ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

SYNTHESIS AND STRUCTURAL STUDIES ON POLYNUCLEAR METAL COMPLEXES DERIVED FROM A NEW MULTIDENTATE LIGAND

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By

Mulugeta Ghiday

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DEDICATION

This piece of work is dedicated to my family, my friends and to my well-wishers.

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ABSTRACT

This study presents the synthesis and characterization of a new multidentate ligand H_6-DHADB and its metal complexes. The ligand, H_6-DHADB is a hydrated Schiff base product formed by the condensation of 2, 4- Dihydroxy-5-acetyl acetophenone (H_2-DAA) and 1,3- diamino propane in 3:2 mole ratio. It possesses four independent chelating sites (OO, ONNO, ONNO, OO) separated by bulky phenyl groups. The metal complexes of H_6-DHADB with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been synthesized from methanolic media at pH ~8. They have been characterized on the basis of elemental analysis, thermal, conductance, IR and electronic spectral studies. The studies have shown that all the metal complexes are non-electrolytes with metal to ligand ratios in 3:1, 2:1 and 2:1 in Co(II), Ni(II) and Cu(II) complexes respectively and 4:1, 2:1, 1:1 in Zn(II), Cd(II) and Hg(II) complexes respectively. Based on IR spectral data, a variety of donor properties of the ligand has been proposed. ONNO, ONNO and OO chelation with cobalt(II); OO and OO chelation with nickel(II); ONNO and ONNO chelation with copper(II); OO, ONNO and OO chelation with zinc (II) and OO chelation with Cd(II) and Hg(II) have been suggested.

Based on electronic spectral data cobalt(II) complex exhibited octahedral, copper(II) complex shows square planar structure and nickel(II), zinc(II), cadmuim(II) and mercury(II) complexes attain tetrahedral geometries.

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ABBREVIATIONS

H_6 - DHADB	1,3- Di- [N-γ-N' (2", 4"- hydroxy-5"-acetyl acetophenimino propyl] acetaldimino-4,6-dihdroxy benzene
M	Molar
mmole	Millimole
IR	Infra-red
Uv	UltraViolet
Vis	Visible
M.p	Melting point
Decomp.	Decomposition point
cm	Centimeter
DMF	Dimethyl formamide
DMG	Dimethyl glyoxime
EDTA	Ethylene diamine tetraacetic acid
CT	Charge Transfer
Λ_M	Molar conductance
S	Siemens
MLCT	Metal to ligand charge transfer
nm	Nanometer
pm	Picometer
C.N.	Coordination number
WL	Wave length

CHAPTER - 1

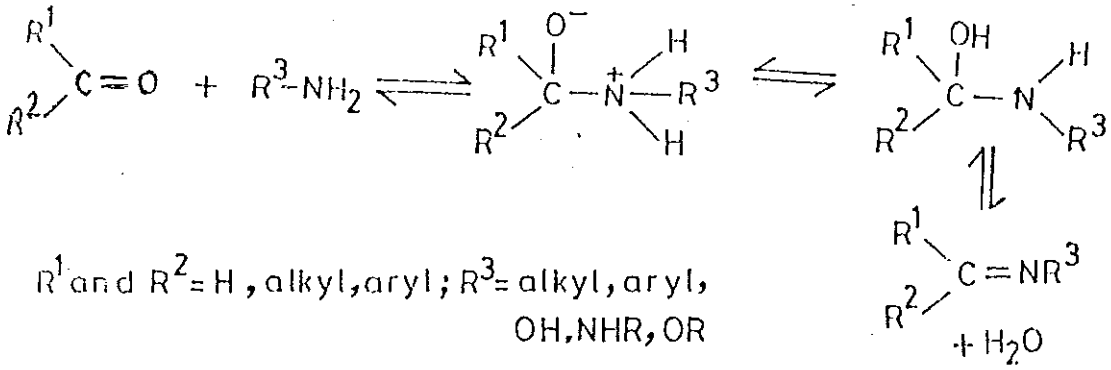
INTRODUCTION

Metal complexes of Schiff's bases have contributed significantly towards the understanding of coordination chemistry [1]. Multimetallic species occupy an important position in modern inorganic chemistry. Metal complexes of Schiff's bases have varied geometries and magnetic properties with valuable applications in several disciplines of science and technology [2-4].

In the area of bio-inorganic chemistry, interest on Schiff's base metal complexes has been very keen due to the role such complexes play in providing synthetic models for the in metalloproteins and enzymes [5]. A wide variety of ligands may be obtained via the schiff's base condensation reactions which vary in denticity, flexibility, nature of donor atoms and in electronic properties. Analytical application of schiff's bases as colorimetric reagents and metal ion indicators in complexometric titrations were reported. Their metal complexes were investigated for fungicidal and bactericidal activities [6-8].

A large number of multidentate ligands have been synthesized and investigated for metal binding characterstics. Several such ligands possessing azomethine(C=N) grouping are widely reviewed by many workers [9-11]. These are usually formed by the condensation of a primary amine with an active carbonyl compound. Schiff's bases which are effective as coordinating ligands have functional groups like -OH, $-NH_2$, -SH, etc sufficiently close to the site of condensation so as to form five or six membered chelate rings on reaction with metal ions. Condensation reactions between dicarbonyls and primary diamines have played an important role in the development of synthetic multidentate ligands [12,13].

Because of the great synthetic flexibility of Schiff's base formation, many ligands of varied structural types can be and have been synthesized and their ligational properties have been extensively studied [14-21]. The proposed mechanism for the formation of azomethine group is given below. It is reversible, progressing through a carbinol amine intermidiate and requires the removal of water.



R^1 and R^2 = H, alkyl, aryl; R^3 = alkyl, aryl, OH, NHR, OR

Literature survey on multidentate ligands having oxygen, nitrogen donor systems reveals, extensive investigation on a number of 'ONN' and 'ONO' donor sequences which have resulted in the formation of multinuclear metal chelates. These metal chelates have been significantly understood with various types of oxygen bridging like phenoxide oxygen bridging, alkoxide oxygen bridging exhibiting characterstic spectral and magnetic properties. The metal complexes of tridentate ligands containing phenoxide or alkoxide centers are mostly dimeric or polymeric in the solid state [22-24]. However, some monomeric complexes like bis-(N-β-dimethyl amino ethyl saliciladiaminato)- copper(II) with a five coordinated [25] geometry are also characterized.

Tetradentate Schiff's bases with 'NNOO' donor set have been widely studied [26]. These diverse ligands usually contain both N and O donor atoms although purely N as well as N, S donors exist [27]. Multidentate ligands having oxygen, nitrogen donor centers reveal an

extensive invetigation in which the formation of polynuclear metal chelates was reported [28]. Several macrocyclic ligands producing homo-di, hetro-di and polynuclear complexes have been documented in literature [29].

The project aims at the preparation and characterization of polynuclear metal complexes derived from a new multidentate ligand. A class of ligands with more than one independent chelating sequence substituted on a single phenyl function can bind two or more metal ions simultaneuosly and form multinuclear complexes. These ligands can be classified into symmetric or unsymmetric systems. They can be bidentates, tridentates or tetradentates. 1,2, 4, 5-tetrasubstituted benzene is a suitable system to initiate this type of investigation. 2,4-dihydroxy-5-acetylacetophenone is one such example,which has been investigated for the formation of metal complexes [13]. Based on analytical, spectral and magnetic studies, it was concluded that this ligand behaves as bis- bidentate, `OO,OO' donor resulting in the formation of polynuclear metal complexes.

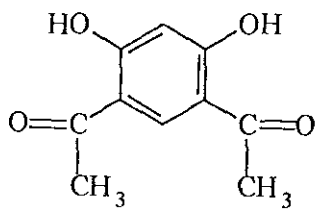


Fig.-1 H_2- DAA

While H_2-DAA is a dibasic bis- bidenate 'OO', 'OO'donor, its dioxime and dihydrazone have been observed to be dibasic bis- bidentate 'ON', 'ON' donors. H_2-DAA can be transformed into

potential multidentate systems by condensation with primary diamines. Di- and poly-amine like ethylene diamine, propylene diamine, diethylene triamine, triethylene tetramine etc are likely to undergo facile condensation with H_2-DAA, to form azomethine derivatives which can acts as chelating ligands towards transition metal ions. Depending on the reaction condition, free ligand may be isolated as monomeric or polymeric product. Synthesis of transition metal complexes having unusual coordination geometries, subnormal magnetic susceptibilities and interesting spectral, thermal and catalytic properties may be accomplished.

SECTION A

LITERATURE SURVEY

A wide variety of multidentate ligands may be obtained via the Schiff's base condensation reaction and metal complexes of these multidentate ligands have been synthesized and investigated. The methods of synthesis are widely reviewed by many workers.

Pfeiffer and Tsumaki, synthesized some important multidentate ligands derived from salicyaldehyde which are shown in the anionic / deprotonated forms in Fig.-2. A wide diversity of coordination geometries and magnetic behaviour has been exhibited [30].

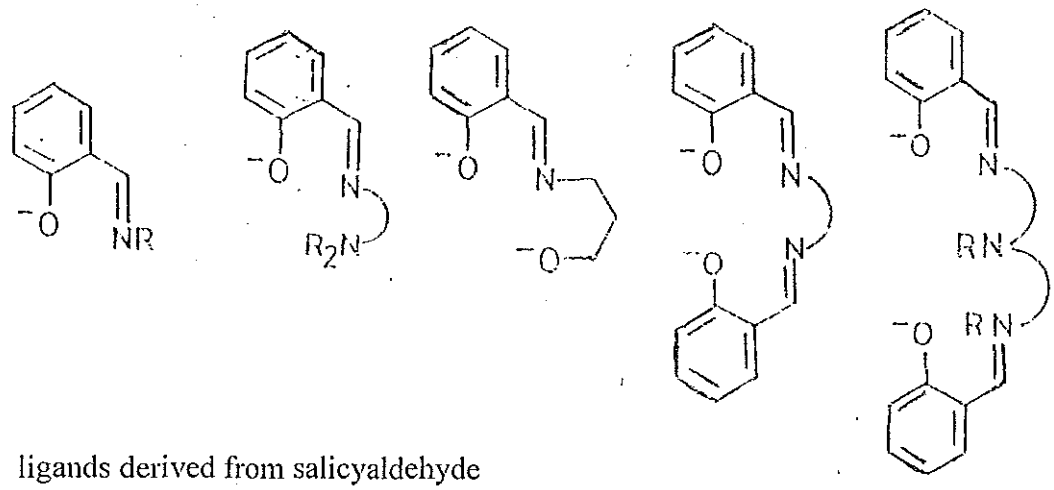
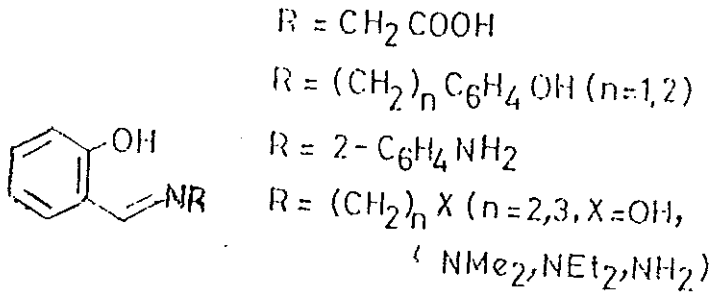


Fig.-2 ligands derived from salicyaldehyde

From the literature survey it is evident that metal complexes of potentially tridentate ligands containing phenoxide or alkoxide [31] centers are mostly dimeric or polymeric in the solid state [48]. Multimetallic species occupy an important position in modern inorganic chemistry. They are ubiquitous in nature as active sites in a variety of metalloenzymes and are playing a significant and expanding role in industry and chemical analysis.



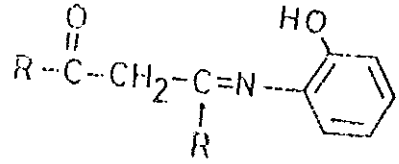


Fig.-3 (a) (b)

Many tridentate Schiff bases have been utilized as anionic ligands having 'NNO' and 'NOO' donor sets [33-36]. Some of them are shown in Fig.-3 (a & b). The ligands derived from substituted acetophenone with three or more metal binding substituents are of great synthetic interest as they can produce polynuclear complexes. Metal complexes of Schiff's bases have varied geometries and magnetic properties. A Schiff's base derived from 2, 4-dihydroxy-5-acetophenone and ethanolamine with 'ONO' donor sequence is reported [37]. Its complexes have binuclear and polynuclear structures. In case of Cu(II) complex the ligand acts as monobasic tridentate with alcoholic oxygen coordinating without deprotonation, where as in Ni(II), Co(II) and Fe(III) complexes it acts as dibasic tridentate. Cu(II) and Fe(III) complexes are suggested to have polynuclear and binuclear structures respectively, with oxygen bridges in an octahedral geometry. Co(II) and Ni(II) have been assigned the trigonal bipyramidal and tetrahedral geometries. Cu(II) and Fe(III) complexes have low magnetic moments as compared to spin only values, due to antiferromagnetic interaction in the solid state.

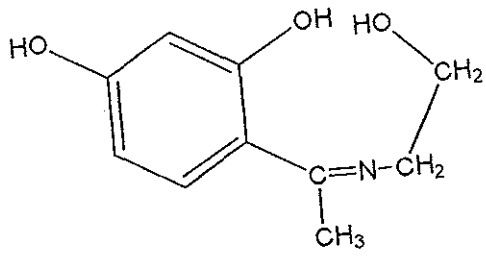


Fig.-4 Ligand derived from 2,4-dihydroxy-5-acetophenone and ethanolamine

A new ligand and its metal complexes with 'ONN' or 'ONO' donor sequence is reported by Rao *et al.* [38]. The ligand N-Salicylidine anthranilamide (H_2-SAA) is of considerable interest owing to amide imino tautomerism. H_2-SAA enolizes to give a dibasic 'ONO'donor set in the divalent metal complexes. It binds to the trivalent metal ion in a non-enolized form using a monobasic 'ONN' donor set. Co(II) is oxidized to Co(III) during complexation. Octahedral geometries are proposed for Cr(III), Mn(II), Fe(III) and Co(III) complexes, while square planar geometries are suggested for the Ni(II) and Cu(II) complexes. Phenoxide bridging in Cr(III), Fe(III) complexes, enoxide bridging in Ni(II) and Cu(II) complexes is proposed. Iron(III) (d^5), cobalt(III) (d^6) and nickel(II) (d^8) complexes are diamagnetic. The nickel(II) complex in square planar stereochemistry and cobalt(III) in low spin octahedral geometry are expected to be diamagnetic. Iron(III) in low spin octahedral configuration (t_{2g}^5) is likely to have a magnetic moment equivalent to one unpaired electron. Each iron(III) ion can undergo spin pairing and thus the complex becomes diamagnetic. The Cu(II) complex, in spite of dinuclear structure exhibits no spin- spin interactions at room temperature, while the Cr(III) complexes, which is also dinuclear structure, exhibits a subnormal magnetic moment. Based on magnetic data metal-metal interactions are inferred only in the iron(III) and chromium(III) species but not in the Cu(II) complexes. One more tridentate dibasic ligand (DHAGLY) derived from dehydroacetic acid and glycine has been prepared and its complexes with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) have been characterized and reported by Rao *et al.* [39]. All the complexes possess octahedral stereochemistry.

Tetradentate Schiff's bases with 'NNOO' donor set have been widely studied. The condensation of two moles salicylaldehyde with one mole of ethylene diamine or of their substituted analogs gives tetradentate Schiff's bases like SALEN [40] as shown in Fig.-5.

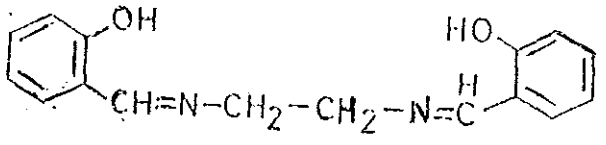
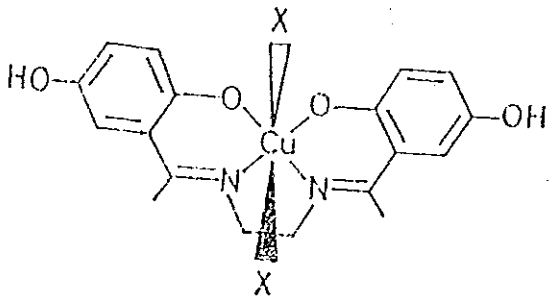


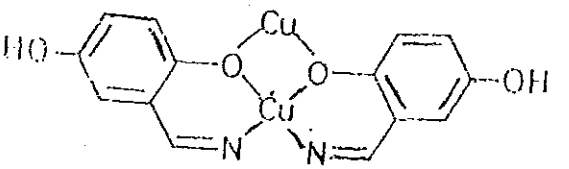
Fig.-5 SALEN

Physiologically active quadridentate Schiff's base derived from dehydroacetic acid (3-acetyl-6-methyl-2H-Pyran-2,4 (3H) dion) and ethylene diamine is (DHAEN) synthesized and its metal complexes were characterized by N.R. Rao *et al.* [41]. The Schiff's base DHAEN and its metal chelates were screened in vitro for their fungicidal activity by adapting agar plate technique against Rhizoctonia Solani and Sarocladium Oryzae, the causative organism or sheeth blight and sheeth rot in rice plants. The study showed that metallation has markedly enhanced the activity. The order of fungal growth inhibition in metal complexes is observed as follows Cu >Ni >Zn>Mn>Co.

Monomeric and dimeric copper(II) complexes of a redox active quadridentate Schiff's base ligand bis-(2,5-dihydroxy acetophenone) ethylenediamine is reported by Yudhvir S.Sharma, H.N. Pandey and Pavan Mathur [42]. The spectral data suggest a distorted tetragonal geometry for Cu(II) ions in the complexes shown in Fig.-6 (a & b).



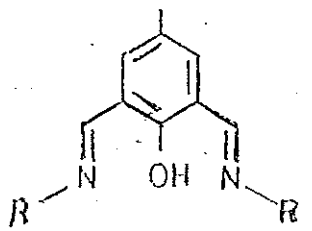
(a)Monomeric Cu(II) complex with bis-(2,5-dihydroxy acetophenone) ethylenediamine



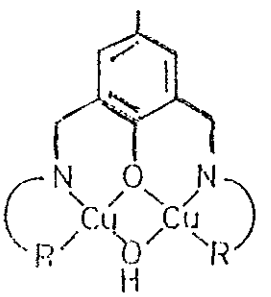
(b) Dimeric Cu(II) complex

Fig.-6 (a &b)

The potentially pentadentate Schiff's base of the type shown in Fig.-7 (a), acts as bis tridentate ligand with respect to a single metal center giving dinuclear Cu(II) complexes as shown Fig.-7(b) [43].



(a) Pentadentate schiff base



(b) Bis- tridentate dinuclear Copper(II) complex

Fig.-7 (a&b)

A hexadentate ligand. the dianion of Schiff's base derived from salicyaldehyde and triethylene tetramine is shown Fig.-8 (a). In a variety of metal complexes, it is forming a distorted octahedral arrangment around the metal ion [44,46].

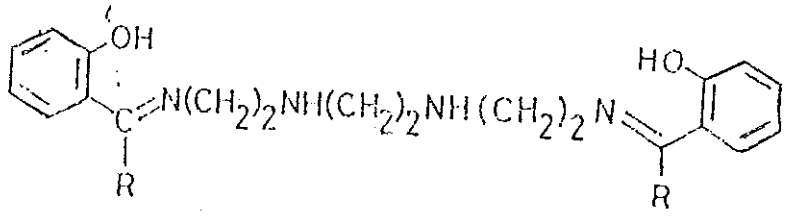


Fig.-8 (a) Hexadentate ligand

Two oxygen atoms occupy the cis position while four nitrogen atoms (two cis amine and two trans imine) complete the coordination sphere. However, it has been shown that the ligand with R=ph gives dinuclear Cu(II) complexes. Each copper(II) ion is bonded to two cis nitrogens and one phenolic oxygen, the fourth coordination site of square planar geometry is provided by an acetate ion [44]. Substitution of the central ethylene diamine bridge with piperazine ring (Fig.-8b) is reported to have imposed steric constrains on the ligand in such away that it gives dinuclear complexes, as shown by the x-ray structure of the di-μ-methoxy dichloro-1,4-peprazine bis (N-ethylene Salicyaldiminato) di iron (III) [45,46]. The predetermined structure of the free Schiff's base in comparison with that in complex shows that conformation of peperazine changes from 'chair' in the free ligand to 'boat' in the complexes.

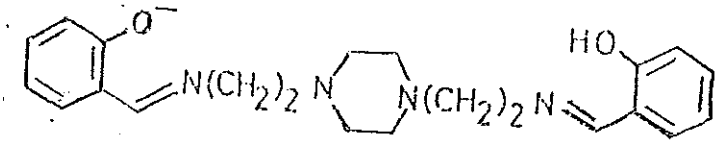


Fig.-8 (b) Piperazine bridged hexadentate ligand

Reaction of bis-N-[2-(1-aziridinyl ethyl salicyladiminato)- Nickel(II)] with KBr yields Ni (SALEN) [47]. During the reaction, an intermediate has been isolated which appeared to be an octahedral nickel (II) complex containing the hexadentate Schiff's base anion shown in Fig.-8(c). In this complex, the nitrogen atoms are mutually trans, the aziridine nitrogen is trans to the ether oxygen, while the phenolic oxygen and the secondary amine nitrogen are trans to each other.

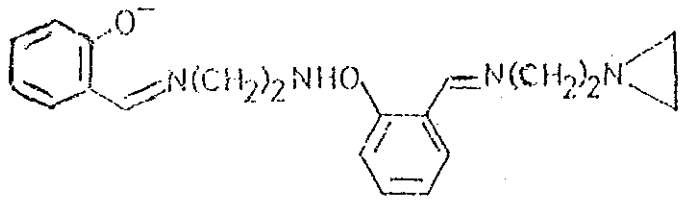
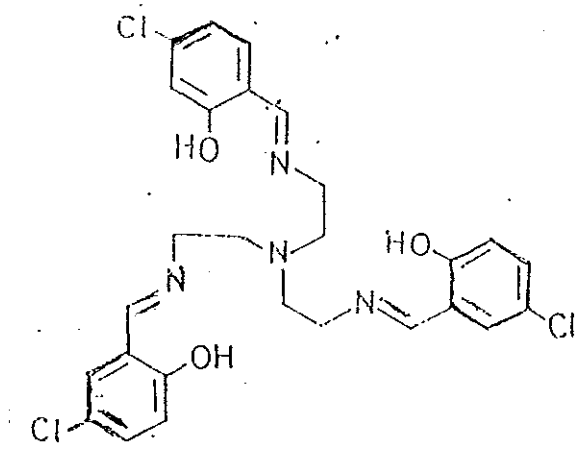
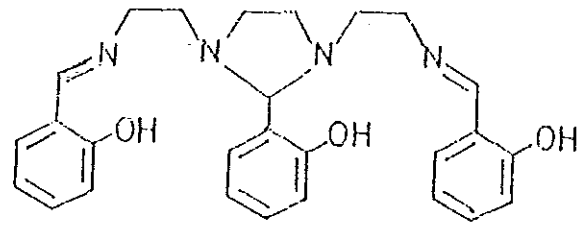


Fig.-8 (c) Hexadentate Schiff's base anion

The potentially heptadentate Schiff's base obtained from tri-(2-amino ethyl) amine and three moles of salicyaldehyde (Fig.-9a) reacts with trivalent metal ions to form neutral 1:1 compounds and in so doing acts as a hexadentate ligand. Heptadentate ligands easily form dinuclear complexes. This is the case with trisalicylidene triethylene tetramine (Fig.-9b) which gives methoxo [48a] and hydroxo [48b] bridged dinuclear Fe (III) complexes.



(a) Heptadentate Schiff's base



(b) trisalicylidene triethylene tetraamine

Fig.-9 (a &b)

Some ligands derived from salicyaldehye and diamine were known to form polymeric complexes with various metal ions. These complexes were reported to be useful as chromatographic supports and absorbents [49]. 5-5'- methylene bis (3-bromo salicyaldehyde) and hexane-1,6- diamine on condensation are reported to form polymeric schiff's base containing 'ONNO' donor sequences. The thermal stabilities of some transition metal complexes with this ligand have been reported [50]. Structurally similar polymeric complexes 'ONNO' donor were reported by Woehrle *et al.* [51]. This polymeric cobalt(II) chelate (as shown in Fig.-10) is found to be an active hetrogeneous catalyst for the valence isomerization of quadricyclane to norbornadiene.

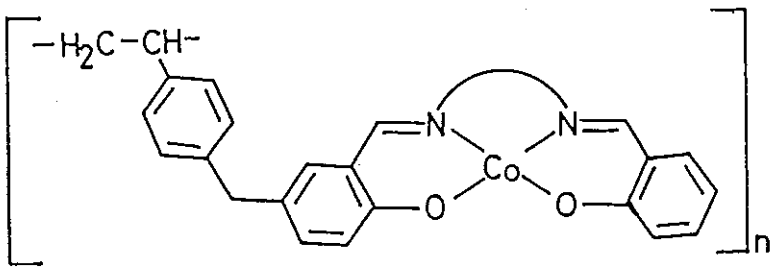
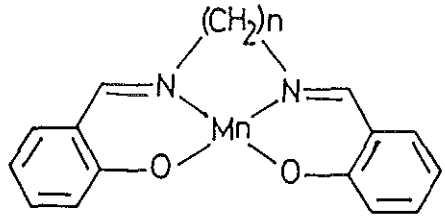


Fig.-10 Polymer Co(II) chelate

In view of the potential usefulness of dioxygen carriers, investigations have resulted in the synthesis of cetrain new cobalt(II) complexes [52]. Manganese(II) complexes with SALEN (Mn SALEN) as shown in Fig.-11 (where SALEN is a ligand derived from salicyaldehyde and ethylenediamine) have been the subject of a number of studies [53,54] and all of them have significantly indicated the presence of antiferromagnetic interactions. Mn(SALEN) oxygenated compound (in pyridine at 20°C) is reported to have given $[Mn(III)\ SALEN(OH)_2]_n$ with effective magnetic moment of 1.92 B.M. per manganese(II) ion which is unusually subnormal.

Fig.-11 MnSALEN complex



Though a large number of metal complexes of potentially tridentate oxygen containing Schiff's bases are dimeric or polymeric in the solid state, some monomeric complexes like bis (N-β - dimethylamino ethyl salicylaldehiminato) copper (II) with a five coordinate [55] geometry are also characterized .

The complex [Ni(L)] derived from an unsymmetrical tridentate Schiff's base formed by successive condensation of o- phenylene diamine with furfuraldehyde and salicylaldehyde has been reported [56]. The complexes Ni(L) where L^{2-} is the dianion of a tetradentate Schiff's base (H_2L) derived from the condensation of o-phenylendiamine with two equivalents of salicylaldehyde has been investigated as a catalyst for olefin epoxidation under phase transfer conditions [57]. Iron(III) complex with acetylacetone and ethanol amine are used as cathodic electrophoretic coatings [58].

A double bridged binuclear iron(III) complex containing inequivalent metal environments is reported by Gary D.Fallon *et al.* [59] using the binucleating ligand [H_3L^A= N-N'- bis salicylidene-1-3- diamino propane-2-ol].

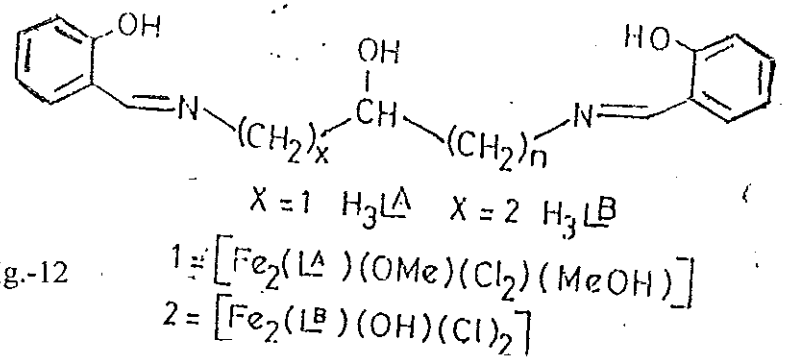


Fig.-12

Metal complexes of bis- bidentate oxygen, nitrogen donor systems have been studied [13]. Starting with Res-diacetonphenone or 2,4- dihydroxy- 5-acetylacetophone, some bis- bidentate and multidentate systems have been obtained by condensing with bases like 2- amino aniline, 2-hydroxy aniline, alcohol amines, hydrazino alcohol, hydrazino ethylcarbazate etc. which may behave either as symmetric bis-chelants or unsymmetric bis-chelants towards transition metal ions like Vo(II), Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). The following ligands and their metal complexes were synthesized.

(I). (N-2- amino phenyl)-5-acetyl-2, 4- dihydroxy acetophenimine (H_2 -APADA)

(II). (N-2-hydroxy phenyl)-5-acetyl-2,4-dihydroxy acetophenimine (H_3-HPADA)

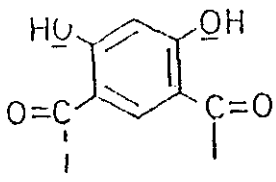
(III). (1,3-di (N-β- hydroxy ethyl) acetyl diimino-4,6-dihydroxy benzene (H_2-DHEADB)

(IV) 1,3-di(N-γ-hydroxy propyl) acetyl diimino-4,6-dihydroxy benzene (H_2 - DHPADB)

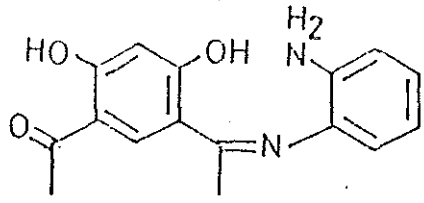
(V). 1,3-diaceto (N-β-hydroxy ethyl hydrazino)- 4,6-dihydroxy benzene (H_2-DAHEHDB)

(VI). N-Carbethoxy-5-acetyl-2,4-dihydroxy acetophenone hydrazone (H_2 -CADAH)

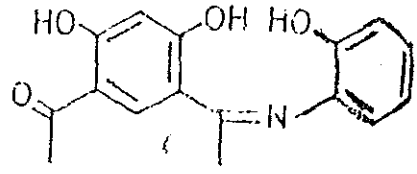
As the ligands possess hydroxy functions which can be deprotonated, they constitute acidic metal binding centers associated with tri or multidentate sequences resulting in metal complexes with significant structural characterstics. Deprotonated phenolic and deprotonated or non-deprotonated alcoholic hydroxy groups can lead to bridging interactions with two or more metal ions and result in the formation of complexes which may exhibit exceptional magnetic properties. Due to unsymmetric spread of binding centers some of these ligands may prefer mixed geometries around the metal ions. The complexes were characterized on the basis of elemental analysis, melting/ decomposition temperature, thermal analysis, conductance measurment, spectral (UV-Vis, IR, EPR) studies and magnetic susceptiblity.



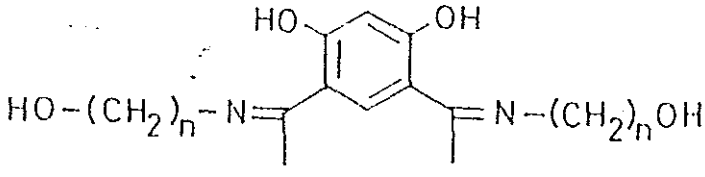
H_2-DAA



H_2-APADA

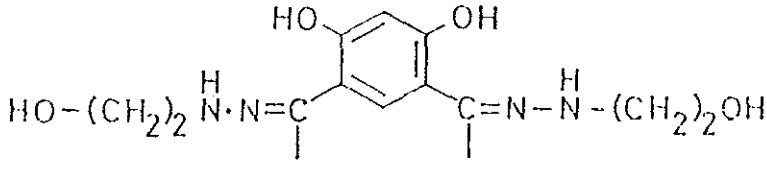


H_3-HPADA

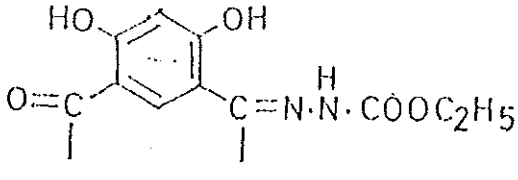


n = 2 – H_2-DHEADB

n = 3 – H_2-DHPADB

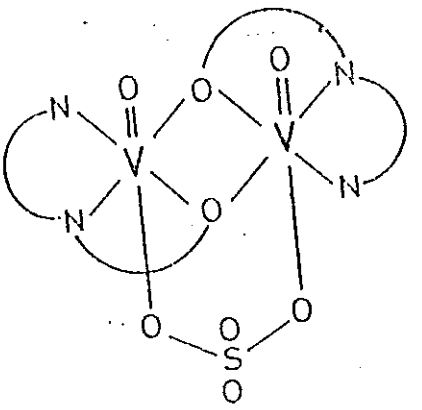


H_2-DAHEHDB



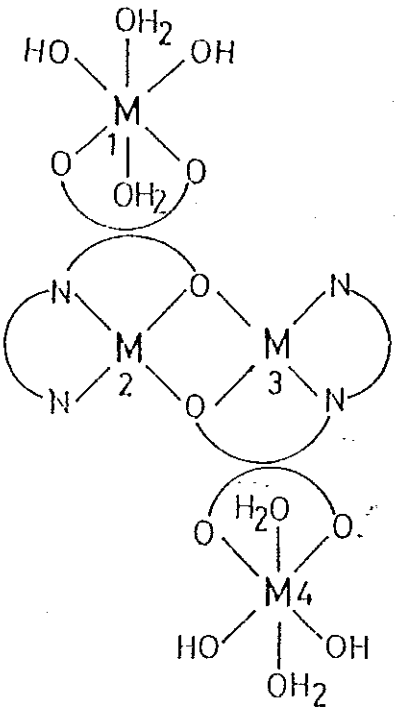
H_2-CADAH

Ligand derived from H_2-DAA



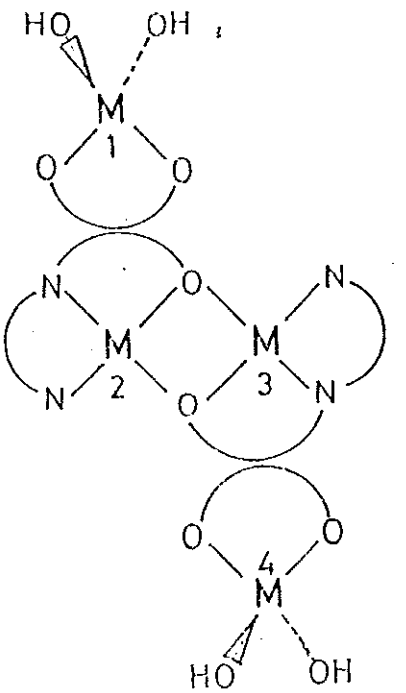
VO(II) Complex of H_2-APADA

Distorted octahedral geometry



Mixed square planar and octahedral geometry

M = Cr(III), Fe(III), Ni(II) and Cu(II)

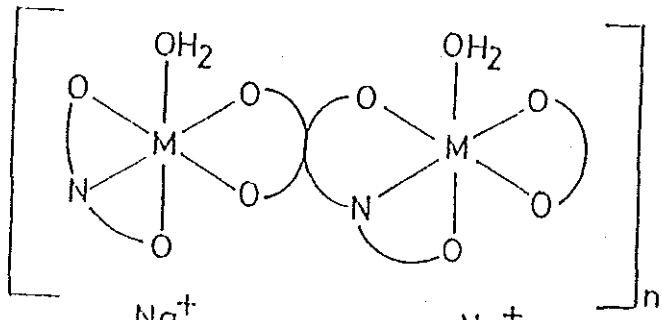


Mixed square planar-tetrahed geometry

M = Mn(II), Co(II)

Zn(II) = highly distorted tetrahedral geomet

Complexes of H_2-APADA



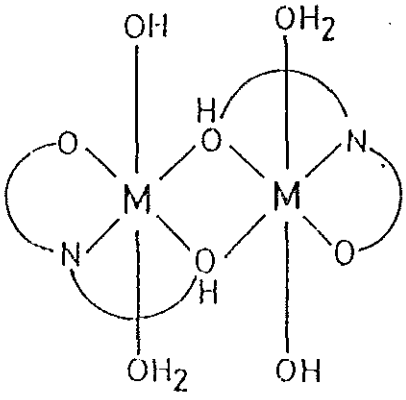
M	n
Mn(II)	3
Co (II)	3
Ni (II)	5
Cu (II)	2
Cr(III) & Fe(III)	3

Na^+ n H_2O Na^+ n H_2O

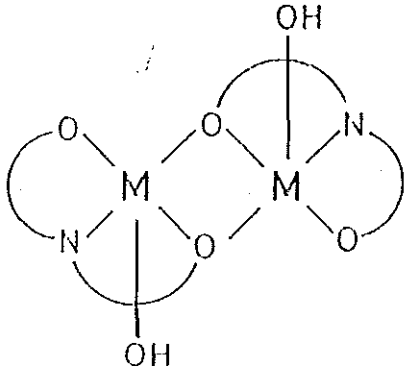
$Na\,[ML(H_2O)].n\,H_2O$

Same structure for Cr(III) and Fe(III) complexes without Na^+

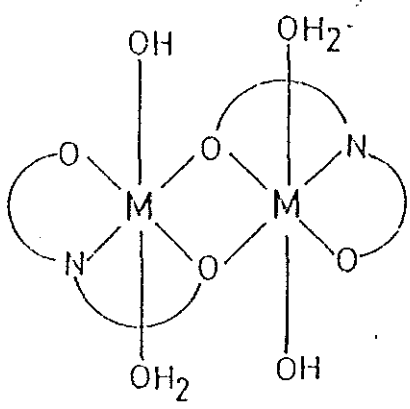
Complexes of H_3-HPADA



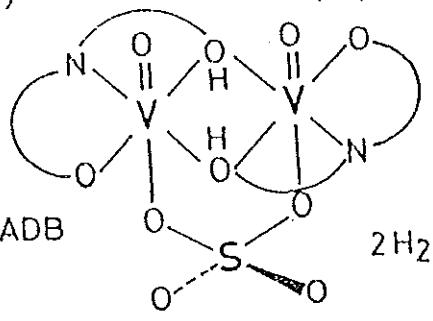
M = Co(II), Ni(II)



M = Fe(III)

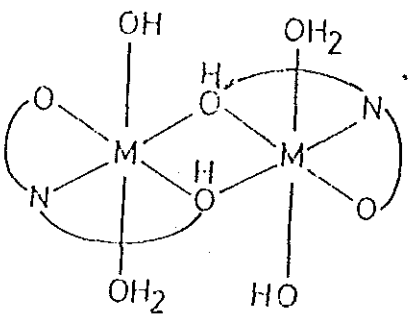


M = Cr(III) - H_2-DHEADB

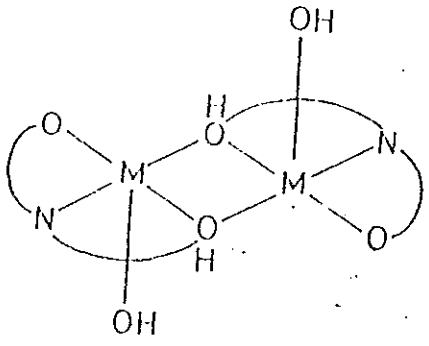


VO(II) - H_2-DHEADB $2H_2O$

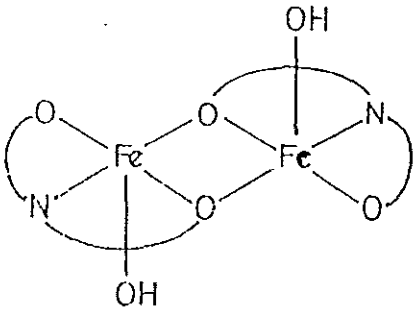
Complexes of H_2-DHEADB

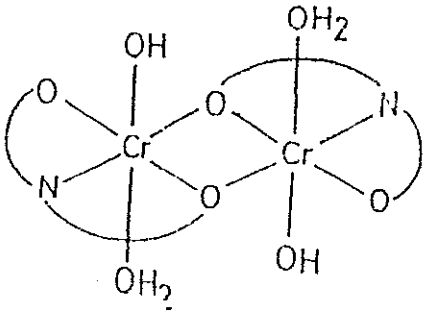


M = Co(II), Ni(II)

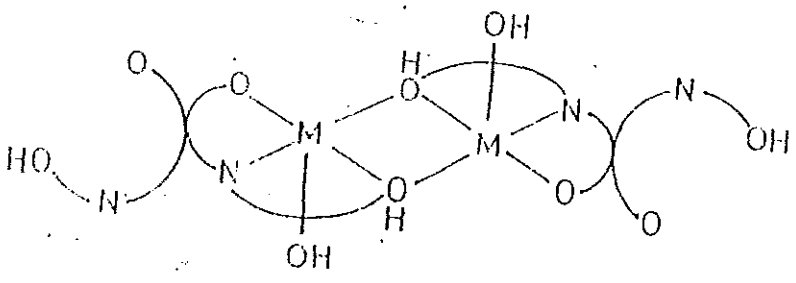


Mn(II), Cu(II), Zn(II)

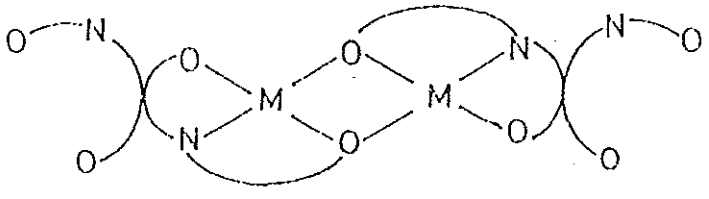




Complexes of H_2-DHPADB



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



M = Cu(II)

Metal complexes of H_2-DAHEHDB

Fig.-13 Structure of bis- chelating ligands and their complexes

SECTION B

SCOPE OF THE PRESENT INVESTIGATION AND OBJECTIVES

Litetrature survey reveals that metal complexes of bis bidentate oxygen, nitrogen donor systems are of considerable structural interest. 1,2,4,5-tetra substituted benzenes with all four substitutions containing metal binding centers are of great synthetic interest as they produce metal complex polymers. Res-diacetophenone or 2,4-dihydroxy-5-acetylacetophone is a symmetric bis-bidentate 'OO-OO' and some bis-bidentate and multidentate systems may be obtained by condensing the same with polyamine like 1, 3-diamino propane. They may behave as potential chelants towards transition metals like cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II). In view of its possible catalytic and heavy metal ion detoxification application, the condensation product of 2,4-dihydroxy acetophenone (H_2-DAA) with 1,3-diaminopropane has been investigated for the formation of polynuclear metal complexes with the metal ions mentioned above.

The basic objectives of the research work is

- to design new synthetic methods to isolate multidentate bis- chelating ligands for the synthesis of metal complexes using lighter transition metal ions and terminal metal ions like cobalt (II), nickel (II) and copper (II) and zinc (II), cadmium (II) and mercury (II) respectively.

-to develop efficient preparative methods for obtaining the transition and non-transition metal complexes

- structural studies on the ligands and metal complexes using analytical and spectral studies.

-to identify metal ions which may effectively be chelated by the ligand.

As the proposed ligand possess hydroxy functions which can be deprotonated, they constitute acidic metal binding centers which are likely to form metal complexes of significant structural characterstics. The complexes will be characterized on the basis of elemental analysis, melting / decompositions temperature, conductance measurments and spectral (IR, UV-Vis) studies.

CHAPTER-2

EXPERIMENTAL SECTION

2.1 CHEMICALS

All the chemicals used were of analar grade. Solvents such as methanol and ethanol (both from Aldrich) were purified with following standard methods [60]. 2,4-dihydroxy-5-acetylacetophenone (H_2-DAA) was prepared in Dr. V.J.T. Raju laboratory, Osmania University, Hyderabad, India using known procedure [61]. Metal salts, $ZnCl_2$ (BDH), $CoCl_2$ $.6H_2O$ and $CuCl_2H_2O$ (Both from Riedel-Haen), $NiCl_2$ (BDH), $CdCl_2H_2O$ and $HgCl_2$ (both from Riedel-de-Haen) and 1,3-diaminopropane (Fluka) were used.

2.2 MATERIALS AND METHODS

Melting points of the products were determined using Bock-Monoscop instrument. The metal complexes have been analyzed for metal and chloride contents using known methods. Cobalt, zinc and cadmium were estimated volumetrically with standared EDTA solution. Nickel and mercury were determined gravimetrically as $Ni(DMG)_2$ and $Hg_5(IO_6)_2$ respectively. Copper was also determined gravimetrically using α-Benzoinoxime as $Cu(C_{14}H_{11}O_2N)$. The chloride contents were estimated in all the complexes gravimetrically as silver chloride [62]. The metal estimations were also repeated by using Atomic Absorption Spectrometer, Spectr AA, from the solutions obtained by digesting the complexes with 3 ml sulfuric acid and 3ml nitric acid and then diluting with distilled water. Carbon, hydrogen and nitrogen analyses were carried out using Elementar Vario EL in the Ethiopian Geological Survey.

The molar conductivities of 10^{-3}M solution of the complexes were recorded using a Phlip Harris conductometer at room temperature.

Infrared spectra were obtained using a Pye-Unican SP-2000 infrared spectrophotometer in the range of 4000-200cm^{-1} as potassium bromide disks. UV-Visible spectrometeric studies of 10^{-3} M solutions of the complexes in the range 200-900 nm were recorded using Spectronic Genesys 2PC at room temperature and the spectra were printed using, Hewlet Packared Deskjet 695C.

2.3 SYNTHESIS OF LIGANDS

In this section, the ligand was prepared using 2, 4-dihydroxy-5- acetylacetophenone (H_2-DAA) as starting material. H_2-DAA on condensation with 1, 3-diaminopropane is expected to form multidentate metal binding systems. The ligand is of significant synthetic interest from chelation point of view, as the oxygen-nitrogen donor centers are expected to be present on the opposite sides of the benzene ring. Further, it was interesting to investigate whether or not the ligand can behave as symmetric multidentate systems.

H_2-DAA and 1,3-diaminopropane were mixed in different mole ratios like 1:1, 2:1 and 1:2 in ethanolic media and each of these mixtures was refluxed for several hours to make preliminary observations. In these attempts, it was observed that two different products could be obtained. Both the products were yellowish in colour, but significantly different in melting/ decomposition temperatures. However, only one of these product was selected on the basis of reaction

conditions and yields.

The selected product was characterized as 3:2 condensation product of H_2-DAA and1,3-diaminopropane named as 1,3-Di-[N-γ-N'-(2",4"-hydroxy-5"-acetylacetopheniminopropyl)] acetaldimino-4,6-dihydroxy benzene, (H_6-DHADB). The experimental details and physico-chemical characterization are discussed in the following sections.

2.3.1 SYNTHESIS OF 2, 4- DIHYDROXY-5-ACETYLACETOPHENONE (H_2-DAA) [61]

To a mixture of freshly fused and powdered zinc chloride (10 g) in 14 ml of dry acetic anhydride (14 ml), 10g of resorcinol was added in small portions while stirring continuosly . The resulting mixture was heated gently on a flame to 140^0 C and maintaining the temperature for fifteen minutes. A red viscous mass was obtained, which was cooled to room temperature and stirred with 80 ml of dil.HCl (V\V 1:1HCl). After a few minutes an orange red crystalline material was separated and filtered, washed thoroughtly with water and dried. The dry pro

2.3.2 SYNTHESIS OF 1, 3-Di-[N-γ-N'(2'',4''-HYDROXY-5''-ACETYL ACETOPHENIMINOPROPYL] ACETALDIMINO-4,6-DIHYDROXYBENZENE (H_6-DHADB)

H_2-DAA (5 mmole) was dissolved in ethanol (20 ml) in a two necked 300 ml round bottom flask and 1,3-propane diamine (6 mmole) was added while refluxing. The mixture was refluxed for one hour to obtain a light yellow product. The reaction mixture was cooled and filtered. The product was washed with ethanol and petroleum ether several times and stored in a desiccator. Yield:- 65%, Decomp.:- 198^{0}C

2.4 SYNTHESIS OF METAL COMPLEXES OF H_6-DHADB

The following general method was employed for the synthesis of metal complexes. To the hot methanolic solution of divalent metal chloride of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) (0.5 mmole in 20 ml) in a two necked round bottom flask, a methanolic suspension of H_6-DHADB (0 .5mmole in 20ml) was added in small portions. A clear solution with distinct colour change was obtained. The pH of the reaction mixture was increased to~8 using 5% (v/v) methanolic ammonia solution and then heated under reflux for four hours. The resulting coloured product was filtered while the solution hot. It was washed with methanol repeatedly and kept in a desiccator (see Table-2 for colour, yields and melting/ decomp.point)

CHAPTER- 3

RESULTS AND DISCUSSIONS

3.1 PHYSICO-CHEMICAL STUDIES OF H_6-DHADB

The ligand is a stable, crystalline, light yellow coloured compound and sparingly soluble in common organic solvents such as acetone, chloroform, methanol carbontetrachloride, 1:4 Dioxane and Dimethyl Sulfoxide. It decomposes partially at 198-200 ^{0}C (probably due to loss of water molecules) and remains stable as light brown coloured substance beyond 200^{0}C.

H_6-DHADB was tested for the presence of primary amine and carbonyl functional groups using azo-dye formation and Brady's reagent respectively [63,64]. The test for primary amine gave negative result, while for that carbonyl funtion was positive. Details of the tests are given below. The test for presence of primary amine function: A small amount (20 mg) of the compound was dissolved in 2N HCl (3-4 ml) and the solution was cooled in ice. To this cold 10% aqueous sodiumnitrite (2 ml) was added. The resultant solution was kept in ice bath for 10 mins and after confirming that an excess of nitrous acid was present (by spotting a drop of the solution on a starch- iodide paper and observing an immediate blue colour). Saturated sodium acetate solution (2 ml) was added and the mixture was poured into a solution of β-naphthanol (0.5g) in 2N sodium hydroxide (6 ml). A primary amine compounds, by coupling with the naphthanol is expected to give a bright red precipitate of an azo-dye (addition of an excess of a diazotized solution to the alkaline β-naphthanol may give a yellowish precipitate of α-nitroso-β-naphthol). As the test did not yield red or yellow precipitate, it was cocluded that the ligand did not contain

the primary amine function [63].

The test for carbonyl function (using Brady's reagent): To 0.05- 0.1g of the substance 3ml of the 2,4-dinitrophenyl hydrazine reagent was added; the mixture was shaken and allowed to stand for 5-10 mins. A crystalline precipitate was formed, indicating the presence of carbonyl group in the ligand [64].

3.1.1 Analytical studies of H_6-DHADB

The C, H, N data of the ligand supports the condensation of H_2-DAA and 1,3-diaminopropane in 3:2 mole ratio and the four water molecules. Based on analytical data the formula $C_{36}H_{50}O_{12}N_4$ is suggested.The elemental analysis of the ligand found and calculated is given in Table-1

Table:-1 Analytical data of H_6- DHADB, (C_{36} H_{50} O $_{12}$ N_4), Calculated (Found)

ligand	Carbon %	Hydrogen %	Nitrogen%
H_6- DHADB	59.10 (58.64)	6.89 (7.05)	7.60 (7.93)

3.1.2 Infra-red Spectrum of the H_6 -DHADB

The IR spectrum of the ligand shows a broad strong multiple band in the region approximated between 2900-3650 cm^{-1} which can be assigned to ν_{OH} (Phen) and ν_{OH} (water) involved in several intra and intermolecular hydrogen bonding interactions [65]. The spectrum also shows another intense relatively broad multistructured band in the regions 1590 - 1650 cm^{-1}. It is assigned to $\nu_{C=N}$ and $\nu_{C=O}$ corresponding to the frequency minimum and frequency maximum respectively [65]. The additional peaks in the region between 1600 and 1650 cm^{-1} could be due to $\nu_{C=C}$, δ_{OH} (phen), δ_{OH} (water), etc [65]. There is a medium intensity multiple band located in the range of 1250- 1260 cm^{-1} which can be assigned to ν_{C-O}, the multiplicity refering to at least two different environments around the phenolic group in the ligand. These features of IR spectrum are consistent with the condensation of H_2-DAA and 1,3- Propylenediamine in a 3:2 mole ratio.

3.1.3 Electronic Spectrum of the ligand H_6-DHADB

The electronic spectrum of the ligand shows bands at 46948, 37878, 33333 and 27777 cm^{-1}. The bands in the high frequency region (46948 cm^{-1}, 37878 cm^{-1}) are more intense than the remaining once. The band observed at 46,948 cm^{-1} is relatively broad. The band at 37,878 cm^{-1} is assigned to $n \rightarrow \pi^*$ transition of the acetyl carbonyl group while those bands at 33,333 and 27,777 cm^{-1} may be assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of azomethine. The band at 46,948 cm^{-1} is due to $\pi \rightarrow \pi^*$ transition of benzene ring [65].

This ligand has been designed and synthesized for the first time with a view to study multidenticity in certain new perspectives. In fact it was intially assumed that H_2-DAA forms 1:1 condensation products with 1,3-proplyenediamine to give symmetric multidenate polymer ligand. But the analytical and spectral data support 3:2 condensation.

The proposed structure of the ligand on the basis of analytical data, IR, electronic spectral data are shown in Fig.-14

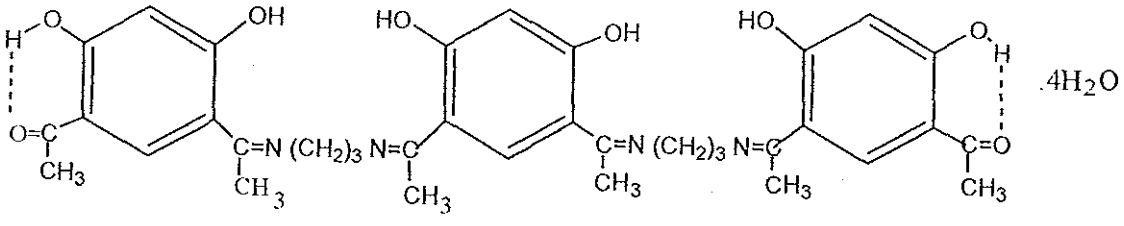


Fig.-14 Structure of H_6-DHADB

3.2 PHYSICO-CHEMICAL STUDIES OF THE COMPLEXES OF H_6-DHADB

The interest on H_6-DHADB ligand stems from the symmetric chelating potentials which are likely to result in polynuclear metal complexes. As this binding sequences on the ligand are grafted on opposite sides of the benzene ring; it will be interesting to examine as to how it picks up metal ions and provides preferential coordination environments around each one of them. The metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) of H_6-DHADB were synthesized from non-aqueous media.

All the metal complexes are coloured and stable to air and moisture. They do not melt, but decompose partially (seeTable-2) while showing colour changes . They have low solubility in most common organic solvents such as DMF, acetone and they decomposes in DMSO on standing for more than three hours.

Table:-2 Physical properties of metal complexes of H_6-DHADB

Complex	Colour	Yield (%)	Decomp. Temp ^{0}C
Zinc(II)	Light yellow	66	260
Mercury(II)	Pale yellow	55	210
Cadmium(II)	Cannery yellow	66	246
Cobalt(II)	Light green	50	213
Nickel(II)	Light brown	50	255
Copper(II)	Light dawn pink	45	220

3.2.1 Analytical data of the complexes of H_6-DHADB

Carbon, hydrogen, nitrogen, metal and chlorine analyses of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes have been done and the data are presented in Table-3. Metal to ligand ratios for Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) are 3:1, 2:1, 2:1, 4:1, 2:1 and 1:1 respectively, which show wide variation both for transition and non-transition metal ions. This probably indicates that all the expected chelating sequences are not approachable for all the metal ions. Particularly, the four water molecules present in free ligand are likely to be strongly locked up with bulk ligand structure, thus, preventing the intimate approach of metal even in methanolic solution. It may be an interesting situation of the ligand which is prefering to chelate water molecules through efficient hydrogen bonding over metal ions in specific geometries. Size of hydrated or solvated metal ions, affinity towards oxygen and nitrogen binding centres, preferred geometric and electronic configurations may be contributing either individually or combinedly to decide these metal ligand stoichiometries. However, it is interesting to note the wide variation in metal ligand stoichiometries. Analytical data also indicates the presence of chloride in Ni(II), Zn(II), Cd(II) and Hg(II) complexes; hydroxide in Co(II) and Zn(II) complexes and ammonia in Co(II), Cd(II) and Hg(II) complexes. All the complexes contain water molecules. The presence of anions in the complexes except the Cu(II) complexes is also indicating variation in the extent of deprotonation of phenolic groups. H_2-DHADB is existing as H_5-DHADB$^-$, H_4-DHADB^{2-}, H_3-DHADB^{3-}, H_2-DHADB^{4-} and DHADB^{6-} in different complexes as suggested by the analytical data.

Table-3 :- Analytical data calculated (found) and conductance data of the metal complexes of H_6-DHADB

Complexes	Carbon%	Nitrogen%	Hydrogen%	Metal%	chloride%	Λ_M (S $cm^2 mole^{-1}$)
Zn_4 (DHADB) OH(Cl) $(H_2O)_2$	43.20	5.59	4.32	26.08	3.55	
	(44.15)	(5.51)	(4.11)	(27.02)	(3.56)	38
Cd_2 (H_4-DHADB) OH Cl(NH_3) (H_2 O)$_5$	42.90	6.96	5.01	22.34	3.53	
	(43.54)	(6.42)	(5.20)	(22.20)	(3.85)	39
Hg (H_5-DHADB) Cl(NH_3) $(H_2O)_5$	46.49	6.99	5.44	20.04	3.55	
	(46.99)	(7.01)	(6.37)	(20. 20)	(4.03)	20
Co_3 (H-DHADB) OH $(NH_3)(H_2O)_6$	44.46	7.19	5.49	18.10		
	(45.61)	(6.51)	(5.92)	(18.05)	-	46
Ni_2 (H_4-DHADB) Cl_2 $(H_2O)_4$	47. 15	6.11	5.28	12.79	7.74	
	(48..08)	(6.56)	(5.93)	(13.90)	(8.04)	35
Cu_2 (H_2-DHADB) $(H_2O)_2$	52.87	6.84	5.18	15.54		
	(52.30)	(5.93)	(5.14)	(16.00)	-	31

DHADB=C_{36} H_{36} O_8 N_4 , Calculated (found)

3.2.2 Conductance studies of metal Complexes of H_6-DHADB

Owing to the low solubility of the complexes, conductance measurments were not possible in common organic solvents. However, freshly made solutions in DMSO or HCOOH (1x 10^{-3}M) recorded very low conductance values which suggest that the complexes are non-electrolytes [66]. Hence, it may be concluded that the anions like chloride and hydroxide as formulated in the complexes are present in the coordination or non-ionizable spheres.

3.2.3 IR Spectra of the metal complexes of H_6- DHADB

The characteristic features of IR spectra (band positions indicated in cm^{-1} frequency units) of metal complexes can be correlated with the specific functional group frequencies of the free ligand. The spectra of the metal complexes show broad bands in the range of 3600-3000- cm^{-1} which are due to hydroxide, water and/or ammonia in the complexes. Some of these water molecules are likely to be present in the coordination sphere of metal ions as evidenced by the medium to low intensity non- ligand bands observed in the range of 1000-850 cm^{-1} and 650-550 cm^{-1} assignable to rocking and wagging mode of coordinating water [67]. Similar features of ammonia coordination are also noted. It is not possible to pin point the changes with respect to ν_{OH} (phenolic) of the ligand, as the ν_{OH} is obscured by the bands due to OH^-, H_2O and/ or NH_3. However, the deprotonation of one or more phenolic groupes can be inferred from the changes observed in $\nu_{C\text{-}O}$ bands and also on account of charge compensation. The strong multiple structured band observed in 1650-1590 cm^{-1} in the free ligand spectrum appears to have been modified in the spectra of the metal complexes. The corresponding band in the spectra of metal

complexes is now observed in the range of 1650- 1550 cm^{-1}. The downward shifts are interpreted in terms of the partcipation of C=N and / or C=O functional groups in coordination. The retention of modified band structures between 1600-1650 cm^{-1} is likely to be due to $\nu_{C=C}$ and $\delta_{O\ H}$ (water) and δ_{NH} (ammonia). Strong evidence in support of phenolic oxygens participation in metal binding is shown by modification of $\nu_{C\text{-}O}$ into multiply split and positively shifted bands in the range 1300-1250 cm^{-1}. These probably could be taken as evidence of phenolic oxygen binding in metal complexes through some of the phenolic groups. Further, bands located in the range 600-200 cm^{-1} could be due to M-O, M-N and M-Cl stretching respectively.

The IR spectral features in 1650-1550 cm^{-1} and 1300-1250 cm^{-1} regions are further elaborated. In the spectra of Co(II), Cu(II) and Zn(II) complexes there is a downward shift in the low frequency end of 1650-1590 cm^{-1} band corresponding to free ligand and is located in the range of 1570-1550 cm^{-1}. This is a strong evidence in support of coordination through azomethine (C=N) nitrogen. In the spectra of Ni(II), Cd(II) and Hg(II) complexes the 1590 cm^{-1} end is unaffected, thus indicating that the azomethine function is not involved in coordination.

The spectra of Zn(II), Cd(II) and Ni(II) complexes show negative shift in the high frequency end of the band which is observed in the range of 1640- 1620 cm^{-1}. This unambiguously supports coordination through the carbonyl oxygen. In the spectra of Co(II) and Hg(II), the corresponding region has two structures at 1650 and 1640 cm^{-1} . This could be suggestive of two type of carbonyls in coordination. In Cu(II) complex the 1650 cm^{-1} band is unaffected and hence no metal binding through carbonyl function can be suggested.

There is complementary evidence with respect to $\nu_{C\text{-}O}$. The band corresponding to $\nu_{C\text{-}O}$'s at 1260- 1250 cm^{-1} in free ligand, shows splitting in the spectra of the complexes. In general the band shows positive shift and appears in the range of 1300-1250 cm^{-1}. The spectra of all the complexes (except that of Zn(II)) show atleast one medium intensity band in the range 1250-1260 cm^{-1}, while other structure appear in the range of 1270-1300 cm^{-1}. These features show that some of the phenolic oxygens are free from metal ion interactions while the others are deprotonated and bonded to metal ions. As the spectrum Zn(II) complexes does not show retention of band structure in 1250-1260 cm^{-1} region but shows band at 1270 cm^{-1}, it depicts deprotonation of all phenoxide oxygens. However, these band positions may not be taken as independent evidence to draw conclusions. Using complementary support from analytical data and non- electrolytic nature from conductance studies, it is proposed that all the phenolic groups are deprotonated and bonded to metal ions in Zn(II) complex, while similar deprotonation and bonding is suggested with five phenolic group in Co(II), four in Cu(II), two in Ni(II) and Cd(II) and one in Hg(II) complexes.

Based on IR spectral data it can be concluded that the ligand behaves as multidentate system employing deprotonated phenolic oxygen, carbonyl oxygen and / or azomethine nitrogens in metal binding. In addition, there are coordinated and lattice water molecules, coordinated ammonia and chloride in the complexes. Involvement of all the azomethine and carbonyl groups in coordination to Zn(II) and only carbonyl functions in coordination of Cd(II) and Hg(II) are concluded. A few more observations on the spectra of Co(II), Ni(II) and Cu(II) complexes can also be made.

The metal to ligand ratio in Cu(II) complexes is 2:1 and in Co (II) complexes, it is 3:1. It is suggested that copper(II) ions get chelated through the tetradentate sequence 'ONNO' of the central part of the ligand while the terminal intramolcular hydrogen bonded carbonyl and phenolic functions are unaffected. But, in cobalt(II) complexes, as the metal ligand ratio is 3:1, it is proposed that the metal ions get chelated at two of the 'ONNO' chelating sites and one of the terminal OO site while leaving the other 'OO'sequence free.

In the spectrum of nickel(II) complex the 1650 cm^{-1} band corresponding to free ligand shows negative shift while the 1590 cm^{-1} end is unchanged, unambiguously suggesting metal binding through the terminal 'OO' chelating sequences, while the middle 'ONNO' sequences do not attract metal ion coordination. It is not clear why such variablity towards the metal ions Co(II), Ni(II) and Cu(II) is exhibited. The non- ligand bands observed in the range of 400- 580 cm^{-1} can be assigned to M-O, M-N stretching. Another non-ligand band at 280 cm^{-1} in nickel (II) complex may be attributed to M-Cl stretching. Based on the IR spectral data Co(II), Ni(II) and Cu(II) complexes with metal to ligand ratio 3:1, 2:1, 2:1 are identified with the following chelation.

-Cobalt (II) complex - ONNO, ONNO and OO chelation

-Nickel (II) complex- OO and OO chelation

-Copper (II) complex- ONNO and ONNO chelation

Table:-4 Characterstic infrared spectral data (band frequency in cm^{-1}) of the complexes of H_6-DHADB

Compound	ν_{OH}(water) +ν_{OH}(phen)	($\nu_{C=O}$ + $\nu_{C=N}$)	ν_{C-O} (phen)	New band s
ligand	2900-3650	1650 - 1590	1250-1260	_
Zn(II) complex	3000-3600	1640- 1570	1270	900,530,410
Cd(II) complex	2900-3650	1630 - 1590	1260,1285	810, 570,420
Hg(II) complex	3000-3600	1650, 1640-1590	1250, 1270,1280	800, 520,400
Cobalt (II) complex	2800-3600	1650- 1570	1260, 1280- 1290,	900, 770, 580, 44
Nickel(II) comple	2900-3600	1620-1590	1260, 1280-1300	890, 550, 480, 400,28
Copper (II) complex	3050- 3600	1650-1550	1260- 1280	600, 550,440,320

Table- 5 Electronic spectra of metal complexes of H_6 - DHADB

Complexes	Electronic spectral band, ν_{max} (cm^{-1})	Assignment
Zinc(II)	27778, 40160, 31250	CT
Cadmium (II)	27624-25000	CT
Mercury (II)	23256	CT
Cobalt (II)	12500, 21739,16666	$^4T_1(F) \rightarrow {}^4T_2(F)$
		$^4T_1(F) \rightarrow {}^4T_1(p)$
		$^4T_1(F) \rightarrow {}^4A_2$
Nickel (II)	20000	$^4T_1(F) \rightarrow {}^4T_1(P)$
Copper (II)	16666-11764	$^2B_1 \rightarrow {}^2B_2$
		$^2B_1 \rightarrow {}^2A_1$
		$^2B_1 \rightarrow {}^2E$

CONCLUSIONS

The metal complexes have been characterized on the basis of analytical, conductance and spectral studies. The studies indicate that Co(II) and Zn(II) which are the lighter transition and the lighter non-transition metal ions respectively used in the investigation are the most effectively chelated metal ions by H_6-DHADB. For non- transition metal ions, an explanation may be given based on mass and size of the metal ions.

As the radius of the metal ion increases from Zn(II)→ Cd(II)→ Hg(II) (88, 109, 116 pm with C.N: 6), the tendency to polarize the binding centres of the ligand decreases [69]. While the smaller Zn(II) can effectively get chelated to the OO, ONNO, ONNO and OO sequences. The bulkier Cd(II), and Hg(II) are not able to do so. They are in contact with only the terminal OO sequences. While Cd(II) can approach both ends of the ligand; Hg(II) is able to bind itself to only one end. This appears to be an interesting features of the study.

Similar reasoning may not justify the behaviour of transition metal ions. Size of hydrated/ solvated metal ions, relative affinities towards binding centers, preferential geomerties, electronic configurations, spin-spin and spin-orbital interactions and ligand steric factors may contribute in deciding the final composition and structures of the complexes. Detailed thermal analysis, NMR, EPR, magnetic susceptibility and X-ray studies help in resolving these features. The structure of these complexes are given in Fig-15

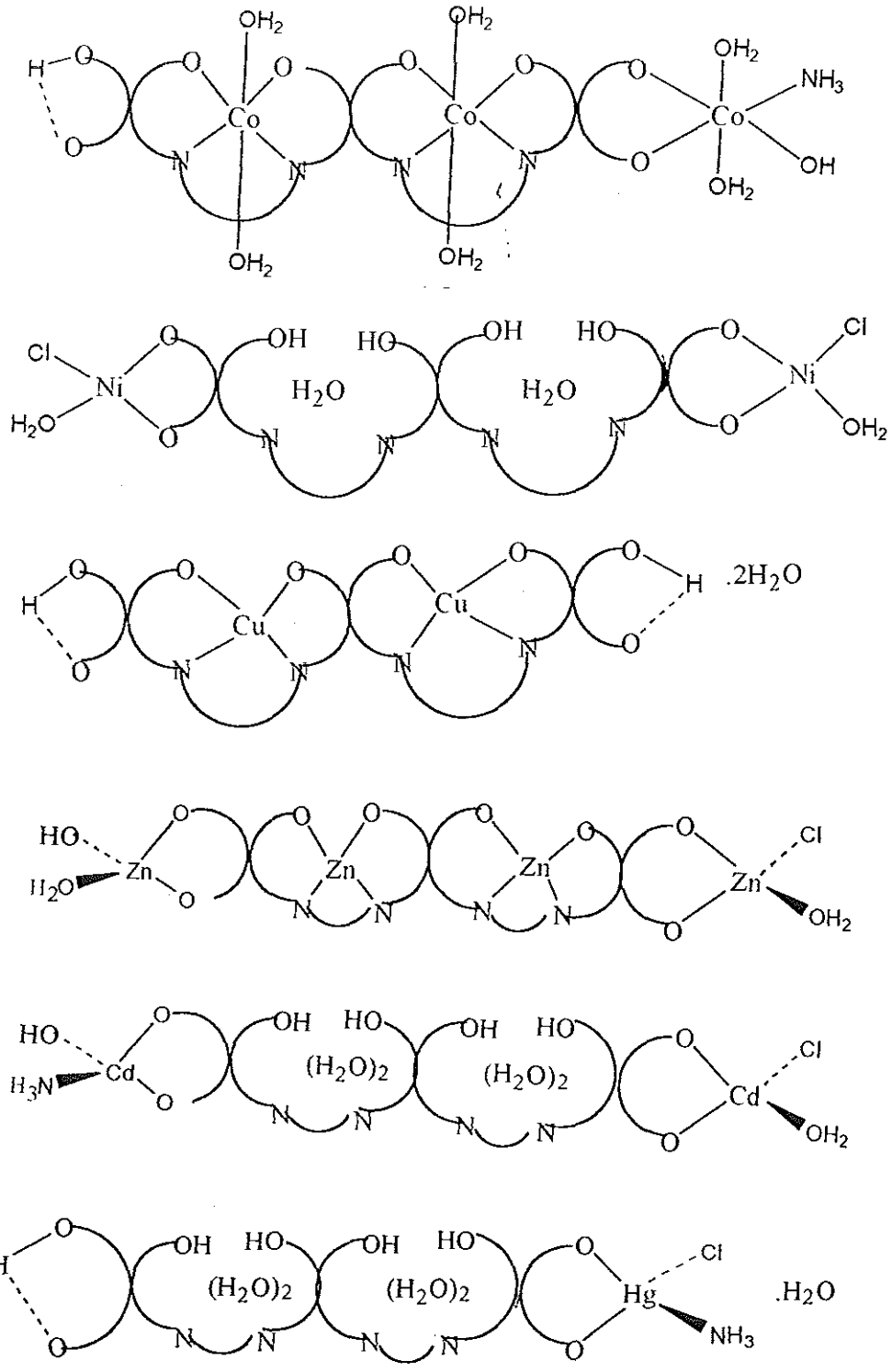


Fig.-15 Proposed structure of metal complexes of H_6-DHADB

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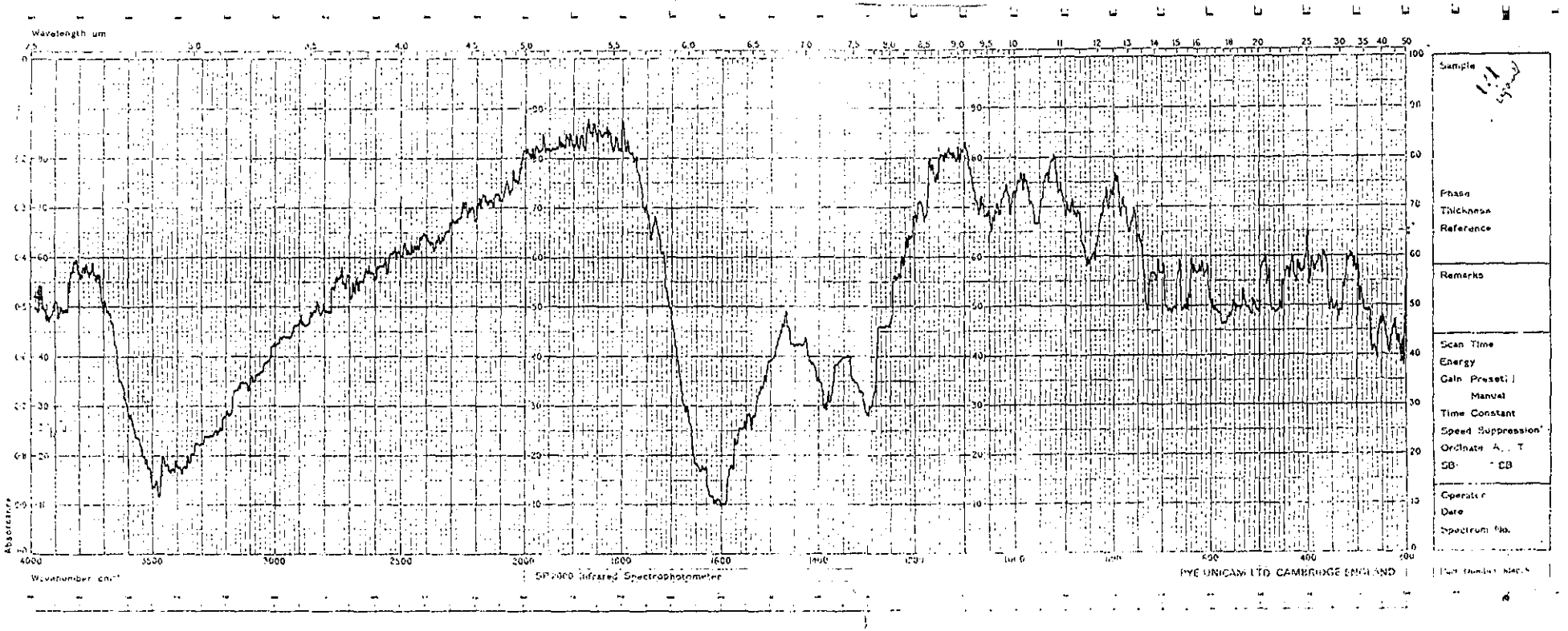
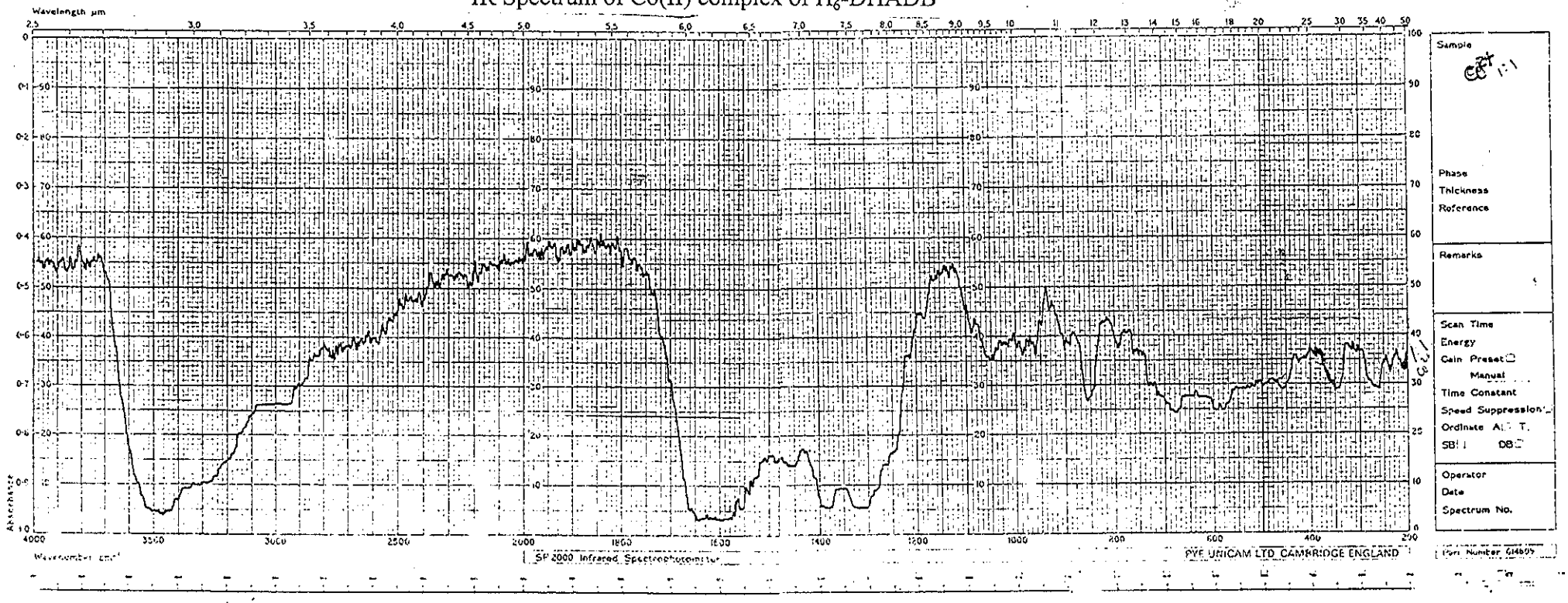
APPENDIX

IR Specrtum of H_6-DHADB



IR Spectrum of Co(II) complex of H_6-DHADB



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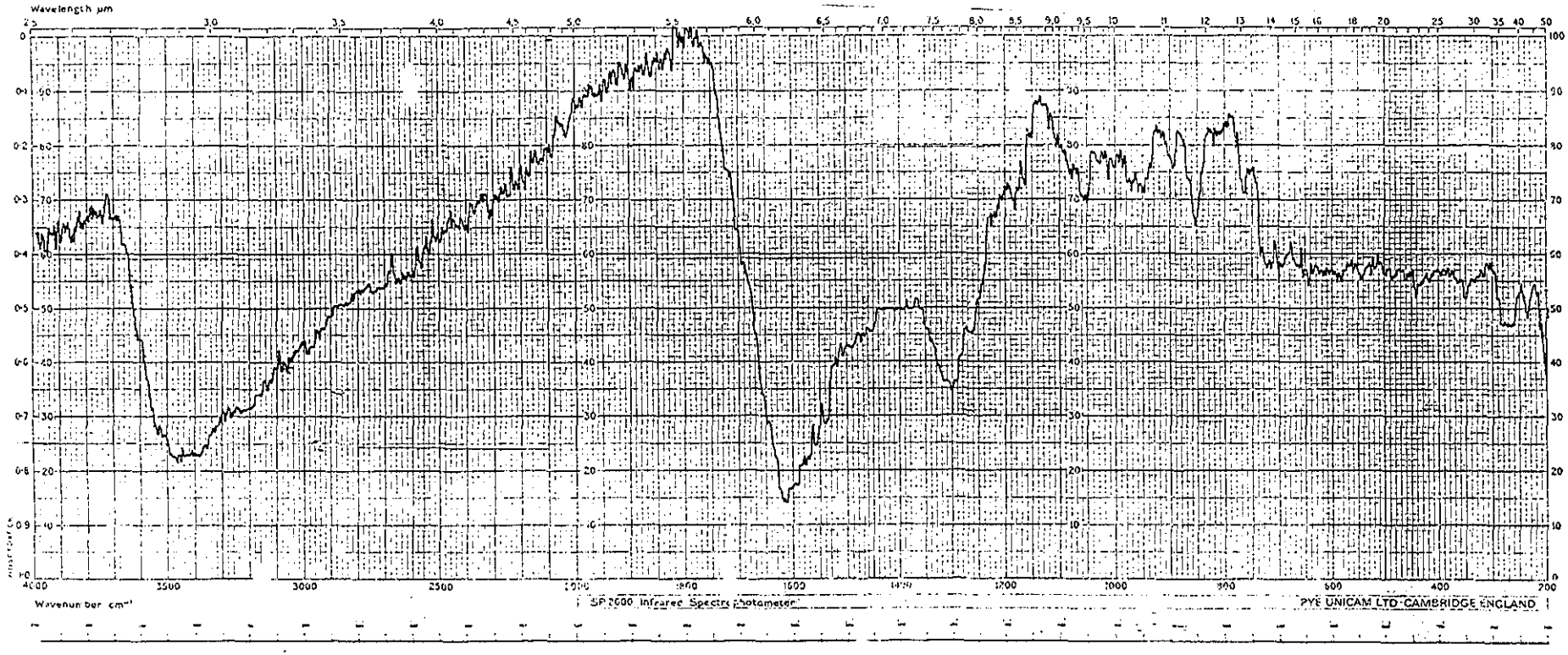

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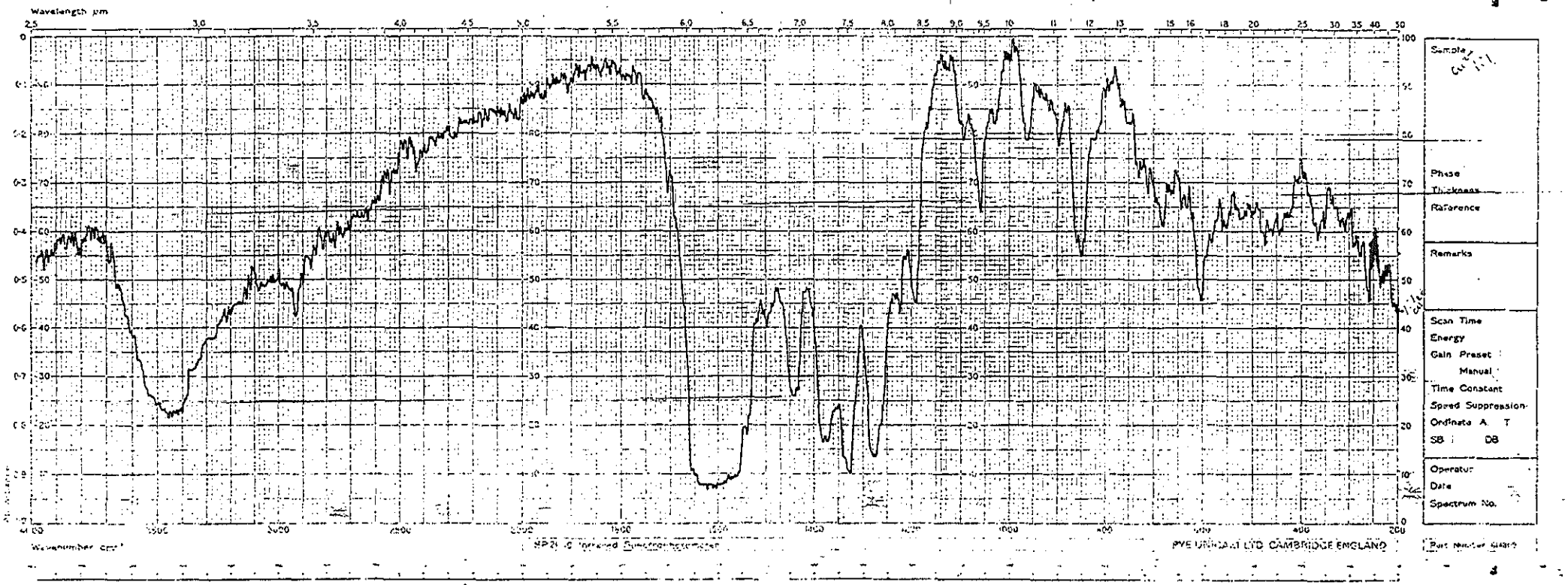

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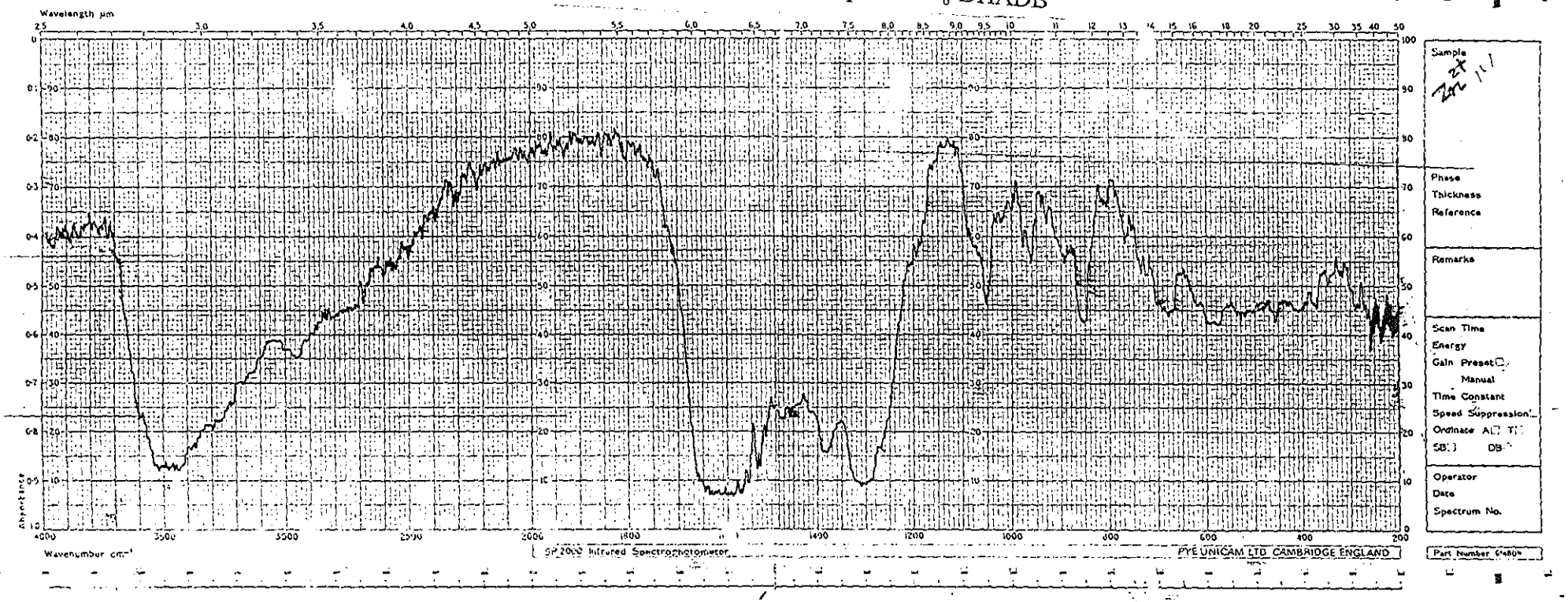

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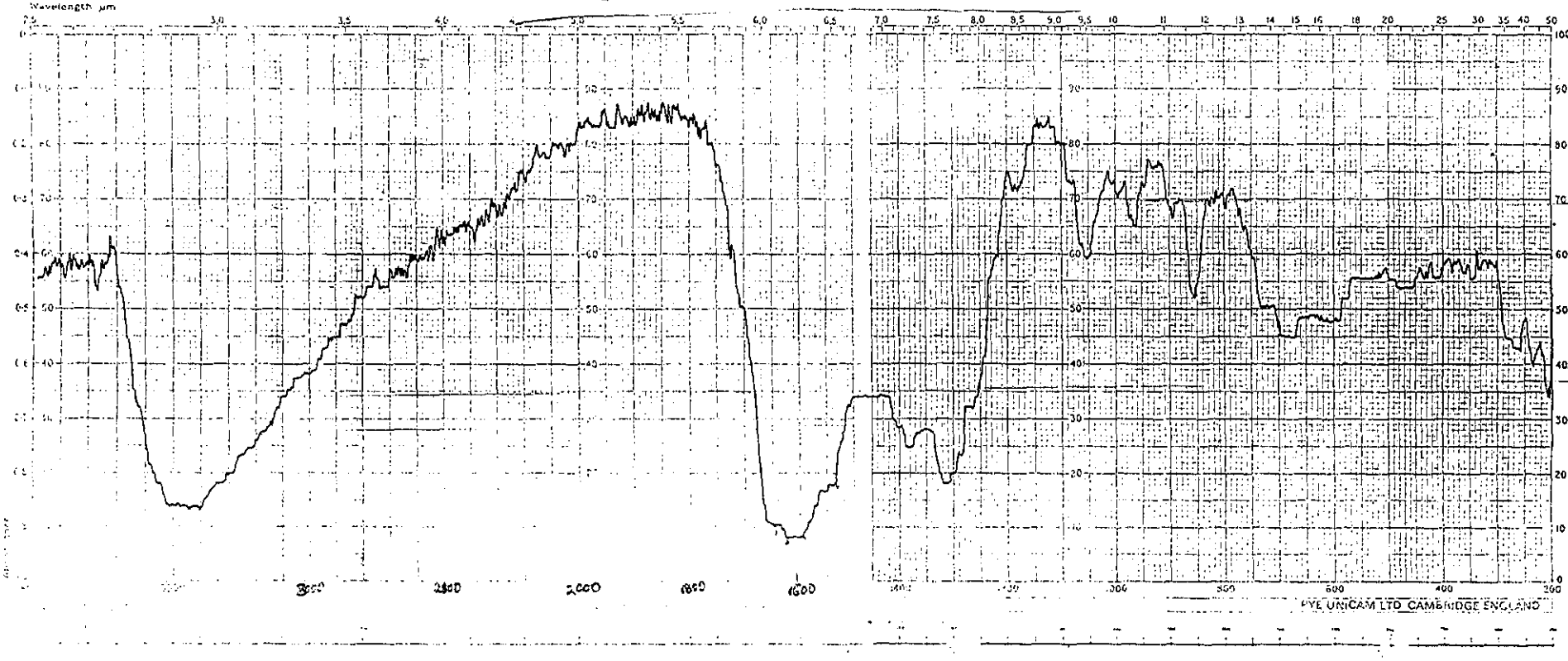

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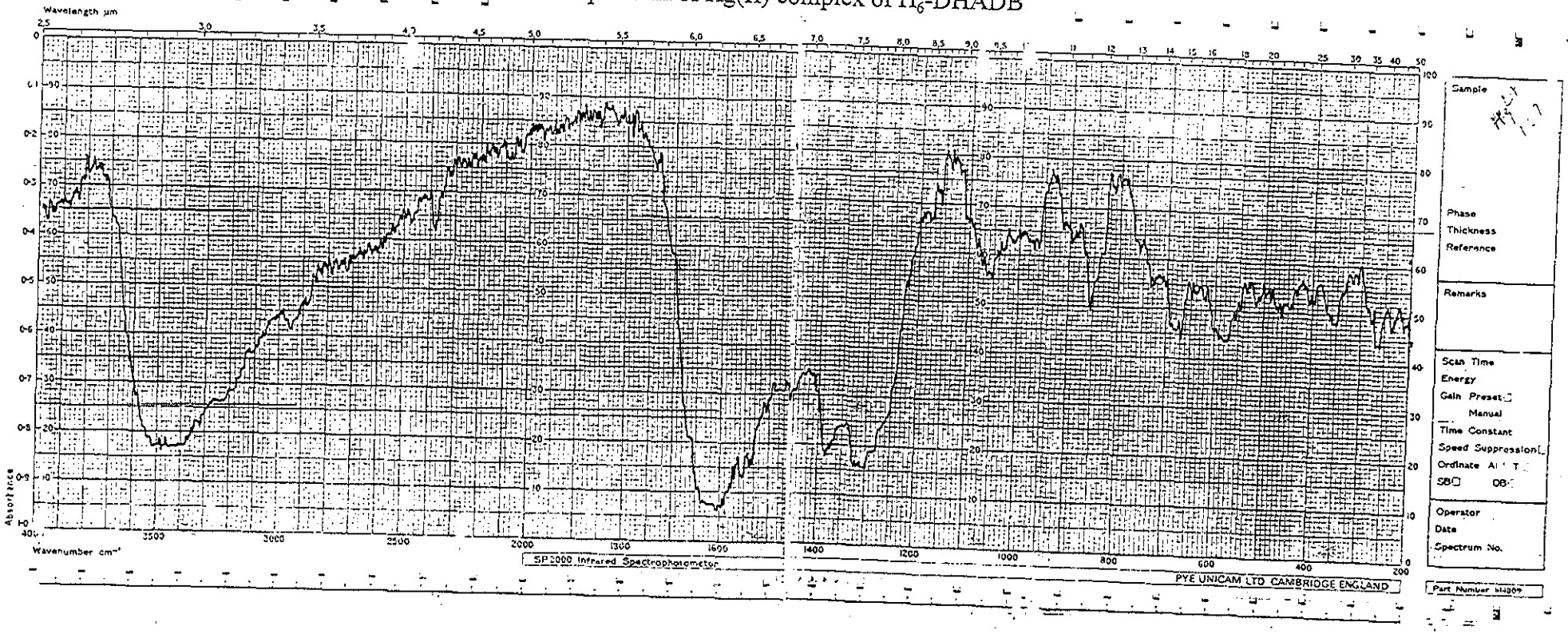

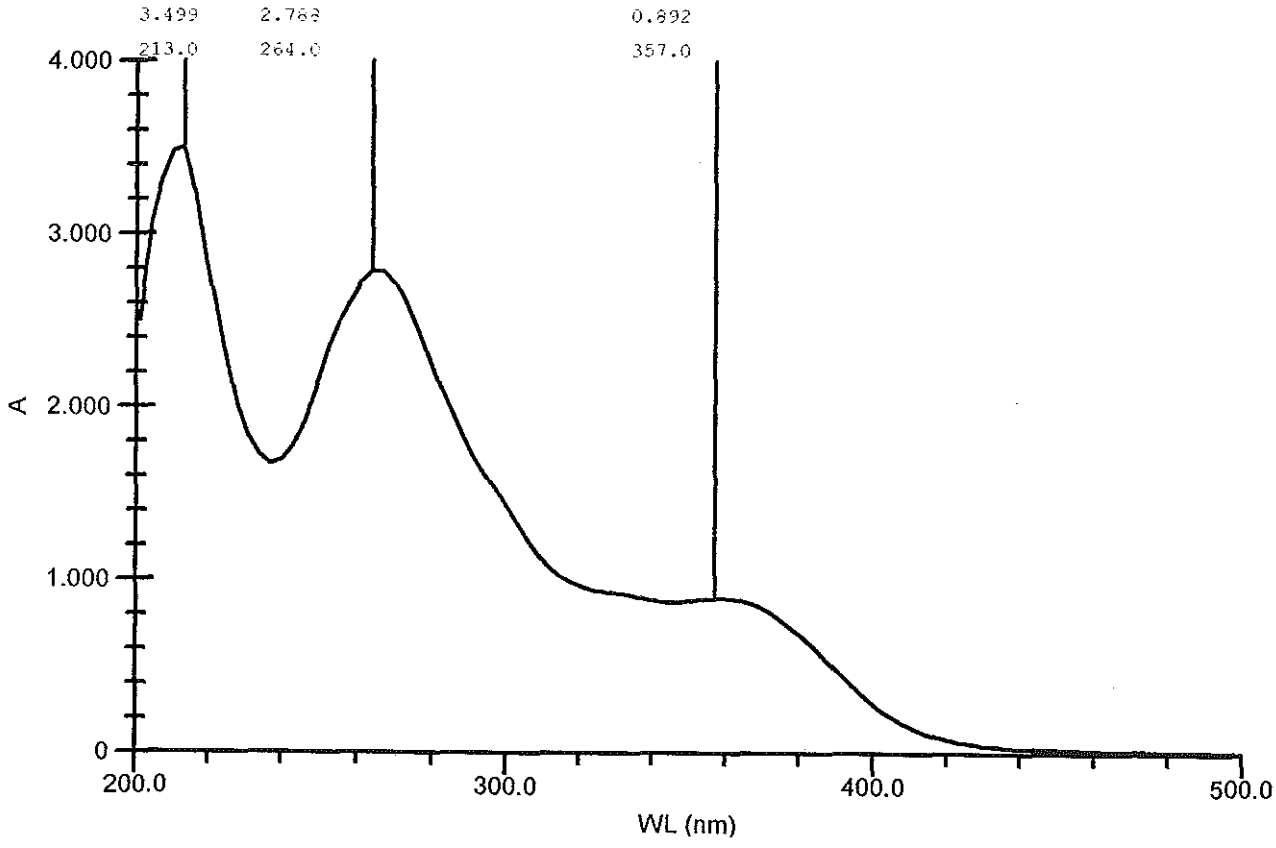

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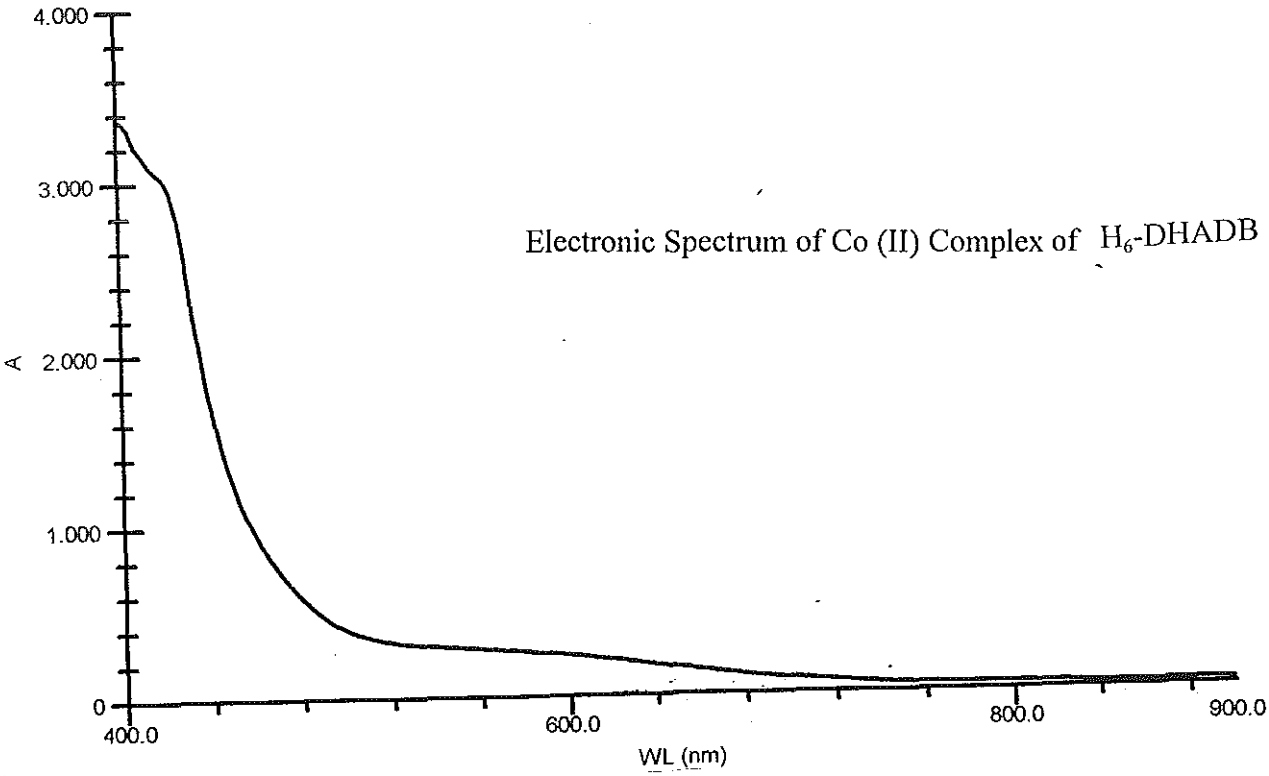

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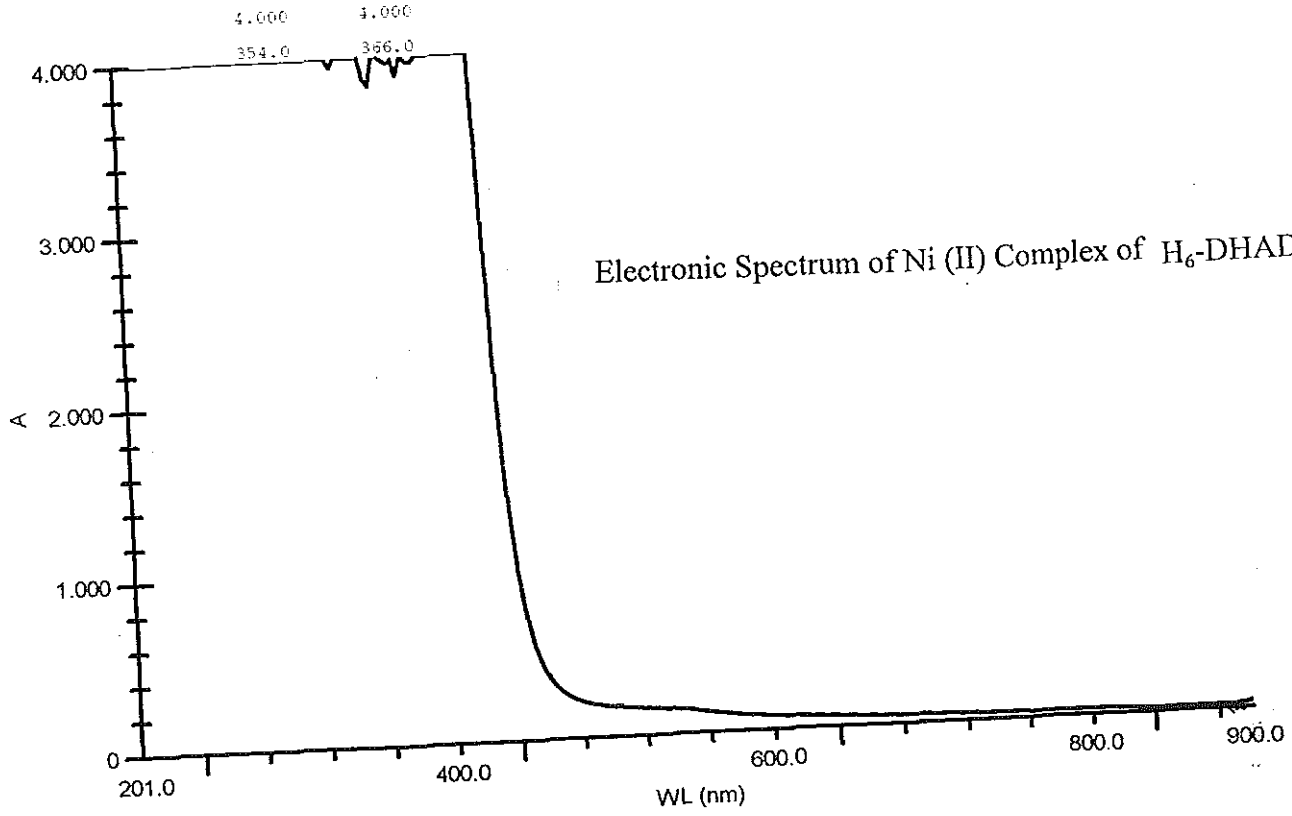

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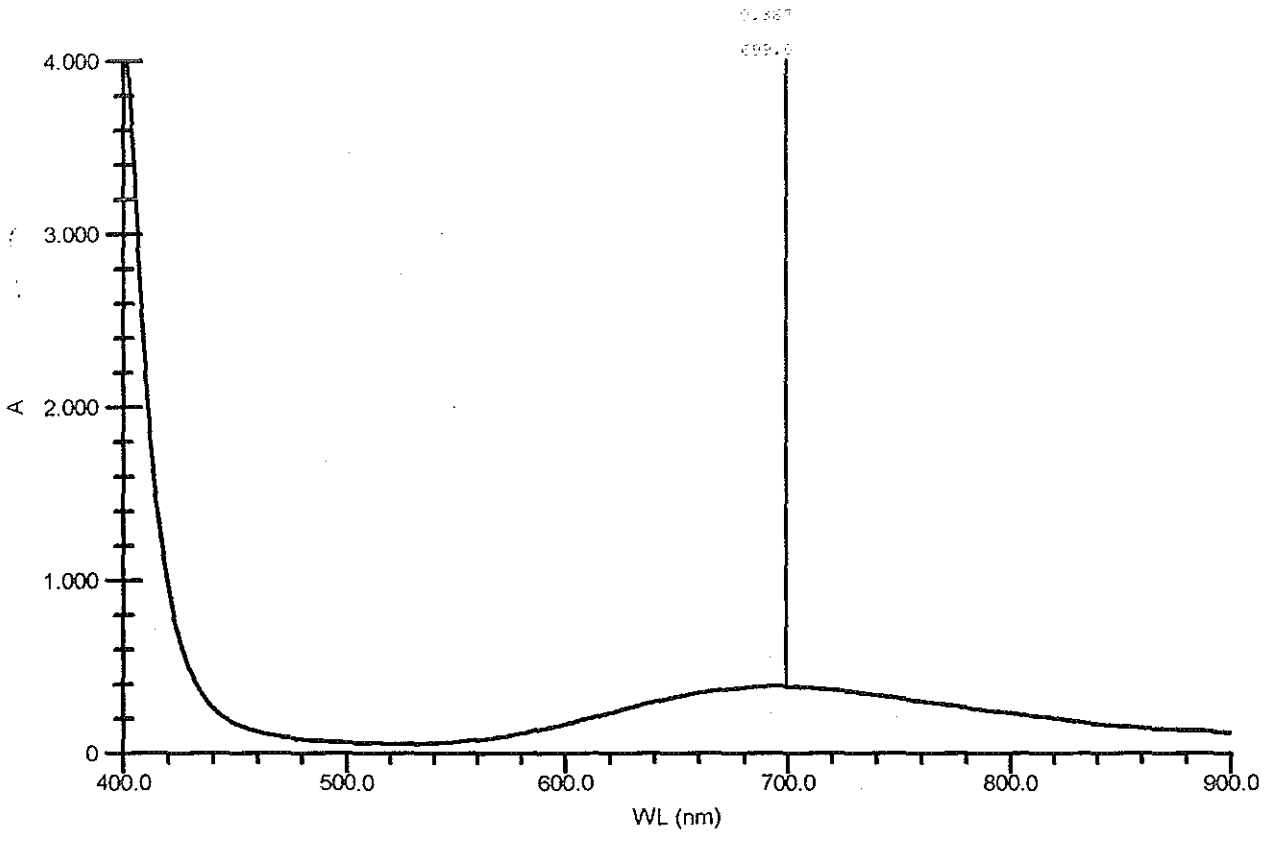

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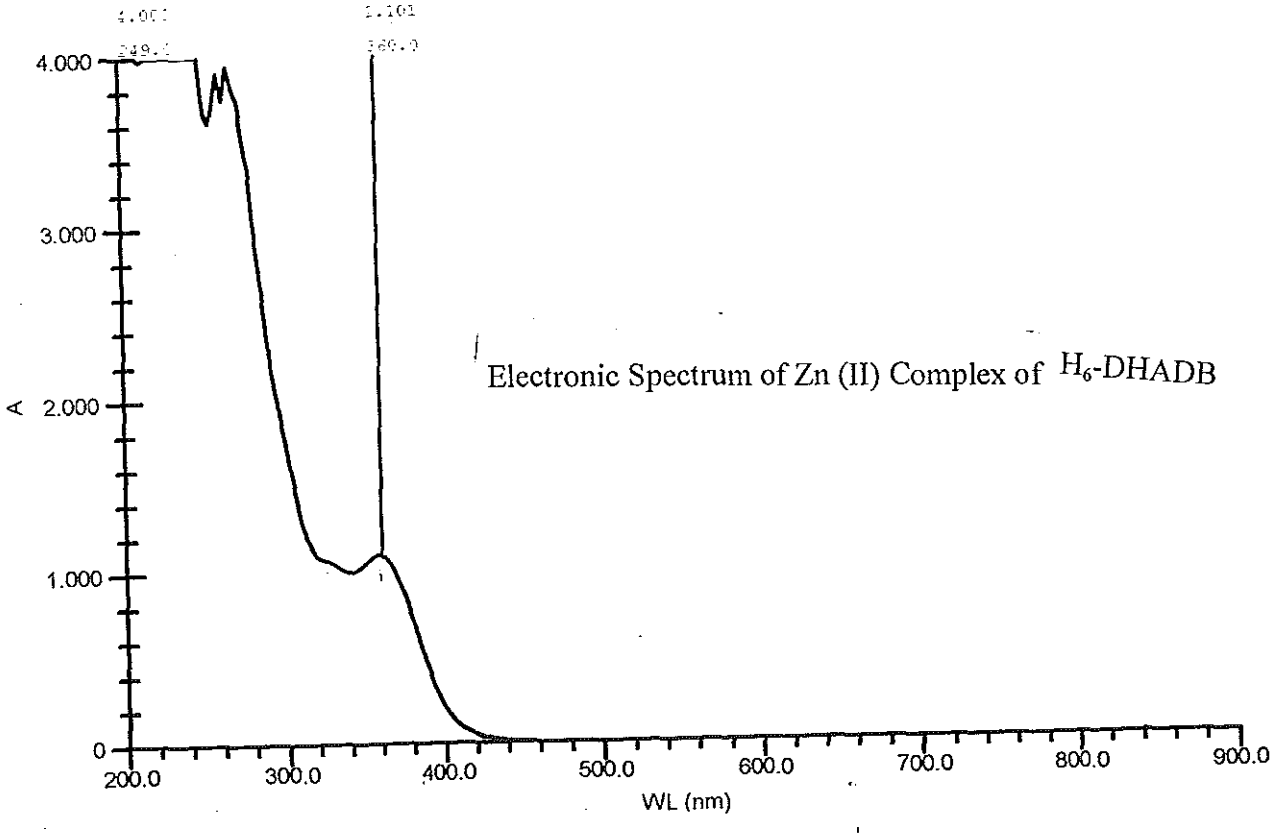

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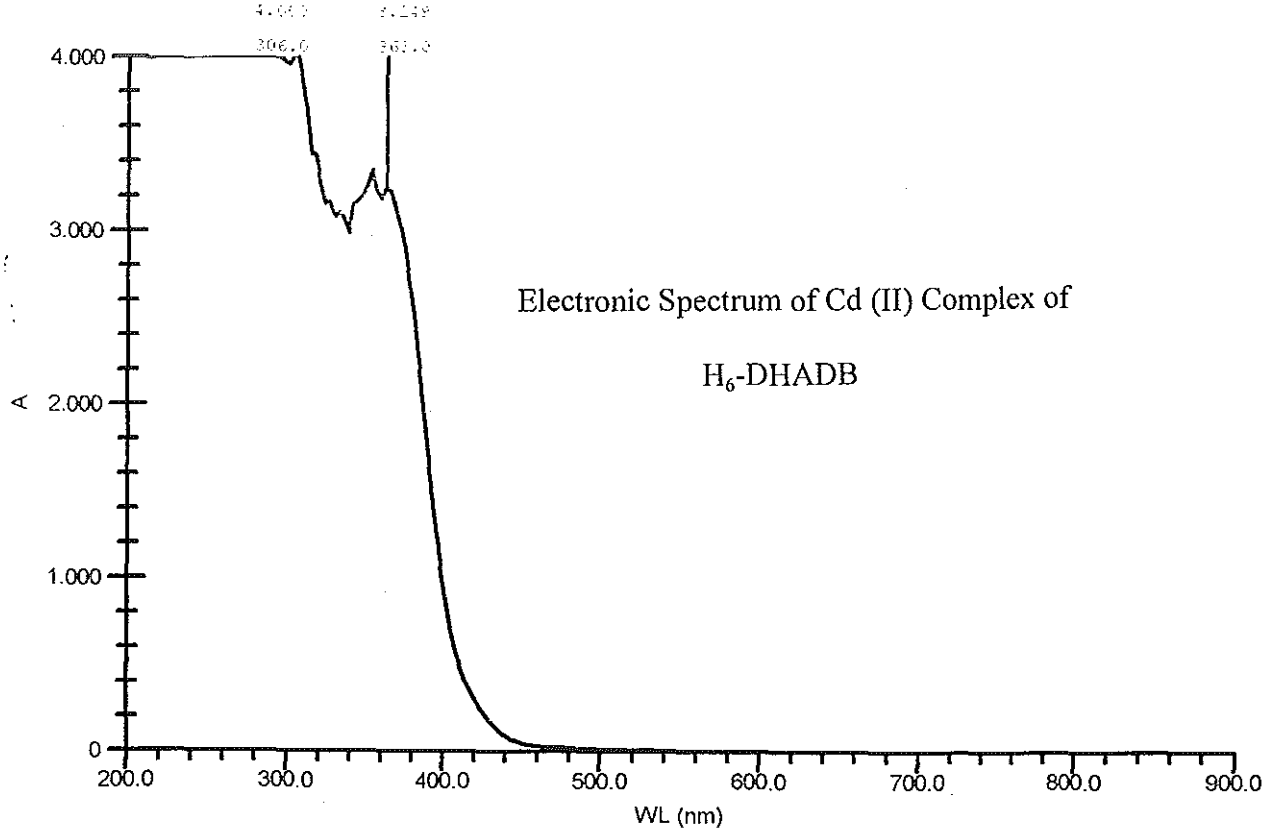

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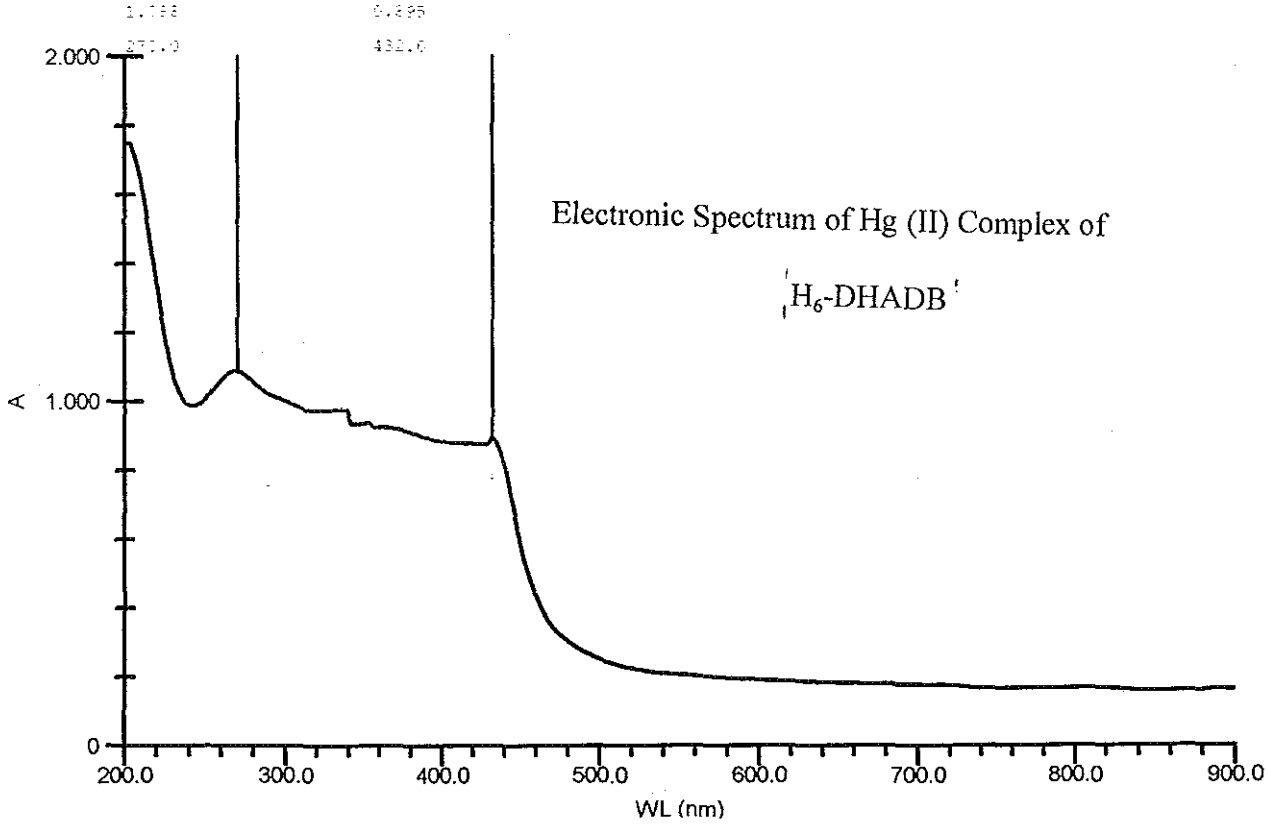

Electronic Spectrum of Hg (II) Complex of H_6-DHADB