1970

Magnetic And Spectroscopic Studies Of Transition Metal Complexes

Hari Shankar Prasad

Recommended Citation

Prasad, Hari Shankar, "Magnetic And Spectroscopic Studies Of Transition Metal Complexes" (1970). *Digitized Theses*. 409.
https://ir.lib.uwo.ca/digitizedtheses/409

MAGNETIC AND SPECTROSCOPIC STUDIES OF TRANSITION METAL COMPLEXES

by

Hari Shankar Prasad

Department of Chemistry

Submitted in partial fulfillment
of the requirement for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Canada
June 1969

ABSTRACT

In Part I, the stereochemistry of nickel(II) complexes of stilbenediamine and related ligands has been discussed. A study of ^1H NMR chemical shifts of stilbenediamine complexes indicates that in solution there exists an equilibrium between diamagnetic and paramagnetic forms of these complexes and that dichloroacetate anions are not coordinated to the nickel atom. The chemical shifts are very much dependent upon the nature of the solvent used. Dimethyl sulfoxide tends to form an addition compound with some of the nickel(II) complexes of stilbenediamine.

The electronic spectra of these complexes has enabled the characterization of two species, namely, diamagnetic and paramagnetic, in solution. The formation of yellow diamagnetic species or blue paramagnetic species in solution depends upon the dielectric constant of the solvents. The bis-meso-2,3-diaminobutane nickel(II) dichloroacetate complex has been found to be octahedral whereas the bis-2,3-dimethyl-2,3-diaminobutane nickel(II) dichloroacetate complex is planar.

Measurements of the magnetic moment of the complexes in solid as well as in solution show that the blue complexes are paramagnetic and the yellow complexes are diamagnetic. The magnetic susceptibility measurements of blue bis-*meso*-stilbenediamine nickel(II) dichloroacetate complex at low temperatures show that the moments are imdependent of temperature, an indication of nickel atoms being octahedrally coordinated.

In Part 2, a series of transition metal complexes of 2,4,5-triphenyl-2-imidazoline(amarine) have been prepared and their properties have been discussed in the light of electronic spectra, magnetic susceptibilities, nuclear magnetic resonance spectra and infrared studies. Zinc(II), cadmium(II) and mercury(II) complexes of amarine differ from the corresponding imidazole complexes in the respect that they do not form the imidazolate type of complexes. Magnetic susceptibility measurements and electronic spectra suggest a halogen-bridged polymeric structure for the bis-2,4,5-triphenyl-2-imidazoline copper(II) halide complexes.

ACKNOWLEDGMENTS

I wish to express my sincere thanks and appreciation to Dr. R. G. Kidd for his invaluable advice and guidance during the course of this work.

I should like to thank the other members of the Faculty and fellow graduate students for their helpful discussions.

I feel indebted to Mr. L.R.Carey for taking some low temperature magnetic moments and to my wife Usha for her help in typing a part of this thesis.

I acknowledge the generous financial assistance of the National Research Council of Canada.

TABLE OF CONTENTS

ABSTRACT iii

ACKNOWLEDGMENTS v

CONTENTS vi

LIST OF TABLES viii

LIST OF ILLUSTRATIONS ix

PART I. THE STEREOCHEMISTRY OF Ni(II) STILBENEDIAMINE COMPLEXES.

Chapter 1. Introduction 1

Chapter 2. Experimental 11

Chapter 3. Results and Discussion 18

- (A) Nuclear Magnetic Resonance Studies 18
  - (i) Diamagnetic Complexes 19
  - (ii) Paramagnetic Complexes 30
- (B) Electronic Spectra 38
  - (i) Survey of Present Knowledge 38
  - (ii) The Effect of Solvent upon Spectra.. 43
  - (iii) Deductions Based upon Observed Dq Values 52
- (C) Susceptibility Studies 54
- (D) Infrared Studies 60

REFERENCES 62

PART 2. TRANSITION METAL COMPLEXES OF AMARINE.

Chapter 1. Introduction 67
Chapter 2. Experimental 72
Chapter 3. Results and Discussion 78
(A) Electronic Spectra 78
(i) Copper Complexes 78
(ii) Cobalt Complexes 82
(iii) Vanadium Complexes 83
(B) Magnetic Susceptibilities 87
(i) Copper Complexes 87
(ii) Cobalt Complexes 88
(iii) Vanadium Complexes 89
(C) Nuclear Magnetic Resonance Studies 89
(D) Infrared Studies 93
(E) Conclusion 98
REFERENCES 100
APPENDIX 102
VITA xii

LIST OF TABLES

PART I.

Table 1. Chemical Analyses of the Ni(II) Complexes ... 16

Table 2. ^1H NMR Chemical Shifts 27

Table 3. Electronic Absorption Spectra of Blue I Ni(ms-stien)$_2$(dca)$_2$.4H$_2$0 44

Table 4. Electronic Absorption Spectra of Ni(II) Complexes in DMSO 46

Table 5. Electronic Absorption Spectra of Ni(II) Complexes in CHCl$_3$ 47

Table 6. Electronic Absorption Spectra of Ni(II) Complexes of 2,3-diaminobutane and 2,3-dimethyl-2,3-diaminobutane 50

Table 7. Magnetic Moments of Yellow I Ni(ms-stien)$_2$-(dca)$_2$.2H$_2$0 56

Table 8. Magnetic Moments of Ni(II) Complexes 57

PART 2.

Table 1. Diffuse Reflectance Spectra and Room Temperature Magnetic Moments 84

Table 2. Principal Infrared Absorption Bands 94

LIST OF ILLUSTRATIONS

PART I.

Figure 1. Blue I Ni(*ms*-stien)$_2$(dca)$_2$.$4H_2O$ 2

Figure 2. Planar Ni(*ms*-stien)$_2$(dca)$_2$ Complex in
Yellow II Crystals 2

Figure 3. Stilbenediamines 4

Figure 4. ^1H NMR Spectrum of *ms*-stilbenediamine 21

Figure 5. ^1H NMR Spectrum of Zn(*ms*-stien)$_2$(dca)$_2$ 21

Figure 6. ^1H NMR Spectrum of Ni(*ms*-stien)$_2$(ClO_4)$_2$ 24

Figure 7. ^1H NMR Spectrum of Ni(*r*-stien)$_2$(ClO_4)$_2$ 24

Figure 8. ^1H NMR Spectrum of Ni(*ms*-stien)$_2$(dca)$_2$.
$2H_2O$ (Yellow I) in DMSO-d_6 25

Figure 9. ^1H NMR Spectrum of Ni(*ms*-stien)$_2$(dca)$_2$.
$2H_2O$ (Yellow I) in $CHCl_3$ 26

Figure 10. ^1H NMR Spectrum of Blue i Ni(*ms*-stien)$_2$-
(dca)$_2$. $4H_2O$ in
(A) DMSO-d_6 32
(B) DMSO 33

Figure 11. ^1H NMR Spectrum of Blue I Ni(*ms*-stien)$_2$-
(dca)$_2$.$4H_2O$ in $CHCl_3$ 33

Figure 12. ^1H NMR Spectrum of Yellow II Ni(*ms*-stien)$_2$(dca)$_2$.
2/3 C_2H_5OH. 4/3 H_2O in $CHCl_3$ 34

Figure 13. ^{1}H NMR Spectrum of Yellow II Ni(<u>ms</u>-stien)$_2$-(dca)$_2$. 2/3 C_2H_5OH. 4/3 H_2O in $CHCl_3$ 35

Figure 14. ^{1}H NMR Spectrum of Ni(<u>l</u>-stien)$_2$(dca)$_2$...... 35

Figure 15. Energy Level Diagram for Octahedral Ni(II) Complexes 39

Figure 16. The Effects of Geometrical Distortions on the Energy Levels of Octahedral Ni(II) 40

Figure 17. Energy Level Diagram for Ni(II) Complexes in Planar D_{4h} Symmetry 41

Figure 18. Electronic Absorption Spectrum of Ni(<u>ms</u>-bn)$_2$(dca)$_2$.2H_2O 48

Figure 19. Electronic Absorption Spectrum of Ni(<u>l</u>-stien)$_2$(dca)$_2$ 49

Figure 20. Temperature versus Reciprocal Magnetic Susceptibility 59

Figure 21. Infrared Sectra 61

PART 2.

Figure 1. Energy Diagram for a Copper(II) ion 79

Figure 2. Electronic Absorption Spectrum of Cu(am)$_2$Br$_2$ 81

Figure 3. Energy Level Diagram for a d^7 ion(Co^{2+}) ... 83

Figure 4. Energy Level Diagram for d^2 Octahedral Configuration 86

Figure 5. Electronic Absorption Spectrum of V(IZH)$_6$Cl$_3$ 86

Figure 6. Imidazole 89

Figure 7. Amarine 90

Figure 8. ^{1}H NMR Spectrum of Amarine in $CDCl_3$ 91

Figure 9. ^{1}H NMR Spectrum of $Hg(am)_2Cl_2$ 91

Figure 10. Structure of Polymeric Compounds of
Zn(II),Cd(II), and Hg(II) 92

PART I

CHAPTER I

INTRODUCTION

During the past few years, considerable effort has been directed towards the elucidation of the molecular structure of the Lifshitz complexes of nickel and the stereochemistry of the metal ion in these compounds. These complexes, which are formed by a large number of nickel salts with meso and racemic 1,2-diamino-1,2-diphenylethane (stilbenediamine = stien) have the general formula $Ni\ (stien)_2X_2$, often containing solvent of crystallisation. It has been found that these complexes exist in either a blue paramagnetic form ($\mu_{eff} = 3.1$ B.M.) or a yellow diamagnetic or sometimes weakly paramagnetic form. The existence of the above forms can be related to the nature of the anion, X, and to a lesser extent to the stereoisomerism of the diamine. The occurrence of both blue and yellow forms containing the same anion, X, becomes more interesting because of the interconvertibility of the two forms.

The relationship among the magnetic properties, colours and structures of the above mentioned compounds is now fairly well understood. The X-ray crystal structure

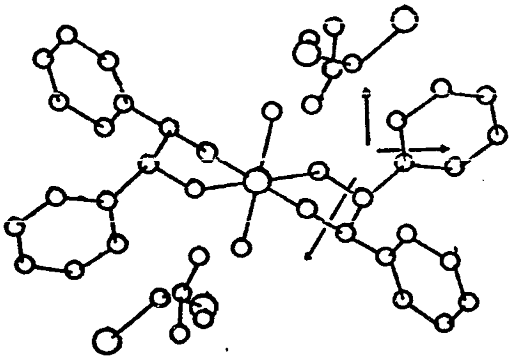


Figure 1. Blue I Ni(*ms*-stien)$_2$(dca)$_2$· 4H$_2$O[1].

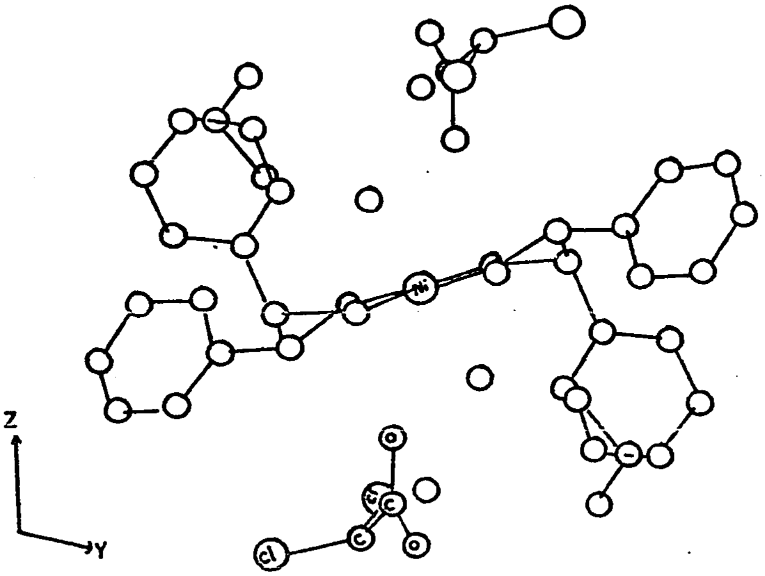
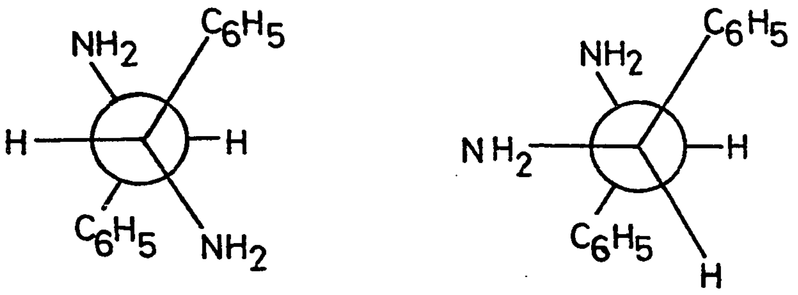


Figure 2. An isolated planar Ni(*ms*-stien)$_2$(dca)$_2$ complex in yellow (II) crystals[1].

analysis of Blue I Ni(ms-stien)$_2$ (dca)$_2$.4H_2O (dca = dichloroacetate) suggests that nickel is octahedrally coordinated and the axial positions are occupied not by dichloroacetate ions, but by two water molecules (Figure 1). Similarly, Yellow (II) Ni(ms-stien)$_2$ (dca)$_2$.2/3 C_2H_5OH.-4/3 H_2O is shown to contain two paramagnetic (in octahedral coordination) nickel atoms and one diamagnetic (planar coordination) nickel atom. An isolated planar Ni(ms-stien)$_2$-(dca)$_2$ complex in Yellow (II) crystals is shown in Figure 2.

As long ago as 1939, Lifshitz, Bos and Dijkema[2] noticed that the colour of these complexes could not be related to the presence or absence of crystal water, as both salts exist in the anhydrous yellow and blue forms, while there are also blue and yellow forms with the same water content. It has been observed[3] that the racemic and active modifications of the base tend to form the blue coordination compounds with nickel salts while the meso modification tends to form the yellow isomer. This difference in behaviour is attributed to stereoisomerism in the metal-base complex; the stable blue form has the two phenyl groups in a trans position (Figure 3a), whereas the cis form (Figure 3b) is unstable owing to steric hindrance between the two phenyl groups and may lead to the isomeric pseudo-coordination compound.

The salts of Ni(ms-stien)$_2X_2$, where the anion X^- is from a weak acid of the type RCOOH (R = H-, CH_3-, CH-, Cl_2-, etc.), are of considerable interest, as they possess[4] different modifications of blue and yellow forms. Ballhausen and Liehr[5] commenting on the anomalous behaviour of these



(a) <u>meso</u> (b) <u>racemic</u> or <u>levo</u>

FIGURE 3. Stilbenediamine.

nickel (II) complexes have suggested a RCO_2^- bridging in the blue pseudo- octahedral complexes, perhaps having the formula $[Ni_2(stien)_4(RCO_2^-)]_2^{++}$ $(RCO_2^-)_2$ and a solid phase break up of the RCO_2^- bridges in the yellow complex forming Ni $(stien)_2^{++}$ groups. Although the suggestion of tetrahedral coordination for the paramagnetic compounds has been made from time to time, it is an established fact that tetrahedral complexes of nickel are usually produced when the steric and/or bonding requirements of ligands make an octahedral configuration unfavourable despite the increased crystal field stabilization energy of this arrangement compared with a tetrahedral arrangement. The stilbenediamine and related ligands do not show any 'steric' reason and hence no preference for tetrahedral coodination.

The behaviour of these complexes in solution (in both coordinating and non-coordinating solvents) is quite interesting. The colour changes which are accompanied by corresponding changes in magnetic properties are similar to those observed in other "anomalous" nickel complexes[6-8]. These complexes, which are diamagnetic in the solid, become paramagnetic in solution or on heating and in some cases show temperature dependent magnetic moments and spectra. Several mechanisms[7,9] have been put forward to explain this type of behaviour but in the present case it has been suggested[2,10] that the variations in colour and magnetism are brought about by changes in the axial environment of the planar $\mathrm{Ni\,(stien)_2^{2+}}$ entity, due to the removal or addition of anions or solvent molecules, causing a change in the tetragonality of the complex. It is also interesting to note that some of these complexes show a dynamic equilibrium between diamagnetic and paramagnetic forms[11].

The nuclear magnetic resonance technique can be an important tool in investigating the effect of addition, substitution or removal of donor ligands at the axial positions of these complexes. The study of diamagnetic species furnished by diamagnetic complexes in solution presents no problem. In the case of paramagnetic ions obtained by dissolving either diamagnetic or paramagnetic complexes in a suitable solvent, the nature of complex ions in solution can be studied with the help of ^1H nuclear magnetic resonance spectra provided conditions are such that either or both the following inequalities are satisfied,

$$\frac{1}{T_1} \gg a \quad , \quad \frac{1}{T_e} \gg a$$

where T_1 is the electron spin relaxation time of the paramagnetic system, T_e is the characteristic exchange time between the paramagnetic and diamagnetic molecules, and a is a nucleus-electron contact-interaction constant. Furthermore, the equilibrium between diamagnetic and paramagnetic forms of the chelate in solution can easily be studied with the help of contact-interaction shifts of the chelates.[12] Contact-interaction shifts are given by

$$\left(\frac{\Delta H}{H}\right)_i = -a_i \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{2SkT[\exp(\Delta F/RT)+3]} \qquad (I)$$

where γ_e and γ_H are, respectively, magnetogyric ratios for the electron and proton, ΔF is the free energy for the diamagnetic $\rightleftharpoons$ paramagnetic equilibrium and the other symbols have their usual significance.

Useful evidence regarding the nature of these compounds can also be obtained from detailed spectroscopic and susceptibility measurements. Furlani and Sartoni[13] have shown from a study of the visible absorption spectra that the nickel atoms are probably octahedrally coordinated in the blue complexes. A comparison of the experimental values with theoretical values obtained by calculations done for various possible structures with the aid of Hartmann's theory of the electrostatic complexes (strong-field and weak-field case); shows a distorted octahedral structure for blue forms with two further ligand groups in <u>cis</u> or <u>trans</u> positions. The three main bands which occur at 10,300 , 16,700 and 26,900 cm^{-1}, are assigned to the three spin-allowed transitions, well established for the majority of octahedral Ni(II) complexes[14]; namely,

$$^3A_{2g} \longrightarrow {}^3T_{2g} \quad (\nu_1);$$

$$^3A_{2g} \longrightarrow {}^3T_{1g} \quad (F)(\nu_2);$$

$$^3A_{2g} \longrightarrow {}^3T_{1g} \quad (P)(\nu_3).$$

The single absorption maximum observed at 22,600 cm^{-1} for yellow diamagnetic complexes is assigned to the transition

$$^1A_{1g} \longrightarrow {}^1A_{2g} \quad (G)$$

A detailed study of electronic spectra of blue and yellow complexes of $Ni(\underline{ms}\text{-stien})_2(dca)_2$ in chloroform and acetone solvents has been done by Nyburg and his coworkers[15]. The addition of water to a solution of the blue complex in acetone favours the formation of the yellow complex in solution and the equilibrium between the two species (diamagnetic and paramagnetic) may be written as

$$\underset{\text{Blue Paramagnetic}}{Ni(\underline{ms}\text{-stien})_2\,(Cl_2CHCOO)_2} + H_2O \rightleftharpoons \underset{\text{Yellow Diamagnetic}}{Ni(\underline{ms}\text{-stien})_2^{2+} + 2\,(Cl_2CHCOO)^-}. \quad (II)$$

The molar extinction coefficient of the absorption band at 22,600 cm^{-1} helps to calculate the amount of yellow diamagnetic form present in the solution.

Recently a great amount of work has been done on the magnetochemical studies of Ni(II) complexes[16-17]. A simple measurement reveals the diamagnetic or paramagnetic nature of the complex under study. These magnetic properties in conjunction with the ligand and crystal field theories of coordination compounds provide pertinent information regarding the stereochemistry of the nickel complexes both in solution and in the solid state. Thus, the anomalous magnetic behaviour of Ni(II) complexes of Schiff's bases has been explained as due to a dynamic equilibrium between two conformations, square planar and tetrahedral. In the case of paramagnetic complexes, the magnetic susceptibilities of the compounds in solution can be measured with the help of the nuclear magnetic resonance technique. Evans[18] has determined the paramagnetic susceptibility of a number of inorganic compounds in aqueous as well as inert solvents. The mass susceptibility, X, of the dissolved substance is given by the expression

$$X = \frac{3\Delta f}{2\pi f m} + X_o + \frac{X_o(d_o - d_s)}{m} \qquad (III)$$

where Δf is the frequency separation between the two lines (line due to pure solvent and the line due to solvent in presence of paramagnetic ion) in cycles/sec., m is the mass of substance contained in 1 ml. of solution, χ_0 is the mass susceptibility of the solvent, d_o is the density of the solvent and d_s that of solution. The advantage of this method is that only a small amount of the sample is required to obtain a reasonable spectrum.

It is not surprising to notice that only a little work has been done on the infrared spectra of the stilbenediamines and their complexes. For the study of these complex molecules, the full theoretical treatment involves difficult and unwieldy computations. However, a comparison can be made with ethylenediamine complexes of transition metals[19]. Goodgame and Hitchman[20] have examined the infrared spectra of the diamagnetic complex $Ni(stien)_2(ClO_4)_2$ with triphenyl phosphine oxide $(C_6H_5)_3PO$, tripheyl arsine oxide $(C_6H_5)_3AsO$ and dimethyl sulfoxide (DMSO) to obtain the information concerning the role of these ligands.

Finally, a study of the chelating tendency of C-substituted ethylenediamines with Ni(II) salts of the type $Ni(RCOO)_2$, where R = Cl_2CH-, C_6H_5CH-, CH_3- etc., is of interest especially from the structural point of view. Ni(II) complexes of ms-2,3-diaminobutane forms only blue complexes whereas 2,3-dimethyl-2,3-diaminobutane forms only yellow diamagnetic complexes.

In this thesis, interest has centered upon:

(a) The study of ^1H nuclear magnetic resonance spectra of these complexes in solution.

(b) A systematic study of electronic spectra of complexes $Ni(L)_2X_2$, where L = <u>meso</u>, <u>racemic</u> and <u>levo</u>-stilbenediamines, 2,3-diaminobutane and 2,3-dimethyl-2,3-diaminobutane.

(c) Magnetic susceptibilities

and finally preparations of some new complexes and their structure determinations.

CHAPTER 2

EXPERIMENTAL

(a) Preparation of ligands:

The following ligands were prepared by the methods already reported in the literature.

(i) meso-stilbenediamine[21]: A mixture of ammonium acetate and benzaldehyde was refluxed for three hours. The white precipitate N-benzoyl-N^1-benzylidine meso-1,2-diphenyl-ethylenediamine (I) thus formed was hydrolysed by dilute sulfuric acid.

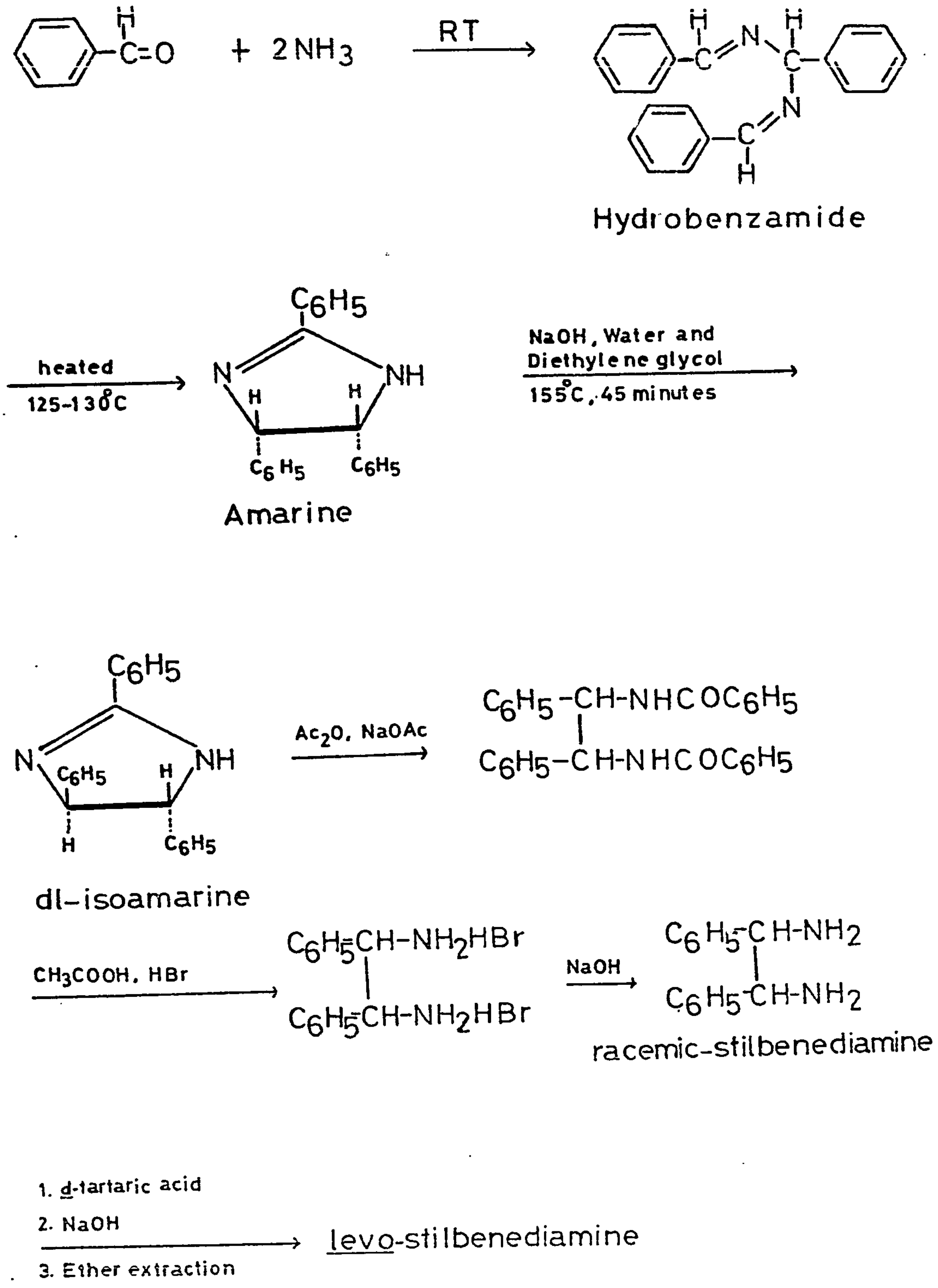
$$2\ \mathrm{Ph.CHO} + 2\ \mathrm{CH_3.COONH_4} \rightarrow \mathrm{Ph.CH(N{:}\underset{(I)}{CHPh}).CHPh.NH.COPh}$$

$$\mathrm{Ph.CH(N{:}CHPh).CHPh.NH.COPh} \rightarrow \mathrm{Ph.CH(NH_2).CHPh(NH_2)}$$

(II)

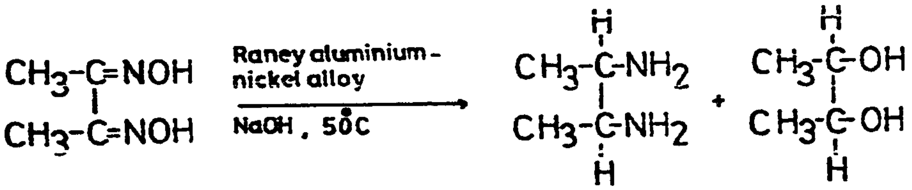
free amine was obtained by neutralising the acid mixture with ammonia. It was then extracted with ether, dried and recrystallised from petroleum ether. m.p. 119°c.

(ii) racemic- and levo-stilbenediamines[22]. These compounds were prepared by the following schemes.



C=O
+ 2NH3
RT
Hydrobenzamide
heated
125-130°C
Amarine
NaOH, Water and
Diethylene glycol
155°C, 45 minutes
dl-isoamarine
Ac2O, NaOAc
C6H5-CH-NHCOC6H5
C6H5-CH-NHCOC6H5
CH3COOH, HBr
C6H5CH-NH2HBr
C6H5CH-NH2HBr
NaOH
C6H5-CH-NH2
C6H5-CH-NH2
racemic-stilbenediamine
1. d-tartaric acid
2. NaOH
3. Ether extraction
levo-stilbenediamine

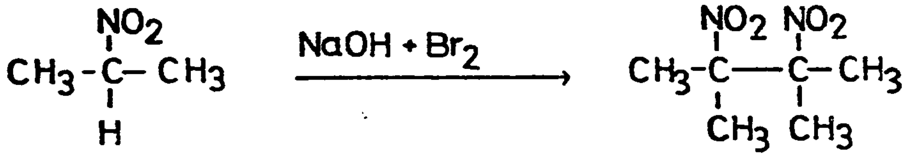
(iii) 2,3-diaminobutane[23].



dimethylglyoxime meso- and DL-2,3-diaminobutane.

<u>meso</u>-2,3-diaminobutane was separated from DL form by fractional crystallisation, <u>meso</u>- form being more soluble in aqueous methanol than the DL-isomer.

(iv) 2,3-dimethyl-2,3-diaminobutane[24].



2-nitropropane 2,3-dimethyl-2,3-dinitrobutane

2,3-dimethyl-2,3-diaminobutane

(b) Preparation of nickel complexes:

Nickel salts of weak acids of the type Ni (RCOO)$_2$, where R = H-, CH$_3$-, CHCl$_2$-, Cl$_2$CH- etc., were prepared by neutralising corresponding acids with an excess of freshly precipitated nickel hydroxide. The temperature of the mixture was always kept below 60°C. The crystals were separated by slow evaporation of the solution and finally dried at room temperature under vacuum.

The complexes were prepared by the methods already described in the literature. Yellow I $Ni(\underline{ms}\text{-stien})_2(dca)_2 \cdot 2H_2O$, was prepared by drying Blue I $Ni(\underline{ms}\text{-stien})_2(dca)_2 \cdot 4H_2O$ at about 80°C under vacuum. Nickel complexes of the type $Ni(L)_2(dca)_2$, where L = racemic- or levo-stilbenediamines were prepared by mixing an alcoholic solution of nickel salt. The crystals were separated by filtration and dried under vacuum. The solid "adduct" of $Ni(stien)_2(ClO_4)_2$ with dimethyl sulfoxide was obtained by dissolving the respective $Ni(stien)_2(ClO_4)_2$ complexes in the minimum volume of hot dimethyl sulfoxide. The resulting solution was left under vacuum over sulfuric acid until a solid formed. This was filtered and dried under vacuum at 70-80°C to constant weight.

With 2,3-diaminobutane and 2,3-dimethyl-2,3-diaminobutane, complexes were obtained from aqueous media.

(c) Analysis of metal complexes:

The complexes were analysed for nickel by precipitating nickel dimethylglyoxime complex from the solution and weighing as such after drying at 120-130°C. Halogens were estimated as silver halides by the standard gravimetric method. Microanalysis for carbon, hydrogen and nitrogen were done by Mr. A.B.Gygli in the microanalysis laboratory, Toronto. The analytical results are shown in Table (I).

(d) Magnetic susceptibility measurements:

Bulk susceptibility measurements were made at room temperature, using a Gouy balance. The Gouy tube was caliberated with $HgCo(NCS)_4$ using the data of Figgis and Nyholm[25]. All measurements were carried out three times, the replicate measurements involving a repacking of the tube. The diamagnetic corrections were computed from Pascal's contants[26]. The susceptibilities of the complexes in solutions were determined from the differences between those of the pure solvents and the solutions, according to the formula

$$\chi_g \text{ complex} = \left[\chi_g(\text{solution}) - \chi_g(\text{solvent})(1-X)\right] / X. \quad \text{---(IV)}$$

where X = fraction by wt. of complex in solution. The determination of paramagnetic susceptibility of the complexes in solution by n.m.r. method was done at 60 Mc/sec. on a Varian A 60 spectrometer using a precision coaxial glass n.m.r. tube obtained from 'The Wilmad Glass Company', Landisville, N.J. In this case the sample dissolved in chloroform was kept in the outer tube and the solvent chloroform in the inner tube which served as a reference. The magnetic moments obtained for various nickel complexes

TABLE 1.

Chemical analyses of the Ni(II) complexes.

Complex	Calculated				Found			
	Ni	Cl	C	H	Ni	Cl	C	H
Ni(ms-stien)$_2$(ClO$_4$)$_2$	8.61	-	49.30	4.72	8.59	-		
Ni(r-stien)$_2$(ClO$_4$)$_2$	8.61	-	49.30	4.72	8.70	-		
Ni(r-stien)$_2$(ClO$_4$)$_2$·4DMSO	5.90	-	43.47	5.67	5.92	-		
Yellow I								
Ni(ms-stien)$_2$(dca)$_2$·2H$_2$O	7.57	-	49.58	4.94	7.61	-	50.49	4.96
Blue I								
Ni(ms-stien)$_2$(dca)$_2$·4H$_2$O	7.2	17.50	47.3	5.16	7.00	17.38	47.50	5.18
Ni(l-stien)$_2$(dca)$_2$	7.94	-	51.99	4.63	8.02	-	52.10	4.60
Ni(r-stien)$_2$(dca)$_2$	7.94	-	51.99	4.63	7.96	-	52.21	4.62
Ni(ms-bn)$_2$(dca)$_2$·2H$_2$O	11.13	26.91	27.35	5.75	11.12	27.11		
Ni(tetrameen)$_2$(dca)$_2$	10.73	25.92	35.13	6.26	10.69	26.13		

are listed in the Table [illegible].

[illegible] Spectroscopic Measurements

Infrared spectra were recorded as [illegible] [illegible] using Beckman [illegible] and Beckman [illegible] spectrometers. Reflectance and solution spectra were obtained with Beckman [illegible] single beam and Beckman [illegible] double beam spectrophotometers. The NMR spectra were run either on a Varian DP-60, a Varian HA-60 or a Varian A-60 high resolution spectrometer. Chemical shift measurements on a DP-60 instrument or on a HA-60 instrument, were made using the audio-side band technique. The chart paper was calibrated by recording the sweep frequencies directly from the spectrometer and subtracting the manual oscillator frequency from the sweep frequencies.

[illegible]

Spectroscopic Measurements

Infrared spectra were recorded on [illegible] [illegible] Model [illegible] [illegible] spectrophotometers. Ultraviolet and visible spectra were obtained with [illegible] [illegible], [illegible] and Beckman DK2 double beam spectrophotometers. The NMR spectra were run either on a Varian A-60, a Varian HA-100 or a Varian [illegible] high resolution spectrometer. Chemical shift measurements on a A-60 instrument or on a HA-100 instrument were made using the audio-side band technique. The chart paper was calibrated by recording the sweep frequencies directly from the spectrometer and subtracting the manual oscillator frequency from the sweep oscillator.

CHAPTER 3

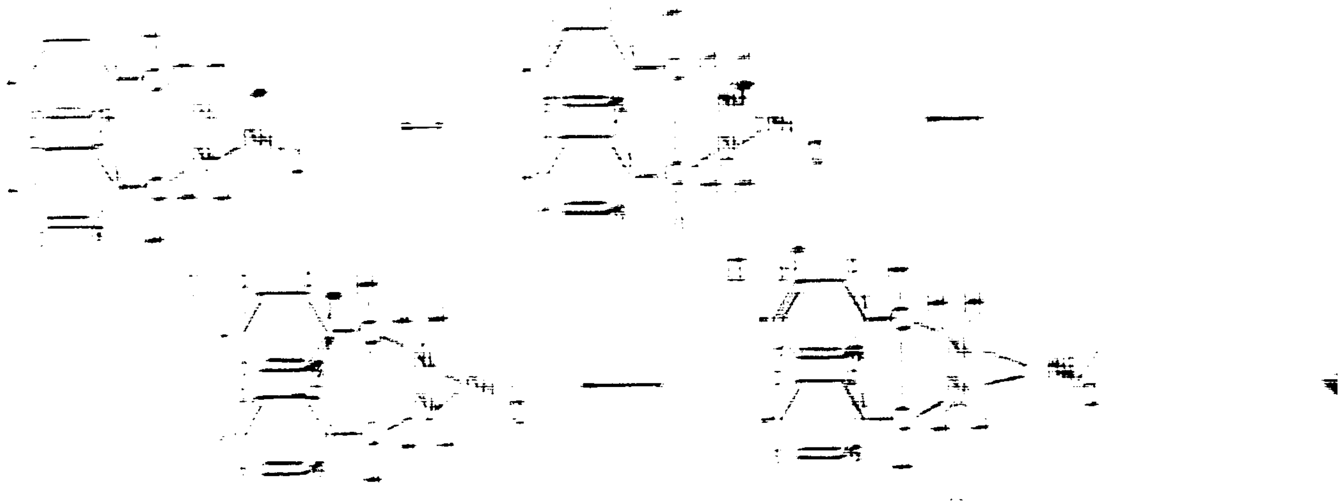
RESULTS AND DISCUSSION

A. Nuclear Magnetic Resonance Studies:

Isotropic ^{1}H resonance shifts of Ni(II) complexes have been reported in the literature[16-17,28,29] and the conditions have been discussed[12,30]. The proton resonance spectra of the stilbenediamine complexes show large shifts to high and low fields relative to the resonance positions of the free base. All contact shifts were measured at 60 Mc. sec. relative to TMS. The spectrum of *ms*-stilbenediamine in two solvents viz. deuterochloroform and dimethyl sulfoxide is shown in Figure 4. The appearance of amino protons at comparatively high field could be explained as due to shielding of these protons by two bulky aromatic rings. The assignments of signals given in Table 1 are based on relative area considerations.

B. Distribution of spin densities.

Eaton, Phillips *et al.*[illegible] have very elegantly described the mechanism for effecting paramagnetic spin densities at different carbon atoms of an aromatic [illegible] in the [illegible] of the [illegible]. The [illegible] of [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] suggested by [illegible] and [illegible][22]. The following valence bond structures involving formal charges are of importance.



I

II

For the odd-alternant chelate ring system these structures predict positive spin densities at 1,3 and 5-carbon atoms, whereas 2-C, 4-C and 6-C acquire negative spin densities through electron correlation effects. Further, McConnell and Chesnut[22] have suggested an indirect π-σ spin polarization mechanism for the transfer of spin densities to the attached protons. Hence, 1-H, 3-H and 5-H will possess [illegible] [illegible] and 2-H and 4-H positive [illegible] [illegible].

[illegible] Diamagnetic complexes

Considered first are the diamagnetic complexes [illegible] [illegible]. In all the spectra, the signal [illegible] [illegible]

[illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] which [illegible] the ligand [illegible] gradually. The [illegible] of [illegible] [illegible] complex in DMSO shows a shift of [illegible] [illegible] [illegible] complex and a shift of [illegible] [illegible] [illegible] with respect to the free ligand (Figure 5). These shifts can be explained easily with the help of [illegible] of [illegible]. This in turn indicated a transfer of negative charge towards the central atom.

(a) [illegible]

The complex [illegible] behaves in the same way as [illegible]. The n.m.r. of this complex in DMSO does not show any [illegible] paramagnetic ion or two different types of dimethyl sulfoxide, i.e. DMSO coordinated to the metal ion and the bulk solvent (Figure 6).

b. [illegible]

The shift of the DMSO peak observed in the [illegible] resonance spectrum of [illegible] in DMSO-[illegible] indicates that either the solvent molecules are coordinated to the metal atom, thereby changing the geometry of the molecule of the complex changes from planar to [illegible] [illegible] (Figure 7). That this complex forms an adduct with DMSO is supported by [illegible] and [illegible]. The adduct has the formula [illegible] and the magnetic moment is [illegible] B.M. Moreover, the electronic spectrum of the complex in DMSO suggests that the complex is octahedrally coordinated in the solution. [illegible]

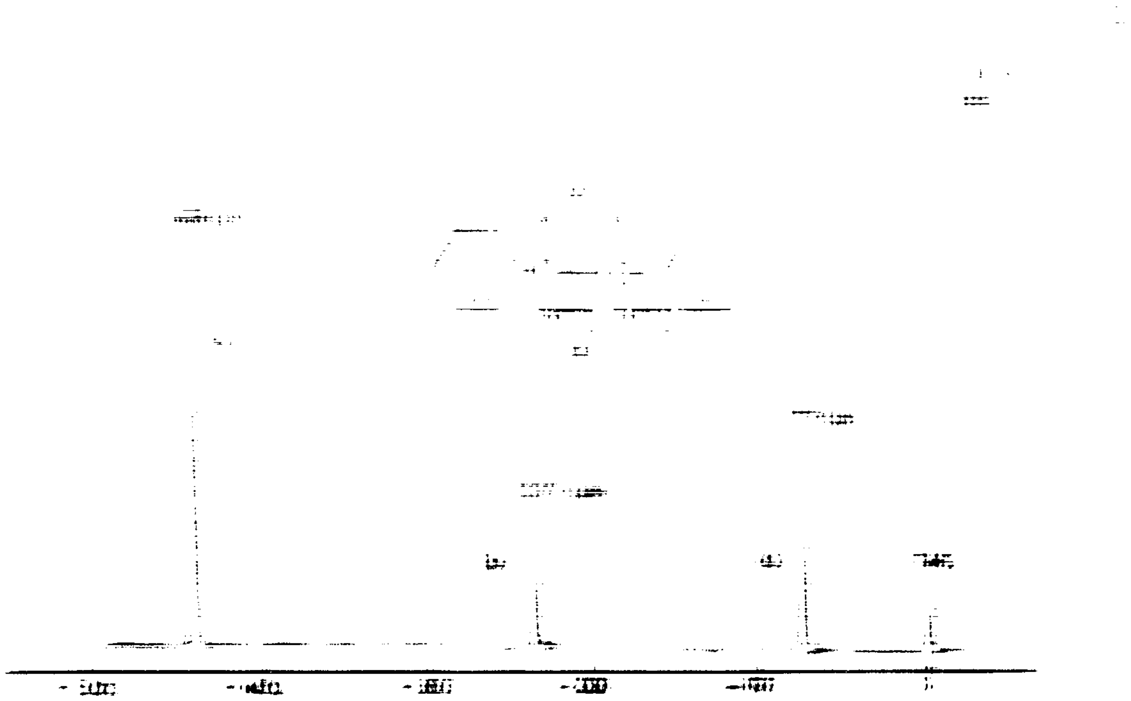
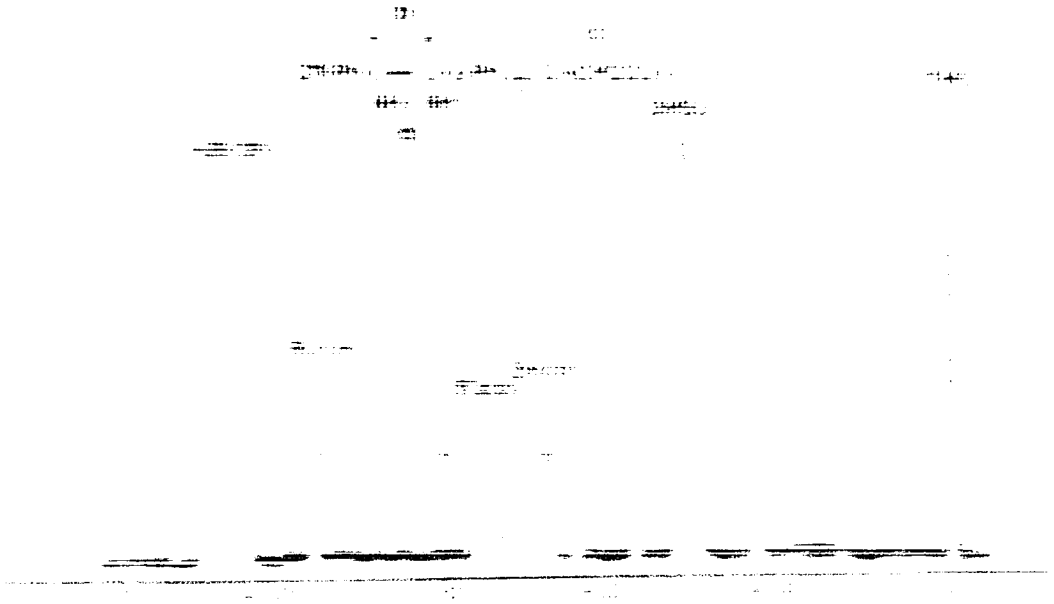
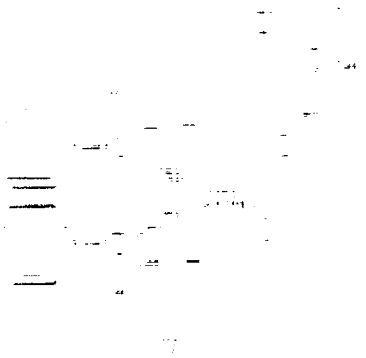


Figure 4. [illegible] NMR Spectrum of [illegible]

in [illegible]



[illegible]



The theory predicts that the [illegible] [illegible] of [illegible] which in structure I will be shifted upfield. Experimentally only one peak is observed on the higher field side which is confirmed as due to $-NH_2$ protons. Similarly, for structure II the water protons will be shifted upfield. The spectrum does not show any evidence of water protons. Therefore, it appears that either the protons in a bonded amino group are exchanging with water protons faster than [illegible] sec^{-1} or the signals due to $-NH_2$ protons and H_2O protons coalesce with each other.

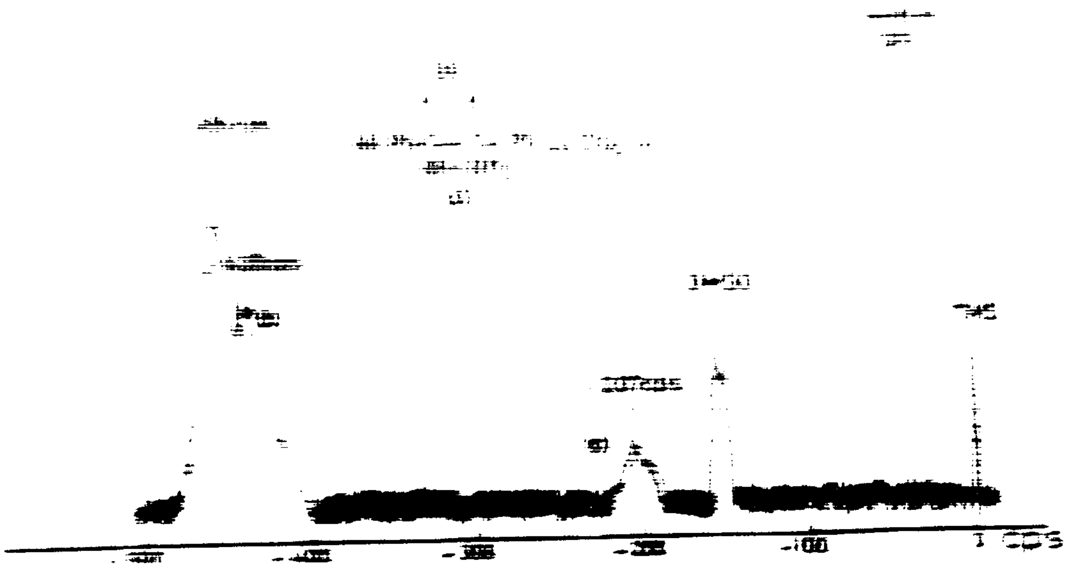


FIGURE 4. ¹H NMR Spectrum of Ni(ms-atien)$_2$(ClO$_4$)$_2$ in DMSO-d$_6$.

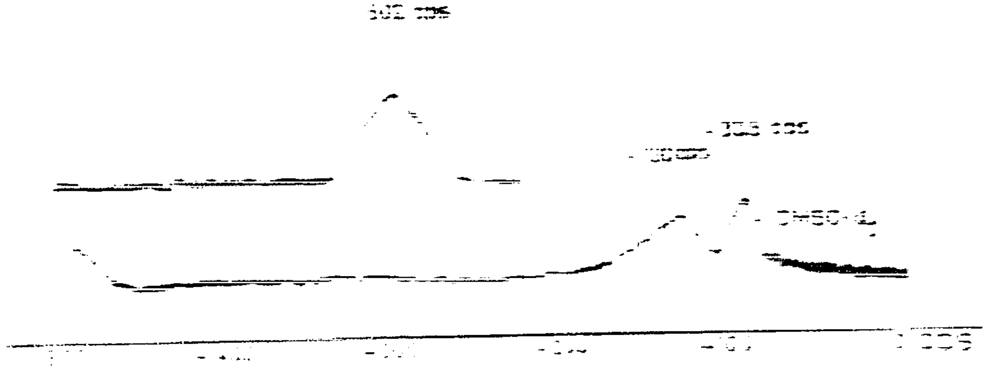


FIGURE 5. ¹H NMR Spectrum of Ni([illegible]-atien)$_2$(ClO$_4$)$_2$ in DMSO-d$_6$.

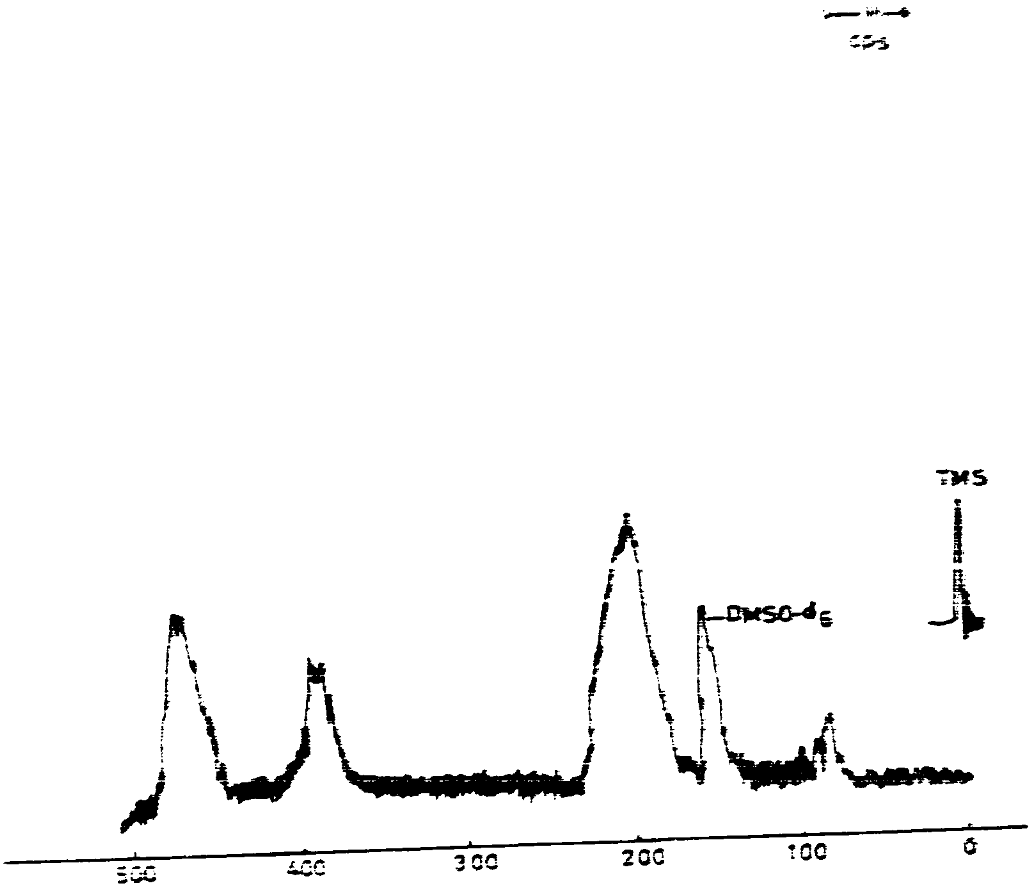


FIGURE 8. ^{1}H NMR Spectrum of Ni(*ms*-stien)$_2$·(dca)$_2$·2H$_2$O (Yellow I) in DMSO-d$_6$.

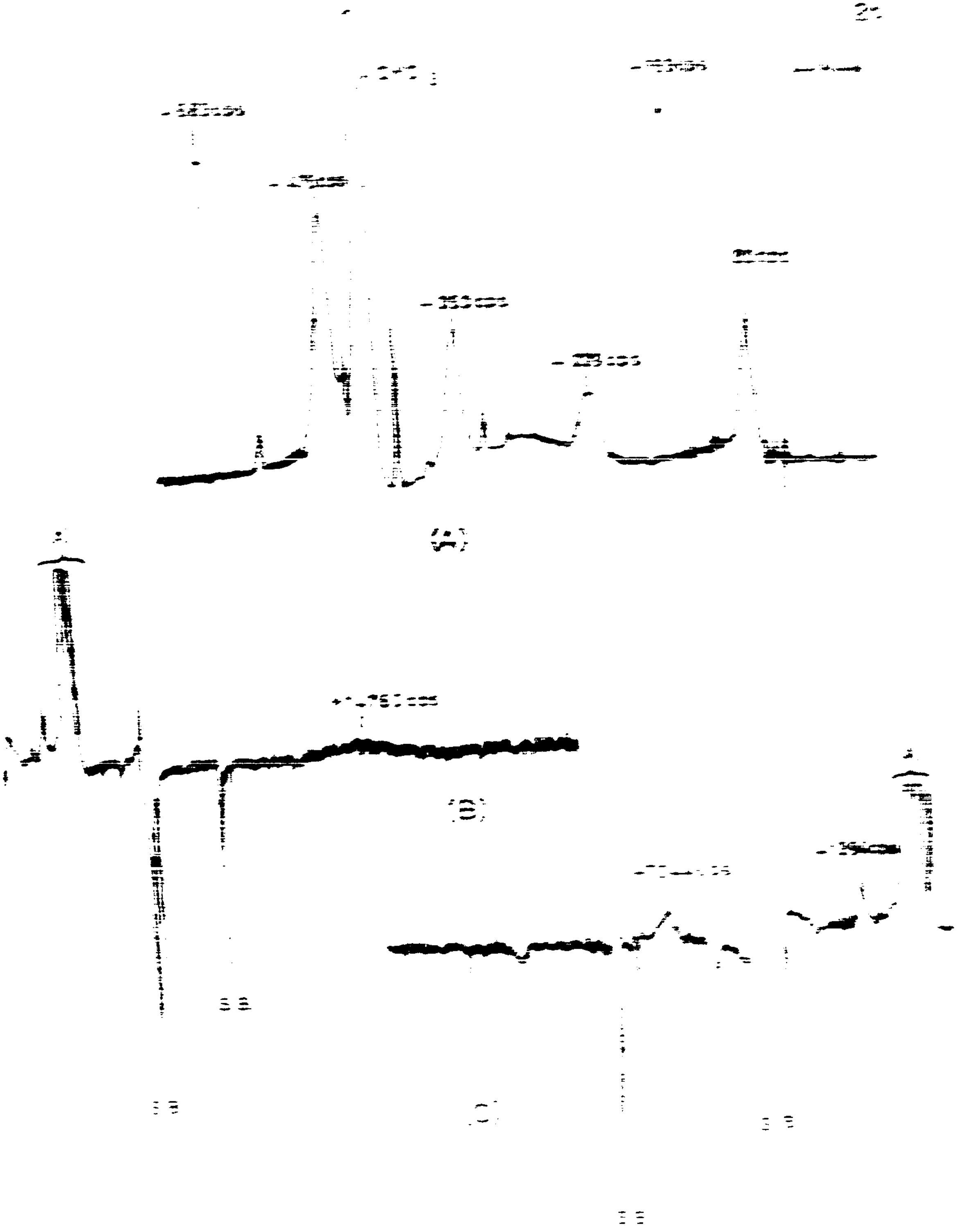


FIGURE 9. ^{1}H NMR Spectrum of [illegible]

(Yellow I) in CDCl$_3$.

TABLE I. ^1H NMR CHEMICAL SHIFTS.

(in cps rel. to TMS)

Compound	Solvent	Resonance peaks	Assignments
ms-stilbenediamine	$CDCl_3$	-77	$-NH_2$
	(and DMSO)	-277	methine protons
		-436	aromatic
r-stilbenediamine	$CDCl_3$	-95	$-NH_2$
		-253	methine protons
		-446	aromatic
$Zn(Cl_2CHCOO)_2$	DMSO	-378	methine protons
Zn(ms-stien)$_2$(dca)$_2$	DMSO	-258	$-NH_2$
		-283	methine(ligand)
		-382	methine (acetate ion)
		-438	aromatic
Ni(ms-stien)$_2$(ClO$_4$)$_2$	DMSO-d_6	-207	$-NH_2$
		-437	methine protons
		-455	aromatic
Ni(r-stien)$_2$(ClO$_4$)$_2$	DMSO-d_6	-93.5	$-CH_3$(DMSO)
		-130	methine protons
		-502	aromatic
Yellow I Ni(ms-stien)$_2$(dca)$_2$· 2H$_2$O	DMSO-d_6	-200	methine(ligand)
		-407	methine (acetate ion)

TABLE 3 (continued).

Compound	Solvent	Resonance peaks	Assignments
		-474	aromatic
Yellow I Ni(<u>ms</u>-stien)$_2$(dca)$_2$· 2H$_2$O	CDCl$_3$ and/or CHCl$_3$	+246ppm	-NH$_2$
		-80	-<u>meta</u>(aromatic)
		-229	
		-353	methine (acetate ion)
		-475	-<u>ortho</u>(aromatic)
		-1294	-<u>para</u>(aromatic)
		-117.4ppm	methine(ligand)
Blue I Ni(<u>ms</u>-stien)$_2$(dca)$_2$· 4H$_2$O	DMSO	+121ppm	-NH$_2$
		-79(triplet)	-<u>meta</u>
		-210(doublet)	
		-393	methine (acetate ion)
		-471	-<u>ortho</u>(aromatic)
		-614	-<u>para</u>(aromatic)
		-77ppm	methine(ligand)
Blue I Ni(<u>ms</u>-stien)$_2$(dca)$_2$· 4H$_2$O	CHCl$_3$	-76(triplet)	-<u>meta</u>
		-227(doublet)	

TABLE 2 (continued).

Compound	Solvent	Resonance peaks	Assignments
		-293(very weak)	$-H_2O$
		-353	methine (acetate ion)
		-473	-*ortho*(aromatic)
		-1313	-*para*(aromatic)
		-117ppm	methine(ligand)
Ni(*l*-stien)$_2$(dca)$_2$	$CHCl_3$	+246ppm	$-NH_2$
		-75(triplet)	-*meta*
		-223(doublet)	
		-328	methine (acetate ion)
		-533	methine(ligand)
		-565	-*ortho*(aromatic)
		-1363	-*para*(aromatic)
Yellow II 3Ni(*ms*-stien)$_2$(dca)$_2$· $2C_2H_5OH$· $4H_2O$	$CHCl_3$	+246ppm	$-NH_2$
		-81	-*meta*(aromatic)
		-224	
		-354	methine (acetate ion)
		-474	-*ortho*(aromatic)
		-1293	-*para*(aromatic)
		-77ppm	methine(ligand)

(ii) Paramagnetic complexes:

(a) Blue I Ni(<u>ms</u>-stien)$_2$(dca)$_2$.4H$_2$O.

It has been pointed out earlier that the electronic spectrum of this complex shows a "mixed" appearance in 95% ethanol solution suggesting the presence in the solution of both the (planar) yellow complex and a blue (octahedral) complex and, probably, an equilibrium between them.

In the NMR spectrum of this complex, an "averaged" resonance, rather than resonances of the two forms is observed. This indicates that interconversion between the two forms is proceeding at a rate in excess of about 10^5 sec^{-1}. The above conclusion is based on the fact that the ^{1}H resonance spectra of this complex in both chloroform and dimethyl sulfoxide are almost the same. Had there been two different types of species in dimethyl sulfoxide solution exchanging slowly enough, one would have two entirely different NMR spectra in these solvents. The assignment of the resonance lines is made as before. The multiplet structure for Blue I Ni(<u>ms</u>-stien)$_2$(dca)$_2$.4H$_2$O, as shown in Figure (10), is a triplet for the meta proton as would be expected from the structure (IV). The doublet at -227cps does not fit well into the above assignment and an explanation is needed here. A study of isotropic proton resonance shifts of triphenyl phosphine complexes of Ni(II) halides by W.DeW. Horrocks, Allen <u>et al.</u>[29] shows that for the complexes where spin-spin splittings are observed, only the <u>para</u> and <u>meta</u> peaks are split, the *ortho* proton resonances being too broad to resolve the splitting, due to the proximity of the metal ion.

(b) Yellow II Ni(*ms*-stien)$_2$(dca)$_2$.2/3 C_2H_5OH.4/3 H_2O.

The presence of the C_2H_5OH molecule does not show in the ^1H resonance spectrum of this complex probably due either to its low concentration in the solution or to its peaks being masked by the signals already present in the spectrum (Figures 12 and 13). The contact shift of methine (ligand) protons (-77ppm) is at higher field than that of methine (ligand) protons of Blue I or Yellow I complexes in chloroform. This proves that this complex is more diamagnetic in chloroform solution which is also supported by the magnetic moment measurement of these complexes in chloroform (Table 8).

(c) Ni(II) complexes of *levo*- and *racemic*-stilbenediamines.

With *levo*- and *racemic*-stilbenediamines, the behaviour of nickel complexes in solution is greatly influenced by the stereoisomerism of the ligands. For example, although the complexes are found to be paramagnetic both in solid and in solution, the shift of methine(ligand) protons shows a marked departure from the corresponding methine shifts of *ms*-stilbenediamine complexes. The assignments of the peaks are made in Table 2.

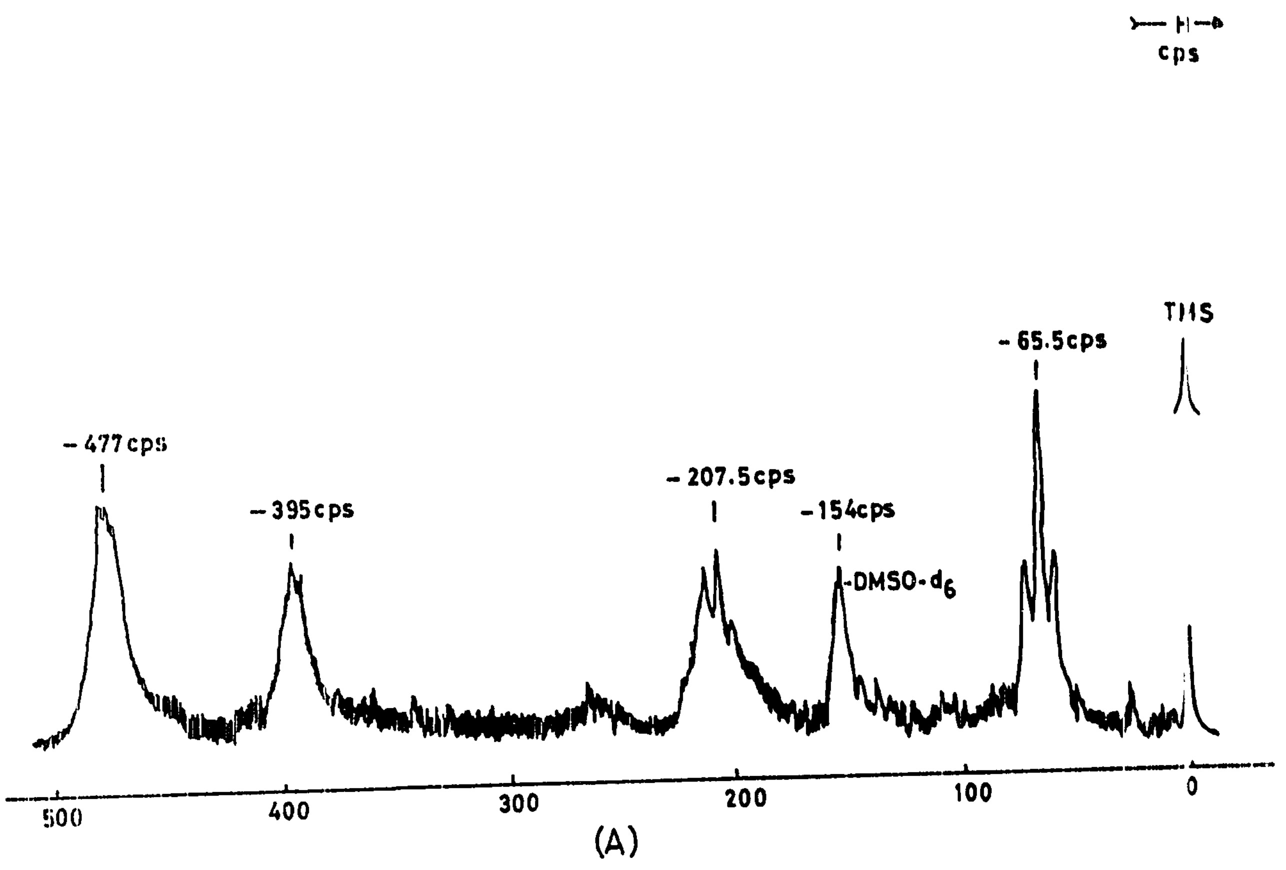


FIGURE 10. ^{1}H NMR Spectrum of Blue I Ni(<u>ms</u>-stien)$_2$(dca)$_2$.4H$_2$O in DMSO-d$_6$.

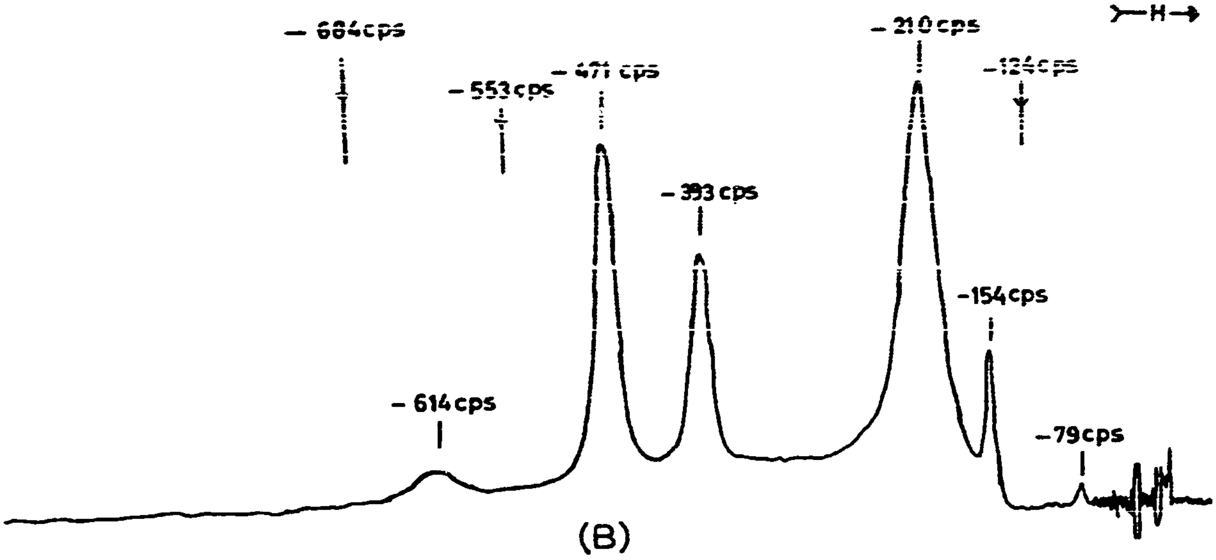


FIGURE 10. ^{1}H NMR Spectrum of Blue I Ni(ms-stien)$_2$-(dca)$_2$.4H$_2$O in DMSO.

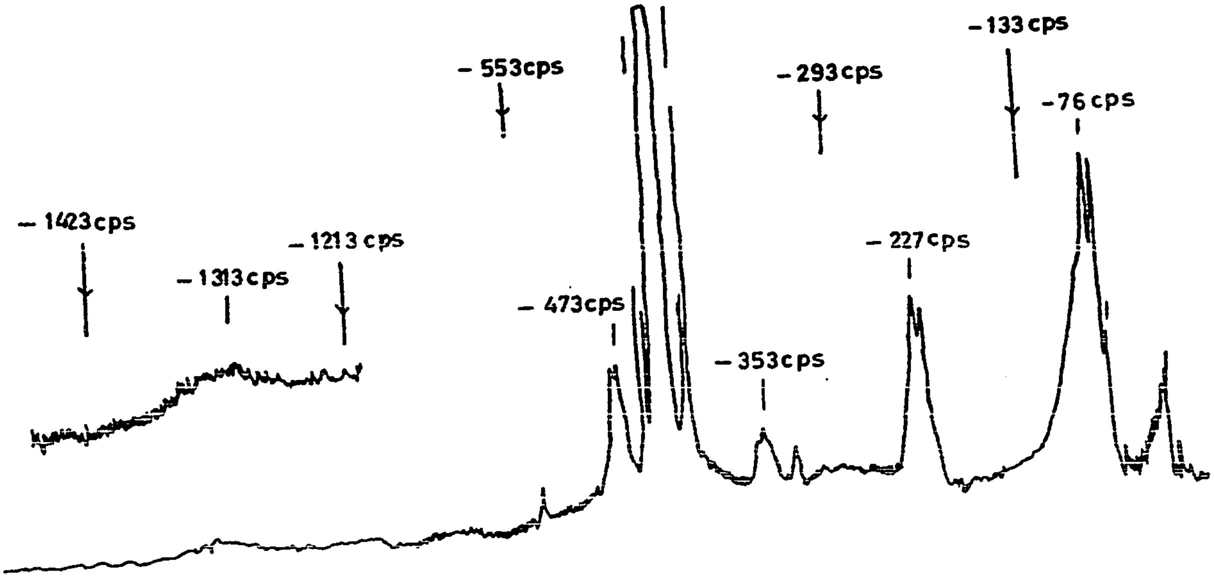


FIGURE 11. ^{1}H NMR Spectrum of Blue I Ni(ms-stien)$_2$-(dca)$_2$.4H$_2$O in CHCl$_3$.

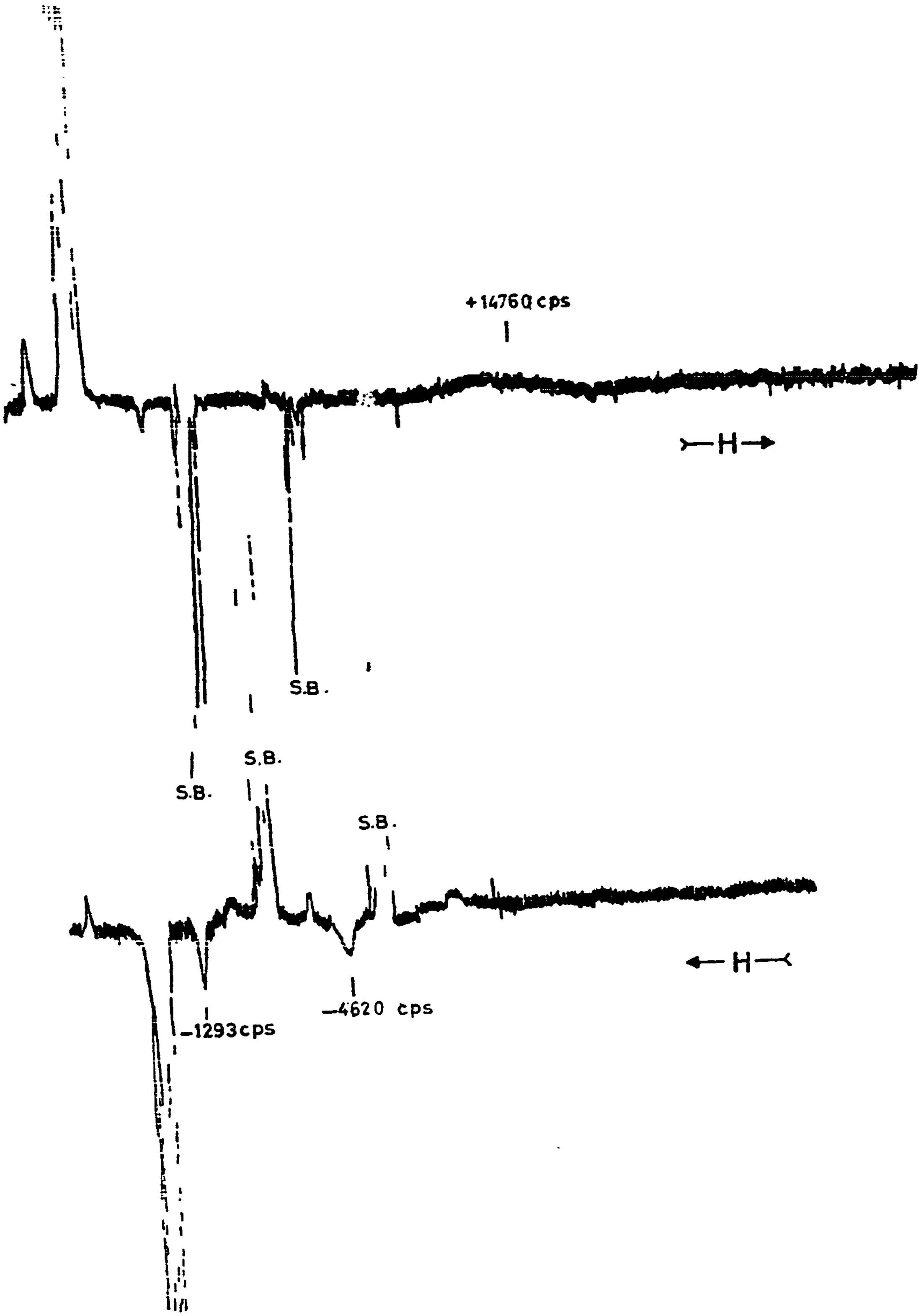


FIGURE 12. ^{1}H NMR Spectrum of Yellow II Ni(ms-stien)$_2$-(dca)$_2$. 2/3 C_2H_5OH. 4/3 H_2O in $CHCl_3$.

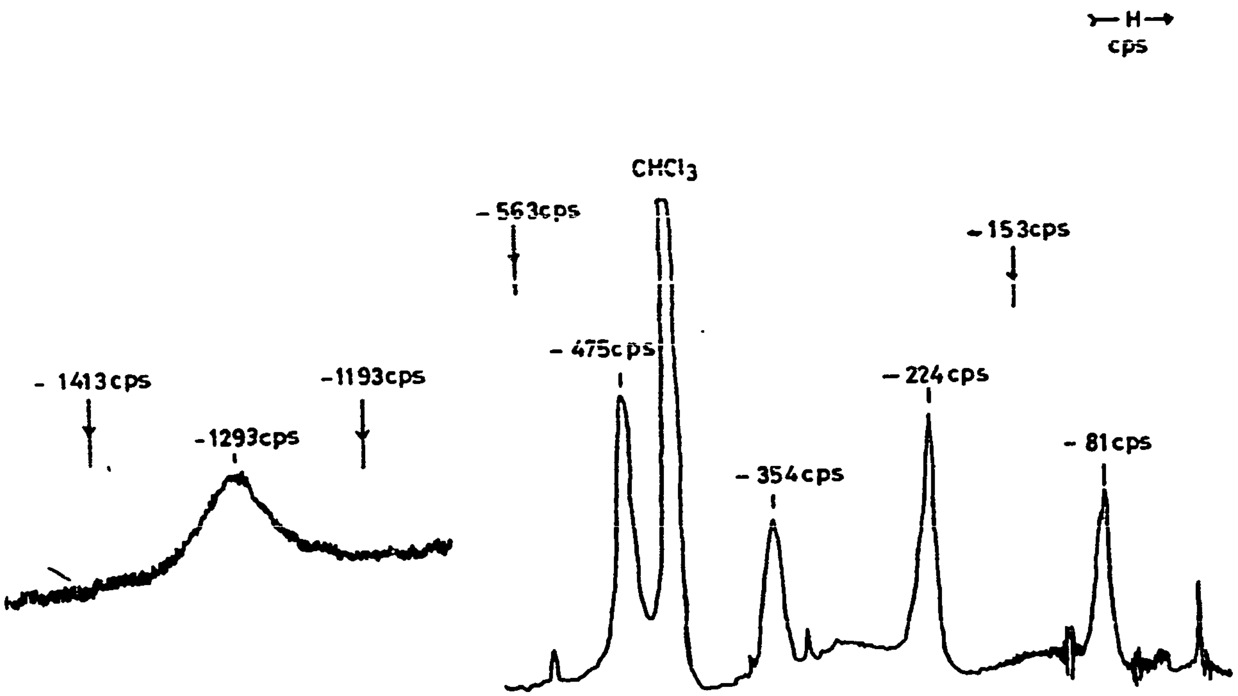


FIGURE 13. ^{1}H NMR Spectrum of Yellow II Ni(<u>ms</u>-stien)$_2$-(dca)$_2$. 2/3 C_2H_5OH. 4/3 H_2O in $CHCl_3$.

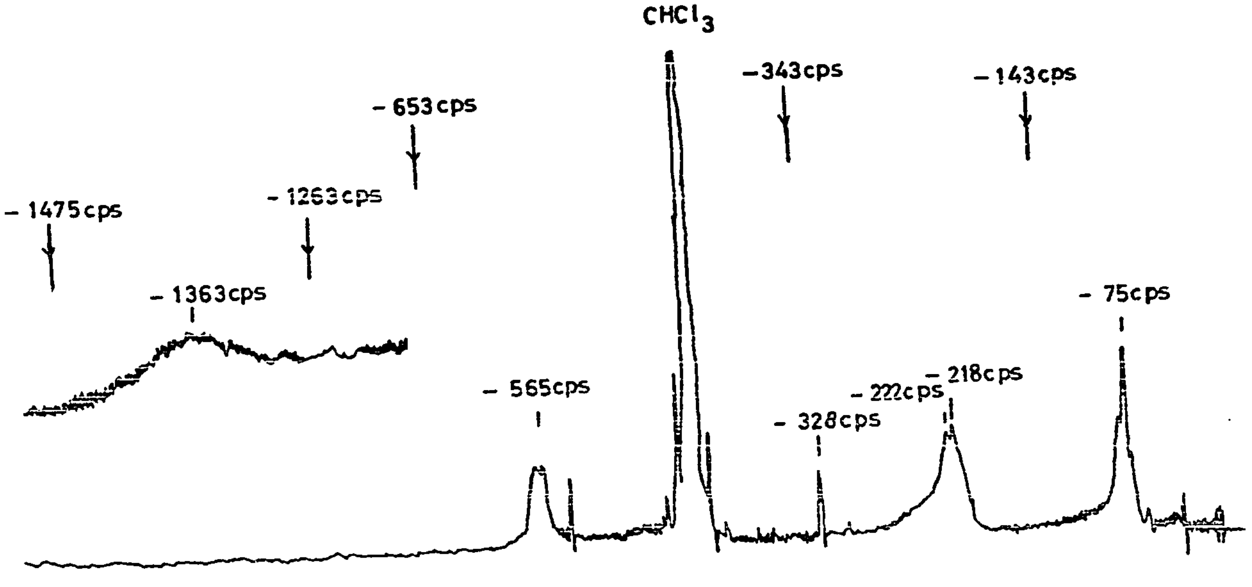


FIGURE 14. ^{1}H NMR Spectrum of Ni(<u>l</u>-stien)$_2$(dca)$_2$ in $CHCl_3$.

If the unpaired spin resides in the σ-system of the ligand, then the shifts are expected to be upfield, attenuating rapidly with increase in the number of bonds between the proton and the paramagnetic ion.

The assumption that as the two phenyl groups are not identical (X-ray analysis), one phenyl group being axial to the ring and the other equatorial; the unpaired spin distribution is a mixture of σ- and π-system is ruled out because of the close resemblence of the ^{1}H resonance spectra of levo- and racemic-stilbenediamines complexes with meso-stilbenediamine complexes. On the basis of σ- and π-spin distribution, the assignment of the ^{1}H NMR of a typical Blue I Ni(ms-stien)$_2$.4H$_2$O complex can be made as

Resonance peaks (in cps rel. to TMS)	Assignment
+246ppm	-NH$_2$
-81(triplet)	-para(aromatic)
-224(doublet)	-meta(aromatic)
-354	methine(acetate ion)
-474	-ortho(aromatic)
-1293	-para(aromatic)
-77ppm	methine(ligand)

The contact shift may arise from another interaction known as a pseudocontact interaction which results from the combined effects of (electron-spin) - (nuclear-spin) coupling, (electron-orbit) - (nuclear-spin) coupling, and electron spin-orbit coupling. It is expected from the equation I (page 7) that the contact interaction shift will depend upon the magnitude of g (where g = Lande' g factor = $1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}$) which in turn depend upon the orientation of the molecule containing the unpaired electron with respect to the magnetic field. If the g value is independent of the orientation of the molecule, it is said to be isotropic and the contact shift measured is due only to the electron-spin - nuclear-spin interaction. In a solution or in a molecule of cubic field symmetry the g value is independent of the orientation of the molecules but in a crystal or in a solid or in a molecule of lower symmetry the g value depends upon the orientation of the molecule and is said to be anisotropic. Thus, if the metal ion possesses anisotropic g factor the dipolar interaction between the electron-spin and the proton fails to average to zero and the resultant shift is known due to pseudocontact interaction. As there is no data available for g values of the complexes of interest, pseudocontact shifts (if any) could not be determined.

(B) Electronic Spectra:

(i) Survey of present knowledge.

For the Ni(II) complexes of stilbenediamine and related ligands, possible geometrical configurations are octahedral (either O_h or D_{4h} symmetry), square planar (D_{4h}) and tetrahedral (T_d). Crystal field theory provides a simple interpretation of the spectra of these Ni(II) complexes in different geometrical environments. The regular octahedral complexes are characterized by the presence of moderately intense bands (ε = 4-10) which result from splitting of triplet ground terms ^3F and ^3P arising from the $3d^8$ configuration of the free ion Ni^{2+}.

The three spin-allowed transitions now well established for octahedral Ni(II) complexes are the following (Figure 15),

$$ {}^3A_{2g}\ (F) \rightarrow {}^3T_{2g}\ (F), \quad \nu_1 = 10\ Dq $$

$$ \rightarrow {}^3T_{1g}\ (F), \quad \nu_2 = (\frac{15}{2})B + 15\ Dq - \frac{1}{2}\left[(\ 15\ B - 6\ Dq\ )^2 + 64(Dq)^2\right]^{\frac{1}{2}} $$

$$ \rightarrow {}^3T_{1g}\ (F), \quad \nu_3 = (\frac{15}{2})B + 15\ Dq + \frac{1}{2}\left[(\ 15\ B - 6\ Dq\ )^2 + 64(Dq)^2\right]^{\frac{1}{2}} $$

where Dq is the ligand field strength parameter and B is a Racah parameter.

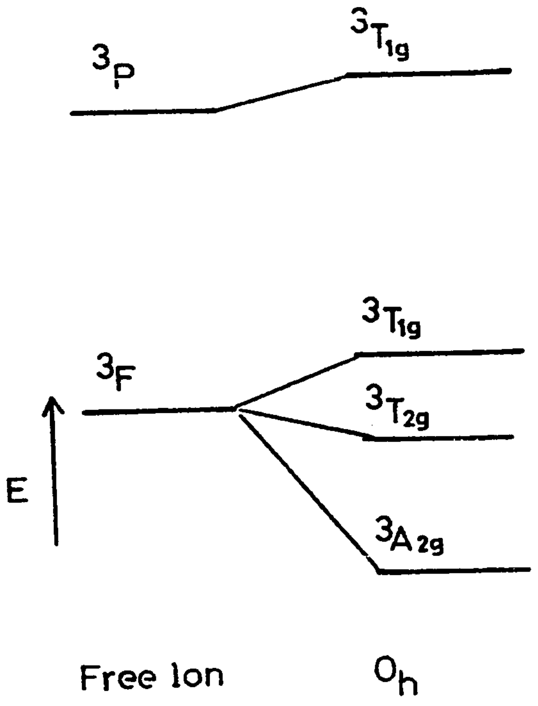


FIGURE 15. Energy level diagram for octahedral nickel (II) complexes[38].

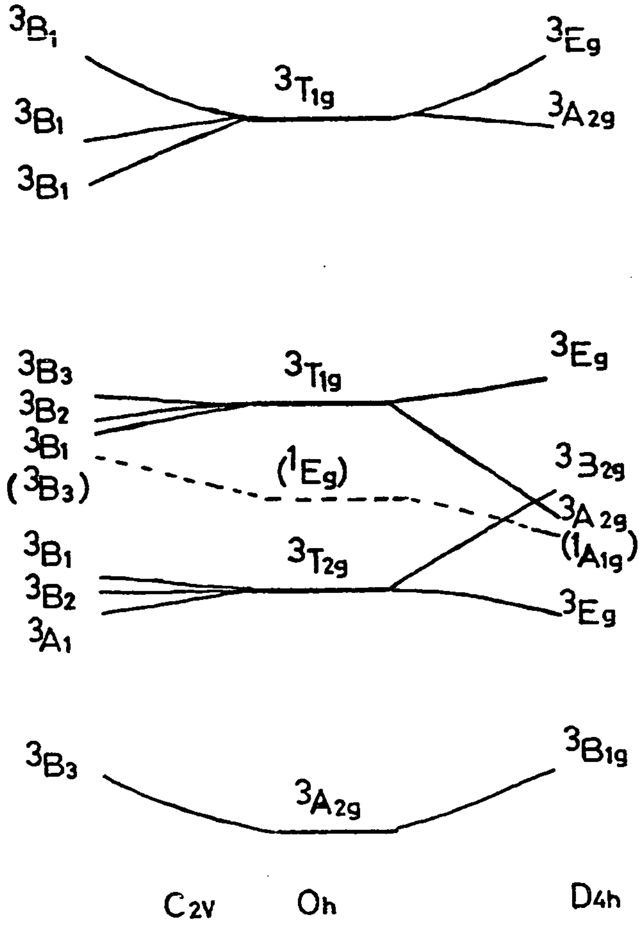


FIGURE 16. The effects of geometrical distortions on the energy levels of octahedral nickel (II)[38].

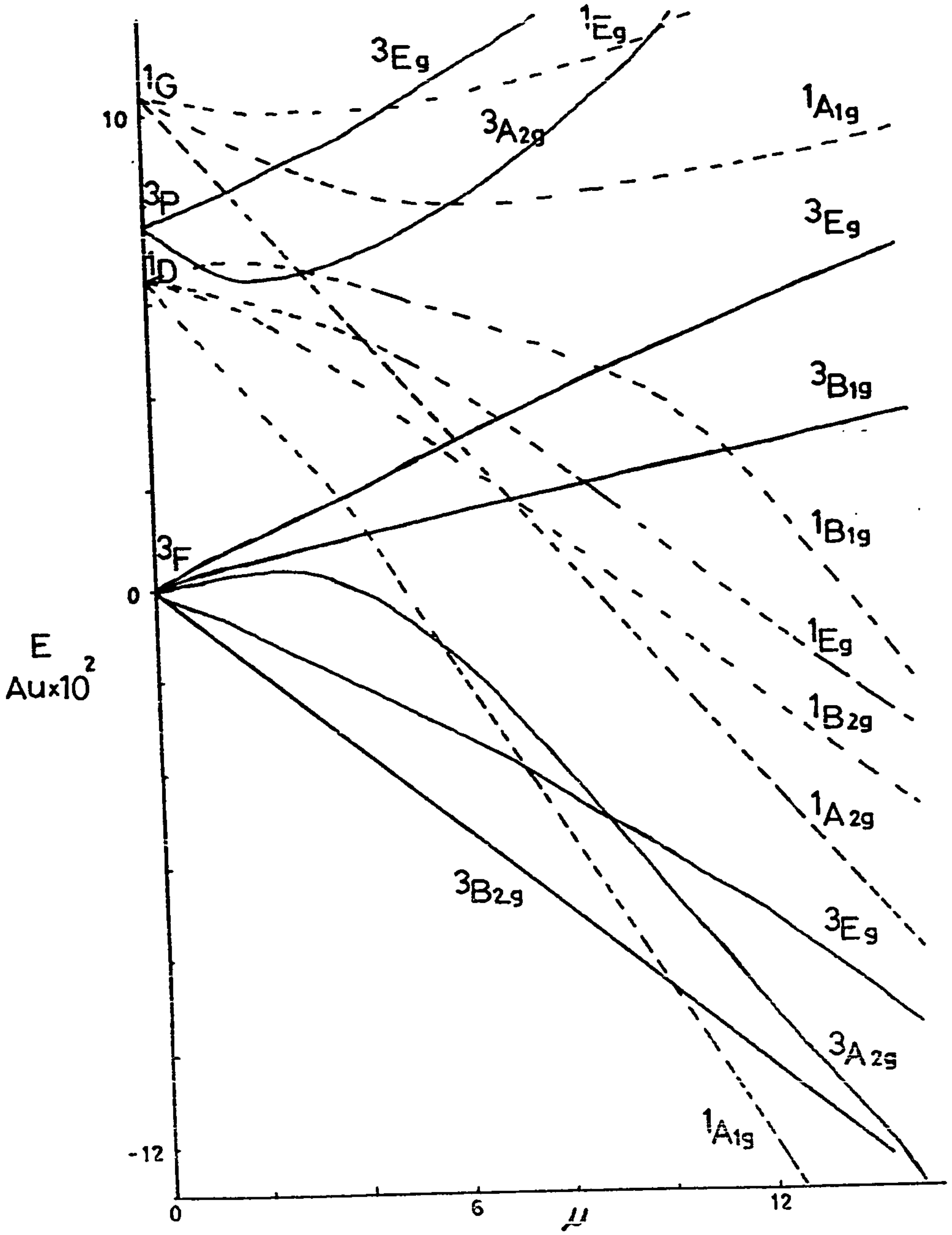


FIGURE 17. Energy level diagram for nickel complexes in planar D_{4h} symmetry[38].

Liehr and Ballhausen[39] have discussed the effect of spin orbit coupling on the splitting of the above energy levels and the intensities of the absorption bands.

In the present case where Ni(II) has coordination number six, the six groups are not of the same kind. Therefore, it might be expected that the absorption bands would show some evidence of deviation of the ligand field from purely O_h symmetry and the absorption spectra could be interpreted using the result of Maki[40] for hexacoordinated Ni(II) complexes of D_{4h} symmetry. The orbital triplets ${}^3T_{1g}$ and ${}^3T_{2g}$ (in O_h symmetry) undergo further splitting (Figure 16) and a large number of transitions are expected in the electronic spectra.

For square-planar Ni(II) complexes the electronic ground state may be either $(e_g)^4\ (a_{1g})^2\ (b_{2g})^2$, a spin-singlet state, term ${}^1A_{1g}$, or $(e_g)^4\ (a_{1g})^2\ (b_{2g})^1\ (b_{1g})^1$, a spin-triplet state, ${}^3A_{2g}$ and an excited state ${}^1A_{2g}$. Ballhausen and Liehr[5,41] have showed by a simple calculation that the low-spin state is stable if the separation between d_{xy} and $d_{x^2-y^2}$ orbitals is more than ca. 10,000 cm^{-1} ie. for high values of ligand field strength. Maki[40] concludes that even a small axial perturbation of Ni(II) complexes of D_{4h} symmetry will destabilize the above singlet state and stabilize the ${}^3B_{2g}$ (F) state, so this becomes the ground state and the complex will show paramagnetic properties.

The energy level diagram for nickel complexes in planar D_{4h} symmetry is shown in Figure 17.

The crystal fields of T_d and O_h symmetries produce the same number of spectroscopic terms when they operate on a given free ion term system. Although it has been pointed out earlier that stilbenediamine and related ligands do not show any 'steric' reason for preferring tetrahedral coordination, an attempt will be made to interpret the spectra where the complex shows a tetrahedral coordination.

(ii) The effect of solvents upon spectra.

It has been observed by Nyburg and his co-workers[1] that the addition of water to a solution of the Blue I Ni(ms-stien)$_2$(dca)$_2$.4H$_2$O in acetone favours the formation of the yellow complex indicating an equilibrium between the two species written by

$$\mathrm{Ni(\underline{ms}\text{-}stien)_2(H_2O)_x(Cl_2CHCOO)_2 + H_2O(aq) \rightleftharpoons Ni(\underline{ms}\text{-}stien)_2^{2+} + 2(Cl_2CHCOO)^-(aq) + H_2O(aq).} \quad \text{(V)}$$

The data in Table (3) show that in general the blue complexes are stable only in solvents of low (ε = 4.8 to 38.57) dielectric constant, and as the dielectric constant of the solvent is increased, dissociation is brought about. The water molecules are removed from the 1st coordination sphere and a planar or strongly tetrahedral yellow complex

TABLE 3.

ELECTRONIC ABSORPTION SPECTRA OF BLUE I Ni(ms-stien)$_2$-(Cl$_2$CHCOO)$_2$, 4H$_2$O.

Medium	Absorption maxima cm^{-1}.	ε_{max}	Dielectric constants $\varepsilon_{20°C}$
Acetone(and	10,400	3.7	20.7(and 4.8)
chloroform)	12,980	2.9	
	17,240	7.3	
	27,070(sh)	18.4	
Nitrobenzene	9,900	3.1	34.82
	12,980	1.2	
	17,240	4.9	
	22,900	8.1	
Nitromethane	10,100	4.7	38.57
	16,130	8.8	
	26,110	19.2	
Dimethyl sulfoxide	10,070	6.1	
(dry)	16,660	5.9	
	22,470	21.1	
	26,660	17.2	
Dimethyl formamide	10,250		109
	16,730		

TABLE 3 (continued).

Medium	Absorption maxima cm^{-1}.	ε_{max}	Dielectric constants ε_{25}°
	22,220		
	26,660		
95% ethanol[42]	10,300	6.5	
	12,650	3.5	
	16,700	7.0	
	27,200(sh)	12.0	

sh = shoulder.

TABLE 4.

ELECTRONIC ABSORPTION SPECTRA OF Ni(II) COMPLEXES IN DIMETHYL SULFOXIDE.

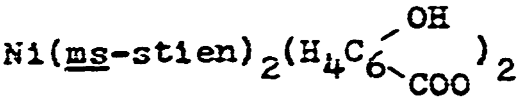
Complex	Absorption maxima cm^{-1}.	$\varepsilon_{\underline{max}}$
 $Ni(\underline{ms}\text{-stien})_2(H_4C_6\overset{OH}{\underset{COO}{}})_2$	10,000	4.3
	16,900	6.7
	22,440(sh)	5.6
Yellow I		
$Ni(\underline{ms}\text{-stien})_2(dca)_2 \cdot 2H_2O$	10,000	7.9
	16,660	6.3
	22,520	23.1
	26,520	17.9
$Ni(\underline{ms}\text{-stien})_2(Ph_2CH_2COO)_2$	10,250	2.6
	16,880	4.2
	26,800	9.2
$Ni(\underline{ms}\text{-stien})_2Cl_2$	16,000	0.4
	22,440	6.0
$Ni(\underline{r}\text{-stien})_2(Cl_2CHCOO)_2$	10,810	12.3
	17,700	9.6
	27,620(sh)	16.0
$Ni(\underline{l}\text{-stien})_2(Cl_2CHCOO)_2$	10,920	12.8
	17,850	12.1
	27,390(sh)	17.1

TABLE 5.

ELECTRONIC ABSORPTION SPECTRA OF Ni(II) COMPLEXES IN CHLOROFORM.

Complex	Absorption maxima cm^{-1}.	ε max
$Ni(\underline{r}\text{-stien})_2(Cl_2CHCOO)_2$	9,750	4.2
	11,390	4.6
	13,070	4.3
	17,850	7.7
	27,390	10.3
$Ni(\underline{l}\text{-stien})_2(Cl_2CHCOO)_2$	9,750	5.4
	11,390	5.3
	13,070	5.3
	17,850	7.2
	27,540(sh)	9.4
Yellow I		
$Ni(\underline{ms}\text{-stien})_2(dca)_2 \cdot 2H_2O$	same as Blue I	

sh = shoulder

FIGURE 18. Electronic Absorption Spectrum of Ni(<u>ms</u>-bn)$_2$(dca)$_2$·2H$_2$O.

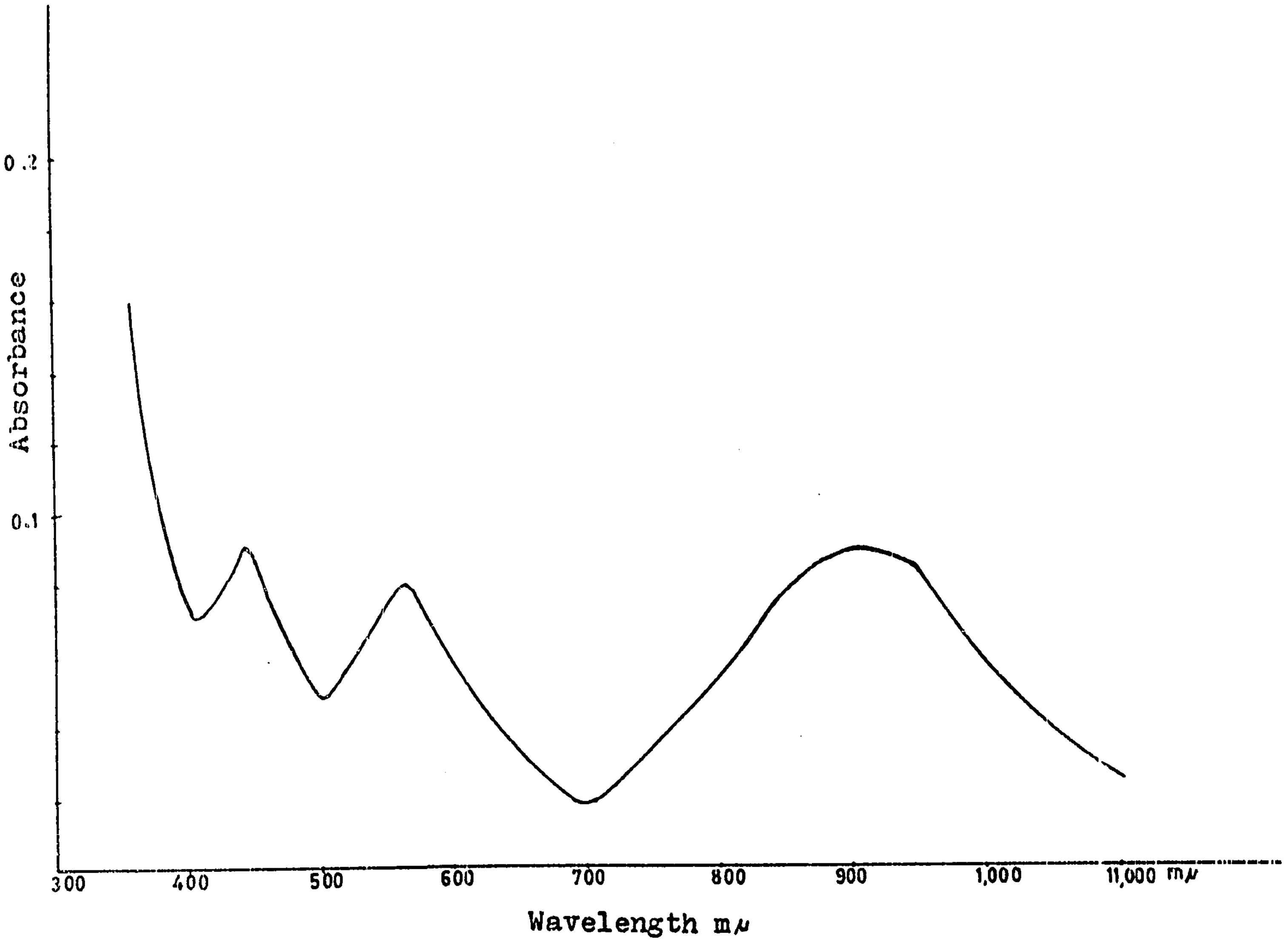


FIGURE 19. Electronic Absorption Spectrum of $Ni(\underline{l}\text{-stien})_2(dca)_2$.

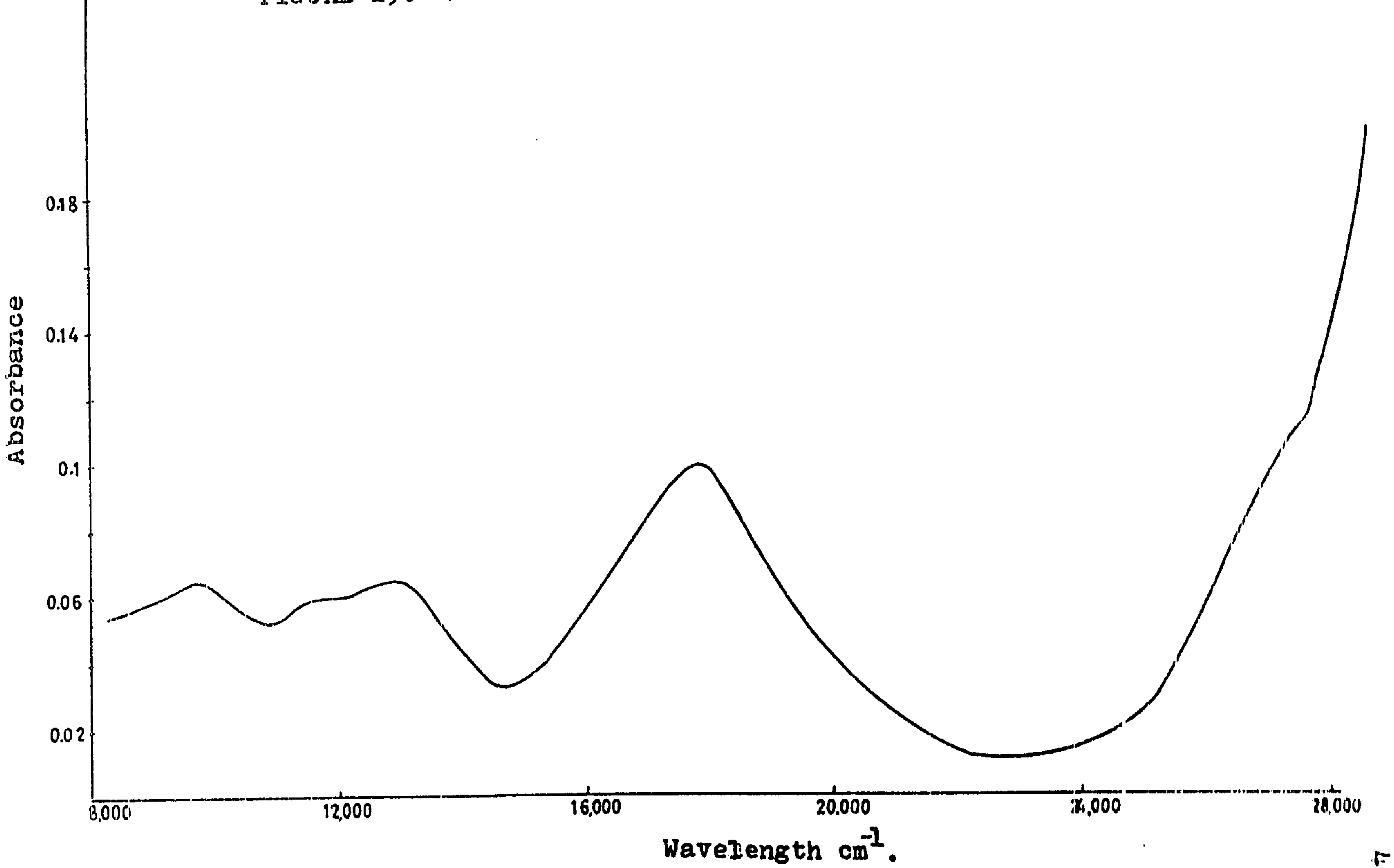


TABLE 6.

ELECTRONIC ABSORPTION SPECTRA OF Ni(II) COMPLEXES.

Complex	Absorption maxima cm^{-1}.	ε max
$Ni(tetrameen)_2(dca)_2$ (in water)	22,470	
$Ni(\underline{ms}\text{-}bn)_2(dca)_2 \cdot 2H_2O$ (in water)	10,990	7.3
	17,880	6.3
	22,520	7.3
	28,210	13.0
$Ni(dca)_2 \cdot xH_2O$ in ethanol	8,610	
	14,290	
	28,170	

is left behind in the solution. It is interesting to note, however, that nitrobenzene having a lower dielectric constant ($\varepsilon = 34.82$) than nitromethane ($\varepsilon = 38.57$) behaves quite differently. The presence of an additional band at 12,980 cm^{-1} ($\varepsilon_{max} = 1.2$) indicates an equilibrium between the two diamagnetic and paramagnetic species similar to (V).

The formation of yellow species in solution is explained by Nyburg as due to steric hindrance of axial positions in the planar complex $\mathrm{Ni}(\underline{ms}\text{-stien})_2^{2+}$, thus preventing the close approach of anions or solvent molecules. An X-ray crystal analysis of Yellow II $\mathrm{Ni}(\underline{ms}\text{-stien})_2(\mathrm{dca})_2 \cdot 2/3\ C_2H_5OH \cdot 4/3\ H_2O$ complex shows that in planar form there is no ligand in the axial position and the nearest atom to the nickel ion is an oxygen atom of the "free" dichloroacetate ion at a distance of 3.25 Å. This steric hindrance of axial positions in the planar complex probably arises due to the shortening of Ni-N bond distance, thus bringing the stilbenediamine molecules closer to the axial positions of the tetracoordinated nickel atom.

Behaviour of dimethyl sulfoxide as a solvent

As dimethyl sulfoxide is a good coordinating solvent, one may expect an exchange between coordinated water (if any) and the solvent molecules. A survey of dimethyl sulfoxide complexes of transition metals suggests that water and dimethyl sulfoxide compete fairly evenly for places in the coordination sphere and also that it is necessary that the concentration of water be low rather than nil in order for it to be excluded. The electronic spectra of these complexes do not show any positive evidence of the solvents being coordinated to the metal ion.

In the case of Ni(II) complexes of levo and racemic-stilbenediamines, the bands are shifted towards high energies which may be an indication of a new complex being formed. In chloroform these complexes behave quite differently. The absorption bands are listed in Table (5). Although the main bands do not show the presence of any shoulders, or pronounced asymmetry, there are two additional bands at 11,390 cm^{-1} and 13,070 cm^{-1} (Figure 19). These bands can not be assigned to the spin-forbidden transitions from the ground state, $^3A_{2g}$ to the singlet, $^1E_g(D)$, but at present no possible explanation seems to be in sight.

Blue complexes of $Ni(\underline{ms}\text{-stien})_2X_2$ where X = C_6H_5-(OH)COO^- and $C_6H_5CH_2COO^-$ behave in the same way as Blue I-$Ni(\underline{ms}\text{-stien})_2(dca)_2 \cdot 4H_2O$ in chloroform and dimethyl sulfoxide.

(iii) Deductions based upon observed Dq values.

The three main bands which occur at 10,300 cm^{-1}, 16,600 cm^{-1} and 26,900 cm^{-1}, are assigned to the three spin-allowed transitions, namely $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1); $^3T_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2); and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3). The values of ν_1 gives Δ

directly (except where this has to be corrected for intermediate coupling due to interaction between $^3T_{2g}(F)$ and $^1E_g(D)$). The band at 12,900 cm^{-1} can be assigned to the spin-forbidden transition from the ground state, $^3A_{2g}$ to the singlet, $^1E_g(D)$.

From the electronic absorption spectrum of $Ni(dca)_2$ in dry ethanol (Table 6), one can assume that the ligand field strength of dichloroacetate ion would be approximately 8,610 cm^{-1}. Also if it is assumed that the ligand field strength of *ms*-stilbenediamine is the same as reported for the complex $Ni(\underline{ms}\text{-stien})_2(ClO_4)_2$[20] (10,930 cm^{-1}) then according to the rule of average environment, if dichloroacetate ions are coordinated to the nickel in the blue complex, one expects to observe the transition $^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$ at 9,490 cm^{-1}.

$$\begin{aligned} \sigma \mathrm{Ni}(\underline{ms}\text{-stien})_2(\mathrm{dca})_2 &\equiv \frac{2}{3}\sigma \mathrm{Ni}(\underline{ms}\text{-stien})_3 + \frac{2}{6}\sigma \mathrm{Ni}(\mathrm{dca})_6 \\ &\equiv \frac{2}{3}(10{,}930\ \mathrm{cm}^{-1}) + \frac{2}{6}(8{,}610\ \mathrm{cm}^{-1}) \\ &\cong 9{,}490\ \mathrm{cm}^{-1} \qquad \text{(VI)} \end{aligned}$$

As the observed values for the blue $Ni(\underline{ms}\text{-stien})_2(dca)_2$ complexes are higher than the calculated value, it shows that the dichloroacetate ions are not coordinated to the nickel atom.

(C) Susceptibility Studies:

The paramagnetism of stilbenediamine complexes is now correctly viewed as due to the presence of slightly perturbed octahedral complex ions rather than tetrahedral complex ions. It is expected that the octahedral complexes would show moments which are given by the term 2.83 (1-$4\lambda/10$ Dq), where $\lambda =$ spin-orbit coupling constant and is equal to $-315\ \text{cm}^{-1}$. In the case of diamagnetic planar Ni(II) chelates, Ballhausen and Liehr[5] suggest the possibility of the existence of magnetic quenching or promotion in order to attain partial paramagnetic character when dissolved in strongly polar solvents such as CH_3OH, DMSO, etc., rather than by conformational equilibria. If this be the case then the molar susceptibility of such solutions should be given by

$$\chi_M = \frac{2g^2\beta^2 N}{3kT}\left[1 + \frac{1}{3}\exp\left(\frac{h\nu_1}{kT}\right)\right]^{-1} + N\alpha \qquad \text{(VII)}$$

where g is the Lande' factor for the $^3B_{1g}$ state, N = Avogadro's number, K the Boltzmann constant, β the Bohr magneton, $N\alpha$ the temperature independent part of the susceptibility and $h\nu_1$ the energy separation of the diamagnetic ground state, $^1A_{1g}$, and the low-lying exited triplet state, $^3B_{1g}$. As no detailed susceptibility vs. temperature studies have been reported in the literature, an attempt was made to carry out this study in chloroform solvent.

Yellow I Ni(ms-stien)$_2$(dca)$_2$. $2H_2O$ complex when dissolved in chloroform becomes paramagnetic showing its characteristic blue colour. The susceptibility measurement at different temperatures(+40°C to -40°C) do not show any appreciable change in its magnetic moment (Table 7). Although these values are slightly higher than those observed for other Ni(II) complexes in chloroform solution, it is unwise to attach great significance to it as these deviations fall within experimental error. However, there is slight indication of the solution becoming more diamagnetic at higher temperature. Unfortunately, the pure diamagnetic complexes, viz. Ni(ms-stien)$_2$(ClO$_4$)$_2$, Ni(ms-stien)$_2$Cl$_2$ and Ni(r-stien)$_2$(ClO$_4$)$_2$ etc. were not soluble in chloroform and although dimethyl sulfoxide is a good solvent for these complexes, low temperature magnetic moment measurements were not possible due to its high freezing point.

It appears, however, that the pure diamagnetic planar Ni(II) complexes attain paramagnetic character by conformational equilibria, supported by the isolation of an adduct compound of the complex.

Blue I Ni(ms-stien)$_2$(dca)$_2$.4H$_2$O shows its magnetic behaviour to follow a Curie-Weiss law with $\theta = -0.3°$(Figure 20). The magnetic moment of this complex at low temperature are listed in Table 8. The moments are independent of temperature as predicted from perturbation of Ni(II) ion in octahedral field. Perturbation of Ni(II) ion in tetrahedral field would show moments - a function of temperature and would depend on the detailed symmetry of the ligand field present. It is interesting to note that in chloroform the magnetic moment of this complex calculated for the formula Ni(ms-stien)$_2$(dca)$_2$$\cdot$4H$_2$O is lower than its magnetic moment in the solid state. It appears that the complex is solvated in chloroform. Lifshitz and his coworkers have reported a complex of composition Ni(ms-stien)$_2$(dca)$_2$$\cdot$2CHCl$_3$ from chloroform solution.

The magnetic moments of other Ni(II) complexes in solid as well as in solution are shown in Table 8. The magnetic moments of these complexes in dimethyl sulfoxide indicate that the complexes are more diamagnetic in this solvent than in chloroform.

TABLE 7.

MAGNETIC MOMENTS OF Ni(ms-stien)$_2$(dca)$_2$$\cdot$2H$_2$O IN CHCl$_3$.

Temperature in °C	μ_{eff} in B.M.
+40	3.58
+23.5	3.68
00.0	3.85
-10.0	3.99
-42	3.92

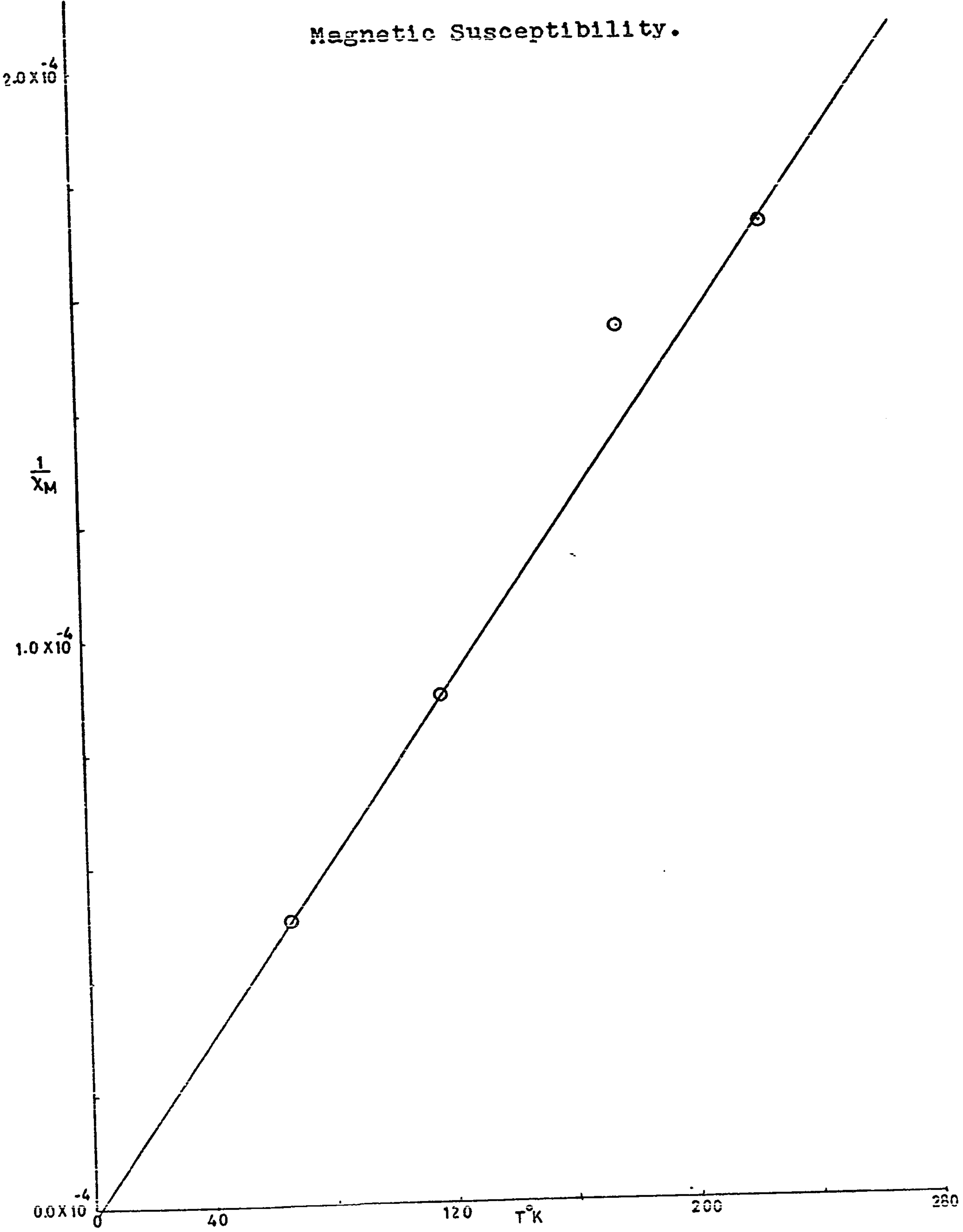
TABLE 8. MAGNETIC MOMENTS OF Ni(II) COMPLEXES.

Complex	Solvent	Temp. °C	μ_{eff} in B.M.
Ni(<u>ms</u>-stien)$_2$(ClO$_4$)$_2$		RT	diamagnetic
Ni(<u>r</u>-stien)$_2$(ClO$_4$)$_2$		RT	diamagnetic
Blue I			
Ni(<u>ms</u>-stien)$_2$(dca)$_2$.4H$_2$O		RT	3.16
		22	3.23
		-48.3	3.25
		-93.6	3.06
		-141.5	3.25
		-194.0	3.24
	CHCl$_3$	RT	2.45
Yellow II			
Ni(<u>ms</u>-stien)$_2$(dca)$_2$.	CHCl$_3$	RT	3.205
2/3 C$_2$H$_5$OH. 4/3 H$_2$O	DMSO	RT	2.36
Yellow I			
Ni(<u>ms</u>-stien)$_2$(dca)$_2$.2H$_2$O		RT	1.98
	CHCl$_3$	RT	3.40
	DMSO	RT	2.70
Yellow II			
Ni(<u>ms</u>-stien)$_2$(dca)$_2$.			
2/3 C$_2$H$_5$OH. 4/3 H$_2$O		RT	2.60
Ni(<u>l</u>-stien)$_2$(dca)$_2$		RT	3.20

TABLE 8 (continued).

Complex	Solvent	Temp. °C	μ_{eff} in B.M.
$Ni(\underline{r}\text{-stien})_2(dca)_2$		RT	3.21
$Ni(tetrameen)_2(dca)_2$		RT	diamagnetic
$Ni(\underline{ms}\text{-bn})_2(dca)_2 \cdot 2H_2O$		RT	3.21

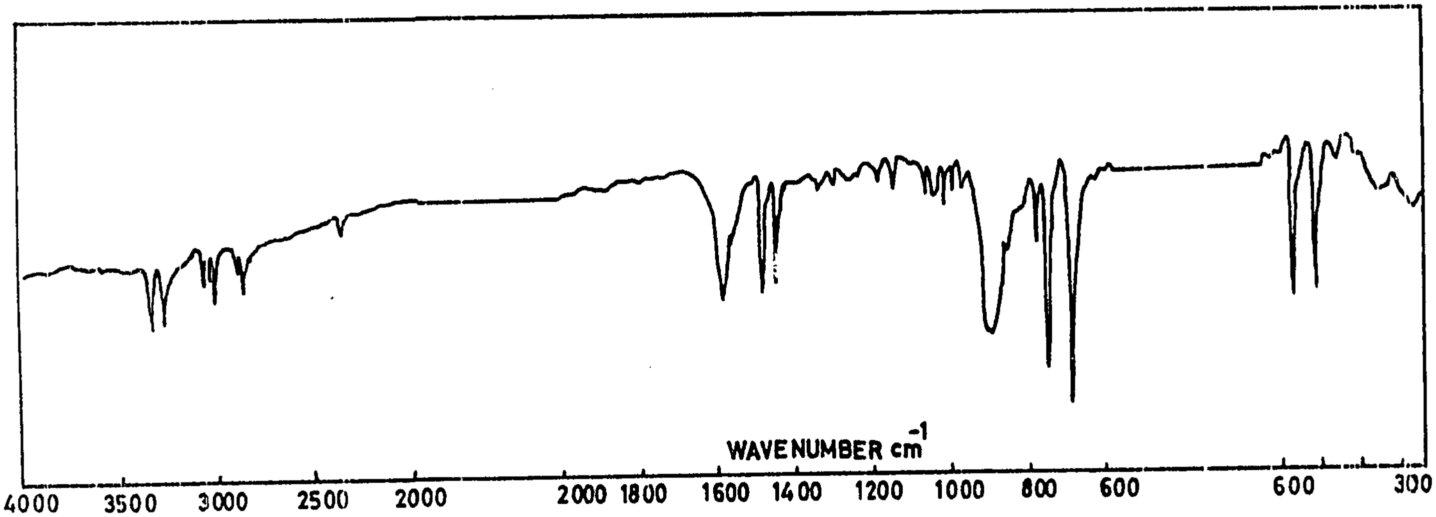
FIGURE 20. Temperature versus Reciprocal Magnetic Susceptibility.



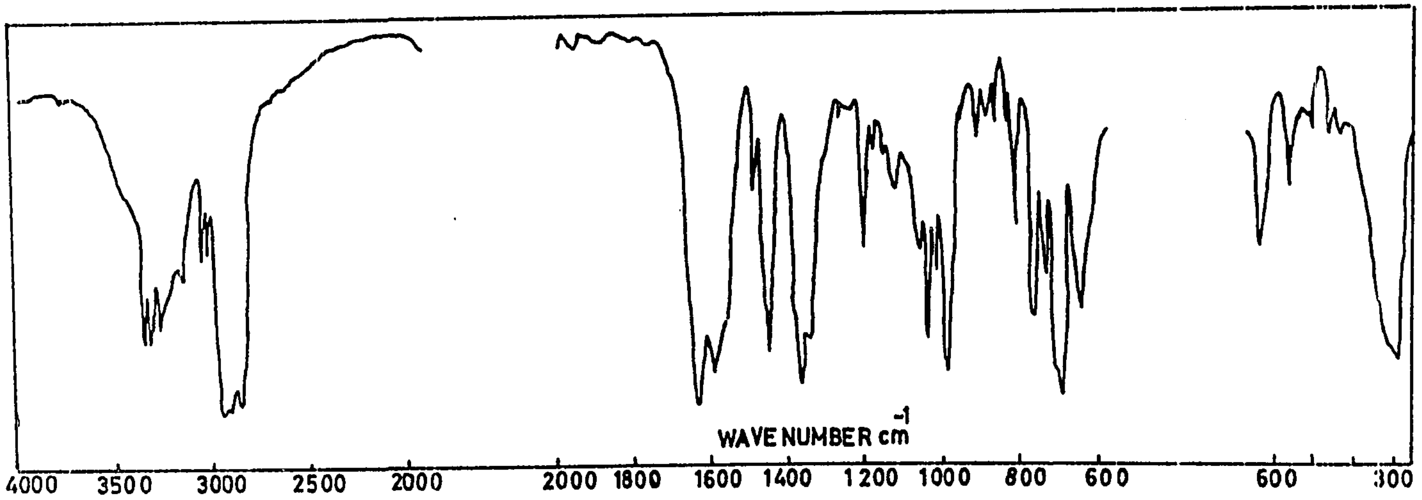
(D) Infrared studies.

The infrared spectra of ms-stilbenediamine and Ni(ms-stien)$_2$(dca)$_2$.4H$_2$O complex are represented in Figure 21. These spectra are so complicated that a definite assignment of M-N stretching vibration in these spectra can not be made easily. However, the band at ca. 450 cm^{-1} appears in almost all the spectra and it may be due to M-N stretching vibrations. The other infrared spectra are shown in the Appendix of this thesis. The spectra are recorded as a means of identifying the complexes rather than assigning the absorption bands.

FIGURE 21. INFRARED SPECTRA.



(a) meso-stilbenediamine in KBr.



(b) Blue I Ni(ms-stien)$_2$(dca)$_2$·4H$_2$O.

REFERENCES

1. S.C. Nyburg and J.S. Wood, Inorg. Chem. 3, 468(1964).
2. I. Lifshitz and J.G. Bos, and K.M. Dijkema, Z. anorg. allgem. chem. 242, 97(1939).
3. I. Lifshitz and J.G. Bos, Rec. trav. chim. 60, 581(1941).
4. C.J. Ballhausen and A.D.Liehr, J. Am. Chem. Soc. 81, 538(1959).
6. J.B. Willis and D.P. Mellor, J. Am. Chem. Soc. 69, 1237(1947).
7. F.A. Cotton and J.P. Fackler, Jr., J. Am. Chem. Soc. 83, 2818(1961).
8. R.H. Holm, J. Am. Chem. Soc. 83, 4683(1961); Part II.
9. L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, J. Am. Chem. Soc. 82, 3487(1960).
10. G. Maki, J. Chem. Phys. 29, 1129(1958).
11. W.C.E. Higginson, S.C. Nyburg, and J.S. Wood, Poc. Chem. Soc. 297(1961).
12. H.M. McConnell and D.B. Chesnut, J. Chem. Phys. 28, 107(1958).

13. C. Furlani and G. Sartoni, Proceedings of Symposium on coordination Chemistry, Rome, 1957, in J. Inorg. Nucl. Chem. 8, 126(1958); C. Furlani, Gazz. chim. ital. 88, 279(1958).

14. C.K. Jørgenson, Acta. Chem. Scand. 9, 1362(1955); ibid. 10, 887(1956).

15. S.C.Nyburg, W.C.E. Higginson and J.S. Wood, Inorg. Chem. 3, 463(1964).

16. R.H. Holm and K. Swaminathan, Inorg. Chem. 2, 181(1963).

17. G.W. Everett, Jr., and R.H. Holm, J. Am. Chem. Soc. 87, 2117(1965).

18. D.F. Evans, J. Chem. Soc. 2003(1959).

19. D.B. Powell and N. Sheppard, J. Chem. Soc. 1112(1961); ibid. 3809(1959); D.B. Powell, Spectrochim. Acta. 16, 241(1960); 17, 68(1961).

20. D.M.L. Goodgame and M.A. Hitchman, J. Chem. Soc. 1404(1968).

21. M.N.H. Irving and R.N. Perkins, J. Inorg. Nucl. Chem. 4, 270(1965).

22. O.F. Williams and J.C. Bailar, Jr., J. Am. Chem. Soc. 81, 4464(1959).

23. F.H. Dickey, W. Fickett, and H.J. Lucas, J. Am. Chem. Soc. 74, 944(1952).

24. R. Sayre, J. Am. Chem. Soc. 77, 6689(1955).

25. B.N. Figgis and R.S. Nyholm, J. Chem. Soc. 4190(1958).

26. B.N. Figgis and J. Lewis in "Modern Coordination Chemistry", J.Lewis and R.G.Wilkins, Ed., Interscience, New York, N.Y. 1960.

27. R.S. Miller and L. Pratt, Discussion Faraday Soc. 34, 88(1962).

28. D.R. Eaton, A.D. Josey, W.D. Phillips and R.E. Benson, Discussion Faraday Soc. 34, 77(1962).

29. Gerd N.La Mar, William DeW. Horrocks, Jr., and Lenard C. Allen, J. Chem. Phys. 41, 2126(1964).

30. R.E. Robertson, in "Determination of Organic Chemistry by Physical methods", edited by F.C. Nachod and W.C. Phillips (Academic Press Inc., New York, 1962), Vol. 2, Chap. 10.

31. D.R. Eaton, A.D. Josey, W.D. Phillips, and R.E. Benson, Mol. Phys. 5, 407(1962).

32. D.R. Eaton, A.D. Josey, W.D. Phillips, and R.E. Benson, J. Chem. Phys. 37, 347,(1962).

33. D.R. Eaton, W.D. Phillips, A.D. Josey, R.E. Benson, and T.L. Cairns, J. Am. Chem. Soc. 84, 4100(1962).

34. D.R. Eaton, W.D. Phillips, and D.J. Caldwell, J. Am. Chem. Soc. 85, 397(1963).

35. D.R. Eaton, A.D. Josey, and W.A. Sheppard, J. Am. Chem. Soc. 85, 2689(1963).

36. E.A. LaLancette, D.R. Eaton, R.E. Benson, and W.D. Phillips, J. Am. Chem. Soc. 84, 3968(1962).

37. D.R. Eaton, A.D. Josey, W.D. Phillips, and R.E. Benson,

J. Chem. Phys. 37, 3513(1963).

38. L. Sacconi in'Transition Metal Complexes', Vol. 4, ed. R.L. Carlin, Marcel Deckker, Inc., New York, 1968.

39. A.D. Liehr and C.J. Ballhausen, Ann. Phys.(N.Y), 6, 134(1959).

40. G. Maki, J. Chem. Phys. 28, 651(1958).

41. C.R. Hare and C.J. Ballhausen, J. Chem. Phys. 46, 788(1964).

42. S.C. Nyburg, W.C.E. Higginson and J.S. Wood, Inorg. Chem. 3, 463(1964).

PART 2

CHAPTER 1

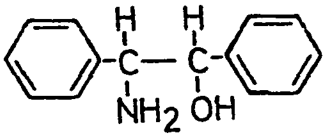
INTRODUCTION

In an attempt to correlate the coordinating ability of stilbenediamine and its derivatives, Hein and Muller[1] observed that acylation of the diamines destroys the coordinating ability of the amines and also that the compounds PhCH(NH_2)CH(OH)Ph (1,2-diphenyl-1-amino-2-hydroxyethane) (I) and amarine (2,4,5-triphenyl-2-imidazoline) (II) are inactive towards nickel. However, with amarine they isolated a complex of Co(II) bromide having a composition $Co(am)_3Br_2$ (am = amarine). This complex was found to be very sensitive towards air and moisture. Nothing has been reported in the literature about the stereochemistry of the above mentioned complex or about the transition metal complexes generally of this heterocyclic ligand.

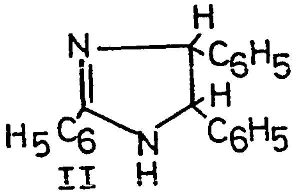
Recently considerable interest has been shown on the bonding properties and synthesis of imidazole (III) and its derivatives with transition metal ions because imidazole shows a close relationship with biological systems e.g. the histidyl residue of proteins. The compound 2,4,5-triphenyl-2-imidazoline is of special interest as on one hand it closely resembles imidazole and on the other it has the same number of possible bonding sites as stilbenediamine. Also amarine has been used for the sensitization of the heart to ventricular fibrillation.

The work of Hein and Muller showed this ligand to behave as a bidentate ligand whereas imidazole and its derivatives are generally monodentate. Therefore, it seemed profitable here to prepare the transition metal complexes of amarine and to compare spectroscopically and magnetically the coordinating properties of this ligand with imidazole and its derivatives.

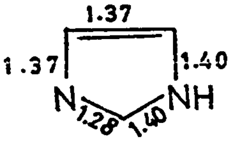
Several studies have been made on the imidazole ring to determine, if possible, which nitrogen is involved in the binding to a transition metal ion. Although Raman and infrared spectra of imidazole[2] suggest the non-equivalence of C=N bonds, n.m.r. results on the ligand indicate that the pyrrole hydrogen exchanges rapidly with the solvent (H_2O) and also with the nitrogen at the 3-position. This amidine tautomerism can also be predicted in the amarine molecule.



I



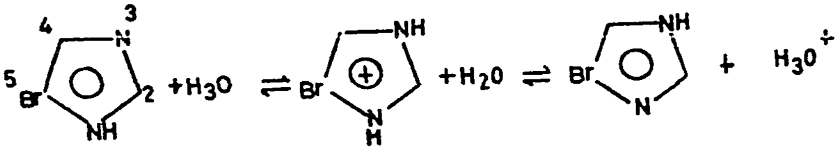
II



III

Eilbeck, Holmes <u>et al</u>.[3-5] have investigated a large number of complexes of imidazole and substituted imidazoles. The differences in structure have been discussed in terms of steric hindrance and basicity of the ligand. For example, in the case of 2-methylimidazole, although the complexes $(MIz)_2CoX_2$ (where MIz = methylimidazole and X = Cl, Br, or I), $(MIz)_2NiBr_2$, and $(MIz)_2NiI_2$ appear to be the same as those found for the corresponding 2-methylpyridine complexes, $(MIz)_2NiCl_2$, $(MIz)_2CuX_2$ (X = Cl or Br), and $(MIz)_4CuCl_2$ are quite different. The tendency of forming hexacoordinated complexes in the latter case is attributed to the larger N-C-CH_3 angle in 2-methylimidazole[6] (130°) than in α-methylpyridine[7] (115°).

Imidazoles containing labile imino-hydrogen and a substituent in the 4- or 5- position are tautomeric systems and react as a tautomeric mixture of the two possible forms[8].

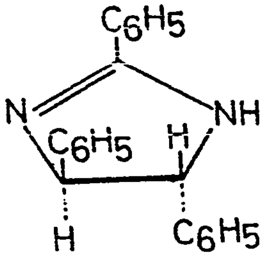


However, in the complexes it is expected that one form of the ligand would be preferred for steric reasons and it has been shown by X-ray studies of $Cu(NO_3)_2(5\text{-methylimidazole})_4$[9] that the molecule coordinates with the substituent in the 5-position. There is no evidence to suggest that any of the complexes contains both 4- and 5- bromoimidazole.

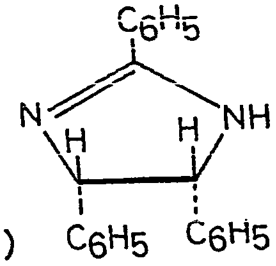
The differences in tetrahedral and octahedral structures of Co(II) and Ni(II) complexes of imidazole with the corresponding pyridine complexes have been discussed[5] in the light of σ(electron donor) and π(electron acceptor) properties of the ligands. Epstein, Straub and Maricondi[10] have studied the Mossbauer spectra of some porphyrin complexes with pyridine and imidazole and to explain the spectra they assumed that imidazole is weaker π-acceptor than pyridine. If π-bonding is so important in the complexes of the type L_2MX_2 (where L = ligand, X = Cl,Br,I etc.), a reduction in the π-acceptor properties of the ligand will tend to increase the charge on the metal atom and thus favour a lower coordination number.

The basicity of the ligand does not seem to be a governing factor in the case of the formation of octahedral and tetrahedral Co(II) complexes. Billing and Underhill[11] have shown that for ligands having a greater basicity than pyridine, the complexes are tetrahedral monomers whilst complexes with ligands of lower basicity possess polymeric octahedral structures. Eilbeck and his coworkers[5] found that the complex $Co(BIz)_2Cl_2$ (BIz = bromoimidazole) has a tetrahedral structure although the basicity of 4(5)-bromoimidazole is much lower than that of pyridine.

The presence of three phenyl groups at 2,4 and 5-positions of 2-imidazoline ring makes the compound a sterically hindered ligand. The two isomeric forms IV and V differ from one another in the respect that in amarine the two phenyl groups at 4 and 5-positions are *cis* to one another whereas in isoamarine they are <u>trans</u>.



(IV) isoamarine



(V) amarine

The solubility of amarine in water or in very dilute acid (hydrochloric) is so low that an ordinary method of determining its basicity fails to produce any result. However, it is interesting to note that in most cases the complexes are readily hydrolysed in presence of excess of ligand.

A study of spectral and magnetic properties of these complexes is required to elucidate the molecular structure and stereochemistry of the transition metal complexes of amarine. In the present thesis, therefore, the preparation and spectral and magnetic properties of Vanadium(III), Co(II), Zn(II), Cd(II) and Hg(II) complexes of amarine are reported. The stoichiometry and stereochemistry of the complexes are discussed in the light of the basicity, steric hindrance and π-bonding properties of the ligand.

A new complex of imidazole with V(III) has been prepared and the stereochemistry is discussed.

CHAPTER 2

EXPERIMENTAL

(a) Purification and drying of solvents:

Earlier[1] preparations of nickel and cobalt complexes of amarine showed that in order to obtain the complexes in a pure state it is necessary to have the solvents rigorously dry.

Benzene was dried by refluxing chemical grade benzene over calcium hydride in dry nitrogen atmosphere. The fraction distilling at 81°C was collected under dry nitrogen.

Anhydrous ethanol was obtained by refluxing absolute alcohol over anhydrous magnesium perchlorate for three days. It was then distilled and collected under nitrogen.

Ether was dried by refluxing anhydrous ether (Mallinckrodt) over calcium hydride followed by distillation.

All of these solvents were stored over Molecular Sieve 4A which had been freshly dried by heating at 200°C in vacuo for one day.

(b) Preparation of ligands:

Amarine was prepared by the method due to [illegible] and [illegible] [illegible] [illegible] the [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]

Anal. Calcd. [illegible] [illegible] [illegible]

Found: [illegible] [illegible] [illegible]

[illegible] Preparation of metal complexes

All the complexes were dried in vacuo at room temperature, unless stated otherwise.

Dichlorobis(2,4,5-triphenyl-2-imidazoline)copper(II). Anhydrous copper(II) chloride (0.4722 g., 1 mol.) was dissolved in the minimum volume of hot absolute alcohol and added to a hot ethanolic solution of 2,4,5-triphenyl-2-imidazoline ([illegible] g., [illegible] mol.). The volume of the mixture was reduced to half by boiling and then allowed to cool. Ether was added gradually to the mixture till crystals [illegible]. The green complex [illegible] on standing [illegible] was filtered off and washed with ether. [illegible]

Anal. Calcd. [illegible]

Found [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] in the minimum volume of hot absolute alcohol and added to a hot ethanolic solution of 1,4,5-triphenyl-2-[illegible] [illegible] mole). The volume of the mixture was then reduced by boiling and then allowed to cool. Ether was added gradually to the mixture till the crystals began to separate. The light green crystals were filtered out, dried at room temperature under vacuum and stored separately. The [illegible] analysis and spectroscopic studies of this complex showed it to be [illegible]. However, this compound was found to be diamagnetic.

To the filtrate some more ether was added when yellow [illegible] crystals started to come out. This was filtered, washed with ether and dried at room temperature under vacuum. [illegible]

[illegible]

then a white crystalline precipitate separated immediately. The precipitate was filtered through a Buchner funnel and recrystallised from hot ethanol. M.Pt. 306.5°C.

Anal. Calcd. C, 68.42 ; H, 4.95 ; Cl, 9.67 ; Zn, 8.92.

Found: C, 68.75 ; H, 5.01 ; Cl, 9.56 ; Zn, 8.62.

Dichlorodi-(2,4,5-triphenyl-2-imidazoline) Hg(II).

This compound was prepared in the same manner as dichlorodi-(2,4,5-triphenyl-2-imidazoline) Zn(II) and was recrystallised from hot absolute alcohol. M.Pt. 221-222°C.

Anal. Calcd. C, 58.04 ; H, 4.14 ; Cl, 8.16.

Found: C, 58.26 ; H, 4.21 ; Cl, 7.93.

Dibromodi-(2,4,5-triphenyl-2-imidazoline) Cd(II).

This compound was prepared as above and recrystallised from hot alcohol. M.Pt. 278-280°C.

Anal. Calcd. C, 58.06 ; H, 4.17 ; Br, 18.37.

Found: C, 58.20 ; H, 4.17 ; Br, 18.52.

Dibromodi-(2,4,5-triphenyl-2-imidazoline) Co(II).

Anhydrous Co(II) bromide (1.3748 g., 1 mole.) was dissolved in about 125 ml. of dry ethanol and added to a solution of amarine ([illegible] g., 3 mole.) in dry benzene. The mixture was kept overnight. The fine needle shaped crystals were separated by decantation, washed with alcohol, filtered and dried at room temperature under vacuum. All the reactions were carried out in dry nitrogen atmosphere.

M. Pt. 310°C.

Anal. Calcd. C, 61.43 ; H, 4.53 ; Br, 19.46.

Found: C, 61.86 ; H, 4.45 ; Br, 19.56.

<u>Trichlorotri-(2,4,5-triphenyl-2-imidazoline) V(III).</u>

Anhydrous V(III) chloride (0.3008 g., 1 mole.) was dissolved in the minimum volume of hot absolute alcohol and added to an alcoholic solution of amarine (2.222 g., 4 mole.). The volume of the mixture was reduced to half and ether was added gradually to the cool solution when brown crystals separated out. This was filtered, washed with ether and dried under vacuum. The colour changed to deep green on standing. M.Pt. 283.5°C.

Anal. Calcd. C, 71.89 ; H, 5.17 ; Cl, 10.1.

Found: C, 73.30 ; H, 5.67 ; Cl, 9.8.

<u>Trichlorohexa-imidazole V(III).</u>

The complex was prepared as trichlorotri-(2,4,5-triphenyl-2-imidazoline) V(III) complex. M.Pt. 204°C.

Anal. Calcd. C, 38.22 ; H, 4.28 ; Cl, 18.79.

Found: C, 38.41 ; H, 4.25 ; Cl, 18.89.

(d) Analysis of metal complexes:

The complexes were analysed for metals by the standard methods outlined in " A Textbook of Quantitative

Inorganic Analysis " by A.I.Vogel. Halogens were estimated as silver halides as usual. Microanalysis for carbon, hydrogen and nitrogen were done by Mr. A.B.Gygli in the microanalysis laboratory, Toronto.

(e) Magnetic susceptibility measurements:

Bulk susceptibility measurements were made at room temperature, using a Gouy balance as described in experimental section of Part I of this thesis. All measurements were carried out three times, the replicate measurements involving a repacking of the tube. The diamagnetic corrections were computed from Pascal's constants.

(f) Spectroscopic measurements:

Infrared spectra were recorded as Nujol mulls using Beckman IR7 and Beckman IR5 spectrometers. Reflectance and solution spectra were obtained with Unicam SP 500 single beam and Beckman DKI double beam spectrophotometers. The NMR spectra were run on a Varian A-60 high resolution spectrometer.

CHAPTER 3

RESULTS AND DISCUSSION

(A) Electronic spectra:

(i) Copper complexes.

The electronic spectra of Cu(II) complexes of imidazole and its derivatives have been reported by Eilbeck, Holmes *et al*.[3-5] In almost all the cases the complexes are found to possess a distorted octahedral structure. A detailed examination of the relationship between the electronic properties of the copper(II) ion in these complexes and the stereochemistry of the ligand environment present has not been possible due to the lack of X-ray crystallographic data available for them. Therefore, in the present case a comparison is made between the shape and position of absorption bands of Cu(II) complexes of amarine with that of absorption bands already reported in the literature for Cu(II) complexes of pyridine, imidazole and its derivatives and therefrom a possible conclusion is drawn.

Energy-level diagram:

The energy-level diagram for ligand fields of D_{4h} (Figure 1) would predict three transitions, while that for

D_{2h} would require four transitions.

The true symmetry of the $Cu(am)_2^{2+}$ should be D_{2h} and that of $Cu(am)_4^{2+}$, D_{4h}. It is expected that for σ-bonding ligands the splitting of the $^2E_g(O_h)$ level will be greater than that of the $^2T_{2g}(O_h)$ level and the $^2B_{2g}$ level will always lie below the $^2E_g(D_{4h})$ level. In D_{4h} symmetry, the three possible energy level sequences which may arise depending upon the degree of tetragonal distortion present, are

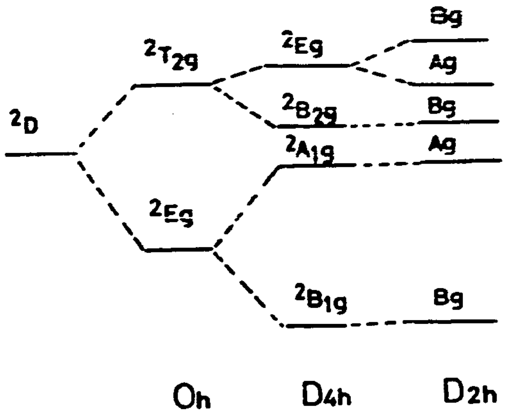


FIGURE 1. Energy diagram for a copper(II) ion in crystal fields of O_h, D_{4h}, and D_{2h} symmetry[13].

(a) $^2E_g > {}^2B_{2g} > {}^2A_{1g} > {}^2B_{1g}$

(b) $^2E_g > {}^2A_{1g} > {}^2B_{2g} > {}^2B_{1g}$

(c) $^2A_{1g} > {}^2E_g > {}^2B_{2g} > {}^2B_{1g}$

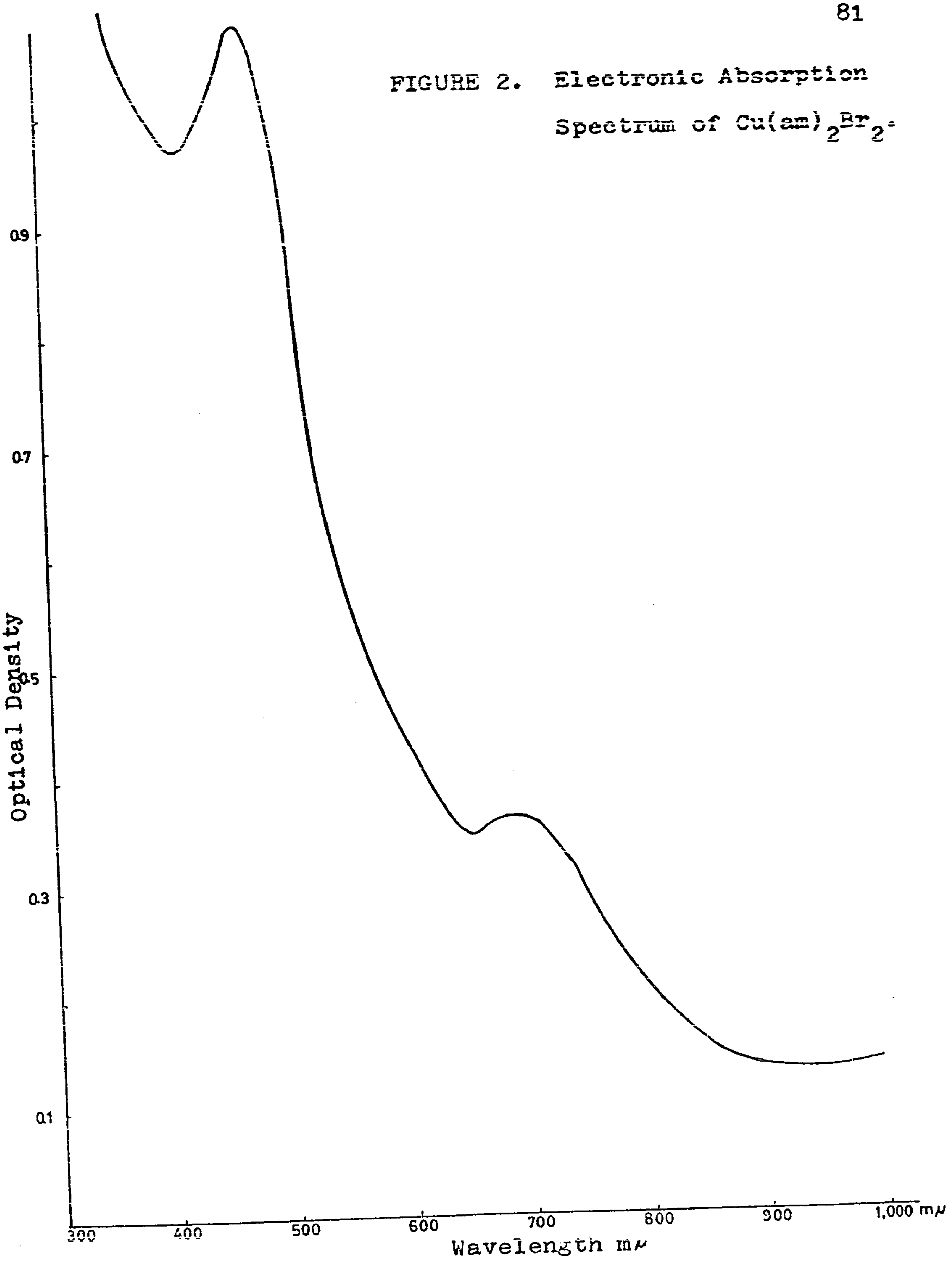
The first case corresponds to a low tetragonal distortion. The transition $^2B_{1g} \rightarrow {}^2E_g$ will be the most intense and the failure to observe a shoulder on the higher frequency side of this band would suggest that sequence (c) is unlikely in these complexes. Similarly D_{2h} symmetry would require four transitions.

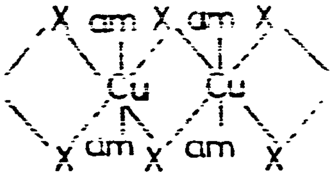
(a) $Cu(\underline{am})_2X_2$ (X= Cl,Br).

The reflectance spectra of these complexes show only two absorption bands, one at 13,300 and the other at about 20,000 cm^{-1}, the latter being shifted to 23,000 cm^{-1} in $Cu(am)_2Cl_2$. A study of crystal spectra of $Cu(py)_2X_2$ (X = Cl,Br,CNS) complexes[14] shows the same number of absorption bands, one at 14,000 cm^{-1} and the other in the near ultraviolet region. The band in the ultraviolet region is related to the charge-transfer band although the absorption intensities are comparable to the metal d-d transitions.

In the present case, however, the intensities of the second absorption band appear to be so low that it does not seem justified to assign these bands as charge-transfer type. Moreover, reflectance as well as the solution spectra of these complexes show another strong absorption band near the ultraviolet region. Thus, the occurrence of the second absorption band at higher energies indicates that amarine is a stronger π acceptor ligand than pyridine or imidazole. A halogen-bridged polymeric structure (A) is suggested for these complexes.

FIGURE 2. Electronic Absorption Spectrum of $Cu(am)_2Br_2$.





(A)

(b) Cu(am)$_4$Br$_2$.

The reflectance as well as the solution spectra of Cu(am)$_4$Br$_2$ in methanol suggest a tetragonally distorted octahedral structure. The four amarine molecules are expected to lie in the xy plane with the anions above and below as has been found in Cu(NO$_3$)(4-methylimidazole)$_4$[15]. The band maxima (15,690 cm^{-1}) are at lower frequencies than in the corresponding imidazole or benzimidazole complexes. This is probably due to the steric hindrance. The Cu-N bond should be longer in this case and hence a weaker field.

(ii) Cobalt complexes.

The reflectance spectra of blue Co(am)$_2$X$_2$ (X = Br,Cl) contains a very intense band at 16,500 cm^{-1} with shoulders at 18,000 and 15,800 cm^{-1}, and a further set of three bands at 8060, 6700 and 5950 cm^{-1}. The spectrum is very similar to that of the tetrahedral Co(imidazole)$_2$Cl$_2$[4] or Co(py)$_2$Br$_2$[16] which has bands at 16,530 and 15,270 cm^{-1}, and 9090, 6800 and 6020 cm^{-1}.

The ground state of Co^{++} in a tetrahedral field is $^4A_2$, followed by $^4T_2$ (F), $^4T_1$ (F) and $^4T_1$(P). Only the transitions $^4A_2 \rightarrow {}^4T_1$ (F) and $^4A_2 \rightarrow {}^4T_1$ (P) are allowed by the selections rule and the band at 16,500 cm^{-1} corresponds

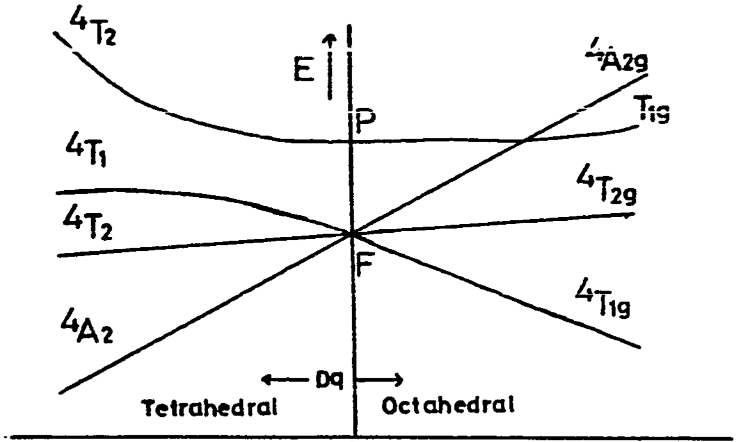


FIGURE 3. Energy level diagram for a d^7 ion (Co^{2+})[17].

to the transitions $^4A_2 \rightarrow {}^4T_1$ (P). The actual symmetry of the complex will therefore be C_{2v}, or lower, and the three near infrared bands can be assigned, in increasing energy, as the $^4A_2 \rightarrow {}^4B_1$, $^4A_2 \rightarrow {}^4A_2$ and $^4A_2 \rightarrow {}^4B_2$. The transitions correspond to the polarization parallel to the Z, Y and X molecular axes, respectively. Lever and Nelson[18] has shown that although the visible band related to transition $^4A_2 \rightarrow {}^4T_1$ (P) is expected to split, this band at about 16,000 cm^{-1} does not split in complexes of this type with C_{2v} symmetry.

(iii) Vanadium complexes.

(a) V(III) (imidazole)$_6$Cl$_3$.

From the energy level diagram (Figure 4) of

TABLE I.

DIFFUSE REFLECTANCE SPECTRA AND ROOM TEMPERATURE MAGNETIC MOMENTS.

Complex	μ_{eff} B.M.	Absorption maxima cm^{-1}	Assignments
$Co(am)_2X_2$ (X = Cl, Br)	4.54	18,000	
		16,500	${}^4A_2 \rightarrow {}^4T_1(P)$
		15,800	
		8,064	${}^4A_2 \rightarrow {}^4B_1$
		6,700	${}^4A_2 \rightarrow {}^4A_2$
		5,950	${}^4A_2 \rightarrow {}^4B_2$
$Cu(am)_4Br_2$	0.26	15,500 (in methanol)	
		5,180	
		4,545(broad)	
$Cu(am)_2Br_2$	1.81	21.270	
		14,280	
$Cu(am)_2Cl_2$	1.45	23,300	
		13,300	
$V(IzH)_6Cl_3$	1.75	22,200	${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$
		14,100	${}^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$
$V(am)_3Cl_3$	diamagnetic	10,470	

V(III), d^2 configuration for octahedral coordination it is expected to observe two absorption bands corresponding to transitions $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ respectively.

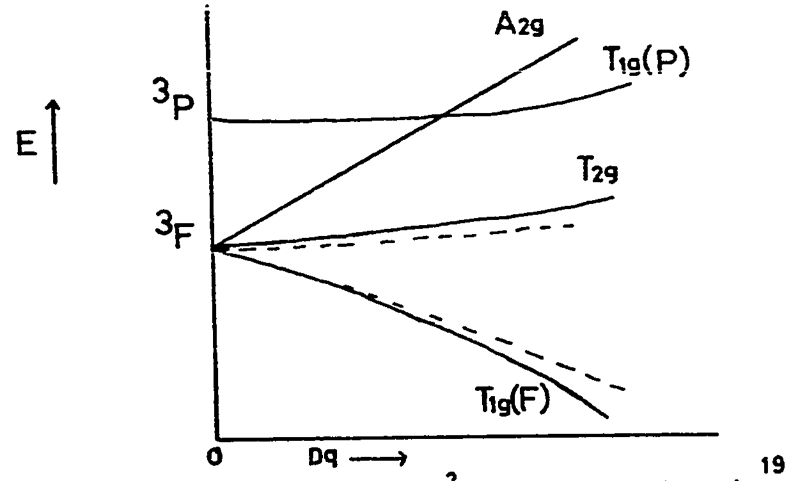


Figure 4. Energy level diagram for d^2 octahedral configuration.

The transition $^3T_{1g}(F) \rightarrow {}^3A_{2g}$ is expected to occur in the ultraviolet region obscured by the charge-transfer transition because even a rough value of Dq estimated from the lowest frequency transition will put this transition at about 37,000 cm^{-1}. The reflectance spectrum of V(IzH)$_6$-Cl$_3$ shows two absorption bands at 13,500 cm^{-1} and 20,000 cm^{-1} respectively. Thus, the spectrum is similar to that of octahedral $[V(H_2O)_6]^{3+}$ which has bands at 17,700 and 25,000 cm^{-1}, the difference being that the bands are shifted to lower frequencies.

(b) V(am)$_3$Cl$_3$.

The electronic spectrum of this complex is

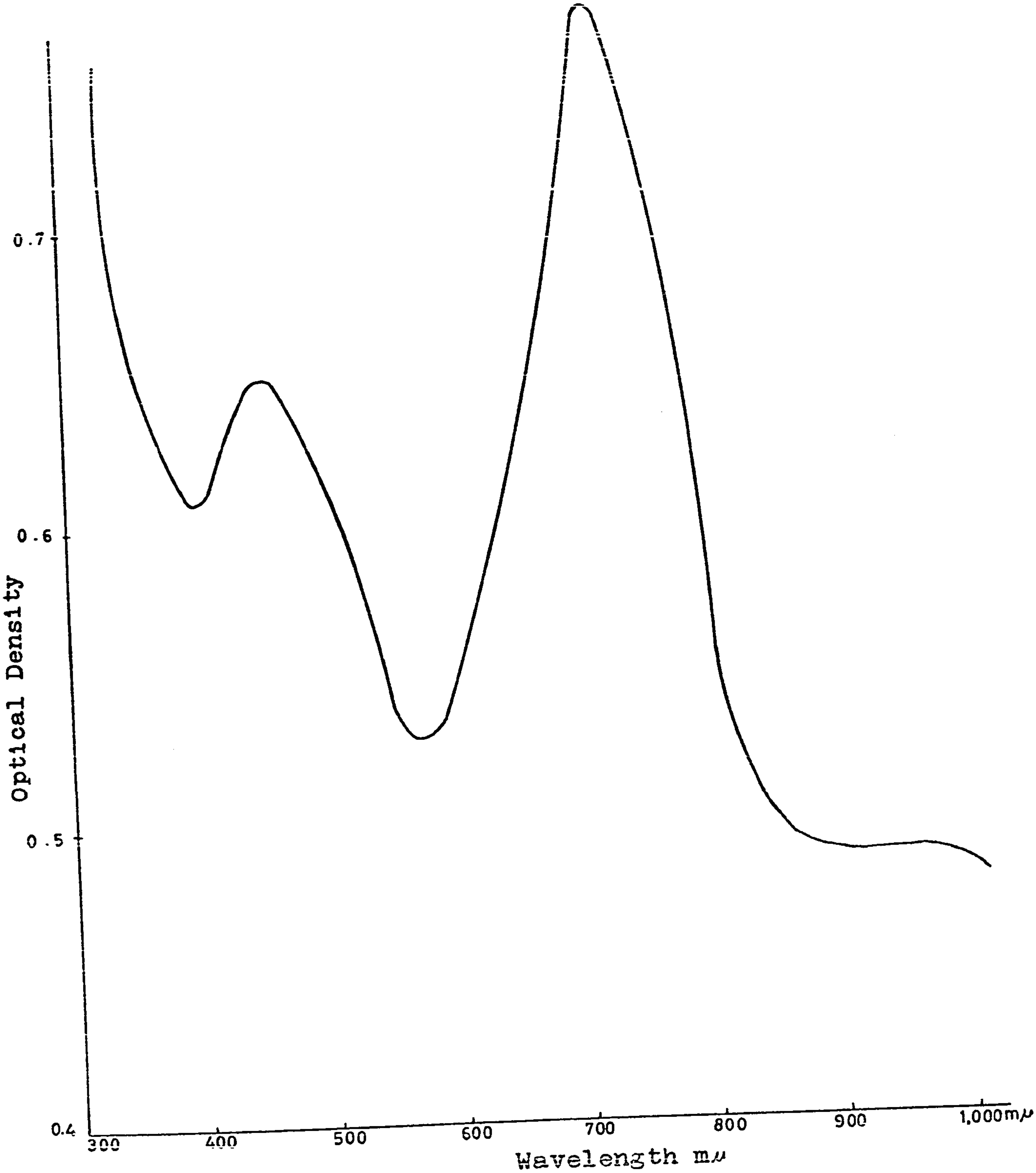


FIGURE 5. Electronic Absorption Spectrum of $V(IzH)_6Cl_3$.

completely different from the corresponding vanadium complex of imidazole. In methanol this complex shows only one absorption band at 10,460 cm^{-1}, the assignment of which is not possible due to uncertainty of the nature of the complex. The complex is diamagnetic at room temperature.

(B) Magnetic susceptibilities.

(a) Copper complexes.

Although the stereochemistry of Cu(II) ion does not have much effect on the average magnetic moment of the complex, the magnetic anisotropy depends upon the details of the ligand fields present. It is expected[20] that most of the copper(II) complexes will have a moment of about 1.9 B.M. at room temperature, with a spin-orbit coupling constant, λ, of -850 cm^{-1}. The magnetic moment of $Cu(am)_2Br_2$ (1.81 B.M. at room temperature is in agreement with the Cu(II) complexes of imidazole and its derivatives already reported in the literature. The magnetic moment of $Cu(am)_2Cl_2$ (1.45 B.M.) is lower than expected. It is surprising to note that the complex $Cu(am)_4Br_2$ is diamagnetic at room temperature. This curious feature of the magnetic behaviour of bivalent copper of seemingly adequate magnetic dilution needs further attention. An attempt to study the spin exchange between the copper atoms, if any, by magnetic moment measurements at low temperature failed to show anything as the magnetic moment of this complex was quite low even at room temperature.

For a tetrahedrally coordinated Cu^{++}, Figgis and Lewis[20] anticipate a moment of 2.2 B.M. at room temperature, which is much higher than the observed values for these complexes. Hence, the possibility of tetrahedrally coordinated Cu(II) is completely ruled out and the complexes essentially possess a tetragonally distorted octahedral structure.

(b) Cobalt complexes.

In a high-spin tetrahedral complex of Co(II), the ground term is $^4A_2$ and the moment is expected to be the spin-value modified by the factor $(1-4\lambda/10Dq)$ and with a TIP term from higher ligand field levels. These effects lead to the magnetic moment between 4.4 and 4.8 B.M. at room temperature. In the case of low-spin octahedral complex the magnetic moment should be close to the spin-only value for one unpaired electron i.e. 1.73 B.M. Similarly, for four-covalent low-spin complexes it is possible to predict a magnetic moment of 1.73 B.M.

The complexes $Co(am)_2X_2(X = Br,Cl)$ which are blue in colour, have the magnetic moment 4.5 B.M. which lies in the range 4.1 - 4.9 B.M. normally observed for tetrahedral cobalt complexes. A tetrahedral geometry is therefore, assigned to these complexes.

(c) Vanadium complexes.

For a V^{3+} ion in a cubic ligand field (octahedral coordination), the magnetic moment is expected to be about 2.7 B.M. at room temperature but $V(IzH)_6Cl_3$ has a magnetic moment of 1.75 B.M. a much lower value. $V(am)_3Cl_3$ appears to be diamagnetic. This unusual behaviour needs a thorough investigation although certain possibilities can easily be ruled out.

(D) Nuclear magnetic resonance studies.

(a) 2,4,5-triphenyl-2-imidazoline.

It has been pointed out earlier that although Raman and infrared spectra of imidazole suggest that there are two different types of nitrogen atoms in the imidazole ring, supported by the non-equivalence of C-N bond; ^1H NMR of the ligand indicates that the pyrrole hydrogen exchanges rapidly with the nitrogen at the 3-position. Hence, in solution the two nitrogen atoms become identical. It is not meaningful, therefore, to try and distinguish which nitrogen is bonded to the metal.

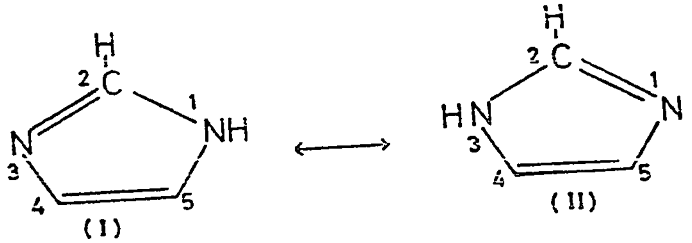


FIGURE 6 . Imidazole.

Amarine being similar to imidazole in structure is expected to show the same type of amidine tautomerism in solution.

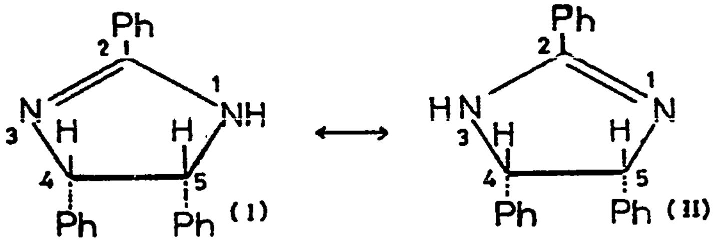


FIGURE 7. Amarine.

The ^1H nuclear magnetic resonance of amarine in $CDCl_3$ is shown in Figure 8. The presence of only one signal at -4.46ppm indicates that the two protons at 4 and 5-positions of the 2-imidazoline ring are equivalent. If there was no tautomeric exchange between structure I and II(Figure 7), the ^1H n.m.r. of this compound would have two different methine protons.

The signal due to the imino proton at -6.0ppm is comparatively at much higher field than the imino proton in imidazole. This can be explained as due to shielding of the =NH protons by phenyl groups. The multiplets at -7.1ppm -7.6ppm and 8.1ppm may be assigned to phenyl groups.

(b) Complexes.

The proton magnetic resonance spectra of Hg(II), Zn(II) and Cd(II) complexes of amarine show them to be different from imidazolate complexes of Zn(II), Cd(II) and Hg(II). Bauman and Wang[21] have suggested that the

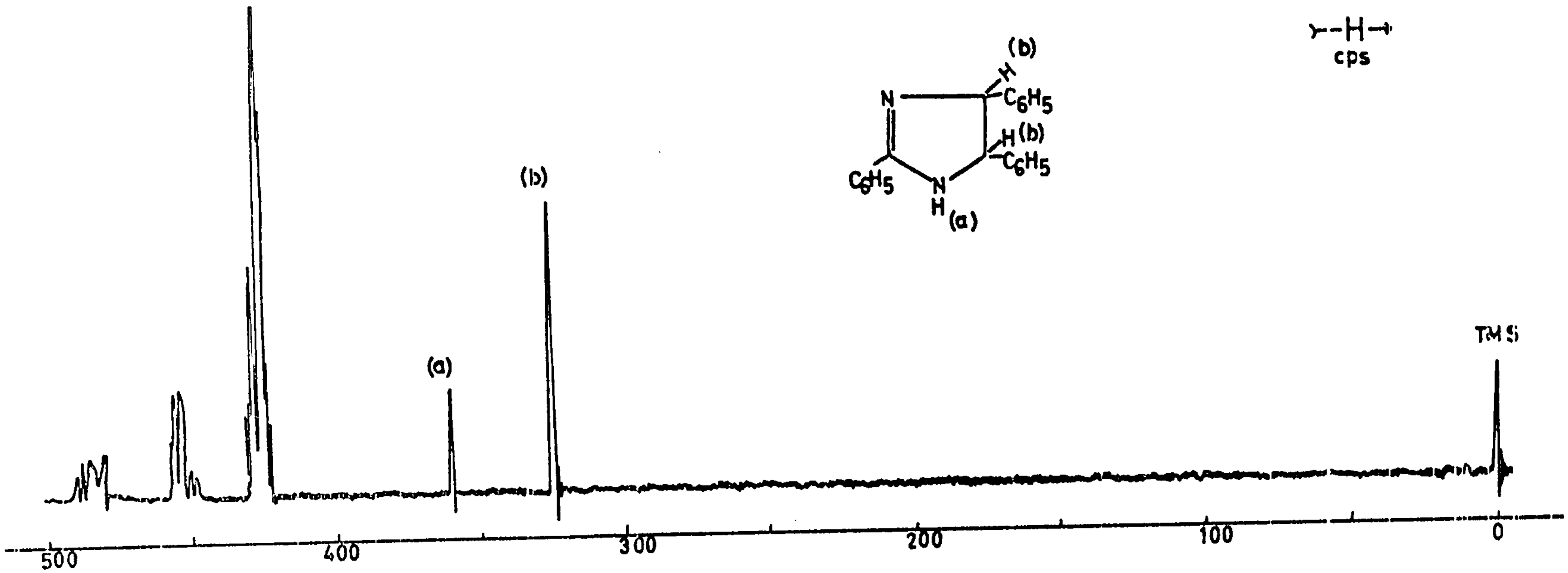


FIGURE 8. ^{1}H NMR Spectrum of amarine in $CDCl_3$ solution.

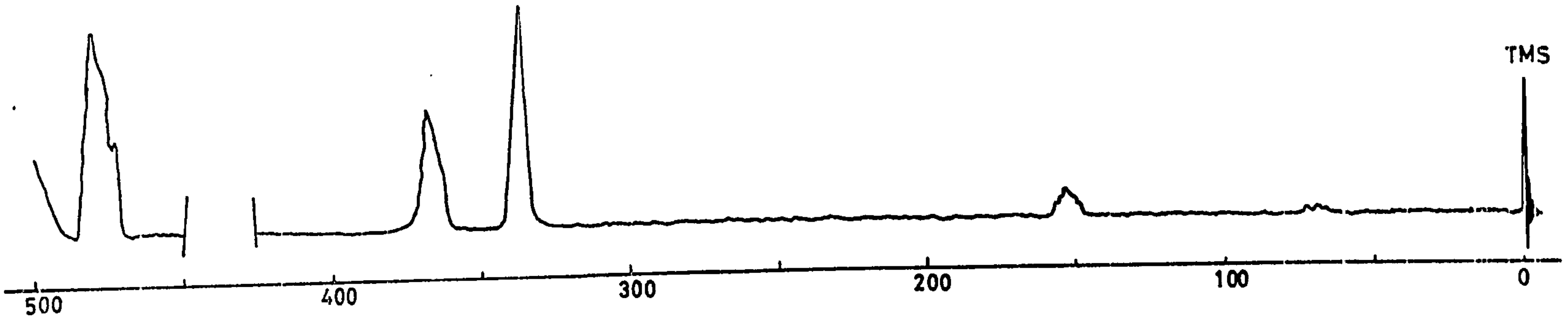


FIGURE 9. ^{1}H NMR Spectrum of $Hg(am)_2Cl_2$ in DMSO-d_6.

ionization of the pyrrole hydrogen in imidazole changes the monodentate imidazole molecule into the bidentate anion and thus the possibility of the formation of polymeric compounds with Zn(II), Cd(II) and Hg(II). The structure is shown schematically in Figure 10; which shows how the metal atoms are linked to the ligand molecules. It is interesting to note that the two nitrogen atoms in the ring are actually indistinguishable.

The presence of the =NH proton signal in the n.m.r spectrum(Figure 9) of metal complexes of amarine suggests that the bonding is through =NH nitrogen. That these complexes are not of the imidazolate type is also supported by chemical analysis and the presence of halogen atoms.

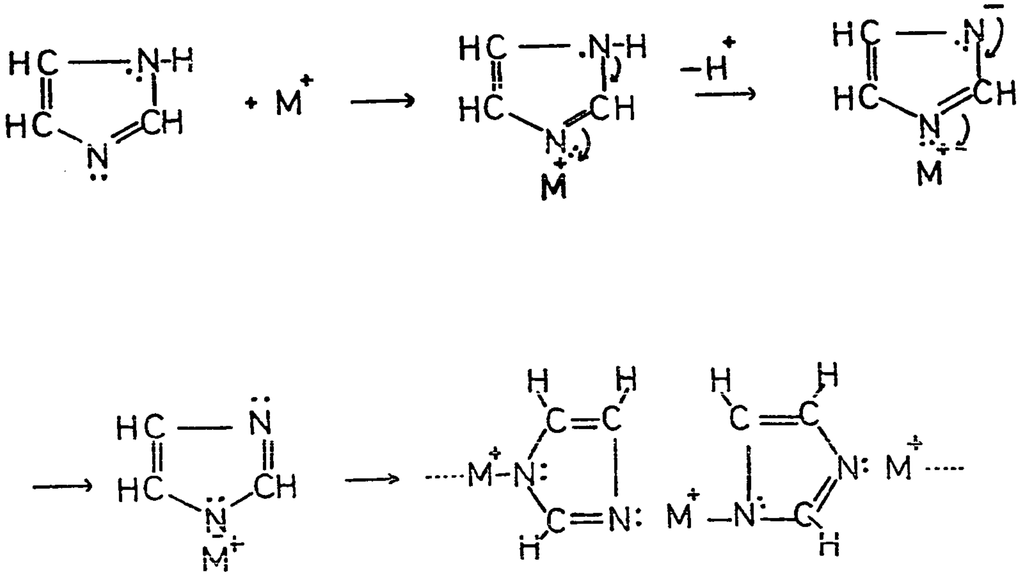


FIGURE 10. Structure of Polymeric complexes of Zn, Cd and Hg(II).

(D) Infrared studies.

The principal infrared absorption bands (300-4000 cm^{-1}) are listed in Table 2. As no detailed study has been made on the infrared spectra of 2,4,5-triphenyl-2-imidazoline compound, interest has centered upon the characteristic bands between 1500-1625 cm^{-1} only, in order to distinguish the metal complexes from their salts. White and Sonnenberg[22] have reported characteristic absorption of aryl-substituted imidazoles. They have assigned the bands at 1600 and 1565 cm^{-1} as due to ring stretching vibrations for phenyl groups. The strong absorption band near 690 cm^{-1} is probably due to C-H out-of-plane deformations for unsubstituted phenyl groups. The band at 3160 cm^{-1} is assigned to the N-H stretching vibration.

The infrared spectra of $M(am)_2X_2$ (where M =Co,Cu,Cd, Hg,Zn, and X = Cl,Br) are very similar to one another and to that of amarine itself. The only difference is that the N-H stretching vibration at 3160 cm^{-1} in the free ligand is shifted to about 3320 cm^{-1}. The X-ray crystal analysis of imidazole[6] shows intermolecular hydrogen-bonding in the solid state. Amarine being similar to that of imidazole is expected to show the similar type of hydrogen-bonding in the solid state. However, in the metal complexes, no hydrogen bonding can occur because one of the nitrogen atoms is coordinated to the metal ion and in all probability the

TABLE 2.

PRINCIPAL INFRARED ABSORPTION BANDS(300-4000 cm^{-1}).

Amarine	$Hg(am)_2Cl_2$	$Zn(am)_2Cl_2$	$Cd(am)_2Br_2$	Assignments
3160s	3320s	3350s(br)	3317s	-NH stretching
3060w	3060w	3060w	3060w	
3030w	3030w	3025w	3015w	
1612s	1610s	1610m	1610m	
1600s	1595s	1590m	1598m	
1565m	1564s	1565m	1565m	
1508m	1505m	1510m	1510m	
	1372s	1375m	1370m	
1328m	1328w		1328w	-CH bending
1275m	1280m	1275m	1282m	
1242m	1250m	1252m	1254m	-Ring breathing
1220m			1210w	
1180w			1142w	
1120m				
1070m	1070m		1072w	-CH bending
			1057w	-CH bending
	1025m	1028m	1026m	
984w	1008m	1012m	1005m	
968w	967w	970w	970w	
915s	913w	916w	912m	
	858w	862w	860m	

TABLE 2 (continued).

Amarine	$Hg(am)_2Cl_2$	$Zn(am)_2Cl_2$	$Cd(am)_2Br_2$	Assignments
780m	775m	778m	778m	
757m	756m	760m	758ms	- CH
742w	738m	738m	740ms	- CH
726m				
	705s	710m	708ms	
688m	690s	692s	690s	
	572s	575m	580s	
550w	555w	540w	555sh	
500m				
	472m	475m	475m	

br = broad, w = weak, s = strong, sh = shoulder,
m = medium , ms = medium strong.

The spectra were recorded in Nujol unless otherwise stated.

TABLE 2 (continued).

$Co(am)_2X_2$ (X= Br,Cl)	$Cu(am)_2Cl_2$	$Cu(am)_2Br_2$	$Cu(am)_4Br_2$	Assignments
3338m	3260s	3270s	3230s	-NH stretching
3058w	3060w	3060w	3060w	
3025w	3040w	3030w	3025w	
1605m	1610m	1605m		
1590m	1595m	1595m	1598s	C C stretching
1550ms	1555m	1555m	1560m	-NH bending
1505m	1508m	1510m	1505m	
1370ms	1374m	1375m	1370m	-CH bending
		1360m	1320m	
1280m	1280m	1280m	1275ms	-Ring breathing
1250ms	1240ms	1242s	1240m	
			1055m	
		1038m	1020m	
		954m	965m	
	914m	915m	910ms	
		855m	858m	
		835m	832m	
775m	775m	775m	775m	
758m	755m	758ms	755m	
	744m	748ms	746m	CH
735ms	730sh	733m	722m	CH
710m		700sh		

TABLE 2 (continued).

Co(am)$_2$X$_2$ (X=Br,Cl)	Cu(am)$_2$Cl$_2$	Cu(am)$_2$Br$_2$	Cu(am)$_4$Br$_2$	Assignments
690s	690s	690s	688s	
570m	575w	575m	570m	
	535w	520w	550w	
		500m		
			495m	

w = weak, s = strong, sh = shoulder, m = medium,
ms = medium strong.

The spectra were recorded in Nujol unless otherwise stated.

pyridine nitrogen atom, by analogy with the imidazole complexes. Hence, the different frequencies for the N-H vibrations with amarine itself are observed. It is important to note that the infrared spectra of $M(am)_2X_2$ (M = Zn,Cd,Hg and X =Cl,Br), are different from the corresponding imidazole complexes. In the case of imidazole complexes the complete absence of both the N-H stretching frequency at 3300 cm^{-1} and the δ(NH) frequency in the region (1400-1450) indicates the absence of the imino hydrogen in these complexes. The presence of N-H stretching frequency in the amarine complexes of these metals definitely proves that they are not of the imidazolate type of compounds. This is also supported by ^1H n.m.r. of these compounds in dimethyl sulfoxide.

(E) Conclusion.

The presence of three phenyl groups at the 2,4, and 5-positions of the imidazoline ring makes the compound a sterically hindered ligand. Although there is a close similarity between the Cu(II) complexes of imidazole and amarine, in the respect that both the ligands form a series of complexes in which 2 or 4 molecules of the ligand are coordinated to the metal atom, the diamagnetic property of $Cu(am)_4Br_2$ distinguishes itself from the Cu(II) complexes of imidazole and its derivatives. The instability of other metal (Mn, Fe, Co, Ni) complexes may be attributed to the steric factor rather than basicity, as the precipitation of metal hydroxides can not be explained simultaneously with halides being coordinated to the metal atom and the formation of metal hydroxides. Thus, Co(II) halides (Br,Cl) form only tetrahedral complexes with amarine and in excess of the ligand the complex tends to hydrolyze. For similar reasons, probably, Zn(II),Cd(II), and Hg(II) halides do not form imidazolate type of complexes. The behaviour of VCl_3 towards the ligand is quite interesting. The diamagnetic properties of the vanadium trichloride-amarine complex needs some further investigation. It is also interesting to note that when the ratio of metal chloride : ligand is 1:2, a white compound believed to be amarine hydrochloride (supported by infrared spectrum and ^1H nuclear magnetic resonance spectrum) is precipitated in absolute alcohol.

REFERENCES

1. Fr. Hein and H. Muller, Z. anorg. allgem. Chem. 283, 172(1956).
2. David Garfinkel and John T. Edsall, J. Am. Chem. Soc. 80, 3807(1958).
3. W.J. Eilbeck, F. Holms, C.E. Taylor, and A.E. Underhill, J. Chem. Soc.(A), 1968, 128.
4. W.J. Eilbeck, F. Holms, and A.E. Underhill, J. Chem. Soc.(A), 1967, 757.
5. W.J. Eilbeck, F. Holms, C.E. Taylor, and A.E. Underhill, J. Chem. Soc.(A), 1968, 1189.
6. S. Martinez-Carrera, Acta Cryst. 1966, 20, 783.
7. B. Bak, J. Rastrup-Anderson, and L. Harsen-Nygaard, Mol. Spectroscopy. 1958, 2, 361.
8. K. Hofmann, 'Imidazole and its Derivatives Part I', Interscience, London. 1953, p-26; M. Charton, J. Org. Chem. 1965, 30, 3346.
9. H. Montgomery and E.C. Lingafelter, J. Phys. Chem. 1960, 64, 831.
10. L.M. Epstein, D.K. Straub, and C. Maricondi, Inorg. Chem. 1967, 6, 1720.

11. D.E. Billing and A.E. Underhill, J. Chem. Soc.(A), 1968, 29.

12. O.F. Williams and J.C. Bailar, Jr., J. Am. Chem. Soc. 74, 944(1952).

13. I.M. Procter, B.J. Hathaway, and P. Nicholls, J. Chem. Soc.(A), 1678(1968).

14. J. Ferguson, Rev. Pure appl. Chem. 1964, 14, 1.

15. H. Montgomery and E.C. Lingafelter, J. Phys. Chem. 1960, 64, 831.

16. J. Ferguson, J. Chem. Phys. 1960, 32, 528.

17. Leslie E. Orgel, 'An Introduction to Transition-Metal Chemistry', John Wiley & Sons Inc. 1960.

18. A.B.P. Lever and S.M. Nelson, Chem. Comm. 1965, 168.

19. Thomas M. Dunn in 'Some Aspects of Crystal Field Theory', Harper and Row, Publishers, New York.

20. B.N. Figgis and J. Lewis in 'Progress in Inorganic Chemistry', Vol. 6, edited by F.A. Cotton, Interscience Publishers, New York, 1964.

21. J.E. Bauman and J.C. Wang, inorg. Chem. 1964, 3, 368.

22. D.M. White and Joseph Sonnenberg, J. Org. Chem.(7), 29, 1926(1964).

APPENDIX I. INFRARED SPECTRA OF Ni(II) COMPLEXES OF <u>meso</u>-STILBENEDIAMINE.

$\underline{\mathrm{meso}}$-stien. in KBr	$\mathrm{Ni(dca)_2 \cdot xH_2O}$ in KBr	$\mathrm{Ni}(\underline{\mathrm{ms}}\text{-stien})_2\mathrm{Cl}_2$ Yellow	$\mathrm{Ni}(\underline{\mathrm{ms}}\text{-stien})_2(\mathrm{ClO_4})_2$ Yellow	Assignments
3345			3270s	$-\mathrm{NH_2}$ st. asymmetric mode
3270			3248sh	$-\mathrm{NH_2}$ st. symmetric mode
			3210s	
3080w		3080w	3128s	
3060w		3020w	3068w	Aromatic =CH st.
3025			3030w	
2900w				≡CH(tertiary) st.
2870w				
	1630s			$-\mathrm{C}{\lessgtr}^{\mathrm{O}}_{\mathrm{O}^-}$ vibrations
1590m		1580s	1590s	-NH def.
1490m		1492m	1492w	C-N vibrations
1450m				C=C skeletal in plane vib.
	1395s	1375s	1375s	

APPENDIX I (continued).

meso-stien. in KBr	Ni(dca)$_2$.xH$_2$O in KBr	Ni(ms-stien)$_2$Cl$_2$ Yellow	Ni(ms-stien)$_2$(ClO$_4$)$_2$ Yellow	Assignments
			1210s	
	1220m			
			1175m	
			1148m	
		1052m	1050s(b)	
				-NH$_2$ wagging
		918m		
900ms(b)				
		815w	815w	
782m	775w			
		748s	742sh	
752s				
	715m	735ms		
				CH out of plane def.
		695s		
692m				-NH$_2$ asymmetric rock.
577s				-NH$_2$ symmetric rocking.
		549m		
524s				
		453ms	495m	
370m(b)				

APPENDIX II. INFRARED SPECTRA OF Ni(II) COMPLEXES OF <u>meso</u>-STILBENEDIAMINE.

$\mathrm{Ni(\underline{ms}\text{-}stien)_2(dca)_2 \cdot 2H_2O}$ (Yellow I)	$\mathrm{Ni(\underline{ms}\text{-}stien)_2(dca)_2 \cdot 4H_2O}$ (Blue I)	Assignments
3365ms	3360ms	$-NH_2$ st. asy. mode
3300m	3330m	$-NH_2$ st sym. mode
3240m	3275m	
	3150w	
3060w	3065w	-Aromatic =CH st.
3030w	3030w	
1630s	1635s	$-\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}-$ vibrations
1585s	1592s	-NH def.
1540w		
1495w	1495w	C-N vibrations
1370sh	1370s	
1364s	1345sh	
1210m	1210m	
1050m	1040m	
980s	990s	
815m	812m	
776sh	765s	
760s	742m	
725m		
695s	695s	

APPENDIX II (continued).

Ni(*ms*-stien)$_2$(dca)$_2$· 2H$_2$O (Yellow I)	Ni(*ms*-stien)$_2$(dca)$_2$· 4H$_2$O (Blue I)	Assignments
560w	568m	
	536m	
524w		
503w		
453w		
	425vw	

b = broad, w = weak, s = strong, v = very, sh = shoulder,
m = medium, ms = medium strong, vw = very weak.
The spectra were recorded in Nujol unless otherwise stated.