METAL COMPLEXES OF AZO-DERIVATIVES OF PYRAZOLONES AND β-DIKETO COMPOUNDS

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By

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CERTIFICATE

This is to certify that this thesis entitled **Metal complexes of azo-derivatives of pyrazolones and β-diketo compounds** is an authentic record of research work carried out by **Mrs. SUSANNAH SETH** 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.K. ARAVINDAKSHAN
(Supervising Teacher)

DECLARATION

I, Susannah Seth, hereby declare that this thesis entitled **Metal complexes of azo-derivatives of pyrazolones and β-diketo compounds** submitted to the University of Calicut in partial fulfilment of the requirements of the Doctoral degree in Chemistry is a bonafide research work done by me under the supervision and guidance of Dr. K.K. Aravindakshan.

I further declare that this thesis has not previously formed the basis for the award of any other degree, diploma or similar title.

C.U. Campus,
12th May 2008.   **SUSANNAH SETH**

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PREFACE

The azo derivatives of pyrazolones and β-diketones find significance in the academic and research fields. Their main application in the industrial field is still the dyeing property. The metal complexes of these azo dyes due to their stability also find a host of applications viz., in the analytical field.

The donor behaviour of multidentate ligands has always captivated the attention of the researchers. Hence, it was found appropriate to investigate the ligational properties of the above mentioned compounds. The emphasis is set on the structural aspects of the ligands and metal complexes with the help of many of the modern instrumental facilities. A possible application of europium complex of the ligand is also envisaged.

The present investigation encompasses the synthesis and characterization of four ligands, phenylazo dimedone (AD), 1-phthalazinyl 3-methyl-2-pyrazolin-5-one (HyPy), phenylazo dehydroacetic acid (ADAA) and antipyrinylazodimedone (DAAP). Five metal complexes in each category have also been synthesised and characterized.

The thesis has been divided into two parts for the sake of convenience. Part I comprises the synthesis and characterization of the ligands and metal complexes. Part II deals with the photophysical studies.

Part I is arranged in six chapters.

Chapter I consists of three sections: Section A unfolds a retrospection of the previous works on azoderivatives of various β-diketones and pyrazolones. A collection of the implementation of the different aspects of the azoderivatives is included in Section B. The objective and scope of the present work is highlighted in Section C.

Chapter II mentions the materials used and the methods adopted for the investigation.

Chapters III, IV, V and VI describes the synthesis, characterization and structural aspects of the four ligands AD, HyPy, ADAA and DAAP, respectively and their metal complexes using various physico-chemical and spectral methods.

Part II consists of two chapters and deals with the possible utility of one of the ligands, AD when complexed with europrium in light emitting devices (LED). There has been plenty of published work on polymers impregnated with europium-chelates during the later half of twentieth century. LED technology is undergoing constant refinement as it is environment friendly and economical. The synthesis and characterization of two europium complexes with phenylazo dimedone (AD) in one and dimedone in the other and their incorporation into four different polymers and the basic

absorption/PL studies have been included in Chapter II of Part II. The work has been undertaken keeping in mind the choice of active material in OLED on the premise that similar results were obtained in other published works.

The references are cited in serial order at the end of each chapter in Part I and the references for Part II are appended at the end of the thesis.

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SYNTHESIS AND CHARACTERIZATION

CHAPTER I

INTRODUCTION

Coordination chemistry is essentially the chemistry of the electron accepting behaviour of metal ions surrounded by ligands. The wide spectrum of colour exhibited by coordination compounds, and the puzzle of their structures which are manifestations of the coordination number of the metal ion and the ligational behaviour of the complexing agents, make their investigation very challenging and at the same time interesting.

Even though the first coordination compound on record[1] is Prussian blue, iron(III) hexacyanoferrate(II), the scientific and systematic development of modern research in coordination chemistry began with Alfred Werner and Sophus Mads Jorgensen. Their attempts to explain the structures of heteroleptic complexes of cobalt(III) with ammonia and chlorine paved way for the extensive proposal of theories.

Coordination compounds find wide applications in the fields of medicine, analytical chemistry, and industry. The present scenario includes small molecule crystallography for structure determination, development of structural outlines and verification of experimental viability using software programmes which employ molecular modelling and other 'in silico' methods.

The applications of new coordination compounds in various other fields are also investigated.

A.   Azo compounds as complexing agents

Azo compounds are characterised by the presence of one or more azo (–N=N–) groups. The formation of azo[2] compounds usually involves the reaction between a diazo species and a coupling agent. The diazo species is obtained by the diazotisation of an aromatic primary amine using nitrous acid or alkyl nitrite[3]. The ease with which the reaction proceeds and the certainty and reactivity of the product, diazonium salt (ArN_2^+), makes it a reliable reaction in academic research and industry[4].

The aryl diazonium ion is a powerful electrophile which gets covalently attached by displacing a proton from a suitable substrate.

$$ArN_2^+ \xrightarrow{\text{H - X}} Ar-N=N-X \ + \ H^+$$
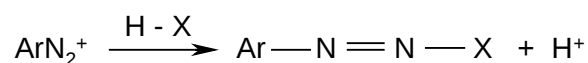
Scheme 1

1. Metal complexes of azo compounds

The versatile ligational behaviour of azo compounds had evoked considerable interest in the past. Both the azo dyes and their metal complexes find applications in dye industry. In some cases the complexes assume more importance due to technical reasons[4], like better fibre affinity, and light

fastness. Moreover, the presence of metals makes the dyes more specific and selective.

Metal complexes of azo compounds are broadly divided into two categories, namely the ones in which the azo group is involved in bonding and the others in which it is not. The former are derived from azo compounds containing donor functions such as OH, NH_2, COOH, SH, etc., in a congenial position so as to form six or five membered chelates (Fig. 1.1).
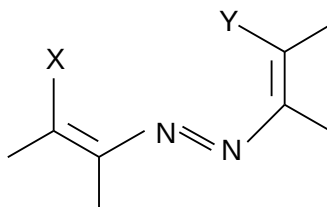
Fig. 1.1

X	Y	Type
H	OH, C=O, NH_2, COOH, SH	bidentate
OH, NH_2 COOH	SH, OH, NH_2, COOH	tridentate

Azo groups show weak donor properties but in conjunction with other strong donors like OH, NH_2 or C=O they form very stable chelates. Their donor properties were in fact proved from the observation that azo benzene having OH or NH_2 group *ortho-* to the azo function formed stable complexes

whereas others with the same groups at *meta* or *para* did not[6]. Therefore, it is understood that in order to form stable complexes, the ligand should have not azo group alone but some other donor atom at β position as well. Some exceptions are the ones which coordinate through the filled π orbital of the –N=N– function.

The stability of the chelates, as mentioned earlier, depends on the number of atoms involved in ring formation. So chelates with five or six membered rings are the most stable ones. For the same reason, complexes of tridentate azo compounds are more stable than the ones of bidentate azo compounds. Moreover, the strongly basic ligands form the most stable complexes and the strongly acidic ones the least stable complexes.

The relative stabilities of some azo dyes in complex formation is represented below (Fig. 1.2).
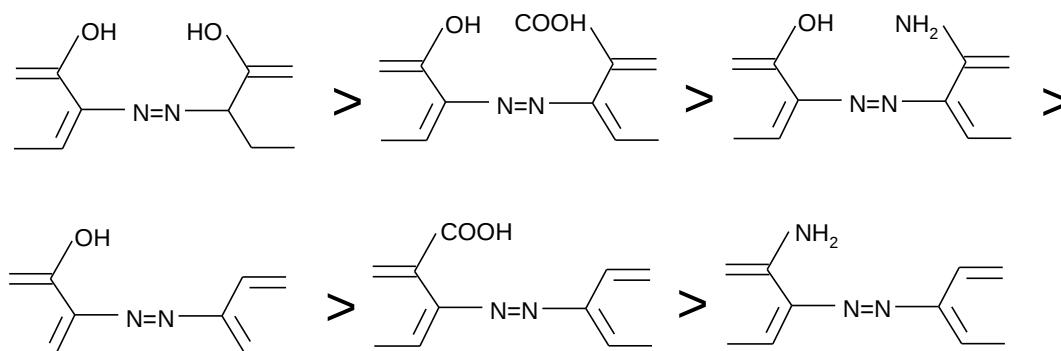
Fig. 1.2

Till 1952, the involvement of the azo nitrogen in bonding with metal ions was indicated as follows (Fig. 1.3).
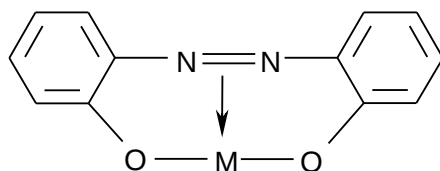
Fig. 1.3

Even though Werner in 1947 proposed a π bonded structure between the azo group and the metal ion, the mode of coordination was not understood until X-ray data were available. It has been proved without doubt that only one nitrogen atom of the azo group[9] is involved in bonding with the metal. The X-ray data of copper(II) complex of phenylazo-2-naphthol indicates that the β-nitrogen atom of the azo group was bonded to the metal as follows (Fig. 1.4).
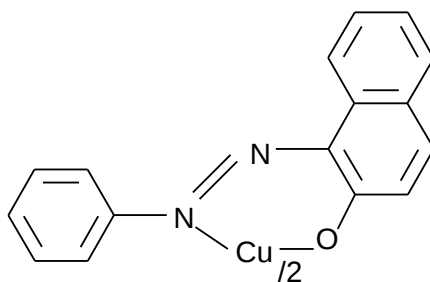
Fig. 1.4

The structural aspects of the metal complexes of diarylazo compounds are exemplified in many a literature[10].

The present investigation is focussed on the synthetic, structural and applicational aspects of two types of monoazo compounds. The first type is derived from diazotised aromatic primary amines and active methylene coupling components such as β-dicarbonyl compounds and their metal complexes. The second category is the pyrazolones, which are formed as a result of cyclisation of the azobetadiketo derivative with substituted hydrazines and their metal complexes.

2. Arylazo derivatives of active methylene compounds

The dye industry mainly makes use of the coupling between aromatic hydroxy compounds and diazotized amines. But still there is another category which can be regarded as the methane derivatives bearing sufficient electron density[11] on the carbon atom for electrophilic substitution to take place. These are referred to as compounds containing active methylene or methine groups.   Of these, the 1,3-dicarbonyls or β-dicarbonyls constitute an important category of coupling reagents. Many important fabric dyes and pigments are prepared from diazo coupling of aryldiazonium ion with 1,3-dicarbonyls.   The well known 'Hansa Yellows' which are obtained by coupling acetoacetanilide[12] and similar 1,3-dicarbonyls with various diazonium salts constitute the prime examples.

The reactivity of the active methylene group of 1,3-dicarbonyls has evoked much interest. The active methylenic carbon in these compounds can act as a nucleophilic centre for the electrophilic attack. The reaction with ArN_2^+ can be represented as Scheme 2.
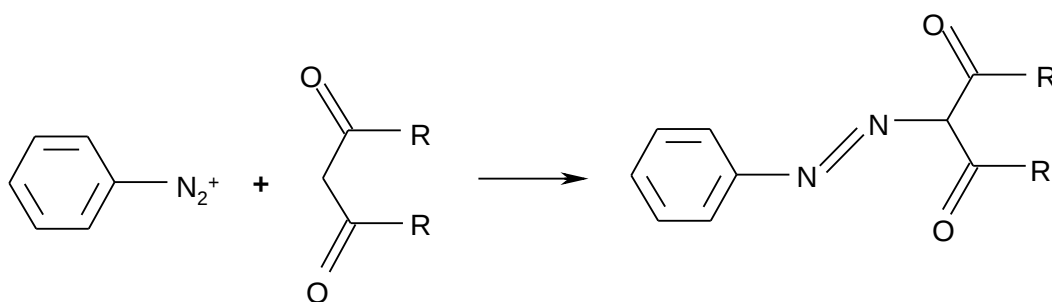
Scheme 2

The resultant product is capable of keto-enol as well as azo-hydrazone tautomerism[13]. The different possibilities are given in Fig. 1.5.
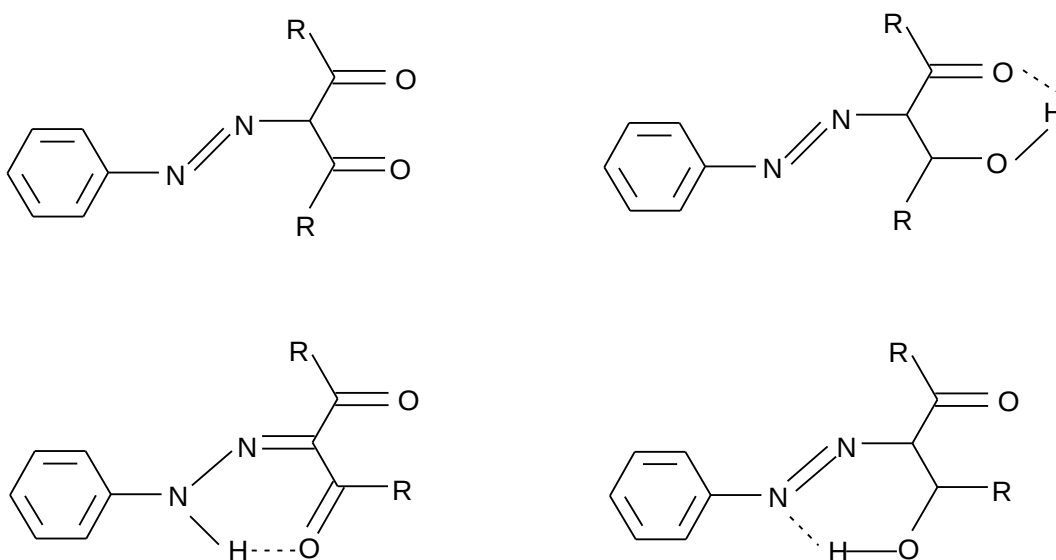
Fig. 1.5

In the case of unsymmetrical 1,3-dicarbonyls, i.e., when the 'R's are different, the possibility of resonating structures increases. Similar situation is also observed when groups like OH, SH, NH_2 or COOH are present on the benzene ring which can form hydrogen bond with the azo group.

3. Metal complexes of arylazo derivatives of β-dicarbonyl compounds

The coupling of a diazonium ion with a bidentate β-dicarbonyl introduces an additional donor atom into the system. However, steric factors[14] prevent the participation of all the donor atoms in chelate formation. It has been shown that these act as good bidentate ligands with only one of the carbonyl groups and one of azo/hydrazonic nitrogen[15] involved in chelate formation.

In the case of arylazo derivatives of heterocyclic 1,3-dicarbonyl compounds, the hetero atom can coordinate to the metal ion, provided it is situated at a vantage position so as to form a 5/6 membered ring. Similar is the case with heteroarylazo derivatives of β-diketones - the hetero atom can contribute electrons towards chelation if appropriately placed. In the case of aryltetrazo derivatives of β-dicarbonyls formed by the coupling of tetrazotised diamines and β-diketones, it is seen that these act as tetradentate ligands - not bonding to the same metal but to different ones rendering them as binucleating ligands.

A number of published works are available on the structural aspects of complexes of azobetadiketones and allied compounds. Reports could be traced back to 1969[16] and many current works are also there. β-diketones, like acetylacetone, benzoylacetone, dibenzoyl methane, methyl/ethyl acetoacetate and malonic ester have been used as coupling agents[17-24, 27-29] and almost in all cases one of the azo nitrogens and one of the keto groups are involved in coordination forming a six membered chelate ring. These compounds act as anionic bidentate ligands.

Cyclic β-diketones, like indane-1,3-dione and cyclohexane-1,3-dione[21] had been made use of to couple with diazotised primary amines. Lycka *et al.*[30] have used acetoacetanilide as the coupling agent and had synthesised and characterised Al(III) complexes. Masoud *et al.* [25,26] had used barbituric acid as a coupling agent. In a recent work, curcuminoids[31], β-diketones with a double bond in the carbon chain have been employed as coupling agent. Reports are also there of the quantum chemical (LCAO) calculations[32] and electrical properties[33] of azo betadiketone complexes. Polymeric binuclear complexes of azobetadiketones had been synthesised by El Beradie and co-workers[34].

4. Arylazo derivative of pyrazolones

Pyrazolones are oxo-derivatives of pyrazoles. Ever since the discovery of the antipyretic action of 1-phenyl-2,3-dimethyl-3-pyrazolin-5-one (Knorr,

1883) the importance of pyrazolones prevails. Soon came tartrazine, 4-(4-sulphophenylazo)-1-(4-sulphophenyl)-5-oxo-2-pyrazolin-3-carboxylic acid (Zeigler, 1884), a synthetic azo dye with pyrazole nucleus. This sparked the synthesis of a series of similar azodyes, used mainly to dye fabrics and it continues to be the major application of azodyes.

Arylazopyrazolones are found to be acting as multidentate chelating ligands. These are found to be existing mainly in three tautomeric forms (Fig. 1.6).

keto (azo)	enol (azo)	(quinone hydrazone)
(a)	**(b)**	**(c)**
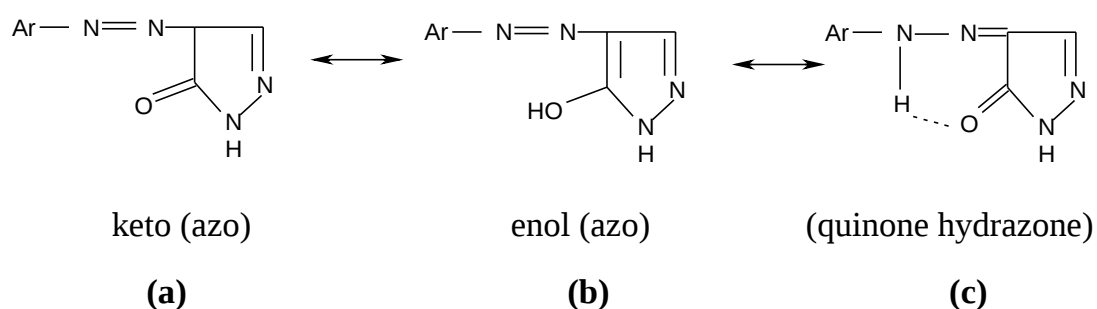
Fig. 1.6

Two more structures can also be drawn. But it has been unequivocally stated[35] that pyrazolones with no substituents on N-2 are all 2-pyrazolones. Therefore, the 3-pyrazolone structures are not mentioned here. The present work is on 4-arylazopyrazolin-5-ones which will be referred to as 'arylazopyrazolone' in the coming discussion.

Arylazopyrazolones can be synthesized in different ways. In one method, the aryl amine is diazotised and coupled with pyrazolone in which

the 4th position is reactive. Another method is the diazotization of amino-pyrazolones, like aminoantipyrine and coupling with aromatic compounds with suitable active electron rich centre. Yet in another method, the pyrazolone is synthesized by cyclisation of hydrazine derivative with β-ketoester followed by coupling with diazotised aromatic amine. The coupling of the diazotised aromatic amine with β-diketoester followed by cyclisation with suitable hydrazine derivative will also yield arylazopyrazolone. The latter methods have the advantage of synthesizing the required arylazopyrazolone with appropriate substituents. In the present work, the synthesis of arylazopyrzolone is carried out by diazotising aromatic amine (aniline) followed by coupling with β-ketoester (methyl acetoacetate) and then cyclising the methyl-2-phenylhydrazono-3-oxobutyrate with a hydrazine derivative, phthalazinyl hydrazine.

5. Metal complexes of arylazopyrazolones

Many researchers have investigated the donor properties of arylazopyrazolones which act as bi/tridentate ligands as the case may be. All the methods mentioned previously have been employed for the syntheses of these compounds. Various studies carried out to characterize these complexes include the stability determination using potentiometric methods, structural investigation using spectral methods, thermal characterization using TG/DTA analyses, minute structural details using single crystal XRD, etc.   Several

applications of arylazopyrazolones have also been reported which will be reviewed in section B of this chapter.

In this section, a selected collection of structural aspects and ligational behaviours of arylazopyrazolones which is a consequence of donor atoms and metal ions will be discussed with appropriate review.

The coordination behaviour of these compounds depends on the azo nitrogen as well as the C=O at 5th carbon atom of pyrazolone ring. These compounds normally behave as bidentate ligands (a of Fig. 1.7). Their denticity will increase depending on the electron rich substituents at *ortho*-position to the azo group. When N–1 of the pyrazolone is substituted with aroyl group, the C=O can also take part in chelation (b of Fig. 1.7).

X = OH, SH, NH$_2$, etc.

(a)

(b)

(c)

Fig. 1.7

13
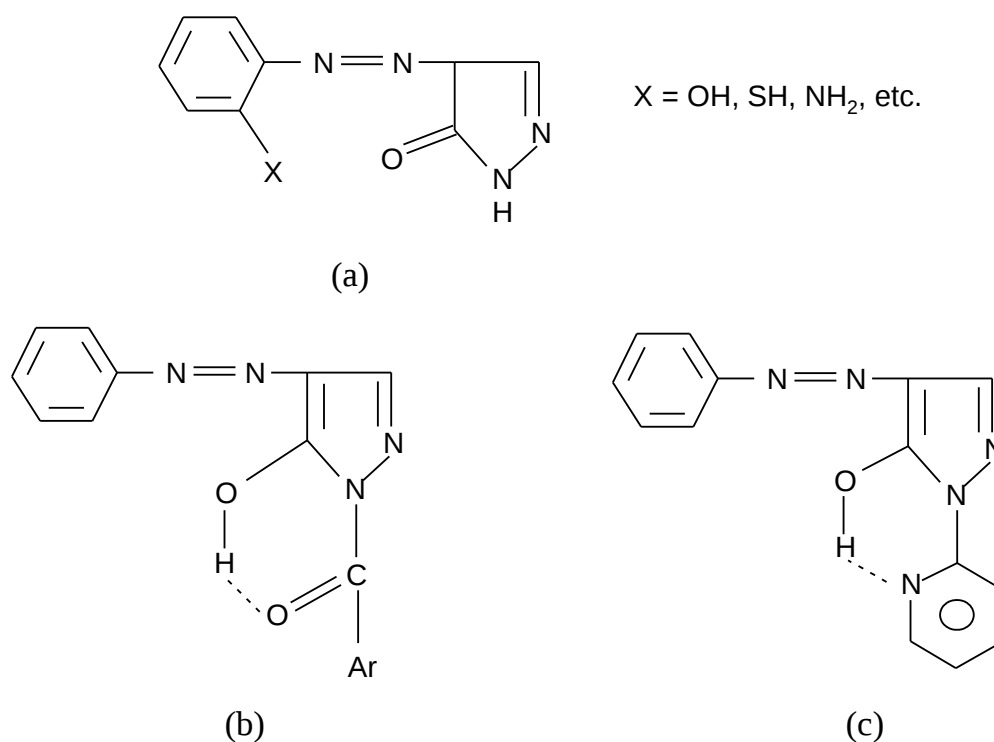
As can be seen from c of Fig. 1.7, the presence of heterocyclic group at N–1 of pyrazolone ring also may affect the denticity of the ligand and the geometry of arylazopyrazolone chelates. The chelating behaviour of these ligands had been thoroughly studied by Snavely *et al.*[36-42]. These works elaborate the stability of metal complexes of simple 4-phenylazopyrazolones and the different substituted ones, where substituents like Cl, I, NO_2, OCH_3, SCH_3, $-OCH_2COOH$, $-N(CH_3)_2$ or $-SO_3H$ enter the position mainly at *ortho-* and in a few cases at *para-* positions of –N=N– group. The authors had established that arylazopyrazolones behave as bi- or tridentate ligands depending on the groups *ortho-* to –N=N–. Moreover, the donor behaviour of N atom in the *ortho-* substituted compound was found to be greater than those with O or S atoms. It was also pointed out[38] that the azo (–N=N–) tautomer prevails rather than –N–N=C hydrazone in 4-azopyrazolone. They had also conducted studies based on IR, NMR and magnetic moment data.

Some contemporary researchers[43] have worked on naphtholazopyrazolone complexes of Cr(III) and have found that these complexes further react with β-diketones, amino acids, etc., to give mixed ligand complexes. The chelating strength of azopyrazolones had been studied by Le Grand and Fernalius[44]. Fouda, A.S *et al.*[45] had synthesized 4-*p*-(N-pyridine-2)sulphanoylphenylazopyrazolone chelates and studied their stability

constant. They had arrived at the conclusion that the stabilities of the complexes increase in the order $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$.

The geometry and stoichiometry of 4-*p*-methoxyphenylazopyrazolone complexes of Ni(II), Co(II), Mn(II) and Cu(II) were investigated by Abdul Latif and Hassib[46]. Studies of similar complexes with La(III), Ce(III), Th(IV), VO_2(VI) were also carried out by the former author[47]. Using spectral and TG/DTA techniques, characterization of 4-ethoxyphenylazopyrazolone complexes had been carried out by Batiu *et al*[48].

The stability constants of the lanthanide complexes of phenylazopyrazolones with different substituents (OCH_3, COOH, NH_2) at *o*-position had been compared by El-Shetary *et al*[49]. They have found that COOH group predominates in coordination behaviour.

Fe(III) complex of quinolinazopyrazolone was assigned a pseudo octahedral structure by Uraev *et al.* [50] using single crystal XRD studies.

Moustafa and Issa[51] elaborated the stoichiometries and structures of 4-(*o*-OH/COOH phenylazo)-1,3-diphenylpyrazolone complexes of Co(II), Ni(II), Cu(II) and Zn(II) by several analytical and spectral techniques. The potentiometric and conductometric studies of transition metal chelates of 4-(4-acetophenyl)-hydrazono-3-methylpyrazolones were also reported[52]. Mubarak[53] had investigated the stability constants of transition metal complexes of 4-sulfamethazineazopyrazolones by potentiometric and

thermodynamic studies and found that the stability constants follow the order,

$Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$.

Stability of 4-(4-nitrophenylazo)-3-methyl-1-(2-hydroxy-3-morpholinopropanyl)pyrazolone and its metal complexes had been elucidated by ElSonbati *et al*[54].

The synthesis and characterization of 4-phenyl-1-(2-benzthiazolyl)-3-methyl pyrazolone and its copper complexes with a variety of substituents on benzene ring had been reported by Emandi *et al*[55].

The single crystal XRD structure together with other spectral studies of 4-(2'hydroxyphenylazo-1,3-methyl 1-phenyl pyrazolone had been illustrated by Banβe *et al*[56].

Complexes of Co(II), Ni(II), Cu(II) and Pd(II) with 3-amino-4-(arylazo)pyrazolone(aryl-*p*–OCH_3/COOH phenyl, *m* CO_2H/NO_2/ CH_3/OH phenyl, and *o*-COOH phenyl) had been synthesized and studied by Masoud *et al*[57].

Bis-phenylazopyrazolone metal complex had been studied by Shetty *et al*[58]. Spectrophotometric studies of actinide complexes with arylazopyrazolones had been by discussed by El Sayed and co-workers[59].

The potentiometric, spectrometric, thermal and conductometric studies of Co(II) complexes of 3-phenyl-4-(arylazo)-pyrazolones, where phenyl

group was substituted at the *para* position with OCH_3, CH_3, H, Cl groups were reported by Hassib and Latif[60].

The spectral and magnetic studies of iron(III) complexes of hydroxyaryl azodyes derived from antipyrine were carried out by Rawther and Nair[61]. They have suggested from the IR data that the OH groups take part in co-ordination together with –N=N– nitrogen and C=O of pyrazolone ring. Radhakrishnan[62] investigated the ligational behaviour of 2,4-dihydroxy phenylazoantipyrine with lanthanide nitrates and pointed out that the –OH group at 2-position was not involved in co-ordination. Similarly, Kuncheria and Indrasenan[63] have reported the naphtholazoantipyrine complexes of Th(IV), where they had observed the involvement –OH group in co-ordination. Later, in their work, Mariamma and Radhakrishnan[64] reported the participation of –OH in coordination in the case of 2,4-dihydroxyphenylazoantipyrine lanthanide perchlorate complexes and pointed out that steric hindrance might be the factor preventing the co-ordination of ClO_4^- which necessitated –OH coordination to satisfy the coordination number of lanthanides. The temperature dependence of the stability of 4-(2-hydroxy-4-methyl-phenylazo)antipyrine and its copper complexes had been observed by El-Sayed *et al*[65].

Harikumaran Nair and Mathew George[66] investigated the spectral, thermal, cyclic voltametric and antibacterial properties of 4-(2-hydroxy-5-

methyl-phenylazo)antipyrine complexes of Ni(II). Studies on mononuclear-and binuclear complexes of antipyrine-4-azo-alphanaphthyl had also been done[67]. Synthesis and spectral characterisation of antipyrine azoimidazoles had been carried out by Senapati *et al* [68].

Shukla and Srivastava[69] synthesized 4-arylazopyrazolones by diazotising anilines, coupling with ethylacetoacetate followed by cyclisation with hydrazine/phenyl hydrazine. The complexes of these ligands with copper(II) and nickel(II) have the anion coordination indicating that the pyrazolones act as neutral ligands.

Kuncheria and Aravindakshan[70] reported the synthesis and characterization of Cu(II) and Co(II) complexes of 1-isonicotinoyl-3-methyl-4-phenylazopyrazolones and have suggested the neutral nature of the pyrazolone ligands.

El-Maraghy *et al*[71a,b]. reported the 1:1 and 1:2 (metal : ligand) complexes of *o*-hydroxyarylazopyrazolones with Eu(III) and Pd(II). An anomalous structure with metal oxygen double bond M=O as in the case of alkoxides was reported in the case of Ni(II) chelates of *o*-methoxypyrazolone. Co(II) complexes of *para* methyl/*ortho* or *para* methoxy/*ortho* carboxyphenylazopyrazolones were synthesized and studied by Verma *et al*[73]. They had proposed the formation of 1:2 complexes with –C=O, N=N groups

participating in the coordination. They had observed participation of –COOH in coordination when it was at *o-* position to –N=N group.

B.   Applications of azo compounds and their metal complexes – a brief review

The term azo is synonymous with dyes. Azo compounds constitute a major share of dyes and pigments. Azo dyes have been adding colour to human thoughts and appearances dating back from the middle of the 19th century after the first synthesis of Aniline yellow (C Mene 1861) followed by Bismarck Brown (Martius 1863). In fact, the synthesis of diazobenzene (Mitscherlich 1834) by the action of alcoholic KOH on nitrobenzene was the inspiration behind the synthesis of azo dyes. Azo dyes contain an azo (–N=N–) group connected to an sp^2 carbon. These dyes do not occur in nature. According to the number of azo groups present, they are termed as monoazo, bisazo, trisazo, etc. Based on the physical and chemical properties, these are further classified as anionic, disperse, azoic, cationic, complex forming, directive, reactive, etc.

Even though many prefer to use the term azo compounds with reference to the hydrazone compounds, strictly speaking, the term azo refers to –N=N– grouping. The discussion here will be restricted to diazonium salts, the precursor of azo dyes and some azobetadiketo and azopyrazolone derivatives, including their metal complexes.

In addition to forming the major reagent in azo coupling reaction, the most widely used industrial reaction in the production of dyes, lakes and pigments, aromatic diazonium salts have recently been found to be having uses in nanotechnology. 4-chlorobenzenediazonium tetrafluoroborate is used in functionalizing[74] nanotubes. Here the diazonium salt covers the surface of the nanotubes with chlorophenyl groups and prevents them from coiling and bundling which is a recurring problem in nanotube technology. They are also found to be useful in functionalizing silicon wafers by forming an aryl mono layer[75]. The diazonium salts are now a days used in metal grafting too[76]. Active methylene compounds, mainly the 1,3-dicarbonyl compounds constitute an important group of coupling reagents in dye industry[77-79].

Apart from being used as dyes, the coupling action resulting in deep colour had been a promising factor for the colorimetric estimation of the coupling agent. Acetoacetate produced by the oxidation of β-hydroxy butyrate in body was estimated with admissible percentage of error by Walker[80a]. Still, the credit of estimating acetoacetate in blood using diazotised *p*-nitrosoaniline goes to Rosenthal (1949), though the pH of the reactions were not specified in his work. The application of diazonium salts as coupling agents for phosphatases in body had been illustrated by Burstone[80b]. Complexes were formed on treatment of the slides of the coupled product with metal salt solution.

Spectrophotometric determination of nitrite ion by treating the sample with *p*-nitroaniline followed by coupling with ethoxyethylenemaleic ester had been reported by Cherian and Narayana[81]. Thenoyl trifluoroacetone was found to be a good coupling agent with a diazotised amine for the spectrophotometric determination of Cu(II)[82,83].

The identification of the toxicity and carcinogenicity of benzidine azodyes had been assessed by De France *et al*[84]. They found that the dye obtained by coupling diazotised benzidine with maleic ester was not converted back to benzidine in body which suggests that the dyes are not mutagenic as the parent amines.

Azobetadiketones have been used as stationary phase in liquid chromatographic separation of metal ions[85].

A mixture of sulpha drugs had been separated by diazotisation followed by coupling with acetylacetone[86] by TLC method.

Azobetaketo dyes have been used in optical wave guides and OLEDs by complexing them with rare earth metals together with some light harvesting heterocycle coligands. The wide cross section of absorption peak of azodyes, especially the betadiketones, in addition to their high ε values make them suitable for the application. The rare earth complexes were incorporated in a suitable matrix, usually a polymer. A modest attempt has

been made on this application in the present work and is included in Part II of this thesis.

Azopyrazolone compounds find their major application in dye industry. Use of tartrazine, many azopyrazolone dyes and their 'metallised' products, i.e., the complexes as dyes were described by Venkataraman[87]. There are reports about Ni(II) and Cr(III) complexes of azopyrazolones used as dyes[88]. Formation of azomethine dyes from 4-arylazopyrazolones was explained by Vittom *et al*[89].

Many dyes find application as biological stains. Tartrazine is used as a counterstain. Many of the hair dyes are made up of azo compounds. The dye, basic yellow is an azo pyrazol derivative [5-hydroxy-3-methyl-1-phenyl-4-(3'-trimethylammoniophenylazo)-pyrazol].

Studies are still continuing[96-98] to exploit the possibilities of newer hues, light fastness, water solubility, etc. of the azo dyes for the evergrowing demand in textile industry.

Pyrazolone red, an azopyrazolone dye has been found good to be used for colouring plasticised PVC[99].

Pyrazolones were reported to be used as couplers to react with phenyline diamines for colour developing image dyes[100] in colour photography.

Azo pyrazolone dyes find many applications other than as colouring agents. There are reports[101] on the deposition of bis-(azopyrazolone) dye on electrodes for the amperometric determination of Ca^{2+}. The method was found to be so sensitive that it could very well be applied to estimate nickel in biological systems.

Another report[102] discusses the amperometric titration of diazotised aromatic amine with 1-phenyl-3-methyl-5-pyrazolone which is useful for the estimation of amines as well as the coupler.

Spectrophotometric determination of thorium with Solochromate Fast Red, an azopyrazolone dye which forms an orange coloured complex with the metal had been described by Korkisch *et al*[103].

Azopyrazolones were also reported to be possessing antitumour[104], antidiabetic[105] and antifungal[106] activities.

The antioxidant properties of azoantipyrine had been illustrated using cyclic voltammetry by Bashkatova *et al*[107].

The extraction of copper from ammonia leach solution using azopyrazolones was described by Emeleus *et al*[108].

Some other applications of azo compounds which are neither β-diketoderivatives nor pyrazolones are also mentioned in the coming passage.

The possibilities of extending the work to azobetadiketones or azopyrazolones can be considered.

A particular dye with boronic acid group had been found to be an effective chemosensor[109] for the presence of monosacharide. This can be applied for the detection of glucose in blood.

Azodyes had been incorporated into concrete[110] by first embedding them in polymers to find out the corrosion possibilities which are mainly due to acidic or chloride influences. Here, the property of azodye to change colour at different pH is made use of.

Congo red which is widely used as a biological stain has been found to bind with HIV protease[111], the sulphonate group interacting with side chains of arginine. This property suggests the possible use of congo red as an antiviral chemical.

Many azo dyes are found to be useful in information processing[112],liquid crystal photoalignment[113], prediction of photoanisotropy[114], as stains in the demonstration of ostetoclasts[115], etc.

From the above review, the wide possibilities of applications of azo dyes are quite obvious. One should venture to exploit the versatility in application with respect to their physical and chemical properties.

As a final note one should always keep in mind the harmful effects of chemicals with which he is working. Azo dyes have been proved to be causing skin cancer by Fare[116] when he painted albino mice with amino azobenzene for about a year. The messy nature of the azodyes which give permanent stain to the cloth, paper, polymer or clay apparatus with which they are in contact must also be kept in mind.

C. Objectives, perspectives and scope of the present investigation

The present investigation aims at working out the ligational behaviour and donor properties of (a) azo-β-diketoderivatives and (b) azopyrazolones. Both are capable of exhibiting azo-hydrazone and keto-enol tautomerisms. The azopyrazolones are formed as a result of cyclisation reaction between an azo-β-diketoester and a hydrazine derivative. The possible application of one of the synthesized ligand has also been investigated by synthesising two rare earth (Eu) complexes with the required modification.

The products obtained by coupling aryldiazonium salts with compounds containing active hydrogens were termed as mixed hydrazones due to the possibility of tautomerism and the reaction was first observed by Meyer and Ambhul[117] when they used ethylacetoacetate and aromatic diazonium salts in alkaline solution. Later, many successful attempts were carried out which continued upto the early part of the 20th century. But the puzzle of the real structure of the product remained unsolved. Russel[118] was

able to prove the structural aspects of 2-phenylhydrazono-1,3-diketones by treating them with diazomethane which resulted in the formation of 3-arylphenylpyrazoles which had known structures. Mention must be made on the work of Japp and Klingmann (1888) who treated equimolar amounts acetoacetic acid and aryldiazonium hydroxide to get hydrazones.

Later it was proved[119] without doubt that the coupling of a diazonium salt to a methinyl carbon gives an unstable azo compound which cleaves to give a hydrazone whereas the coupling product of the same diazonium salt to a methylene carbon was a relatively stable hydrazone. The isolation of azocoupled product of Japp Klingemann reaction was conducted by Yao and Resnick[120] by careful concentration of the reaction mixture under reduced pressure at low temperatures.

Hydrazones are characterised by the presence of triatomic grouping >C=NH. They can behave as neutral or anionic ligands and coordinate through azomethine nitrogen (>C=N–) or the hydrazone nitrogen (>N–H). Denticity increases by the presence of other corodinating groups in proximity of the nitrogen atom. Metal 1,3-diketonates are known to undergo many electrophilic substitution reactions, typical of aromatic compounds, because of the quasi-aromatic C_3O_2M ring system present in these chelates. This accounts for their stability too.

In the case of heterocyclic azo compounds such as pyridylazo and thiazolylazo compounds, the pyridine and thiazole ring systems have lower resonance stablisation energy compared to their carbocyclic analogues[121]. Therefore, azo derivatives of heterocycles may exist in the azo form itself rather than the hydrazone form. The reduction patterns of azopyrazolones studied by polarographic and cyclic voltammetric studies[122,123] indicated the presence of an azo structure.

The present work comprises the studies of four ligands and their transition metal complexes. The ligands are (i) phenylazo dimedone, AD (ii) N-1-phthalazinyl phenylazo pyrazolone, HyPy (iii) phenylazo dehydro acetic acid, ADAA and (iv) antipyrinyl azo dimedone, DAAP. The metals chosen are those of the first transition series. Two europium complexes have also been synthesised for photophysical studies. Even though the ligands, HyPy and ADAA had been synthesised earlier by other researchers[*], the ligational behaviour of these compounds has not yet been explored. The ligand AD bears similarities with other reported[#] works but the metal complexes are, to the best of our knowledge anew.

The prime objective of the present work is to have a detailed analysis of the ligands and their metal complexes with respect to their structure based

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[*] [#]References are mentioned in the concerned chapters.

on microanalytical, magnetic, spectral and thermal analysis. The single crystal XRD data of one of the ligands, AD have also been included.

In addition to the structural aspects, the possible photophysical application of one of the ligand AD when complexed to europium with 1,10-phenanthroline as coligand has also been looked into. The photophysical features of two europium complexes of the above type (one with dimedone and the other with phenylazo dimedone) have been investigated, keeping in mind their possible application in light emitting diodes or optical fibre amplifiers. The details are included in Part II of this thesis.

The azo compounds find a host of applications besides their dyeing aspects. Many arenas like analytical, metallurgical, medicinal, etc., are yet to be explored. Azo-β-diketones and azopyrazolones, the ligands of choice in the present investigation can also find similar applications.

Pyrazolones had long been in use as medicines. Starting from antipyrine, amino pyrine (4,4-dimethylamino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one), dipyrone (sodium salt of 2,3-dimethyl-1-phenyl-5-oxo-2-pyrazolin-4-methylamino methane sulphonic acid), sulphamipyrine (dipyrone derivative), phenyl butazone (4-butyl-1,2-diphenyl-3,5-pyrazolidine dione) are some to mention a few. Though many of the pyrazolone drugs were used due to their antipyretic and antiinflammatory action, almost all are banned in many of the countries due to their harmful side effects, like aplastic anaemia.

These are now considered as outdated medicines, their place being taken up by paracetamol, ibubrufen, etc.

However, the medicinal aspects of the ligands and complexes synthesised during the present work can be investigated. They are sure to exhibit antipyretic, antiinflammatory and antimicrobial activities due to the presence of pyrazoline and phthalazinyl moieties. Oral or intravenous drugs with azo group are not used in current medical practice. But they may at least find some peripheral applications.

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CHAPTER II
MATERIALS AND METHODS

A brief description of the reagents used and methods adopted for the characterization of the compounds are included in this chapter. The models of the instruments with a note on their operational settings are also provided. Only those compounds which could be isolated in stable and analytically pure form are reported in this thesis.

A.   Reagents

All the chemicals used for synthetic purposes were of Analar grade. Solvents like methanol, acetic acid, acetone, dichloromethane and chloroform were purchased from E Merck and used as received. Commercial ethanol was purified by distillation and used. The metal salts used for the synthesis of complexes were acetate of Co(II), Ni(II) and Cu(II) and chlorides of Cr(III), Fe (III) and Zn (II).

B.   Ligands and complexes

1.   Ligands

In the present investigation four different ligands belonging to the group azo-β-diketones and azo pyrazolones have been synthesized and characterised. These are (i) phenylazo dimedone, (AD) (ii) N-1 phthalazinyl

azopyrazolone, (HyPy) (iii) phenyl azo dehydro acetic acid, (ADAA) and (iv) anti pyrinylazo dimedone, (DAAP).

The azo β-diketones were synthesized by diazotising the appropriate primary amine and coupling[2] with β-diketone. HyPy has been synthesized by cyclising the azo coupled product of the above reaction with hydralazine hydrochloride. The details of the synthesis are given in the respective chapters.

2. Complexes

All the complexes were synthesized by adding metal salt solutions to ligand solutions in appropriate metal: ligand mole ratio (1:2 for divalent metals and 1:3 for trivalent metals). The resultant mixture was refluxed on a steam bath for about 3 h. The details of the procedure are described in the relevant chapters.

C. Instruments

The following instruments were utilized for the physico chemical analyses of the compounds.

a)   JASCO UV-Visible spectrophotometer

b)   JASCO FTIR spectrophotometer 4100

c)   JEOL SX 102/DA-6000 Mass spectrometer for FAB and Micromass
       Quattro 11 triple quadrupole mass spectrometer for ESI methods.

d)   Vario EL III CHNS analyser

e)   ICPAES-IRIS intrepid IIX SP, Thermo electron corporation

f)   NMR – 400 MH$_z$ Varian Mercury NMR

g)   Magway magnetic susceptibility balance, Sherwood scientific, UK

h)   Perkin Elmer Diamond TG/DTA

i)   Single crystal XRD – Bruker AXS (Kappa Appex II)

D.   Methods

UV-visible spectra were recorded using 10^{-3} M solutions of ligands and complexes in methanol. The solvent, methanol was taken as reference and the scanning was done in 200-800 nm range.

IR spectra of the compounds were recorded by making thin KBr discs with the compound. The scanning range was 4000-400 cm^{-1}.   The standardisation of the instrument was done with PS film.

The FAB mass spectra were obtained using Argon as the FAB gas, accelerating voltage, 10 kV and *m*-nitrobenzyl alcohol (NBA) as matrix. The spectra were taken from SAIF, CDRI, Lucknow.

The ESI mass spectra were measured by dissolution of the sample in methanol with ESI capillary set at 3.5 kV and voltage 40V. The spectra were obtained from SAIF, CDRI, Lucknow.

The elemental percentage analyses of C, H and N were carried out at STIC, Kochi. Some of the metal percentage analyses were conducted at STIC, Kochi using ICP-AES spectrometer using argon as the conductor gas for plasma state at a core temperature of 9000 K. The other metal percentages were determined by adopting standard procedure[3] as outlined below.

The complex was digested with a mixture of conc. HNO_3 and 70% perchloric acid (2 or 3 drops) till all the white fumes subsided. It was then made upto a known volume and this solution was used for the estimation of metal ions. The metals, copper (as CuCNS), cobalt (as $Hg[Co(NCS)_4]$), nickel (as nickel dimethylglyoxime) and iron (as Fe_2O_3) were estimated by gravimetric methods. Zinc was estimated complexometrically with EDTA and Eriochrome blackT indicator. Chromium was estimated spectrophotometrically[4] after oxidising to dichromate. Chloride has been estimated by Volhard's method by fusion with Na_2CO_3 followed by decomposition in HNO_3.

The NMR spectra were obtained using $CDCl_3$ as solvent and TMS as internal standard from SAIF, IIT, Bombay and Department of Chemistry, Madurai Kamaraj University.

Magnetic susceptibility was determined at room temperature on Magway susceptibility instrument which was calibrated[5] using $Hg[Co(NCS)_4]$.

Thermogravimetric studies, TG/DTG and DTA were carried out at STIC, Kochi in nitrogen atmosphere with a heating rate of 10°C/min.

Single crystal X-ray diffraction of one of the ligands was performed for collection of data regarding unit cell parameters, space groups and structural details like bond distances, bond angles, torsion angles about bonds and dihedral angles between planes. The instrument with a gonimeter of Kappa geometry and CCD diffractometer equipped with Mo Kα source was used. The software Shel XTL-S was used for structure determination. The facility at SAIF, IIT Madras was utilised for this purpose.

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CHAPTER III

SPIRO 5,5-DIMETHYL-1,2,3-CYCLOHEXANE TRIONE-2-PHENYL HYDRAZONE AND ITS METAL COMPLEXES

Spiro 5,5-dimethyl-1,3-cyclohexane dione (dimedone) finds a large variety of applications in chemistry and allied fields. Dimedone analogues are found to mimic natural amino acids (Fig. 3.1).

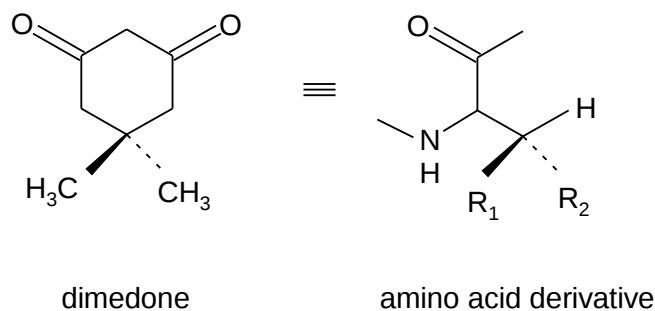dimedone   amino acid derivative

Fig. 3.1

The scope of synthesising such peptide libraries is being attempted at by current researchers.

Dimedone being a betadiketone with more enol content acts as a promising ligand through the two donor oxygens. The active methylene group can be allowed to couple with diazonium salts there by increasing the number of donor atoms.

Eventhough there are reports[1,2] of the substituted phenylazo derivatives of dimedone and its metal complexes, the unsubstituted aniline has so far not been reported to be used in diazo coupling reaction with dimedone. Hence the present study has been carried out by diazo coupling unsubstituted aniline with dimedone to form phenylazo dimedone (AD) (LH).
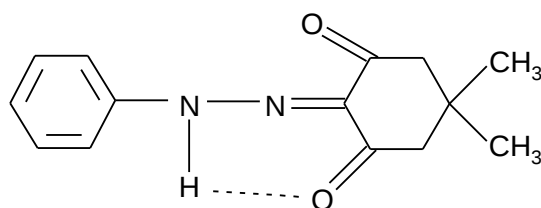

Fig. 3.2. Phenylazo dimedone, AD (LH)

The structural aspects of this ligand and its Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes have been explained using various physico-chemical techniques like elemental analyses, electronic, IR, NMR and mass spectral methods. The single crystal XRD data of the ligand is also included.

A. Synthesis of phenylazo dimedone (AD)

Aniline (0.01 mole) was diazotised with $NaNO_2$ (0.01 mole) and HCl (0.025 mole) at a temperature of ~ 0-5°C. Excess acid was removed by the addition of urea. The mixture was stirred for half an hour maintaining the temperature at ~ 0-5°C. This solution of phenyl diazonium chloride was added drop wise with stirring to a well cooled solution of dimedone (0.01 mole) in ethanol when lemon-yellow coloured phenylazo dimedone

precipitated out. The pH of the solution was adjusted to about 6.5 using sodium acetate. The solution was stirred for another half an hour and the precipitate was filtered, washed with water, recrystallised from methanol and dried over anhydrous $MgSO_4$ in a desiccator. The purity of the compound was checked by TLC technique (yield 85%, m.p. $120^{o}C$).

B. Synthesis of metal complexes

The metal salts used for the synthesis were chlorides of Fe(III) and Zn(II) and acetates of Co(II), Ni(II) and Cu(II). The metal to ligand ratio used was 1:2 for divalent metal complexes and 1:3 for trivalent metal complexes.

A methanolic solution of the metal salt (0.001 mole) was added slowly in drops with stirring to a methanolic solution of phenylazo dimedone (0.002 mole/0.003 mole as the case may be). This mixture was refluxed for about 2h on a steam bath. The complex precipitated on cooling and was filtered, washed with water and dried over anhydrous $MgSO_4$ in a desiccator. The complexes were recrystallised from methanol or methanol-CH_2Cl_2 mixture.

C. Results and discussion

1. Characterization of the ligand

The ligand AD was a lemon-yellow non-hygroscopic solid which formed good crystals on crystallisation. Just like other azo compounds, it also changed its colour to orange red on increasing the pH.

a) Analytical data

The elemental percentages and other physical data are included in Table 3.1. The percentages of C, H and N showed close agreement with the molecular formula $C_{14}H_{16}N_2O_2$.

Table 3.1.   Physiochemical data of phenylazo dimedone

Ligand	Colour	Yield (%)	MP (°C)	Element percentage Found (Calc.)			Electron spectral data λ_{max} (nm)
				C	H	N	
Spiro 5, 5-dimethyl-1,2,3-cyclohexane-trione-2-phenyl hydrazone (Phenylazo dimedone) (AD) (LH)	Lemon yellow	85	120	68.69 (68.35)	6.11 (6.56)	11.29 (11.48)	286, 342, 386, 510, 686

b) Spectral data

The electronic, IR, NMR and mass spectra of the ligand AD were utilized to ascertain the structure.

i) Electronic spectrum

The electronic spectrum shows all the peaks expected of a monophenyl hydrazone[1]. A weak band at 286 nm and a strong absorption band at 386 nm are clear indications of a hydrazone form. The azo form is excluded as a strong K band[2] at 270-280 nm, which is characteristic of an azo form is absent

in the spectrum of the compound under investigation. The band at 510 nm may be due to a chelated ketonic[3] structure.

ii) IR spectrum

The IR spectrum of the ligand shows almost all bands expected of an azo betadiketone compound.

The intense bands in the carbonyl region 1673 and 1623 cm^{-1} confirmed the presence of diketo groups. The shift of these bands to a lower region compared to that expected for β diketones ($\sim$ 1700 cm^{-1}) may be attributed to the conjugation of the >C=O groups with >C=N (of hydrazone form). A band at still lower frequency may be due to the stretching of another >C=O involved in a hydrogen bonding with >NH.

No absorption bands were seen $\sim$ 3600 cm^{-1} (free-OH) or $\sim$ 3500 cm^{-1} (free-NH). However, the presence of a broad band at $\sim$3400 cm^{-1} indicated hydrogen bonded OH....N or H-N ....O groups.

The νC=N absorption occurs at the same region as that of C=O. In non-conjugated systems, νC=N absorption normally appears between 1690 and 1650 cm^{-1}. In conjugated systems it shifts to lower frequency. The band at 1590 cm^{-1} may be due to conjugated stretching of C=N. The important IR bands and their assignment are included in Table 3.3.

Table 3.2. IR spectral bands, ν (cm^{-1})

Wave number, (ν)	Assignment
~3400	N-H.....O
3052	=C-H (aromatic)
2954	asy C–H str.
2931	sym C–H str.
1673(s)	C=O (in conjugation with C=N)
1623 (s)	C=O (hydrogen bonded with NH)
1590	C=N
1507	C=C str (aromatic)
1455	C-H def (>CH$_2$)
1394	C-H def [(CH$_3$)$_2$C]
752(s)	C-H def.
690	monosubstd. aromatic ring

iii) ^{1}H NMR Spectrum

The ^{1}H NMR spectrum supports well the hydrazone structure of the ligand. In the azo form, there should be a peak corresponding to $\geqslant$CH group flanked by two >C=O groups at ~3.2 - 3.5 ppm which was absent in the NMR spectrum of phenylazo dimedone (Fig. 3.3).
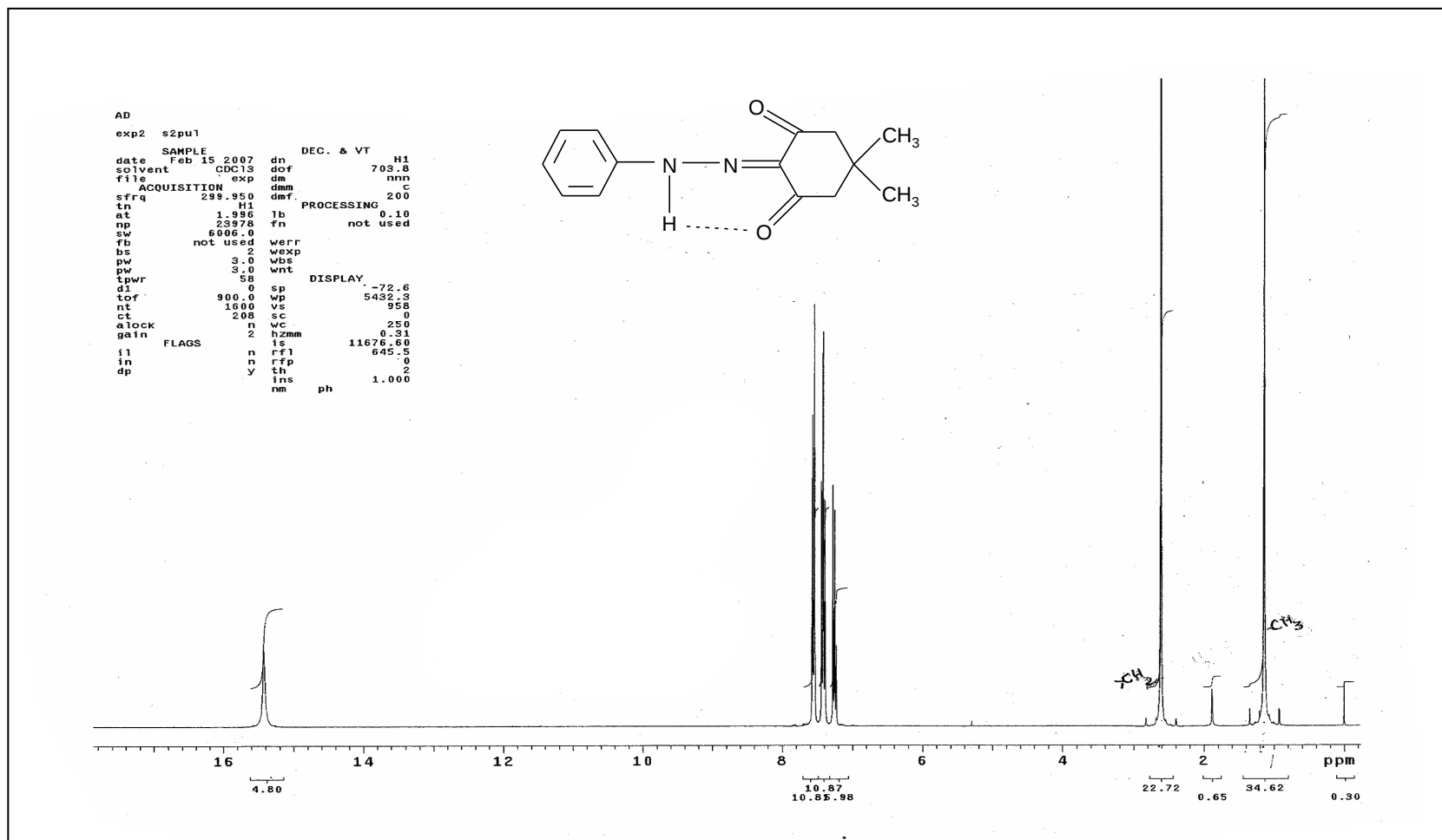
Fig. 3.3. ¹H NMR spectrum of phenylazodimedone

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N-H proton signal of hydrazone group is observed at 15.4 ppm which gives additional evidence to the hydrazone structure in which the absorption occurs at 3-5 ppm lower[4] than the azo-hydroxy resonance structure. Moreover, there are reports that an NH....O hydrogen bond is preferred to an OH....N hydrogen bond when both are possible[5-7].

In addition to the above peaks, the unmistatable[8] peaks of CH_3 (1.9 ppm), CH_2 (~2.6 ppm) and aromatic pattern (~ 7.2 - 7.6 ppm) are also present.

iv) Mass spectrum

Invetigations[9] have ruled out the disturbance of equilibrium (keto-enol or azo-hydrazone) after electron bombardment in a mass spectrometer.

The mass spectrum (Fig. 3.4) of phenylazo dimedone is pronounced by the presence of base peak at m/z 245 which is the $(M+1)^+$ ion. The other peaks of importance are m/z 217 $[(M+1)-(C_2H_4)]$, m/z 152 $[(M+1) - C_6H_5NH)$ which is an additional support to the hydrazone structure; where –HN–N= cleavage occurs.

Had it been the azo (N=N) form, the cleavage between N=N would not have occured. Moreover, the absence of an $(M-N_2)^+$ peak[10] also points to the absence of an azo group. The other important peaks are at m/z 124 (M+1-$(C_6H_5NH+two CH_3)^+$, and m/z 94 $(C_6H_5N^+H_3)$.
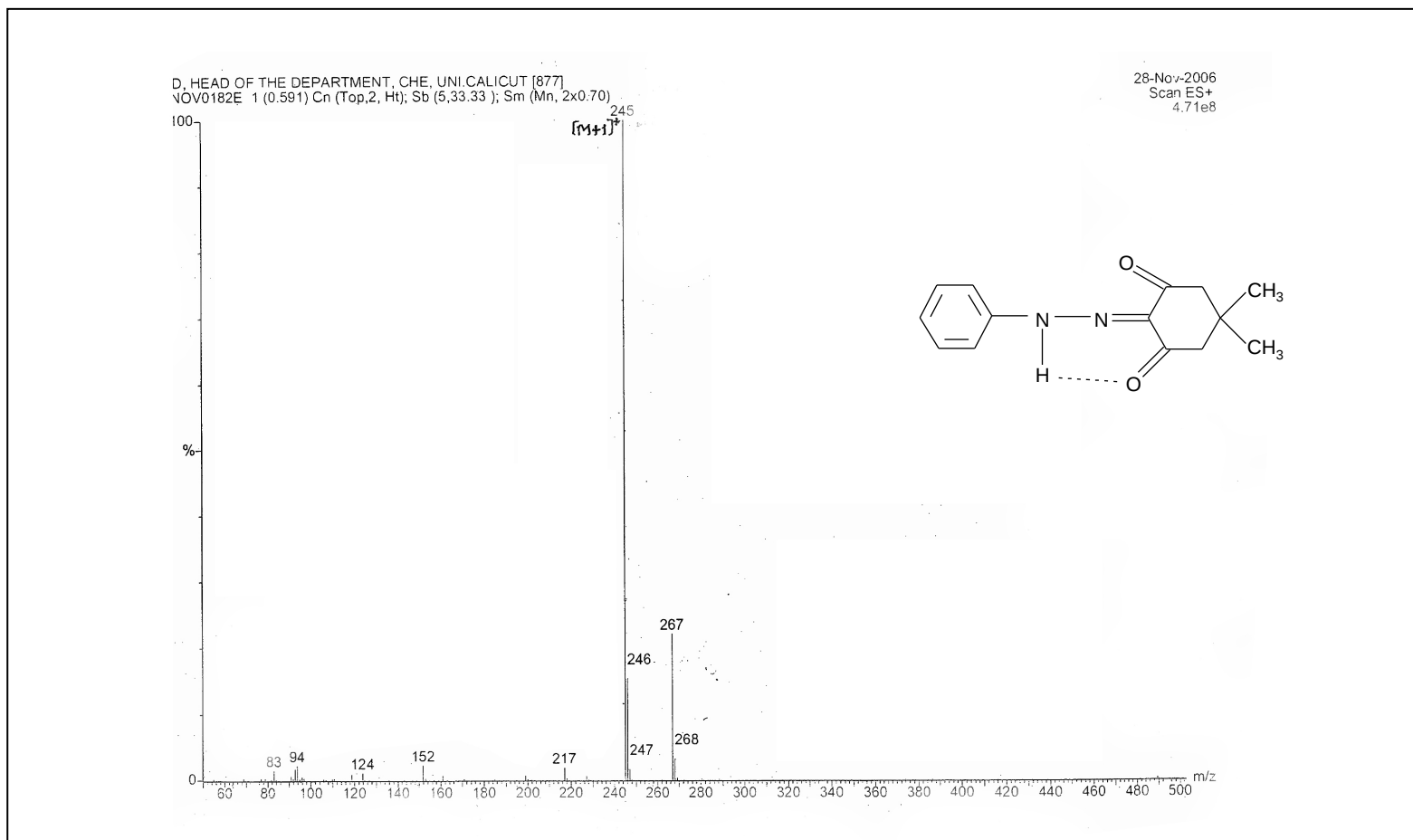
Fig. 3.4. ESI mass spectrum of phenylazo dimedone

c) Single crystal XRD data

The single crystal of the ligand has been obtained by slow evaporation of the purified substance in CH_2Cl_2 + CH_3OH mixture at room temperature. The data collection was done by cutting a suitable piece of size 0.3 x 0.2 x 0.2 mm and mounting on a goniometer using glass fibre. 10766 reflections were collected and 2011 were used for structure determination. The structure was solved by direct method using SHELXL software and refined by full matrix least squares against F^2. The computer graphics was of ORTEP model (Fig. 3.5). The general data are included in Table 3.3.
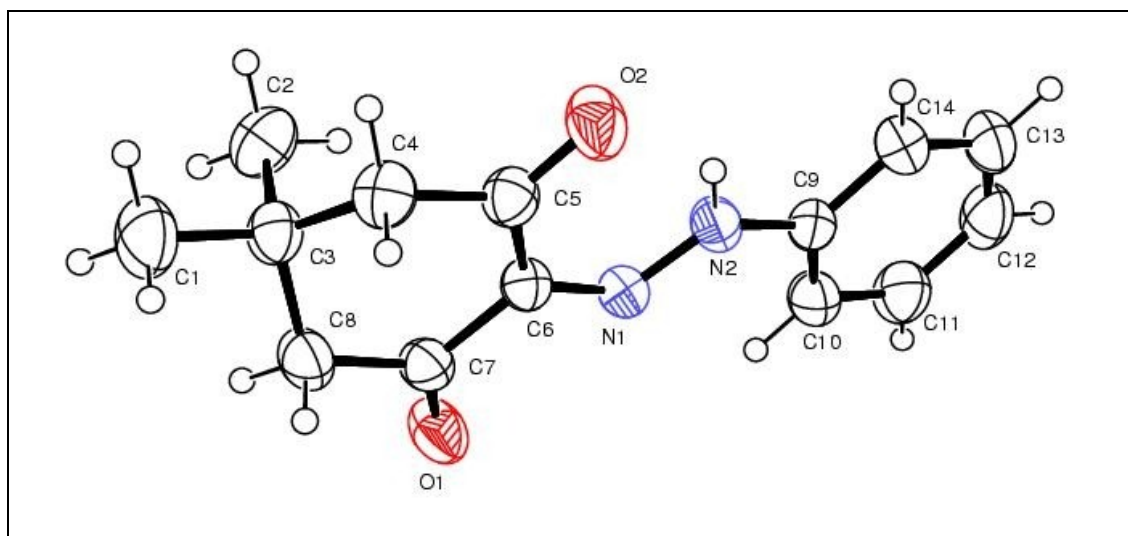

Fig. 3.5. ORTER representation of AD

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Table 3.3. Single crystal XRD data of AD

Empirical formula	$C_{14}H_{16}N_2O_2$
F.W	244.29
Temperature	293 K
Wave length (MoK$_\alpha$)	0.71073 A^o
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions (A^o) a = 10.7285 b = 5.8431 c = 20.8152	
α = 90.000 β = 96.946 γ = 90.000	
z value = 4	
Density (calc.)	1.253 Mg/m^3
Volume (A^3)	1295.28 (8)
Reflections collected/used	10766/2011
Residuals (all data) R$_1$	0.0526, ωR$_2$ = 0

Bond lengths between various atoms are also available in the data. The following table (Table 3.4) gives the bond lengths between selected atoms. The bond lengths in phenyl group and dimedone moiety are not shown in the table. The numbering is in accordance with the ORTEP computer representation.

Table 3.4. Bond length between selected atoms

Bond	Bond length (A°)
C(6) – N(1)	1.322
N(1) – N(2)	1.2987
N(2) – H(2)	0.94
C(5) – O(2)	1.2340
C(7) – O(1)	1.2149
C(9) – N(2)	1.406

C(6) - N(1) is a double bond. C(5) - O(2) length is greater than C(7) - O(1). Eventhough both are carbonyl oxygens of dimedone, the higher value of C(5) - O(2) may be due the single bond character of the bond as O(2) is hydrogen bonded to H(2) of N(2).

Further evidence is provided by the details of the hydrogen bond shown below.

N(2) - H(2) ..... O(2)   angle 136.5^0

bond length - N(2) - H(2) 0.94 A°

H(2) ... O(2) 1.00 A°

2. Charaterization of metal complexes

Phenylazo dimedone forms well defined complexes with Fe(III), Co(II), Ni(II), Cu(II) and Zn(II). Attempts to make Cr(III) complex were not successful . Fe(III) complex was obtained in poor yield, may be because of the steric reasons. Still, all the complexes synthesised have been purified by

recrystallisation. These were found to be nonconducting. Ni(II) and Zn(II) complexes were diamagnetic. The μ_{eff} values of all other complexes complied well with the expected values. An attempt has been made to arrive at the structure of the complexes on the basis of elemental analyses, electronic IR, ^{1}HNMR and mass spectral data. The physico-chemical data, electronic spectral absorption positions and magnetic moment values are given in Table 3.5.

Table 3.5. Physico-chemical, electronic spectral and magnetic data of complexes

Sl. No.	Compound	Colour	Yield (%)	MP (°C)	Elemental Analysis (%) found (calc)				Magnetic moment μ (B.M.)	Electronic spectra λ_{max} (nm)
					C	H	N	M		
1.	[FeL$_3$]	Brown	30	165	64.02 (64.22)	5.57 (5.74)	10.26 (10.70)	6.53 (7.12)	5.91	290,340,500
2.	[CoL$_2$]	Pinkish brown	70	200	61.10 (61.65)	5.15 (5.51)	10.28 (10.27)	10.62 (10.81)	3.82	288,380,512,690
3.	[NiL$_2$]	Brown	60	250	61.00 (61.68)	5.41 (5.51)	10.43 (10.28)	10.57 (10.77)	D	292,230,450,564
4.	[CuL$_2$]	Olive green	70	215	61.36 (61.41)	5.99 (5.46)	9.98 (10.19)	11.19 (11.56)	2.10	288,384,686
5.	[ZnL$_2$]	Yellow	50	130	60.23 (60.94)	5.98 (5.44)	10.06 (10.16)	11.26 (11.85)	D	288,380,510

M – Metal; D – Diamagnetic; L – monoanion of AD(LH).

a) *Electronic spectral data and magnetic behaviour*

The electronic absorption bands of all the complexes bear close resemblance with those of the ligand. This showed that no structural alteration has occured on complexation. However, a slight shift in the absorption maxima of >C=O and >C=N bands were seen, may be because of the involvement of these groups in co-ordination. Not much information could be gained from electronic spectra. Still some assignments are carried out here. Trivalent iron has a tendency to have CT bands in the near UV which have many shoulders extending to the visible region which make the interpretation difficult. The magnetic moment was typical of an octahedral geometry viz. 5.91 B.M.

Cobalt complex was brown in colour with a pink tinge. This is typical of an octahedral geometry. The band at 512 may be due to $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ in an octahedral environment. But the magnetic moment value (3.82 B.M) was found to be too low for an octahedral geometry.

Nickel complex was brown and diamagnetic. The bands at 330 ($^1A_{1g} \rightarrow {}^1B_{1g}$) and 292 (C-T) also indicated the square planar geometry of the complex.

Copper complex was olive green in colour as expected and a band corresponding to the absorption was observed at 686 nm[12]. The explanation of

the spectrum was rather difficult owing to enveloping of bands. However, this can be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition in a square-planar geometry. The magnetic moment obtained (2.10 B.M.) was within the range (1.75 – 2.20 B.M.) expected for magnetically dilute square-planar copper(II) complexes.

b) IR spectra

The position of the free carbonyl stretching band of the ligand was only marginally (~ 30 cm^{-1}) altered in the spectra of complexes, showing that it was still free in the complexes. The band corresponding to hydrogen bonded carbonyl group has been lowered, that may be assigned to metal bonded carbonyl group. A new band at ~ 440 may be assigned[13] to νM–O and the band at ~ 560 may be assigned to νM–N.

All other bands in the ligand such as those at 3060 (aromatic C–H) 2959 and 2850 (C–H str.) 1394 (gem dimethyl C-H def) were retained in the spectra of the complexes. Important bands and assignments are given in Table 3.6.

Table 3.6. Important IR spectral bands (cm^{-1}) and their assignment

Sl. No.	Compound	Free νC=O	Chelated νC=O	νC=N	νM-N	νM-O
1.	[FeL$_3$]	1658	1547	1590	554	439
2.	[CoL$_2$]	1660	1546	1595	564	439
3.	[NiL$_2$]	1658	1547	1591	582	447
4.	[CuL$_2$]	1642	1520	1590	519	440

5.	[ZnL$_2$]	1659	1546	1592	553	444

c) ^{1}H NMR spectrum

^{1}H NMR spectrum of the diamagnetic ZnL$_2$ complex has been recorded and given in Fig. 3.6. The prominent feature of the spectrum was the absence of N-H peak[14] (~ 15δ) which was present in the ligand NMR spectrum. This was a clear indication of coordination through N to metal replacing H. Other peaks were the same as that of ligand NMR spectrum.

d) Mass spectrum

The ESI mass spectrum of Copper(II) complex was found to be having very conspicuous M$^+$ (m/z 550) peak which affirms the stoichiometry ML$_2$. The base peak (m/z 245) is that of the ligand. The (M+2) peak must be due to the isotope of copper, ^{65}Cu (abundance 30.9%). The spectrum is included as Fig. 3.7.

D. Conclusion

In this chapter, the synthesis and characterization of the ligand, phenylazo dimedone AD, (LH) and its Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes have been discussed. The structure of ligand has been confirmed with single crystal XRD data and by other physico-chemical methods. An attempt has been made to suggest the structures of the complexes with the support of mass spectrum of one of the complexes, CuL$_2$ and other spectral techniques.
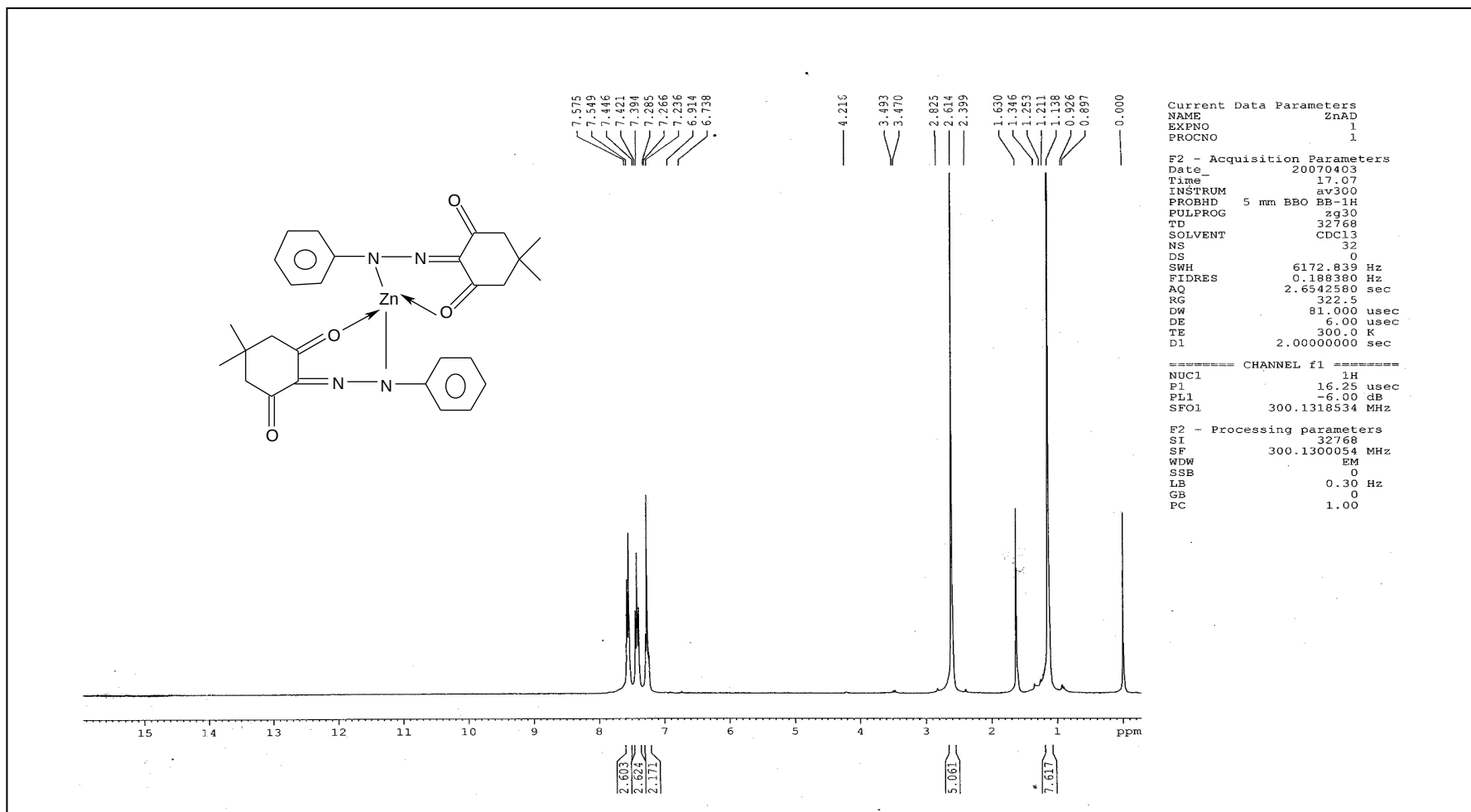
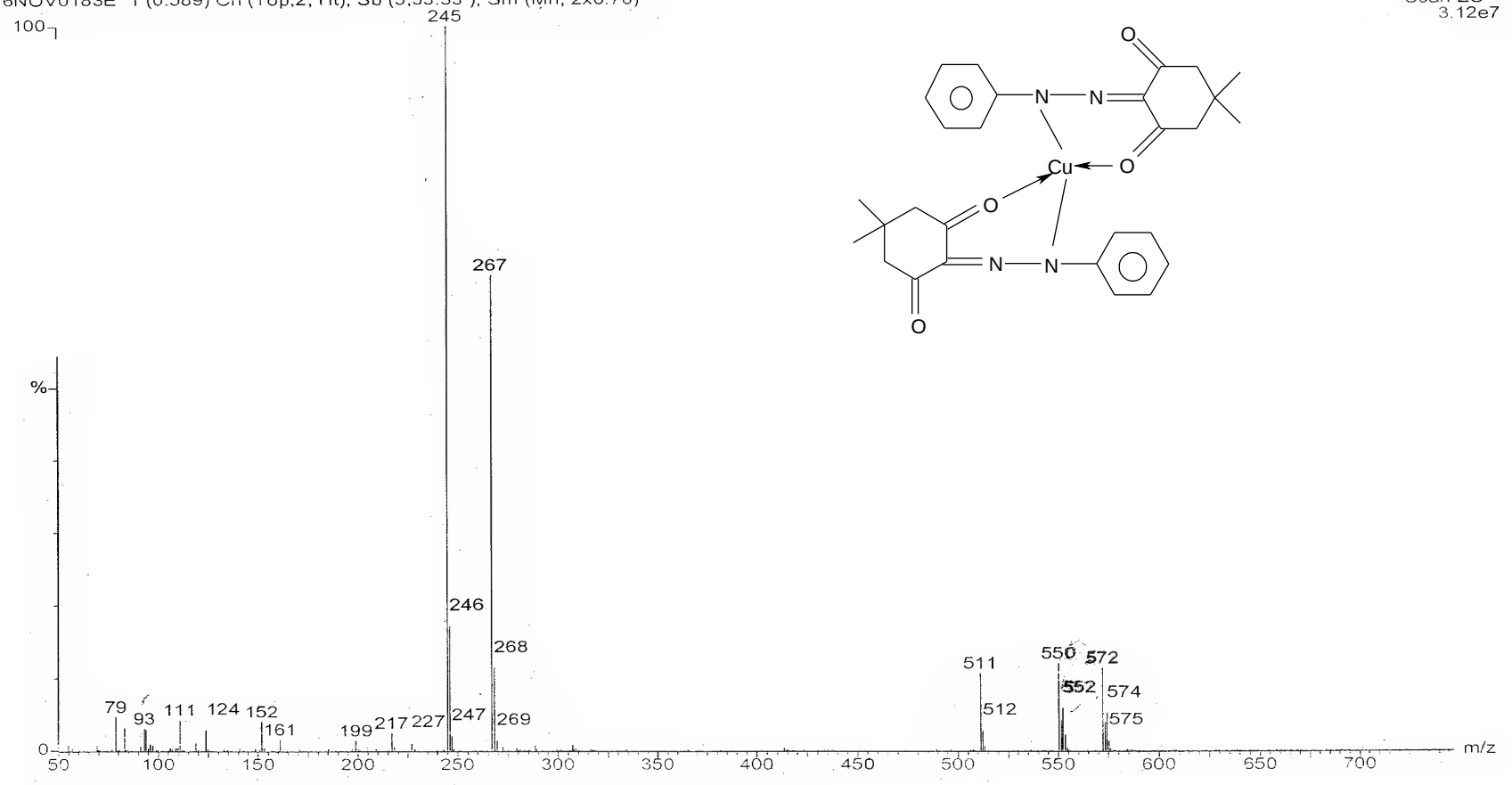**Fig. 3.6. ¹H NMR spectrum of ZnL₂**

Fig. 3.7. ESI mass spectrum of CuL$_2$

The single crystals of metal complexes were not obtained despite several attempts.   From the available data, it is clear that the ligand acts as monovalent, bidentate and coordinating through nitrogen and oxygen of the carbonyl group involved in hydrogen bonding, replacing the H with metal ion. Octahedral geometry has been assigned to Fe(III) and Co(II) complexes, and square-planar geometry to Ni(II) and Cu(II) complexes.   The four-coordinate Zn(II) complexes may be tetrahedral in geometry.
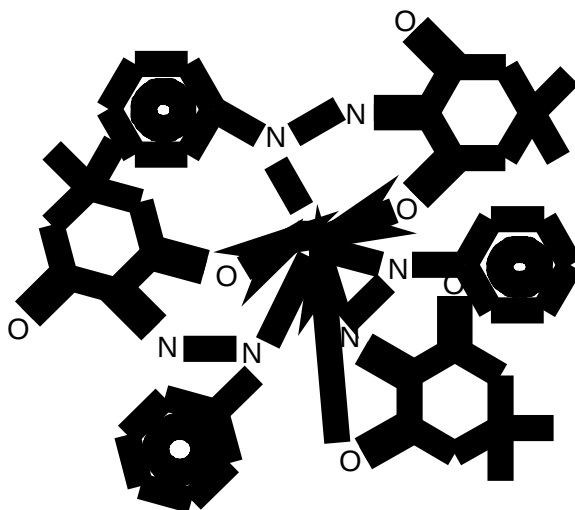

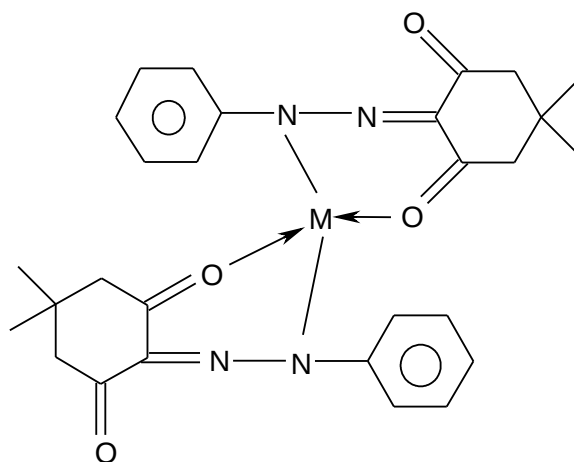**Fig. 3.8. Proposed structure of octahedral Fe(III) complex, [FeL$_3$]**

Fig. 3.9. Proposed structure of square-planar Ni(II) / Cu(II) complexes, [ML$_2$]
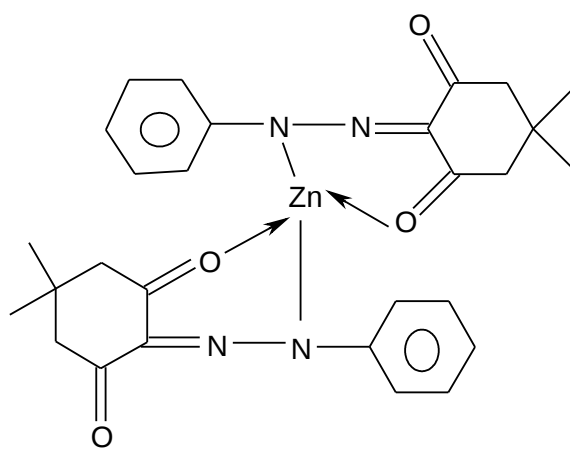

Fig. 3.10. Proposed structure of tetrahedral Zn(II) complex, [ZnL$_2$]

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CHAPTER IV

3-METHYL-4-(PHENYLHYDRAZONO)-1-PHTHALAZINYL-2-PYRAZOLIN-5-ONE AND ITS METAL COMPLEXES

1-phthalazinyl hydrazine (hydralazine) is used as an antihypertensive under the trade name aprasoline.
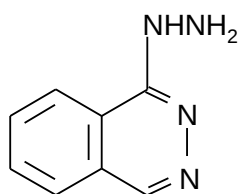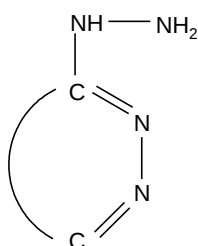

Fig. 4.1. Hydralazine

It holds the credit of being the first medicinal compound containing a hydrazino group. Druey and Marxes[1] have attributed the antihypertensive action of hydralazine and its derivatives to the presence of

group.

The ligand, N-1-phthalazinyl phenylazo pyrazolone which is named systematically as 3-methyl-4-(phenyl hydrazono)-1-phthalazinyl-2-pyrazolin-5-one (HyPy), (LH) has been synthesised by diazocoupling aniline with

methylacetoacetate and then cyclizing the product with hydralazine. The synthesis of this compound is reported[2] earlier even though a detailed characterization has been lacking. The ligational behaviour of the compound has not been reported yet and hence its complexes with Cr(III), Fe(III), Ni(II) and Cu(II) have been synthesised and characterized in the present investigation.

A. Synthesis of N-1-phthalazinyl phenylazo pyrazolone (HyPy)

The ligand has been synthesised in two steps.

**1. Synthesis of methyl-2-phenylhydrazono-3-oxobutyrate**

Aniline (0.01 mole) was diazotised by dissolving in 1:1 HCl and adding $NaNO_2$ (0.01 mol) solution keeping the temperature at ~ 0-5ºC. This diazonium chloride solution was added drop wise with stirring to a well cooled ethanolic solution (0.01 mol) of methyl acetoacetate. The pH was kept at 7. The orange coloured oily liquid was stirred for 0.5 h keeping the temperature low and the solidified product was filtered, washed with water, dried, recrystallised from methanol. This product was dried over anhydrous $MgSO_4$ and verified for purity (TLC).
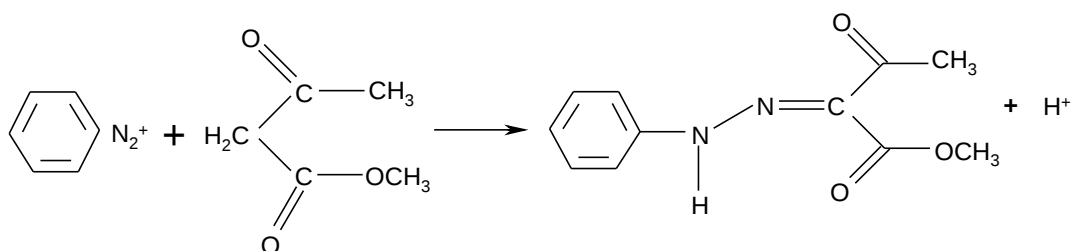
Scheme 4.1

2. Synthesis of 3-methyl-4-(phenylhydrazono)-1-phthalazinyl-2-pyrazolin-5-one (HyPy)

Methyl-2-phenylhydrazono-3-oxobutyrate (Phenylazo methylaceto-acetate) solution (0.003 mole) was prepared in glacial acetic acid. Hydralazine hydrochloride (0.003 mole) in minimum quantity of distilled water was added drop wise to the above solution. One drop of conc. H_2SO_4 was also added and the mixture was kept under reflux for 10h on a steam bath. The product was checked for cyclisation reaction using neutral $FeCl_3$ solution which imparts a deep red colouration indicating the presence of pyrazolone (aromatic-OH) moiety. The ligand was filtered, dried, purified by recrystallisation from methanol and kept in a desiccator over anhydrous $MgSO_4$.

(HyPy)
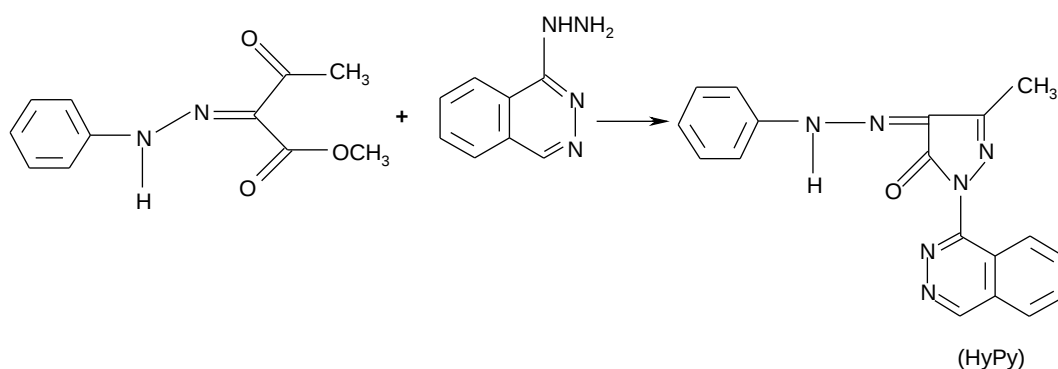
Scheme 4.2

B. Synthesis of metal complexes

The metal complexes were synthesised by mixing solutions of metal salts and ligand in methanol in 1:2 or 1:3 molar ratio for divalent and trivalent metals, respectively. The resultant mixture was refluxed on a steam bath for 3h. The precipitated complexes were filtered while warm, washed with water and acetic acid successively and dried over anhydrous $MgSO_4$ in a desiccator.

Copper(II) gave two complexes, different in colour, stoichiometry, spectral- and TG data. The brown complex was obtained when the solution was diluted with water. Both copper complexes were analysed and characterised. All the complexes were found to be paramagnetic in nature.

C. Results and discussion

1. Characterization of the ligand

Arylazo pyrazolin-5-ones are shown[3] to be existing in the hydrazone form. On the basis of a detailed investigations, the ligand HyPy was also

assigned a hydrazone structure. The analytical and electronic spectral details of the ligand are shown in Table 4.1.

Table 4.1. Physico-chemical and electronic spectral data of HyPy

Compound	Colour	Yield (%)	MP (°C)	Elemental Analysis Found (Calc.) %			Electronic spectral data λ_{max} (nm)
				C	H	N	
3-Methyl-4-(phenyl hydrazono)-1-phthalazinyl-2-pyrazolin-5-one (HyPy) (LH)	Yellow	50	110	65.95 (65.45)	4.92 (4.20)	25.86 (25.45)	286, 308, 380, 512

a) Analytical data

The elemental percentages of the compound were found to be in good agreement with the molecular formula $C_{18}N_6OH_{14}$.

b) Spectral data

i) Electronic spectrum

The electronic spectrum of the ligand was not having an absorption band at ~270-280 which is very characteristic of an azo structure. Hence it must be existing in the hydrazone form.

ii) IR spectrum

The IR spectrum showed a broad band at 3408 cm^{-1} which may be assigned to the stretching of NH (hydrogen bonded) as observed in phenylhydrazono ketones. Two strong bands at 1698 cm^{-1} indicated[4] C=O (exocyclic) conjugated with C=N. The band at 1546 cm^{-1} could be attributed to >C-NH-N = (not cyclic)[5] system. The IR bands and their assignments are shown in Table 4.2.

Table 4.2. IR spectral bands, ν (cm^{-1})

Compound	exocyclic C=O	C=C	NH–N =	C–N
HyPy	1698	1600	1546	1454

iii) ^{1}H NMR spectrum

The ^{1}H NMR spectrum (Fig. 4.2) of HyPy showed a low field signal at ~14 ppm for acidic proton. Other prominent signals were at 7.47, 7.45 8 ppm due to phthalazinyl protons as shown in the spectrum which were very much in accordance with the reported[3] values. Other peaks were at 7.25 - 7.30 ppm (unsymmetrical pattern - phenyl) and 2.5 ppm (-CH$_3$). The absence of a signal at ~ 6.48 ppm (C-4 proton)[6] also indicated a hydrazone structure.
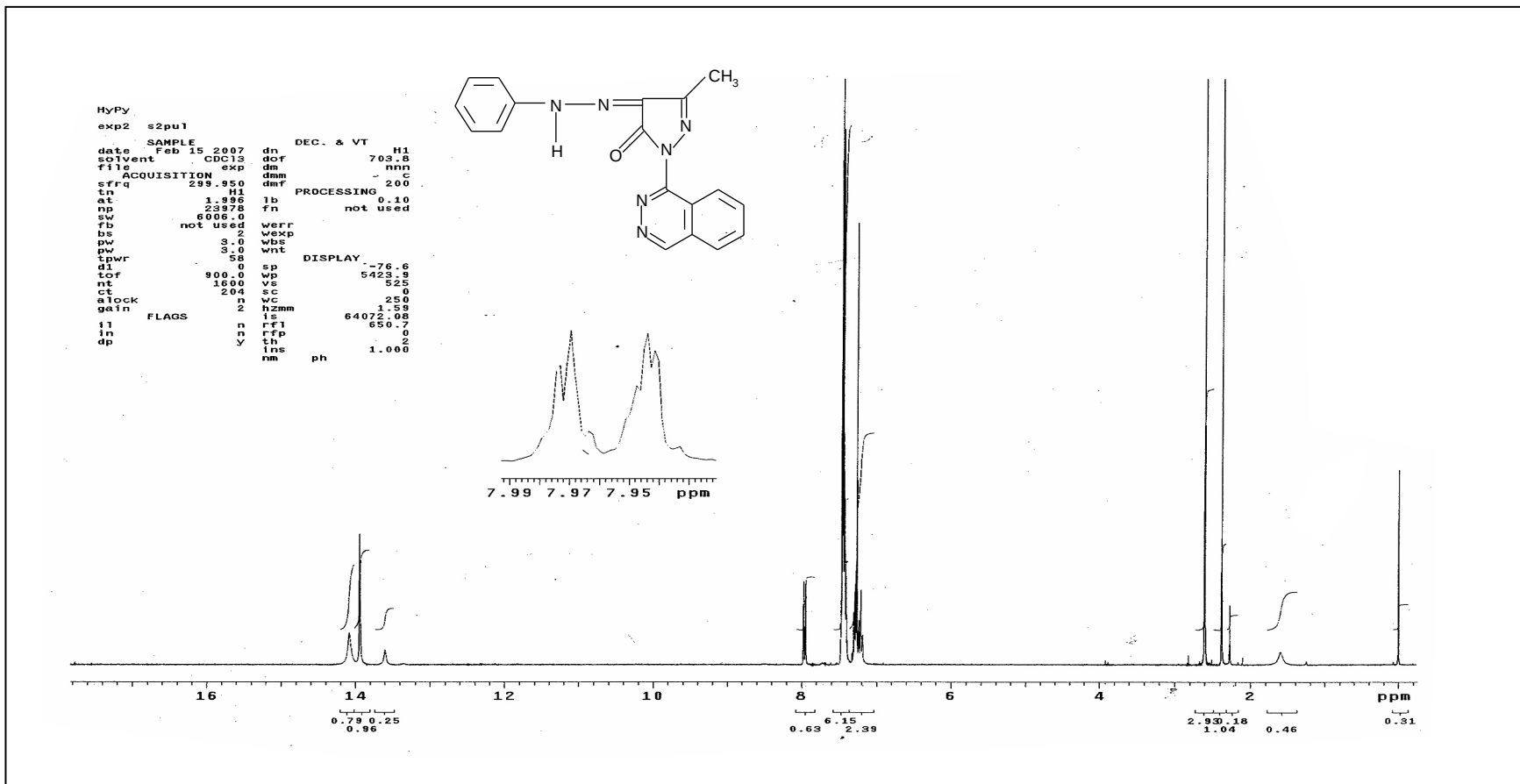
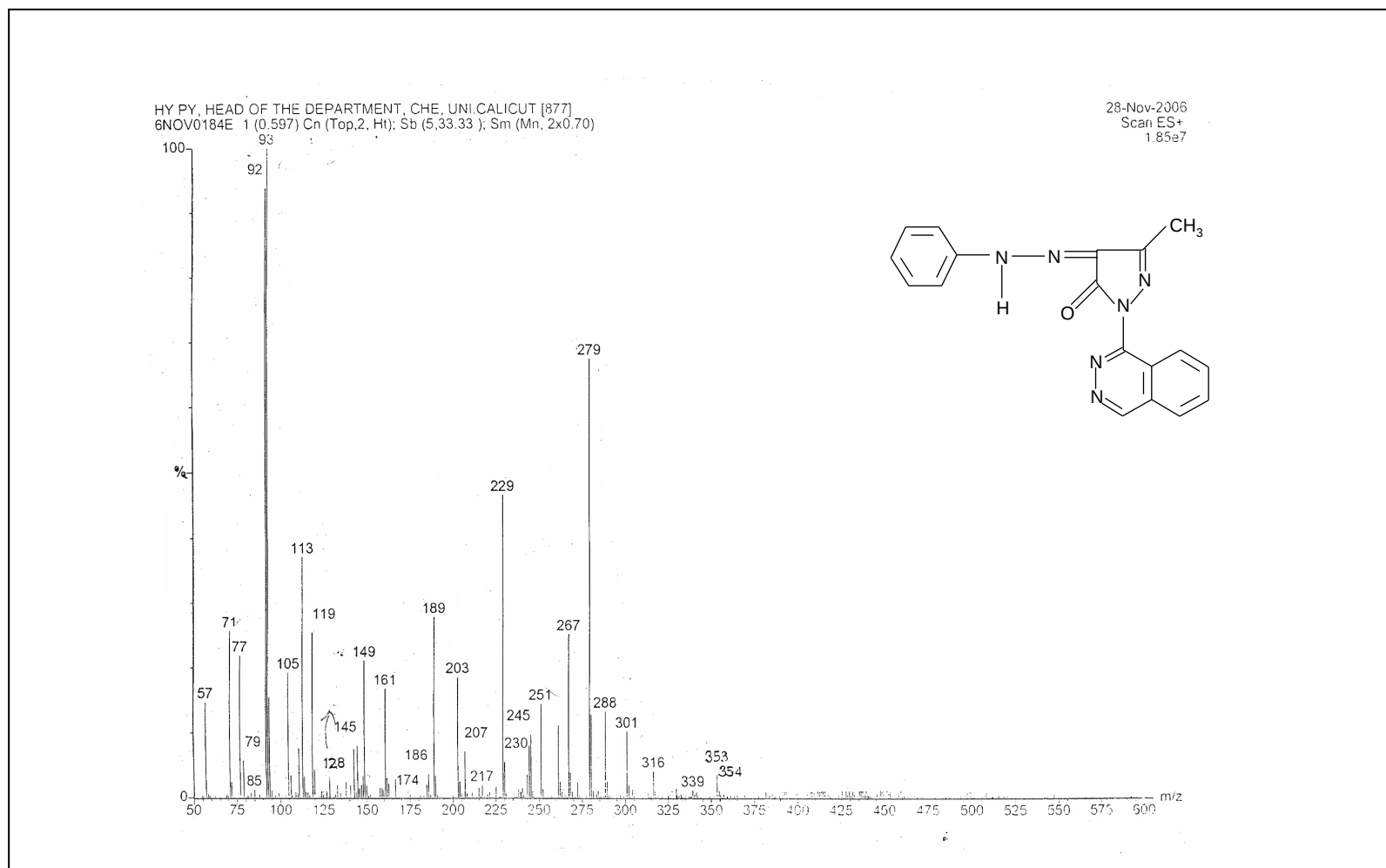**Fig. 4.2.** ^{1}H NMR spectrum of HyPy

Fig. 4.3. ESI mass spectrum of HyPy

iv) Mass spectrum

The mass spectrum of the ligand, HyPy showed all the expected peaks. The molecular ion peak was present at m/z 330, even though not marked by the instrument, may be due to the low percentile value. It is expected to have a low value due to the bulky pendant like phthalazinyl ($C_8H_5N_2$) group. All the other expected peaks were present in the spectrum at m/z 93 (bp, $C_6H_8N^+H_2$), 77 ($C_6H_5^+$), 128 ($C_8H_5N_2^+$), 203 (M-$C_8H_5N_2$)$^+$ etc. The base peak and m/z 93 and the absence of (M-N_2) peak clearly point to a hydrazone[7] structure rather than an azo structure. The spectrum is entered as Fig. 4.3.

Based on the above evidences, the probable structure of the ligand can be depicted as in Fig. 4.4.
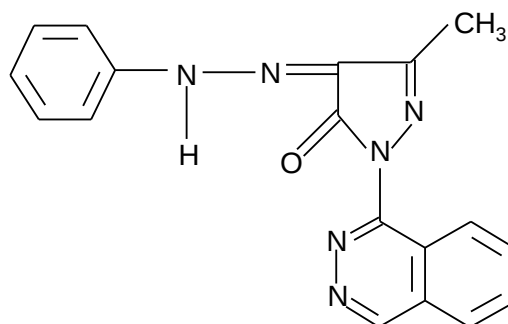
Fig. 4.4. N1-phthalazinyl phenylazo pyrazolone (HyPy) (LH)

2. Characterization of metal complexes

Complexes of Cr(III), Fe(III), Ni(II) and Cu(II) have been synthesised in the present study. All have anions coordinated to the metal ions. The physico-chemical and magnetic moment data are presented in Table 4.3. The complexes were found to be paramagnetic with μ_{eff} values as expected for the proposed geometry.

Table 4.3. Physico-chemical, electronic spectral and magnetic data of complexes

Sl. No.	Compound	Colour	Yield (%)	M.P. (°C)	Elemental analysis found (cal.) %					Magnetic moment μ (B.M.)	Electronic spectral data λ_{max} (nm)
					C	H	N	M	X		
1.	[Cr(LH)Cl$_3$]	Dark green	40	200	43.90 (44.30)	2.88 (2.87)	17.97 (17.20)	10.04 (10.87)	20.62 (21.85)	3.72	286, 312, 410, 576, 686
2.	[Fe(LH)Cl$_3$]	Yellowish brown	40	170	43.83 (43.96)	2.92 (2.65)	17.59 (17.10)	11.56 (11.37)	21.06 (21.68)	5.91	288, 314, 412, 514, 630
3.	[Ni(LH)(OAc)$_2$(H$_2$O)]	Brown	60	>300	50.58 (50.39)	3.51 (3.81)	16.61 (16.01)	11.01 (11.18)	--	2.95	286, 310, 386, 676
4.	[CuL(OAc)(H$_2$O)$_2$]	Dark brown	40	190	49.31 (49.18)	3.09 (3.89)	17.68 (17.21)	13.26 (13.02)	--	2.1	280, 316, 512, 680
5.	[Cu(LH)(OAc)$_2$H$_2$O]	Pista green	50	215	50.15 (50.00)	3.81 (3.98)	15.81 (15.91)	12.32 (12.03)	--	1.76	288, 314, 514

LH = HyPy; X = Cl,   M = metal L = mono anion of HyPy (LH)

a) *Electronic spectral data and magnetic behaviour*

Chromium(III) complex was dark green in colour. The magnetic moment value of 3.72 B.M. suggested an octahedral geometry[8]. The conspicuous electronic spectral bands were at 400 nm due to $^4A_{2g}(P) \rightarrow {}^4T_{1g}(F)$ and 576 nm due to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transitions which gave additional support to octahedral geometry of the complex.

Fe(III) complex showed spectral bands which were overlapped with CT bands. The bands observed at 530 nm could very well be due to $^4A_{1g} \rightarrow {}^6T_{1g}$ transition. The magnetic moment value of 5.91 B.M. indicated octahedral geometry.

The spectrum of Ni(II) complex was very conspicuous with bands at 386 nm and 676 nm which were due to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions respectively. These are characteristic of octahedral geometry. The magnetic moment value of 2.95 B.M also pointed to octahedral geometry for Ni(II) complexes.

The brown coloured copper complex showed bands at the lower end of the visible region. This complex registered a magnetic moment of 2.10 B.M.

The green copper complex showed less number of bands than the brown complex. The magnetic moment of the complex was 1.76 B.M.

b) IR spectra

In the IR spectra of the complexes, the band at ~ 1550 cm^{-1} is a clear indication of chelated C=O, suggesting involvement of carbonyl oxygen of pyrazolone ring in coordination. Moreover, the band at 1698 cm^{-1} in the ligand spectrum has disappeared in the spectra of the complexes. The bands around 1400 cm^{-1} indicated C=N. The lower bands at 580 and 520 cm^{-1} were due to νM-N and νM-O, respectively.[10] The important IR spectral bands and their assignment are shown in Table 4.4.

Table 4.4. Important IR spectral bands (cm^{-1}) and their assignments

Sl. No.	Compound	Chelated νC=O	Chelated νC=N	νM-N	νM-O
1	[Cr(LH)Cl$_3$]	1556	1498	557	507
2	[Fe(LH)Cl$_3$]	1554	1507	578	510
3	[Ni(LH)(OAc)$_2$H$_2$O]	1550	1499	581	509
4	[CuL(OAc)(H$_2$O)$_2$]	1547	1498	582	490
5	[Cu(LH)(OAc)$_2$H$_2$O]	1547	1498	582	507

e) Mass spectra

Mass spectra of the two copper complexes showed the parent ion peaks at 488 and 528 for the brown coloured and green coloured complexes, respectively. Both spectra showed fragment peaks due to the detachment of $C_8H_5N_2$(phthalazinyl) and $C_4N_2OH_3$(pyrazolonyl) groups. The ESI mass

spectrum of the brown coloured copper complex (Fig. 4.5) agreed well with the structural formula [CuL(OAc)(H$_2$O)$_2$]. The values of prominent m/z peaks were 488(M$^+$), 469(M–H$_2$O), 450(M–twoH$_2$O], 301 [M–(C$_8$H$_5$N$_2$+OAc)], 279 (M–C$_8$H$_5$N$_2$–OAc–H$_2$O), 203 [M-(C$_8$H$_5$N$_2$+C$_4$N$_2$OH$_3$+OAc)] 243 [M–(C$_8$H$_5$N$_2$+C$_5$N$_2$H$_3$–H$_2$O)] - base peak), 185 [M–(C$_8$H$_5$N$_2$+C$_5$N$_2$H$_3$+H$_2$O–OAc)], 92 (C$_6$H$_5$N$^+$H), 77 (C$_6$H$_5$$^+$), etc. Additional M+1, M+2, etc. peaks were also present.

The FAB mass spectrum of green copper complex (Fig. 4.6) agreed well with the structural formula [CuLH(OAc)$_2$H$_2$O]. The prominent m/z values are 528 (M$^+$), 474 (M-CH$_3$ COO), 416 (M-2 x CH$_3$COO), 154 - Base peak [M-(2xCH$_3$COO+H$_2$O+C$_8$N$_2$H$_5$(Phthalazinyl)+C$_6$H$_5$N$_2$], 107 (C$_6$H$_5$N$_2$$^+$)78(C$_6H_5$)$^+$.

d) Thermal data

Thermal analyses curves of two copper complexes [CuL(OAc)(H$_2$O)$_2$] and [Cu(LH)(OAc)$_2$H$_2$O] are shown in Fig. 4.7.

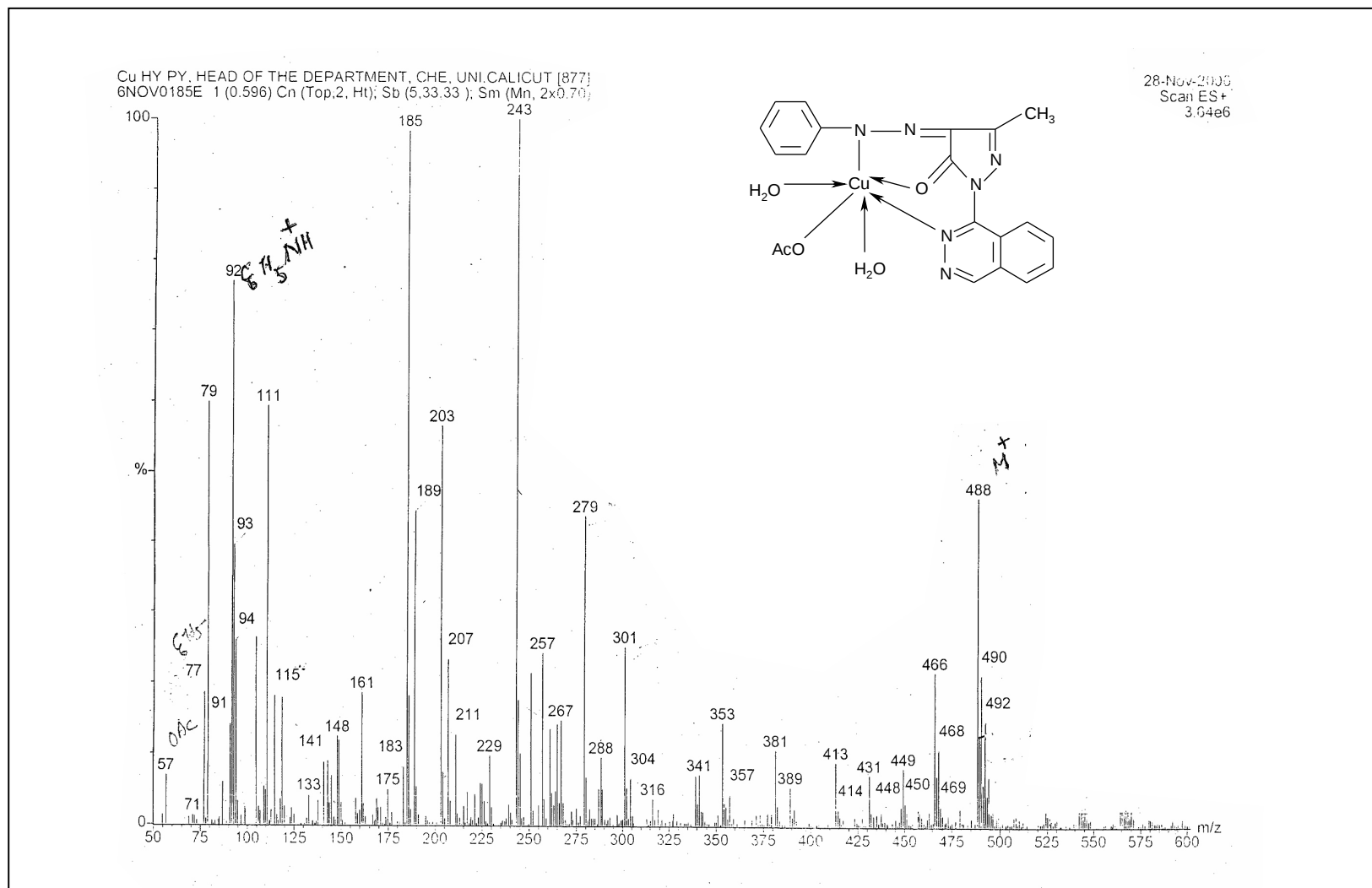The decomposition pattern is summarized in the following Table 4.5.
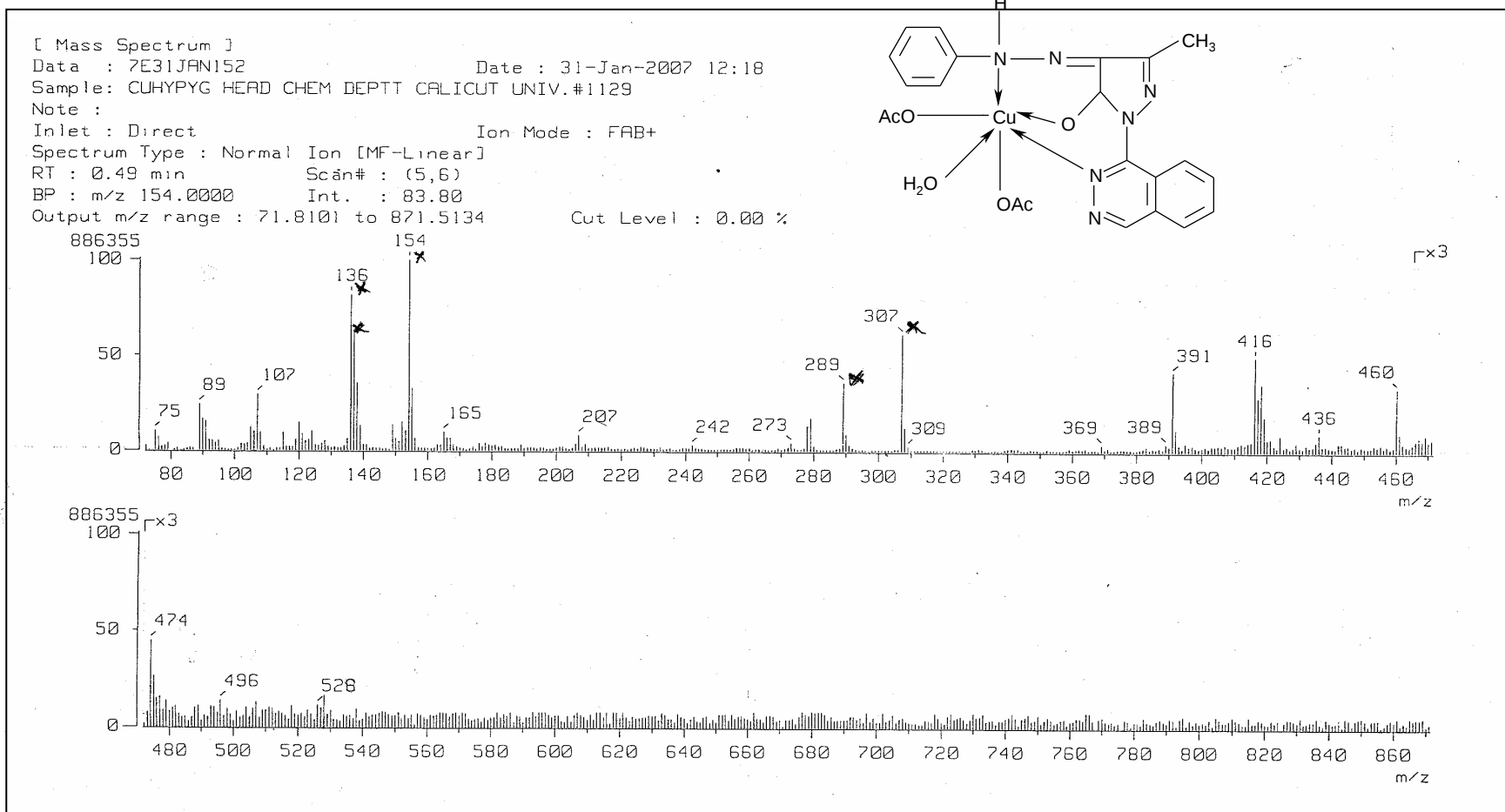
Fig. 4.5. ESI mass spectrum of [CuL(OAc)(H₂O)₂]
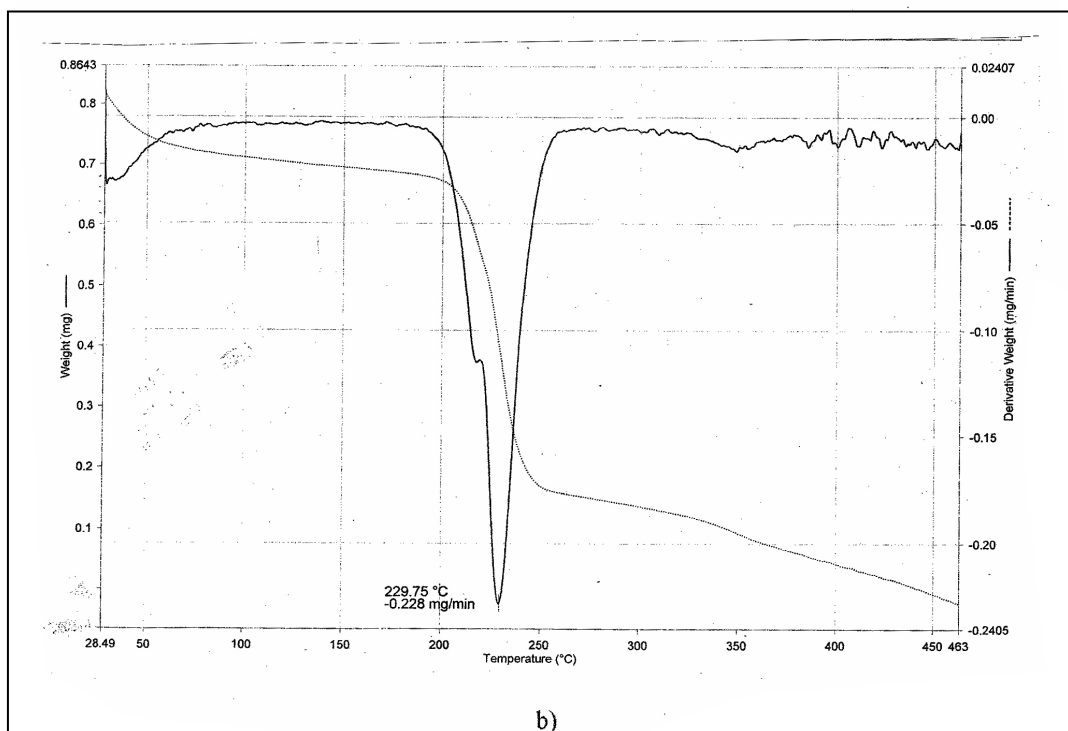
Fig. 4.6. FAB mass spectrum of [Cu(LH)(OAc)₂H₂O]
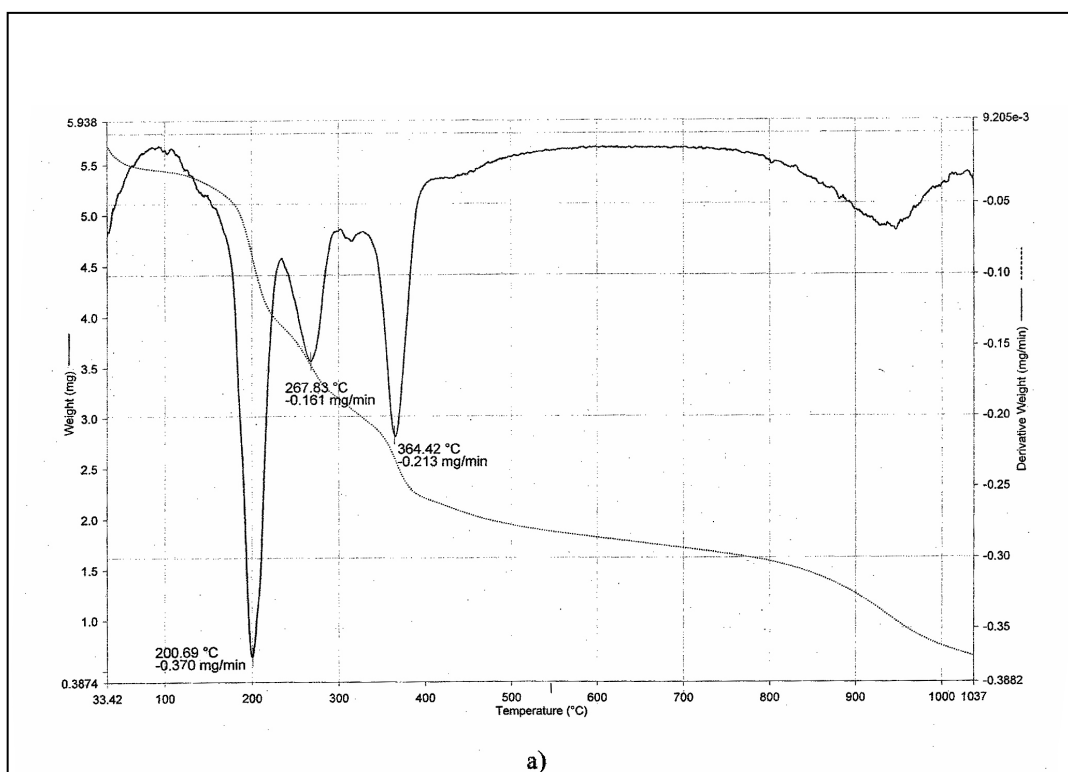
Fig. 4.7. TG/DTG traces of
(a) [CuL(OAc)(H$_2$O)$_2$] and (b) [Cu(LH)(OAc)$_2$(H$_2$O)]

Table 4.5. Decomposition data of copper complexes

Complex	Colour	F.W	Decomposition stage	Decomposition temp (^{o}C) DTG	Mass loss % from TG (Calc)	Decomposition pattern
[CuL(OAc)(H$_2$O)$_2$]	Brown	488	Stage 1	200.7	19.25 (19.47)	loss of CH$_3$COO + two H$_2$O
			Stage 2	364.4	54.3 (48.9)	loss of (CH$_3$COO + two H$_2$O + phthalazinyl + CH$_3$)
			Stage 3	400.6	61.3 (64.5)	loss of (CH$_3$COO + two H$_2$O + phthalazinyl + CH$_3$ + C$_6$H$_5$)
			Stage 4	900.6	78 (83.6)	Final residue CuO
[Cu(LH)(OAc)$_2$H$_2$O]	Green	528	Stage 1	215.8	72.9 (78.5)	(loss of two CH$_3$COO + H$_2$O + phthalazinyl + C$_6$H$_5$N$_2$ + CH$_3$)
			Stage 2	364.5	90.7 (84.5)	Final residue CuO

As can be observed from the TG traces, both Cu(II) complexes are stable upto 200°C. In both cases, the coordinated H$_2$O as well as the CH$_3$COO$^-$ detached at about same temperature, ~ 200°C. The complex in which HyPy was acting as a monoanionic ligand was found to retain this ligand upto a temperature of 900°C. This was well expected because of the stronger attachment (covalent) than a dative bond. The decomposition patterns agreed very well with the structural formulae suggested for the Cu(II) complexes.

D. Conclusion

From the above discussion, the versatile nature of the ligand HyPy is very obvious. Phenylazo pyrazolones can act as tridentate ligands when the N–1 of the pyrazolone is possessing a substituent with suitable hetero atom. Thus in the present case the nitrogen of the phthalazinyl group is also found to be taking part in coordination making it a tridentate neutral ligand. One exception has been observed in the case of the brown coloured copper(II) complex $[CuL(OAc)(H_2O)_2]$ in which it acts a tridentate monoanionic ligand. This is well expected as the complex was formed on dilution with water. Therefore, based on the different physico-chemical evidence, the complexes are assigned the following octahedral geometry.

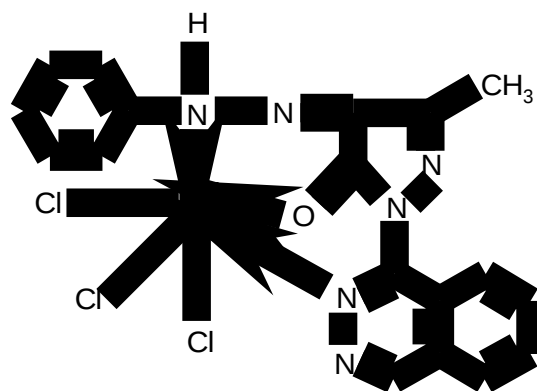**Fig. 4.8. Proposed structure of the complex [M(LH)X₃]**
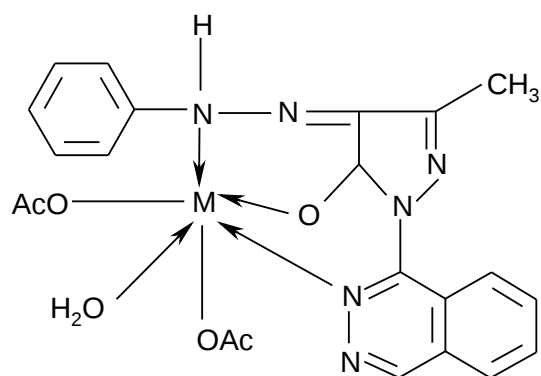
where M = Cr(III) / Fe(III), X = Cl

Fig. 4.9. Proposed structure of octahedral [M(LH)(OAc)$_2$(H$_2$O)]

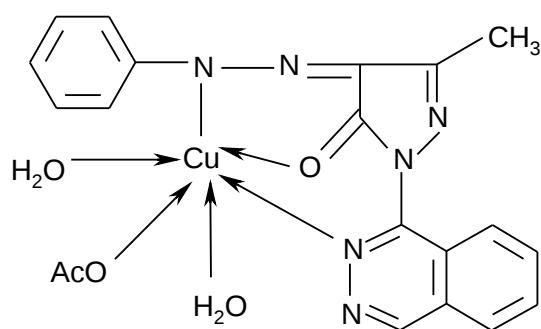where M = Cu(II) / Ni(II)

Fig. 4.10. Proposed structure of octahedral [CuL(OAc)(H$_2$O)$_2$]

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CHAPTER V

3-ACETYL-5-AZOPHENYL-4-HYDROXY-6-METHYL-PYRAN-2-ONE AND ITS METAL COMPLEXES

The structure of dehydroacetic acid had been a subject of controversy ever since its discovery in 1866. The accepted structure[1] is in the form of a β,β'-tricarbonyl as 3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione as in Fig. 5.1.
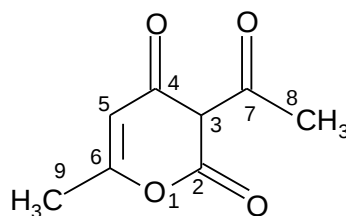

Fig. 5.1

However, it has been proved[2] that in solution it exists as a completely enolised species as in Fig. 5.2.
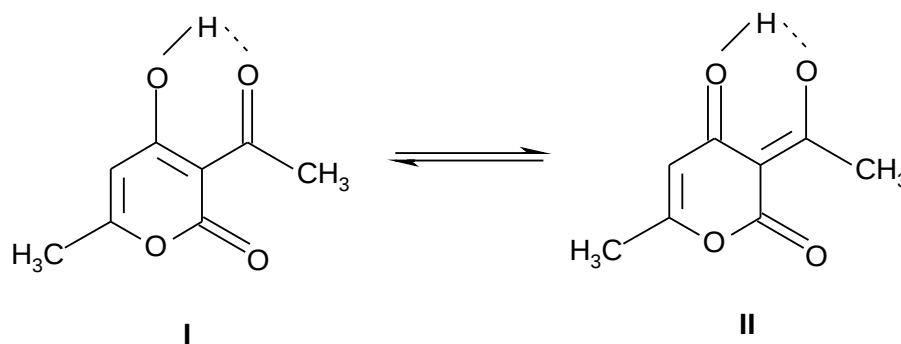

Fig. 5.2

In the solid form, structure I predominates.

Structure I suggests that like phenols, dehydroacetic acid (DAA) can couple with diazonium salts at C-5 and some reports[4,5] are available on the condensation of DAA with diazotised derivatives of aniline, substituted anilines, benzidine, etc. Even though reported works are available on metal chelate of DAA[6], no work has so far been done on chelates of azoderivatives of DAA. In chelates of dehydroacetic acid, the acidic proton of structure II has been found to be replaced by metal ions with molecular formula $M(DAA)_2(solvent)_2$.

In the present work it has been found that one of the azo nitrogens also takes part in coordination. Chelates of Cr(III), Fe(III), Ni(II), Cu(II) and Zn(II) have been synthesised and characterized by elemental analysis, magnetic susceptibility measurements, electronic, ^{1}H NMR, FABmass, IR-spectral and thermal (TG/DTG) analytical techniques.

A. Synthesis of phenylazo dehydroacetic acid (ADAA)

Aniline (0.01 mole) was diazotised and this solution of diazonium salt was added slowly drop wise to a well cooled alkaline solution of DAA (0.02 M). The mixture was allowed to stand for 0.5 h. The brick red product of phenylazodehydroacetic acid, ADAA (LH) was filtered, washed successively with very dilute HCl and water and recrystallised from methanol. Stored over anhydrous $MgSO_4$ in a desiccator (yield 60%, m.p. 50ºC).

B. Synthesis of metal complexes

To a methanolic solution of ADAA, the metal salt solution, also in methanol was added drop wise with stirring. The mixture was refluxed on a steam bath for about 1 h. The metal salt to ligand ratio was kept at 1:2 / 1:3 for bivalent/trivalent metals, respectively. The precipitated complex was filtered, washed with water, methanol and dried. The complexes were recrystallised from CH_2Cl_2–CH_3OH mixture and stored over anhydrous $MgSO_4$ in a desiccator (yield, 60%, m.p. 50°C).

C. Results and discussion

1. Characterization of the ligand

The ligand was a brick red amorphous solid. The colour of the ligand was so intense that the complexes formed were also deep coloured.

a) Analytical data

Physical- and analytical data are given in Table 5.1.

Table 5.1. Physico-chemical and electronic spectral data of phenylazo-dehydro acetic acid

Compound	Colour	Yield (%)	M.P. (°C)	Elemental analysis found (cal.) %			Electronic spectral data λ_{max} (nm)
				C	H	N	
3-Acetyl-5-phenylazo-4-hydroxy-6-methyl-pyran-2-one (ADAA) (LH)	Brick red	60	50	61.70 (61.77)	4.26 (4.41)	9.95 (10.29)	260, 278, 370

The elemental percentages of the ligand were found to be in fine agreement with molecular formula $C_{14}N_2O_3H_{12}$.

b) Spectral data

i) Electronic spectrum

The electronic spectrum of the ligand, ADAA was conspicuous with the band at 278 nm which is characteristic of an azo form. The other bands of importance were at 260 (carbonyl) and 370 (N=N–).

ii) IR spectrum

The broad band at 3445 cm^{-1} showed the presence of hydrogen bonded OH. The band at 1599 cm^{-1} is typical of an –N=N– group. The free acetyl carbonyl absorption was found at ~ 720 cm^{-1} and the ring C=O at 1657 cm^{-1}. The band due to C–O–C stretch of the pyrone was observed at 1125 cm^{-1}. The important IR bands are enlisted in Table 5.2.

Table 5.2. IR spectral bands, ν (cm^{-1})

Compound	C=O acetyl	C=O ring	N=N	C=C aromatic
Phenylazo dehydro acetic acid (ADAA)	1720 (s)	1657 (s)	1599 (m)	1550 & 1490 (m)

iii) ^{1}H NMR spectrum

^{1}H NMR spectrum of ADAA (Fig. 5.3) showed all the peaks expected of dehydroacetic acid[6] except the peaks at C-5 where the proton has been substituted by a phenylazo group. The peak at 15.68 ppm belonged unmistakably to the acidic proton of OH at C-4 and other prominent peaks were 7.48 nm (unsymmetrical pattern, aromatic), 2.7 ppm for H_S on C-8 and 2.4 ppm for H_S on C-9.

iv) Mass spectrum

The mass spectrum of ADAA (Fig. 5.4) showed the M$^+$ peaks at m/z 272. The peaks at 244 pertained to $(M–N_2)^+$ which is very characteristic of an azo group. The base peak at m/z 149 indicated the fragment $[M–(C_6H_5N_2 + OH)]^+$. Other prominent peaks are marked in the spectrum. So based on the above evidences the probable structure of ADAA was found to be as depicted in Fig. 5.5, which is in conformity with other findings[4,5].
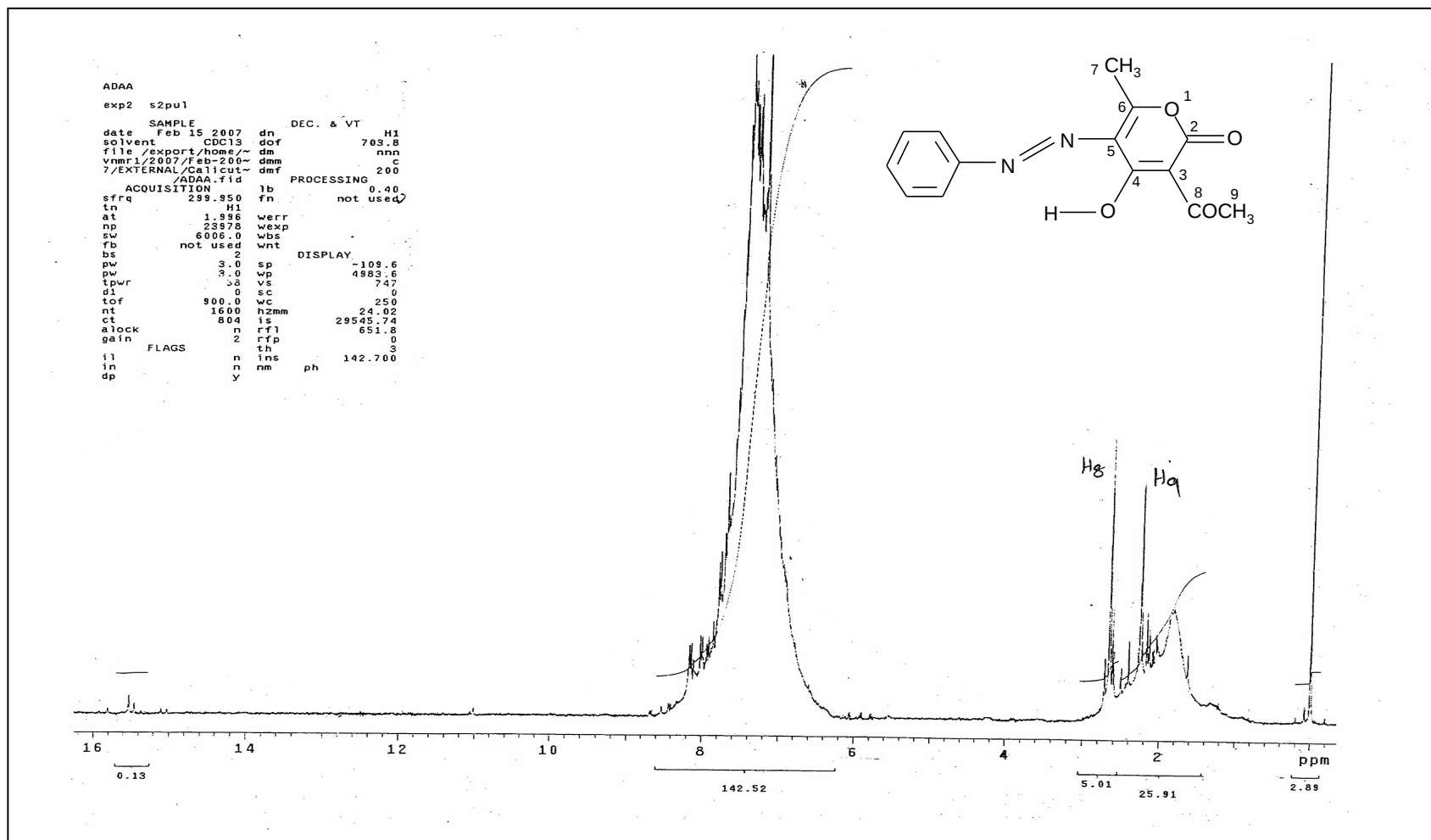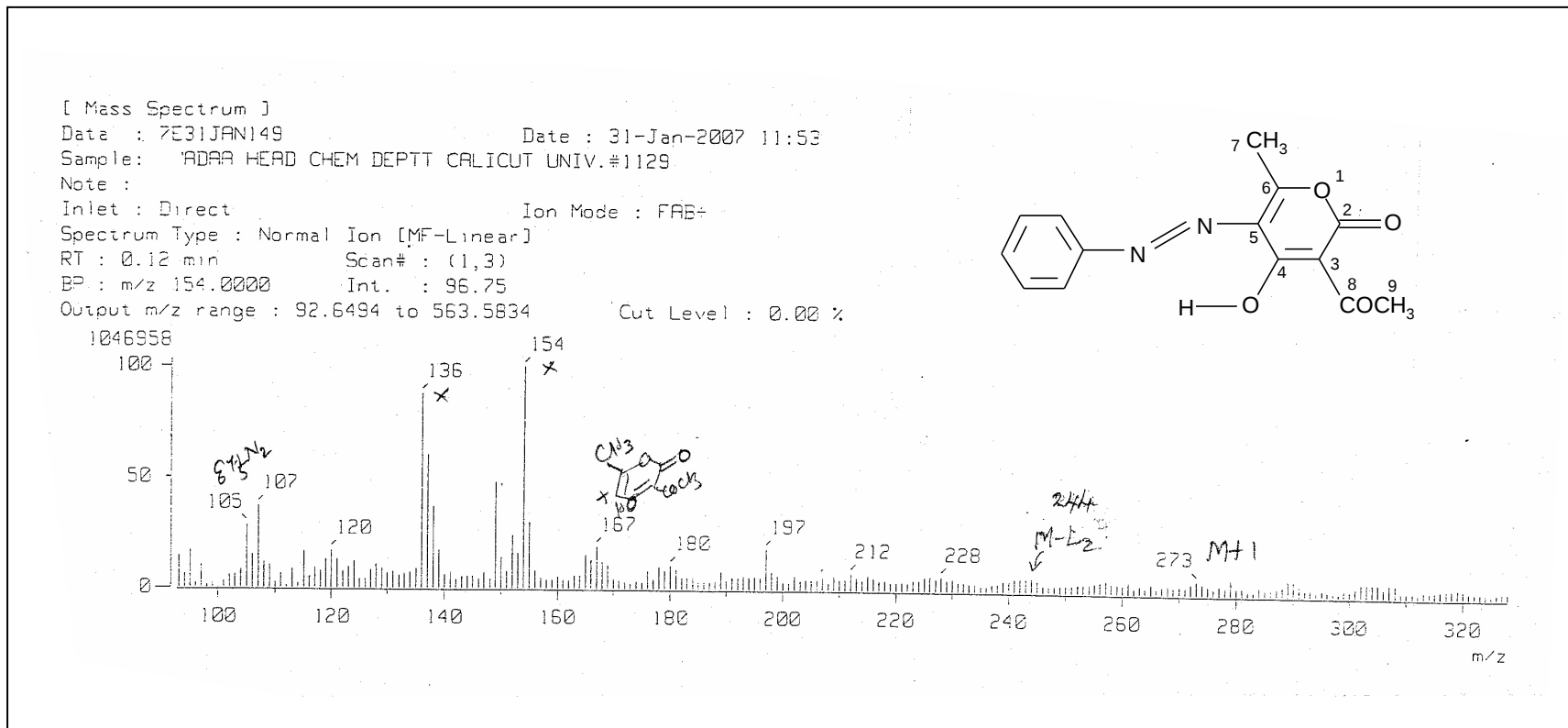
Fig. 5.3. ^{1}H NMR spectrum of ADAA

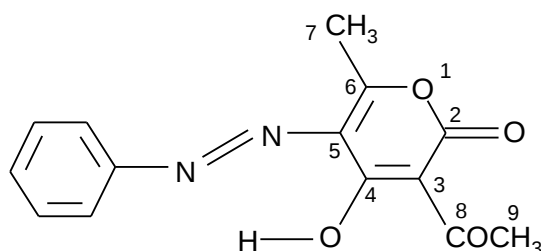**Fig. 5.4. FAB mass spectrum of ADAA**

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Fig. 5.5. 3-Acetyl-6-methyl-4-hydroxy-5-phenylazo-pyran-2-one (ADAA) (LH)

2. Characterization of metal complexes

ADAA formed stable complexes with Cr(III), Fe(III), Ni(II), Cu(II) and Zn(II). In all the complexes one of the azo nitrogens took part in coordination together with oxygen of the enolic OH. The Zn(II) complex was diamagnetic and all others showed expected magnetic moment values. All complexes were deep red / brown in colour.

a) *Electronic spectral data and magnetic behaviour*

The elemental analysis, magnetic moment and electronic spectral values are summarised in Table 5.3.

Chromium(III) complexes were dark brown in colour. The magnetic moment value of 3.76 B.M. suggested an octahedral geometry. The prominent electronic spectral bands include 380 nm ($^4T_{1g}(F) \rightarrow A_{2g}(F)$) and 570 nm ($^4A_{2g}(F) \rightarrow \, ^4T_{2g}(F)$) which also pointed to an octahedral geometry.

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Fe(III) complex spectrum was difficult to interpret due to CT bands. The magnetic moment value of 5.85 B.M. indicated an octahedral geometry.

The spectrum of Ni(II) complex had almost all of the peaks expected for an octahedral geometry. The bands at 376 nm ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$) and 680 nm ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$) were very conspicuous. The magnetic moment value of 2.92 B.M. also confirmed the octahedral geometry.

The copper(II) complex exhibited bands at 316 and 682 which were characteristic overlapped bands of copper complexes. The magnetic moment value of the complex was 2.10 B.M.

Table 5.3. Physico-chemical and electronic spectral data of complexes

Sl. No.	Compound	Colour	Yield (%)	MP °C	Elemental analysis found (calc.) %					Magnetic moment μ B.M.	Electronic spectral data λ_{max} (nm)
					C	H	N	M	X		
1	[Cr(L)$_2$Cl(H$_2$O)]	Dark brown	65	80	51.53 (51.89)	4.10 (4.32)	8.98 (8.65)	8.65 (8.03)	5.69 (5.48)	3.76	276, 314, 380, 570
2	[Fe(L)$_2$Cl(H$_2$O)]	Dark brown	65	140	51.15 (51.58)	4.26 (4.29)	8.14 (8.59)	8.13 (8.58)	5.71 (5.45)	5.85	278, 310, 370, 514
3	[Ni(L)$_2$(H$_2$O)$_2$]	Dark brown	70	160	52.72 (52.75)	4.82 (4.71)	8.84 (8.79)	9.74 (9.22)	--	2.82	278, 312, 376, 680
4	[Cu(L)(OAc)H$_2$O]	Dark brown	70	> 300	46.64 (46.60)	4.12 (3.88)	3.79 (3.90)	15.38 (15.42)	--	2.10	278, 316, 377, 682
5.	[Zn(L)$_2$]	Maroon	65	210	55.01 (55.32)	3.55 (3.62)	9.76 (9.22)	10.25 (10.76)		D	278, 310, 370, 512

L = monoanion of LH, ADAA, M = Metal; D = Diamagnetic, X = Cl

b) IR spectra

The IR spectra of all complexes showed the acetyl carbonyl stretch more or less at the same position indicating the absence[7] of coordination through this carbonyl oxygen. But there was a marked lowering of the band due to stretch of the ring C=O suggesting coordination through this oxygen. The N=N stretch also has lowered from ~ 1600 to 1570 cm^{-1} pointing to coordination through azo nitrogen. The important IR stretching bands of the complexes are listed in Table 5.4.

Table 5.4. Important IR spectral bands ν(cm^{-1}) and their assignments

Sl. No.	Compound	Acetyl νC=O	Chelated νC=O	Chelated νM=N–	νM–N	νM–O
1	[Cr(L)$_2$Cl(H$_2$O)]	1719	1645	1572	587	444
2	[Fe(L)$_2$Cl(H$_2$O)]	1716	1643	1570	582	446
3	[Ni(L)$_2$(H$_2$O)$_2$]	1709	1645	1574	582	447
4	[Cu(L)(OAc)(H$_2$O)]	1714	1650	1573	542	440
5	[Zn(L)$_2$]	1718	1641	1566	584	456

The appearance of two new bands at lower wave numbers around 580 and 440 cm^{-1} may be an indication of M–N and M–O bonds, respectively.

c) ^{1}H NMR spectrum

The ^{1}H NMR spectrum (Fig. 5.6) of the diamagnetic Zn(II) complex exhibited all the peaks of the ligand except the enolic OH peak at ~ 15.58 ppm. This indicated the coordination through enolic oxygen[8] where the metal has replaced H leading to the formation of a six membered chelate. Other peaks of importance were at 2.48 (s) (acetyl proton), 2.62 ppm (s) (methyl protons at C-6).

d) Mass spectrum

The mass spectrum (Fig. 5.7) of the Cu(II) complex showed M+1 peak at 413 which conformed the M+1 of $[CuL(OAc)(H_2O)]$. Other prominent peaks were 394 $(M–H_2O)$, 375 $[M–(H_2O + N_2)]$ which supports the azo structure, 244 $(LH–N_2)$ 168 $(LH–C_6H_5N_2)$ 149 BP, $[LH-(C_6H_5N_2+OH)]$.

e) Thermal data

The thermal decomposition curves of the complexes $[Cu(L)(OAc)(H_2O)]$ and $[Ni(L)_2(H_2O)_2]$ are given in Figure 5.8. The decomposition pattern is summarised in Table 5.5.

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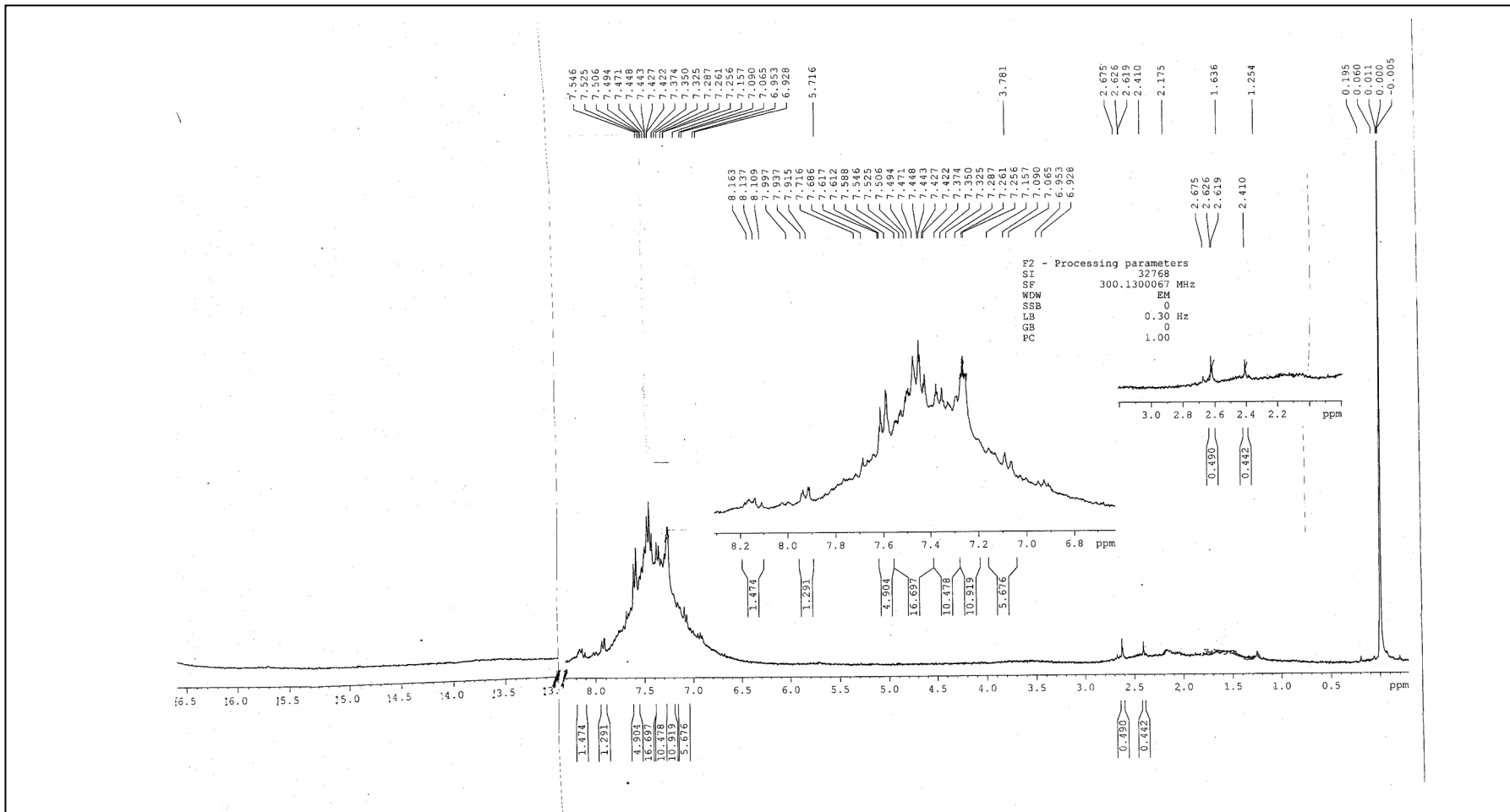
Fig. 5.6. ^{1}H NMR spectrum of ZnL$_2$
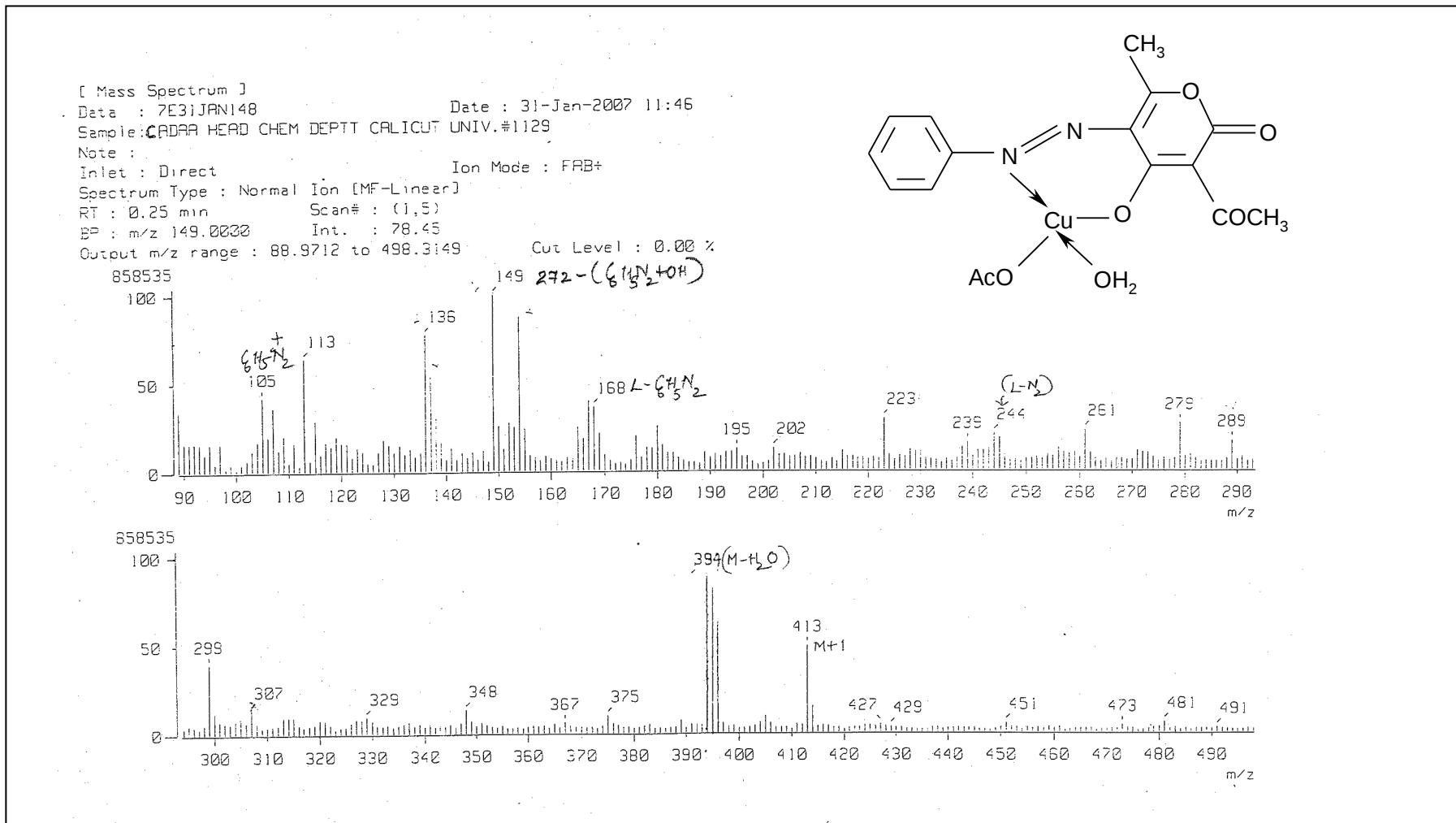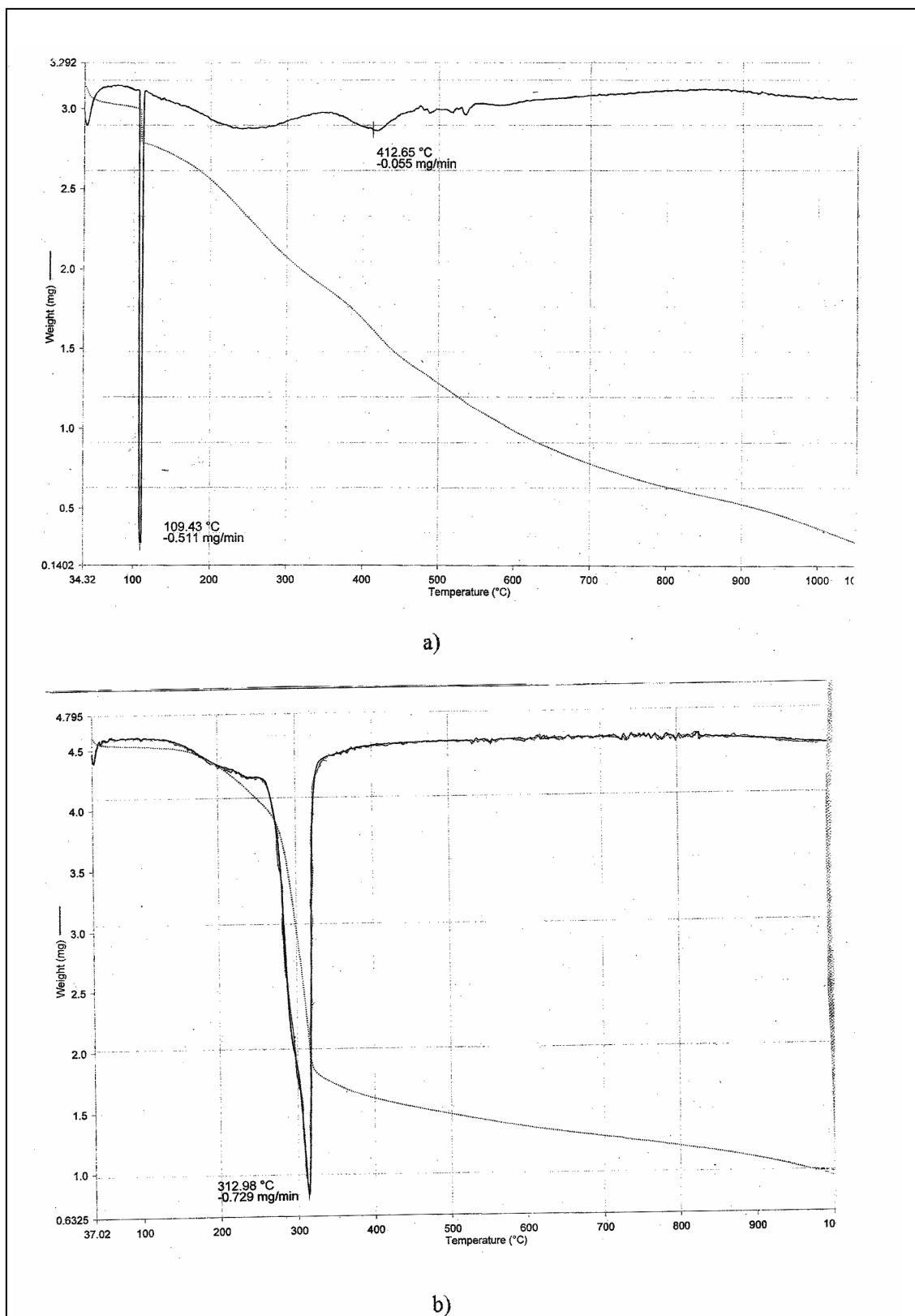
104

Fig. 5.7. FAB Mass Spectrum of [CuL(OAc)(H₂O)]

Fig. 5.8. TG/DTG Traces of
(a) [Ni(L)$_2$(H$_2$O)$_2$] and (b) [Cu(L)(OAc)(H$_2$O)]

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Table 5.5. Decomposition data of nickel and copper complexes

Complex	F.W.	Decompo-sition stage	Decompo-sition tempera-ture (^{o}C)	Mass loss % TG (calc.)	Decompo-sition pattern
[Cu(L)(OAc)(H$_2$O)]	412	Stage 1	181.9	3.8 (4.4)	Loss of H$_2$O
		Stage 2	281.5	18.5 (18.6)	Loss of (H$_2$O+OAc)
		Stage 3	1000.1	86.1 (80.7)	Final residue CuO
[Ni(L)$_2$(H$_2$O)$_2$]	636	Stage 1	160.6	9.2 (5.7)	Loss of two H$_2$O
		Stage 2	1001.2	88.2 (88.3)	Final residue NiO

It can be observed from the data that both of the complexes are stable upto 150°C. Above this temperature, decomposition begins slowly. After the loss of coordinated OAc/H$_2$O, the final stage is attained at a very high temperature of ~ 1000°C. This is a clear indication of the strong binding nature of the ligand ADAA. The degradation pattern strongly supports the proposed molecular formulae as the percentages of mass loss at different stages are very close to the calculated values.

D. Conclusion

In all the synthesised complexes, ADAA (LH) was found to be acting as a bidentate monoanionic ligand. All complexes except the Zn(II) complex were found to be accommodating other ligands to satisfy co-ordination number/electrovalency. Zinc was found to be attached to two ligand moieties, thus satisfying both primary and secondary valencies. The Cr(III), Fe(III) and Ni(II) complexes were found to assume octahedral geometry and the Cu(II) and Zn(II) complexes, tetraheral geometry. The probable geometries of the complexes can be represented as in Figures 5.9, 5.10 and 5.11.
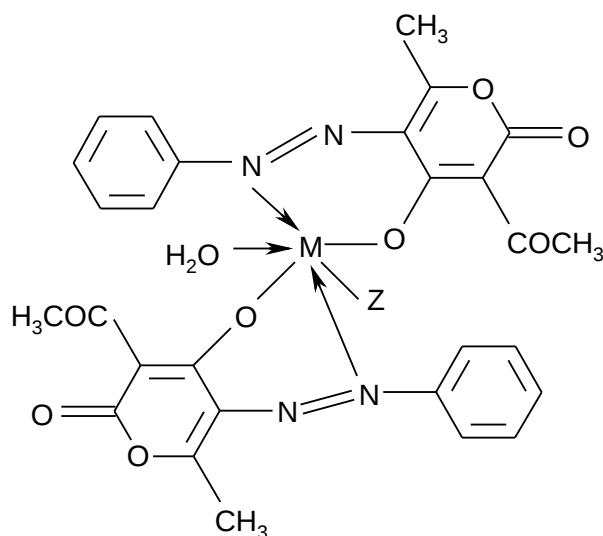

Fig. 5.9. Proposed structure of octahedral complexes

where M = Cr(III) / Fe(III) / Ni(II)
Z = Cl when M = Cr(II) / Fe(III)
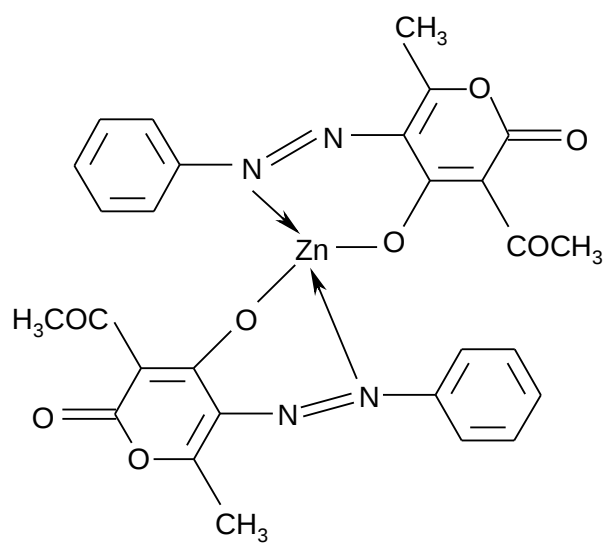Z = H_2O when M = Ni(II)

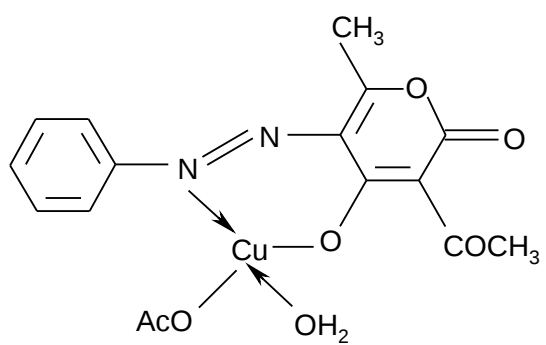**Fig. 5.10. Proposed structure of tetrahedral complex [ZnL$_2$]**

Fig. 5.11. Proposed structure of tetrahedral complex [CuL(OAc)(H$_2$O)]

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CHAPTER VI

2,3-DIMETHYL-4-(2-HYDRAZONO-SPIRO-5,5-DIMETHYL 1,3-CYCLOHEXANE DIONO) 1-PHENYL-3-PYRAZOLIN-5-ONE AND ITS METAL COMPLEXES

Azopyrazolones, viz., azoantipyrine derivatives of 1,3-dicarbonyls[1] form an important group of dyes. Eventhough these can be easily synthesised by the diazotisation of 4-aminoantipyrine (Fig. 6.1) followed by coupling with a β-dicarbonyl compound, the reports[2-4] on the ligational behaviour of these compounds are scanty. Moreover, the nature of N-N-C linkage is reported either as the azo or the hydrazono by different researchers.
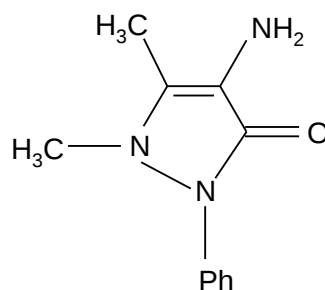

Fig. 6.1. 4-Aminoantipyrine

In the present investigation, the compound 2,3-Dimethyl-4-(2 hydrazonospiro-5,5-dimethyl-1,3-cyclohexanediono) 1-phenyl-3-pyrazolin-5-one (antipyrinylazodimedone) (DAAP) (LH) was found to be having a hydrazono structure. The physico-chemical and spectral evidences are given in the following discussion.

A. Synthesis of antipyrinylazodimedone (DAAP)

4-amino antipyrine (0.01 mole) was diazotized by dissolving in dilute (1:1) HCl and adding $NaNO_2$ solution (0.01 mole) drop wise with brisk stirring. The temperature of the system was always maintained at ~ 0-5°C. This diazonium chloride solution was added slowly in drops to an ethanolic solution of dimedone (0.01 mole) when the yellow precipitate of antipyrinylazo dimedone (DAAP) was formed. The product was highly soluble in water and hence over dilution and repeated washing with water were avoided. The pH of the solution was kept at ~ 6.5. The product was dried over anhydrous $MgSO_4$ in a desiccator. Recrystallisation was done in methanol (Yield 80% , M.P: 210°C).

B. Synthesis of metal complexes

The ligand, DAAP was dissolved in methanol and to this solution metal salt solution in aqueous-methanol was added slowly drop-wise with stirring. The metal to ligand mole ratio was maintained at 1:2 or 1:3 depending on the valency of the metal. The mixture was kept over a steam bath for 1.5 h. The solution was kept aside to bring down temperature and the precipitated metal complexes were filtered while hot, washed with water and ethanol and dried over anhydrous $MgSO_4$ in a desiccator. Recrystallisation was done in CH_2Cl_2 - CH_3OH mixture.

C.   Results and discussion

1.   Characterization of the ligand

Spectra of the azo-derivatives of pyrazolones have been studied[5-7] extensively and the conclusion was that azopyrazolin-5-ones have the hydrazono structure and azopyrazolin-3- and- 4-ones have azo-hydroxy structure.
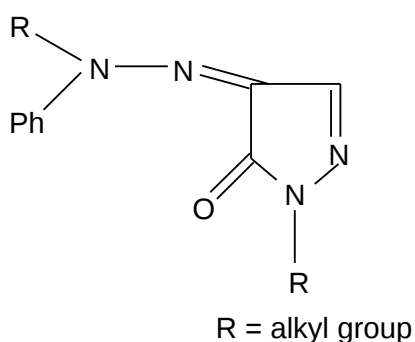

R = alkyl group

Fig 6.2. Hydrazono structure

But in the present situation, as N-2 of the antipyrinyl moiety is substituted, the pyrazolone is a 3-pyrazolin-5-one and the two possible structures are represented below.
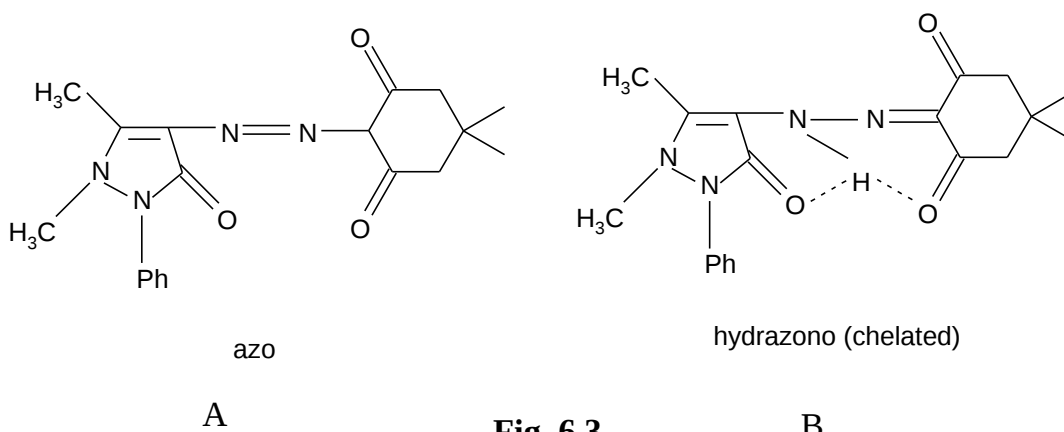

azo

A   **Fig. 6.3**   B

a) Analytical data

The physical and analytical data of the ligands are given in Table 6.1. The elemental percentages conform to the molecular formula $C_{18}N_4O_3H_{22}$.

Table 6.1. Physico-chemical and electronic spectral data of DAAP

Compound	Colour	Yield (%)	MP (°C)	Elemental analysis (%) found (Cal)			Electronic Spectral data λ_{max} (nm)
				C	H	N	
2,3-Dimethyl-4-(2- hydrozono spiro 5,5-dimethyl-1,3-cyclohexanediono) 1 phenyl-3-pyrazolin-5-one (DAAP) (LH)	Yellow	80	210	64.19 (64.59)	5.68 (6.21)	15.50 (15.81)	310, 384, 510, 684

b) Spectral data

i) Electronic spectrum

The absence of a band at ~ 270-280 nm indicated the absence of azo structure in the ligand. The strong band at 384 nm confirmed the hydrazone structure of the compound.

ii) IR spectrum

IR spectrum showed two bands of strong intensity at 1665 and 1625 cm^{-1} which could be attributed to the free β-dicarbonyl and the chelated >C=O

group respectively. The band due to pyrazoline carboxyl stretching vibration was observed at lower frequency than at the expected region. The band at 1540 cm^{-1} could be assigned to C=C–NH–N=(not cyclic) system[9]. The broad band at 3450 cm^{-1} indicated strong intramolecular hydrogen bonding of acidic proton. The IR data are presented in Table 6.2.

Table 6.2. IR spectral bands ν (cm^{-1})

Compound	Free >C=O	Chelated >C=O	C=C–NH–N=	C–N
DAAP	1665	1625	1540	1422

iii) ^1H NMR spectrum

The ^1H NMR spectrum (Fig. 6.4) of DAAP showed a low-field signal at ~ 15 ppm due to the acidic proton. Other prominent signals were at ~ 7.4 ppm (unsymm. pattern, aromatic) and 3.28 ppm (–N–CH_3), both conform to literature[9] data of antipyrine. Signals at 2.68 ppm (other –CH_3 of antipyrine moiety), 2.78 ppm (H_2C< of dimedone) and 1.28 ppm (*gem* dimethyl of dimedone) were also very conspicuous.

iv) Mass spectrum

The mass spectrum (Fig. 6.5) of DAAP did not have an (M-N_2)$^+$ peak which showed the absence of azo group. Hence a hydrazone structure was strongly indicated. The BP at m/z 154 ($C_8NO_2H_{10}$)$^+$, indicated the dimedone azo fragment. The (M+1)$^+$ peak was very conspicuous at 355 m/z.
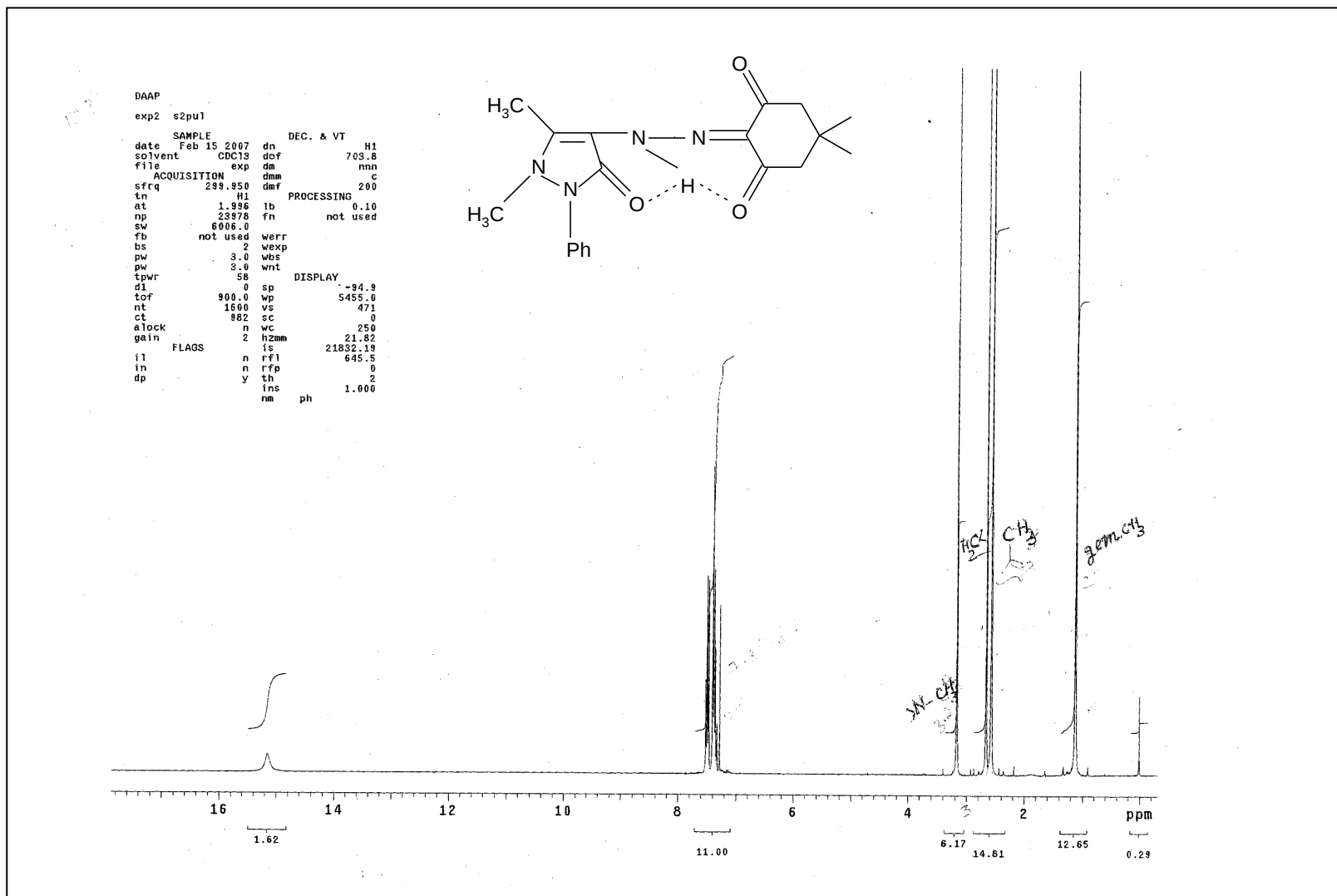
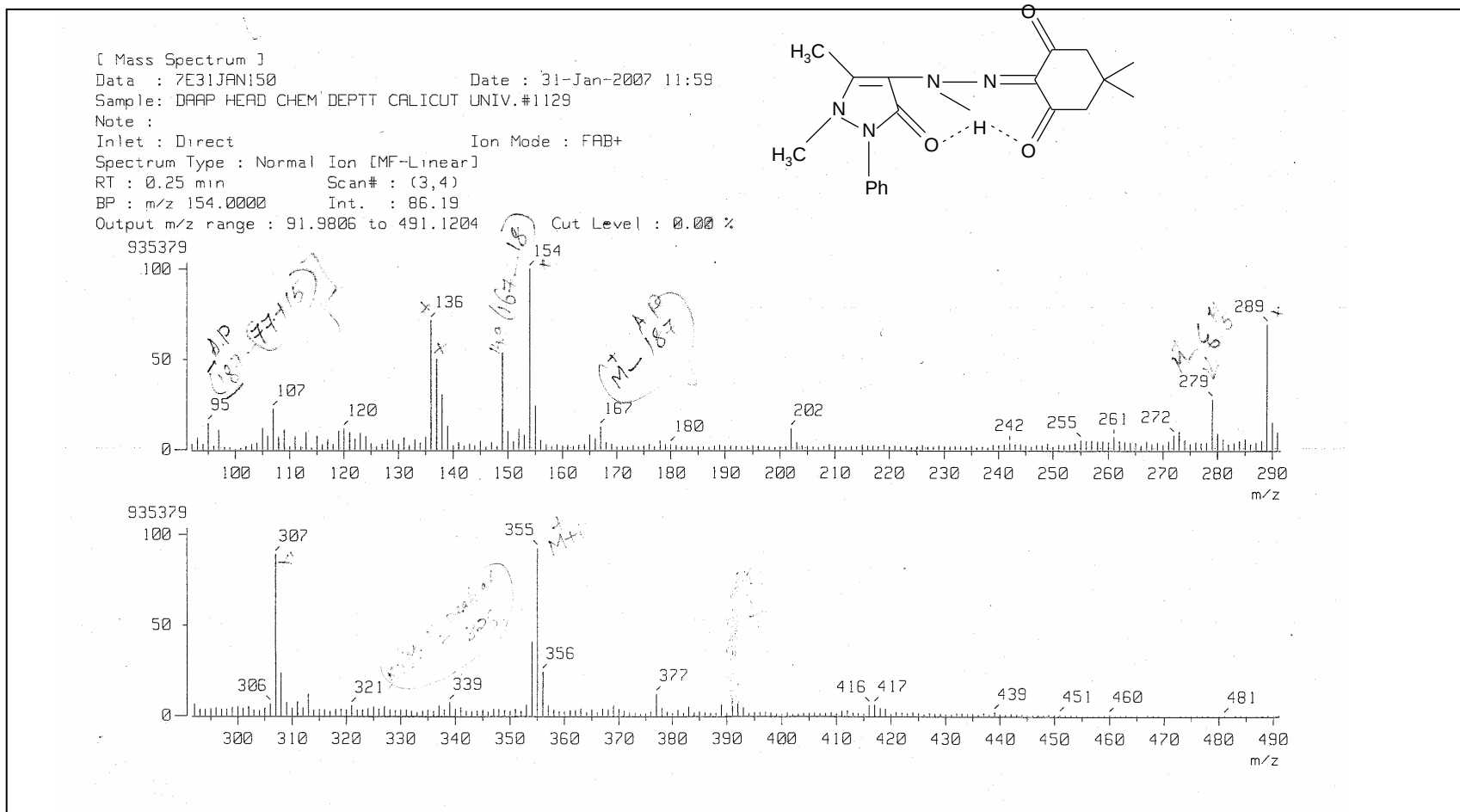**Fig. 6.4.   ¹H NMR spectrum of DAAP**

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Fig. 6.5. FAB mass spectrum of DAAP

Other important peaks are: m/z 279 (M-C_6H_5)$^+$, m/z 167 ($C_8N_2O_2H_{10}$) and m/z 95 (187 –C_6H_5–CH_3). The peaks marked with x sign are matrix peaks as provided by the instruction manual. Therefore the structure for DAAP was assigned as in Fig. 6.3(B).

2. Characterization of metal complexes

Well defined complexes of Cr(III), Fe(III), Ni(II), Cu(II), and Zn(II) have been synthesised and characterised. Fe(III) and Cr(III) complexes were found to contain anion (Cl$^-$). Zn(II) complex was diamagnetic in nature.

Cr(II) complex was found to be slightly conducting indicating that Cl$^-$ may well be placed out of the coordination sphere. Fe(III) complex was non conducting and the two Cl$^-$ ions were considered to be within the coordination sphere. Complexes of Ni(II), Cu(II) and Zn(II) were also non conducting.

Table 6.3. Physico-chemical and electronic speectral data of complexes

Sl. No.	Compound	Colour	Yield (%)	M.P. (°C)	Elemental Analysis found (calc.) (%)					Magnetic moment μ_{eff} B.M.	Electronic spectral data λ_{max} (nm)
					C	H	N	M	X		
1.	[Cr(L)$_2$Cl]	Dark Green	50	270	57.10 (57.61)	5.20 (5.31)	14.62 (14.75)	6.92 (6.55)	4.96 (4.47)	3.79	260, 310, 400, 570, 680
2.	[Fe(L)Cl$_2$]	Brown	60	170	47.31 (47.51)	4.39 (4.38)	11.77 (11.64)	11.93 (11.67)	14.85 (14.79)	5.94	288, 310, 416, 516, 630
3.	[Ni(L)$_2$]	Greenish Brown	65	280	59.72 (59.63)	5.73 (5.49)	14.78 (14.65)	7.26 (7.68)	--	2.84	286, 314, 390, 670
4.	[Cu(L)$_2$]	Brown	70	240	59.63 (59.10)	5.66 (5.70)	14.36 (14.52)	7.98 (8.26)	--	1.74	286, 310, 388, 508, 786
5.	[Zn(L)$_2$]	Yellow	70	290	59.38 (59.12)	5.22 (5.71)	14.97 (14.52)	8.23 (8.47)	--	D	288, 310, 512, 680

L = Mono anion of DAAP (LH); M - metal, X = Cl, D = Diamagnetic

a) Electronic spectral data and magnetic behaviour

Chromium(III) complex was dark green in colour. The magnetic moment of 3.79 B.M. confirmed the presence of 3 unpaired electrons and octahedral geometry. The prominent electronic spectral bands at 260 nm ($^4A_{2g}(F) \rightarrow T_{1g}(P)$), 400 nm ($^4T_{1g}(F) \rightarrow A_{2g}(F)$) and 570 nm ($^2A_{2g}(F) \rightarrow {}^4T_{2g}(F)$) were very conspicuous and obviously suggested an octahedral geometry.

Explanation of the spectrum of Fe(III) complex was difficult due to overlap of CT- and visible bands. But the magnetic moment value (5.94 B.M.) clearly indicated an octahedral geometry.

The spectrum of Ni(II) complex was characteristic of an octahedral geometry with prominent bands at 390 nm ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and 676 nm ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$). The magnetic moment of 2.84 B.M. also suggested an octahedral geometry.

The Cu(II) complex was brown in colour due to strong CT bands tailing off into the blue end of the visible region. The magnetic moment value (1.74 B.M.) lies well within the expected range (1.7 - 2.2 B.M.).

The Zn(II) complex was diamagnetic and the spectral peaks were all similar to those of the ligand as d-d transitions were absent.

b) IR spectra

The free C=O band at 1665 cm^{-1} in the ligand was retained around 1660 cm^{-1} indicating its non involvement in co-ordination. The lowering of band at 1625 to 1590 cm^{-1} suggested coordination through >C=O and the C=N band is visible ~ 1550 cm^{-1}. Two new bands at ~600-560 cm^{-1} and 460-440 cm^{-1} indicate M-N and M-O stretching vibration respectively. The broad band at ~3400 cm^{-1} in the ligand spectrum has disappeared in the spectra of complexes, indicating involvement of hydrogen bonded nitrogen in metal coordination where the H has been replaced by M.

The important IR bands and their assignment are given in the table below.

Table 6.4. Important IR spectral bands (cm^{-1}) and their assignments

Sl. No.	Compound	Free C=O	Chelated C=O	Chelated C=N	M-N	M-O
1.	[Cr(L)$_2$Cl]	1661	1591	1545	582	435
2.	[Fe(L)Cl$_2$]	1660	1591	1540	562	450
3.	[Ni(L)$_2$]	1652	1594	1560	555	439
4.	[Cu(L)$_2$]	1641	1595	1578	609	468
5.	[Zn(L)$_2$]	1659	1591	1548	564	447

c) ¹H NMR spectrum

The ^1H NMR spectrum (Fig. 6.6) of $[Zn(L)_2]$ showed no peak at ~15 ppm showing that the acidic proton has been replaced by metal ion. All other peaks, viz., unsymmetrical pattern at ~ 7.28 ppm (aryl), two singlets at 2.8 and 3.2 ppm ($-NCH_3$ & $C-CH_3$) and broad singlet at 1.6 ppm ($-CH_2$) confirm the presence of ligand moiety. The doublet (instead of a singlet) at ~ 1 ppm of the *gem* dimethyl groups may be due to the strain in the molecule as a result of coordination of two ligands.

d) Mass spectra

ESI mass spectrum (Fig. 6.7) of $[Cu(L)_2]$ and FAB mass spectrum (Fig. 6.8) $[Zn(L)_2]$ showed molecular ion peaks at 770 and 771, respectively. $(M+2)^+$ peaks (isotopic) are also prominent for Cu(II) complex. In both cases, the base peaks were the $[ML]^+$ peak showing the displacement of acidic proton during chelation.

The peaks at 120 and 105 in both the ligand and the chelate may be due to the fragmentation typical[11] of pyrazolones as shown in scheme 6.1.
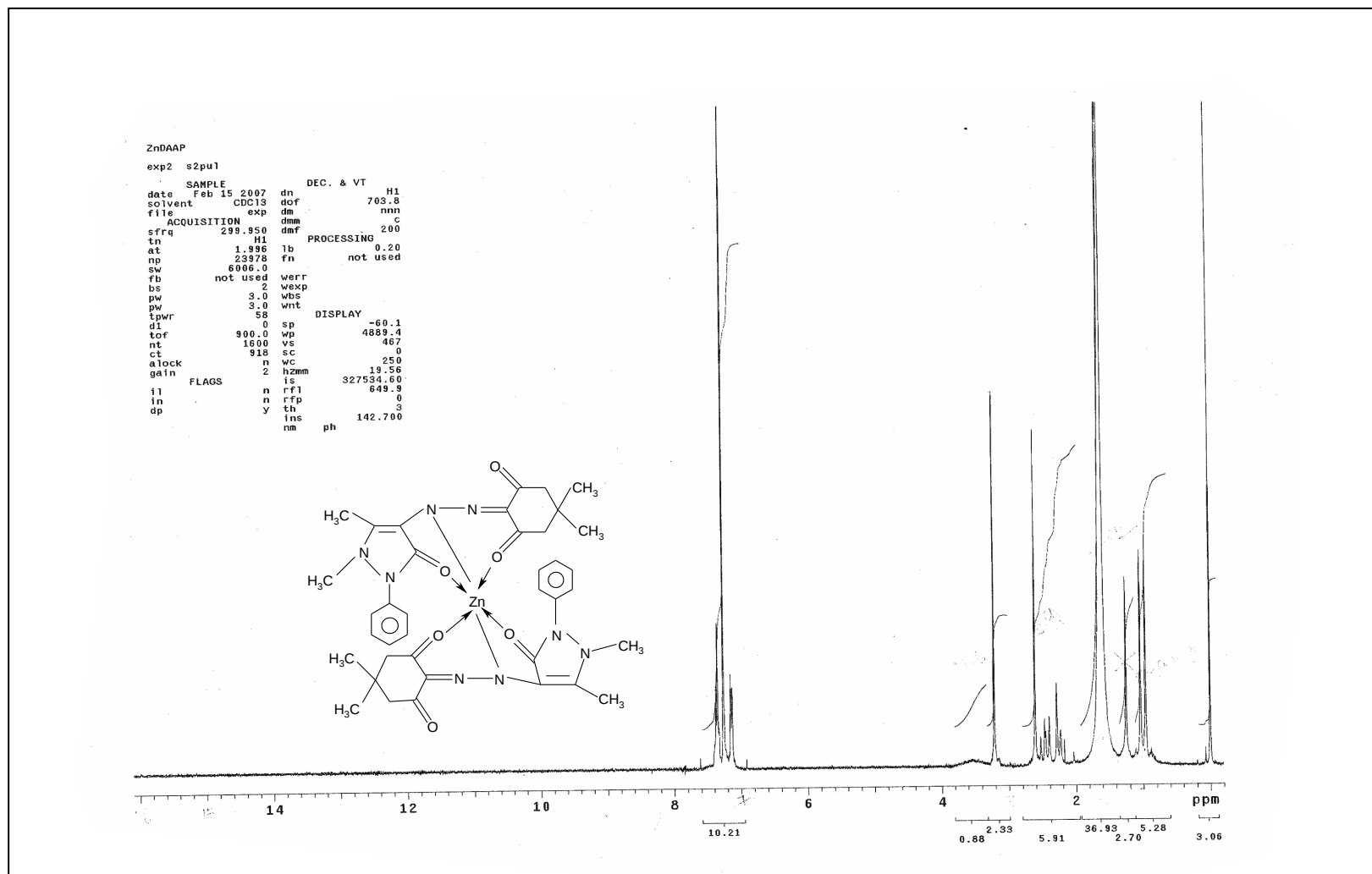
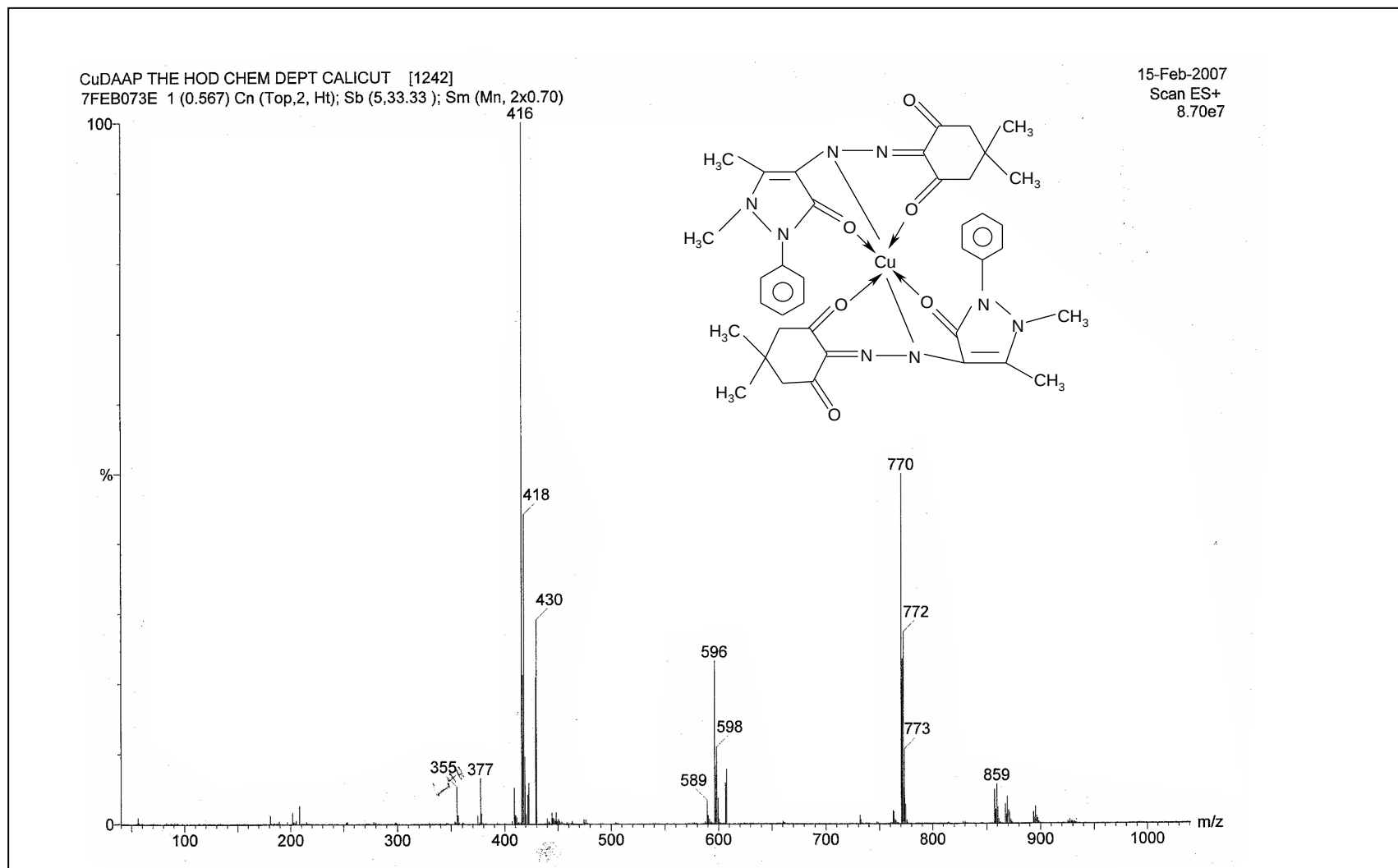**Fig. 6.6.** ^{1}H NMR spectrum of ZnL$_2$
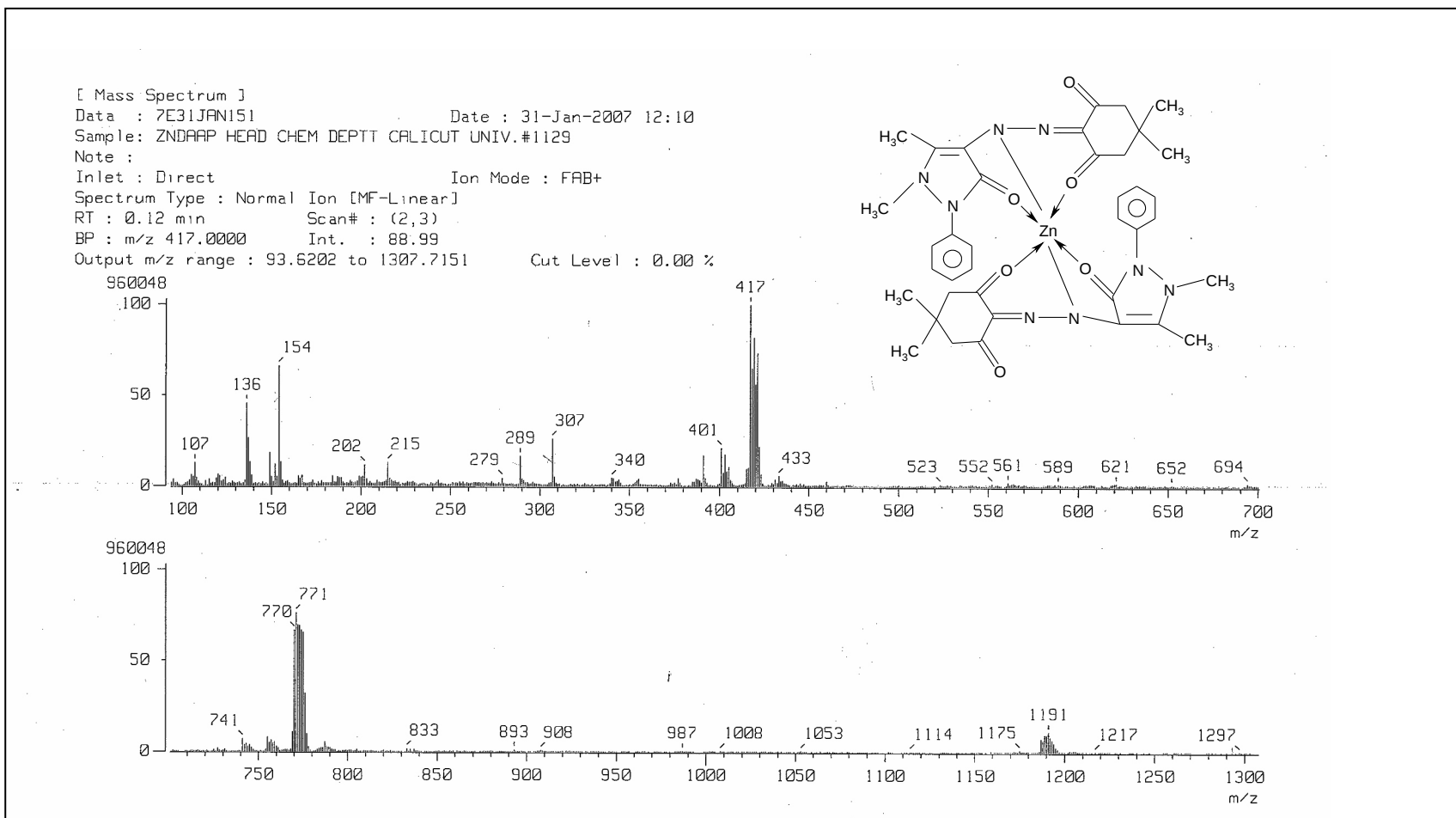
Fig. 6.7. ESI mass spectrum of CuL₂

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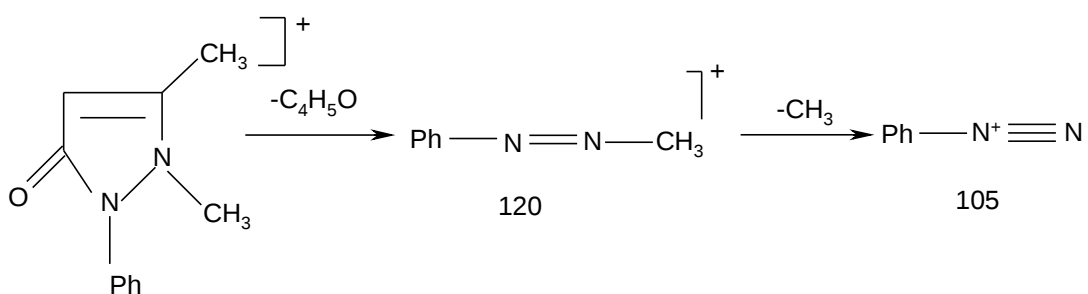**Fig. 6.8. FAB mass spectrum of ZnL₂**

Scheme 6.1

The absence of an M-N$_2$$^{1+}$ peak ruled out any azo structure. Other prominent peaks ascertaining the structure are shown in the spectrum.

D. Conclusion

The above physico chemical data confirmed the stoichiometric ratio of 1:2 (metal: ligand) for Ni(II), Cu(II) and Zn(II) complexes. Whereas, the trivalent metals form complexes with different metal to ligand ratio. Moreover, these metals were found to be accommodating simple anions (chloride) to satisfy the valencies. The stioichiometric ratio of metal : ligand : chloride for Cr(III) complex was 1:2:1 and that for Fe(III) complex was 1:1:2. The halide ion has been suggested to be out of the coordination sphere in Cr(III) complex and in Fe(III) complex the Cl$^-$ ion are well within the coordination sphere.

Hence the following structure may be assigned to the complexes of DAAP.
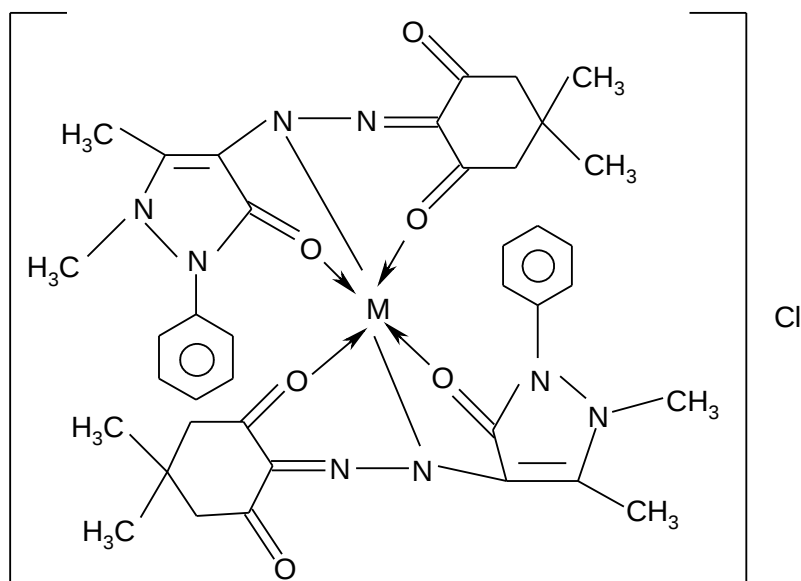
Fig. 6.9. Proposed Structure of octahedral [CrL$_2$]Cl
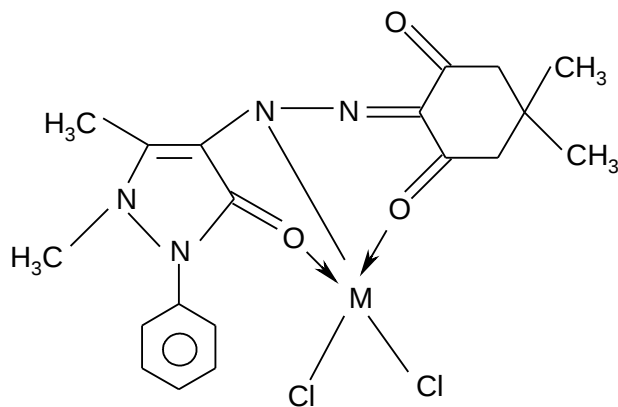
Fig. 6.10. Proposed structure of octahedral [FeLCl$_2$]
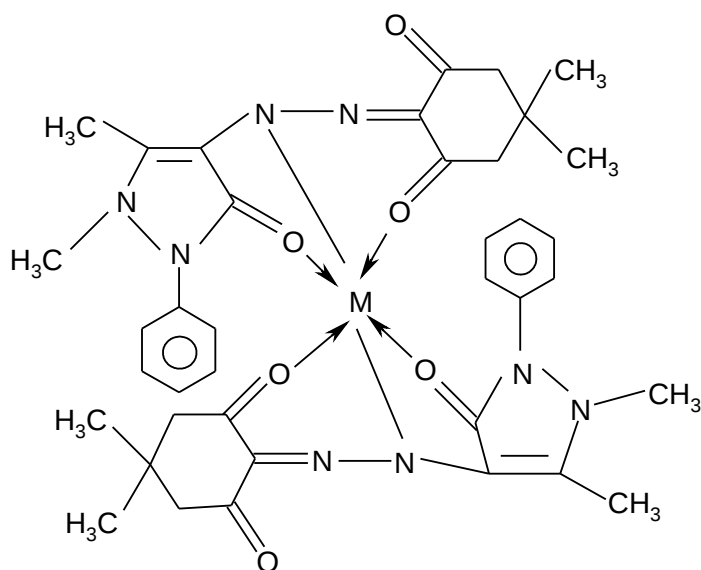
Fig. 6.11. Proposed structure of octahedral complex [ML$_2$],
where M = Ni(II) /Cu(II) / Zn(II)

Thus, the ligands function as monobasic tridentate species in their bivalent metal complexes forming annulated chelate rings with metal atoms. The involvement of pyrazolone carbonyl, one of the hydrazono nitrogens and one of the dimedone carbonyl was also indicated. It can also be seen that the tautomeric form of the ligand is retained in the metal complexes too. All the complexes were assigned octahedral geometry. The sixth corodination in Fe(III) complex may be satisifed by some other neighbouring interaction.

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PART II

PHOTO PHYSICAL STUDIES

CHAPTER I

INTRODUCTION

Fluorescence is the property of some atoms or molecules to absorb radiation at a particular wave length and subsequently emit light of longer wave length after a brief interval. This phenomenon had been described for the first time in 1852 by the British scientist Sir George G. Stokes. The fluorescing molecules are termed as 'probes', or 'fluorochromes' or sometimes as 'dyes'. A 'flurophore' is a fluorochrome that is attached to a larger molecule like polymer or protein.

A fluorophore in the excited state (donor) can transfer its energy to the neighbouring chromophore (acceptor) nonradiatively through long range dipole-dipole interactions over distances measured in nanometers. This is referred to as 'Resonance Energy Transfer (RET). RET is possible whenever the emission band of the fluorophore overlaps the absorption band of the acceptor. The separation between the donor and acceptor must also be less than 10 nm. This principle is made use of in the present work in which the polymer host transfers its energy to the embedded europium chelate which in turn emits radiation at ~613 nm.

A. Fluorescent compounds as guest molecules - an overview

From the mid 1960s[1,2] dyes have been used in lasers which can emit both in the pulsed and the continuous wave forms. Hundreds of dyes have been demonstrated to lase measurably covering a spectral range from UV to near IR. Dyes have been found to exhibit fluorescence in the solid, liquid or gas phases. However, liquids though preferred due to their high optical quality and suitability to be used in different concentrations pose the problem of requirement in large quantities causing disposal problems. Many of these solvents are toxic, carcinogenic and even expensive. Moreover, liquid solvents require cells with larger dimensions and other associated difficulties like leakage, spilling, etc., are also encountered with.

Therefore, attempts were made to overcome these problems by incorporating the organic molecules into solid matrices. Most of the recent work has been done in inorganic glasses[3] and transparent polymers[4-6]. Still, it must be kept in mind that dyes have a tendency to photodecompose.

Inorganic glasses have the advantages of better thermal properties like high thermal conductivity, low thermal expansion and higher damage threshold than polymers. But polymers are more easy to handle, less expensive, flexible and can be made into very thin films which require small quantities of the guest molecules. Polymers also exhibit better solvent compatibility with the embedded organic molecules and have superior optical

homogeneity. New modified fluorinated polymers[7,8] have high threshold of damage and stabilities higher than those of inorganic glasses. Optical fibres made of polymers have greater flexibility and core diameter than conventional methods of data transport.

Ever since Weissman[9] discovered the visible fluorescence of Eu(III) betadiketonate complex in 1942, the lanthanide ions hold a special place in photonics. Lanthanide chelates, especially the β-diketonates find a wide range of applications in tuneable lasers, amplifiers for optical communications, light emitting active layers in multi layer organic light emitting diodes (OLEDS) and efficient light conversion molecular devices[10] (LCMDS) in fluoroimmuno assays, photovoltaic devices, etc. They also find a place in finger print tracing and in fluorescent marking of currency, like the Euro. While typical fluorophores such as fluorescein have a half-life of 5-6 n secs, lanthanide chelates stay at excited state for about 10^5 times longer. This significantly enhances sensitivity and also dramatically reduces back ground fluorescence. Lanthanide chelates have wider stokes shift (about 200-300 nm) than other fluorophores. They have sharp emission peaks which are independent of the structure of the ligand. Moreover, they are stable upto seven years, if stored properly. However, it is seen that temperature and radiations tend to decrease their stability. Many chelates have water

molecules coordinated to the metal ion which quench emission. Some chelates are even prone to 'ligand evaporation'.

The luminescence of lanthanide complexes and their photophysics were systematically studied in the beginning of 1960s[11-15] and continue to draw attention in recent years too.

B. Principles involved in the fluorescence of lanthanide chelates

Lanthanides have different number of 4f electrons, their electronic configuration indicated as $4f^{0-15}5d^{0-10}s^{1-2}$. Since 4f electrons are shielded from the environment, the properties of lanthanides[16] closely resemble each other.

Fluorescent rare earth chelates are divided into three main groups according to their fluorescent characteristics.

1.   The strong fluorescent group (Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}chelates).

2.   The weak fluorescent group (Ce^{3+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} chelates).

3.   The non-fluorescent group (La^{3+}, Gd^{3+} and Lu^{3+} chelates).

Excitation and emission occur by the following process. First, the ligand is excited to higher energy state (S_1) by the ultraviolet light. Next, by intersystem crossing, energy is transferred to the triplet state (T_1) and from there to the excited state of the Lanthanide ion. In the case of europium, the

excited state is ^5D. Therefore, when the metal returns to the ground state ^7F, fluorescence is emitted[17].

The transitions of Eu^{3+} in solution are given below.

Transition		λ emission (nm)
^5D_o	$\rightarrow$ ^7F_o	580
	$\rightarrow$ $^7F_1$	590
	$\rightarrow$ $^7F_2$	613
	$\rightarrow$ $^7F_3$	650
	$\rightarrow$ $^7F_4$	690
	$\rightarrow$ $^7F_5$	710

A strong fluorescence is observed in the case of β-diketonate ligands as they suppress the deactivation process that is caused by energy transfer to the solvent molecules. Therefore, the ligand chosen should have high absorbance for the complex to exhibit fluorescence.

C. Incorporation of lanthanide chelates into polymer matrices

The incorporation of lanthanide chelates into vinylic hosts[18] was reported as early as in 1962, almost at the same time when their optical properties were analysed.

The concept of lanthanide luminescence when embedded in polymers is pictorially depicted as follows.
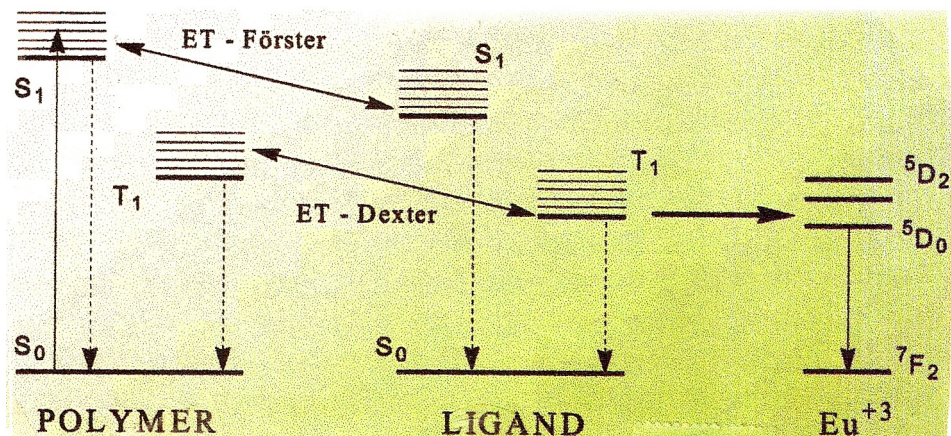

**Fig. 1(II) Background energy transfer -
polymer to ligand to lanthanide**

While synthesising lanthanide chelates for optical applications, one part of the ligand is usually designed to bind strongly and shield the lanthanide ion against quenching. β-diketones, cryptands, calixarenes, cyclodextrins, crown ethers, etc, are used for the purpose. In addition to β diketones, organic chromophores like N-heterocycles are also used to complex with the lanthanide ions. These light harvesting moieties enhance absorption cross section of Ln^{3+} absorption bands which are otherwise narrow ($\Delta\lambda$ <1 nm) and weak (ϵ< $1M^{-1}$ cm^{-1}). These are also termed as 'antennae molecule's as they transfer energy towards the central metal ion[19]. Pyridines,

bipyridine, 1,10-phenanthroline, etc., are some examples for antennae molecules.
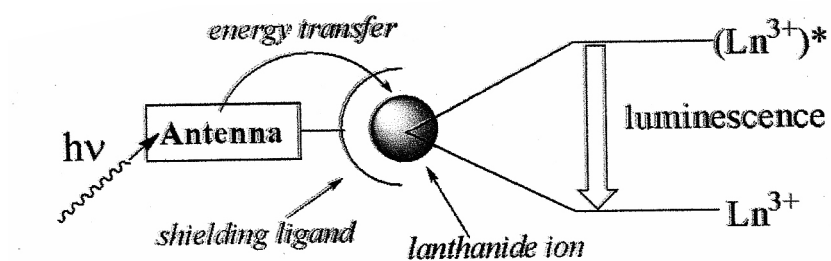

Fig.2(II) Pictorial representation of lanthanide complexes in photophysical phenomenon

Lanthanides have the unique property of emission which is independent of the matrix into which they are embedded provided one succeeds in incorporating them. Obviously, when this difficulty in doping is taken into account, chelates of lanthanides are preferred to their simple salts in studies involving polymer matrices as it is hard to find a solvent compatible with the ion as well as the polymer.

CHAPTER II
EUROPIUM CHELATE AS EMITTER IN OPTICAL DEVICES

For long distance communication it is necessary to compensate the attenuation (link loss) in fibre by regeneration of the signal at every 50-150 km using optical amplifiers. An amplifying medium contains a material capable of luminescence at the signal beam wave length.

The present work is focussed on β-diketonate complexes of europium with 1,10-phenanthroline as coligand. The luminescence phenomena in the visible region is not disturbed by vibrational C-H overtone absorptions of the matrix. Moreover, for the same reason, polymers have their low loss windows in the spectral region ~ 600 nm, which is also one of the standard wave lengths[20] in optical telecommunications. Therefore, europium, one of the strongest emitters among the lanthanides which fluoresce at 613 nm is chosen for the study. The high quantum yield of europium chelates when compared to the weak fluorescent group (due to a large difference in energy levels of excited and ground states which avoids non-radiative transition) also rationalises the choice of the metal ion. Organic dyes exhibit wide absorption cross section σ, and wide spectral range of absorption $\Delta\lambda$. Therefore, the azo dye, phenylazodimedone was chosen to complex with europium and 1,10-phenanthroline was chosen as the antenna molecule.

A comparison of the photophysical properties of dimedone when co-ordinated to europium with 1,10-phenanthroline as coligand is also conducted.

There has been plenty of work[21-32] in the field of optical/electrical properties of lanthanide β-diketones and the antennae ligands incorporated into glass/silica or polymer matrices. When the excitation/luminescence peak of plain polymers show proximity to the absorption peaks of the complexes in films, it can be suggested[33] that these polymers work well to become hosts for europium complexes to be used as active material in POFA and OLEDS. Verification of these applications requires the laborious process of fabricating optical fibre/diode and testing the electroluminescent behaviour. Lack of technical know how and sophisticated instruments prevent one from delving deep into the intricate details. So the basic minimum study of casting thin polymer films and obtaining the absorption and PL spectra were carried out in the present work. In almost all of the previous works, the chelates were introduced into the monomers and then polymerisation was initiated using a catalyst. Hence, the chelates make a covalent linkage with the polymer chain. Even though this makes a stronger attachment of the chelate towards the polymer chain, the process is not as easy as the present work. The doping in the present study is carried out by adding the chelate as such into the polymer solution and there is no covalent linkage between the chelate and the

polymer. Moreover, in this work the chelate to polymer ratio could be adjusted unlike as in the other studies.

Another feature of the present work is that the use of azo β-diketones as ligands. Even though a few reports[34-36] are there of employing azo β-diketones, not much work has been done with these ligands. These organic dyes have the additional advantage of wide absorption cross sections which extend the absorption-emission overlap region.

A comparison is also done using the same β-diketone sans the azo coupled moiety. The results are discussed towards the end of this chapter.

A. Experimental methods

A general description of the four polymers chosen for this study and the instruments used for different analyses are given below. A brief outline of the method for the synthesis of the two complexes is also provided.

1. Materials

The chemicals used, the β-diketones dimedone (loba) and thenoyl trifluoroacetone (Emerck) o-phenanthroline (Merck) $EuCl_3$ (alfa aeser) were of standard AnalaR grade. The solvents, methanol and chloroform used were from E Merck and were used as received. Ethanol was purified by distillation and used.

a) Polymer hosts

The oligomer, PEG was purchased from E Merck. Other polymers were of synthetic grade.

i) Ethylene vinyl acetate (EVA)

Polyethylene vinyl acetate (EVA) or acetate is a copolymer of ethylene and vinyl acetate. The weight percentage of vinyl acetate varies from 10-40%, the rest being ethylene. EVA is a thermoplastic with good clarity, gloss, low-temperature toughness and stress-crack resistance. EVA finds application in foam padding in foot-wear, in drug delivery devices and in photovoltaics as an encapsulation material for silicon cells.
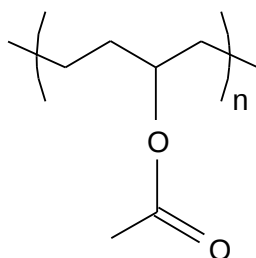

Fig. 3(II) EVA

ii) Polystyrene (PS)

Polystyrene (PS) is an aromatic polymer formed by the polymerisation of styrene.
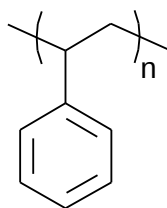
Fig. 4(II) PS

This is a thermoplastic and finds application in industry as a substitute for fibre. Apparatus made of PS is used in biomedical research laboratories.

iii) *Polymethyl methacryalate (PMMA)*

Polymethyl methacrylate (PMMA) or poly (methyl 2-methyl propenoate) is a transparent thermoplastic. Other names of PMMA are plexiglass, perspex, Acrylex, acrylic glass or acrylic. It is a good alternative to glass. It transmits UV radiation down to 300 nm and IR up to 2800 nm. It finds application as light shades in automobiles, in helmet visors, IOL used in cataract surgery laser discs and also in semiconductor research and industry.
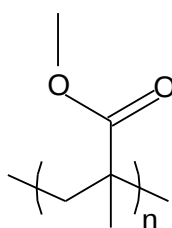

Fig. 5(II) PMMA

iv) Polyethylene glycol (PEG)

Polyethylene glycol (PEG) is chemically synonymous with polyethylene oxide (PEO) as both have the same monomeric unit with the latter having higher molecular mass.
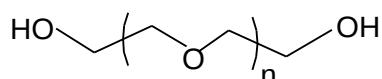

Fig. 6(II) PEG

This oligomer is prepared by the polymerisation of ethylene oxide with ethylene glycol. PEG is available in different categories as the range of monomeric units varies. PEG 400 is used in the present work which has molecular weight in the range 380-420. PEG finds application as polar stationary phase in GC, virus concentrator in microbiology, PEG bound vaccine for Hepatitis C in medicine, etc.

2. Instruments

(a)   Elementar Vario EL III CHNS analyser

(b)   Jasco UV/vis spectrophotometer. V-550

(c)   Jasco FTIR spectrophotometer - 4100

(d)   Micromass Quattro II triple quadrapole mass spectrometer.

(e)   Magway magnetic susceptibility instrument, Sherwood Scientific, UK.

(f)   SEM JEOL - JSM - 6300 Microscope.

(g)   Perkin Elmer, Diamond TG/DTA instrument.

(h)   Elico SL 174 spectrofluorometer

3. Methods

Metal (Eu) percentage was obtained by standard method[36] after igniting the chelates to oxide, digesting with conc. HCl, diluting to known volume and estimating by complexometry method using EDTA as titrant and xylenol orange as indicator which changes colour from purple to pale yellow at the end point.

C, H, N percentages were obtained by microanalyses at STIC, Kochi.

UV-visible and PL spectra were taken in methanolic solution for quantum yield studies and thin film strips were used for the doped polymer studies.

FTIR spectra were taken as KBr discs for characterisation of chelates and as circular film strips for doped polymer studies.

ESI mass spectra were obtained with samples dissolved in methanol and ESI capillary at 3.5 kv, cone voltage 40 v. The spectra were taken from SAIF, CDRI, Lucknow.

Magnetic moments were determined at room temperature ~ 26°C using Magway magnetic susceptibility instrument calibrated[37] using $Hg[Co(NCS)_4]$

SEM micrographs were taken with electron microscope operating at accelerating voltage 20-30 kv using polymer films (1 cm x 1 cm) sputtered with a thin layer of gold.

TG analyses were carried out in inert (N_2) atmosphere at heating rate of 10^oC/min at STIC, Kochi.

4. Synthesis of ligands and complexes

a) Ligands

The ligands used in the present investigation were dimedone (D), phenylazodimedone (AD) and 1,10-phenoantharoline (phen). Dimedone and 1,10-phenanthroline were used as purchased. Phenylazo derivative of dimedone was synthesised as described in Chapter III of Part I of this thesis. It has been characterised by elemental analysis, IR, UV, NMR and mass spectral and single crystal XRD techniques.

b) Complexes

i) Europium complex [Eu(AD)$_3$phen]

To a 2M solution of sodium hydroxide in 5 mL ethanol, 0.005 mol of phenylazodimedone was added followed by 0.002 mol of 1,10-phenanthroline and the solution was stirred until complete dissolution. Europium(III) chloride (0.002 mol) in ethanol was added drop wise when a deep-pink precipitate separated out. Stirring was continued for 4-5 h and the precipitated chelate

was filtered, washed with ethanol and dried over $MgSO_4$ in vacuum desiccator and recrystallised from methanol.

ii) Europium complex [Eu(D)$_3$phen]

This chelate was synthesised exactly in the same method as above except that dimedone was used instead of phenylazodimedone. The recrystallisation and drying conditions were also the same as described above.

B. Results and discussion

1. Characterization of Complexes

Elemental analysis data (Table 1) confirmed the molecular formula $EuC_{54}N_8O_6H_{56}$ for the chelate [Eu(AD)$_3$phen] and $EuC_{36}N_2O_6H_{44}$ for the chelate [Eu(D)$_3$phen] with 1:3:1 stoichiometry of metal: β-diketone/ azoβ-diketone : o phen. The paramagnetic nature and magnetic susceptibility values at room temperature were typical[38] of europium complexes.

Table 1. Physico-chemical data of the complexes

No	Complex	Colour	Yield %	MP °C	Mag. moment B.M	Elemental analyses found (calc) %				Electronic spectral data λ_{max} (nm)
						C	H	N	Eu	
1	[Eu(AD)₃phen]	deep pink	45	145	3.03	60.36 (60.90)	5.74 (5.26)	10.11 (10.53)	14.13 (14.29)	290, 380, 510
2	[Eu(D)₃phen]	pale yellow	41	240	3.24	56.63 (56.45)	5.59 (5.85)	3.46 (3.72)	20.67 (20.21)	260, 370, 520

The IR stretching bands consisted of all the expected values for free C=O, chelated C=O metal nitrogen and metal oxygen. νC=N band was observed only for [Eu(AD)$_3$phen] which further confirmed the hydrazono β-diketone moiety (see Table 2).

Table 2. Important IR stretching bands of europium chelates (cm^{-1})

Complex	Free C=O	Chelated C=O	C=N	M-N	M-O
[Eu(AD)$_3$phen]	1658	1547	1615	582	447
[Eu(D)$_3$phen]	1659	1547	nil	604	439

The electron spray ionisation (ESI) mass spectra of the complexes are given in figures 7(II) and 8(II). The spectra are having very prominant M+1 peaks at 1065 for [Eu(AD)$_3$phen] and at 753 for [Eu(D)$_3$phen] together with M+2 peaks. This strongly confirms the molecular formula. Moreover, the peaks at m/z 959 (M$^+$-C$_6$H$_5$N$_2$), 839 B.P (M$^+$-(C$_6$H$_5$ x 2 + CH$_3$), 691 (M$^+$-(o-phen + C$_6$H$_5$ N$_2$+ CH$_3$ x 6-2H) for [Eu(AD)$_3$phen] confirms the stoichiometry of 1:3:1 w.r.t Eu: phenylazodimedone : o-phenanthroline.
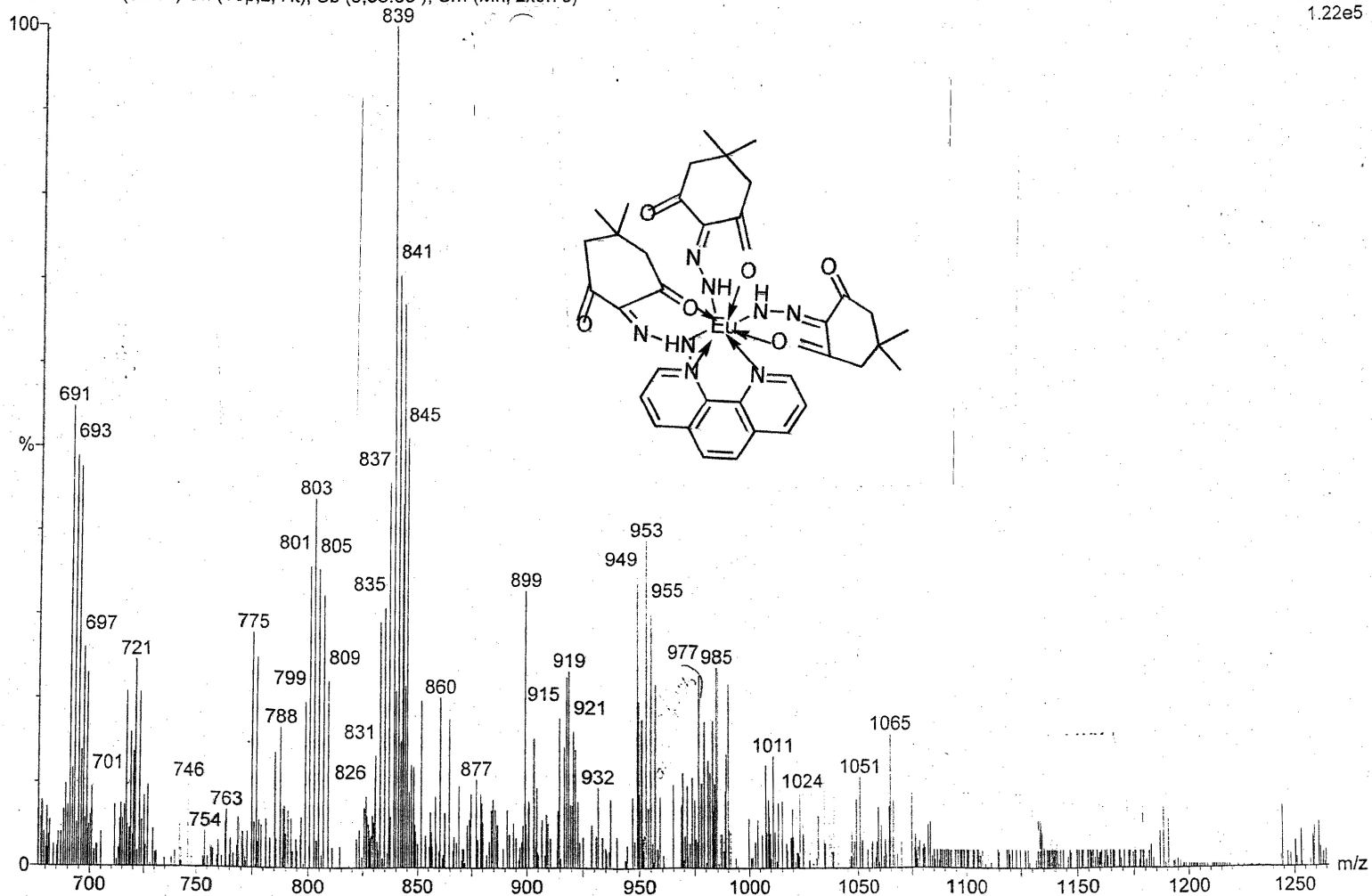
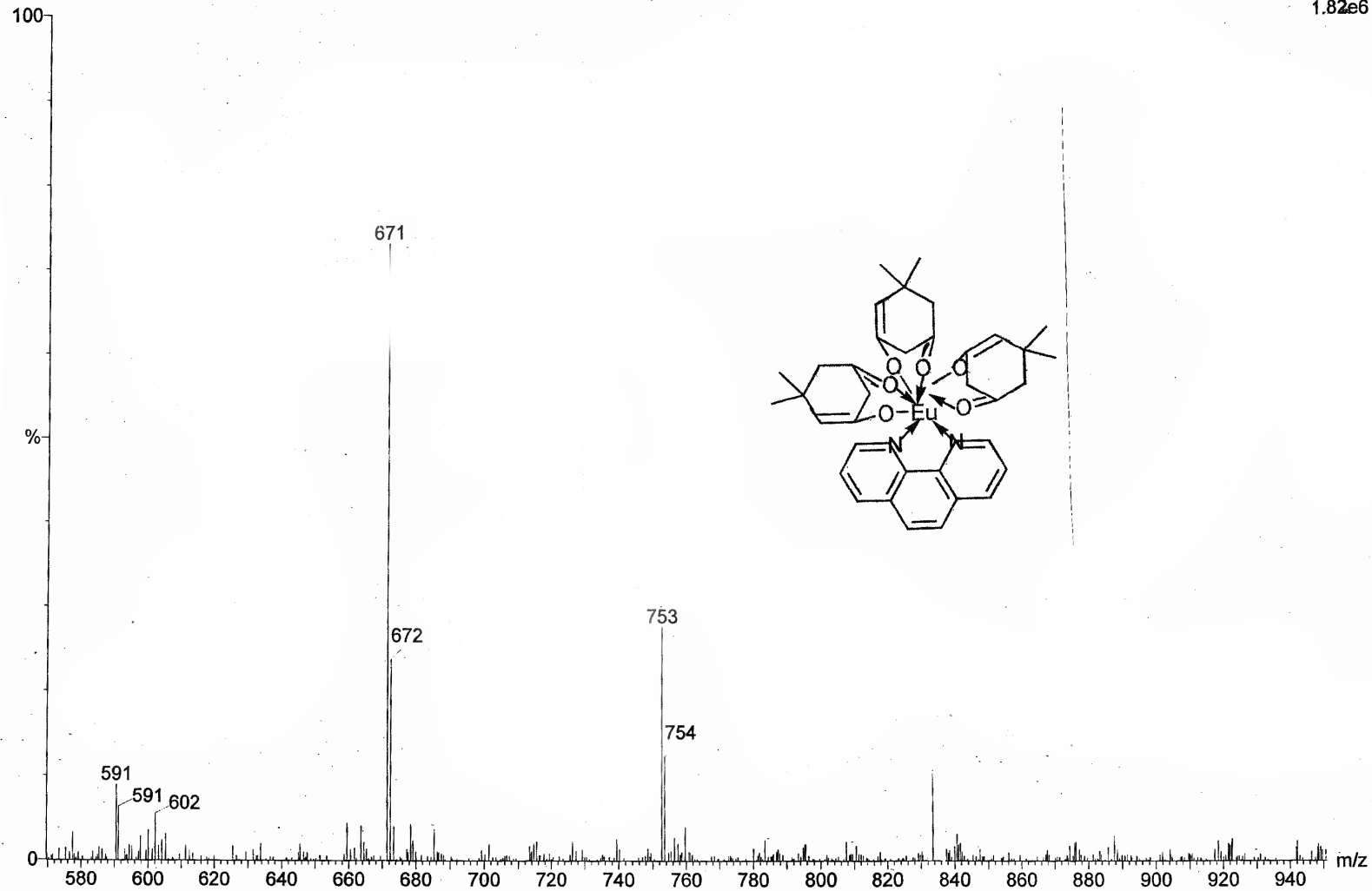Fig.7(II)   ESI mass spectrum of [Eu(AD)₃phen]

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Fig.8(II)   ESI mass spectrum of [Eu(D)₃phen]

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2. Fluorescence quantum yield studies

Fluorescence quantum yield is one of the most important optical properties of fluorescent materials. It is the essential parameter to express the fluorescent characteristics. Even though other methods like time resolved fluorometry[39] are prevalent, the time tested conventional method of comparing with a standard is found to be easier and reliable.

The standard chosen in this work was europium thenoyltrifluoro acetonate, $[Eu(TTA)_3(H_2O)_2]$ which has been synthesised solely for this purpose. The synthesis was done as per reported[40] procedure and the chelate was characterised: (mp 163°C, Eu percentage - 16.89 (found), 17.85 calc.).

The quantum yield of $[Eu(TTA)_3(H_2O)_2]$ is taken[41] as 0.19 for a $10^{-3}M$ solution in ethanol at 25°C.

The following equation was made use of for calculation of quantum yield.

$$\phi_{sample} = A_{sample} \in_{st} c_{st} \phi_{st} / A_{st} \in_{sample} c_{sample}$$

where ϕ - quantum yield

A = Area of fluorescence peak of europium complex at 613 nm.

c = concentration of the solution.

$\in$ = molar absorption coefficient

Subscript st - refers to standard.

The ϕ values for the complexes were obtained as 0.2754 and 0.2543 for [Eu(AD)$_3$phen] and [Eu(D)$_3$phen], respectively.

$$\phi Eu(AD)_3 \text{ phen} = 0.2754$$

$$\phi Eu(D)_3 \text{ phen} = 0.2543$$

This shows that both are having appreciable quantum yield with values higher than that of [Eu(TTA)$_3$(H$_2$O)$_2$]. So both chelates are suitable for optical applications in POFA/OLED.

3. Polymer films and optical studies

a) Casting

The polymers EVA, PS and PMMA were made into thin films after dissolving in CHCl$_3$, by stirring at a temperature of ~ 50°C and allowing to evaporate on shallow dishes at room temperature. The doping of the chelate was done by dissolving it in methanol and adding to a solution of the polymer in CHCl$_3$. It was then poured into shallow dishes and allowed to evaporate at room temperature. While preparing the polymer solution, stirring was carried out for 1 h to confirm homogeneity. The chelate to polymer ratio was 1:5 by weight. The films were kept in separate polythene sheets in a desiccator.

The liquid oligomer PEG-400 was used as such and doping was done by dissolving the chelate by stirring for 1 h. This oligomer was chosen taking

into account the possibility of converting it into solid matrix by sol-gel process[42]. This can be attained by mixing with silica gel and the transparent solid thus formed is found to retain all the photophysical characteristics of original liquid. However, the conversion of PEG to solid matrix was not attempted in the present work due to lack of expertise.

b) Absorption spectral analyses

The IR spectra of plain - and the doped polymers are shown in Fig. 9(II). It can be seen that the original peaks of polymers are retained in more or less the same way in the doped ones showing that the complexes are not covalently linked to the polymer chain.

The UV-visible spectra of the doped polymers showed the ∂_{max} at ~ 350 which is characteristic of europium β-diketonate complexes. The spectra are shown in Fig. 10(II).

c) Scanning Election Microscopy (SEM) of doped polymer films

SEM is mainly aimed at observing the surface morphology of materials. SEM micrographs of two doped polymer films are presented here - one with [Eu(D)$_3$phen] doped in EVA and the other with [Eu(AD)$_3$phen] doped in PS. The single films of size 1 cm x 1 cm sputtered with Au paste were used as sample and data acquired over ~ 5-10 min. Since scattering

from thin films are weak (~25% of the incident beam is scattered) all possible

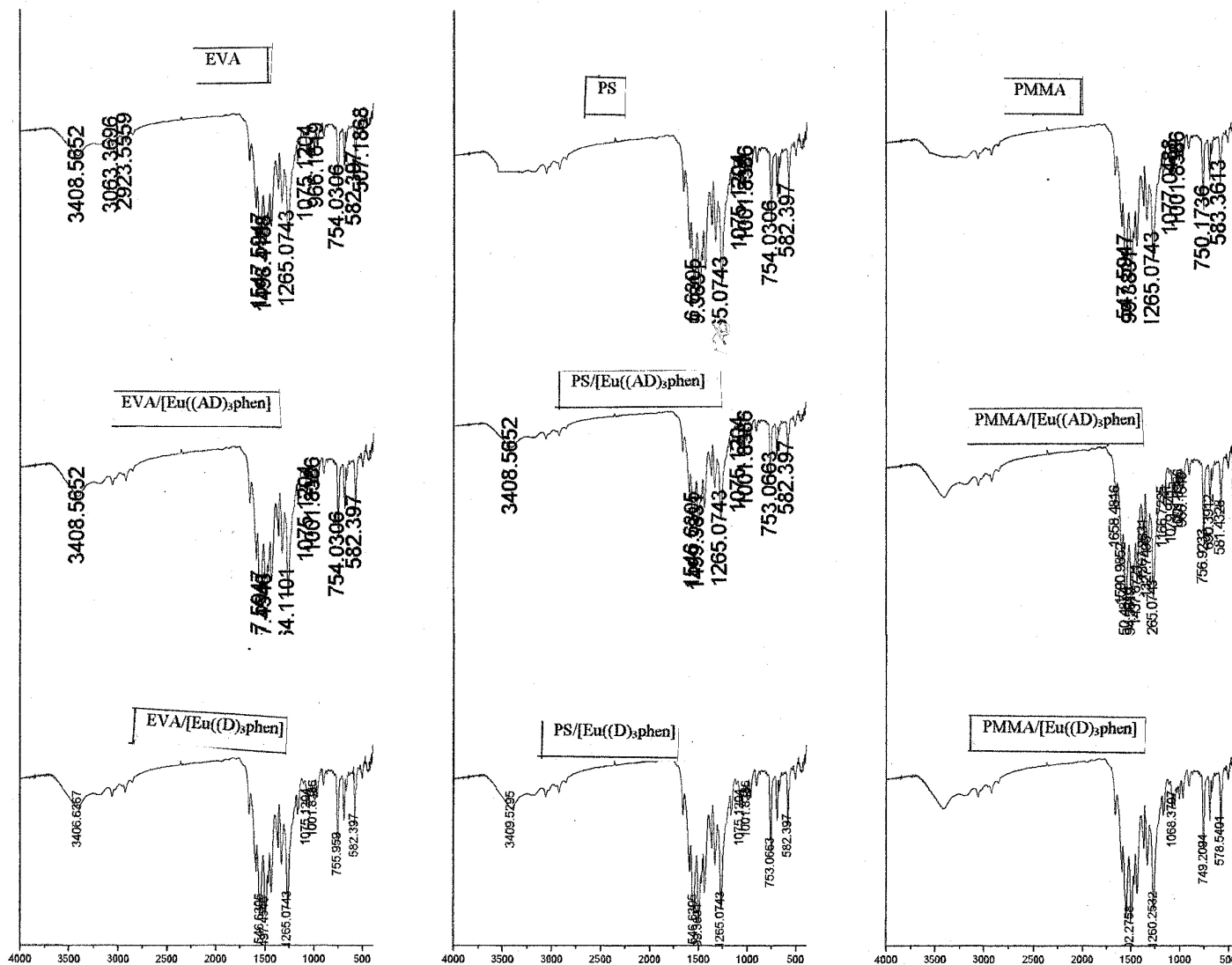care had been taken to reduce background scattering.

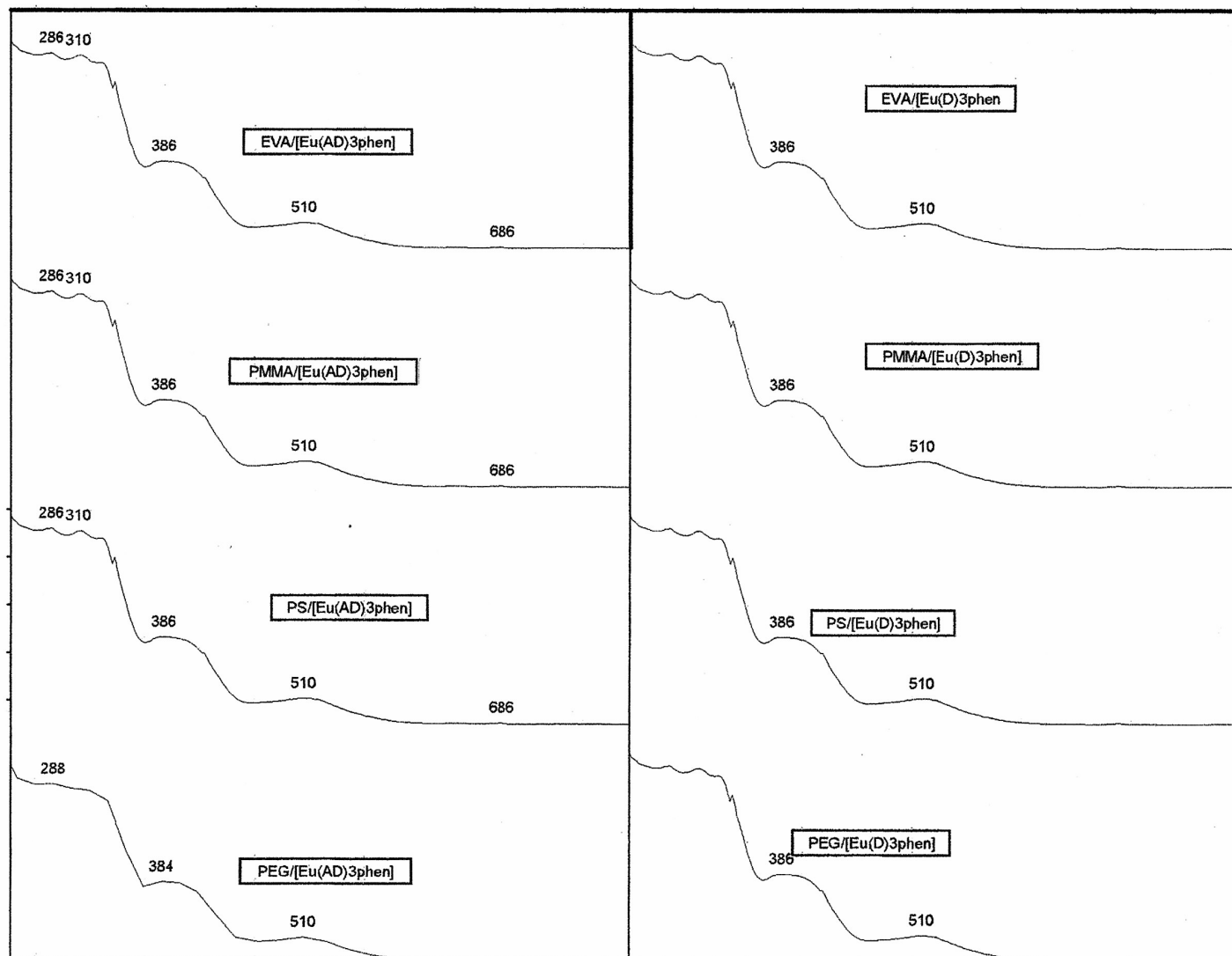**Fig.9(II)   IR spectra of plain and doped polymer films**

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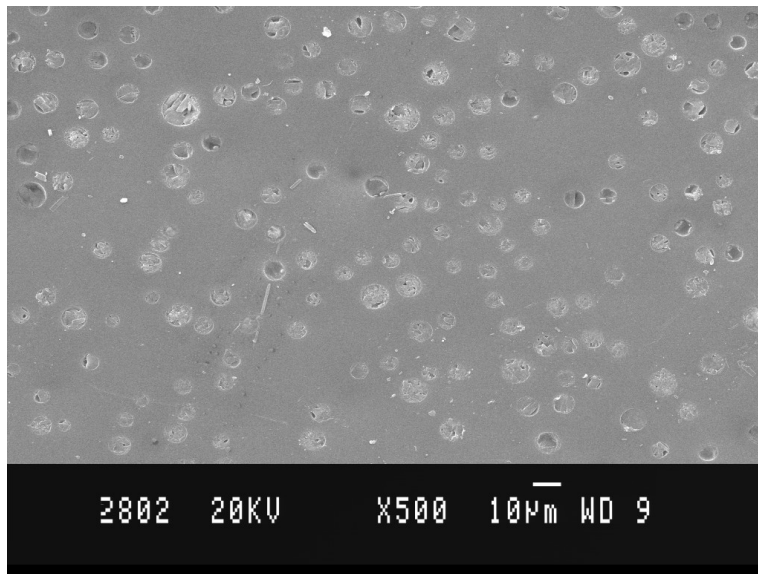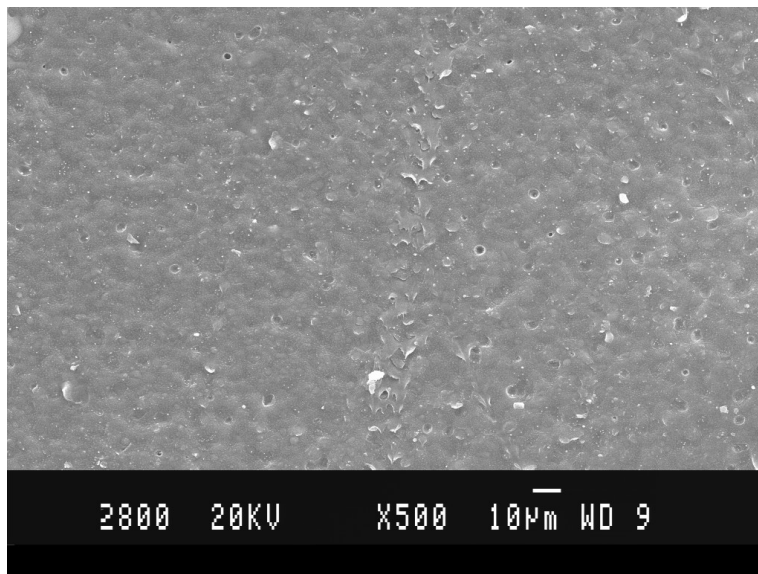**Fig.10(II) UV-visible spectra of doped polymers**

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Fig. 11(II) (a) Photograph of polymer films doped with [Eu(AD)$_3$phen] and [Eu(D)$_3$phen]

PS [Eu(AD)₃phen]

EVA/[Eu(D)₃phen]

Fig. 11(II)(b) SEM Micrographs of doped polymers

The SEM micrographs clearly indicate a flat surface. The surface roughness and film thickness were almost approximated to <10 run and ~200 nm, respectively, although accurate prediction of these values requires an AFM instrument. The pictures show a uniform distribution of the doped material which is a clear indication of how well these layers can perform if used in POFA or OLEDS which require uniform emission. The doped particle size is also very conspicuous, 6-7 μm for [Eu(AD)$_3$phen] and 4-6 μm for [Eu(D)$_3$phen]. This was assessed from the scale bar (10 μm). The SEM analyses were done after 5-6 months of storage of the films which showed the keeping qualities of the films.

d) Thermal analyses of doped polymers

The simultaneous thermogravimetric (TG/DTG) and differential thermal (DTA) analyses of the three polymer, EVA, PS and PMMA, each doped with [Eu(AD)$_3$phen] and [Eu(D)$_3$phen] were carried out.

The thermal analysis of the oligomer PEG could not be conducted as it was in the liquid form. All analyses had been done in inert atmosphere (N$_2$) as the presence of oxidants may accelerate the decomposition process.

The decomposition mechanism of the host polymers had been observed to be end chain scission (E) for PMMA and either end chain or random chain scission (E/R) for EVA and PS.

Fig.12(II) TG/DTG/DTA curves of a)EVA/[Eu(AD)₃phen] and b)EVA/[Eu(D)₃phen]

In figure a):
- 351.08 °C −0.180 mg/min
- 472.11 °C −1.390 mg/min
- a)

In figure b):
- 350.02 °C −0.203 mg/min
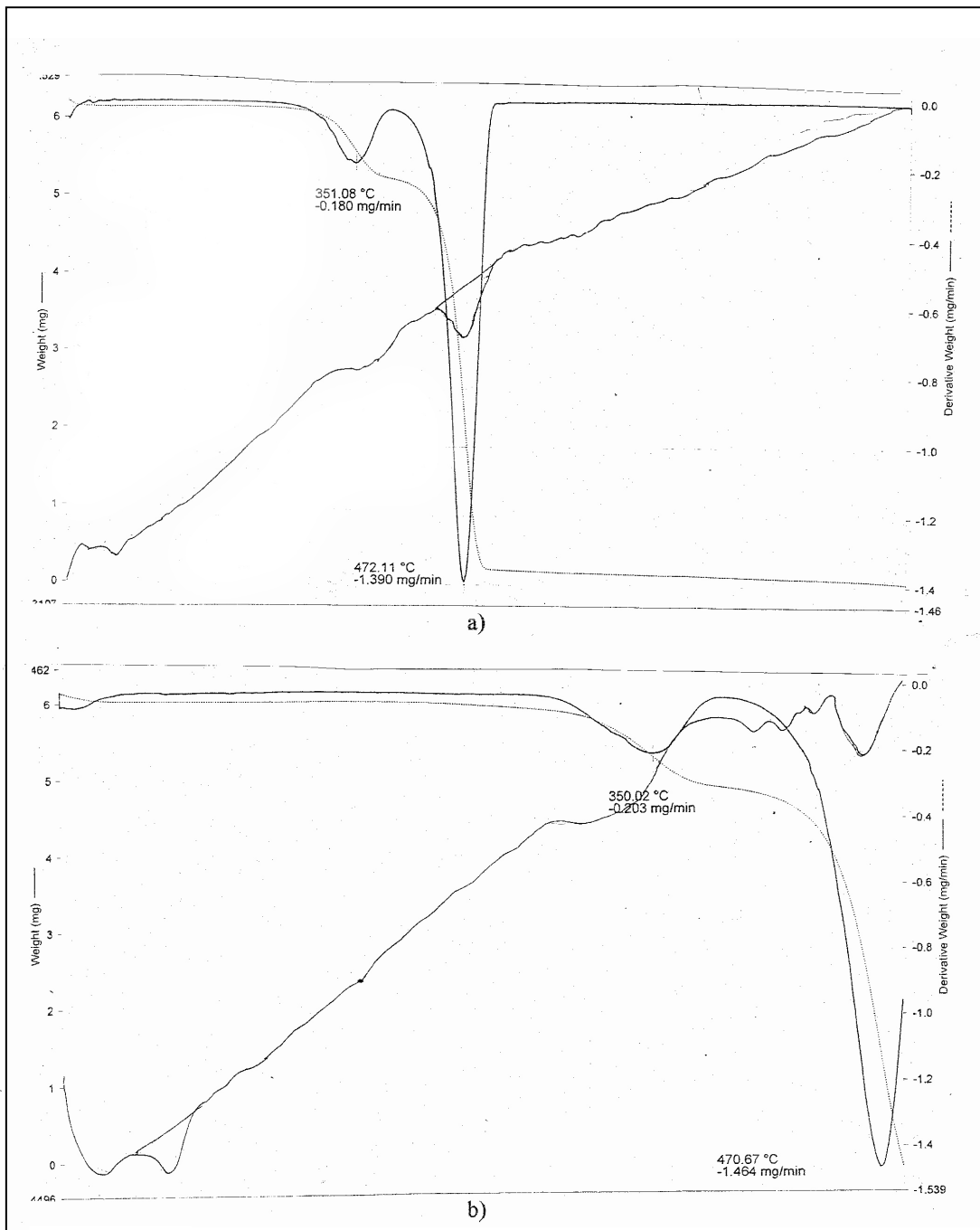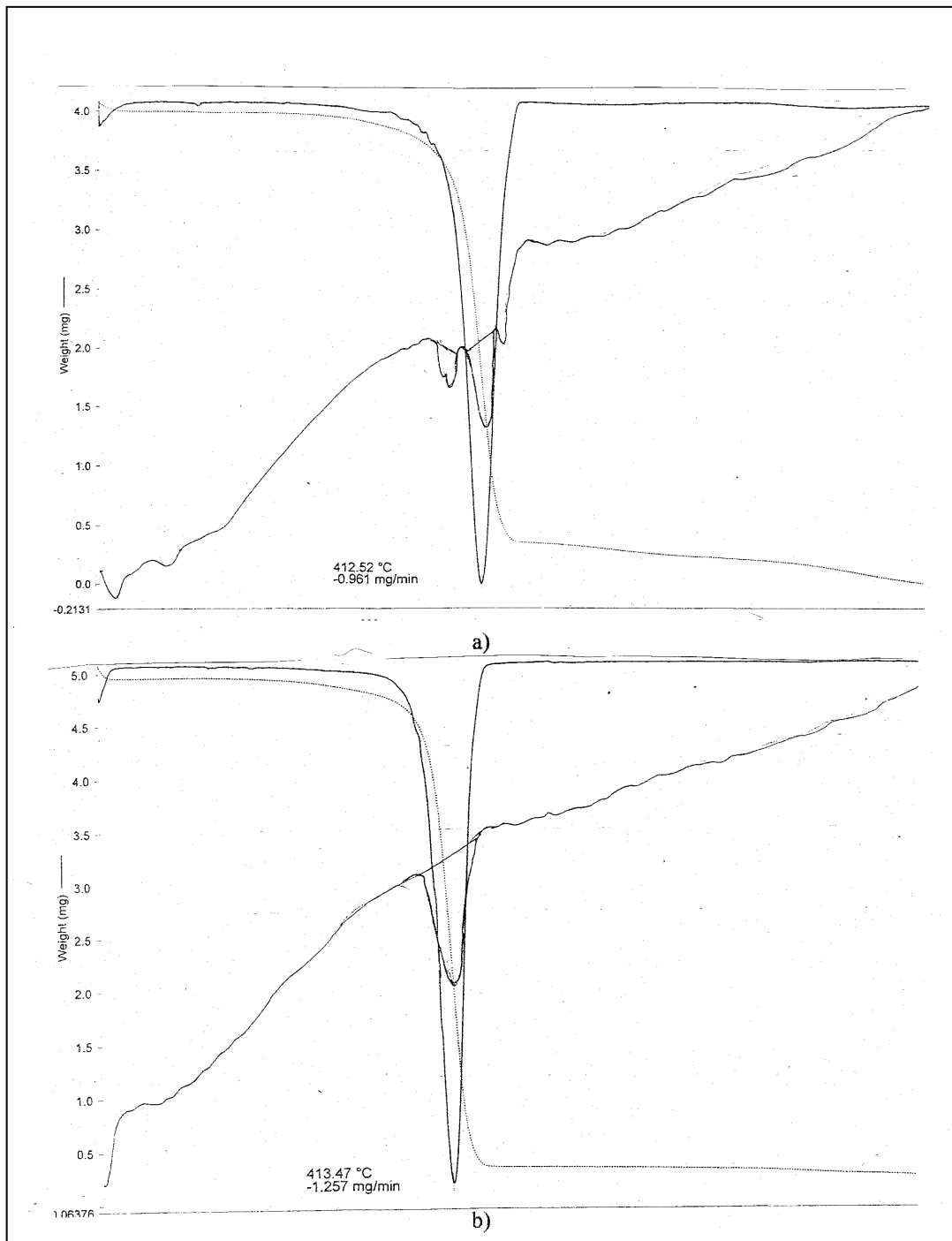- 470.67 °C −1.464 mg/min
- b)

159

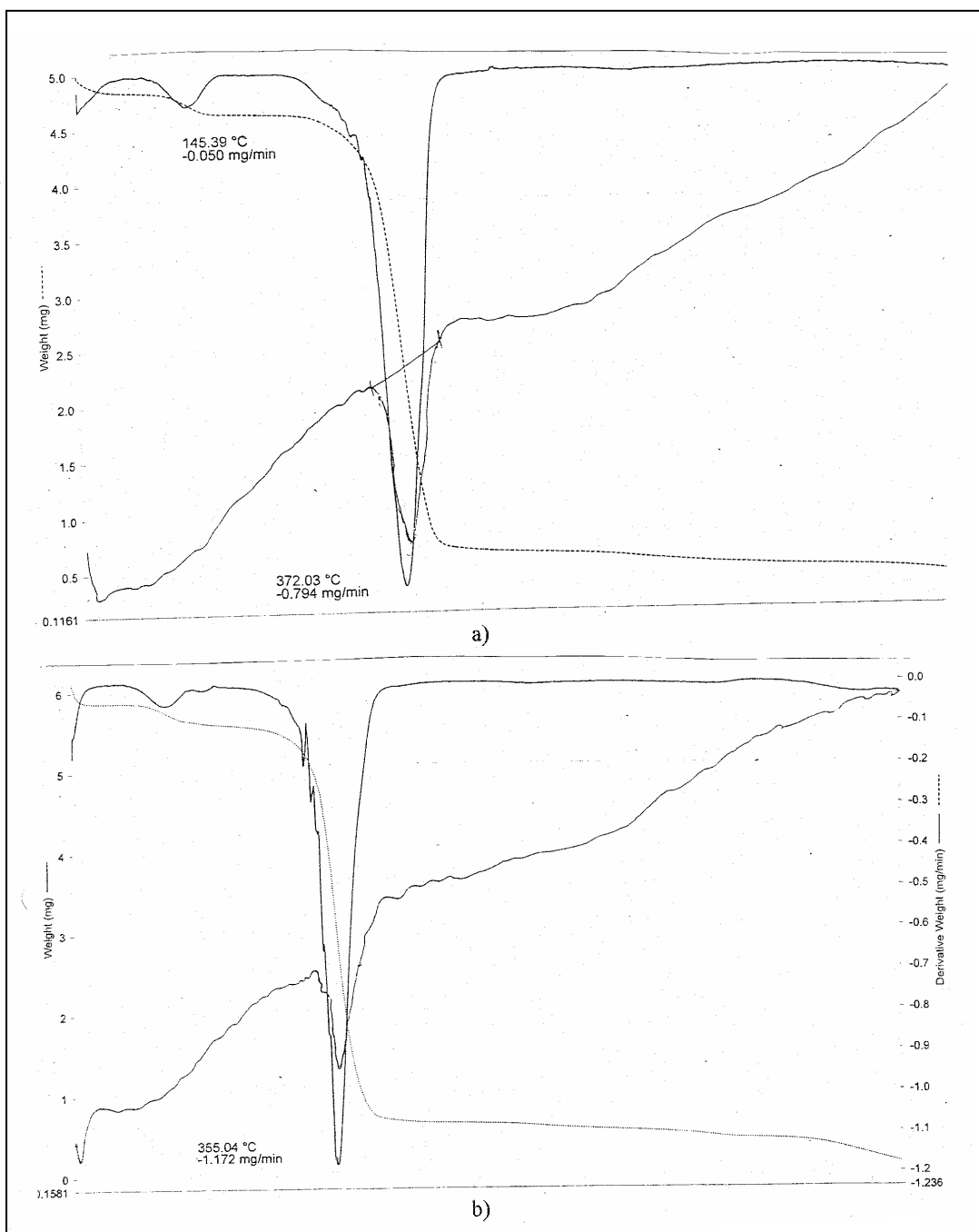**Fig.13(II) TG/DTG/DTA curves of a)PS/[Eu(AD)₃phen] and b)PS/[Eu(D)₃phen]**

Fig.14(II) TG/DTG/DTA curves of a)PMMA/[Eu(AD)₃phen] and b)PMMA/[Eu(D)₃phen]

The decomposition pattern of the undoped host and the doped polymers are discussed below. The decomposition data of undoped polymers were taken from published literature[43-45].

Table 3. Thermal stability data of EVA and doped EVA

Material	T_1 (°C)	T_{max1} (°C)	T_2 (°C) RW_2 (%)	T_{max2} (°C)	T_3 (°C), RW_3 (%)	DTA peak (°C)
EVA	290	335	405, 82	470	490, 15	
EVA/[Eu(AD)$_3$phen]	290	370	424, 81.5	469	492 2.8	472 (endo)
EVA/[Eu(D)$_3$phen]	291	363	429, 73.6	470	482, 0.2	358 (endo)

RW = Residual weights; T_1, T_2, T_3 initial degradation temperatures of the three stages; T_{max1} and T_{max2} = temperatures at which maximum weight loss occur.

The thermal stabilities of the doped polymes showed that the temperature withstanding capacities of the host polymer were retained. T_{max1}, of the doped polymers are 30-40 degrees higher than that of plain EVA. This was a clear indication of the decelaration of heating rate and hence the slow response of the doped polymers towards temperature changes.

Table 4. Thermal stability data of PS and doped PS

Material	T_1 (°C)	T_{max1} (°C)	T_2, RW_2 (°C, %)	DTA peak (°C)
PS	275	398	430, 15.0	410 (endo)
PS/[Eu(AD)$_3$phen]	310	414	432, 12.8	383 (endo), 414 (endo)
PS/[Eu(D)$_3$phen]	270	415	440, 7.9	415 (endo)

RW = Residual weight. T_1 & T_2 initial degradation temperatures of two stages. T_{max}, = temperature at which maximum weight loss occurs.

From the above table it is clear that the thermal stabilities of the doped polymers are comparable to the undoped host polymer PS. The initial degradation temperature of the polymer when doped with [Eu(AD)$_3$phen] is higher. The temperature at which maximum weight loss occurs, T_{max} is also high for the doped polymers.

Table 5. Thermal stability data of PMMA and doped PMMA

Material	T_1 (°C)	T_{max} (°C)	T_2, RW_2 (°C, %)	T_{max2} (°C)	T3, RW_3 (°C, %)	DTA peak (°C)
PMMA	250	310	320, 86.0	380	400, NIL	320 (endo) 430 (exo)
PMMA/[Eu(AD)$_3$phen]	260	314	321, 86.9	378	411, 14.6	373 (endo)
PMMA/[Eu(D)$_3$phen]	252	316	320, 84.6	360	407, 12.1	359 (endo)

RW = Residual weight; T_1, T_2, T_3 initial degradation temperatures of three stages; T_{max} Temperature at which maximum weight loss occurs.

The above data clearly indicate that the thermal stability of the undoped polymer PMMA is retained in the doped ones. The initial degradation temperatures of PMMA/[Eu(AD)$_3$phen] are higher than the host polymer.

The thermal studies were conducted in order to have an idea of the applicability of the doped polymers in optical devices. It has been found that the polymers, despite hosting a hygroscopic complex show good thermal stability and do not absorb moisture even when kept air exposed.

e) Optical studies

The photoluminescence spectra of plain polymers are shown in Fig. 15(II). The absorption maxima of the complexes doped in polymers and the peaks are compared in Table 6.

Table 6.   Comparison of PL peak of plain polymers with absorption peaks of doped polymers

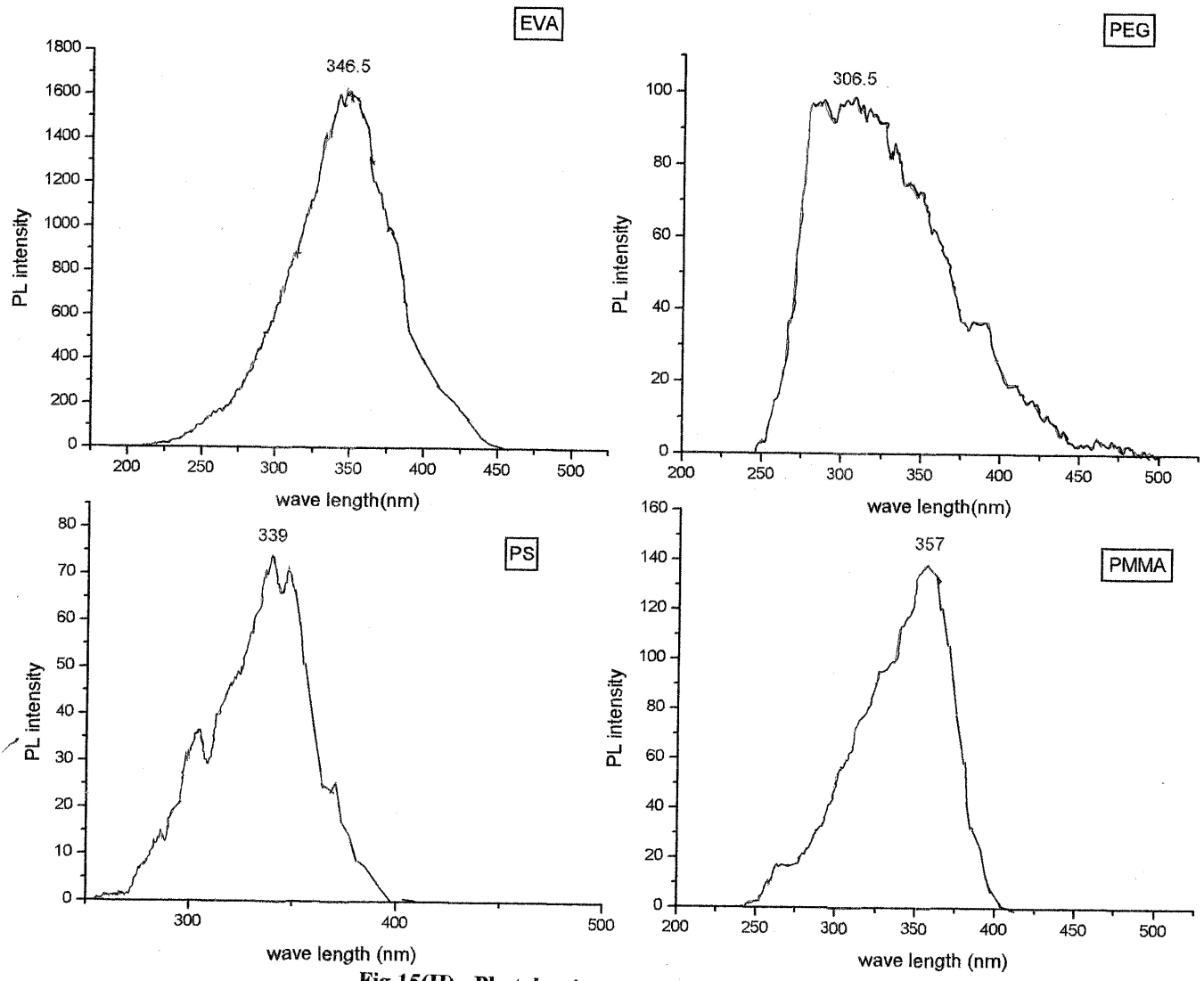| Polymer	PL peak (nm)	Absorption max (nm) with embedded chelate	
		[Eu(AD)$_3$phen]	[Eu(D)$_3$phen]
EVA	346.5	386	386
PS	339	386	386
PMMA	357	386	386
PEG	306.5	384	386

Fig.15(II) Photoluminescence spectra of plain polymers
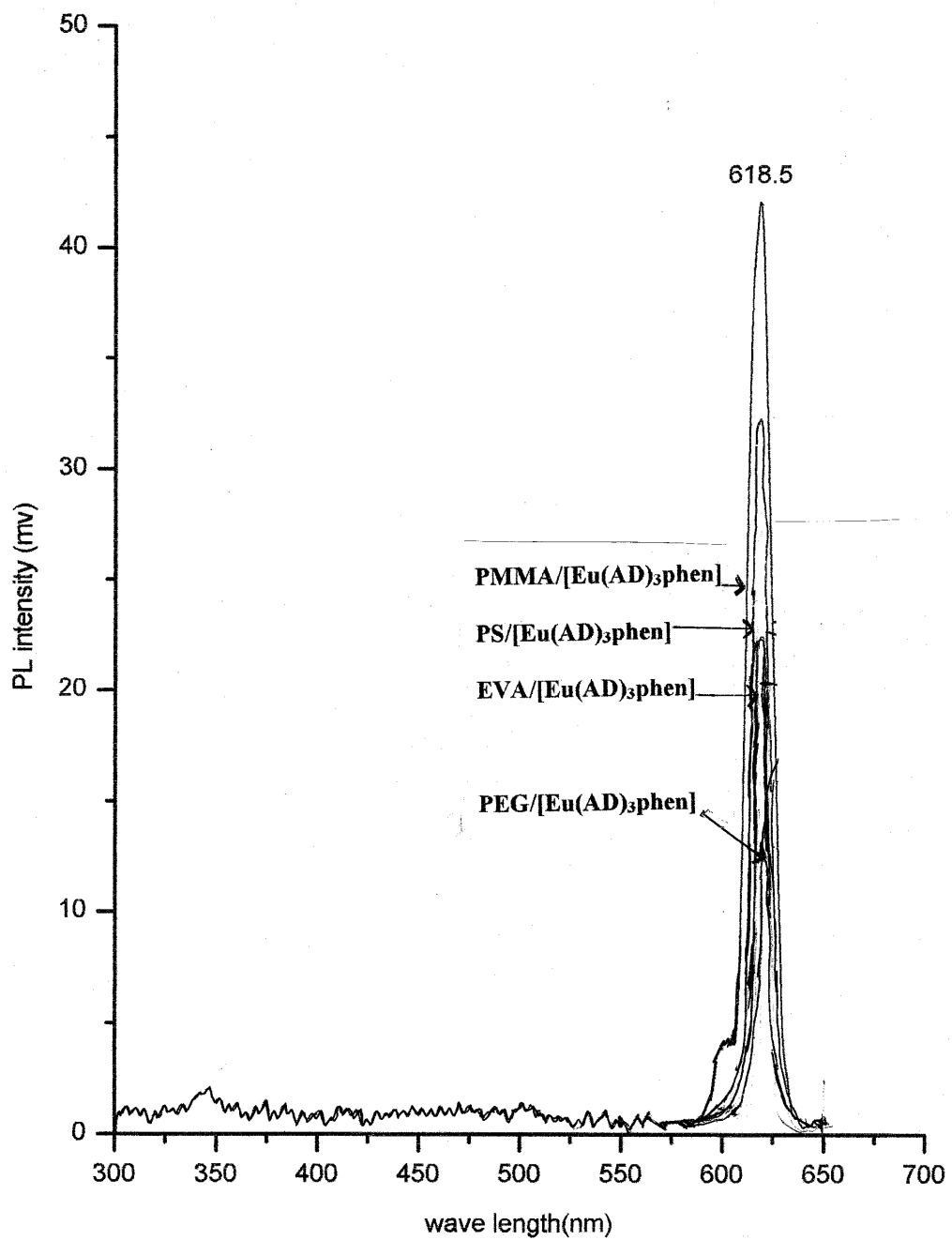
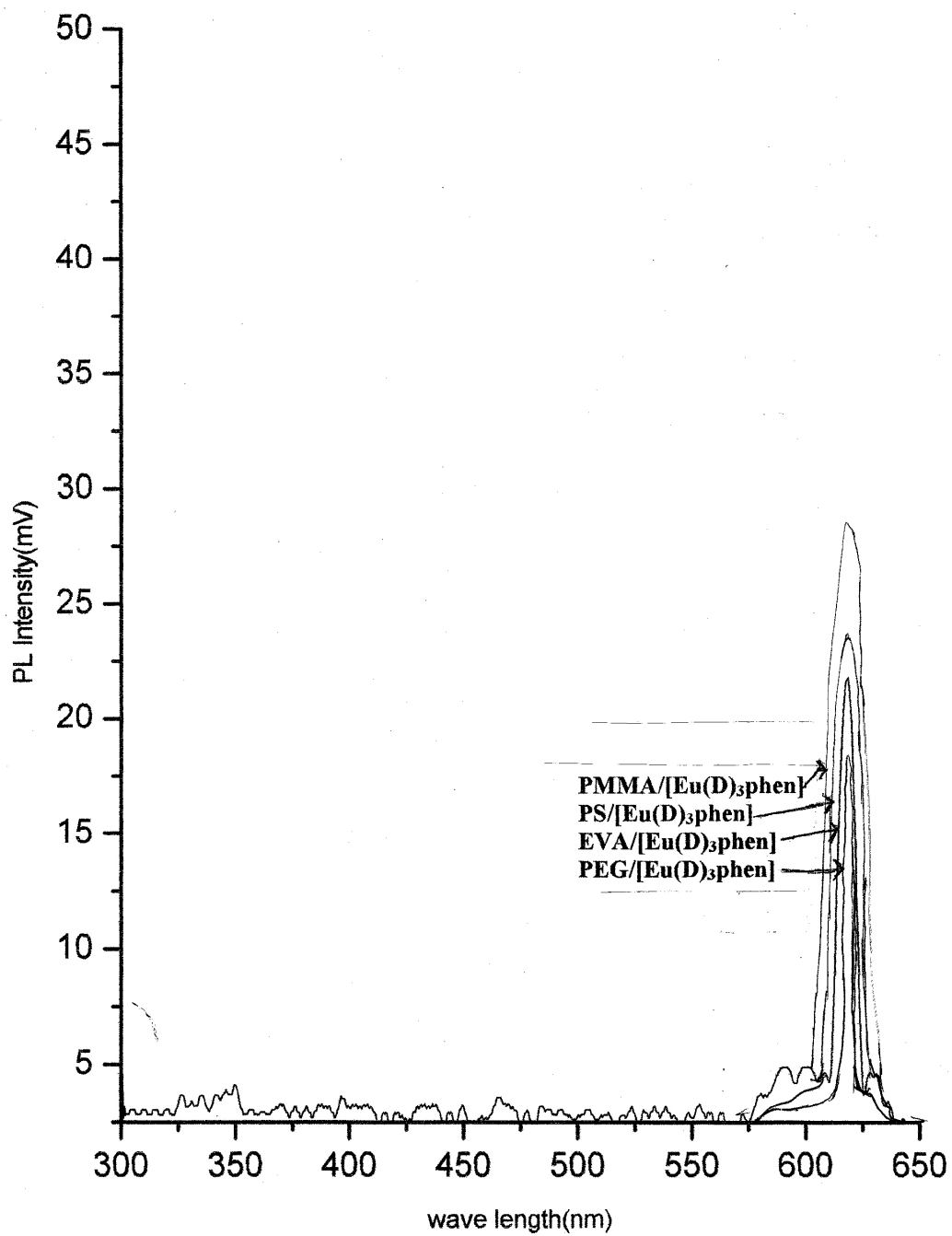Fig.16(II) Photoluminescence spectra of polymers doped with [Eu(AD)₃phen]

Fig.17(II) Photoluminescence spectra of polymers doped with [Eu(D)₃phen]

The proximity and overlap of the absorption peaks of the complexes doped in different polymers and the PL peak of plain polymers is a clear indication of how these doped polymers may work well with POFA or OLEDS.

Of the four polymers chosen, PMMA gave the best result with the PL peak showing more proximity to absorption peaks which were constant at 386 nm.

The PL peaks of the doped polymers are shown in Fig. 16(II) and Fig. 17(II).

All show the peak at ~ 618 nm which is characteristic of europium irrespective of the matrix into which it is incorporated. Here also the polymer PMMA is found to be the best host allowing a high intensity fluorescence emission where as in others there is a considerable amount of intensity decrease. The complex [Eu(AD)$_3$phen] shows more intensity than [Eu(D)$_3$phen] which may be due to the presence of azogroup in the former.

C. Conclusion

The present work though done with the basic minimum amenities in this laboratory shows the possibility of using rare earth chelates doped as such into polymer host for applications like POFA /OLEDS. The use of EVA for this purpose has not been reported earlier. This polymer is very cheap though it may not perform as good as the modern perfluorinated or deuterated

polymers which are very costly. The multibillion dollar business involved in OLEDS and POFA require more customised polymers[46] which are synthesised specially for the purpose. Still, our attempt is aimed at finding an application to the ligands synthesised in the present work using easily available polymers.

D. Scope

This method can be extended to other azo betadiketones or other rare earths and the applicability can be checked by fabricating POFA, wave guides or OLEDS. The place of OLEDS is now slowly being replaced by phosphor dots which are better emitters. Still the unique emission characteristics of rare earth chelates will make them dominate the field of photophysics in the years to come.

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