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CONTENTS AND STUDIES OF SOME METAL COMPLEXES  
OF DIHYDROCARBAZIN ACID DERIVATIVES

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PRESENTED TO  
THE UNIVERSITY OF INDIA FOR COMPUTERISED

DEGREE OF DOCTOR  
IN CHEMISTRY

[PARTLY BY PAPER AND PARTLY BY SEMINAR]

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1973

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**SYNTHESIS AND STUDIES OF SOME METAL COMPLEXES  
OF DITHIOCARBAZIC ACID DERIVATIVES**



**A THESIS SUBMITTED TO  
THE UNIVERSITY OF POONA FOR THE DEGREE OF  
MASTER OF SCIENCE  
IN CHEMISTRY  
[PARTLY BY PAPERS AND PARTLY BY RESEARCH]**

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1979

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CHAPTER I : GENERAL INTRODUCTION

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1

This thesis presents work on the synthesis and characterization of several new metal complexes with sulphur-nitrogen chelating ligands, phenyldithiocarbamic acid, S-methyl-N-(phenyl)ethylidendithiocarbazate and S-methyl-N-(ferrocenyl)ethylidendithiocarbazate.

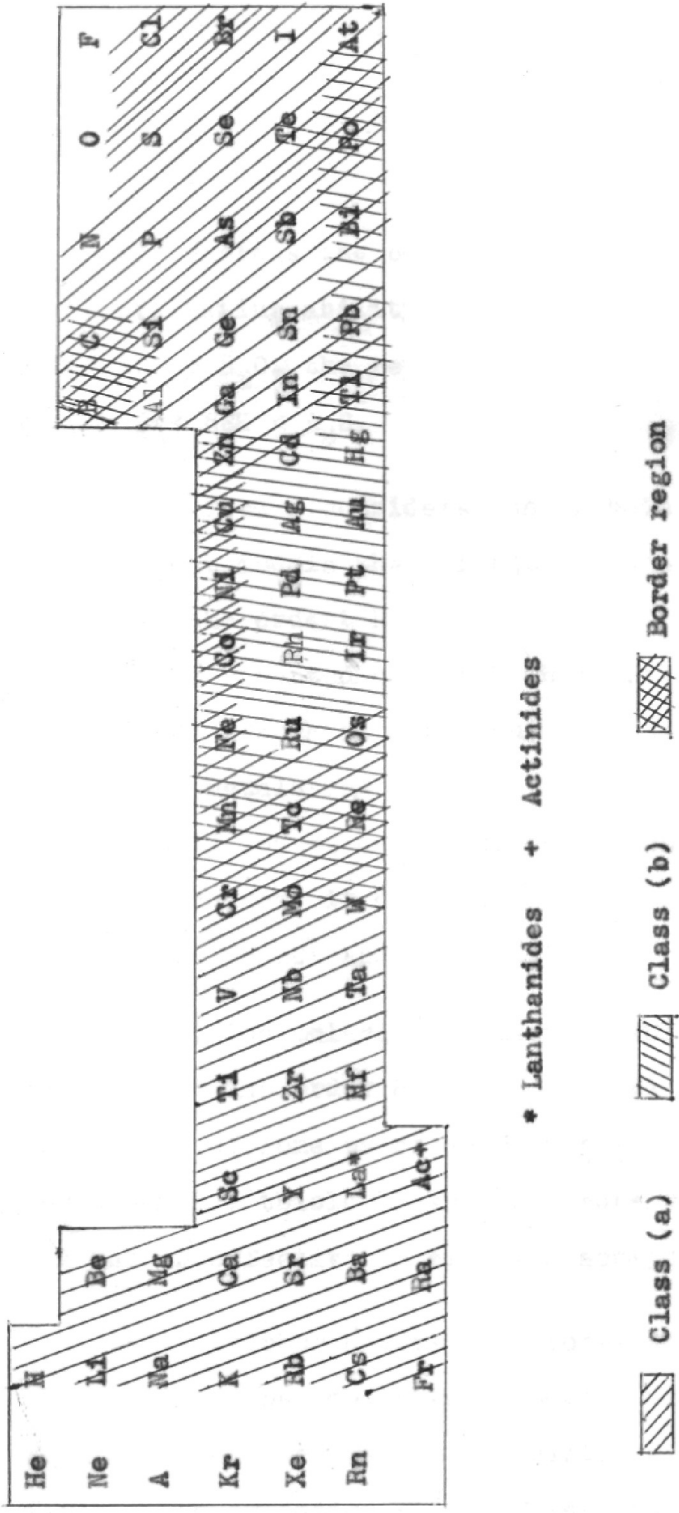
Our understanding of coordination compounds dates from the time of Alfred Werner, the 1913 Noble prize winner who is regarded as the Father of coordination chemistry. Coordination chemistry is primarily concerned with metal complexes. Metal complexes play a very important part in our lives. Since the study of metal complexes contributed greatly to our understanding of chemical bond and of inorganic chemistry as a whole, for many years these compounds were of interest to the theoretical and inorganic chemists only. Subsequently, metal complexes have played vital roles in analytical chemistry. Today, metal complexes are of vital importance in the syntheses of organic chemicals, in polymerization processes and in our understanding of biological processes. Furthermore, the current interest of organic compounds containing sulphydryl and disulphide groups stems from the fact that sequestering agents remove metallic ions and the resulting nonionic organometallic complex is less toxic and more rapidly excreted than the metallic ions.

As we know, a metal complex is formed when a number of ions or molecules combine with a central metal atom or ion to form an entity in which the number of atoms directly attached to the central atom exceeds the normal valency (oxidation state) of this atom. Metal complexes may be neutral (no charge), cationic (positively charged), or anionic (negatively charged). The groups bonded to the central metal atom are called ligands. A ligand may be attached to the central atom by more than one donor atom, thus forming a heterocyclic ring, in which case the ligand is termed as a chelating agent and the resulting complex a metal chelate.

From a survey of the relative affinities of ligand atoms for metal ions, Ahrland, Chatt and Davies<sup>1</sup> divided metals into two classes, (a) and (b). Class (a) includes metals forming more stable complexes with ligands whose donor atoms are the first row elements (N,O,F) and class (b) includes those preferring to bond to ligands having second-row elements as donor atoms, (P,S,Cl) as shown in Fig.1.

For good many years, in the synthesis and study of metal complexes, ligands with oxygen and nitrogen donor atoms received far greater attention as compared to those with sulphur donor atom. However, in recent years, the interest in ligands with sulphur donor atom has considerably enhanced.

In a review article, Livingstone and Akbar Ali<sup>2</sup> have made some general observations regarding particular features of sulphur as a donor atom, which are as follows:



\* Lanthanides + Actinides

 Class (a)    
  Class (b)    
  Border region

Fig. 1. Classification of acceptor atoms in their normal-valent states.



(i) Whereas the permanent dipole moment and the coordinating ability decrease in the order:  $H_2O > ROH > R_2O$ , the reverse order holds for sulphur, viz.  $H_2S < RSH < R_2S$ .

(ii) From a consideration of both electrostatic and covalent models the strength of bonding to a metal ion is in the order:  $RO^- > RS^-$  and  $R_2O > R_2S$ . However, sulphur has vacant d orbitals which can be used for  $d_{\pi}-d_{\pi}$  bonding such as can occur with the latter transition metals and with the early transition metals in unusually low oxidation states. Consequently, if  $\pi$ -bonding occurs, it can cause a reversal of the order to  $RS^- > RO^-$  and  $R_2S > R_2O$ .

(iii) The polarizabilities of sulphur donors decrease in the order  $S^{2-} > RS^- > R_2S$ ; furthermore, the number of lone pairs decreases in the same order. Consequently, thiole ligands are more polarizable but not as effective  $d_{\pi}$  electron acceptors as thioethers.

(iv) Sulphur donors bind more strongly to (b) class metals than do oxygen donors. Class (b) metals form a triangular area in the centre of the Periodic Table. The oxidation state of the metal affects the

degree of (b) character which is strongest for transition metals in low oxidation states i.e., metals having non-bonding d electrons and thus capable of forming  $d_{\pi}-d_{\pi}$  bonds by donating a pair of electrons to the ligand.

(v) The spectrochemical series of ligands is arranged according to the spectroscopic splitting parameter  $\Delta$  or  $10 Dq$ . Although some sulphur donors including S-bonded  $SCN^{-}$ ,  $(RO)_2PS_2^{-}$ , and  $S^{2-}$  have a low position in the series near  $Cl^{-}$ ,  $R_2S$  falls in the middle of series, probably between  $H_2O$  and N-bonded  $SCN^{-}$ , while S-bonded  $SO_3^{2-}$  has a late position near  $NO_2^{-}$ . The position of  $RS^{-}$  has not been established.

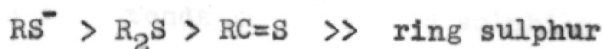
(vi) Sulphur ligands occupy a late position in the nephelauxetic series which is, in effect, a measure of the degree of covalent bonding between metal and ligand. The series of donor atoms (arranged according to decreasing values of  $1-\beta$ ) is roughly  $F < O < N < Cl < B < S \sim I < Se$ .

(vii) The low-spin  $d^8$  ions, palladium (II), platinum(II) and gold(III) and the  $d^{10}$  ions copper(I), silver(I), gold(I) and mercury (II) have

high stability constants when complexed with sulphur ligands. Being typically (b) class, they form strong  $\sigma$ -bonds with soft ligands and also  $d_{\pi}$ - $d_{\pi}$  bonds by donation of a pair of electrons to the ligand.

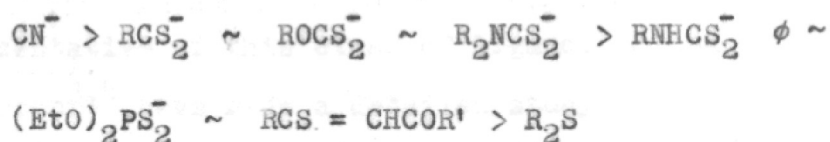
(viii) Thiols but not thioethers cause spin-pairing in complexes of cobalt(II) and nickel(II).

(ix) Sulphur atoms in heterocyclic rings have very poor coordinating ability due to the pseudo-aromatic nature of the ring which has the two-fold effect of causing the lone pairs on the sulphur atom to be less available for donation and the  $\pi$ -orbitals to be less capable of accepting electrons from the metal. Towards (b) class and borderline metals the coordinating ability of the various types of sulphur donors is



(x) All ligands except the "hardest-base" fluoride ion, cause spin-pairing of cobalt(III). Thiols, monothio- $\beta$ -diketones and other charged sulphur ligands, such as diethyl dithiophosphate,

but not thioethers or thiones, cause spin-pairing of nickel(II). However, only the "softest" bases such as cyanide ion, diarsine, and certain charged sulphur ligands cause spin-pairing of iron(III). A series denoting the decreasing ability to cause spin-pairing is:



It has been further observed by Livingstone and Akbar Ali that what has been stated about complexes of sulphur ligands applies also to complexes of sulphur-nitrogen chelating ligands. However, the nitrogen atom tends to lower the solubility of the complexes in non-aqueous solvents so that complexes of sulphur-nitrogen ligands are, in general, either sparingly soluble or insoluble in non-polar solvents.

At present quite a good number of sulphur-nitrogen chelating ligands bonding to the metal through both nitrogen and sulphur are known. They may be classified into:

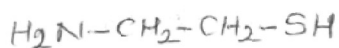
1) Sulphur-nitrogen chelating ligands having a Thiolo group

These ligands are usually bidentate and bonding of a metal to these ligands takes place through S by replacement of the thiolo hydrogen atom and through N by coordination.

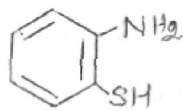
2-Aminoethanethiol (a) is the simplest representative of this class of ligand. Jicha and Busch<sup>3,4</sup> have made a detailed study of the complexes of 2-aminoethanethiol.

2-Aminobenzenethiol(b) is another important ligand of this class<sup>5,6</sup>. 2-(2-Mercaptoethyl)-pyridine (c)<sup>7,8</sup>, 8-mercaptoquinoline (d)<sup>9-11</sup> and thiosemicarbazide (e)<sup>12,13</sup> are also some ligands of this class which have received much attention.

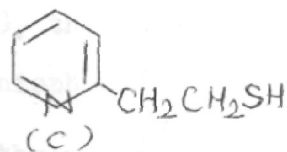
Dithiocarbazic acid (f) and several of its derivatives, metal chelates of some of which have been reported in next two chapters, also belong to this class. It may be noted, however, that the metal chelates of these ligands and the thiosemicarbazide have the NNCS backbone, whereas the metal chelates of the ligands (a), (b), (c) and (d) have NCCS backbone.



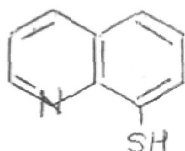
(a)



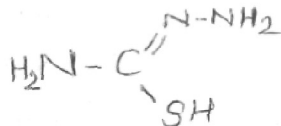
(b)



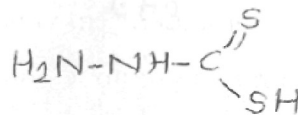
(c)



(d)



(e)

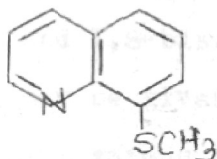


(f)

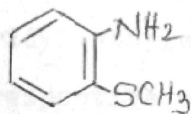
2. Chelating ligands with nitrogen and thioether sulphur as donors

Bidentate, tridentate, tetradentate and even quinquedentate and sexadentate ligands in this class have been reported. Both sulphur and nitrogen are coordinatively bonded to the metal in the metal complexes with these.

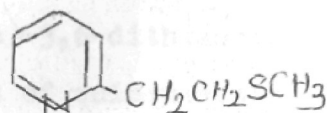
8-Methylquinoline (g), o-methylthioaniline (h) and 2-(2-methylthioethyl)pyridine (i) are some of the well-known bidentate ligands of this class.



(g)

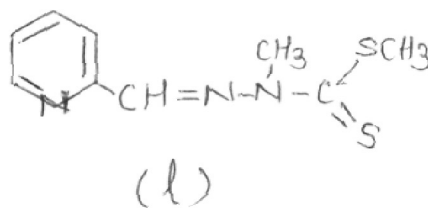
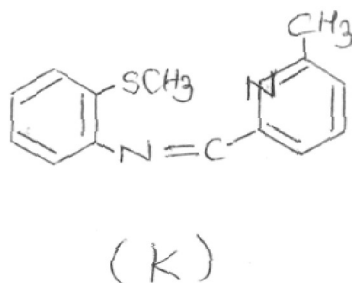
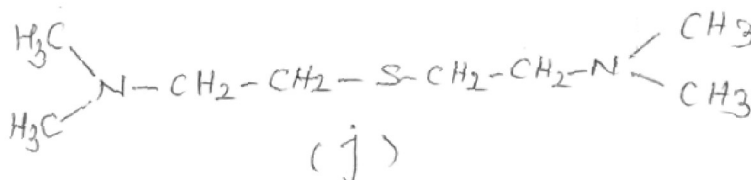


(h)

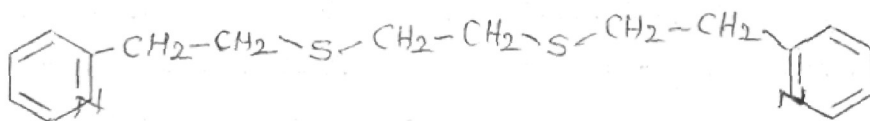


(i)

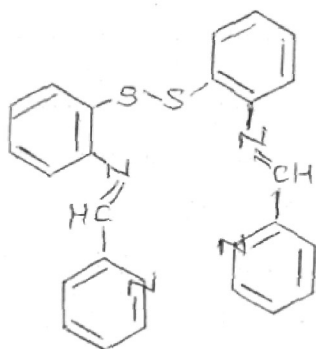
Bis(2-dimethylaminoethyl)sulphide<sup>14</sup> (j), the Schiff bases 6-methylpyrid-2-yl-N-(2'-methylthiophenyl)-methyleneimine (k) and  $\alpha$ -N-methyl-S-methyl- $\beta$ -N-(2-pyridyl)methylendithiocarbamate<sup>15</sup> (l) are examples of tridentate ligands of this class.



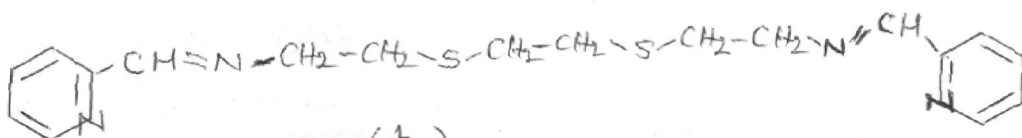
As an example of some of the quadridentate ligands of this class, mention may be made of 1,8-bis(2-pyridyl)-3,6-dithiaoctane<sup>16</sup>(m). Similarly  $\alpha, \alpha'$ -[dithiobis-(*o*-phenylenitrilo)]di-2-picoline<sup>17</sup>(n) and 1,8-bis( $\alpha$ -pyridylmethyleneamino)-3,6-dithiaoctane<sup>18</sup>(p) may be given as respective examples of quinquedentate and sexadentate ligands.



(m)



(n)



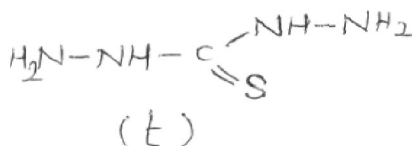
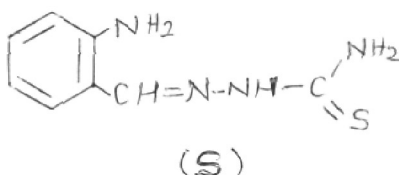
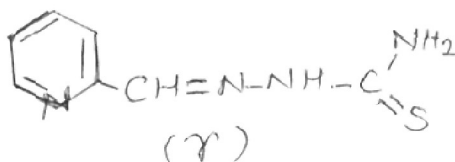
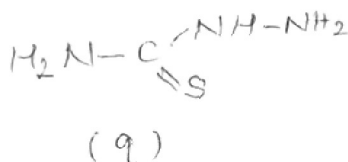
(p)

### 3. Chelating ligands with nitrogen and thione sulphur as donors.

Several ligands of this class have been reported. In this case also, both sulphur and nitrogen are co-ordinatively bonded to the metal in metal complexation.

A common example of this class of ligands is thiosemicarbazide in keto-form (q) of which many metal complexes are known<sup>19-22</sup>. Some Schiff base derivatives of this thiosemicarbazide, like pyridine-2-aldehyde thiosemicarbazone (r) and o-aminobenzaldehyde thiosemicarbazone<sup>23</sup> (s), also belong to this class.





Thiocarbohydrazide<sup>24</sup> (t), the next higher homologue of thiosemicarbazide, is also a ligand of this class.

#### Uses of sulphur-nitrogen ligands and their metal complexes

It has already been mentioned that metal complexes are at present playing vital role in our understanding of biological processes. Metal complexes of sulphur-nitrogen ligands have received considerable attention in this respect and some such complexes have been studied for carcinostatic and antiviral activity as stated below:

French and co-workers<sup>25-27</sup> studied the carcinostatic activity of a number of thiosemicarbazones containing nitrogen heterocycles and they suggested that these compounds, by loss of a proton from their tautomeric thiol form, act as tridentate chelating agents, sequestering metal ions which are involved in carcinogenesis.

Kethoxal bis(thiosemicarbazone) (KTS) has marked carcinostatic action<sup>28</sup>. The cytotoxicity of KTS is enhanced by the presence of copper and zinc ions and it has been shown<sup>29</sup> that the copper(II) chelate of KTS is involved in the cytotoxic action of KTS.

Isoquinoline-1-carboxaldehyde thiosemicarbazone has a broad range of carcinostatic activity and a low toxicity<sup>26</sup>. A very active anti-leukaemia reagent reported is 5-hydroxypyridine-2-carboxaldehyde thiosemicarbazone<sup>30</sup>. Among the few anti-viral drugs known are the isatin thiosemicarbazones which probably act by binding strongly to copper<sup>31</sup>.

The preparation and the biological applications of some metal complexes of dithiocarbazic acid,  $H_2NNHCS_2H$ , have been the subject of some patents<sup>32,33</sup>. A considerable number of metal complexes of ligands derived from dithiocarbazic acid have been tested for carcinostatic activity and the complexes  $Pd(H_2NN = CSSMe)_2$ ,  $Cr(C_5H_4NCH = NNMeCSSMe)Cl_3$  and  $Cu(C_5H_4NCH = NN = CSSMe)Cl$  have shown antitumour activity<sup>34</sup>.

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CHAPTER II : METAL CHELATES OF PHENYLDITHIO-  
CARBAZIC ACID

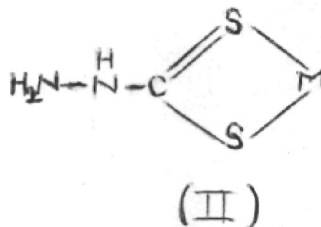
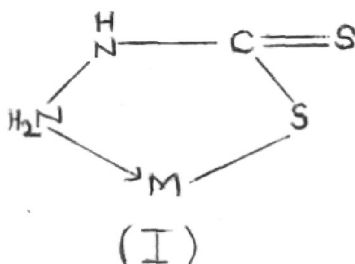
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### Abstract

Complexes of copper(II), nickel(II), palladium(II), zinc(II), cadmium(II), mercury(II), tin(II), lead(II), chromium(III), oxovanadium(IV) and silver(I) with the ligand phenyldithiocarbazate,  $\text{PhNHNHCSS}^-$ , have been obtained by reaction of ammonium salt of phenyldithiocarbazic acid with metal salts in aqueous solution. Except the nickel(II) and zinc(II) phenyldithiocarbazates, all the metal complexes have been synthesized for the first time. Data on infrared and electronic spectral studies as well as on magnetic measurements carried out wherever possible, have been presented and discussed for characterization of the compounds. The ligand has been found to chelate to the metal through  $\beta$ -nitrogen atom and thio sulphur atom.

INTRODUCTION

Of late, sulphur-containing ligands, in particular sulphur-nitrogen chelating ligands have attracted much attention because of their growing importance in bioinorganic chemistry<sup>1-4</sup>. Dithiocarbamate,  $H_2NNHCSS^-$  and its substituted derivatives have been less thoroughly studied as ligands as compared to other well-known dithioanions such as dithiocarbamates,  $R_2NCSS^-$ , xanthates,  $ROCSS^-$  and dithiophosphates,  $(RO)_2PSS^-$ . Livingstone and coworkers<sup>5</sup> have investigated some metal complexes of dithiocarbazic acid and have assigned them the N-S bonded structure I, discarding the alternate S-S bonded structure II.



Tarli and co-workers<sup>6</sup> synthesized and studied nickel(II) and zinc(II) complexes of dithiocarbazic acid and some of its derivatives including phenyldithiocarbamate,  $C_6H_5NHNHCSS^-$ . This prompted us to synthesize and study the complexes of phenyldithiocarbamate with several

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other metal ions which have not been reported so far. Herein is described the synthesis of phenyldithiocarbazato complexes of silver(I), copper(II), nickel(II), zinc(II), cadmium(II), mercury(II), lead(II), tin(II), palladium(II), chromium(III) and oxovanadium(IV). Studies on infrared and electronic spectral measurements and also on magnetic measurements carried out for characterizing the compounds synthesized are also reported. All the compounds except the nickel(II) and zinc(II) complexes have been isolated for the first time.



## EXPERIMENTAL

### Materials and methods:

All the chemicals used were of A.R. grade and solvents were used after purification and distillation by standard methods<sup>7</sup>.

The infrared spectra of the compounds in nujol mull were recorded on a Perkin Elmer Spectrophotometer, model 221, using sodium chloride prism. The ultra violet and visible spectra of the compounds in potassium bromide discs were recorded on UV-VIS specord model No.445069 spectrophotometer. The diffuse reflectance spectral measurements were carried out on a Unicam SP model 500 spectrophotometer with magnesium carbonate as a standard. The magnetic susceptibilities were determined by Faraday method<sup>8</sup>. The apparatus was calibrated with mercury(II) tetrathiocyanato cobaltate<sup>9</sup>.

### Syntheses

#### Preparation of ammonium phenyldithiocarbazate:

This ammonium salt of the ligand was prepared by the method described in the literature<sup>10</sup> by reacting 21.6 g phenyl hydrazine with 45.7 g of carbon disulfide in ethanolic medium below 0°C and passing a strong current of ammonia. The white product was filtered, washed with alcohol and sucked dry. Yield, 25 g ; m.p. 121°-122°C (reported 122°C).

Bis(phenyldithiocarbazato)nickel(II):

An aqueous solution (5 ml) of nickel(II) chloride hexahydrate (0.594 g, 0.0025 mole) was added to the filtered aqueous solution (30 ml) of ammonium phenyldithiocarbazate (1.006 g, 0.005 mole) with stirring. An olive green precipitate was immediately formed. The mixture was stirred for 30 minutes and filtered, the precipitate washed thrice with 15 ml portions of water and twice with 10 ml portions of absolute alcohol, sucked dry and kept over KOH in a desiccator under vacuum for two days. Yield, 0.86 g (81%), m.p. 152°C.

Bis(phenyldithiocarbazato)palladium(II):

An aqueous solution (15 ml) of sodium tetrachloropalladate (1.470 g, 0.005 mole) was added to an aqueous solution (50 ml) of the ammonium salt of the ligand (2.012 g, 0.01 mole), with stirring. A brown solid formed was stirred for 30 minutes, collected on a filter and washed with three portions of 15 ml water followed by two portions of 10 ml absolute alcohol. It was dried under vacuum over KOH for two days. Yield, 2.0 g (85%), m.p. 192°C.

Bis(phenyldithiocarbazato)copper(II):

Cupric chloride dihydrate (0.426 g, 0.0025 mole) was dissolved in 10 ml water. Ammonium phenyl

dithiocarbazate (1.006 g, 0.005 mole) was dissolved in 25-30 ml water. On adding cupric chloride solution to the ligand salt solution with stirring a deep green compound was immediately formed. It was stirred for 30 minutes, collected on a filter, washed thrice with 15 ml portions of water and twice with 10 ml portions of absolute alcohol, sucked dry and dried over KOH in a vacuum desiccator for two days. Yield, 0.85 g (85%), m.p. 146°C.

Mono(phenyldithiocarbazato)silver(I):

To 30 ml aqueous solution of the ligand salt (1.006 g, 0.005 mole) was added 10 ml aqueous solution of silver nitrate (0.849 g, 0.005 mole) with stirring. A light brown solid so obtained was filtered off after stirring the mixture for 30 minutes. It was washed thrice with 15 ml portions of water, twice with 10 ml portions of absolute alcohol and dried over KOH in a desiccator under vacuum for two days. Yield, 1.2 g (85%), m.p. 145°C.

Bis(phenyldithiocarbazato)zinc(II):

Zinc acetate dihydrate (0.549 g, 0.0025 mole) in 10 ml aqueous solution was added to 30 ml aqueous solution of the ligand salt (1.006 g, 0.005 mole) with stirring. A light pink compound thus obtained

was stirred for 30 minutes, collected on a filter, washed thrice with 15 ml portions of water and twice with 10 ml portions of absolute alcohol and dried over KOH in a desiccator under vacuum for two days. Yield, 0.9 g, (83%), m.p. 148°C.

Bis(phenyldithiocarbazato)cadmium(II):

Cadmium chloride dihydrate (0.570 g, 0.0025 mole) in 10 ml aqueous solution was added to 30 ml aqueous solution of the ligand salt (1.006 g, 0.005 mole) with stirring. A light pink compound obtained was stirred for 30 minutes. It was filtered off, washed with three portions of 15 ml water followed by two portions of 10 ml absolute alcohol, and dried over KOH in a desiccator under vacuum for two days. Yield, 1.0 g (83%), m.p. 149°C.

Bis(phenyldithiocarbazato)mercury(II):

Mercuric chloride (0.678 g, 0.0025 mole) in 50 ml aqueous solution was added to 30 ml aqueous solution of the ligand salt (1.006 g, 0.005 mole) with stirring. A light olive green product formed was stirred for 30 minutes, collected on a filter, washed thrice with 15 ml portions of water and twice with 10 ml portions of absolute alcohol and dried over KOH in a desiccator under vacuum for two days. Yield, 1.2 g (85%), m.p. 118°C.

Bis(phenyldithiocarbazato)oxovanadium(IV):

Vanadyl chloride dihydrate, 50% aqueous solution (0.434 g, 0.0025 mole) was added to 30 ml aqueous solution of the ligand salt (1.006 g, 0.005 mole) with stirring. An olive green product so formed was stirred for 15 minutes, filtered off, washed thrice with 15 ml water and twice with 5 ml absolute alcohol and dried over KOH in a desiccator under vacuum for two days. Yield, 0.7 g (63%), m.p. 150°C.

Tris(phenyldithiocarbazato)chromium(III):

Chromic chloride hexahydrate (0.444 g, 0.0017 mole) dissolved in 10 ml water was added to 30 ml aqueous solution of the ligand salt (1.006 g, 0.0051 mole) with stirring. A light violet product was formed. It was stirred for 30 minutes, filtered off, washed with three portions of 15 ml water followed by two portions of 5 ml absolute alcohol and dried over KOH in a desiccator under vacuum for two days. Yield, 1.0 g (63%), m.p. 190°C.

Bis(phenyldithiocarbazato)tin(II):

Stannous chloride dihydrate (0.564 g, 0.0025 mole) in 2 ml water was added to 30 ml aqueous solution of the ligand salt (1.006 g, 0.005 mole) with stirring. A light yellow solid formed was stirred for 30 minutes, filtered off, washed thrice with 15 ml portions of water and twice with 10 ml portions of absolute alcohol and

dried over KOH in a desiccator under vacuum for two days. Yield, 1.0 g (83%), decomp.  $140^{\circ}\text{C}$ .

Bis(phenyldithiocarbazato)lead(II):

Lead acetate trihydrate (0.95 g, 0.0025 mole) in 10 ml aqueous solution was added to 30 ml aqueous solution of the ligand salt (1.006 g, 0.005 mole) with stirring. A light yellow product which precipitated out was stirred for 30 minutes, filtered off, washed thrice with 15 ml portions of water and twice with 10 ml portions of absolute alcohol and dried over KOH in a desiccator under vacuum for two days. Yield, 1.2 g, (85%), decomp.  $147^{\circ}\text{C}$ .

The data on the elemental analysis of the above synthesized compounds are given in Table I.

Table I

## Metal Chelates of Phenylthiocarbamic acid

No.	Name of the compound	Metal %	C %	H %	N %	S %
1.	Ammonium phenylthiocarbazate	-	41.01 (41.70)	5.97 (5.50)	20.53 (20.87)	31.51 (31.85)
2.	Bis(phenylthiocarbazato)nickel(II) $Ni(C_7H_7N_2S_2)_2$	13.51 (13.80)	39.73 (39.54)	3.98 (3.32)	13.01 (13.17)	29.97 (30.15)
3.	Bis(phenylthiocarbazato)palladium(II) $Pd(C_7H_7N_2S_2)_2$	22.90 (22.50)	36.18 (35.55)	3.51 (2.98)	11.70 (11.85)	26.71 (27.12)
4.	Bis(phenylthiocarbazato)copper(II) $Cu(C_7H_7N_2S_2)_2$	14.12 (14.78)	39.98 (39.08)	3.83 (3.26)	13.13 (13.03)	29.04 (29.82)
5.	Mono(phenylthiocarbazato)silver(I) $Ag(C_7H_7N_2S_2)$	36.81 (37.07)	28.52 (28.88)	2.90 (2.42)	9.22 (9.62)	22.55 (22.03)
6.	Bis(phenylthiocarbazato)zinc(II) $Zn(C_7H_7N_2S_2)_2$	15.13 (15.14)	39.11 (38.92)	3.67 (3.27)	12.71 (12.97)	29.38 (29.69)
7.	Bis(phenylthiocarbazato)cadmium(II) $Cd(C_7H_7N_2S_2)_2$	24.39 (23.47)	35.36 (35.11)	3.00 (2.95)	12.36 (11.70)	26.14 (26.78)
8.	Bis(phenylthiocarbazato)mercury(II) $Hg(C_7H_7N_2S_2)_2$	35.51 (35.37)	-	-	9.01 (9.88)	22.01 (22.61)

Table I (contd.)

9.	Bis(phenyldithiocarbazato)oxovanadium(IV) $\text{VO}(\text{C}_7\text{H}_7\text{N}_2\text{S}_2)_2 \cdot \text{H}_2\text{O}$	10.63 (11.28)	37.25 (37.23)	3.81 (3.57)	11.20 (12.41)	28.11 (28.40)
10.	Tris(phenyldithiocarbazato)chromium(III) $\text{Cr}(\text{C}_7\text{H}_7\text{N}_2\text{S}_2)_3 \cdot 2\text{H}_2\text{O}$	8.55 (8.16)	39.55 (39.55)	4.01 (3.95)	13.19 (13.18)	29.91 (30.16)
11.	Bis(phenyldithiocarbazato)tin(II) $\text{Sn}(\text{C}_7\text{H}_7\text{N}_2\text{S}_2)_2$	24.01 (24.46)	35.15 (34.65)	3.16 (2.91)	12.09 (11.55)	26.59 (26.43)
12.	Bis(phenyldithiocarbazato)lead(II) $\text{Pb}(\text{C}_7\text{H}_7\text{N}_2\text{S}_2)_2$	37.36 (36.12)	29.84 (29.30)	2.76 (2.46)	10.43 (9.77)	22.11 (22.36)

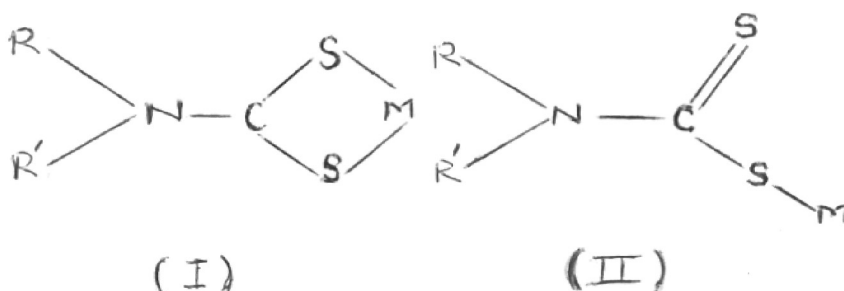
Values in parentheses are calculated values.



## RESULTS AND DISCUSSION

Tarli and co-workers<sup>6</sup> have reported the occurrence of two different chromophores for low-spin square planar nickel(II) dithiocarbazates, the chromophore  $[\text{NiS}_4]$  in which the bonding of the dithiocarbazate ligand to the metal is through both S (as in metal dithiocarbamates) and the chromophore  $[\text{NiN}_2\text{S}_2]$  with bonding through N and S (as in thiosemicarbazides). Whereas the chromophore suggested for the nickel complex of dithiocarbazic acid  $\text{Ni}(\text{H}_2\text{NNHCS}_2)_2$  is  $[\text{NiN}_2\text{S}_2]$ , the one suggested for the nickel complex with phenyldithiocarbazate is  $[\text{NiS}_4]$ . In support of the chelation through both S atoms, these authors have made mention of a strong absorption band near  $1550 \text{ cm}^{-1}$  in the infrared spectrum of the complex with  $[\text{NiS}_4]$  chromophore, which they have assigned to a vibration containing mainly of CN with a substantial double bond C=N contribution. According to these authors, the band due to CN vibration in the case of  $[\text{NiN}_2\text{S}_2]$  chromophore occurs at a lower frequency ( $1505\text{-}1485 \text{ cm}^{-1}$ ), with a splitting. These observations are in agreement with those of Livingstone and co-workers<sup>5</sup> who have also drawn analogy between metal dithiocarbazates and metal dialkyldithiocarbamates. With N,N-dialkyldithiocarbamates, the  $\nu(\text{C-N})$  frequency has been used to distinguish between disulphur chelation(I) and unidentate sulphur

coordination(II). Where disulphur chelation occurs,  $\nu(\text{CN})$  is found within the range  $1490\text{-}1590\text{ cm}^{-1}$ , while with unidentate sulphur coordination, the frequency is observed in the range  $1460\text{-}1490\text{ cm}^{-1}$ .



Although coordination through both S atoms has been suggested for nickel(II) phenyldithiocarbamate complex<sup>6</sup>, in the case of phenyldithiocarbamate complexes with nickel(II) and several other metal ions isolated by us, the coordination appears to take place through N and S on the basis of our infrared spectral studies of these compounds. The infrared absorption frequencies of the ligand (ammonium salt) and its various metal complexes are given in Tables II-VII. The spectra are given in Figs. 1-8. It may be noted that the synthetic methods followed by us were different from those of Tarli and co-workers.

The infrared spectra of all the metal complexes show strong bands with splitting in the region

Table II

Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of (A) ammonium phenyldithiocarbazate (B) tris(phenyldithiocarbazato)-chromium(III)dihydrate.

A	B	Possible assignments
3480 bw	3500 bw	NH stretching
3230 sh	3250 bm	
3100 bs	3100 w	
2920 bs*	2920 bs*	C=C Aromatic vibrations
1595 m	1598 s	
1480 w	1510 sh )	C-N stretching
1460 m*	1488 s )	
1370 s*	1460 s*	
1285 w	1370 sh*	
1225 m	1300 m	
1170 w	1240 s	
1140 w	1170 m	
1100 m	1150 w	
1070 m	1100 w	
1000 s	1070 s	C-S stretching
	1015 sh )	
	1005 s )	
890 m	885 m	
845 w	840 m	
755 s	755 s	C-H out of plane bending
715 w		
690 m	690 s	C-S stretching
660 w	660 w sh	
630 w		

\* Nujol peak

Table III

Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of  
 (A) bis(phenyldithiocarbazato)nickel(II) and  
 (B) bis(phenyldithiocarbazato)palladium(II).

A	B	Possible assignments
3250 s	3235 s	NH stretching
3050 w	3035 w	
2920 bs*	2920 bs*	
1598 s	1595 s	C=C aromatic ring vibrations
1505 sh )	1500 sh )	
1485 s )	1488 m )	C-N stretching
1460 s*	1460 s*	
1370 m*	1360 s*	
1310 w		
1285 w	1250 m	
1170 m	1170 w	
1090 m	1070 w	
1010 sh )	1000 sh )	
985 s )	995 s )	CSS <sup>-</sup> stretching
885 m	880 w	
855 m	830 w	
755 s	750 s	C-H out of plane bending
715 w	715 w	
690 m	685 s	C-S stretching
660 w	670 w	
630 w	650 w	

\* Nujol peak

Table IV

Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of  
 (A) bis(phenyldithiocarbazato)oxovanadium(IV)  
 monohydrate and (B) mono(phenyldithiocarbazato)silver(I).

A	B	Possible assignments
	3295 s	
3255 bs	3255 s	NH stretching
3050 w	3045 w	
2920 bs*	2920 bs*	
2070 s		V=O stretching overtone
1640 m		
1600 s	1600 s	C=C aromatic vibrations
1510 sh )	1505 sh )	
1490 s )	1490 s )	C-N stretching
1465 s*	1465 s*	
1370 s*	1370 s*	
1300 w	1300 w	
1245 m	1235 m	
1140 m	1170 w	
1070 w	1075 w	
995 sh )	995 sh )	CSS <sup>-</sup> stretching
975 bs )	970 s )	
885 w	880 w	
750 s	745 s	C-H out of plane bending
690 m	690 m	C-S stretching
665 w sh	650 w	

\* Nujol peak

Table V

Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of  
 (A) bis(phenyldithiocarbazato)copper(II) and  
 (B) bis(phenyldithiocarbazato)lead(II).

A	B	Possible assignments
	3330 s	
3298 s	3290 s	NH stretching
3235 s	3170 s	
3045 w	3040 w	
2920 bs*	2920 bs*	
1600 s	1600 s	C=C aromatic ring vibrations
1510 sh )	1505 sh )	
1490 s )	1490 m )	C-N stretching
1465 m*	1460 s*	
1370 m*	1370 m*	
1300 w	1300 m	
1240 m	1240 bm	
1140 w	1140 w	
1070 w	1070 m	
985 sh )	980 s )	CSS <sup>-</sup> stretching
970 s )	955 sh )	
880 w	880 w	
745 s	750 s	C-H out of plane bending
	715 w	
690 s	690 w	C-S stretching
635 w	655 w	

\* Nujol peak

Table VI

Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of  
 (A) bis(phenyldithiocarbazato)zinc(II) and  
 (B) bis(phenyldithiocarbazato)cadmium(II)

A	B	Possible assignments
3305 m	3298 s	
3250 s	3220 s	NH stretching
3080 bs	3050 w	
2920 bs*	2920 bs*	
1600 s	1600 s	C=C aromatic ring vibrations
1510 sh )	1505 sh)	
1490 s )	1490 s )	C-N stretching
1460 m*	1460 s*	
1365 m*	1370 bm*	
1300 m	1300 m	
1285 m		
1235 m	1240 m	
1145 w	1140 m	
1080 w	1070 m	
1000 s )	990 s )	CSS <sup>-</sup> stretching
975 s )	970 s )	
875 w	880 m	
750 s	745 s	C-H out of plane bending
680 m	690 s	C-S stretching
650 w sh	655 m	

\* Nujol peak

Table VII

Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of  
 (A) bis(phenyldithiocarbazato)tin(II) and  
 (B) bis(phenyldithiocarbazato)mercury(II)

A	B	Possible assignments
	3330 s	
3285 s	3265 s	NH stretching
2920 bs*	2920 bs*	
3040 w	3040 w	
1595 s	1595 s	C=C aromatic ring vibrations
1505 sh)	1505 sh )	
1485 m )	1485 m )	C-N stretching
1455 m*	1455 m*	
1365 m*	1365 m*	
1295 m	1295 w	
1240 m	1235 m	
1070 w	1085 w	
990 sh)	1020 sh )	
980 s )	1010 s )	CSS <sup>-</sup> stretching
880 w	885 w	
750 s	750 s	CH out of plane bending
690 m	690 m	C-S stretching
660 w	660 w	

\* Nujol peak



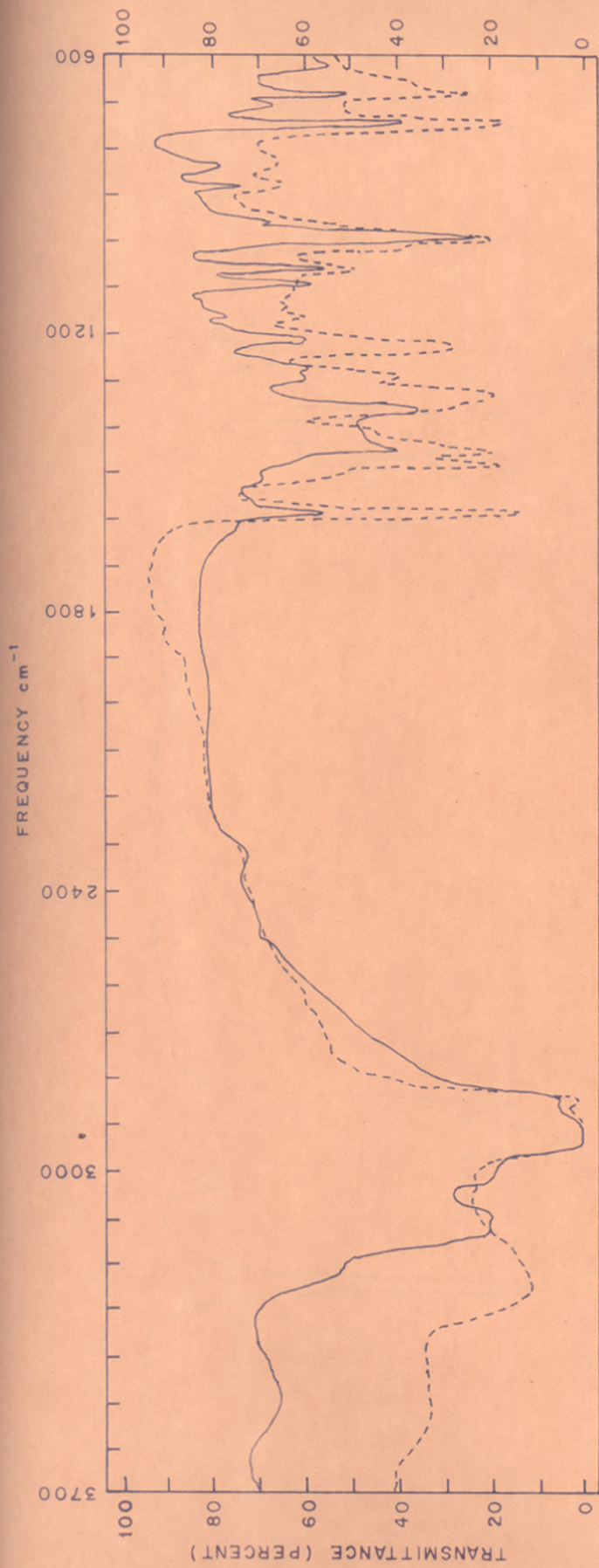


FIG. 1 INFRARED SPECTRA IN NUJOL MULL OF  
— AMMONIUM PHENYL DITHIOCARBAZATE  
- - - TRIS ( PHENYL DITHIOCARBAZATO )  
CHROMIUM (III) DIHYDRATE

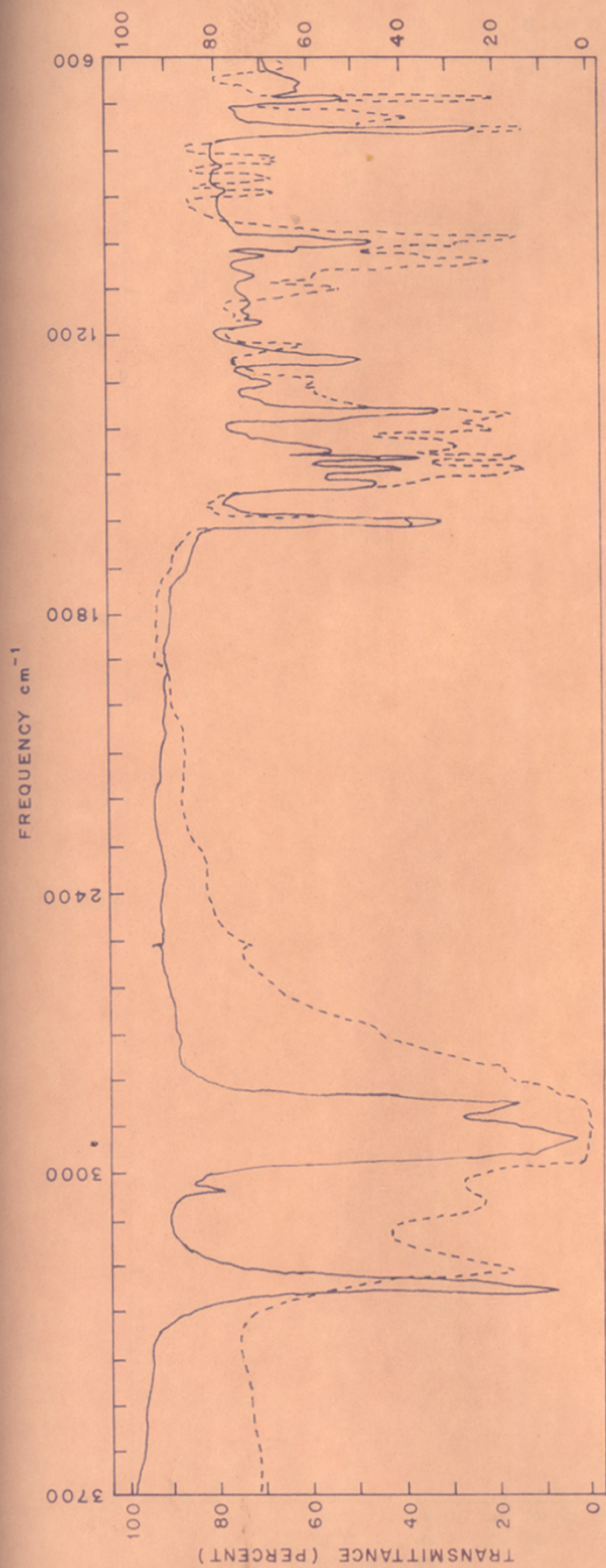


FIG. 2 INFRARED SPECTRA IN NUJOL MULL OF  
--- BIS (PHENYL DITHIOCARBAZATO) NICKEL (II)  
— BIS (PHENYL DITHIOCARBAZATO) PALLADIUM (II)

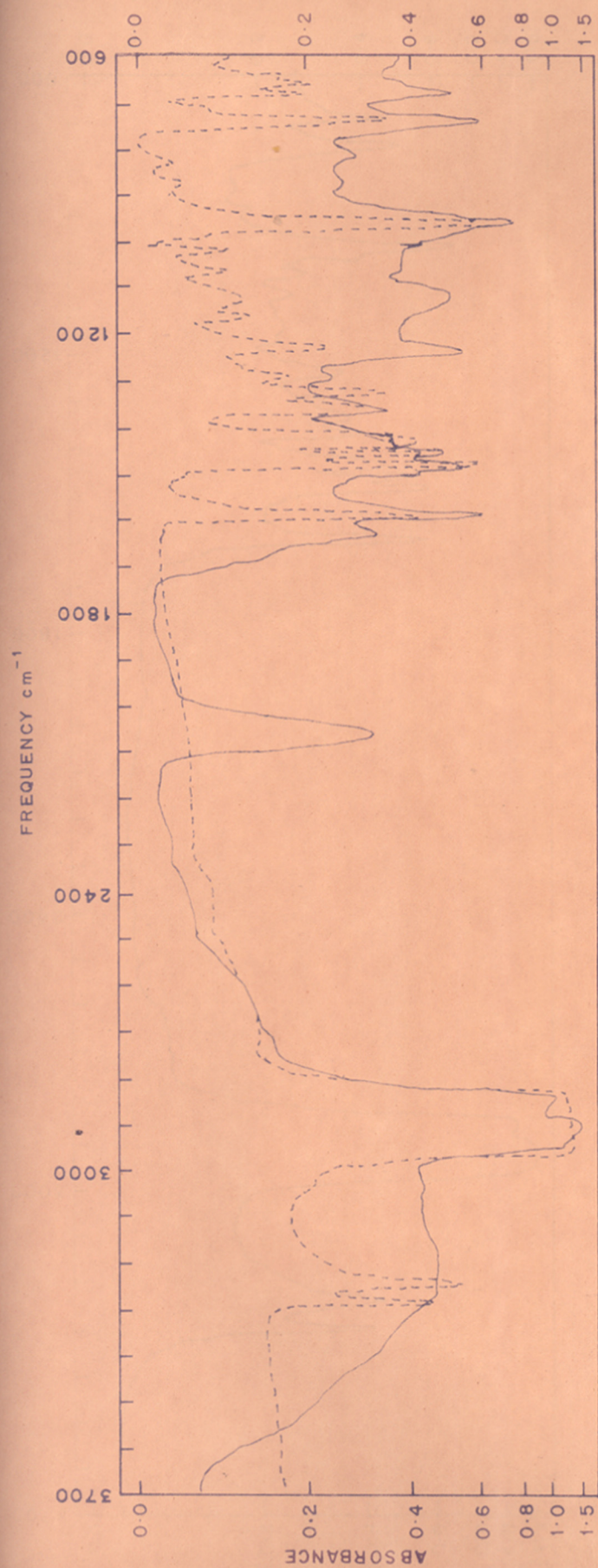


FIG. 3 INFRARED SPECTRA IN NUJOL MULL OF  
— BIS ( PHENYL DITHIOCARBAZATO ) OXO  
VANADIUM (IV) MONOHYDRATE AND  
---- MONO(PHENYLDITHIOCARBAZATO) SILVER (I)

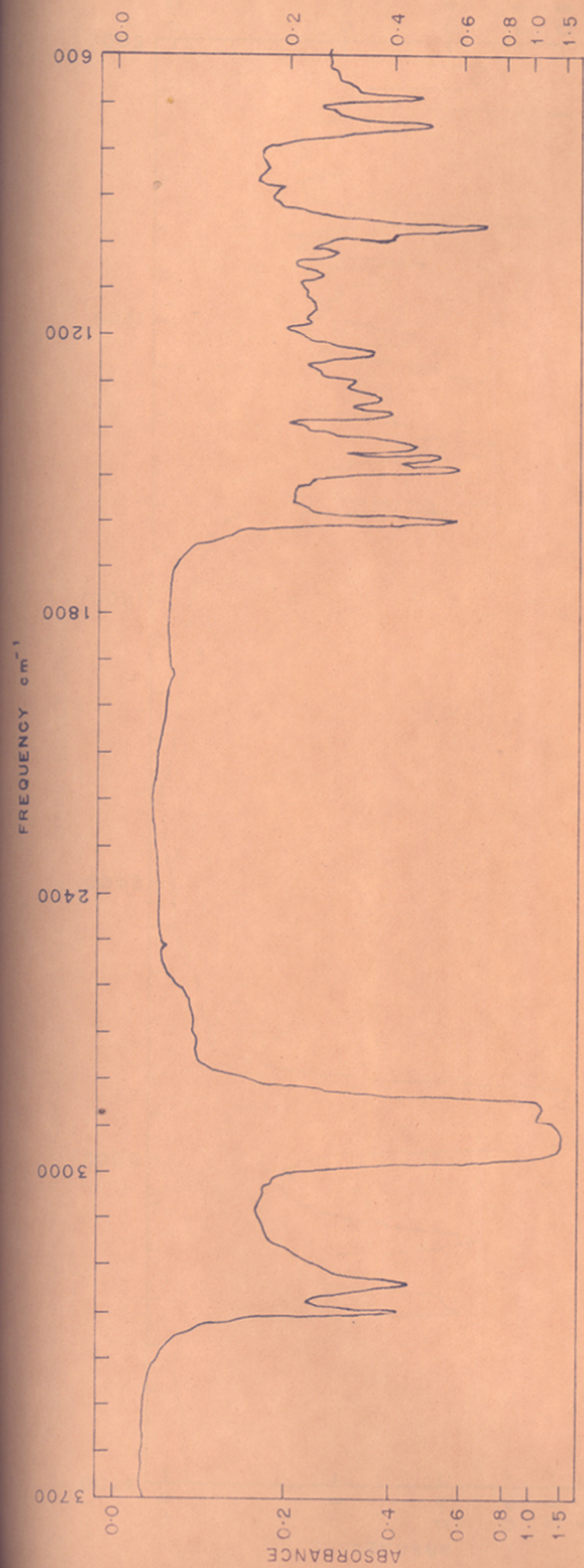


FIG. 4 INFRARED SPECTRUM IN NUJOL MULL OF  
— BIS ( PHENYLDITHIOCARBAZATO )  
COPPER ( II )

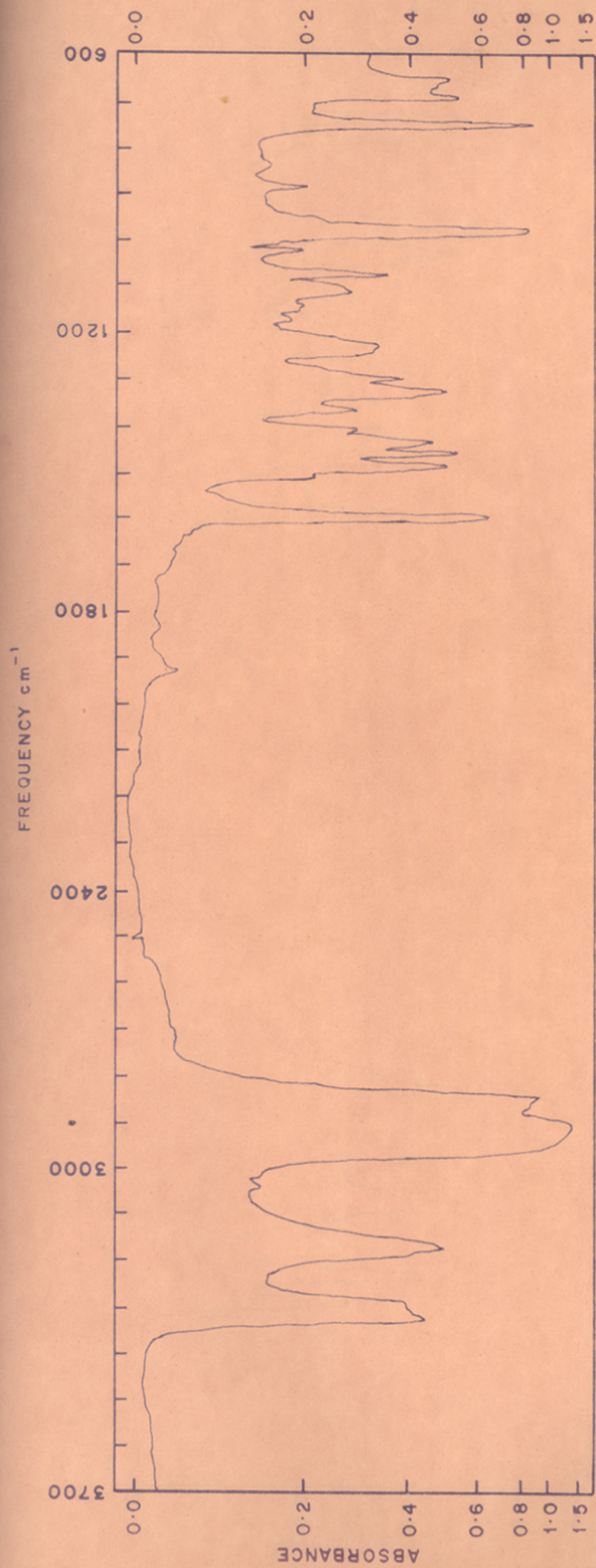


FIG. 5 INFRARED SPECTRUM IN NUJOL MULL OF  
BIS (PHENYL DITHIOCARBAZATO) LEAD (II)

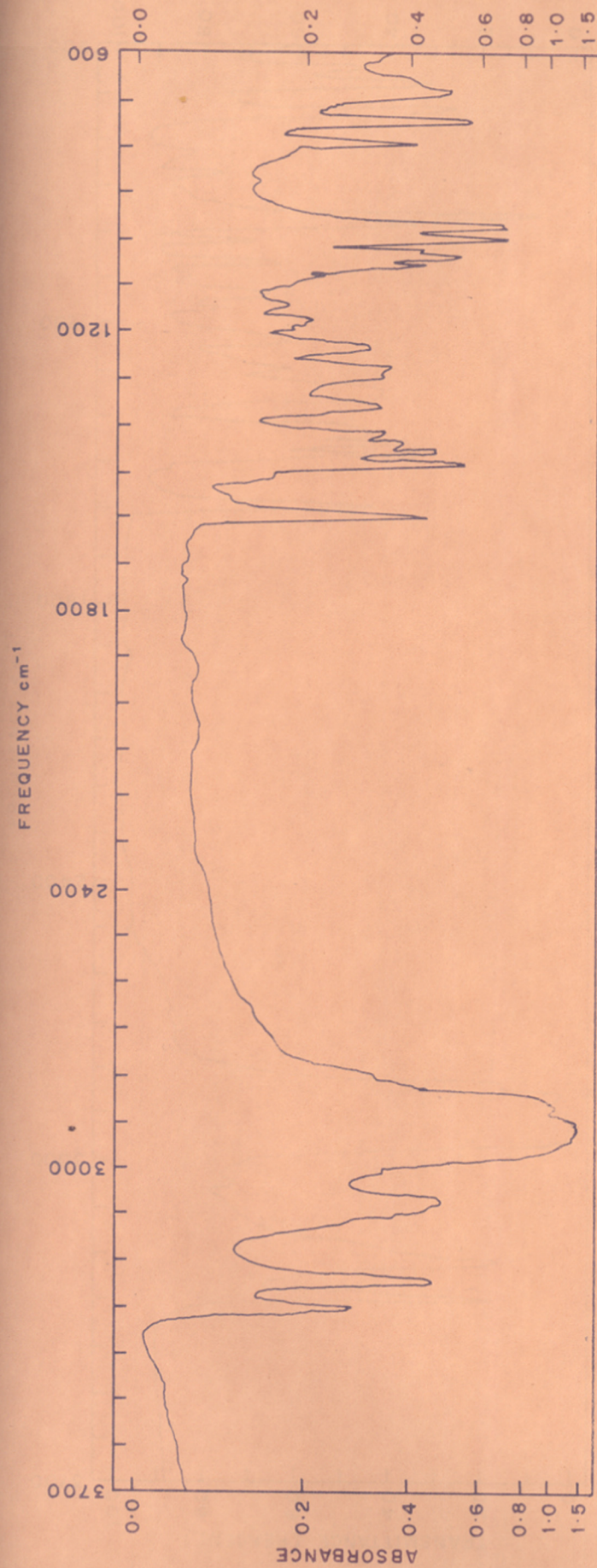


FIG. 6 : INFRARED SPECTRUM IN NUJOL MULL OF  
BIS (PHENYL DITHIOCARBAZATO) ZINC (II)

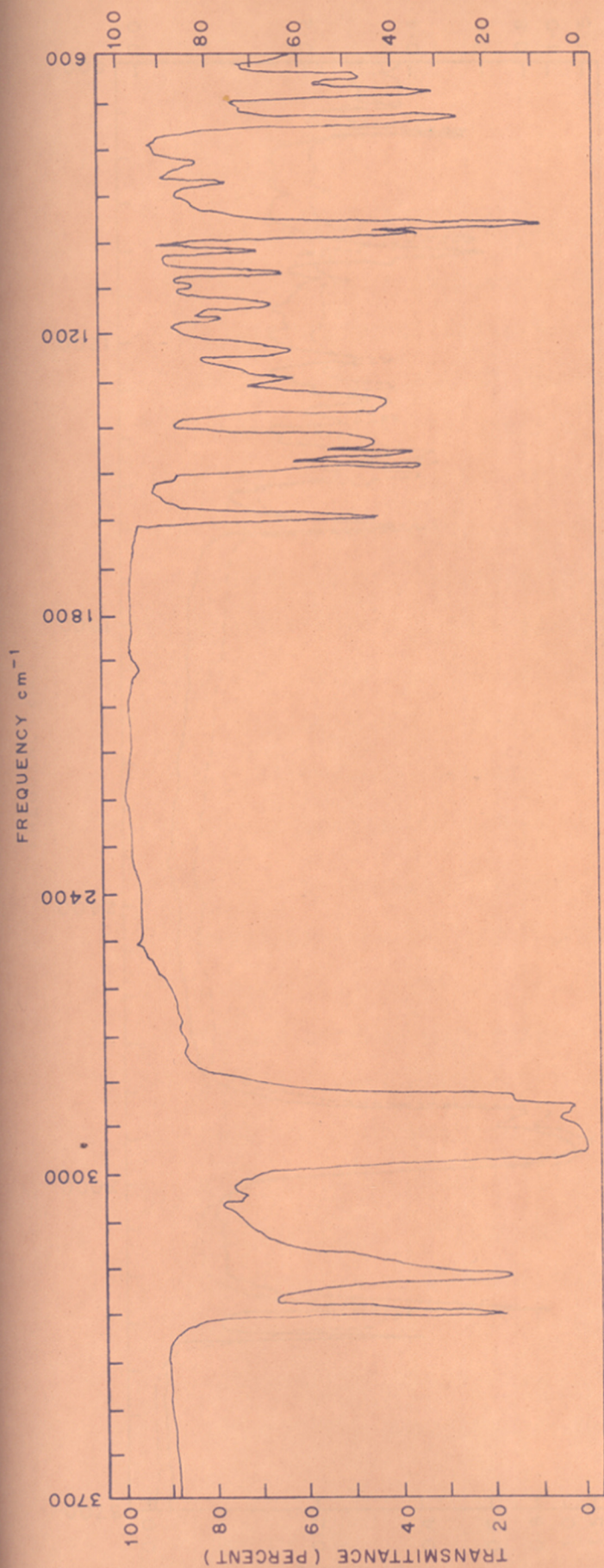


FIG. 7 INFRARED SPECTRUM IN NUJOL MULL OF  
BIS (PHENYL DITHIOCARBAZATO) CADMIUM (II)

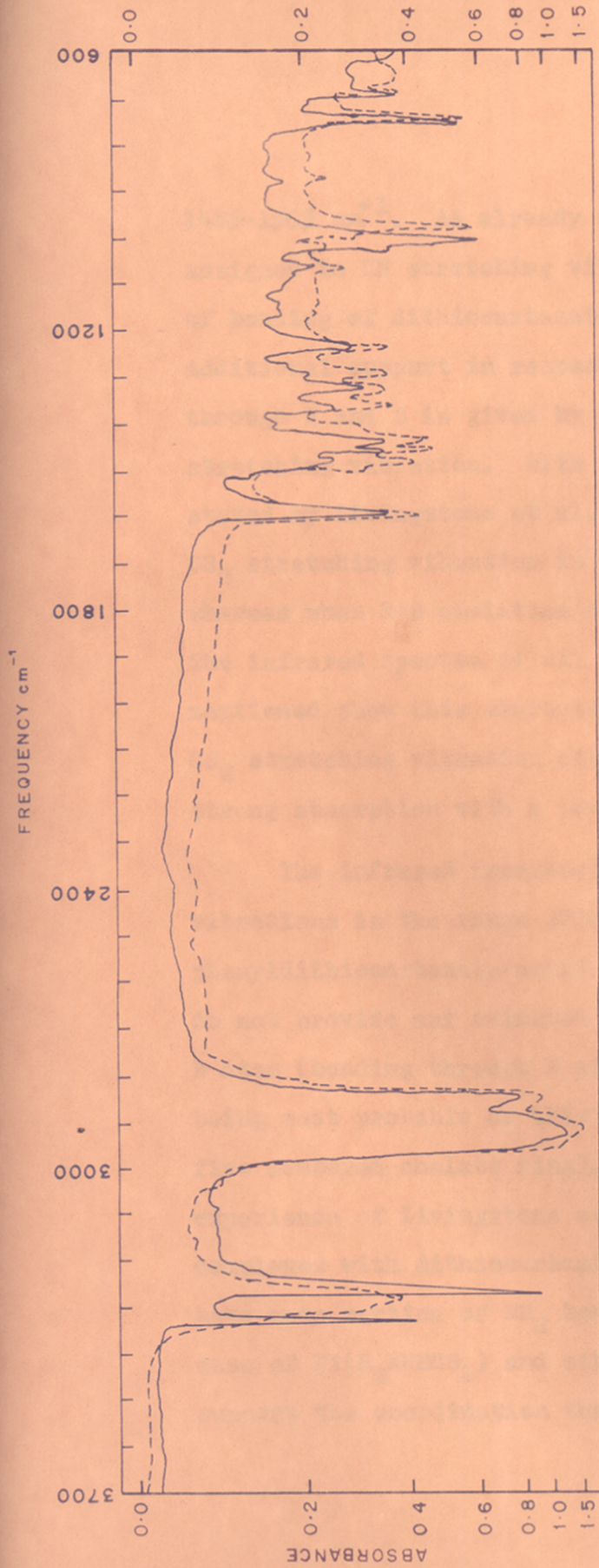


FIG. 8 : INFRARED SPECTRA IN NUJOL MULL OF  
----- BIS (PHENYL DITHIOCARBAZATO) TIN (II) AND  
——— BIS (PHENYL DITHIOCARBAZATO) MERCURY (II)



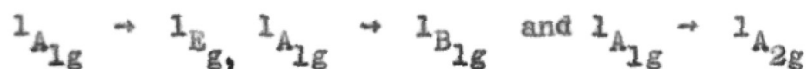
1485-1505  $\text{cm}^{-1}$ . As already stated above these bands, assigned to CN stretching vibration, are indicative of bonding of dithiocarbazate on metal through N and S. Additional support in respect of this coordination through N and S is given by the characteristic  $\text{CS}_2$  stretching vibration. With disulphur chelation, as stated by Livingstone et al.<sup>5</sup>, a single band for  $\text{CS}_2$  stretching vibration is usually found at  $\sim 1000 \text{ cm}^{-1}$ , whereas when N-S chelation occurs this band is split. The infrared spectra of all the metal complexes mentioned show this characteristic splitting of  $\text{CS}_2$  stretching vibration either as a doublet or as a strong absorption with a shoulder around  $1000 \text{ cm}^{-1}$ .

The infrared frequencies absorbed by NH stretching vibrations in the range  $3230-3000 \text{ cm}^{-1}$  in the case of phenyldithiocarbazate-metal complexes isolated by us, do not provide any evidence regarding bonding through N atom (bonding through N attached to phenyl group being most probable as this can give a more stable five membered chelate ring). This has also been the experience of Livingstone et al.<sup>5</sup> in the case of metal complexes with dithiocarbazic acid. However, Tarli et al.<sup>6</sup> have made mention of  $\text{NH}_2$  bending vibrations, in the case of  $\text{Ni}(\text{H}_2\text{NNHCS}_2)$  and other allied complexes, to support the coordination through  $\beta$ -N atom. They found

the bands due to  $\text{NH}_2$  bending vibrations sharper and at lower frequencies after complexation.

A band of good intensity showing absorption at frequency  $2070 \text{ cm}^{-1}$  in the infrared spectrum of bis(phenyldithiocarbazato)oxovanadium(IV) attracts attention since this band is not observed in the spectra of all other metal complexes. This band may be considered to be due to overtone of  $V=O$  stretching frequency. A medium intensity band at  $2061 \text{ cm}^{-1}$  was observed by Miller and Cousins<sup>11</sup> in the infrared spectrum of vanadium oxytrichloride and it has been assigned by them to overtone of the absorbed frequency at  $1035 \text{ cm}^{-1}$  due to  $V=O$  stretch.

The bis(phenyldithiocarbazato)nickel(II) isolated by us has been found to be diamagnetic suggesting a low-spin square planar structure for it. The diffuse reflectance spectrum of this complex (Fig.9) shows a broad band with maxima at  $23600 \text{ cm}^{-1}$ , a small band at  $18500 \text{ cm}^{-1}$  and a shoulder at  $15400 \text{ cm}^{-1}$ . These bands may be assigned to the spin-allowed d-d transitions



respectively. These electron transitions are normally expected for low-spin square planar  $d^8$  metal complexes<sup>12</sup>.

The absorption spectrum of the compound in KBr pellet (Fig. 12) gives bands with maxima at  $30500\text{ cm}^{-1}$ ,  $27000\text{ cm}^{-1}$ ,  $23700\text{ cm}^{-1}$  and  $15800\text{ cm}^{-1}$ . While the first two bands may be assigned to charge-transfer or ligand absorptions, the other two may be respectively assigned to  $1A_{1g} \rightarrow 1E_g$  and  $1A_{1g} \rightarrow 1A_{2g}$  d-d transitions.

The bis(phenyldithiocarbazato)copper(II) complex isolated was found to have the magnetic moment of 1.68 B.M., a value quite close to that according to spin-only formula for one unpaired electron. According to Ray and Sen<sup>13</sup>, the four-coordinated copper(II) complexes can be divided into two groups: one with moment values lying between 1.72 and 1.82 B.M. and the other with higher moment values between 1.90 and 2.20 B.M. They have stated that the copper(II) complexes in the first group with magnetic moment values closer to the spin-only value (1.73 B.M.) for one unpaired electron are all  $dsp^2$  square planar, the lower moment value resulting from more or less complete quenching of the orbital contribution of the single unpaired electron raised to the outermost  $4p$  level of the atom, where it is fully exposed to the electric field of the neighbouring atoms and ions, away from the nucleus screened by the coordinating

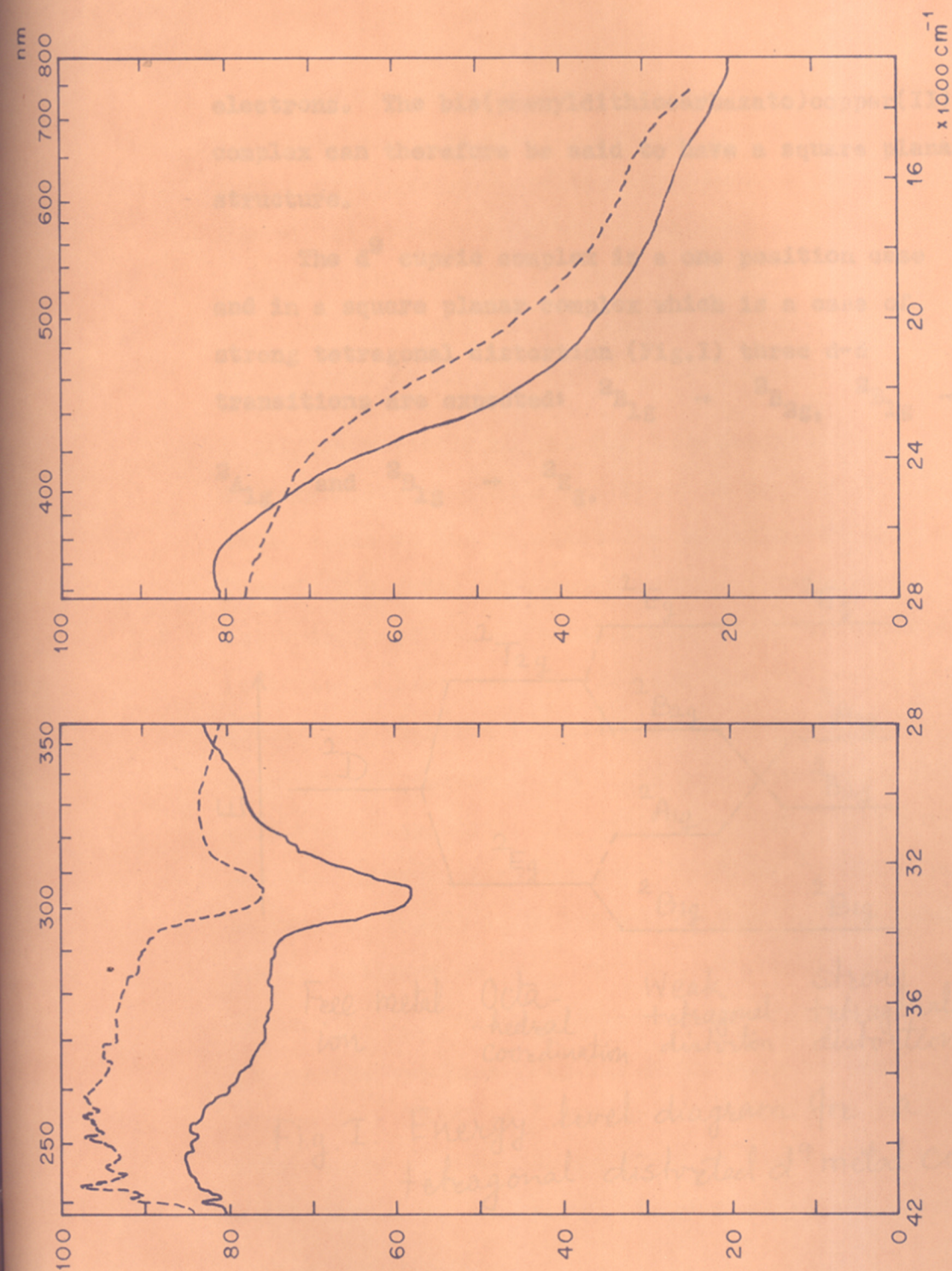


FIG. 12 : ABSORPTION SPECTRA IN KBr PELLET OF

— BIS (PHENYL DITHIOCARBAZATO) NICKEL (II) AND

----- BIS (PHENYL DITHIOCARBAZATO) OXO VANADIUM (IV) MONOHYDRATE

electrons. The bis(phenyldithiocarbazato)copper(II) complex can therefore be said to have a square planar structure.

The  $d^9$  cupric complex is a one position case and in a square planar complex which is a case of strong tetragonal distortion (Fig.1) three d-d transitions are expected:  ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ,  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$ .

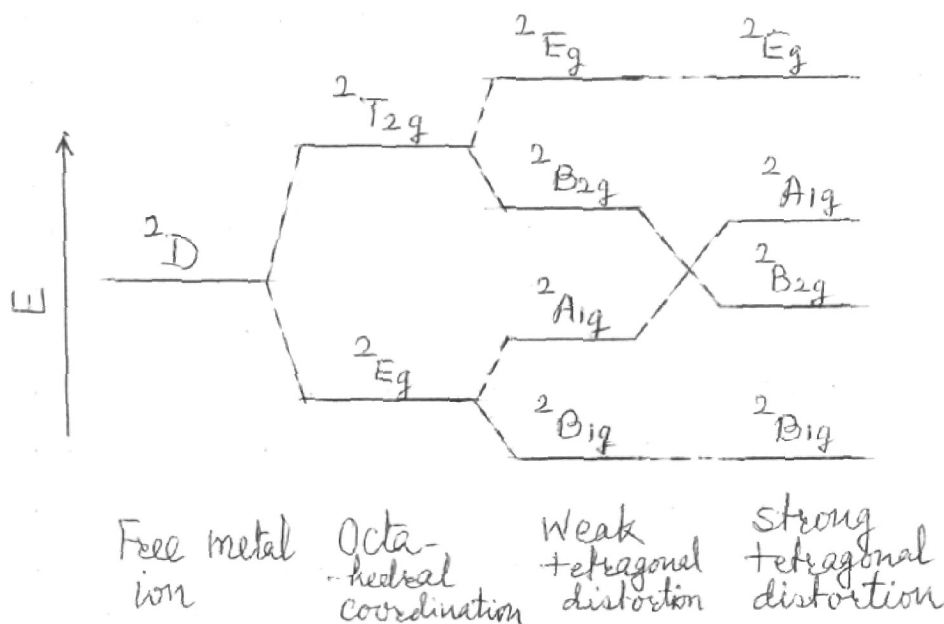


Fig.1. Energy level diagram for a tetragonal distorted  $d^9$  metal complex.

The diffuse reflectance spectrum of bis(phenyl-dithiocarbazato)copper(II) (Fig.9) shows a band with maxima at  $17500\text{ cm}^{-1}$  and its absorption spectrum in KBr pellet shows a band with maxima at  $16000\text{ cm}^{-1}$ . A band in this region is normally found in the electronic spectrum of square planar copper(II) complexes and may be assigned to  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  d-d transition.

The magnetic moment for tris(phenyldithiocarbazato)chromium(III) was found to be 3.88 B.M., a value close to the expected one according to spin-only formula for three unpaired electrons, indicating an octahedral structure for this compound. The diffuse reflectance spectrum (Fig.10) and the KBr pellet absorption spectrum (Fig.11) are also consistent with this structure. Two bands are observed in the reflectance spectrum, one with maxima at  $\sim 19000\text{ cm}^{-1}$  and the other with maxima at  $\sim 15000\text{ cm}^{-1}$ , which can be said to result from d-d transitions<sup>14</sup>. The former may be assigned to  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  transition and the latter to  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  transition. The KBr pellet absorption spectrum (Fig.11) shows only one band with maxima at  $\sim 15000\text{ cm}^{-1}$  due to d-d transition and two other bands with maxima at  $27800\text{ cm}^{-1}$  and  $30500\text{ cm}^{-1}$  which may be due to charge transfer or ligand absorptions.

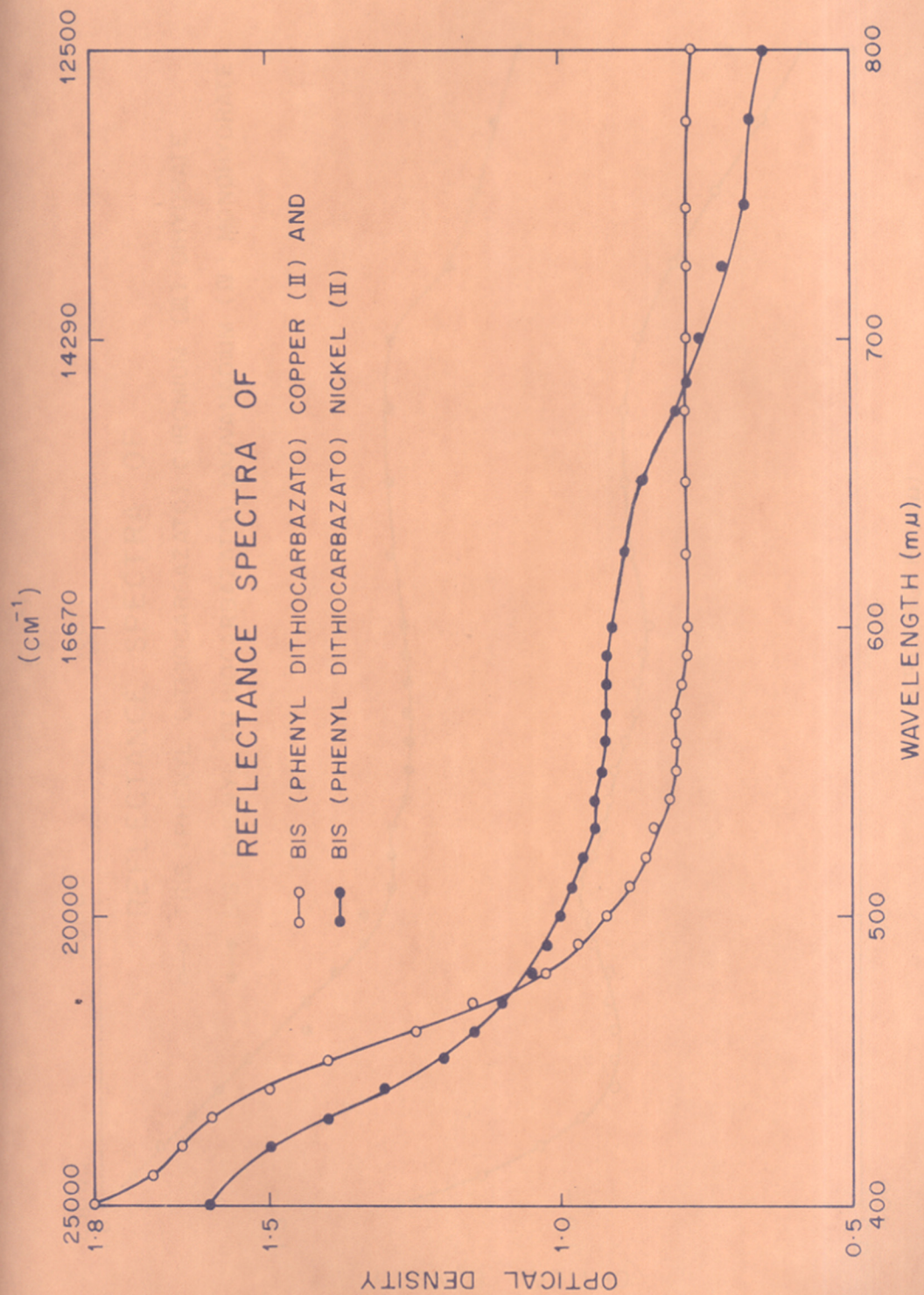


FIG. 9

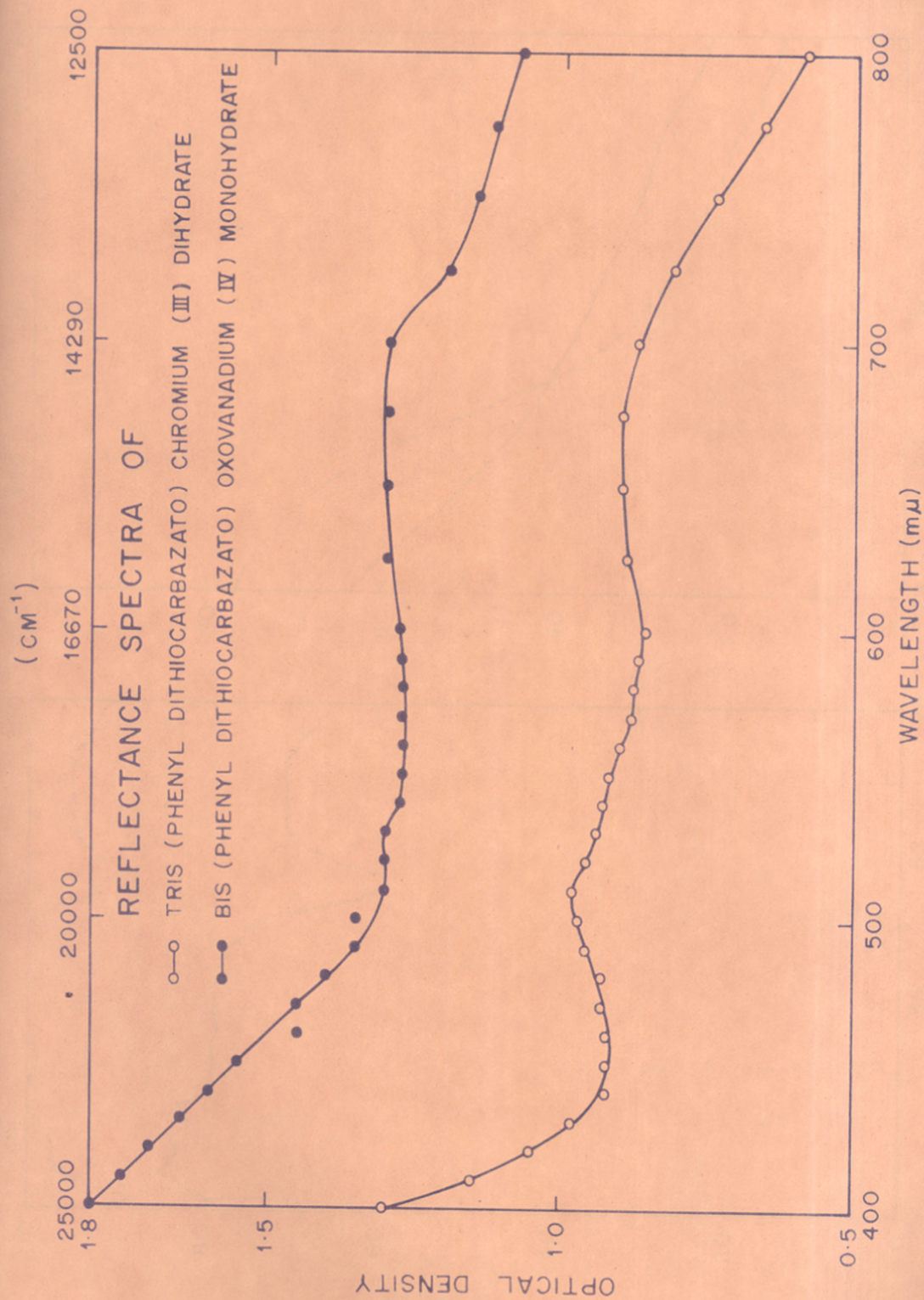


FIG. 10



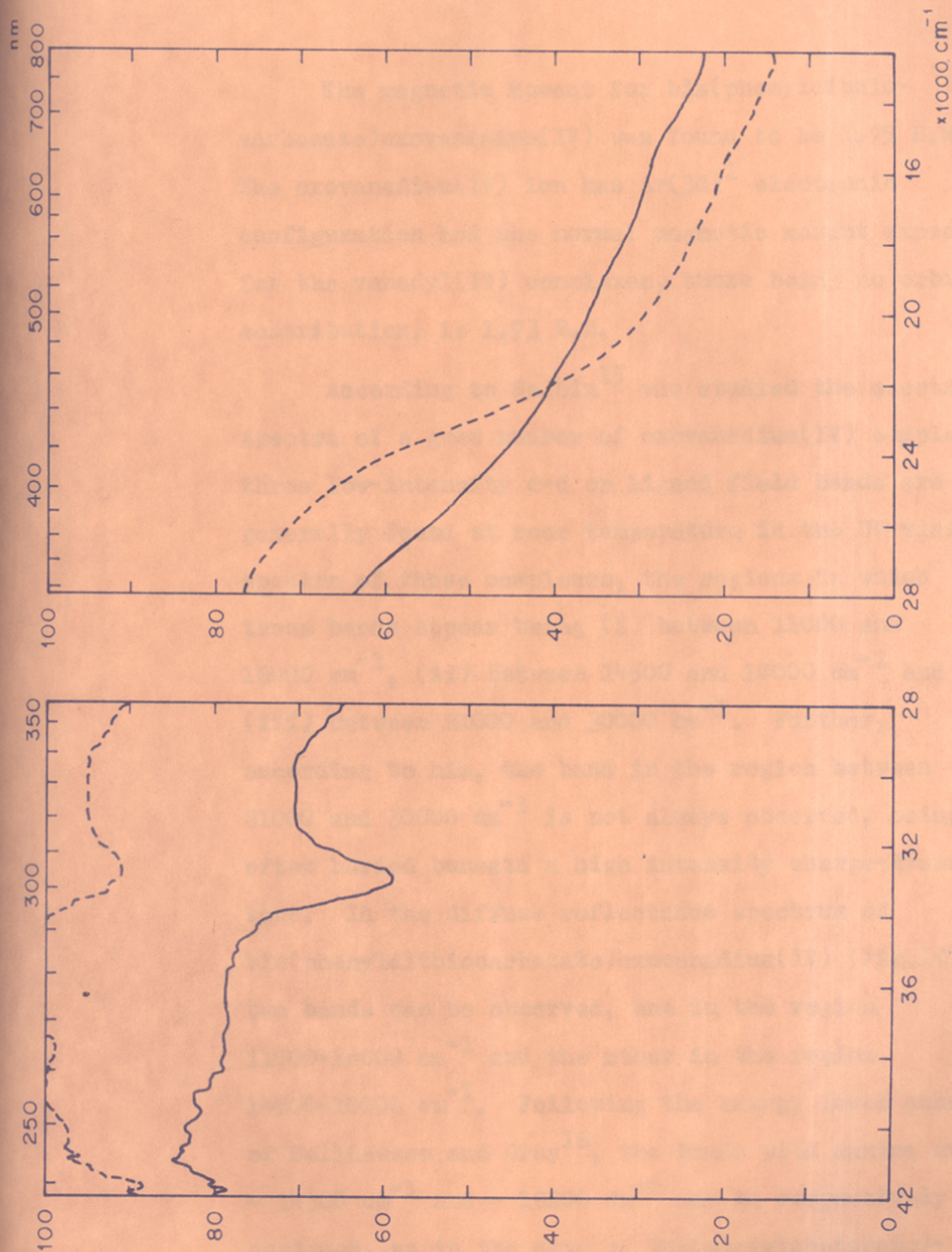


FIG. 11 : ABSORPTION SPECTRA IN KBr PELLET OF

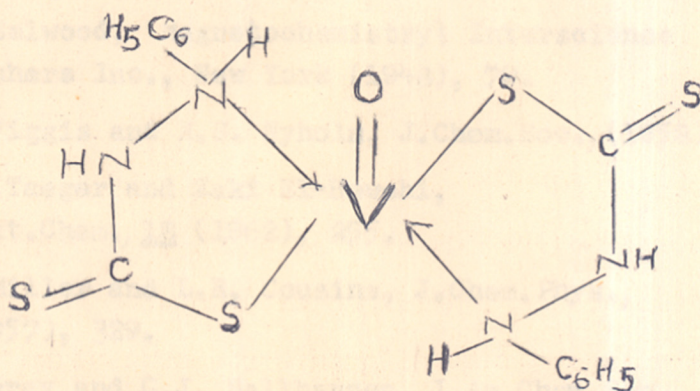
----- BIS (PHENYL DITHIOCARBAZATO) COPPER (II).

——— TRIS (PHENYL DITHIOCARBAZATO) CHROMIUM(III) DIHYDRATE.

The magnetic moment for bis(phenyldithiocarbazato)oxovanadium(IV) was found to be 1.75 B.M. The oxovanadium(IV) ion has  $Ar(3d)^1$  electronic configuration and the normal magnetic moment expected for the vanadyl(IV) complexes, there being no orbital contribution, is 1.73 B.M.

According to Selbin<sup>15</sup> who studied the electronic spectra of a good number of oxovanadium(IV) complexes, three low-intensity d-d or ligand field bands are generally found at room temperature in the UV-visible spectra of these complexes, the regions in which these bands appear being (i) between 11000 and 16000  $cm^{-1}$ , (ii) between 14500 and 19000  $cm^{-1}$  and (iii) between 21000 and 30000  $cm^{-1}$ . Further, according to him, the band in the region between 21000 and 30000  $cm^{-1}$  is not always observed, being often buried beneath a high intensity charge-transfer band. In the diffuse reflectance spectrum of bis(phenyldithiocarbazato)oxovanadium(IV) (Fig.10) two bands can be observed, one in the region 11000-16000  $cm^{-1}$  and the other in the region 14500-19000  $cm^{-1}$ . Following the energy level scheme of Ballhausen and Gray<sup>16</sup>, the bands with maxima at  $\sim 14300$   $cm^{-1}$  and  $\sim 18800$   $cm^{-1}$  may be respectively assigned, as in the case of bis(acetylacetonato)-oxovanadium(IV)<sup>17</sup>, to  ${}^2B_2 \rightarrow {}^2E(I)$  and  ${}^2B_2 \rightarrow {}^2B_1$

d-d transitions. The absorption spectrum of the compound in KBr pellet (Fig.11) shows three bands with maxima at  $30500\text{ cm}^{-1}$ ,  $24100\text{ cm}^{-1}$  and  $14900\text{ cm}^{-1}$ . Whereas the band with maxima at  $30500\text{ cm}^{-1}$  may be assumed to be purely charge-transfer in origin, the band with maxima at  $24100\text{ cm}^{-1}$  can be said to be due to either charge-transfer or charge-transfer plus  ${}^2B_2 \rightarrow {}^2A_1$  d-d transition. The band with maxima at  $14900\text{ cm}^{-1}$  may be assigned to  ${}^2B_2 \rightarrow {}^2E(I)$  d-d transition. The structure of the compound may be written as:



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CHAPTER III : METAL CHELATES OF S-METHYL-N-(PHENYL)-  
ETHYLIDENDITHIOCARBAZATE AND S-METHYL-N-  
(FERROCENYL)-ETHYLIDENDITHIOCARBAZATE

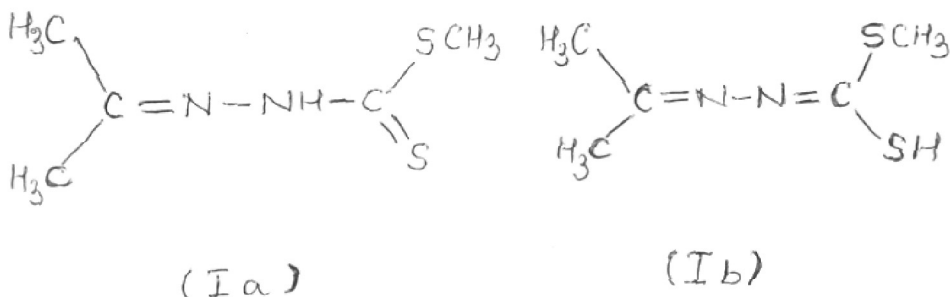
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### Abstract

Two new Schiff bases derived from S-methyl ester of dithiocarbazic acid, and acetophenone and acetyl ferrocene have been synthesized. Mass spectral fragmentations, NMR and IR spectra of these compounds of the type  $RC(CH_3)=N-N=C(SCH_3)SH$  (where R = phenyl or ferrocenyl) have been studied. Both the compounds act as ligands and their metal complexes of the type  $M(N-S)_2$  where (N-SH = Schiff base) with copper(II), nickel(II) and palladium(II) have been isolated and characterized by spectral (NMR, IR and electronic) and magnetic measurement studies.

## INTRODUCTION

In one of a series of papers on metal chelates of dithiocarbamic acid and its derivatives, Livingstone et al.<sup>1</sup> have reported the synthesis of a bidentate ligand, S-methyl-N-isopropylidendithiocarbamate (Ia), a Schiff base derivative obtained by condensation of S-methyl ester of dithiocarbamic acid with acetone.



The synthesis of stable crystalline complexes of this ligand with copper(II), nickel(II), palladium(II), platinum(II) and cobalt (III) has also been reported. According to these authors, the ligand exists in thione form (Ia) in the solid state, but in solution it probably exists in equilibrium with its tautomeric thiol form (Ib) and consequently, by the loss of the thiol proton, acts as a singly negatively charged bidentate ligand by coordinating to a metal ion via the mercapto-sulphur and the nitrogen bound to the isopropylidene group.

In this Chapter we describe the synthesis of two analogous Schiff base ligands, S-methyl-N-(phenyl)-ethylidendithiocarbazate and S-methyl-N-(ferrocenyl)-ethylidendithiocarbazate. These two compounds have been isolated for the first time. Mass spectral fragmentations, NMR and infrared spectra of these compounds have been discussed. Syntheses of complexes of these ligands with copper(II), nickel(II) and palladium(II) as well as their spectral and magnetic data are also reported.



## EXPERIMENTAL

### Materials and Methods

The S-methyl ester of dithiocarbazic acid and acetylferrocene were prepared in the laboratory according to literature methods<sup>2,3</sup>. The acetophenone used (L.R., B.D.H.) was freshly distilled before use. Metal salts used were of analytical reagent grade. Solvents used were purified and dried wherever necessary, by standard procedures<sup>4</sup>.

The infrared spectra of the ligands and complexes in nujol-hexachlorobutadiene mulls were recorded on a Perkin Elmer spectrophotometer model 221, using sodium chloride prism. The nmr spectra of the compounds were recorded on a Varian Associates Model T-60, with tetramethyl silane as internal standard. The UV-visible spectra of the compounds were recorded on UV-VIS specord model No.445069 spectrophotometer. The mass spectra of the ligands were recorded on a CEC 21-110B (USA) double focussing mass spectrometer. The magnetic susceptibilities were determined by Faraday method<sup>5</sup>. The apparatus was calibrated with mercury(II) tetrathiocyanatocobaltate<sup>6</sup>.

### Preparation of the ligands

#### 1. S-methyl-N-(phenyl)ethylidendithiocarbazate:

This was obtained by condensation of S-methyl-dithiocarbazate with acetophenone.

a) Preparation of S-methyldithiocarbamate:

This was prepared according to the method of Bahr and Schleitzer<sup>2</sup>. To a solution of 11.4 g of KOH in 75 ml alcohol (95%), 12.4 g of hydrazine hydrate (80%) were added and the mixture was cooled in ice and 15.2 g of cooled carbon disulfide (diluted with equal volume of alcohol) was added to it maintaining the temperature below 5°C. Potassium dithiocarbamate which separated as the oil, was dissolved in 40% alcohol and reacted with 29 g of methyl iodide below 0°C by shaking the mixture vigorously. The white crude product was recrystallised from benzene. Yield, 6 g (25%), m.p. 83°C. (reported, 84°C). Found: C, 20.00, H, 4.93; N, 22.90; S, 52.31%. Calculated for  $C_2H_6N_2S_2$ : C, 19.64; H, 4.95; N, 22.93; S, 52.48%.

b) Condensation of S-methyl dithiocarbamate with acetophenone:

6.15 g (0.05 mole) of acetophenone was added to a solution of 6.1 g (0.05 mole) of S-methyldithiocarbamate in 75 ml ethanol. The clear yellow solution was covered with a watch glass and heated on a water-bath for 30 minutes. The solution was concentrated to half of its original volume and cooled to 0°C for 30 minutes. The tiny yellow crystals separated were filtered, sucked dry and recrystallised from ethanol.

Yield, 6 g (53%), m.p. 150°C. Found: C, 53.17; H, 5.69; N, 11.95; S, 28.94%. Calculated for  $C_{10}H_{12}N_2S_2$ : C, 53.55; H, 5.36; N, 12.50; S, 28.63%.

2. S-methyl-N-(ferrocenyl)ethylidendithiocarbamate:

This was obtained by condensation of S-methyl-dithiocarbamate with acetylferrocene.

a) Preparation of ferrocene:

This was prepared according to the method described in Inorganic Syntheses<sup>7</sup>.

A 500 ml three necked flask, equipped with a stirrer, was charged with 240 ml of tetrahydrofuran and 100 g of potassium hydroxide powder. While the mixture was slowly stirred and the flask was flushed with nitrogen gas from one side neck, 22 ml (0.268 mole) of cyclopentadiene was added. The other side neck was fitted with a  $CaCl_2$  guard tube and the main neck was fitted with a 100 ml dropping funnel and 26.0 g (0.130 mole) of iron(II) chloride tetrahydrate in 100 ml of dimethyl sulfoxide was placed in the dropping funnel. This solution was added drop-wise with stirring during 1 hr. The stopcock of the funnel was closed and the stirring was continued for another 30 minutes. The nitrogen stream was stopped and the mixture was added to a mixture of 360 ml of 6 M HCl

and approximately 400 g ice. The slurry was stirred for 15 minutes, the precipitate was collected on a filter and washed with four 25 ml portions of water. The product was allowed to dry in air overnight. Yield, 21.25 g, (89%), m.p.  $174^{\circ}\text{C}$  (reported,  $173-174^{\circ}\text{C}$ ). Found: C, 63.14; H, 5.33; Fe, 30.6%. Calculated for  $\text{C}_{10}\text{H}_{10}\text{Fe}$ : C, 63.57; H, 5.42; Fe, 30.02%.

b) Preparation of acetyl ferrocene:

This was prepared essentially by the method described in literature<sup>3</sup>. To 18.6 g of ferrocene was added 40 ml acetic anhydride and 4 ml of 85% phosphoric acid. The mixture was heated at  $100^{\circ}\text{C}$  for 10 minutes, cooled and poured on 200 g ice. The mixture was allowed to stand overnight. It was neutralized with 40 g sodium carbonate monohydrate dissolved in 40 ml of water. The resulting pasty mass was cooled in an ice bath and filtered, washed with water, sucked dry and dried over  $\text{P}_2\text{O}_5$  in desiccator under vacuum. The product was recrystallised from petroleum ether. Yield, 14 g, (57%), m.p.  $85^{\circ}\text{C}$  (reported,  $85-86^{\circ}\text{C}$ ). Found: C, 64.23; H, 5.89; Fe, 24.91. Calculated for  $(\text{C}_{10}\text{H}_9\text{COCH}_3)_2\text{Fe}$ : C, 63.17; H, 5.26; Fe, 25.0.

c) Condensation of S-methyldithiocarbamate with acetyl ferrocene:

A solution of 0.82 g (0.0067 mole) of S-methyl-

dithiocarbazate in 30 ml absolute ethanol was added to a 15 ml ethanolic solution of 1.5 g (0.0066 mole) of acetyl ferrocene. The mixture was heated under reflux for 1.5 hr. and allowed to stand at 5-10°C for 24 hrs. The solid formed was collected on a filter, washed well with small quantities of cold alcohol and dried in vacuo at room temperature. Shining red crystals were obtained. Yield, 1.15 g (53%), m.p. 124°C. Found: C, 51.01; H, 4.92; N, 8.01; S, 19.11; Fe, 15.92%. Calculated for  $C_{14}H_{16}N_2S_2Fe$ : C, 50.60; H, 4.82; N, 8.44; S, 19.30; Fe, 16.81%.

Preparation of the metal complexes

Bis[S-methyl-N-(phenyl)ethylidendithiocarbazato] copper(II) monohydrate:

A hot ethanolic solution (5 ml) of 0.426 g (0.0025 mole) of cupric chloride dihydrate was added to a hot ethanolic solution (50 ml) of 1.12 g (0.005 mole) of acetophenone Schiff base. A greenish yellow solid was formed. It was digested on water-bath for 20 minutes, collected on a filter, washed well with ethanol and dried in vacuo over KOH. Yield, 0.8 g (61%); m.p. 287°C. Found: C, 44.92; H, 5.02; N, 10.90%; S, 24.10; Cu, 12.33%. Calculated for  $(C_{10}H_{11}N_2S_2)_2Cu \cdot H_2O$ : C, 45.38; H, 4.56; N, 10.60; S, 24.29; Cu, 12.03%.

Bis[S-methyl-N-(phenyl)ethylidendithiocarbazato]nickel(II):

Nickel chloride hexahydrate (1.18 g, 0.005 mole) dissolved in 15 ml absolute ethanol was added to 190 ml ethanolic solution of the ligand (2.24 g, 0.01 mole) with stirring. The greenish brown clear solution was stirred at room temperature for two hrs. when a greenish black compound separated out. It was collected on a filter, washed 4-5 times with 15 ml portions of absolute ethanol, sucked dry and dried over KOH in vacuo. The compound was recrystallized from chloroform. Yield, 0.5 g, (25%); the compound does not melt upto 360°C. Found: C, 48.58; H, 4.60; N, 11.04; S, 24.24; Ni, 11.54%. Calculated for  $(C_{10}H_{11}N_2S_2)_2Ni$ : C, 47.52; H, 4.39; N, 11.09; S, 25.37%; Ni, 11.61%.

Bis[S-methyl-N-(phenyl)ethylidendithiocarbazato]palladium(II):

To the warm ethanolic solution (90 ml) of the ligand (1.12 g, 0.005 mole) was added a warm aqueous solution (5 ml) of sodium tetrachloropalladate (0.735 g, 0.0025 mole) with stirring. The orange red clear solution yielded an orange coloured compound after fifteen minutes stirring. After stirring

further for fifty minutes, the solid was collected on a filter, washed with two portions of 15 ml ethanol and dried over KOH in vacuo. It was recrystallised from chloroform. Yield, 0.7 g (50%). The compound does not melt upto 360°C.

Found: C, 44.05; H, 4.33; N, 10.47; S, 23.14; Pd, 19.01%.  
 Calculated for  $(C_{10}H_{11}N_2S_2)_2Pd$ : C, 43.42; H, 4.01; N, 10.14; S, 23.18; Pd, 19.24%.

Bis[S-methyl-N-(ferrocenyl)ethylidendithiocarbazato]-copper(II) monohydrate:

Cupric acetate monohydrate (0.24 g, 0.0012 mole) dissolved in 20 ml absolute ethanol was added to 50 ml ethanolic solution of acetyl ferrocene Schiff base (0.8 g, 0.0024 mole). The mixture was stirred for 4 hrs. and allowed to stand overnight. The black solid formed was collected on a filter, washed well with ethanol and dried in vacuo at room temperature. Yield, 0.75 g (84%). Found: C, 45.22; H, 4.19; N, 7.07; S, 17.11; Cu + Fe, 23.38%.

Calculated for  $(C_{14}H_{15}N_2S_2Fe)_2Cu.H_2O$ : C, 45.20; H, 4.30; N, 7.53; S, 17.23; Cu + Fe; 23.57%.

Bis[S-methyl-N-(ferrocenyl)ethylidendithiocarbazato]-nickel(II):

Nickel chloride hexahydrate (0.396 g; 0.0011 mole)

dissolved in 5 ml ethanol was added to 50 ml warm ethanolic solution of the ligand (0.8 g, 0.0024 mole) with stirring. A brown compound was immediately formed. It was stirred for 1 hr., filtered, washed twice with two 15 ml portions of ethanol and dried over KOH in vacuo. The compound was recrystallised from chloroform. Yield, 0.61 g (50%). The compound does not melt upto 360°C. Found: C, 47.53; H, 4.61; N, 7.44; S, 17.54; Ni + Fe, 23.88%. Calculated for  $(C_{14}H_{15}N_2S_2Fe)_2Ni$ : C, 46.63; H, 4.19; N, 7.77; S, 17.78; Ni + Fe, 23.57%.

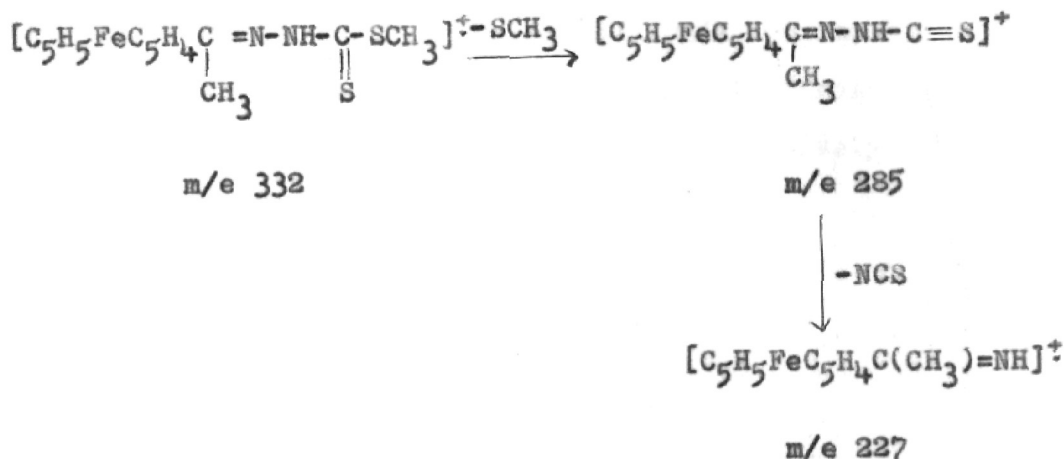
Bis[S-methyl-N-(ferrocenyl)ethylidendithiocarbazato]-palladium(II):

A warm solution of sodium tetrachloro palladate (0.735 g, 0.0025 mole) in 5 ml water was added to 50 ml warm ethanolic solution of the ligand (1.66 g, 0.005 mole) with stirring. An orange red product formed immediately was stirred for 1 hr., collected on a filter, washed well with ethanol and dried over KOH in vacuo. The compound was recrystallised from chloroform. Yield, 1.25 g (88%). The compound does not melt upto 360°C. Found: C, 43.99; H, 3.90; N, 6.59; S, 16.42; Pd + Fe, 28.10%. Calculated for  $(C_{14}H_{15}N_2S_2Fe)_2Pd$ : C, 43.73; H, 3.93; N, 7.28; S, 16.68; Pd + Fe, 28.36%.

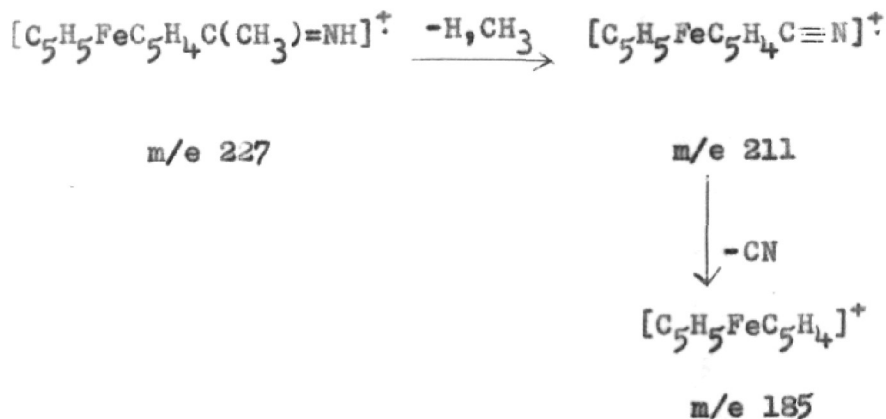


## RESULTS AND DISCUSSION

The mass spectra of the ligands, S-methyl-N-(phenyl)ethylidendithiocarbazate and S-methyl-N-(ferrocenyl)ethylidendithiocarbazate, showed molecular ion peaks respectively at m/e 224 and at m/e 332. The mass spectral fragmentation patterns of the two ligands were, however, somewhat different from one another in the region of interest, that is, the region between the molecular ion peak and phenyl ion peak in the case of acetophenone Schiff base compound and that between molecular ion peak and ferrocenyl ion peak in the case of acetylferrocene Schiff base. Besides the molecular ion peak, only four major ion peaks (relative intensity > 10%) were observed in this region of the spectrum of acetylferrocene Schiff base compound (Table II). The ion peak at m/e 285 can be said to be due to loss of -SCH<sub>3</sub> group by the molecular ion and, as shown,



this ion in turn seems to undergo loss of -NCS group to give the ion peak at m/e 227. The peaks at m/e 211 and m/e 185 can be assigned to the ions formed by the plausible fragmentations:



In the mass spectrum of acetophenone Schiff base compound, eight major ion peaks, in addition to that of molecular ion, were observed in the region mentioned (Table I). In this case also the molecular ion undergoes loss of -SCH<sub>3</sub> group, which accounts for the ion peak at m/e 177. The peaks at m/e 209 and m/e 147 can be ascribed to the ions resulting from the loss of methyl and phenyl radicals respectively by the molecular ion:

Table I

Mass spectrum of S-methyl-N-(phenyl)ethyliden-  
dithiocarbazate.

S.No.	m/e	relative abundance %
1	224	93
2	209	100
3	177	89
4	147	62
5	133	56
6	118	84
7	104	69
8	91	90
9	77	84

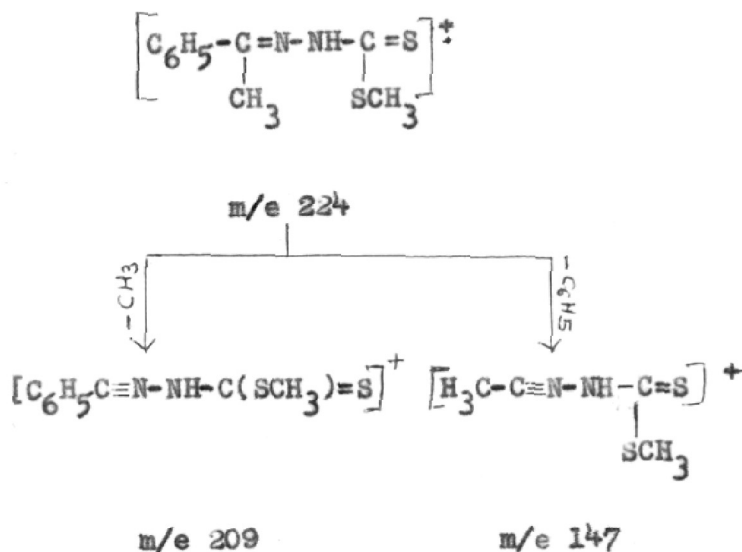
Peaks of less than 10 p.c. intensity are not given

Table II

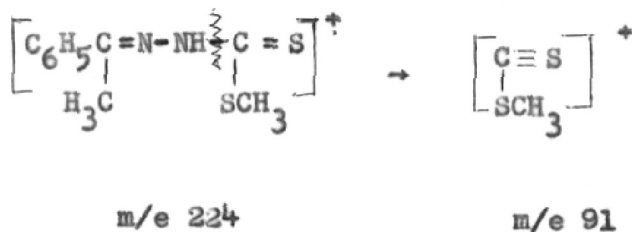
Mass spectrum of S-methyl-N-(ferrocenyl)-  
ethylidendithiocarbamate.

S.No.	m/e	relative abundance %
1	332	20
2	285	100
3	227	71
4	211	93
5	185	100

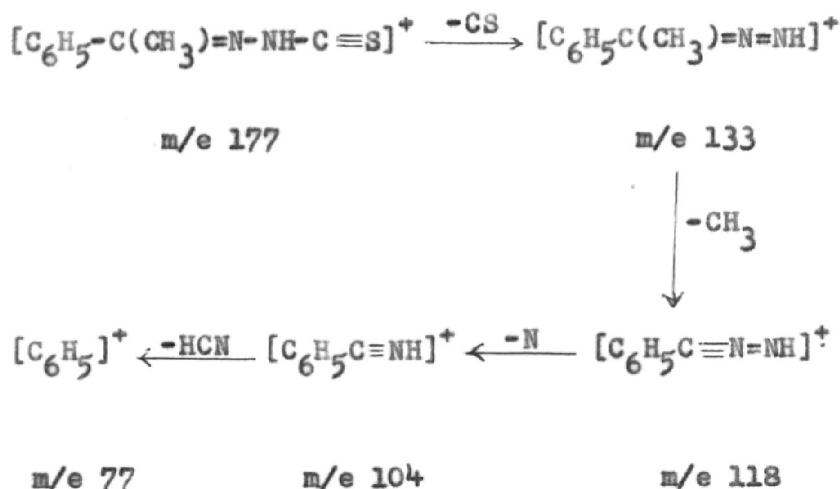
Peaks of less than 10 p.c. intensity are not given



The molecular ion appears to undergo also rupture, as shown, resulting in the ion peak at m/e 91:



The ion peaks at m/e 133, m/e 118, m/e 104 and m/e 77 can be explained on the basis of the plausible fragmentation pattern:



The NMR spectrum of the acetophenone Schiff base in deuteriochloroform (Fig.6) shows two sharp singlets, one at  $\tau$ 7.70 and the other at  $\tau$ 7.37 (each corresponding to three protons as per proton integration ratio), due to methyl protons. It also shows a complex in the range  $\tau$ 3 and  $\tau$ 2 (corresponding to five protons) due to phenyl protons and a broad peak at  $\tau$ 0.1 (corresponding to one proton) ascribable to NH proton. But the spectrum of the acetylferrocene Schiff base compound in deuteriochloroform (Fig.9) shows two sharp doublets, at  $\tau$ 7.75 and  $\tau$ 7.35 (each doublet corresponding to three protons) due to methyl protons. In addition a complex peak in the range  $\tau$ 6 and  $\tau$ 5 (corresponding to nine protons) due to

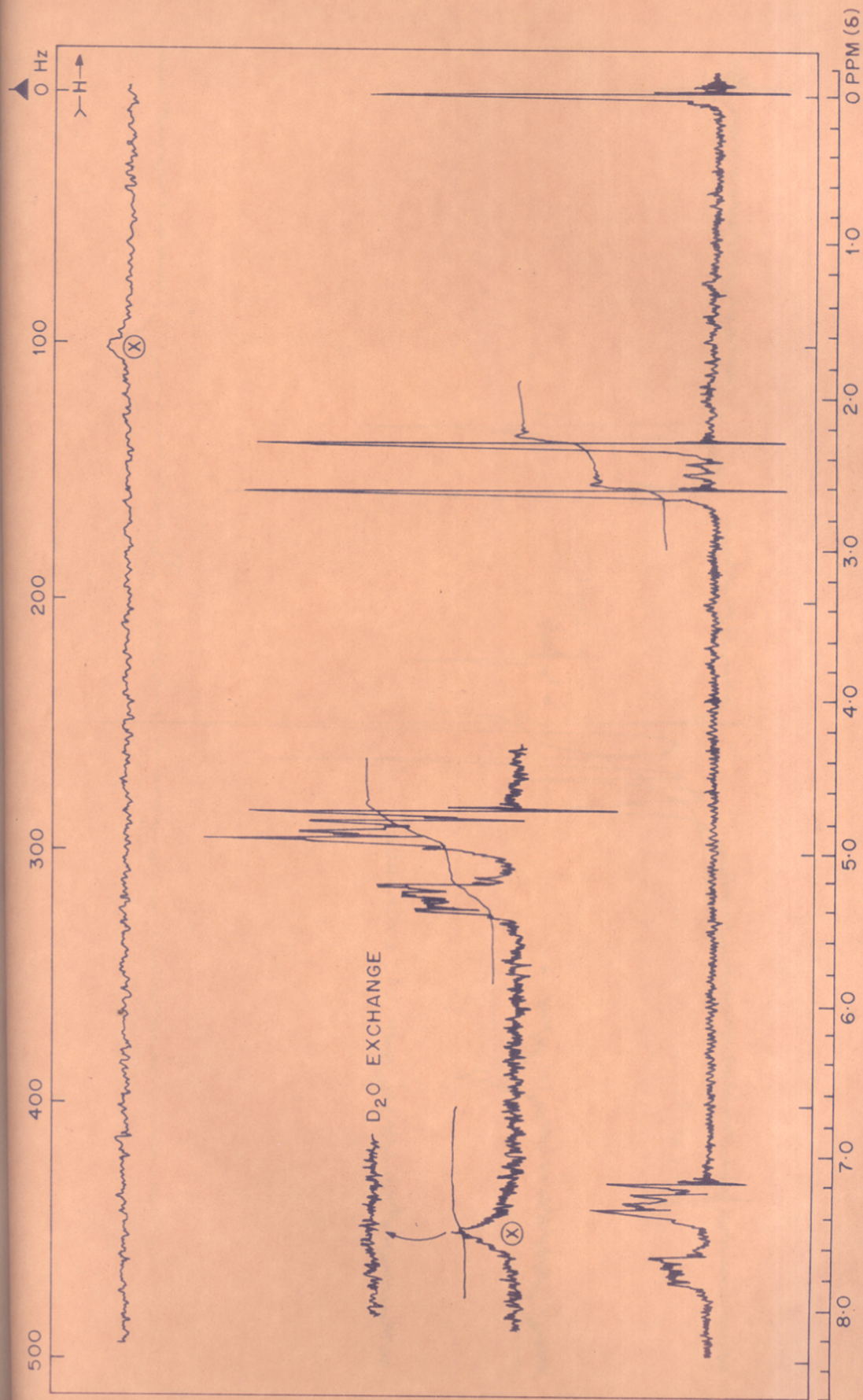
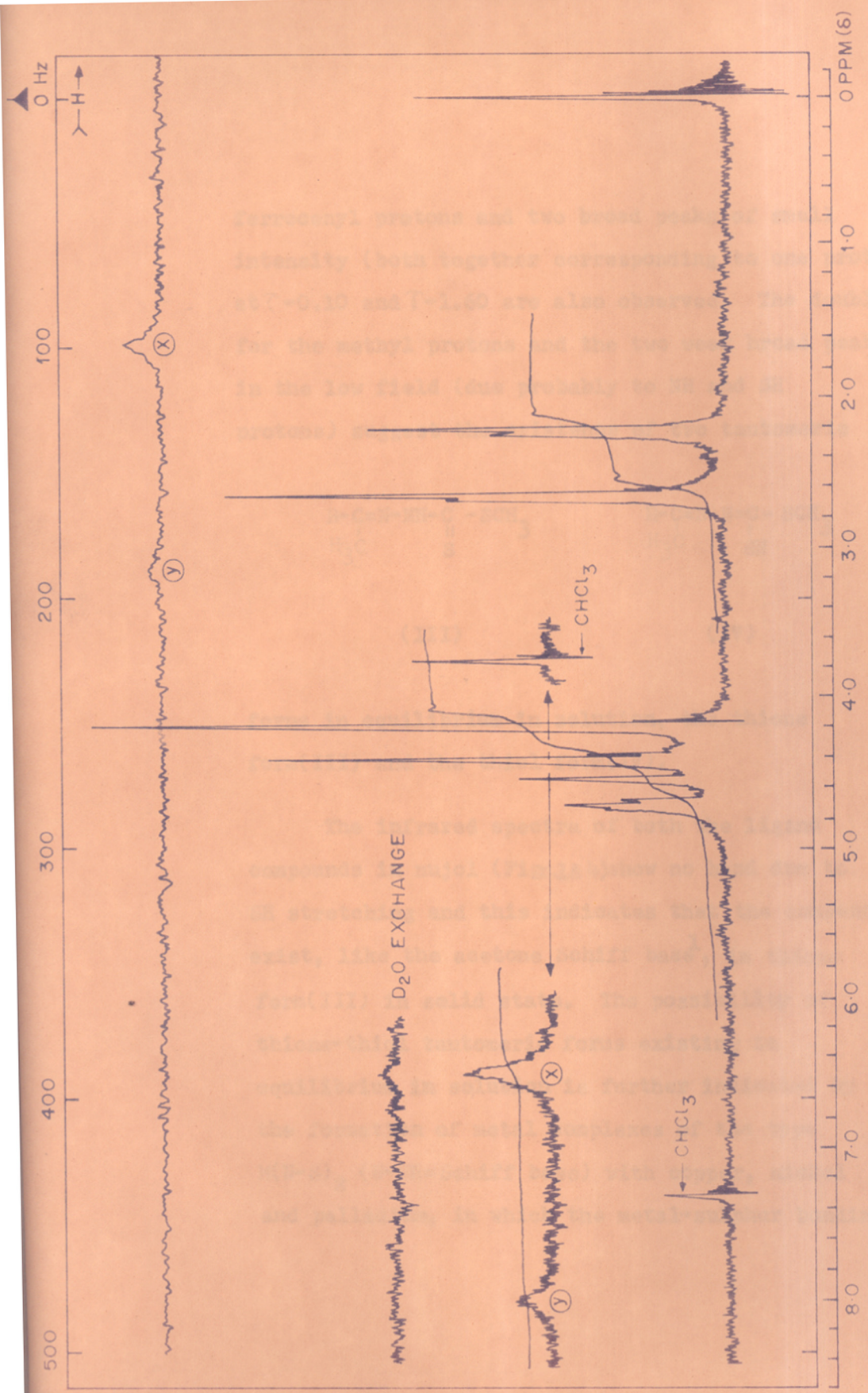


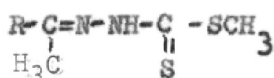
FIG. 6 : NMR SPECTRUM OF  
 S-METHYL-N-(PHENYL) ETHYLIDEN DITHIOCARBAZATE  
 IN  $CDCl_3$

FIG. 9 : NMR SPECTRUM OF  
S-METHYL-N-(FERROCENYL) ETHYLIDEN DITHIOCARBAZATE  
IN  $CDCl_3$

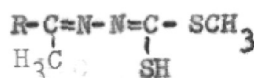




ferrocenyl protons and two broad peaks of small intensity (both together corresponding to one proton) at  $\tau$ -0.10 and  $\tau$ -1.60 are also observed. The doublets for the methyl protons and the two weak broad peaks in the low field (due probably to NH and SH protons) suggest the existence of two tautomeric



(III)



(IV)

forms in equilibrium in solution, the thione form(III) and the thiol form(IV).

The infrared spectra of both the ligand compounds in nujol (Figs 1 & 4) show no band due to SH stretching and this indicates that the compounds exist, like the acetone Schiff base<sup>1</sup>, in thione form(III) in solid state. The possibility of thione-thiol tautomeric forms existing in equilibrium in solution is further indicated by the formation of metal complexes of the type  $\text{M}(\text{N-S})_2$  (N-SH=Schiff base) with copper, nickel and palladium, in which the metal-sulphur bonding

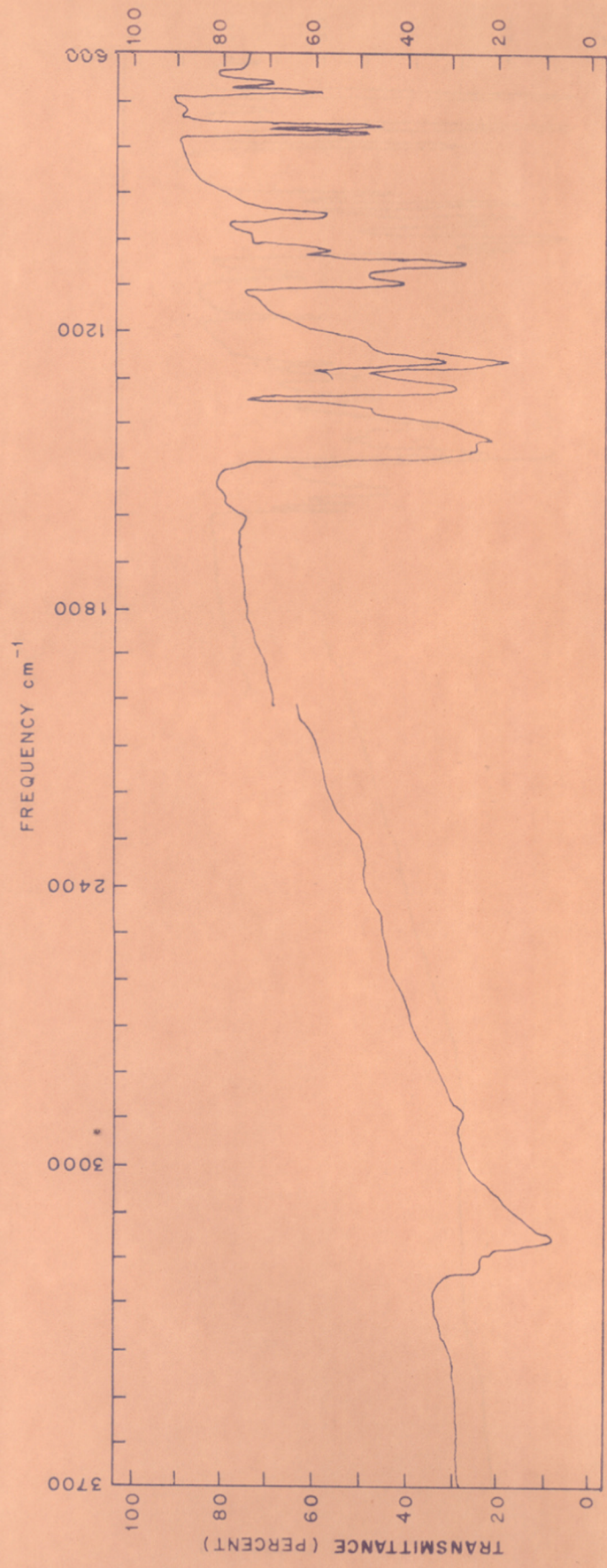


FIG. 1 INFRARED SPECTRUM IN HEXACHLOROBUTADIENE/NUJOL MULL OF  
S - METHYL - N - ( PHENYL ) ETHYLIDENDITHIOCARBAZATE

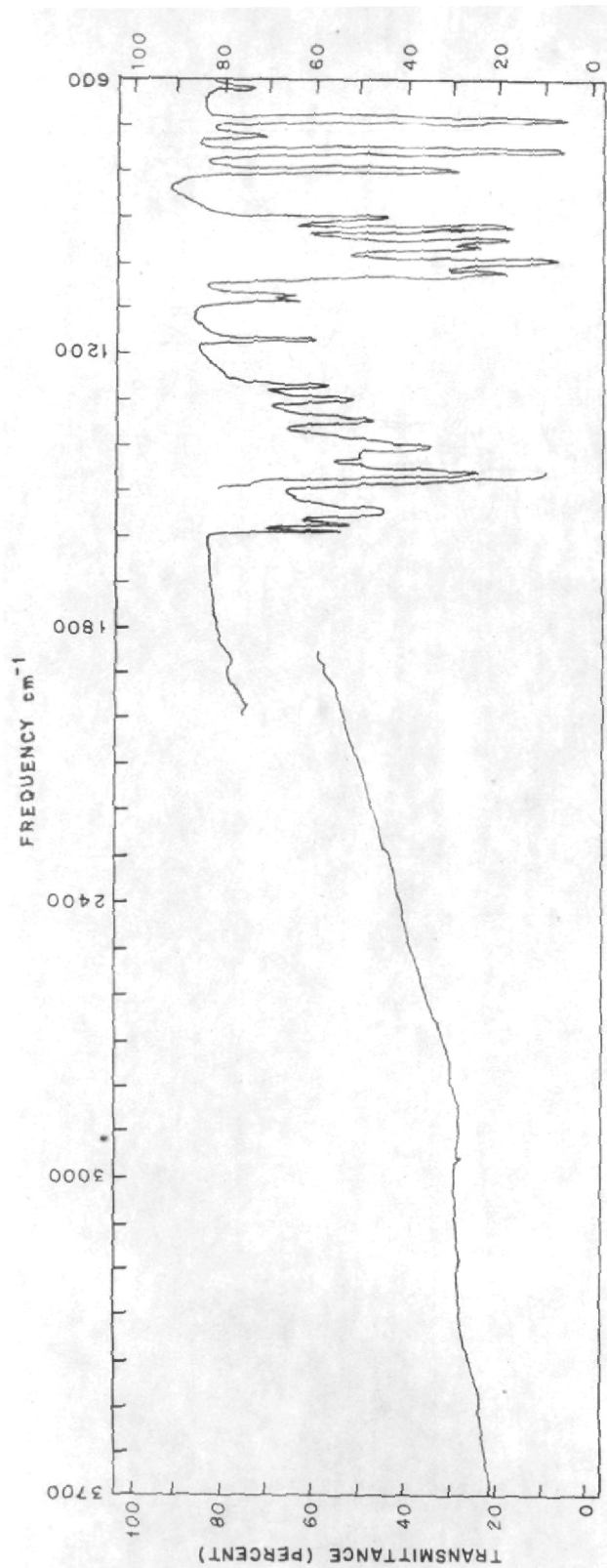


FIG. 2 INFRARED SPECTRUM IN HEXACHLOROBUTADIENE/NUJOL MULL OF  
BIS [S - METHYL - N - (PHENYL) ETHYLIDENDITHIOCARBAZATO]  
COPPER (II) MONOHYDRATE

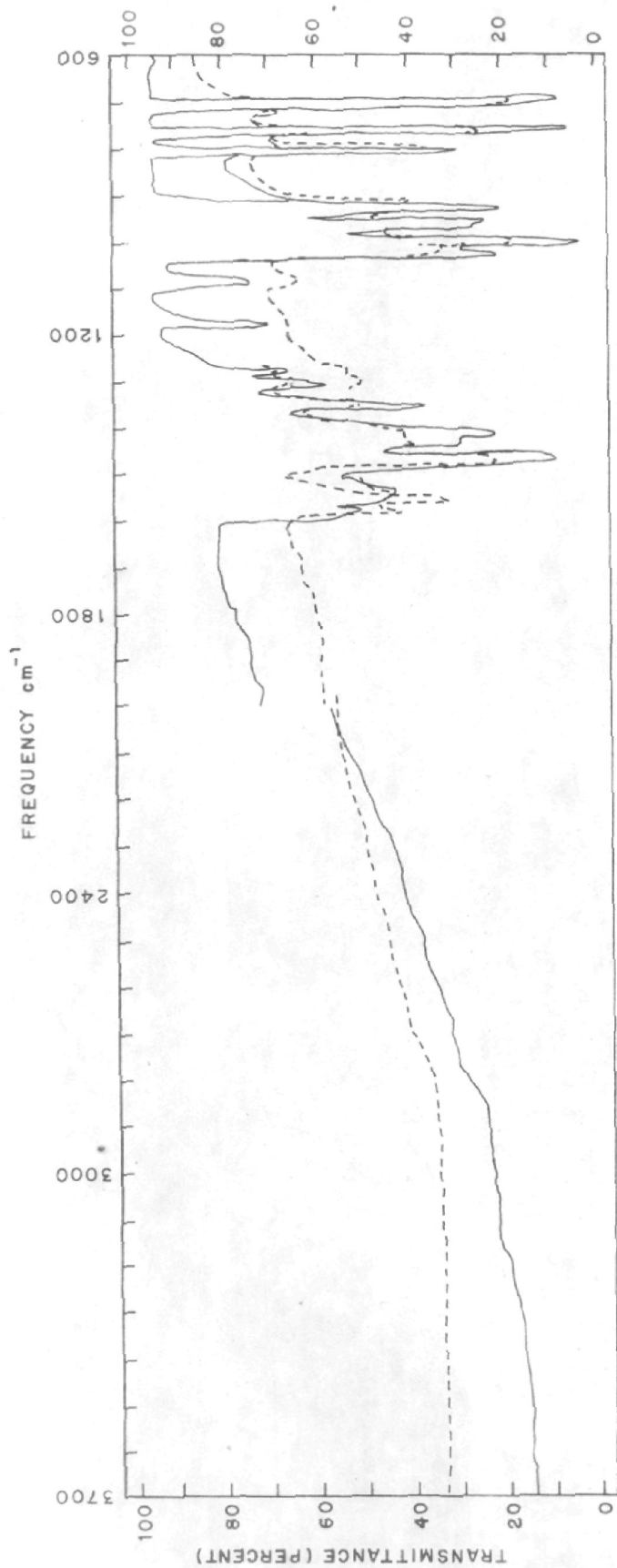


FIG. 3 INFRARED SPECTRA IN HEXACHLOROBUTADIENE/NUJOL MULL OF  
 — BIS [S-METHYL-N-(PHENYL) ETHYLIDEN DITHIOCARBAZATO]  
 NICKEL (II) AND  
 - - - BIS [S-METHYL-N-(PHENYL) ETHYLIDEN DITHIOCARBAZATO]  
 PALLADIUM (II)

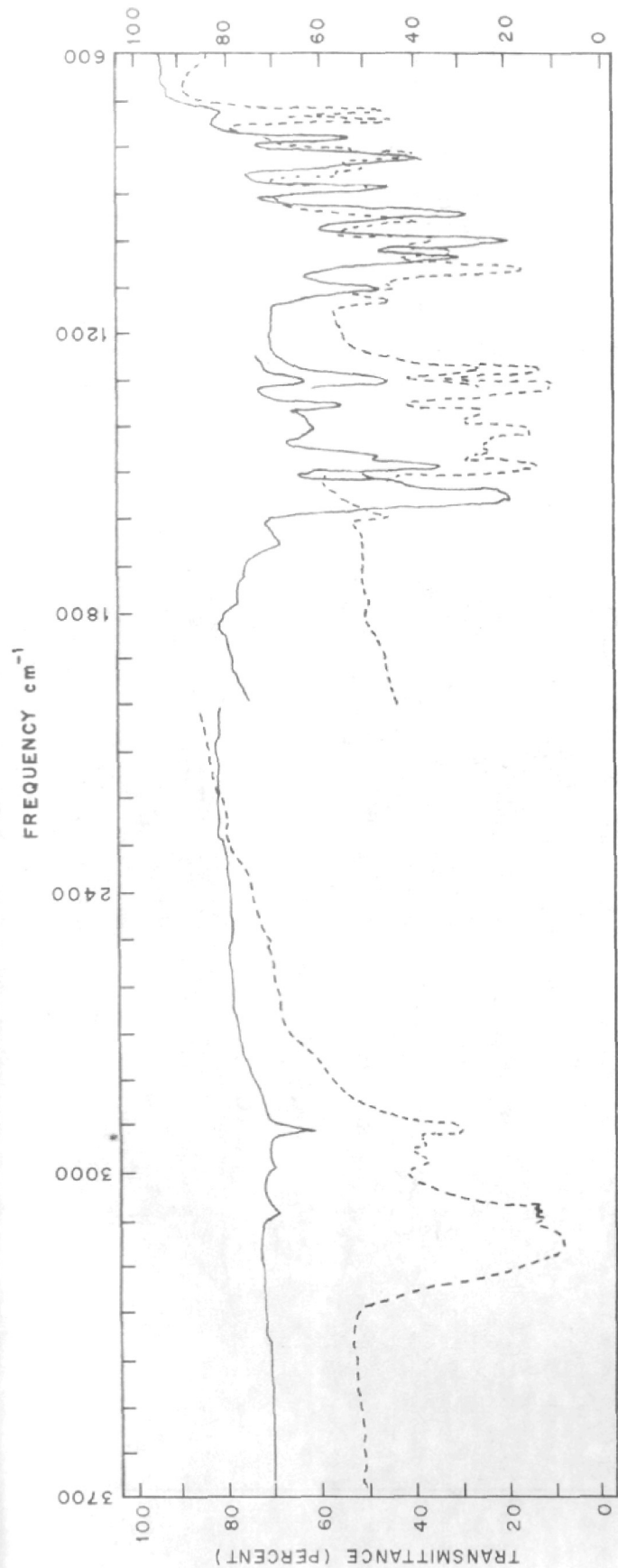


FIG. 4 INFRARED SPECTRA IN HEXACHLOROBUTADIENE/NUJOL MULL OF  
---- S - METHYL - N - (FERROCENYL) ETHYLIDENDITHIOCARBAZATE  
— BIS [S - METHYL - N - (FERROCENYL) ETHYLIDEN DITHIOCAR-  
BAZATO] COPPER (II) MONOHYDRATE

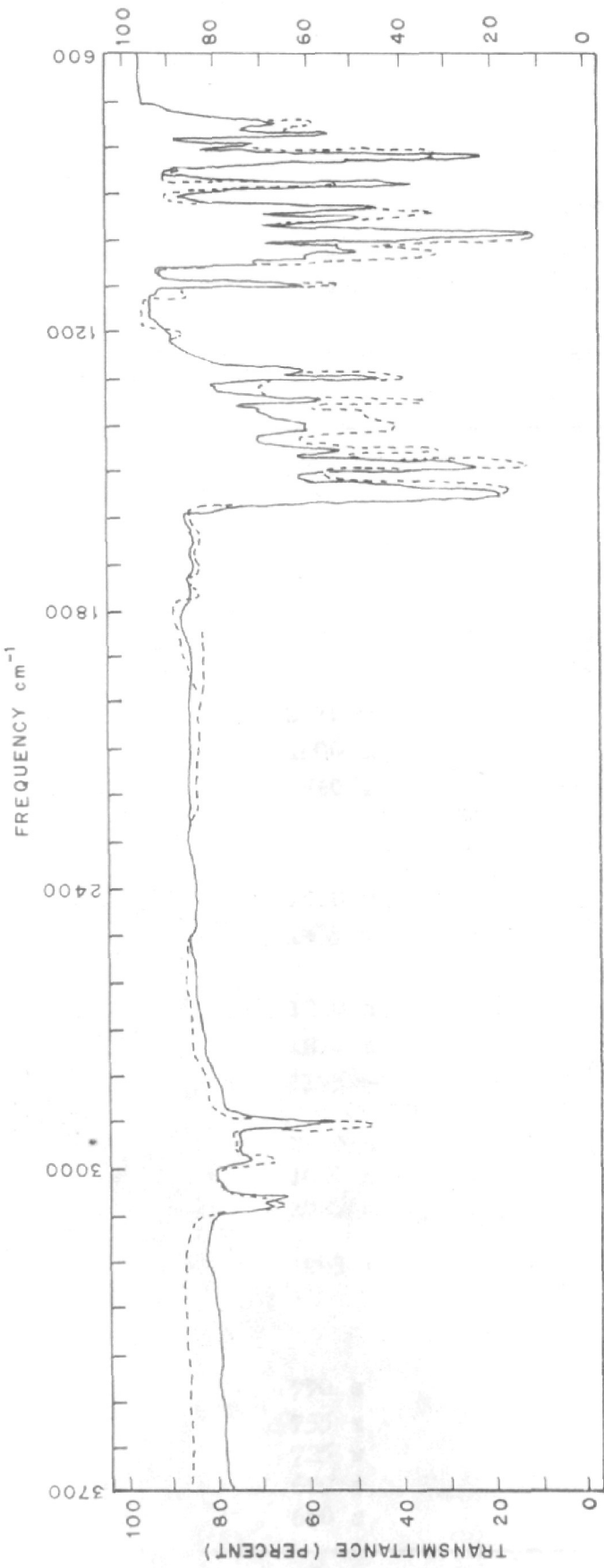


FIG. 5 INFRARED SPECTRA IN HEXACHLOROBUTADIENE/NUJOL MULL OF  
 ---- BIS [S-METHYL-N-(FERROCENYL)ETHYLIDENDITHIOCARBAZATO]  
 NICKEL (II) AND  
 ——— BIS [S-METHYL-N-(FERROCENYL)ETHYLIDENDITHIOCARBAZATO]  
 PALLADIUM (II)

Table III

Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of  
 A) S-methyl-N-(phenyl)ethylidendithiocarbazate and  
 B) S-methyl-N-(ferrocenyl)ethylidendithiocarbazate.

A	B
3235 m	
3170 s	3160 bs
	3100 w
	3090 w
	3075 w
	2980 m
	2940 m
2910 m	2910 m
1600 m	1620 bw
1560 w	1590 m
	1495 sh
	1485 m
1460 m	1455 m
1435 m	1415 m
	1365 m
1320 s	1310 s
1270 s	1280 s
1175 w	
	1125 m
1100 m	1100 m
1050 s	1060 s
1025 m	1020 m
	1000 s
945 s	955 s
	890 s
	850 m
	815 s
770 s	735 s
755 s	720 s
725 w	
680 s	
660 s	

Table IVInfrared absorption frequencies ( $\text{cm}^{-1}$ ) of

- A) bis[S-methyl-N-(phenyl)ethylidendithiocarbazato]-  
Cu(II) monohydrate,  
B) bis[S-methyl-N(phenyl)ethylidendithiocarbazato]-  
Ni(II) and  
C) bis[S-methyl-N-(phenyl)ethylidendithiocarbazato]-  
Pd(II).

A	B	C
2910 bw	2900 bw	2900 bw
1595 m	1590 m	1605 m
1580 m	1575 m	1580 m
1555 bm	1545 m	1560 m
1475 s	1470 s	1470 s
	1435 m	1435 m
1415 m	1415 s	1415 s
1355 s	1355 s	1350 s
1305 m	1300 m	1300 m
1280 m	1275 m	1275 m
1170 s	1175 s	1175 w
1080 m	1080 m	1080 m
1030 s	1020 m	1025 m
1010 s	1005 s	1005 s
960 s	960 s	960 s
935 s	930 s	930 s
	910 m	910 m
805 s	800 s	800 s
765 s	760 s	760 s
715 w	720 w	720 w
695 s	690 s	690 s



Table V

- Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of
- A) bis[S-methyl-N-(ferrocenyl)ethylidendithiocarbazato] Cu(II) monohydrate,
- B) bis[S-methyl-N-(ferrocenyl)ethylidendithiocarbazato] Ni(II) and
- C) bis[S-methyl-N-(ferrocenyl)ethylidendithiocarbazato] Pd(II).

A	B	C
3085 bw	3085 bm	3085 bm
2995 w	2990 bm	2990 bm
2985 w	2960 bw	2960 bw
2915 m	2920 s	2920 s
1650 bw	1650 bw	1630 bw
1550 bs	1560 bs	1560 bs
1495 sh	1495 s	1490 s
1485 s	1460 s	1460 s
1400 bw	1410 bs	1410 bs
1350 m	1350 s	1350 s
1300 s	1300 s	1300 s
1120 w	1120 m	1120 w
1100 m	1100 s	1100 s
1035 s	1035 m	1030 m
1000 s	1000 s	995 s
940 s	945 s	940 s
885 s	885 s	885 s
820 s	820 s	825 s
775 s	775 s	775 s
-	755 s	755 s

takes place through the replacement of thiol proton. The metal-sulphur bonding through the replacement of thiol proton is supported by NMR and infrared spectra of the metal complexes with both the ligands. The NMR spectra of the nickel(II) and palladium(II) complexes in deuteriochloroform (Figs. 7 and 8) and (Figs. 10 and 11) show no peaks due to NH (or SH) proton and this has been confirmed by  $D_2O$  exchange. In the infrared spectra of all the metal complexes (Figs. 2,3 and 5) bands due to NH stretching (observed at  $\sim 3160-3235\text{ cm}^{-1}$  in the spectra of ligands) are absent.

The magnetic measurements showed the nickel complexes with both the ligands to be diamagnetic. This indicates the nickel complexes to be square planar. It is known that the palladium(II) complexes strongly demand tetra-coordinate square planar configuration and the palladium(II) complexes with both the ligands were found to be diamagnetic as expected. The magnetic moment of copper(II) complex with acetophenone Schiff base was found to be 1.66 B.M. and that of copper(II) complex with acetylferrocene Schiff base was found to be 1.82 B.M. These values show that the complexes belong to the group of  $dsp^2$  square planar type four-coordinate copper complexes

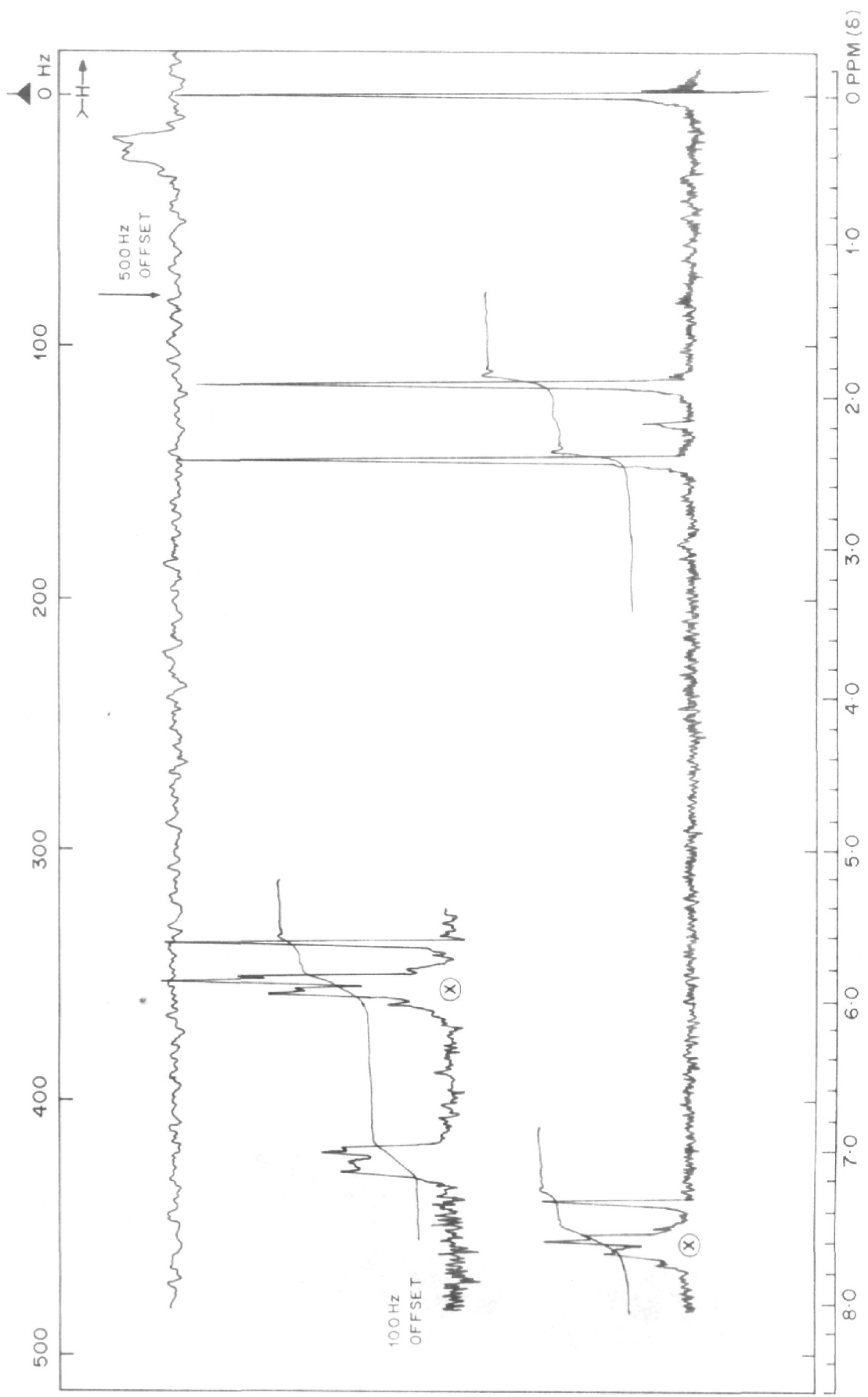


FIG. 7 : NMR SPECTRUM OF

BIS [S-METHYL - N - (PHENYL) ETHYLIDEN ETHYLIDEN DITHIOCARBAZATO] NICKEL (II) IN  $CDCl_3$

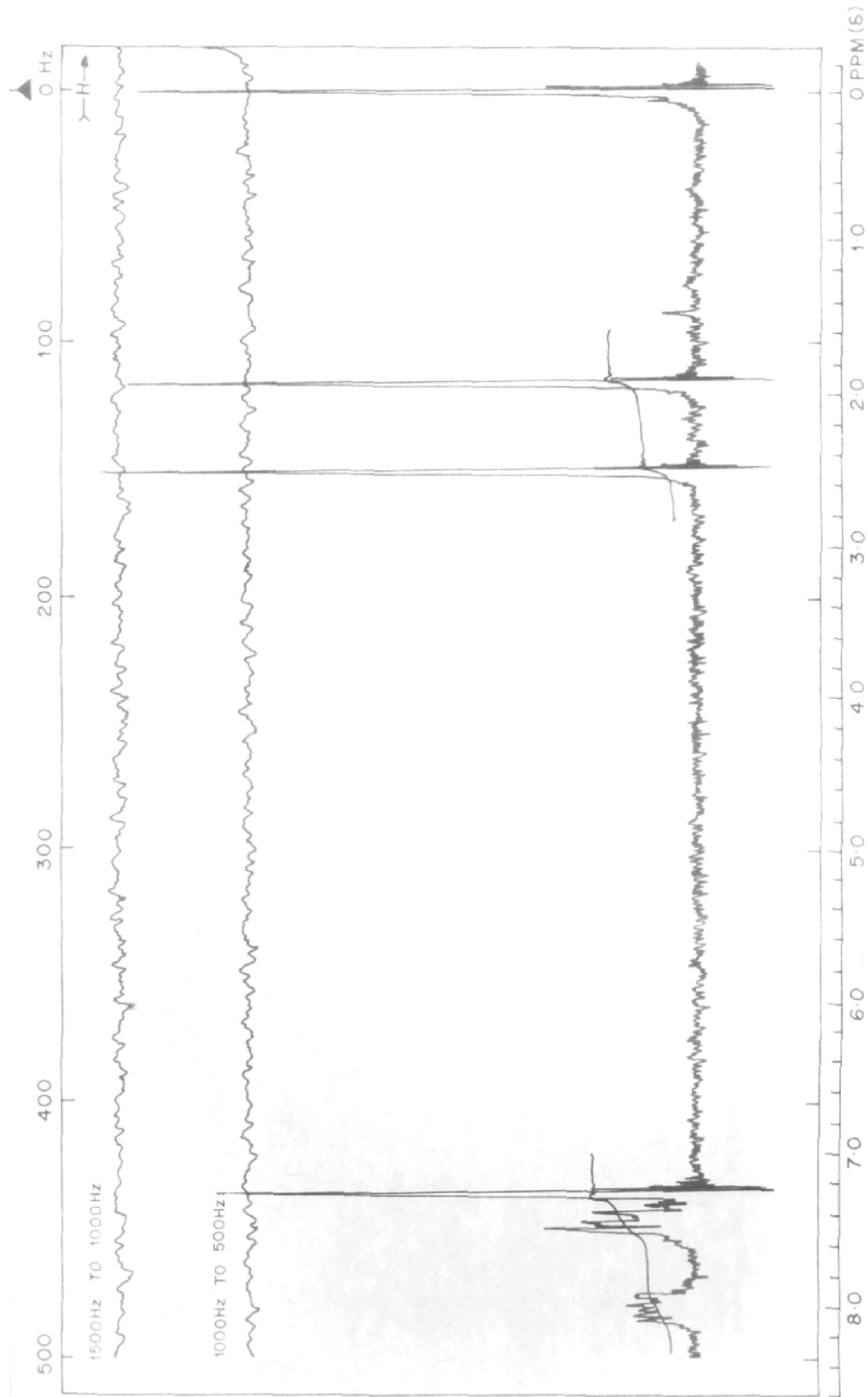


FIG. 8 : NMR SPECTRUM OF  
 BIS [S-METHYL-N-(PHENYL)ETHYLIDEN DITHIOCARBATO]  
 PALLADIUM (II) IN  $CDCl_3$

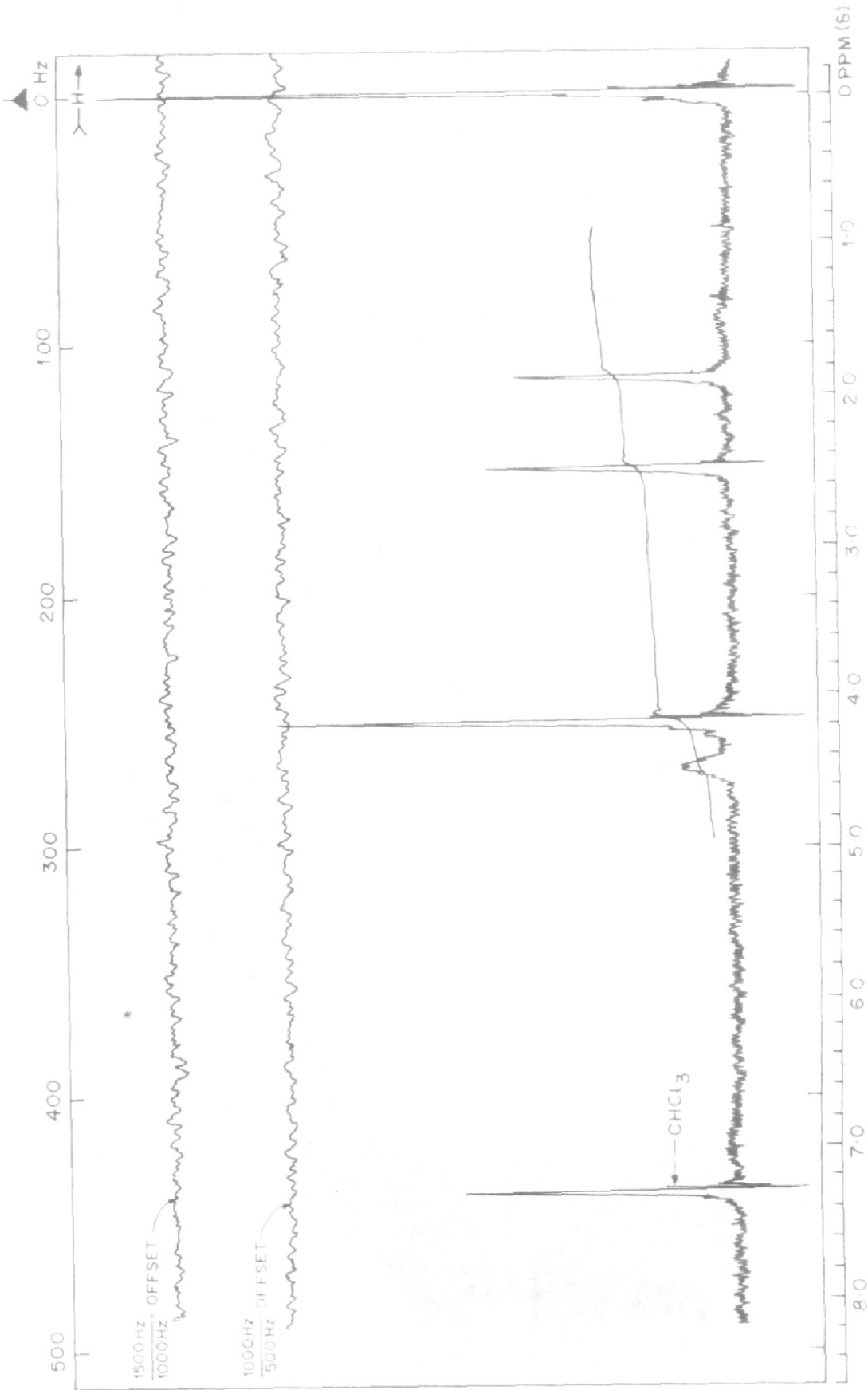


FIG. 10: NMR SPECTRUM OF  
 BIS [S-METHYL - N - (FERROCENYL) ETHYLIDEN DITHIOCARBAZATO]  
 NICKEL (II) IN  $CDCl_3$

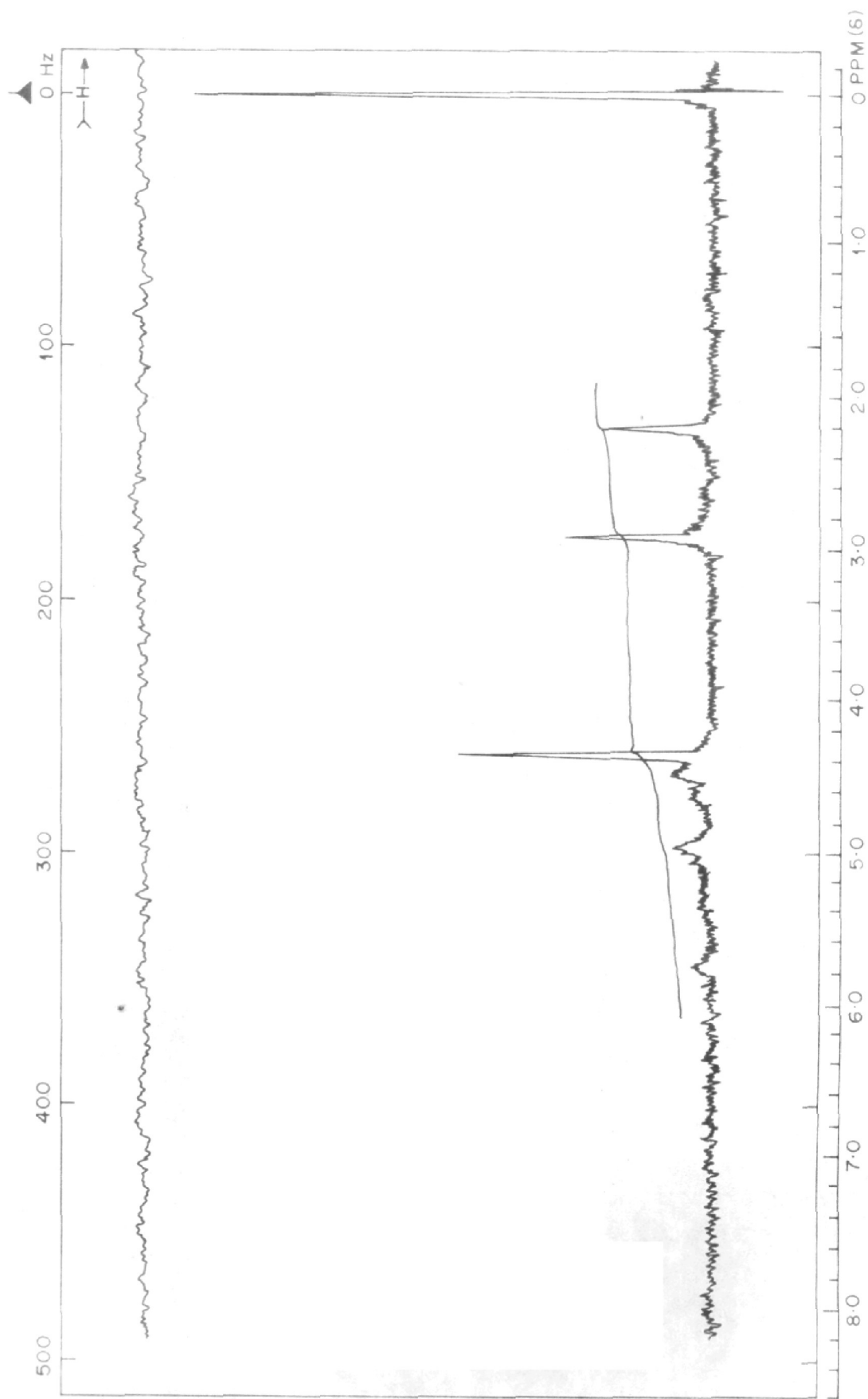


FIG. 11 : NMR SPECTRUM OF

BIS [S-METHYL -N- (FERROCENYL) ETHYLIDEN DITHIOCARBAZATO]  
PALLADIUM (II) IN TRIFLUOROACETIC ACID.

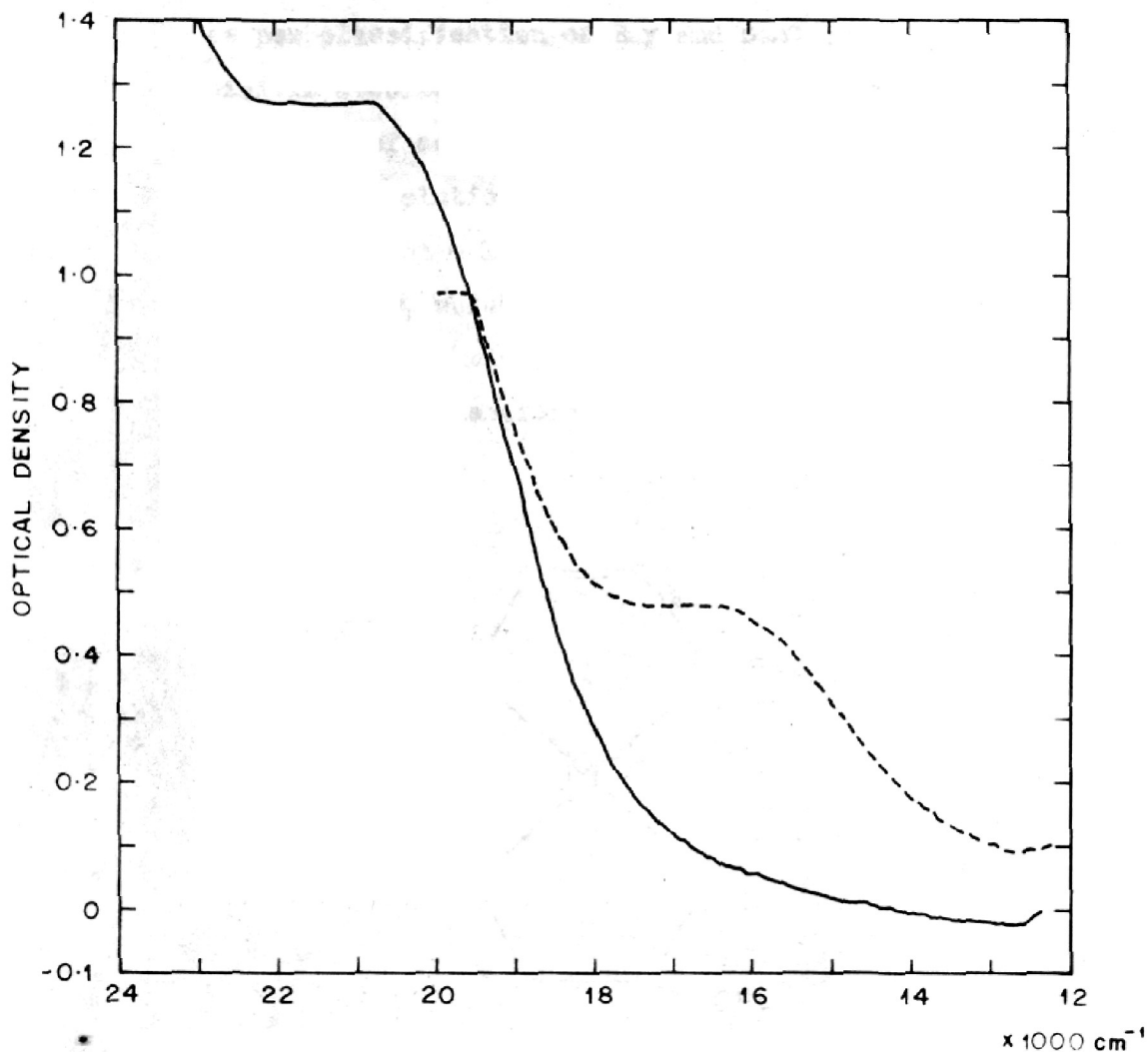
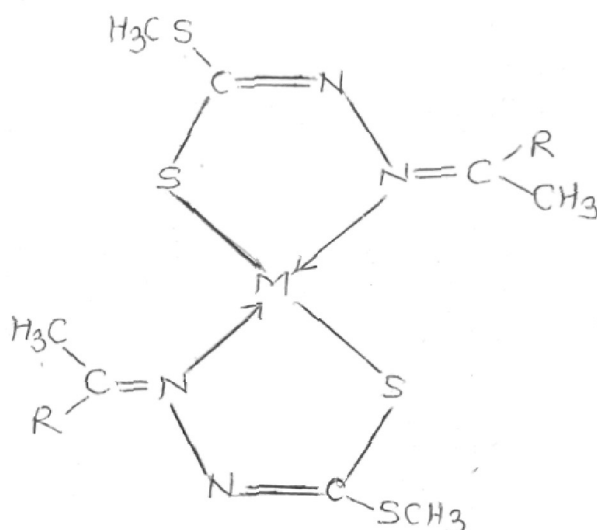


FIG. 12 : ABSORPTION SPECTRA IN  $\text{CHCl}_3$  OF

- BIS [S-METHYL-N-(FERROCENYL) ETHYLIDEN-DITHIOCARBAZATO] COPPER (II) MONOHYDRATE.
- BIS [S-METHYL-N-(FERROCENYL) ETHYLIDEN-DITHIOCARBAZATO] NICKEL (II).

as per classification of Ray and Sen<sup>8</sup>. The visible absorption spectra of copper and nickel complexes of acetylferrocene Schiff base in chloroform solution (Fig. 12) show absorption bands with maxima at  $\sim 16000 \text{ cm}^{-1}$  and  $\sim 21000 \text{ cm}^{-1}$  respectively, which is in keeping with the square planar configuration. The structure of all these complexes may therefore be written as -



Where  $M = \text{Cu(II)}, \text{Ni(II)}$  or  $\text{Pd(II)}$  and  
 $R = \text{phenyl}$  or ferrocenyl group.



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