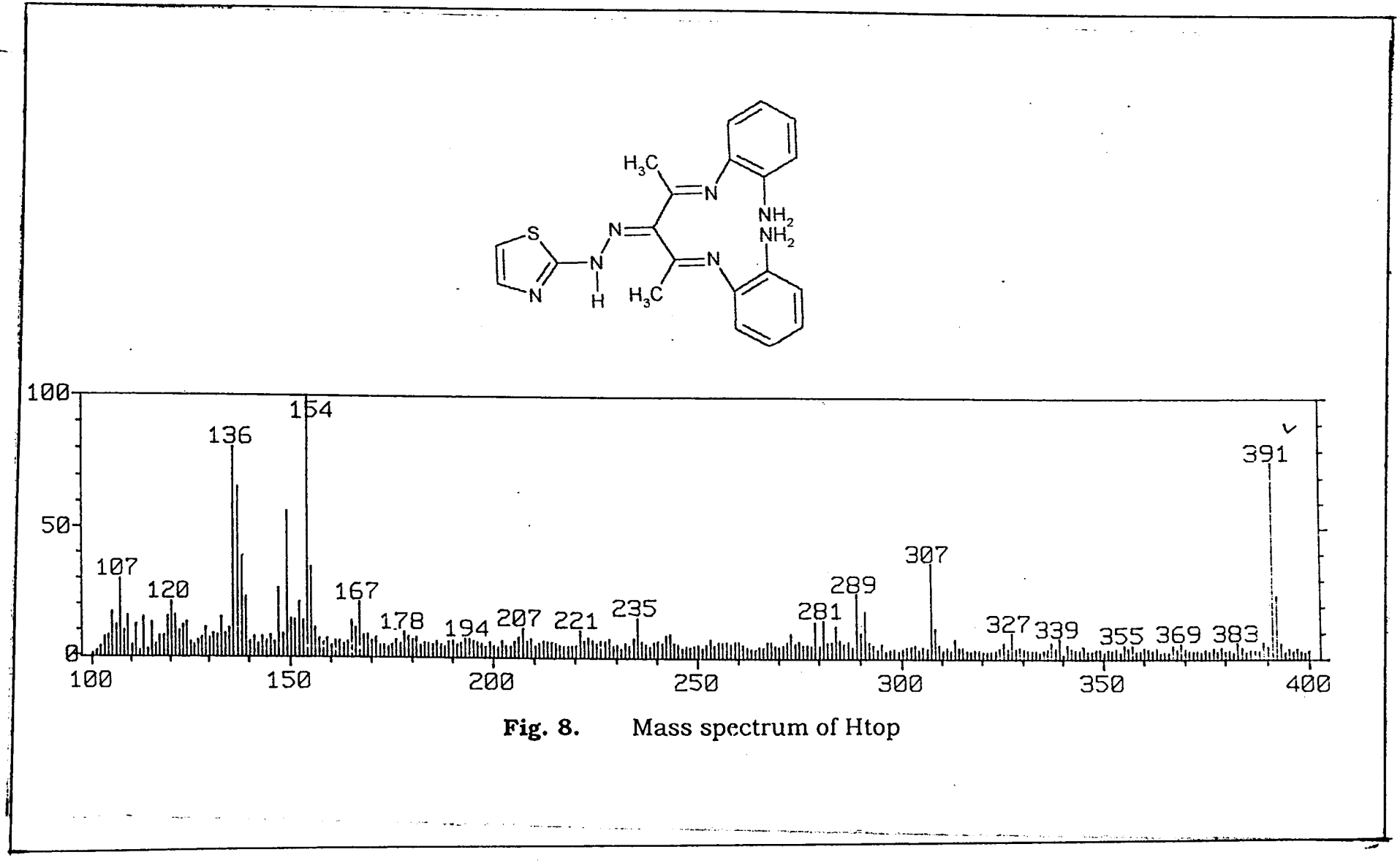
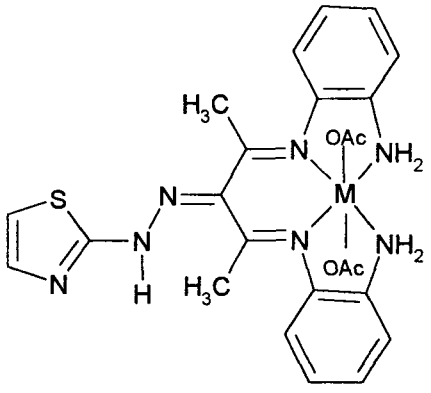


Fig. 8. Mass spectrum of Htop

Infrared spectra

A characteristic feature of the spectra of all the complexes is the presence of a comparatively strong new band at ~ 1630 cm^{-1} and another band at ~ 1300 cm^{-1}. The position of the bands due to the stretching of C=N groups shifted appreciably to low frequencies. Since the complexes contain coordinated acetate groups the band at ~ 1630 and ~ 1300 cm^{-1} can safely be assigned to the stretching of C=O (free) and C–O coordination respectively of the unidentate coordinated acetate groups. The unidentate coordination is indicated by the large difference (Δ ~ 330 cm^{-1}) between the two bands. This is further confirmed from the presence of a new medium intensity band at ~ 420 cm^{-1} in the spectra of all the complexes.

Since some of the νC=N bands of the free ligand shifted to lower values suggest the involvement of at least two of the C=N groups in coordination with metal ion. The ring νC=N of 2-thiazolyazo-2,4-pentanedione usually shows absorption at 1615 cm^{-1}. For steric reasons all the four C=N groups cannot be simultaneously engage in boding with the same metal ion. Therefore the most probable mode of bonding of the ligand with the metal ion will be as in structure **14**.



14

The ligand behaves as tetradentate neutral N_4 donor with the formation of two five membered and one six membered chelate ring with the metal ions is clearly indicated from the ir spectral data. Evidently the metal ion will be in a square planar environment of the four nitrogens of the schiff base and the two acetate groups occupy the *trans* positions of an overall octahedral structure. The appearance of atleast two new bands in the 500-550 cm^{-1} in the complexes are probably due to νM-N vibrations in addition to a slightly broadened band at ~ 3200 cm^{-1}. This may be due to weak hydrogen bonding possible of these type of compounds. Important bands and their probable assignments are given in table 12.

Nmr spectra

The proton nmr spectrum of zinc(II) complex also support the structure **14** of the complex. Thus the hydrazone NH proton signal remained almost unaffected in the spectrum of the complex.

Similarly the NH_2 proton signals appeared at slightly low field compared to the free ligand. The methyl group signals of the ligand appeared at δ 2.65 and 2.70 ppm. A new six proton signal present at $\delta \sim 2.1$ ppm is due to the coordinated acetate methyl group. The aryl protons are observed in the 6.70 - 7.80 ppm range.

B. Synthesis and characterisation of thiazolylazoacetylacetone-bismeta-phenylenediimine, Htmp, and its metal complexes.

Experimental

Synthesis of Htmp

Meta-phenylenediamine in ethanol (1.08 g, 0.01 ml, 20 ml) was added to an ethanolic solution of thiazolyazocetylacetone (2.11 g, 0.01 mol, 20 mL) and the mixture was refluxed for about 2 h. The resulting solution was concentrated to half the volume and cooled. The crystalline product formed was filtered and recrystallised from hot methanol to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

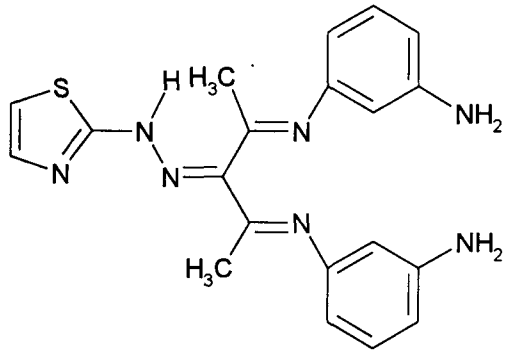
Nickel(II), copper(II) and zinc(II) complexes of the compound were prepared as given below.

A concentrated aqueous solution of metal(II) acetate (0.01 mol) was added to a methanolic solution (0.01 mol, 20 mL) of the ligand and the mixture was refluxed for ~ 2 h on a boiling water bath and the volume was reduced to half. The precipitated complex was filtered, washed with excess water and recrystallised from hot methanol.

Results and discussion

Characterisation of Htmp

The observed elemental analytical data of the compound given in table 13 suggest that one molecule of thiazolazoacetylacetone reacted with two molecules of 1,3-diaminobenzene. The compound shows sharp melting point and is soluble in common organic solvents. The ir, ^1H nmr and mass spectral data of the compound is compatible with the structure **15** of the compound.



15

Infrared spectra

In the spectrum of the compound no band assignable to free or hydrogen bonded acetyl carbonyl is observed. In the region 1600-1800 cm^{-1} showed three strong bands at 1628, 1616 and 1610 cm^{-1}. Since these bands cannot originate from the stretching of acetyl carbonyl groups, they can confidently be assigned to various νC=N vibrations of structure **15** of the compound. From a comparison of

the reported spectra of thiazolazoacetylacetone and related compound[149] the band at 1628 cm^{-1} arises from the stretching of the thiazole C=N group and the bands at 1616 and 1610 cm^{-1} are respectively due to the imine and hydrazone C=N functions.

TABLE 13

Analytical and physical data of Htmp and its complexes

Compound	Yield %	M.P. °C	μ_{eff} B.M.	Elemental analysis % Found / (Calcd.)			
				C	H	N	M
Htmp	701	178		61.00 (61.38)	5.78 (5.37)	26.00 (25.06)	--
[Co(Htmp)(OAc)$_2$]	70	> 300	3.72	49.44 (50.71)	4.34 (4.75)	16.94 (17.25)	9.89 (10.37)
[Ni(Htmp)(OAc)$_2$]	75	> 300	2.85	51.04 (50.73)	4.34 (4.75)	17.00 (17.26)	10.01 (16.33)
[Cu(Htmp)(OAc)$_2$]	75	> 300	1.78	49.44 (50.30)	4.98 (4.71)	16.95 (17.11)	11.88 (11.09)
[Zn(Htmp)(OAc)$_2$]	70	> 300	--	49.44 (50.13)	4.32 (4.70)	17.00 (17.06)	12.00 (11.38

That the compound contain unassociated N–H bands is evident from the presence of broadened bands at 3300 and 3450 cm^{-1}. The slightly broadened nature of these peaks suggest that the intramolecular hydrogen boding in the compound is not so predominant and is only very weak N–H...N compared to O–H...N or C=O...H–N. The spectrum is given in figure 9. The observed values are given in table 14.

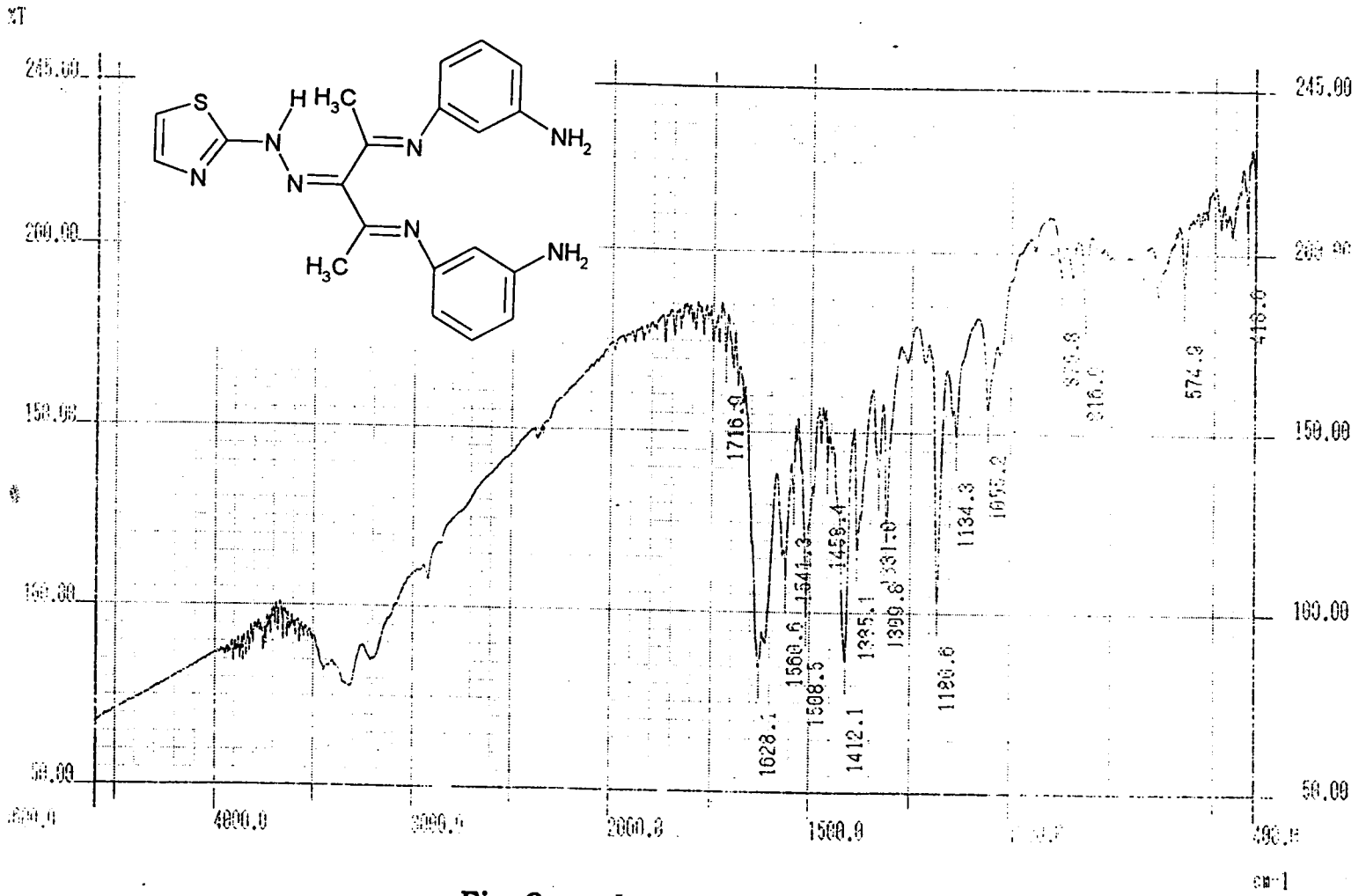


Fig. 9. Ir spectrum of Htmp

Nmr Spectra

The ^1H nmr spectrum of the compound shows the absence of any signal due to N–H...O or O–H...N hydrogen banded proton. However the spectrum is characterised by the presence of a one proton signal at δ 8.29 due to an NH proton which is only slightly associated with the neighbouring electronegative atom of the molecule. The presence of two proton signal at 2.88 and 2.89 ppm of the spectrum can be assigned to the NH_2 proton of structure **15**. The methyl proton appeared at δ 2.60 ppm and the aryl proton in the region 7.13 - 8.03 ppm.

TABLE 14

Characteristic ir band of Htmp and its metal complexes

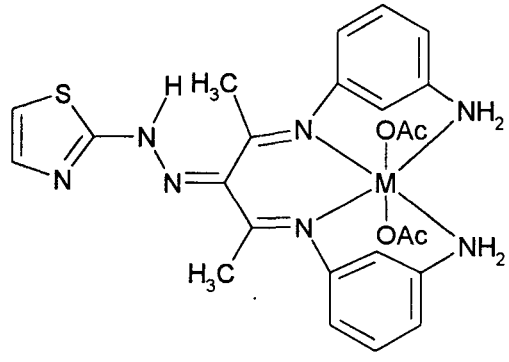
Compound	νCO	νCO	νC=N	δN–H	νC–N	νM–N
Htmp			1628 1616 1610	1538 1520	1282 1275 1268	--
[Co(Htmp)(OAc)$_2$]	1632	1305	1620 1610 1595	1535 1515	1268 1252 1235	528 510
[Ni(Htmp)(OAc)$_2$]	1630	1315	1618 1508 1592	1528 1522	1274 1262 1251	522 515
[Cu(Htmp)(OAc)$_2$]	1628	1328	1615 1605 1598	1527 1519	1265 1248 1228	532 510
[Zn(Htmp)(OAc)$_2$]	1622	1320	1622 1612 1600	1535 1508	1280 1268 1260	515 505

Mass Spectra

The mass spectrum of the compound is reproduced in figure 10. One of the most prominent peak in the spectrum is due to the molecular ion at m/z 391. Thereby confirming the proposed structure **15** of the compound. Other important peaks in the spectrum are due to the elimination of N_2, CH_3CN, $PhNH_2$, thiazole, etc. groups from parent ion.

Characterisation of metal complexes

The ligand formed well defined crystalline complexes with Co(II), Ni(II), Cu(II) and Zn(II) metal ions. All complexes behave as non-electrolytes in dmf and do not contain the anion of the metal salt used for their preparations. The observed carbon, hydrogen and nitrogen percentages together with the metal content given in table 13 can be accounted by considering the $[M(Htmp)(OAc)_2]$ stoichiometry of the complexes. The ir, ^1H nmr and mass spectral data, discussed below, is in agreement with the nature of bonding of the ligand in the complexes as in structure **16**.



16

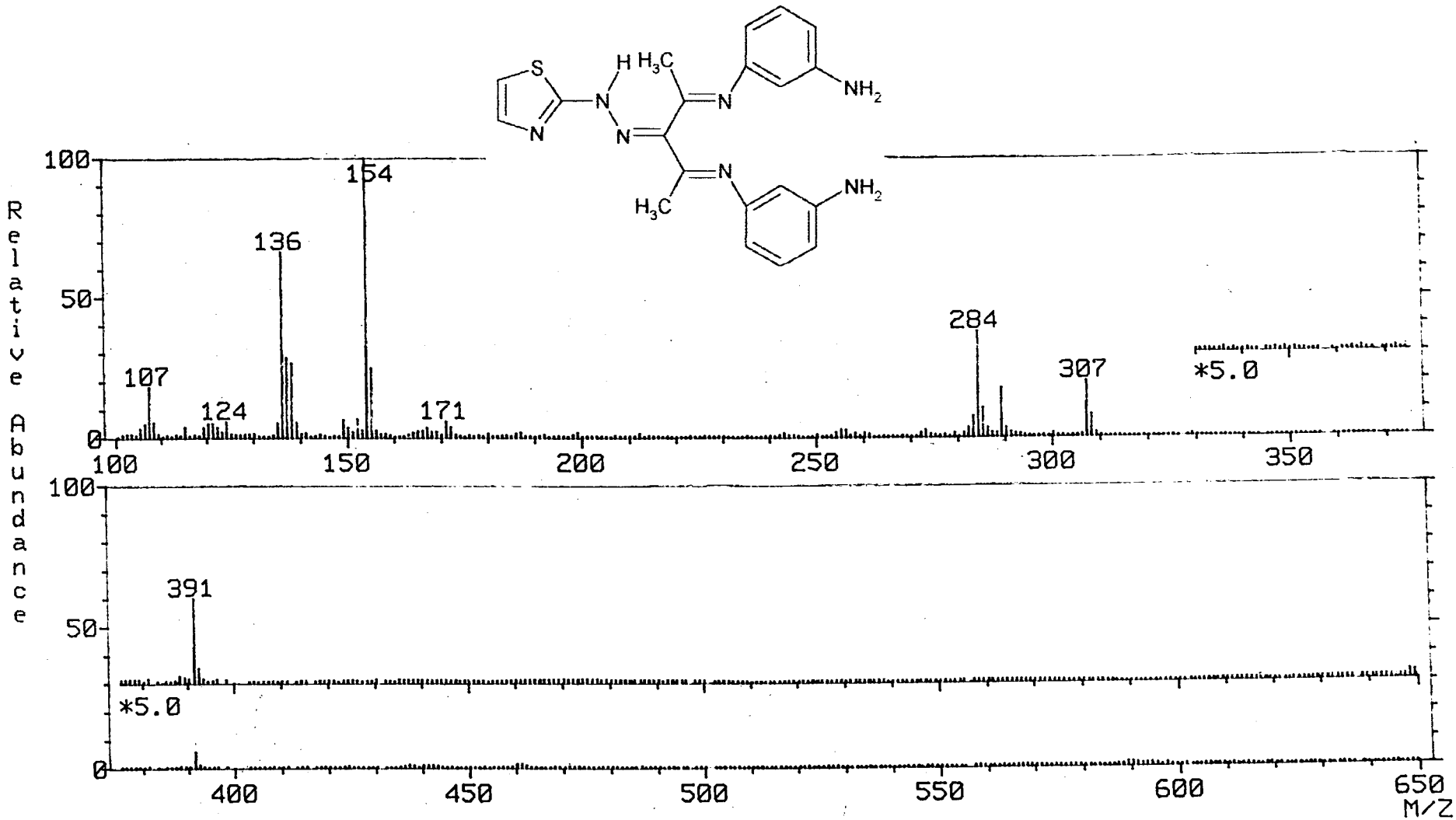


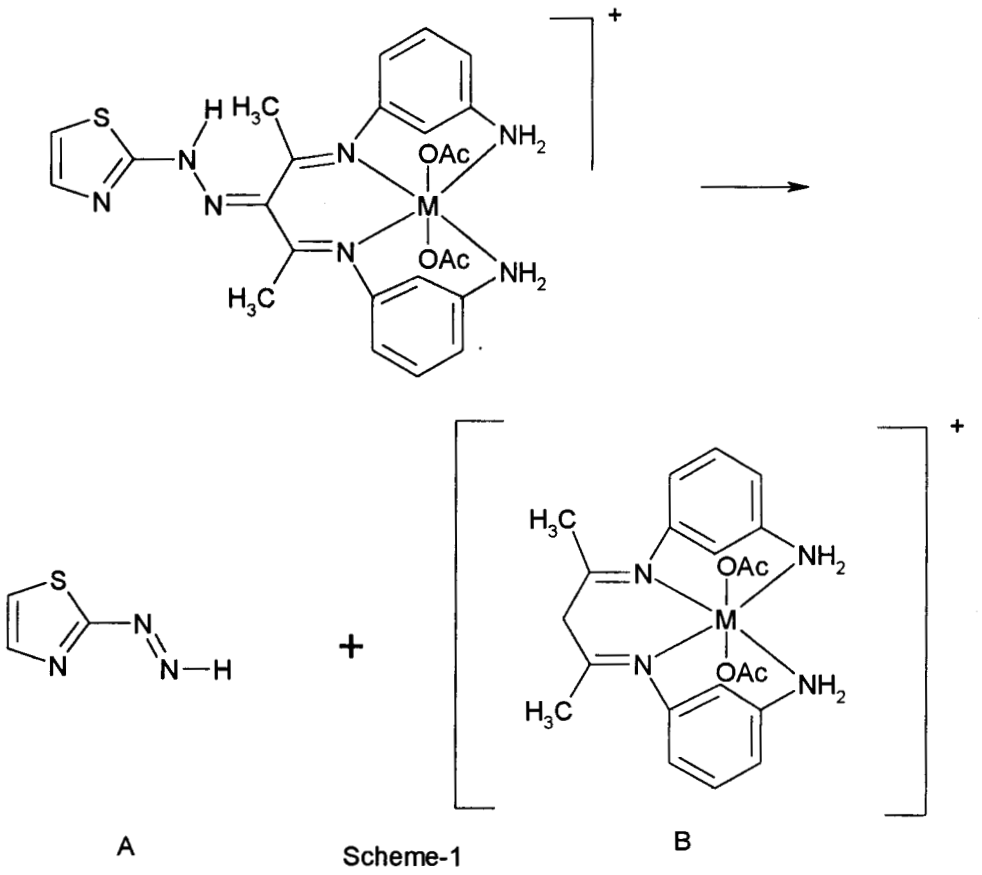
Fig. 10. Mass spectrum of Htmp.

The ir spectra of the complexes displayed three prominent bands in the 1590-1800 cm^{-1} region. The band at ~ 1630 cm^{-1} can be assigned to the stretching of C=0 of the monodentate coordinated acetate group and the bands at ~ 1620 and 1610 cm^{-1} are respectively due to thiazole C=N and the hydrazone C=N. The medium intensity band at ~ 1595 cm^{-1} originate from the metal bonded C=N groups. The broad band in the region 3200-3500 cm^{-1} of the free ligand cleared up and several bands appeared in the region assignable to the various νN-H vibrations. The spectra of all the complexes contain additional bands at ~ 425 cm^{-1} and ~ 550 cm^{-1} due to νM-O and νM-N absorptions. Important bands and their probable assignment are given table 14.

In the proton nmr spectrum of the zinc(II) complex the signal at δ 8.29 only marginally shifted indicating that this proton is not replaced by the metal ion. The NH_2 proton signals shifted to low field indicating the involvement of these groups in complex formation. The integrated intensity and position of the methyl protons are in conformity with the structure of the complexes.

The mass spectrum of the copper(II) complex showed the presence of a peak due to molecular ion at m/z 572 and 574. However the most intense peak in the spectrum is at m/z 459. The appearance of this peak can be accounted by elimination of the

fragment A, with the formation of stable ion B from the molecular ion as in scheme 1. The spectrum is reproduced in figure 11. Other fragments in the spectrum can be accounted by the elimination of CH_3, CH_3COO, $PhNH_2$, etc. from B.



Scheme 1

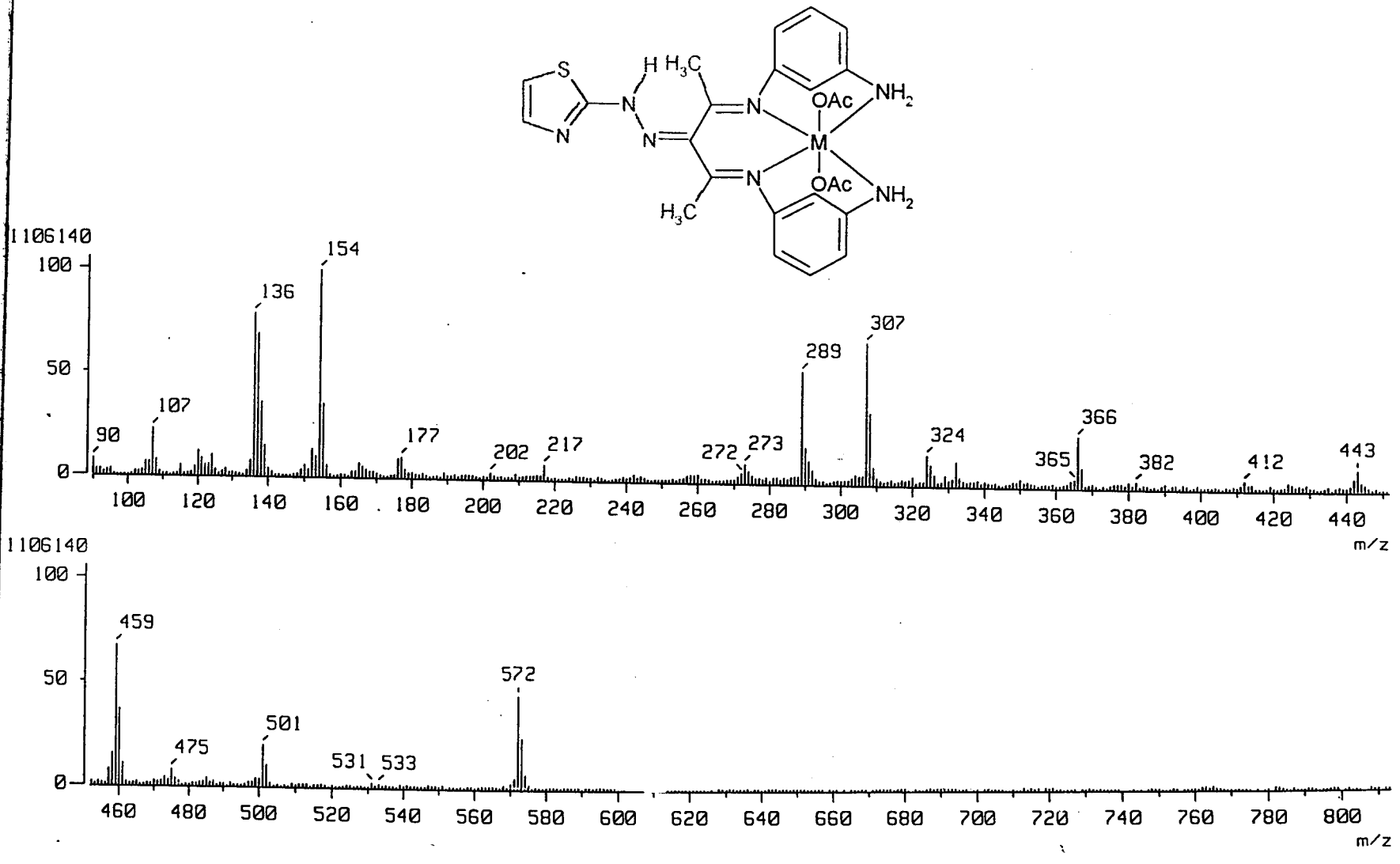


Fig. 11. Mass spectrum of [$CuHtmp(OAc)_2$]

C. Synthesis and characterisation of thiazolylazoacetylacetone *para*-phenylenediimine, H_2tpp and its metal complexes

Experimental

Synthesis of H_2tpp

A hot ethanolic solution of *para*-phenalenediamine (1.08 g, 0.01 mol, 20 mL) was added to an hot ethanolic solution of thiazolylazoacetylacetone (2.1 g, 0.01 mol, 20 mL) and the mixture was refluxed on a boiling water bath for ~ 4 h. The volume was reduced and the solution poured into crushed ice with vigorous stirring. The crystalline product formed was filtered and recrystallised from hot methanol twice to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

Ni(II), Cu(II) and Zn(II) complexes of the compound were prepared by the following method.

A concentrated aqueous solution of metal(II) acetate (0.01 mol) was added to an ethanolic solution of the ligand (0.01 mol, 20 mL) and the mixture refluxed on a boiling water bath for ~ 4 h and the precipitated complex was filtered, washed with excess water and then with methanol, dried in vacuum.

Results and discussion

Characterisation of H_2tpp

The schiff base condensation reaction between 1,4-diaminobenzene and thiazolazoacetylacetone yielded a crystalline compound with sharp melting point and soluble in common organic solvents. The observed C, H and N percentage given in table 15 clearly suggest that unlike the 1,2- and 1,3-diaminobenzene, one molecule of 1,4-diaminobenzene reacted with two molecules of thiazolazoacetylacetone to form the schiff base. The ir, ^1H nmr and mass spectral data of the compounds also agree well with this observations.

TABLE 15

Analytical and physical data of H_2tpp and its complexes

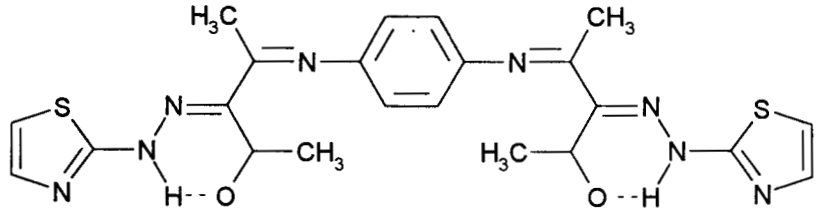
Compound	Yield %	M.P. °C	Elemental analysis % Found/(Calcd.)			
			C	H	N	M
H_2tpp	70		52.84 (53.65)	3.95 (4.06)	21.34 (22.76)	--
$[Ni_2(tpp)_2]$	60	> 300	47.45 (48.13)	3.00 (3.28)	21.30 (20.41)	10.90 (10.70)
$[Cu_2(tpp)_2]$	65	> 300	48.00 (47.69)	3.48 (3.25)	21.00 (20.23)	11.88 (11.47)
$[Zn_2(tpp)_2]$	65	> 300	47.78 (47.53)	3.56 (3.24)	19.82 (20.16)	11.94 (11.77)

Infrared spectra

The infrared spectrum of the compound consists of a strong band at 1655 cm^{-1}. The origin of this band can only be attributed to the stretching of acetyl carbonyl group. The νCO of free acetyl carbonyl usually appears in the 1700-1720 cm^{-1} conjugation decreases the value to the range 1670-1700 cm^{-1}. Further shift to lower values is possible when C=0 is H-bonded to O–H or N–H groups. In general C=0...H–N shows much lower value than C=O...H–O hydrogen bonding. This has been well established, in the case of arylazo derivative of several 1,3-diketones.[183,184] Thus the exact values of acetyl carbonyl stretching depends on the degree of conjugation and also on the type of intramolecular H-bonding and its strength.

In the compound under study the νC=0 vibration observed at low value suggest that the carbonyl group is a part of highly conjugated system and also it is involved in strong intramolecular hydrogen bonding of the type C=O...H–N. The spectrum of the compound in the 1600-1650 cm^{1} region also displayed three medium intensity bands at 1608, 1615 and 1630 cm^{-1}. From a comparison of the spectral data of compounds discussed in earlier sections these bands can be assigned to νC=N of hydrazone, imine and thiazole groups respectively.

In the region 2000-4000 cm^{-1} no band appeared assignable to νNH or various νC-H. Instead the spectrum showed a broad band in the range 2500-3500 cm^{-1} (fig. 12) which indicate the existence of strong intramolecular hydrogen bonding in the compound. Thus the ir spectrum strongly favour the structure **17** of the compound. The observed values are given in table 16.



17

Nmr spectra

The ^1H nmr spectrum of the compound is characterised by the presence of low field two proton signal at δ 14.82 ppm. This signal can readily be assigned to intramolecularly hydrogen bonded NH protons of structure **17**. The methyl protons of H_3C–C=N at δ 2.63 (6H) and that of H_3C–C=0 at δ 2.52 (6H) ppm present in the spectrum also agree with the structure. The phenyl proton signals in the range 7.260-7.50 and the thiazyl protons in the range 6.85 - 7.10.

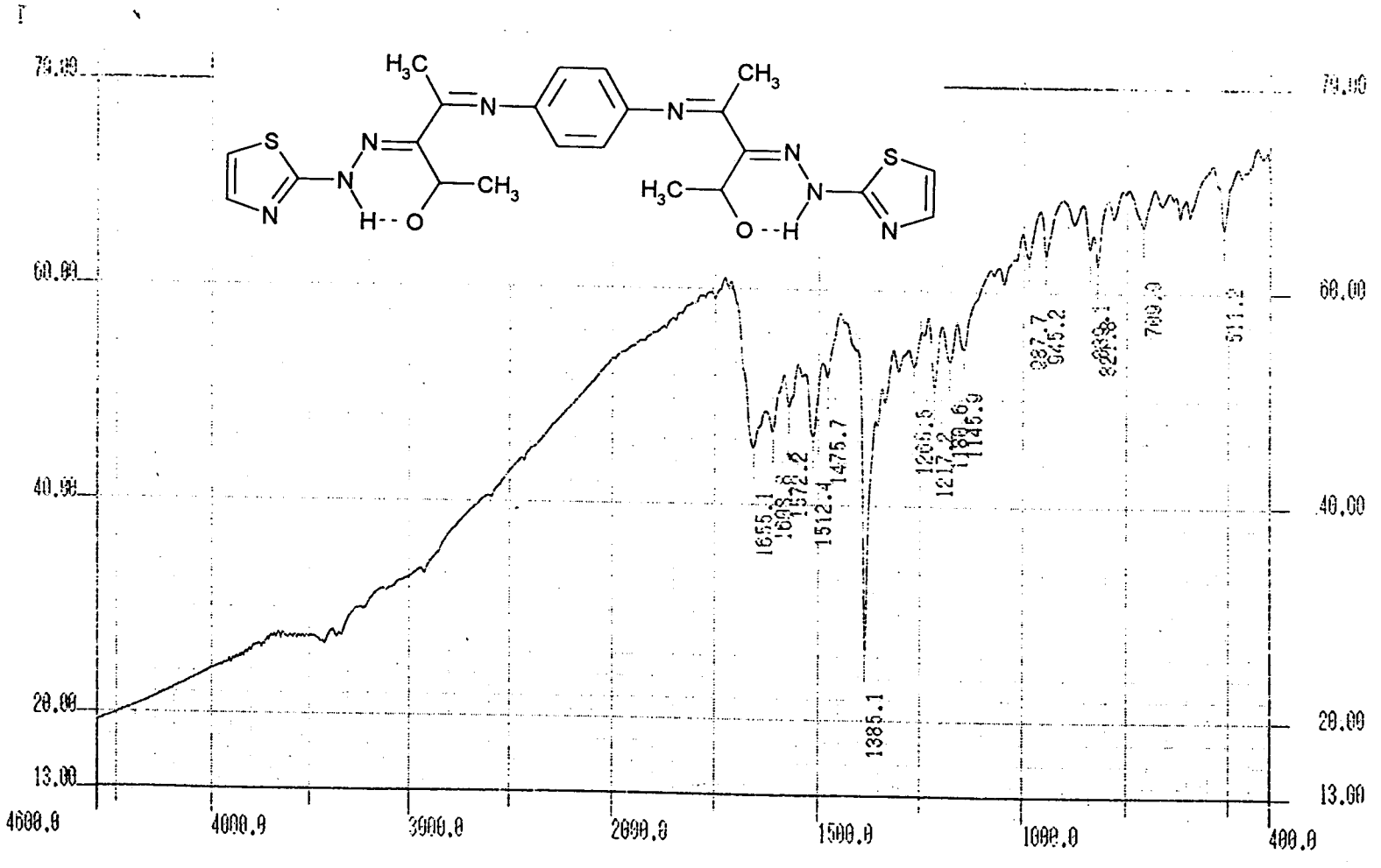


Fig. 12. Ir spectrum of H_2tpp.

TABLE 16

Characteristic ir spectral data of Htap and its metal complexes (stretching bands, cm^{-1})

Compound	C=O	C=N	C–N	M–N	M–O
H_2tap	1655	1630, 1615 1608	1282 1269	--	--
[Ni_2(tap)$_2$]	1560	1612 1600 br	1285 1260	532 525	432 422
[Cu_2(tap)$_2$]	1558	1615, 1608 1600	1278 1255	538 520	428 430
[Zn_2(tap)$_2$]	1562	1610, 1605 1598 br	1275 1265	442 528	435 418

Mass spectra

The FAB mass spectrum of the compound is given in figure 13. The spectrum shows an intense $(P+1)^+$ peak at m/z 495 corresponds to the molecular mass of the compound. Peaks due to the elimination CH_3, CH_3CO etc from molecular ion are marked in the spectrum. However the base peak in the compound is due to a fragment at m/z 302. The origin of the fragment can be explained by the probable formation of the stable ion from the molecular ion as given in structure **17.**

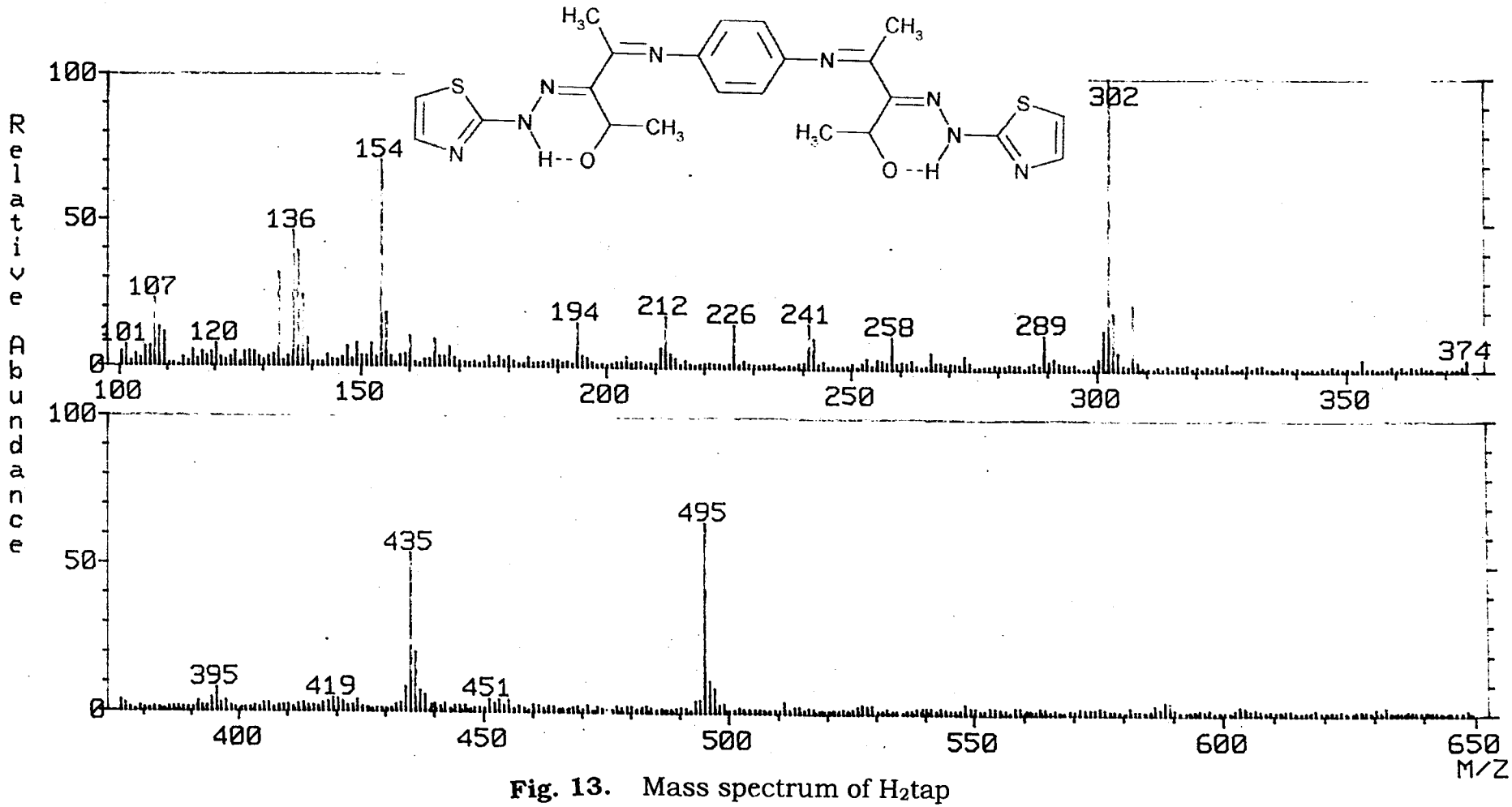


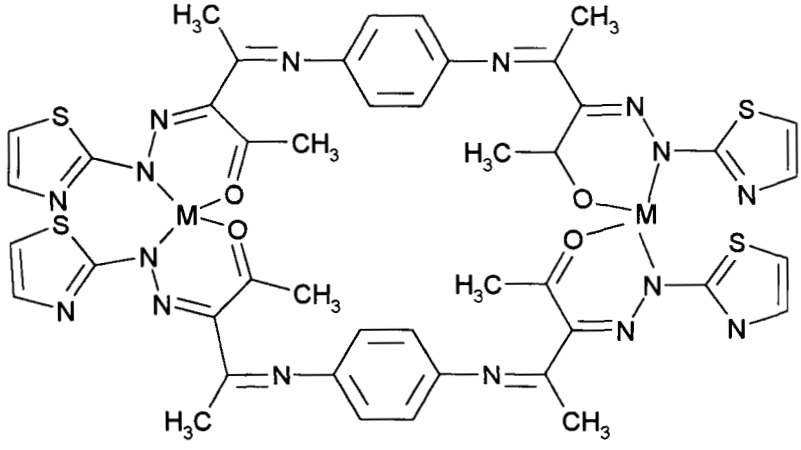
Fig. 13. Mass spectrum of H_2tap

Characterisation of metal complexes

Nickel(II), copper(II) and zinc(II) ions formed stable metal complexes with H_2tap. The C, H, N and metal content of complexes are given in table 15. The data indicate 1:1 stoichiometry of all the complexes. The copper(II) complexes show normal paramagnetic moment and the nickel(II) and zinc(II) complexes are diamagnetic. Conductivity measurements indicate that all the complexes are 'non-ionic'. Molecular weight of the complexes determined by Rast's method suggest $[M_2L_2]$ composition. The ir, ^{1}H nmr and mass spectral data of the complexes are discussed below.

Infrared spectra

The ir spectra of the complexes are compatible with the structure that would result if the intramolecularly hydrogen bonded hydrazone protons are replaced by the metal ion as in structure **18**.



Thus the position of the intramolecularly hydrogen bonded acetyl carbonyl of the free ligand disappeared in the spectra of all complexes and instead a new band appeared at ~ 1560 cm^{-1} assignable to metal bonded carbonyl function. The C=N bands of the uncomplexed ligand also shifted to lower value. That the replacement of intramolecularly hydrogen bonded hydrazone hydrogen by metal ion is clearly indicated from the disappearance of the broad free ligand band in the 2500-3500 cm^{1} in the spectra of all the complexes. Instead several weak and medium intensity bands appeared in the region due to the stretching of various C–H groups. Another prominent feature of the spectra of all the complexes, compared to the ligand spectra is the presence several new bands in the 420-450 cm^{-1} and 520-550 cm^{-1} regions assignable to νM-O and νM-N vibrations respectively. Important ir bands and their probable assignments are brought out in table 16.

Nmr spectra

In agreement with the structure **18** proposed, the ^{1}H nmr spectra of the diamagnetic nickel(II) and zinc(II) complexes, the low field signal due to the chelated hydrazone hydrogen of the free ligand disappeared. The spectra of the complexes displayed two signals at ~ 2.50 ppm and ~ 2.65 ppm of equal intensity assignable to methyl protons. The integrated intensity of the signal correspond to 12H.

This is expected of structure **18** of the complex. The phenyl and thiazolyl protons appeared as a complex multiplet in the 6.80-7.80 ppm region. Thus both the ir and nmr spectra support structure **18** of the complexes.

Electron spin resonance (esr) spectroscopic studies of copper(II) complexes

Electron spin resonance spectral data of paramagnetic metal complexes highly instructive in revealing the nature of metal-ligand bond, particularly the covalent character.[187] It has been well established that 'g' values are sensitive to the covalent nature of the metal-ligand bond. In general the g value above 2.3 shows ionic character and lower values indicate covalent character.[188,189]

The g_{av} values of the three copper(II) complexes of the thiazolylazoacetylacetone phenylenediimines are given below:

Complex	g_{av}
$[Cu(Htop)(OAc)_2$	2.098
$[Cu(Htmp)(OAc)_2]$	2.090
$[Cu_2(tpp)_2]$	2.080

The data indicate that the complex of the Sciffbase thiazolylazoacetylacetone *para*-phenylenediimine have greater covalent character. This is not unxpected considering the proposed

structure of the complex. In this structure extensive delocalisation is possible compared to the other complexes.

The esr spectrum of $[Cu_2(tpp)_2]$ was recorded also in solution. The spectrum showed four peaks each evidently due to the coupling of the electron spin with the spin of the ^{63}Cu nucleus (I = 3/2). The peaks are broad and have the appearance of ill-resolved multiplets. This can be attributed as due to hyperfine splitting of the coordinated nitrogens of the ligand.

CHAPTER 4

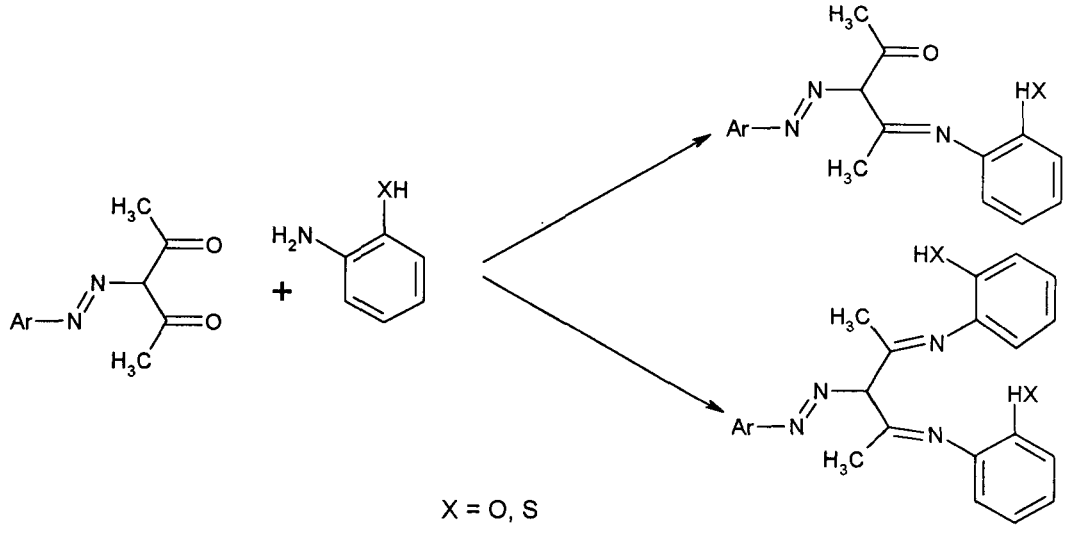
METAL COMPLEXES OF SCHIFF BASE LIGANDS DERIVED FROM THE 3-ARYLAZO-2,4-PENTANEDIONES WITH 2-AMINOPHENOL AND 2-AMINOTHIOPHENOL

CHAPTER 4

METAL COMPLEXES OF SCHIFF BASE LIGANDS DERIVED FROM THE 3-ARYLAZO-2,4-PENTANEDIONES WITH 2-AMINOPHENOL AND 2-AMINOTHIOPHENOL

Phenylazo- and thiazolylazo-2,4-pentanediones on reaction with 2-aminophenol and 2-aminothiophenol yielded a new series of polydentate schiff base ligand systems that form stable chelate complexes with a number of metal ions. The synthesis and characterisation of these ligands and their metal complexes are considered in this chapter.

Two types of condensation reaction are possible for the 3-arylazo-2,4-pentanediones with 2-aminophenol and 2-aminothiophenol. Without considering the actual tautomeric forms, the reaction can be represented as below.



Scheme 1

Careful analysis of the spectral and analytical data of the compound obtained (presented in the results and discussion section) revealed that the final product depends not only on the aryl group but also on the XH group (X = 0, S) of the amino compound. Thus the reaction led to some new ligand systems. However it is to be pointed out that in all the cases only one product was formed. Therefore the synthesis and characterisation of these four Schiff base ligands and their metal complexes are presented separately in this chapter.

A. Synthesis and characterisation of phenylazoacetylacetone aminophenol, H_2paa and its metal complexes

Experimental

Synthesis of H_2paa

Phenylazoacetylacetone was synthesised as reported by the diazo-coupling of aniline with acetylacetone as given in chapter 2.

An ethanolic solution of 2-aminophenol (1.09 g, 0.01 mol, 20 ml) was added to an ethanolic solution of phenylazoacetylacetone (2.04 g; 0.01 mol, 20 mL). The mixture was refluxed on a boiling water bath for ~ 5 h and kept over night. The solution was then poured into hot water (~ 70°C) with vigorous stirring. The precipitated compound was filtered and washed with hot water. It is recrystallised from hot methanol twice to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

The Ni(II), Cu(II), Zn(II) complexes of the compound was prepared by the following methods.

A concentrated aqueous solution of metal(II) acetate (0.001 mol) was added to an ethanolic solution of the ligand (0.001 mol, 20 mL) and the mixture was refluxed for ~ 2 h on a boiling water bath.

The precipitated complex was filtered, washed with water and then with methanol and dried in vacuum.

Results and discussion

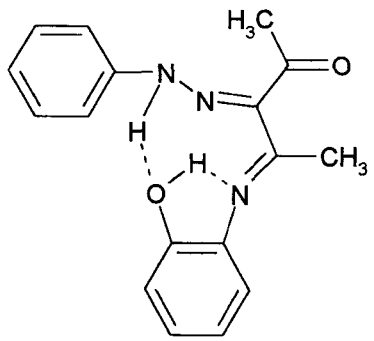
Characterisation of H_2paa

Elemental analytical data of the reaction product of phenylazoacetylacetone with 2-aminophenol (Table 1) suggest that the condensation has occurred in the 1:1 ratio. The observed ir, nmr and mass spectral data of the compound are in agreement with structure **1**. The spectral data are discussed below.

Infrared spectra

The ir spectrum of the compound in the 1600-1800 cm^{-1} region is characterised by the presence of two strong bands at 1678 cm^{-1} and 1624 cm^{-1} and a slightly broadened intense band at 1591 cm^{-1}. The 1678 cm^{-1} band is undoubtedly due to a conjugated free acetyl carbonyl stretch and the 1624 cm^{-1} band can be assigned to the stretching of the C=N functions. The νC=C vibration appeared as a broad band with maximum at 1591 cm^{-1}. The broad band observed in the 2500-3500 cm^{-1} is due to the involvement of the acidic NH and OH protons in strong intramolecular hydrogen bonding. The most important conclusion that can be derived from the ir spectrum is that the compound contain one conjugated acetyl carbonyl group.

Further the phenolic OH and hydrazone NH protons are intramolecularly hydrogen bonded as in structure **1**.



1

Nmr spectra

The ^1H nmr spectrum of the compound shows two one proton singlet at δ 15.45 and δ 10.80 ppm which indicates that the compound contain two acidic protons. The appearance of this signals in the low field also suggest their involvement in strong intramolecular hydrogen bonding. The methyl proton signals are observed as two singlets at δ 2.32 (3H) and δ 2.58 (3H). Absence of any signal due to methine proton support the hydrazone form of the compound. The aryl protons appeared in the range 6.8-7.8 ppm as a complex multiplet.

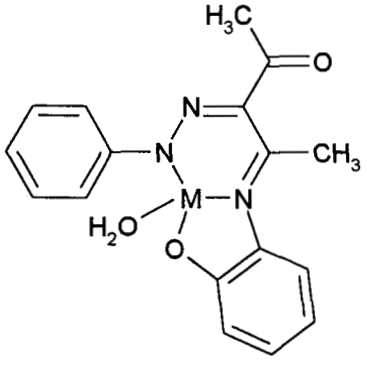
Mass spectra

The mass spectrum of the compound shows intense molecular ion peak at m/z 295 in agreement with the structure 1. Peaks due

to the elimination of CH_3CO (m/z 45), C_6H_5NH (m/z 92), C_6H_5O (m/z 93), C_6H_5 (m/z 77) from the molecular ion are, all present in spectrum. Thus the observed spectral data fully support structure **1** of the compound.

Characterisation of metal complexes

Nickel(II), copper(II) and zinc(II) ions formed well defined complexes with **H_2paa**. The observed C, H, N and metal percentages suggest their 1:1 metal ligand stoichiometry (Table 1). All the complexes are non electrolyte in dmf and do not contain the anion of the metal salt used for their preparation. The Ni(II) and Zn(II) complexes are diamagnetic and Cu(II) complexes showed a magnetic moment of 1.78 BM. The ir, nmr and mass spectral data can be conveniently explained by considering the structure **2** of the complexes.



2

TABLE 1

Analytical and Physical data of H_2paa and its complexes

Compound	M.P. °C	Elemental analysis (%) Found / (Calcd.)			
		C	H	N	M
H_2Paa	72	69.00 (69.15)	5.44 (5.76)	14.10 (14.23)	--
[Ni(Paa)(H_2O)]	> 300	52.34 (55.18)	4.76 (4.59)	11.58 (11.36)	14.96 (15.87)
[Cu(Paa)(H_2O)]	> 300	55.00 (54.46)	4.86 (4.53)	11.37 (11.21)	16.80 (16.96)
[Zn(Paa)(H_2O)]	> 300	54.90 (54.20)	4.76 (4.51)	11.28 (11.15)	17.59 (17.37)

Infrared spectra

The acetylcarbonyl band of the ligand at 1678 cm^{-1} remained almost unaffected in the spectra of all the complex which indicate that the carbonyl group is not involved in bonding with the metal ion. The band at 1628 cm^{-1} due to νC=N shifted to lower wave number and appeared as a new band at ~ 1600 cm^{-1} in the spectra of all the complexes. The broad free ligand band in the region 2500-3500 cm^{-1} cleared up in the spectra of all the complexes and instead several medium intensity bands assignable to various aliphatic and aromatic νC-H vibrations appeared. This suggest that the intramolecularly hydrogen bonded OH and NH protons are replaced by metal ion as in structure **2**. Spectra of all the complexes show

additional medium intensity bands in 420-450 cm^{-1} and 500-550 cm^{-1} presumably due to νM-O and νM-N vibrations. That the complex contain coordinated water molecule is clearly indicated from the presence of band at ~ 3500 cm^{-1} in the spectra. Important bands are tabulated in table 2.

TABLE 2

Characteristic ir data of H_2paa and its complexes

Compound	νC=O	νC=N	νC=C	νM–O	νM–N
H_2Paa	1678s	1624s	1591br	--	--
[Ni(Paa)(H_2O)]	1672s	1601s	1585, 1592, 1595	428, 437	532, 540
[Cu(Paa)(H_2O)]	1675s	1509s	1582, 1588, 1592	422, 440	530, 542
[Zn(Paa)(H_2O)]	1680s	1604s	1595, 1590	420, 432	522, 535

Nmr spectra

In the proton nmr spectra of the diamagnetic zinc(II) and nickel(II) complexes the low field signal due to the NH and OH protons disappeared. This unequivocally suggest that these protons are replaced by the metal ion. The integrated intensities of the methyl proton signal agree well with [ML] stoichiometry of the complexes.

Mass spectra

The mass spectrum of the copper (II) complex is given in figure 1. The spectrum clearly indicate a peak at m/z 358 and another peak at m/z 360 in the 3:1 ratio. This peaks correspond to the $[Cu(paa)]^+$ ion in expected natural abundance of ^{63}Cu and ^{65}Cu. Peaks due to the elimination of CH_3CO, C_6H_5NH, C_6H_5O etc. from P^+ are also appeared in the spectrum. Thus all available spectral data fully support structure **2** of the complexes.

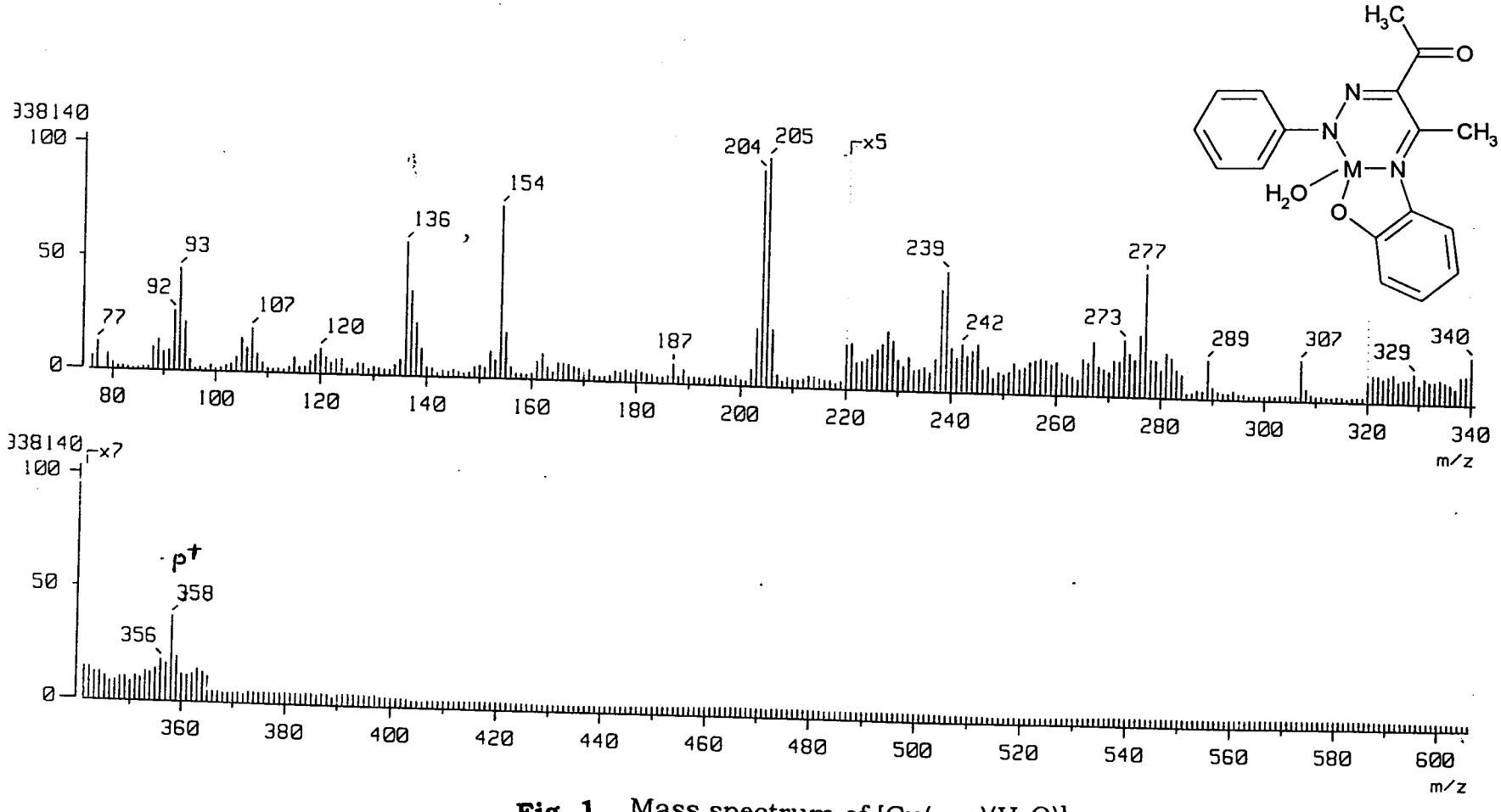


Fig. 1. Mass spectrum of [Cu(paa)(H_2O)]

B. Synthesis and characterisation of phenylazoacetylaetone aminothiophenol, H_2pat and its metal complexes

Experimental

Synthesis of H_2Pat

An ethanolic solution of 2-aminothiophenol (1.25 g, 0.01 mol, 20 mL) was added to an ethanolic solution of phenylazoacetylacetone (2.04 g, 0.01 mol, 20 mL) in ethanol. The mixture was refluxed on a boiling water bath for ~ 4 h. Volume was reduced and the precipitated compound filtered. It was recrystallised from hot methanol to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

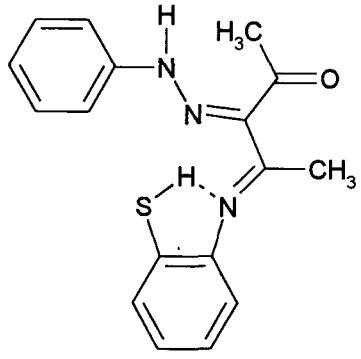
The Ni(II), Cu(II), Zn(II) complexes were prepared by the following methods.

A concentrated aqueous solution of metal(II) acetate (0.001 mol) was added to an ethanolic solution of the ligand (0.001 mol, 20 mL) and the mixture was refluxed for ~ 4 h on a boiling waterbath and cooled to room temperature. The precipitated complex was filtered, washed with water and then with methanol and dried in vacuum.

Results and Discussion

Characterisation of H_2pat

The analytical data of the reaction product of phenylazoacetylacetone with 2-aminothiophenol suggest a 1:1 condensation. The ir, nmr and mass spectral data are in agreement with structure **3** of the compound. The spectral data are discussed below.



3

Infrared spectra

The ir spectrum of the compound displayed in figure 2 shows three strong bands at 1672 cm^{-1}, 1622 and 1612 cm^{-1} (br). The former band is undoubtedly due to νC=O of CH_3CO and the latter bands can be assigned to νC=N vibrations. The νC=C vibrations of the aromatic rings are observed as several medium intensity bands in the 1550-1600 cm^{-1} region.

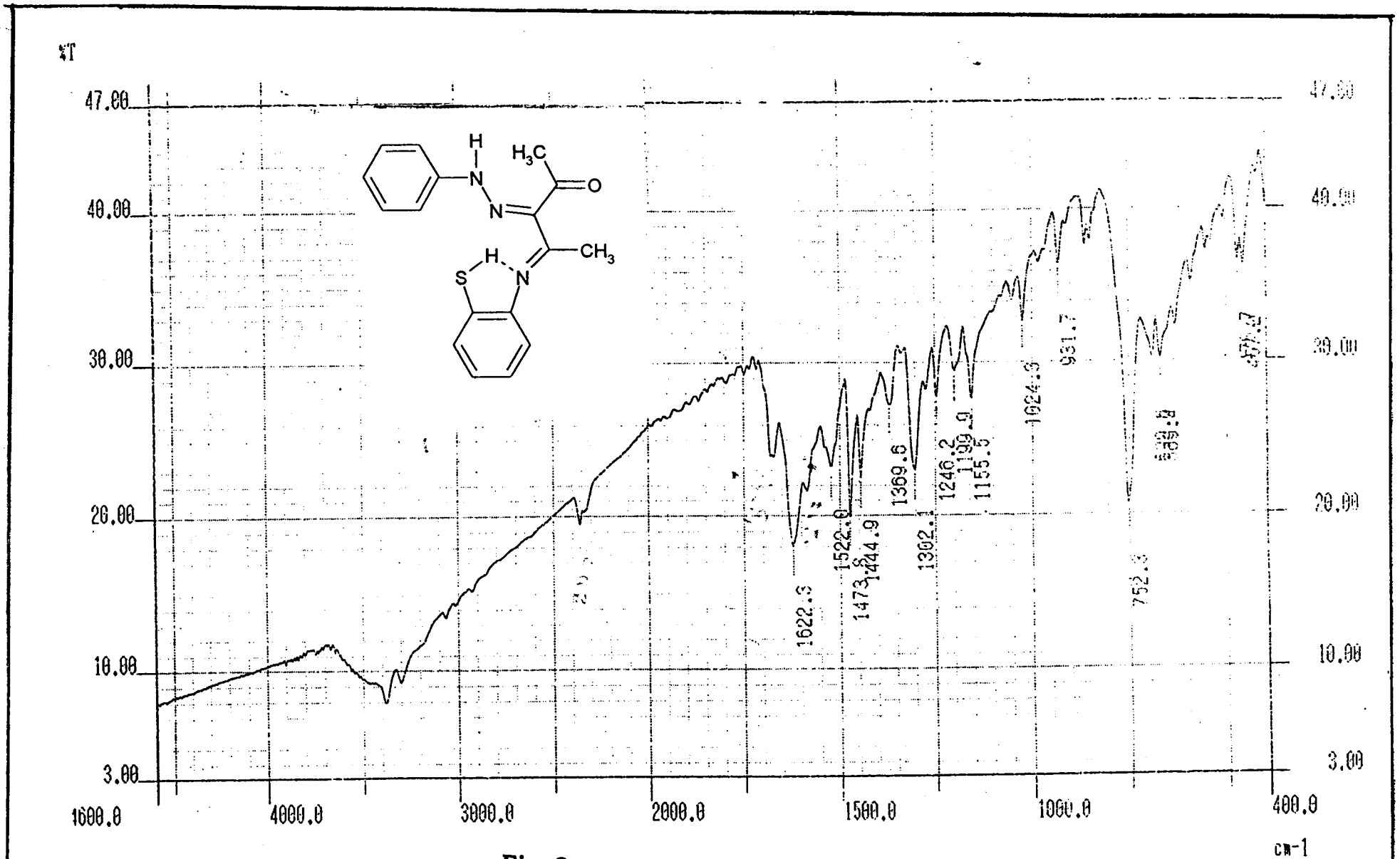


Fig. 2. Ir spectrum of H_2pat

TABLE 3

Analytical and physical data of H_2Pat and its complexes

Compound	M.P. °C	Elemental analysis % Found / (Calcd.)			
		C	H	N	M
H_2Pat	62	65.22 (65.59)	5.24 (5.46)	13.23 (13.50)	
[Ni(Pat)(H_2O)]	> 300	55.00 (55.48)	3.99 (4.07)	11.22 (11.42)	15.96
[Cu(Pat)(H_2O)]	> 300	53.92 (54.76)	4.00 (4.02)	11.20 (11.27)	16.82 (17.05)
[Zn(Pat)(H_2O)]	258	54.01 (54.48)	3.98 (4.00)	11.11 (11.21)	17.44 (17.46)

The SH stretching frequency of thiophenols usually appears in the region 2550-2600 cm^{-1}. Electron donor groups such as NH_2 decreases this value. In the spectrum of H_2pat a slightly broad medium intensity band appeared at 2425 cm^{-1} assignable to νS-H. In the 3000-3800 cm^{-1} region shows a broad band due to the intramolecularly hydrogen bonded NH proton. The deformation vibration of NH is observed at 1545 cm^{-1}.

Nmr spectra

The ^1H nmr spectrum of the compound showed a one proton signal at δ 14.2 ppm due to hydrogen bonded NH proton. Another one proton signal appeared at δ 6.2 ppm is probably due to the SH

group. The methyl proton signal are at δ 2.62 (3H) and δ 2.78 (3H) and the aryl protons in the range δ 6.8-7.5 ppm.

Mass spectra

Although the mass spectrum of the compound (Fig. 3) displayed a peak due to the molecular ion at m/z 311, the base peak in the spectrum is at m/z 248. The formation of this fragment can conveniently be explained by considering the elimination of the $(CH_3)_2S$ from the molecular ion[177] and the formation of a stable ion of m/z 248.

Characterisation of metal complexes

The ligand **H_2pat** formed crystalline stable complex with nickel(II), copper(II) and zinc(II) ion. The analytical and physical data of the complexes are given in table 4. The data suggest $[M(pat)H_2O]$ stoichiometry of the complex. The copper(II) complex shows paramagnetic moment of 1.79 BM and the other complexes are diamagnetic. The electrolytic conduction behaviour suggest their neutral nature. The ir, nmr and mass spectral data of the complexes suggest the structure **4** in which the acidic NH and SH protons are replaced by the metal ion. The spectral data are discussed below.

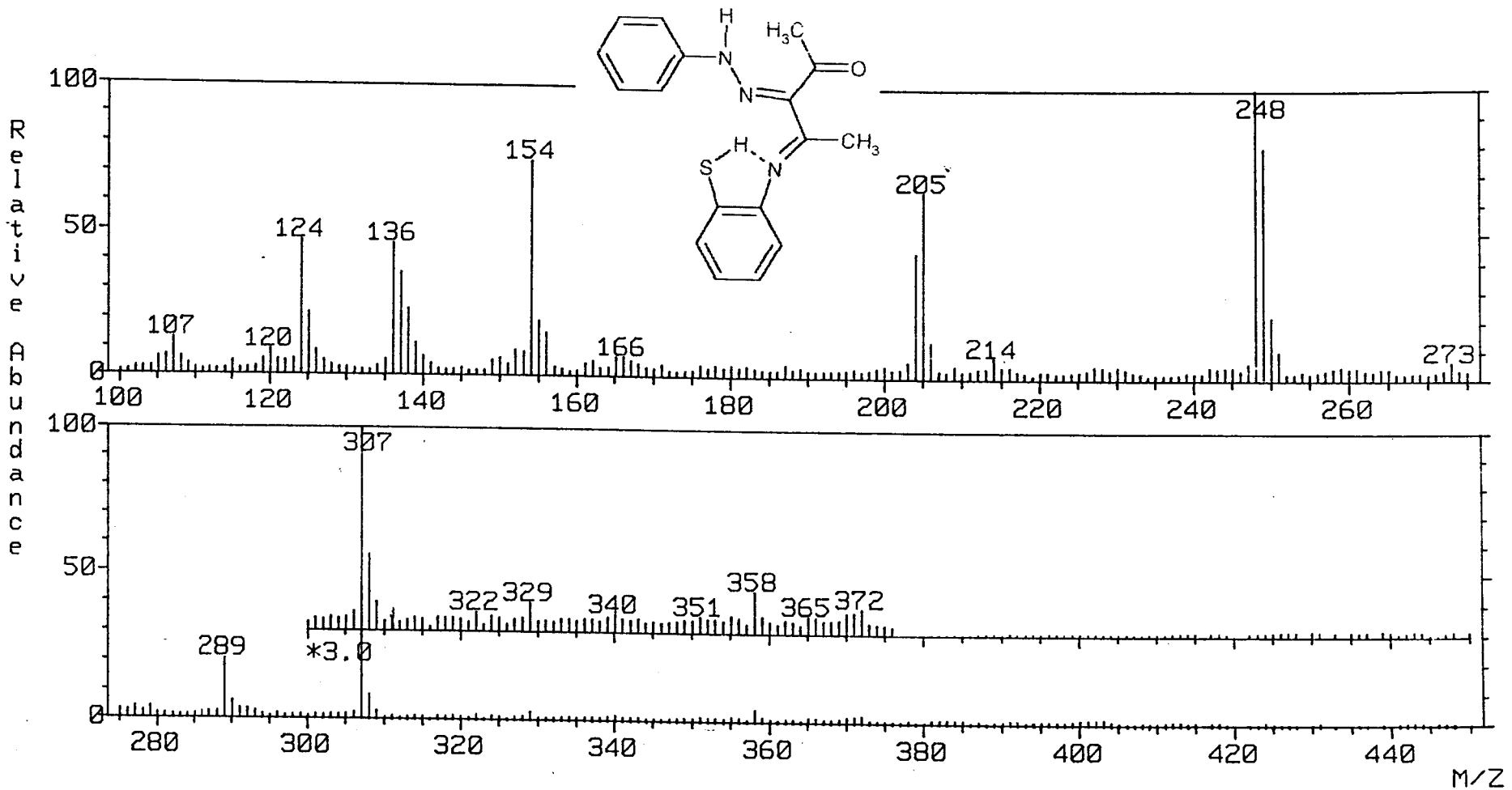
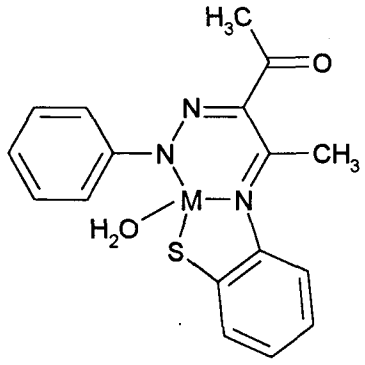


Fig. 3. Mass spectrum of H_2pat.



4

TABLE 4

Characteristic ir data (cm^{-1}) of H_2pat and its complexes

Compound	νC=O	νC=N	νC=C	νM–O	νM–N
H_2Pat	1672	1622, 1612	1592, 1598	--	--
[Ni(Pat)(H_2O)]	1675	1585, 1605	1590, 1595	428	522
[Cu(Par)(H_2O)]	1668	1582, 1602	1590, 1594	420	528
[Zn(Pat)(H_2O)]	1670	1580, 1610	1598, 1600	415	530

Infrared Spectra

The ir spectra of all the complexes are characterised by the presence of a strong band at ~ 1670 cm^{-1} and no other band is observed in the 1600-1800 cm^{-1} region. Thus it appears that the acetyl carbonyl of the free ligand remained almost unaffected in complexes also. That is the carbonyl group is not involved in bonding with the metal ion. The band at 1622cm^{-1} of the free ligand disappeared and instead a new band appeared at ~ 1580 cm^{-1} in the spectra of all complexes. This clearly suggest that the C=N group of the ligand is involved in banding with the metal ion.

Another characteristic feature of the spectra of all the complexes is the disappearance of the broad free ligand peak at 2425 cm^{-1} due to νSH vibration. Similarly the broad free ligand band in the region 2800-3500 cm^{-1} vanished and several weak bands appeared in the range 2500-3800 cm^{-1}. These observations suggest that the NH and SH protons are replaced by the metal ion during complexation. Thus the observed ir spectra strongly suggest that the thiol sulphur, the imino nitrogen and the hydrazone nitrogen are involved in the metal co-ordinate bond formation. This is further evident from the presence of new bands in the low frequency region (400-600cm^{-1}) assignable to νM-N and νM-O vibrations. Presence of coordinated water in the complex is also indicated from the presence of a band at ~ 3450 in the spectra of complexes. Important spectral bands are given in table 4.

Nmr Spectra

In the ^1H nmr spectra of the diamagnetic nickel(II) and zinc(II) complexes, the one proton signals at δ 14.2 and at δ 6.2 due respectively to NH and SH protons of the free ligand are not observed. This indicates that these protons are replaced by the metal ion during complex formation. The methyl and aryl proton signals are shifted slightly to low field and the integrated intensities

of these signals agree well with the formulation of the complex as in structure **4**.

Mass Spectra

The mass spectrum of the copper (II) complex clearly showed a prominent peak at m/z 372 assignable to the 1:1 stoichiometry. Similarly the peak due to ^{65}Cu of the complex appeared at m/z 374 at the expected intensity corresponding to the natural abundance of ^{63}Cu and ^{65}Cu. Other prominent peaks appeared in the spectrum are due to the elimination of CH_3CO, CH_3, C_6H_5, C_6H_5N etc. from the molecular ion. Thus ir, nmr and mass spectral data fully support the dibasic tridentate co-ordination of the complexes as in structure **4**.

C. Synthesis and Characterisation of thiazolylazoacetyl-acetoneaminophenol, H_2tap and its metal complexes

Experimental

Synthesis H_2tap

Thiazolylazoacetylacetone was synthesised by the diazo-coupling of 2-aminothiazole with acetylacetone as given in chapter 2. An ethanolic solution of 2-aminophenol (1.09 g, 0.01 mol, 20 mL) was added to an ethanolic solution of thiazolylazoacetylacetone (2.13 g 0.1 mol, 20 mL) and refluxed on a boiling water bath for ~ 8 h. The volume was reduced and poured the mixture to crushed ice with vigorous stirring. The precipitate formed was filtered and recrystallised from hot methanol twice to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

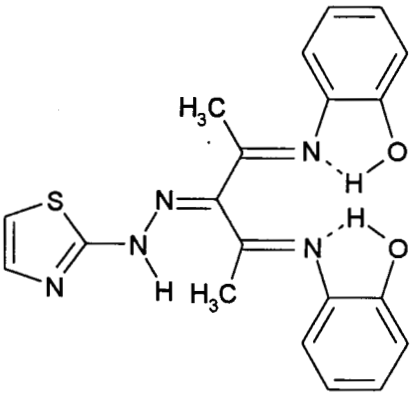
The Ni(II), Cu(II), Zn(II) complexes are prepared by the following methods.

A concentrated aqueous solution of metal(II) acetate was added to an ethanolic solution of the ligand (0.001 mol, 20 mL) and the mixture was refluxed for ~ 4 h on a boiling water bath. The solution was kept overnight. The precipitated complex was filtered, washed with water thoroughly then with methanol and dried in vacuum.

Results and discussion

Characterisation of H_2tap

The observed elemental analytical data of the condensation product of thiazolylazoacetylacetone with 2-aminophenol given in table 5 clearly suggest that two moles of aminophenol reacted with one mole of thiazolylazoacetylacetone. This together with the recorded ir, nmr and mass spectral data conform to the structure **5** of the schiff base formed.



5

Infrared data

In the ir spectra of **H_2paa** and **H_2pat** presence of a strong band due to the stretching of the acetyl carbonyl group at ~ 1670cm^{-1} was the most characteristic feature. However in the spectrum of **H_2tap** no such band assignable to the stretching of conjugated free acetyl carbonyl was observed. This indicates that both the carbonyl group

of thiazolylazoacetylacetone are condensed with 2-aminophenol. The spectrum of the compound in the 1600-1800 cm^{-1} region displayed three medium intensity band at 1605, 1615 and 1625 cm^{-1} assignable respectively to the stretching of the hydrazone C=N, CH_3-C=N and the thiazole ring C=N respectively. These assignments are based from a comparison of the reported spectra of thiazolylazoacetylacetone, phenylazoacetylacetone and 2,(2-hydroxy-phenylazo)-2,4-pentanedione with the spectrum of **H_2tap**. That the phenolic OH groups are involved in strong intramolecular hydrogen bonding is clearly evident from the presence of a broad band in the region 2500-3800cm^{-1} in the spectrum of **H_2tap**. A prominent band appeared at 1542 cm^{-1} is assignable to the deformation vibration of the hydrazone NH function.

TABLE 5

Analytical and Physical data of H_2tap and its complexes

Compound	M.P. °C	Elemental analysis % Found / (Calcd.)			
		C	H	N	M
H_2tap	125	60.94 (61.06)	4.56 (4.83)	17.48 (17.80)	--
[Ni(tap)]	> 300	52.94 (53.37)	3.12 (3.78)	15.23 (15.57)	12.94 (13.05)
[Cu(tap)]	> 300	52.20 (52.80)	3.15 (3.74)	15.00 (15.40)	13.82 (13.97)
[Zn(tap)]	> 300	52.00 (52.59)	3.23 (3.72)	15.14 (15.33)	14.00 (14.33)

Nmr Spectra

The ^1H nmr spectrum of the compound displayed a slightly broadened two proton signal at δ 12.18 ppm and a one proton signal at δ 13.5 ppm. These three signals in the low field are undoubtedly due to acidic protons. From a comparison of the reported spectra of arylazo derivatives of 1,3-diketones it can be stated that the signal at δ 12.18 ppm is due to intramolecularly hydrogen bonded phenolic group and the signal at δ 13.5ppm from the resonance of an NH proton involved in a conjugated molecular system. The spectrum of the compound also displayed two three proton signal at δ 2.35 ppm and δ 2.58 ppm due to two methyl group of the structure **7**. The aryl proton signals are observed in the 6.68-7.90 regions.

TABLE 6

Characteristic ir data (cm^{-1}) of H_2tap and its complexes

Compound	νC=N	δNH	νM–O	νM–N
H_2tap	1625, 1615, 1605	1542	--	--
[Ni(tap)]	1622, 1602, 1560	1545	432, 420	550, 538
[Cu(tap)]	1620, 1605, 1565	1538	422, 415	555, 540
[Zn(tap)]	1622, 1600, 1570	1540	428, 418	545, 530

Mass spectra

The formation of the compound as in structure **5** is well confirmed from the presence of an intense P^+ peak in its mass spectrum. The spectrum is reproduced in figure 4. Fragments corresponds to the elimination of C_3H_2NS, $C_3H_3N_2$, $C_3H_3N_3S$, C_6H_5-O from the parent ion are all appeared in the spectrum. Thus the observed, ir, nmr and mass spectral data fully support structure **5** of the compound.

Characterisation of metal complexes

The C, H, N and metal percentages of the Ni(II), Cu(II) and Zn(II) complexes of **H_2tap** are given in table 5. The data clearly indicate the formation of 1:1 complexes with the metal ions. Since their conductivity in dmf 10^{-3}m solution suggest the neutral nature of the complex. Thus it appears that two of the three acidic proton of **H_2tap** has been replaced by the metal ion during complexation. There are several distinguishing features in the ir, nmr and mass spectral data of the complexes compared to spectra of the complex discussed in the previous section. However the spectra of the complexes of **H_2tap** can satisfactorily be explained by considering the structure **6** of the complex.

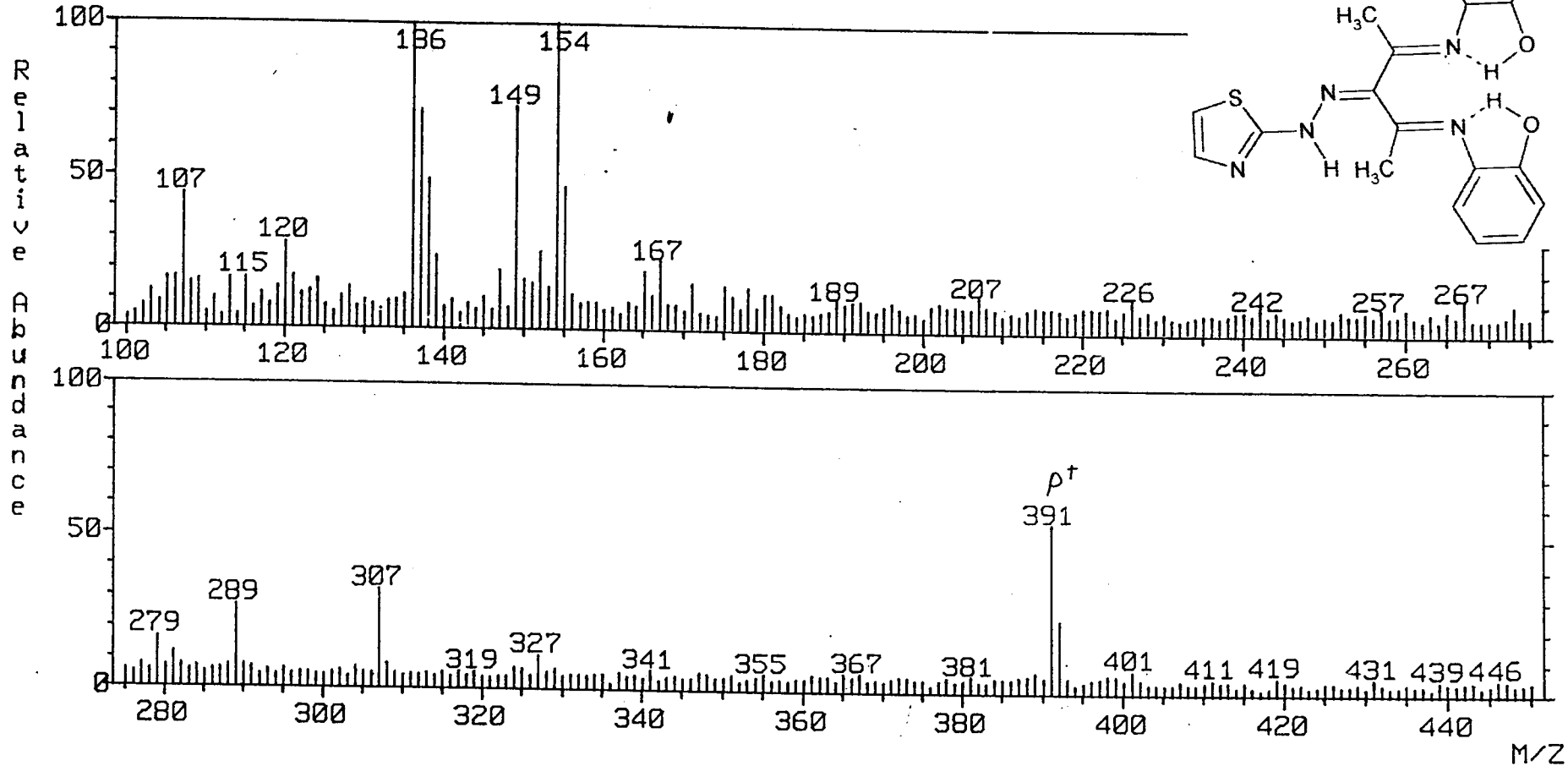
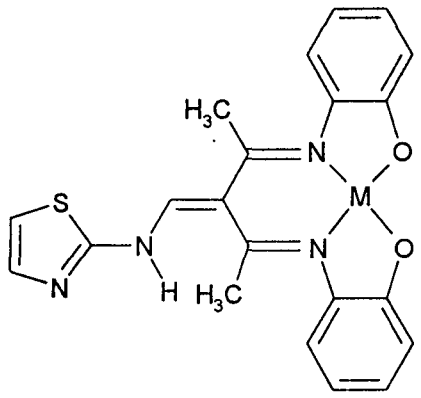


Fig. 4. Mass spectrum of H_2tap.



6

The most important evidences regarding the formulation and the nature of bonding as given structure **6** of the complexes of **H_2tap** were derived from their ^{1}H nmr of the diamagnetic Ni(II) and Zn(II) complexes and the mass spectrum of the copper(II) complex. The ^{1}H nmr spectra of the complexes are characterised by the presence of a low field one proton signal at δ 14.75 ppm and two three proton signals at δ2.28 and 2.36ppm in addition to several multiplet signals in the region δ 6.50-7.95 ppm due to aryl protons. The signals due to the phenolic proton of the free ligand are disappeared in the spectra of the complexes. The signal due to the hydrazone proton remained almost unaltered in the spectra of the complexes. This clearly support the fact that only the phenolic hydrogen are replaced by metal ion as in structure **6**, and the hydrazone NH proton remained as such. The two three proton signals observed in the high

field region are due to the two methyl groups of the complexes as given in structure **6**.

The mass spectrum of the copper (II) complex is given in figure 5. The spectrum clearly show the presence of a molecular ion peak in accordance with the structure 6. Other important peaks appeared in the spectrum are due to the elimination of thiazole, Tz-NH, etc. from the molecular ion.

The ir spectra of all complexes are also in agreement with the structure **6**. Thus the νC=N bands shifted appreciably to low wave numbers indicating the involvement of these groups in bonding with the metal ion. The bending mode of hydrogen NH remained almost unaffected in the spectra of complexes suggest that this group is excluded from the complexation. The broad free ligand band in the region 2500-3800 cm^{-1} almost vanished in thespectra of complexes and instead several weak and medium intensity band appeared in this region assignable to νN-H and various νC-H vibrations. Important ir bands and their assignments are given in table 6.

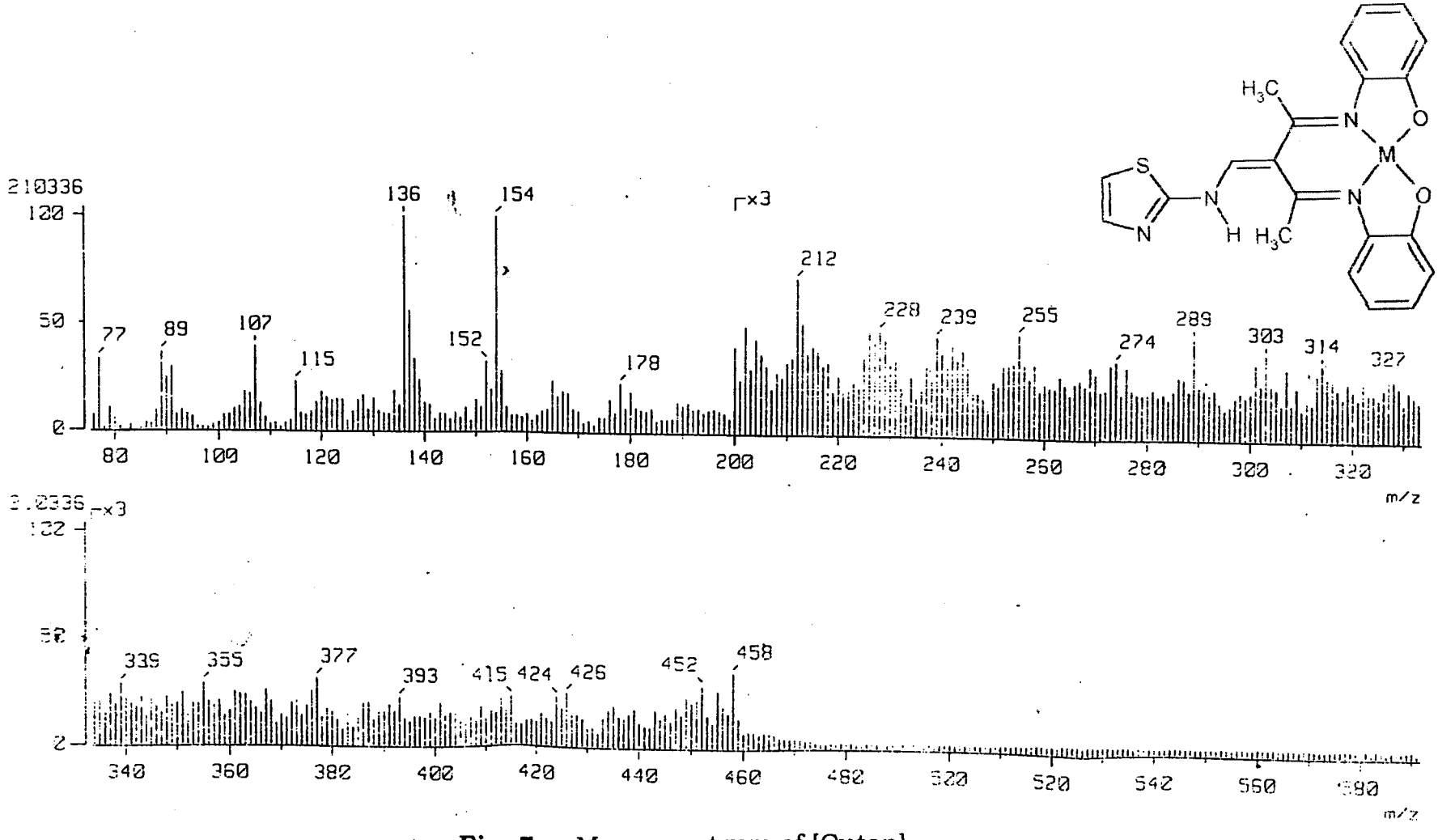


Fig. 5. Mass spectrum of [Cutap]

D. Synthesis and Characterisation of thiazolylazoacetyl-acetone-thiophenol and its metal complexes

Experimental

Synthesis of H_2tat

Thiazolylazoacetylacetone was prepared as reported. To an ethanolic solution of thiazolylazoacetylacetone (2.11 g, 0.01 mol, 20 mL) added 2-aminothiophenol (0.1 g 0.01 mol) drop by drop. The solution was stirred for ~ 9 h in a closed flask maintaining the temperature at 50-55°C. The crystalline product formed was filtered and recrystallised from hot methanol to get chromatographically (tlc) pure compound.

Synthesis of metal complexes

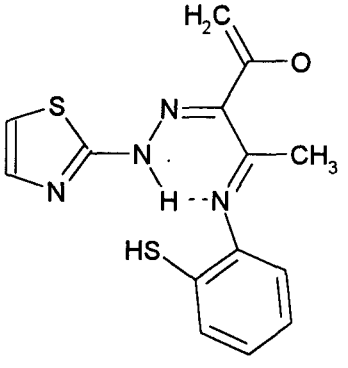
The Ni(II), Cu(II), Zn(II) complexes were prepared by the following methods.

A concentrated aqueous solution of metal(II) acetate (0.001 mol) was added to an ethanolic solution of the ligand (0.001 mol, 20 mL) and the mixture was refluxed for ~ 3 h on a boiling water bath. The precipitated complex was filtered washed several times with water and then with ethanol and dried in vacuum.

Results and discussion

Characterisation of thiazolylazoacetylacetoneaminothiophenol and its metal complexes

The analytical and spectral data of the reaction product of thiazolylazoacetylacetone with 2-aminothiophenol are in agreement with structure **7** of the compound.



7

The compound formed 1:1 complexes with Ni(II), Cu(II) and Zn(II) ions. The analytical and other details of the complexes are also included in table 7. The ir, nmr and mass spectral data of the ligand and complexes are discussed below.

Infrared spectra

The ir spectrum of the ligand displayed a strong band at 1670 cm^{-1} due to νC=O of the conjugated acetyl carbonyl. The three medium intensity band observed in the 1600-1630 cm^{-1} region of the

spectra can be assigned to the various νC=N vibrations. The broad band in the region 2500-3500 cm^{-1} suggest the presence of strong intramolecular hydrogen bonding. The SH stretching band is observed at 2420 cm^{-1}.

TABLE 7

Analytical and Physical data of H_2tat and its complexes

Compound	M.P. °C	Elemental analysis % Found / (Calcd.)			
		C	H	N	M
H_2tat	130	52.44 (52.83)	4.22 (4.40)	17.33 (17.61)	--
[Ni(tat)(H_2O)]	> 300	44.00 (44.83)	3.21 (3.20)	14.00 (14.94)	15.78 (15.66)
[Cu(tat)(H_2O)]	> 300	43.45 (44.26)	3.00 (3.16)	14.12 (14.75)	16.00 (16.74)
[Zn(tat)(H_2O)]	220	43.84 (44.04)	3.02 (3.15)	14.44 (14.68)	16.95 (17.14)

In the spectra of complexes the band at 1670 cm^{-1} remained almost unaffected. However the bands due to C=N shifted appreciably to lower wave numbers.[190] This indicate the involvement of these groups in complex formation. Further the appearance of a new medium intensity in 500-550cm^{-} region of the spectra are due to νM-N vibration. That the NH and SH protons are replaced by metal ion is evident from the disappearance of broad free ligand band on the 2500-3500 cm^{-1} region. Instead several weak bands appeared in

this region due to various νC-H groups. Further the band due to νSH is also absent in the spectra of complexes. Important ir bands are given in table 8.

TABLE 8

Characteristic ir spectral data (cm^{-1}) of H_2tat and its complexes

Compound	νC=O	νC=N	νM–O	νM–N
H_2tat	1670	1630, 1618, 1610	--	--
[Ni(tat)(H_2O)]	1672	1620, 1608, 1595	422	532
[Cu(tat)(H_2O)]	1668	1618, 1605, 1598	418	528
[Zn(tat)(H_2O)]	1675	1615, 1602, 1595	430	520

Nmr spectra

The nmr spectrum of the ligand contain two one proton signals at 9.25 and 5.85 ppm respectively due to the strong hydrogen bonded NH and SH protons. In metal complexes these signals are absent indicating their replacement by metal ion. The methyl proton signals appeared as two three proton signals at at 2.58 and 2.72 ppm and the aryl protons as multiplets in 6.5-7.8ppm. These signals are shifted slightly to low field in metal complex.

Mass spectra

Mass spectrum of the Schiff base given in figure 6 which shows an intense P^+ peak in agreement with the structure **7**. The mass spectrum of the copper(II) complex also exhibited peaks

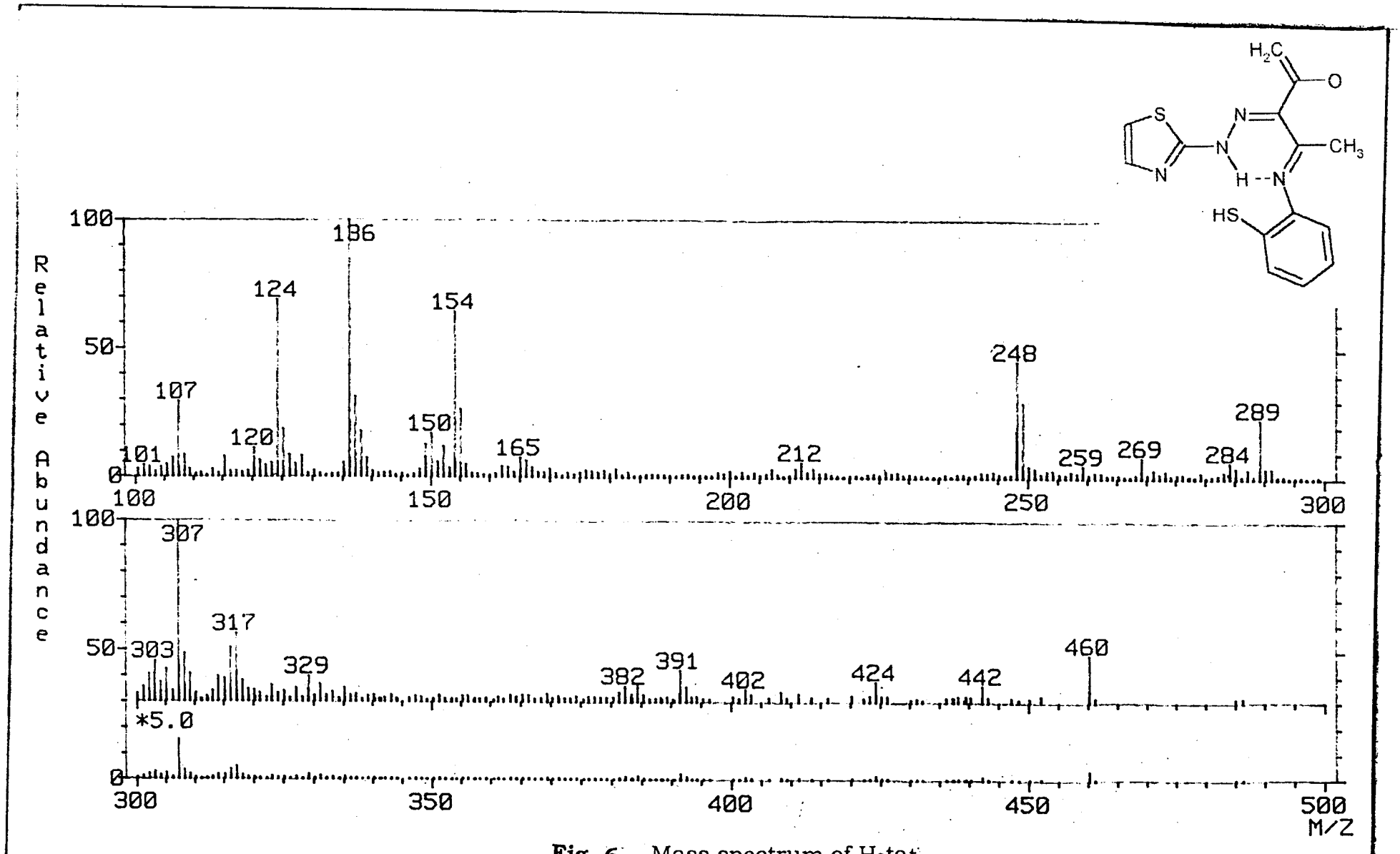
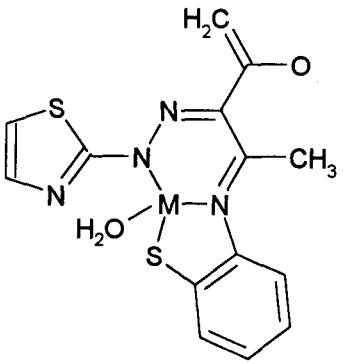


Fig. 6. Mass spectrum of H_2tat

corresponding to [Cu(tat)(H_2O)] stoichiometry in expected intensities of ^{63}Cu and ^{65}Cu. Thus all available evidences support the structure **8** of the complexes.



8

Esr spectral data

Esr spectra of the copper(II) complexes of the schiff bases were taken at liquid nitrogen temperature. The spectra gave four well resolved peaks due to the copper hyperfine interaction. The $g_{||}$, $g_{\perp}$, $A_{||}$ and $A_{\perp}$ values obtained are given in table.

Compound	$g_{\|\|}$	$g_{\perp}$	$A_{\|\|}$	$A_{\perp}$
			x 10^4 cm^{-1}	
[Cu(paa)(H_2O)]	2.172	2.052	210	25
[Cu(pat)(H_2O)]	2.171	2.075	202	26
[Cu(tap)]	2.160	2.065	183	38
[Cu(tat)(H_2O)]	2.182	2.068	198	28

From the data it is evident that the metal-ligand bonds have considerable covalent character. The A values observed indicates

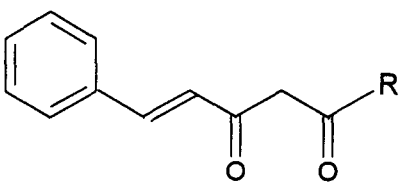
that odd electron density is less on [Cu(tap)] compared to the other three chelates. This would mean that delocalisation of metal d electrons is greater in [Cu(tap)] compared to the other three complexes. This is justifiable of the complex in view of the proposed structure where delocalisation is more facile.

SUMMARY

Two most important reactions of 1,3-diketones and metal 1,3-diketonates are (a) the electrophilic substitution at the 2-carbon atom of 1,3-diketone moiety and (b) nucleophillic attack of an amine at the carbonyl function. These two properties of 1,3-diketones have been properly exploited in the design and synthesis of a large number of ligand systems having wide applications in diverse fields of chemical and biological sciences.

The first type of reactions have been well demonstraetd in the case of the diazo-coupling reaction between 1,3-diketones and the powerful electrophile, aryldiazonium salt. Thus hundreds of such compounds and their metal complexes have been studied and a number practical applications have been developed for such compounds. The second type of reactions of 1,3-diketones have been meticulously employed in the design and synthesis of numerous schiff base ligand systems that can act as model compounds in several biochemical systems. These aspects of 1,3-diketone and their metal derivatives along with the need for further investigation in this direction have been briefly outlined in **chapter 1** of the Thesis.

Majority of the reported studies are confined to synthetic 1,3-diketones in which the diketo function is attached to alkyl/aryl/ heteroaryl groups. However, these types of studies on naturally occurring 1,3-diketones such as curcuminoids (the active chemical constituents present in the herbaceous Indian medicinal plant turmeric), where the diketo function is attached to olefinic linkages have not received as much attention as they deserve. In the present investigation synthesis and characterisation of arylazo derivatives of three typical 1,3-diketones **1a-c**, in which the diketo function is attached to alkenyl groups are studied (**chapter 2, section 1**).



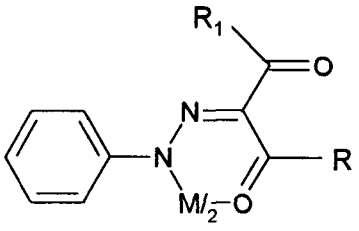
1

1a R = –CH = CH – C_6H_5

1b R = $–CH_3$

1c R = $–C_6H_5$

Based on ir, nmr and mass spectral data it has been shown that the phenylazo derivatives exist in the intramolecularly hydrogen bonded keto-hydrazone form, whereas the thiazolylazo derivatives in the azo-enol form. These compounds function as monobasic bidentate in which one of the hydrazone/azo nitrogen(s) and keto/enol oxygen(s) are involved in bonding with the metal ion as in structure **2** and **3**.



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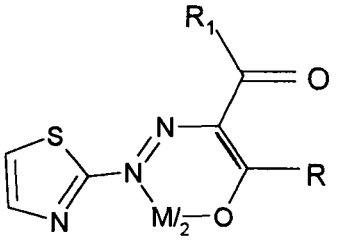


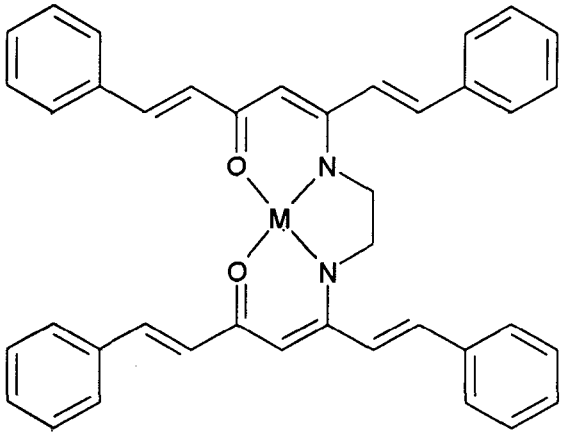
3

$R = R_1 = -CH=CH-C_6H_5$

$R = CH_3 \quad R_1 = -CH=CH-C_6H_5$

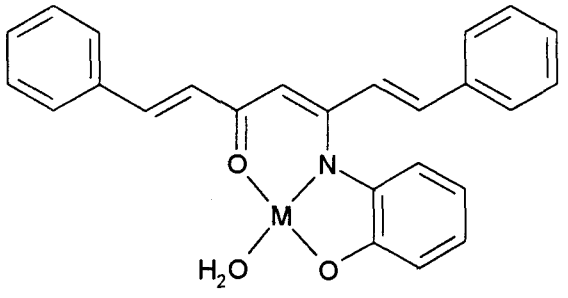
$R = CH = CH-C_6H_5 \quad R_1 = C_6H_5$

In **chapter 2, section 2**, metal complexes of schiff bases of the unsaturated 1,3-diketone **1a** are discussed. The Schiff base obtained by the condensation between **1a** and ethylenediamine exist in the intramolecularly hydrogen bonded keto imine form. The ir, nmr and mass spectral data of the Cu^{2+} and Ni^{2+} complexes of the Schiff base supported the tetradentate coordination as in structure **4**.



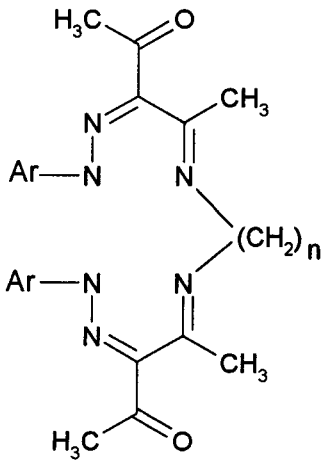
4

Schiff's base obtained by the condensation of **1a** with 2-aminophenol has been found to exist in the keto-imine form in which both the N–H and phenolic –OH are intramolecularly hdyrogen bonded with the cinnamoyl carbonyl group. Dibasic tridentate nature of the compound in its complexes with Cu(II) and Ni(II) have been established on the basis of various spectral data (structure **5**).



5

A series of polydentate ligand systems have been synthesised and characterised by the reaction of 3-phenylazo- and 3-(2-thiazolylazo)-2,4-pentanediones with 1,2-diaminoethane, 1,3-diaminopropane and 1,6-diaminohexane (**chapter 3, section 1**). Various spectral and other evidences fully support structure **6** of compounds. The tetradentate N_4 coordination of these compounds as in structure **7** has been clearly established on the basis of analytical and spectral data.



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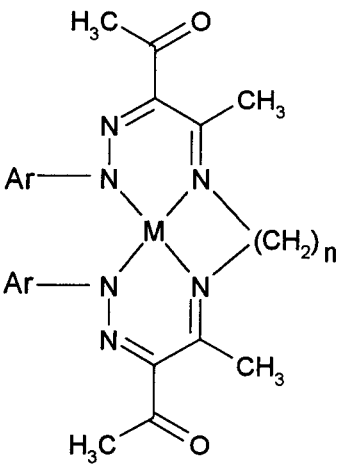

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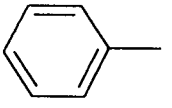

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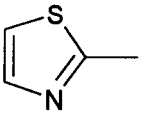
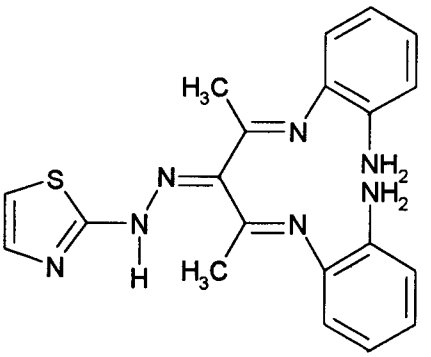


Reaction of 3-(2-thiazolylazo)-2,4-pentanedione with 1,2-, 1,3- and 1,4-diaminobenzene yielded three new schiff base ligands (**section 2, chapter 3**). Spectral and analytical evidences unequivocally showed that the products have the structure **8, 9** and **10**. Formation of stable metal complexes of structures **11, 12** and **13** has also been established on the basis of spectral and other data.



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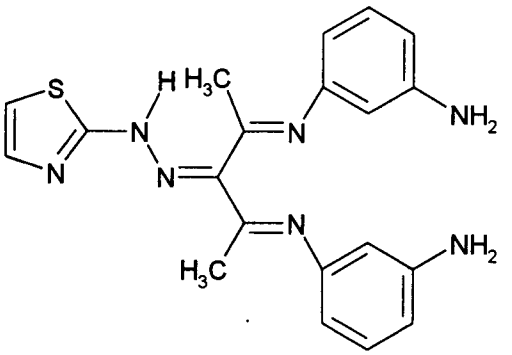

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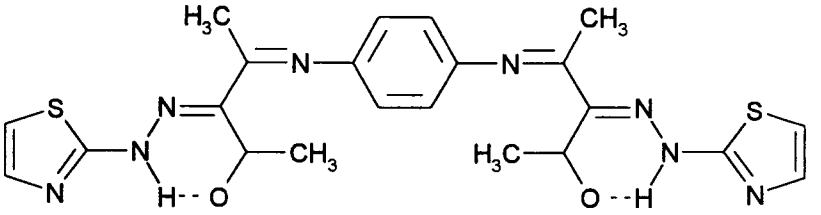

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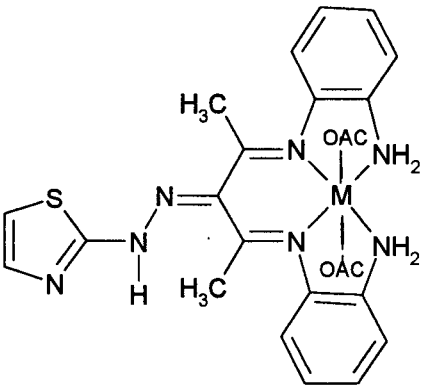

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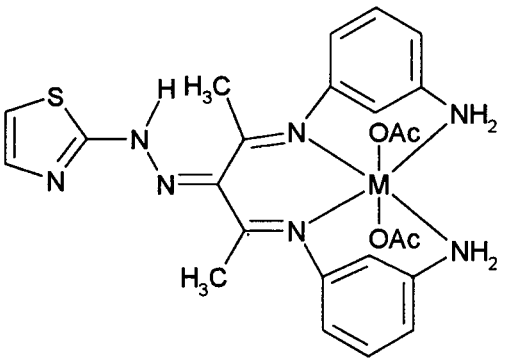

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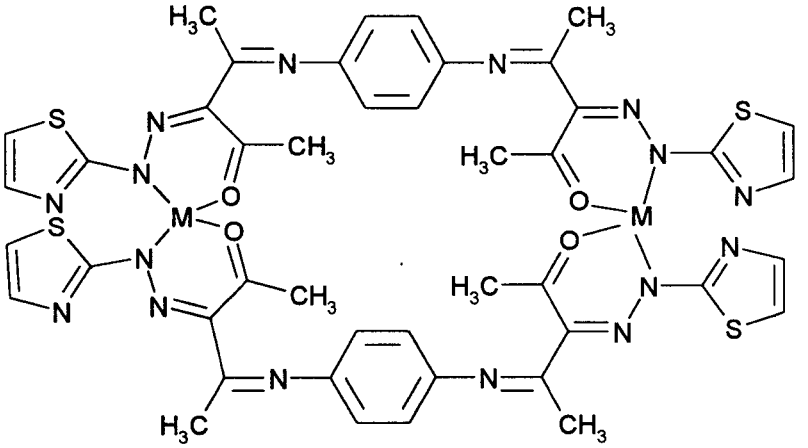
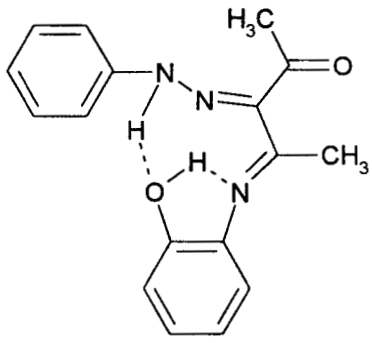


13

2-Aminophenol and 2-aminothiophenol on Schiff base condensation with 3-phenylazo- and 3-(2-thiazolylazo)-2,4-pentanedione resulted in the formation of the following ligand systems of structures **14-17** and these compounds form stable complexes of structures **18-21.** Details on the synthesis and characterisation of these compounds have been discussed in **chapter 4** of the thesis.



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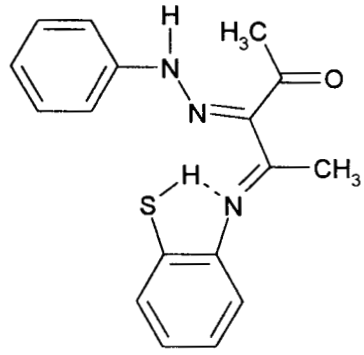

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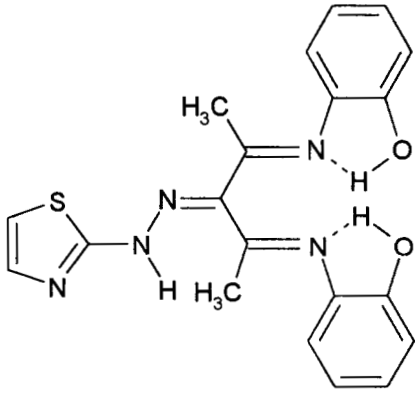

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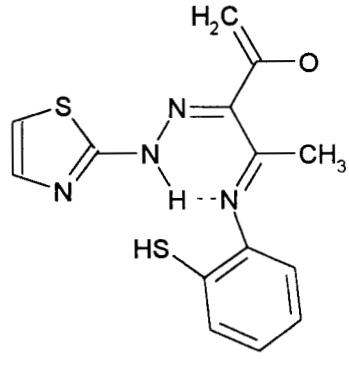

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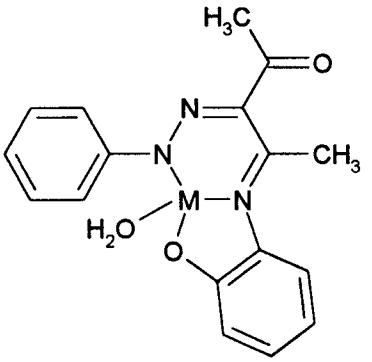
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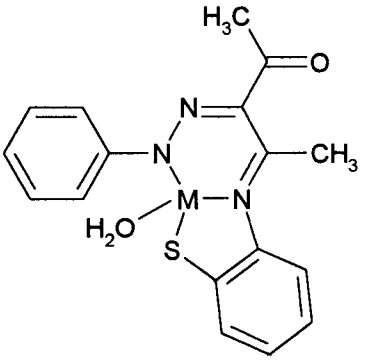
H2O
O

18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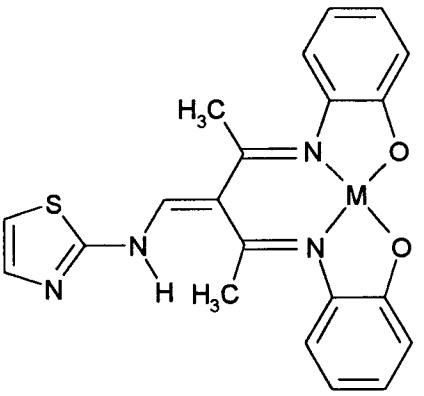
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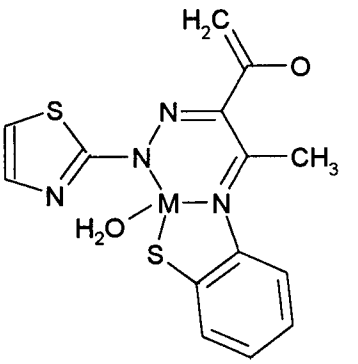
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21

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