

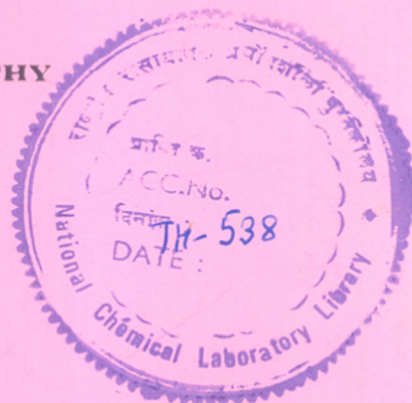
**STUDIES ON THIOSEMICARBAZONES, SOME
NITROGEN, SULPHUR CONTAINING
HETEROCYCLIC LIGANDS AND THEIR
METAL COMPLEXES**

A THESIS
SUBMITTED TO THE
UNIVERSITY OF POONA
FOR THE DEGREE OF
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(IN CHEMISTRY)

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BUD

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Form 'A'

Certified that the work incorporated in the thesis
"Studies on Thiosemicarbazones, some Nitrogen, Sulphur
Containing Heterocyclic Ligands and Their Metal Complexes"
submitted by Mr. Anil Purushottam Budhkar, was carried
out by the candidate under my supervision. Such material
as has been obtained from other sources has been duly
acknowledged in the thesis.

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Finally, I wish to dedicate this thesis to 'SHRI SAI' and to my parents.


(A.P. Budhkar)

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CHAPTER I : INTRODUCTION

A. General Introduction

The area of coordination and organometallic chemistry has been widely developed in the last three decades. Not only has an upsurge taken place in experimental studies, but there has also been a renewed interest in the structure of these complexes, and in corresponding advances in the elucidation of structure and bonding. Complexes are playing increasingly important roles in industry, ranging from anticorrosion agents and soil treatment agents, to medicinal agents, which certainly testify for their importance in contemporary life. The biologically important complexes, such as chlorophyll, hemoglobin and vitamin B₁₂ - all with very complex structures and also the wide application of transition metal salts and complexes as catalysts in syntheses of several important organic compounds like styrene and other petrochemicals suggest a need by all chemists the study of the principles of coordination and organometallic chemistry.

The phenomenon of complex formation is really a very general one, but it is markedly noted among the transition metal ions. The formation of a complex is the result of a Lewis-acid base type of interaction, in which one atom with a vacant orbital (generally the metal) attracts the electron pair on another atom (generally a

non-metal). For bonding to occur as a result of such an interaction, the metal must possess vacant orbitals and these orbitals must be symmetrically correct, sterically available and of reasonably low energy. Since transition metal ions generally meet these requirements best, they form complexes so readily.

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 valence (oxidation state) of this atom. Metal complexes may be neutral (no charge), cationic (positively charged), or anionic (negatively charged). The groups bonded to 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 called a chelating agent and the resulting complex a metal chelate. The number of ligands attached to the metal atom constitutes its coordination number and the ligands are characterised as mono, bi, tri or multidentate ligands depending on the number of donor sites (atoms) present in the ligands.

In two excellent reviews^{1,2} on metal complexes of ligands containing sulphur, selenium, tellurium, nitrogen,

or oxygen as donor atoms, Livingstone has discussed the particular features of these ligands in details, some of which are narrated below.

1. Sulphur donors bind more strongly to class b metals than do oxygen donors.

2. 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 π orbitals to be less capable of accepting electrons from the metal.

3. The permanent dipole moment and the coordinating ability decrease in the order: $\text{H}_2\text{S} < \text{RSH} < \text{R}_2\text{S}$.

4. The polarizabilities of sulphur donors decrease in the order $\text{S}^{2-} > \text{RS}^- > \text{R}_2\text{S}$. Consequently thiole ligands are more polarizable but not as effective $d\pi$ electron acceptors as thioethers.

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

6. 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 complexes with sulphur ligands. Being typically

class b, they form strong σ -bonds with soft ligands and also $d\pi-d\pi$ bonds by donation of a pair of electrons to the ligand.

All the above main features about complexes of sulphur ligands are also applicable to 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. These ligands appear to give rise to a smaller reduction in the interelectronic repulsion energy than sulphur-sulphur ligands. This presumably is due to nitrogen having a low position compared to sulphur in the nephelauxetic series.

Organometallic compounds are formed by attachment of organic groups to metal atoms by metal-carbon bonds. These are almost invariably covalent and the bonding electrons are highly delocalised. Although molecular orbital diagram for some simple organometallic compounds like tungsten hexamethyl $[W(CH_3)_6]$ and tungsten hexacarbonyl $[W(CO)_6]$ could be easily drawn because of the high symmetry of the attached organic residues; it has been found impossible or extremely difficult to draw M.O. diagrams for the molecule as a whole, in case

of several organometallic species. It was noticed about sixty years ago that a large number of stable carbonyls had 18 electrons in the metal ligand bonding system and it has also been found possible to explain the stability of a large number of organometallic compounds by electron counting methods.

There are six pairs of electrons in the (mainly ligand) orbitals and six electrons in the (mainly metal) π orbitals in $W(CO)_6$ following 18 electrons stability rule. Another example would be iron pentacarbonyl $Fe(CO)_5$, where each CO is considered to donate two electrons to the metal ligand bonding and the iron atom has eight electrons in its valence shell ($3d^6 4s^2$) again giving a total of 18. Further support comes from the observation that unstable vanadyl hexacarbonyl $[V(CO)_6]$ (17 electrons) readily takes up an electron to give $[V(CO)_6]^-$ - 18 electrons. On the basis of these observations, the eighteen electrons rule is postulated as follows:

"The sum of the electrons on the metal and the electrons donated by the ligands should equal the atomic number of the inert gas next after the metal in the Periodic Table or the number of electrons in the valence shell of the metal plus the number contributed by the ligands should equal 18".

Such compounds have a greater stability than equivalent compounds with a different number of electrons. This effective atomic number or 18 electron rule is essentially a rule of thumb, and is unreliable for ionic complexes, but covers a very large percentage of organometallic compounds of transition metals, irrespective of their symmetry.

Tentative explanations of the success of the rule have been proposed, of which the most reasonable is that the metal has nine atomic orbitals in its valence shell (five d, one s and three p), and that the most stable bonding arrangement will be for it to form nine bonding and nine antibonding orbitals, with all the bonding orbitals filled - corresponding to 18 electrons in the valence shell. Some force is given to this statement by the fact that, for the first row elements, the rule works best in the middle of the 3d series, where 3d, 4s and 4p orbitals are closest in energy.

The majority of the exceptions to the rule are 16 electron compounds well known for d^8 metal ions e.g., $[\text{Ni}(\text{CN})_4]^{2-}$ and the rule does not exclude the possibility of other species.

B. The chemistry of nickel(II) complexes

In the classification of metals by Ahrlund et al.³, nickel(II) is on the border-line between class a and class b. It forms stronger complexes with the lighter halogens, thus exhibiting class a character towards the group VII elements, but mild class b character is displayed towards group VII elements as ligand atoms. Nickel(II) complexes are known with a six coordinate octahedral configuration, with five-coordinate square pyramidal or trigonal bipyramidal structures, and with four-coordinate square-planar or tetrahedral configurations; these configurations are often only approximately regular. It is a peculiarity of nickel(II) chemistry that complexes of one configuration can often be easily converted to other configurations. This structural lability implies that the free energy difference between different stereochemical forms is usually small.

Square planar nickel(II) complexes

Numerous nickel(II) complexes have been investigated by X-ray crystallography. Square planar nickel(II) complexes are mainly formed with ligands capable of highly covalent bonds and having strong π -bonding character. In bis(dimethylglyoximate)nickel(II), the distance between

nickel atoms of adjacent molecules is only 3.2 \AA^4 . As a natural consequence of the d^8 configuration, the planar ligand set causes one of the d orbitals (dx^2-y^2) to be uniquely high in energy and the eight electrons can occupy the other four d orbitals and leave the strongly antibonding orbital vacant. In tetrahedral coordination, on the other hand, occupation of antibonding orbitals is unavoidable. With the congeneric d^8 systems Pd^{II} and Pt^{II} this factor becomes so important that no tetrahedral complex is formed. Planar complexes of nickel(II) are invariably diamagnetic. They are frequently red, yellow or brown owing to the presence of an absorption band of medium intensity in the range 450-600 nm, but other colours do occur when additional absorption bands are present.

Five coordinate nickel(II) complexes

A considerable number of both trigonal-bipyramidal and square-pyramidal complexes occur and high and low spin examples of each geometry are known, the former having two and the latter having no unpaired electrons. In the diamagnetic complexes the donor atoms of the ligands are CO, P, As or S, that is, the atoms of low electronegativity which therefore form delocalized coordination bonds easily. The magnetic moments of the high-spin complexes range from 3.2 to 3.4 B.M. All the

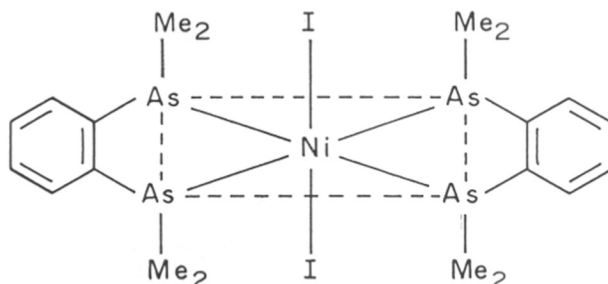
high spin complexes contain strongly electronegative elements N and/or O as ligand atoms. In many cases one or two halide ions, complete the set of coordinating atoms in both high and low spin complexes; $[\text{Ni}(\text{Me}_6\text{tren})\text{Br}]^+$
 $[\text{Me}_6\text{tren} = \text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3]$
 is high spin, but replacement of ligand N atoms by P, As, S, Se etc. causes larger ligand field splittings and stabilizes the low spin configuration. Bis(acetone-thiosemicarbazone)nickel(II) chloride monohydrate is the first high spin pentacoordinated species determined by X-ray⁵ where there are only two S atoms, two N atoms and a chloride ion in the coordination. *Sphered*

Octahedral nickel(II) complexes

The maximum coordination number of nickel(II) is six. Several nickel(II) complexes with octahedral geometry have been studied for which the magnetic moment usually found lie between 2.9 and 3.3 B.M. Even though the great majority of six-coordinate nickel(II) compounds are paramagnetic, there is a very restricted group of diamagnetic compounds for which six-fold coordination has been proposed. The diamagnetism of these six coordinate complexes has been attributed to the presence of a strong component of lower symmetry in the ligand field.

The six-coordinate diamagnetic compound for which the structure has been determined by X-ray⁶ (as shown

below) is the complex of nickel iodide with *o*-phenylenebisdimethyl arsine. The Ni-I distance of 3.21 Å is greater than the sum of the covalent radii (2.67 Å). The weak nature of these two bonds together with the very different positions occupied by I and As in the spectrochemical series ($I \ll As$) leads to a strong tetragonal ligand field in this compound creating a situation very similar to that in four-coordinate planar complexes which are in fact diamagnetic.



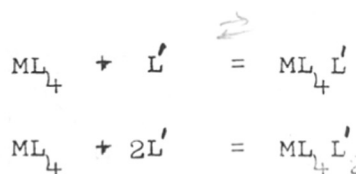
Anomalous properties of nickel(II) complexes

A considerable number of nickel(II) complexes do not behave as expected on the basis of this structure for which they have been termed 'anomalous' in the past. In fact, all these anomalies are satisfactorily explained on the basis of following three main structural changes:

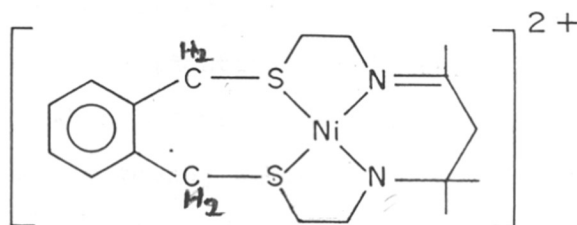
1. Formation of five and six-coordinate complexes by addition of ligands to square ones

For any square complex NiL_4 , the equilibria with

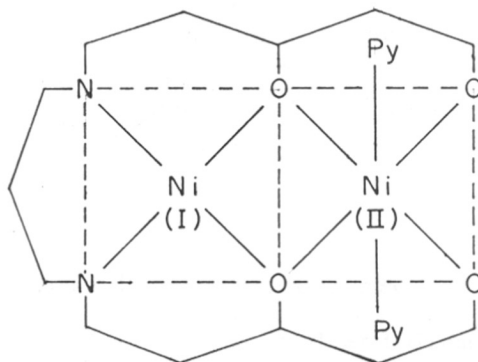
additional ligands L' must in principle exist as follows:



In the case where $L = L' = CN$, only the five-coordinate species is formed, but in most cases equilibria strongly favour the six-coordinate species that have trans structures and two unpaired electrons. Busch and others⁷ have synthesised and characterised series of compounds based on $[NiL]^{2+}$ as shown below.



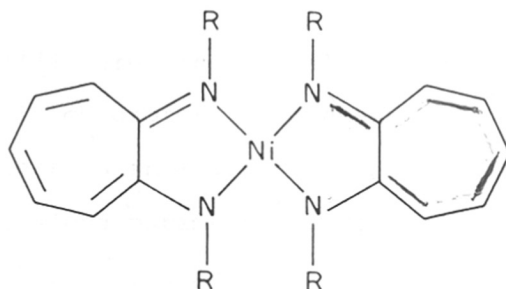
An interesting complex with structure as given below contains low spin square coordinated and high spin octahedrally coordinated nickel atoms⁸.



2. Square-tetrahedral equilibria and isomerism

Nickel(II) complexes of certain stoichiometry, namely, the bis(halo)bis(phosphino) and bis(salicylaldiminato) types may have either square or tetrahedral structures depending on the identity of ligands. For instance, in NiL_2X_2 , when $\text{L} = \text{triphenylphosphine}$, tetrahedral structures are found, whereas the complexes with trialkylphosphines generally give square complexes.

Planar-tetrahedral equilibria in compounds as shown below have been characterised by n.m.r. In the tetrahedral forms unpaired electron spin density from the nickel atom is introduced into the ligand π system, which results in large shifts in the positions of the various protons nuclear magnetic resonances.

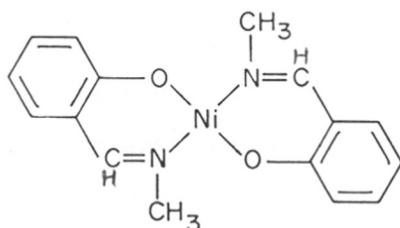


In some instances, two crystalline forms of the compound, one yellow to red and diamagnetic, the other green or blue with two unpaired electrons are isolated. In ^{the} case of $\text{Ni}[\text{C}_6\text{H}_5\text{CH}_2)(\text{C}_6\text{H}_5)_2\text{P}]_2 \cdot \text{Br}_2$ both tetrahedral and square planar forms are found together in the same crystalline substance.

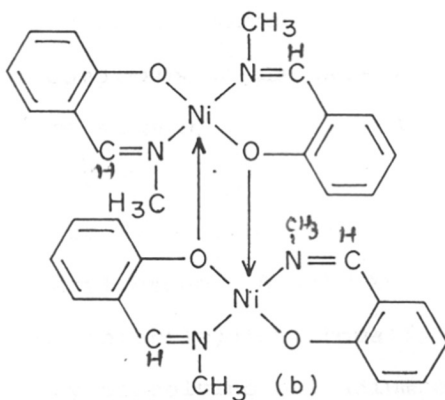
3. Monomer-Polymer Equilibria

In many cases four coordinate complexes associate or polymerise, to give species in which the nickel ions become five or six coordinate. In some cases the association is very strong and the four coordinate monomers are observed only at high temperatures; in others the position of the equilibrium is such that both red, diamagnetic monomers and green or blue, paramagnetic polymers are present in a temperature and concentration-dependent equilibrium around room temperature⁹. Partial dimerisation, to give five coordinate, high-spin nickel(II) complex is known to be the cause of anomalous behaviour in some instances. Thus, although N-(n-alkyl)salicylaldiminato complexes

of nickel(II) are, in general, planar, diamagnetic monomers in chloroform or benzene, when the alkyl group is CH_3 there is an equilibrium between the diamagnetic monomer (a) and paramagnetic dimer (b); for which the proposed structures are:



(a)



(b)

C. Chemistry of palladium(II) and platinum(II) complexes

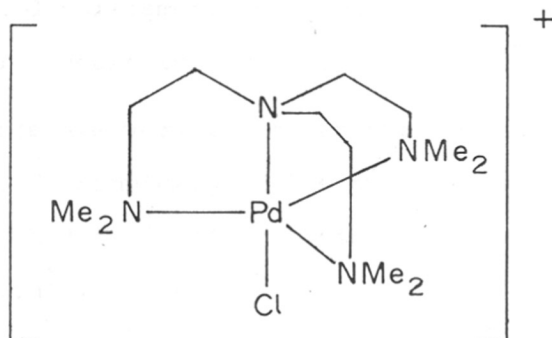
As a rule Pd(II) and Pt(II) show a preference for nitrogen (in aliphatic amines and in NO_2), halogens, cyanide and heavy donor atoms (P, As, S, Se) and relatively small affinity for oxygen and fluorine. The strong binding of the heavy atoms donor is due in

great measure to the formation of metal-ligand π bonds by overlap of filled $d\pi$ orbitals on the metal with empty $d\pi$ orbitals in the valence shells of the heavy atoms. Palladium(II) complexes are somewhat less stable in both the thermodynamic and the kinetic sense than their platinum(II) analogues but otherwise the two series of complexes are usually similar. Cyanide ions, nitro groups, and carbon monoxide are bound involving π bonding, which results from overlap of filled metal $d\pi$ orbitals with empty $p\pi$ antibonding molecular orbitals of these ligands. In such complexes, there is usually considerable similarity of nickel to palladium and platinum.

There is an enormous number of palladium and platinum complexes of the general formula $MXYL_1L_2$, where X and Y are anionic groups and L are neutral donor ligands such as NR_3 , PR_3 , SR_2 , CO and alkenes. In addition to ions such as Cl^- and SCN^- , X or Y may also be H or an alkyl or aryl group. A well known compound of palladium is bis(benzonitrile)dichloropalladium(II), $[PdCl_2(C_6H_5CN)_2]$ obtained by dissolving palladium chloride in the ligand and crystallizing.

Five coordinate complexes of palladium(II) and platinum(II)

Several stable five coordinate complexes¹² of Pd(II) and Pt(II)¹ have been isolated of the type shown below.



A five coordinate platinum(II) complex with monodentate ligands $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ which is well known catalyst for the hydrogenation of ethylene and some other olefinic compounds. The catalytic reaction is based on the ready dissociation of the complex in solution, prompted by the trans effect of SnCl_3^- which leaves vacant sites for coordination of olefin and hydrogen.

Octahedral complexes of palladium(II) and platinum(II)

Palladium and platinum generally have similar chemistries in the II oxidation state. Usually they have square planar configuration. However, weaker bonds are formed in the vacant octahedral sites. In solutions, these positions may be occupied by solvent molecules and

in catalytic reactions of these metal complexes or in ligand displacement reactions, initial attack presumably occurs in the axial positions.

There are very few octahedral palladium(II) and platinum(II) complexes of the type $\text{trans-MI}_2(\text{diars})_2$ [$\text{M} = \text{Pd}^{\text{II}}$ and Pt^{II} , diars = diarsine], which dissociate in solution¹⁰.

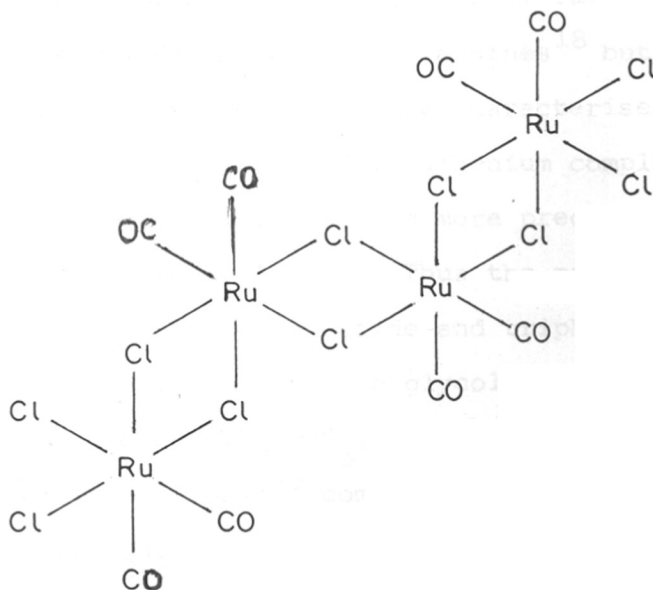
D. Chemistry of ruthenium(II) complexes

Hydrated ruthenium trichloride, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ($x = 3$), precursor for most of the ruthenium compounds, is soluble in a large number of organic solvents and hence many organic groups can be directly introduced. Although various methods have been suggested for the preparation of $\text{RuCl}_2(\text{CO})_2$ ¹¹⁻¹⁴, the most facile method is the one proposed by Chatt et al¹⁵. Although there was some doubt about the composition of the 'red carbonyl solution' prepared by Chatt et al., I.R. monitoring of the reaction established that the major species of the red solution obtained on passing carbon monoxide through a refluxing ethanolic solution of ruthenium trichloride was $[\text{RuCl}_2(\text{CO})_2]_n$ ¹⁶. The polymerisation occurs through chlorine bridges and carbon monoxide is in the cis position as indicated by a CO linked structure¹⁷.

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The IR absorption values for ruthenium chloro-carbonyls reported in literature are not the same.

A few selected values are listed below:

<u>Species</u>	ν ($C\equiv O$) cm^{-1}	<u>Reference</u>
$[RuCl_2(CO)_2]_n$	2076, 2018	28
	2068, 1997	16
	2157, 2148	
$[RuCl_2(CO)_3]_2$	2097, 2086	
	2148, 2088	
	2068, 2095	28

Many ruthenium triphenylphosphine and triphenylarsine complexes were earlier prepared from ruthenium trichloride and substituted phosphines or arsines¹⁸ but the products were either mixtures or poorly characterised. Many of the structures proposed for ruthenium complexes by early workers were later revised as more precise tools for analysis became available. Thus the product of reaction between ruthenium trichloride and triphenylphosphine in a boiling solvent (ethylene glycol, 2-methoxy ethanol) was reported as $\text{RuCl}(\text{PPh}_3)_3$. Later it was shown to be the hydrido carbonyl¹⁹ complex with the formula $\text{RuHClCO}(\text{PPh}_3)_3$. Vaska et al.²⁰ later reported a series of complexes of ruthenium containing CO, halogen and substituted phosphine, arsine or stibine. Thus ruthenium trichloride and triphenylarsine in 2-methoxy-ethanol under reflux conditions gave $\text{RuCl}_2(\text{CO})(\text{AsPh}_3)_3$. In all these reactions it was shown that ruthenium abstracts CO from alcohol even under mild conditions and substituted phosphines act as reducing agents.

It was shown that carbonyl complexes could be prepared by passing CO gas into an alcoholic solution of ruthenium trichloride¹⁵. A series of ruthenium carbonyl compounds with the general formula $\text{RuCl}_2(\text{CO})_2(\text{MR}_3)_2$, where M = P or As and R = alkyl or

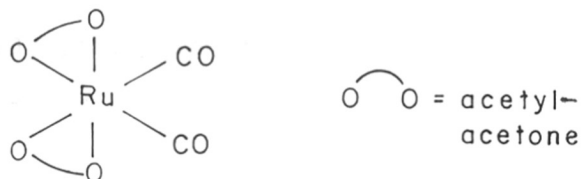
aryl was prepared by this method followed by the addition of a tertiary phosphine or arsine. The complexes were shown to be hexa-coordinated with both chlorines cis to each other. The CO groups were found to be either in cis or in trans position. However, the cis position was more stable and the transformation could be effected either thermally or by recrystallisation from suitable solvents.

Hexa-coordinated complexes²¹ with the general formula $\text{RuCl}_2(\text{CO})_2(\text{MEt}_3)_2$, [M = P, As or Sb] were obtained by cleavage of the chlorine bridges in $[\text{RuCl}_2(\text{CO})_2]_n$ by triethyl-phosphine, -arsine or -stibine. I.R. spectra of these complexes showed three CO absorption bands indicating a cis-trans mixture. Repeated crystallisation from acetone in many cases yielded pure cis complexes with only two CO absorptions.

Carbonylation of hydrated ruthenium trichloride in methanol²² gave a dimer $[\text{RuCl}_2(\text{CO})_3]_2$, which with THF produced an adduct $\text{RuCl}_2(\text{CO})_3 \cdot \text{THF}$. This adduct on reaction with substituted phosphines, arsines, diphos, pyridine, etc. gave hexa-coordinated complexes replacing one CO group and the THF group yielding compounds with the general formula $\text{RuCl}_2(\text{CO})_2(\text{L})_2$.

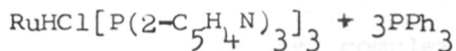
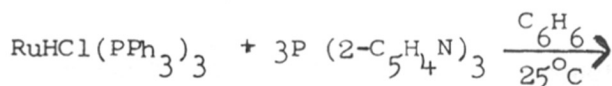
Bis-(acetylacetonato)dicarbonylruthenium²³ was prepared by the reaction of dodecacarbonyl triruthenium and acetylacetonone in THF in an autoclave at 150°C.

The complex was assigned the following structure with acetylacetonone acting as a bidentate chelating ligand on the basis of IR and ^1H nmr spectral studies.



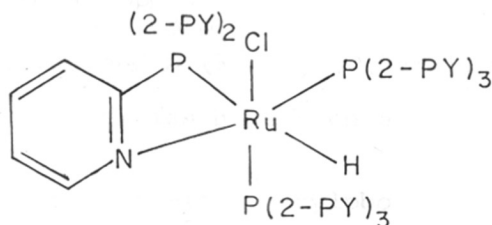
Replacement of triphenylphosphine^{in $\text{RuHCl}(\text{PPh}_3)_3$} with equivalent ligands can produce five coordinate analogues of the hydrido complex. Thus, excess diphenyl(sodium m-phenylenesulphonate)phosphine replaces all three triphenylphosphine ligands to give a water soluble homogeneous hydrogenation catalyst. If the solvent for the reaction is changed from ethanol to aqueous tetrahydrofuran, the product is $\text{RuHCl}[\text{Ph}_2\text{P}(\text{m-C}_6\text{H}_4\text{SO}_3\cdot\text{Na})]_3\cdot 2\text{H}_2\text{O}$. The latter complex is also an active catalyst in alkene hydrogenation at 80°C ²⁴.

Total replacement of triphenylphosphine ligands also occurs when tris(2-pyridyl)phosphine is reacted with $\text{RuHCl}(\text{PPh}_3)_3$:



The product however, is six-coordinate by virtue of one tris(2-pyridyl)phosphine ligand being bidentate.

The compound has the structure



Two of the three triphenylphosphine ligands in the hydrido complex are displaced by one molecule of the dimethylphosphinocarborane, $1\text{-PMe}_2\text{-1,2-C}_{10}\text{B}_2\text{H}_{11}$, when this ligand is added to a suspension of $\text{RuHCl}(\text{PPh}_3)_3$ in refluxing toluene. The yellow orange product was claimed to be a useful catalyst for the incorporation of deuterium into other boron hydrides and their transition metal complexes²⁵.

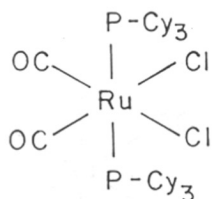
If $\text{RuHCl}(\text{PPh}_3)_3$ is allowed to react with carbon monoxide in benzene¹⁹ or N,N-dimethylacetamide²⁶ or hexane²⁷, the six coordinate dicarbonyl complex cis- $\text{RuHCl}(\text{PPh}_3)_2(\text{CO})_2$ is formed. Abstraction of carbon monoxide from organic reagents yields the six-coordinate monocarbonyl complex $\text{RuHCl}(\text{PPh}_3)_3(\text{CO})$.

A series of halogeno-carbonyl complexes of ruthenium have been prepared by decarbonylation of formic acid by ruthenium chloride. The complexes synthesised included $[\text{RuCl}_2(\text{CO})_3]_2$, $[\text{RuCl}_4(\text{CO})_2]^{2-}$ and $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$. The vibrational spectra have been analysed and $\nu(\text{Ru-C})$, $\nu(\text{Ru-Cl})$ and the metal carbonyl frequencies have been assigned²⁸.

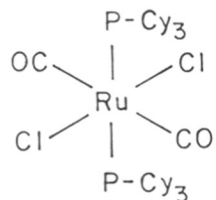
Dichlorotris-(triphenylphosphine)ruthenium(II) is one of the few penta-coordinated Ru(II) complexes synthesised. It has been prepared by reacting ruthenium trichloride and triphenylphosphine in a lower primary or secondary alcohol. X-ray analysis of the compound has shown that it has a distorted square pyramidal structure; the trans chlorine and phosphorus atoms with ruthenium at the centre form the base and the third phosphine group at the apex completes the pyramid²⁹. If the above reaction is carried out in a higher primary alcohol, a carbonyl complex is obtained by abstracting CO from alcohol³⁰.

The carbonyl triphenylphosphine complex, $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, reacted with a carboxylic acid in boiling benzene giving the bis-monodentate carboxylate³¹. The reaction between a ~~secondary~~ phosphine and ruthenium trichloride in ethanol gave $\text{RuCl}_2(\text{HPPH}_2)_4$ ³².

When tricyclohexylphosphine is added to the red carbonyl solution, the complex $\text{RuCl}_2(\text{CO})(\text{P-Cy}_3)_2$ is obtained³³. The same complex is obtained as a byproduct when tricyclohexylphosphine is added to a 2-methoxyethanol solution of ruthenium trichloride cooled to 0° . The complex has a square pyramidal geometry. On reaction with CO two isomers are obtained:



(i)



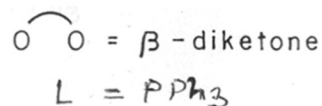
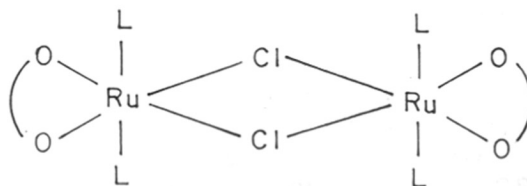
(ii)

o-Styryl diphenylphosphine, $\left[\text{C}_6\text{H}_4(\text{PPh}_2)(\text{CH}=\text{CH}_2) \right]$
 and o-styryl diphenylarsine $\left[\text{C}_6\text{H}_4(\text{AsPPh}_2)(\text{CH}=\text{CH}_2) \right]$
 reacted with an alcoholic solution of ruthenium
 trichloride to give $\text{RuCl}_2(\text{ligand})_2$. Both the group V
 atoms and vinyl groups are coordinated to ruthenium
 and there are three isomers. The coordinated vinyl
 group can be replaced with CO and the resulting complex
 has the ligand as a monodentate moiety coordinated
 through the group V atom³⁴.

It has been shown that the complexes of the type
 $\text{RuX}_2(\text{CO})_2(\text{PPh}_3)_2$ undergo cis-trans isomerisation by
 ordinary light and more often by UV radiation. The
 cis form is more stable and thermal transformation
 takes place through a third isomer³⁵:



Natarajan and Agarwala^{36,37} have isolated $\text{RuH}(\text{acac})(\text{CO})(\text{PPh}_3)_2$ and $[\text{RuCl}(\text{acac})(\text{CO})(\text{PPh}_3)_2]$ compound where acac = β -diketones. They have assigned them octahedral geometry by infrared and electronic spectral studies. with the following structure, which was however, found to be incorrect.

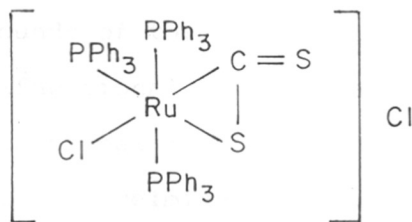
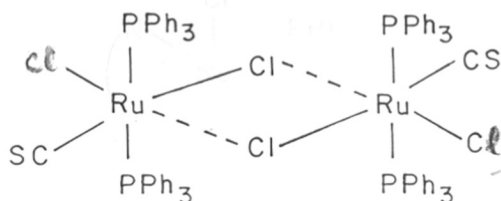


Many mono-nuclear ruthenium complexes containing nitrogen donors are prepared by halogen bridge cleavage of halo carbonyl complexes. Thus $[\text{RuX}_2(\text{CO})_2]_n$ reacts with pyridine, 2,2'-bipyridyl, 1,10-phenanthroline or nitriles to yield complexes of the formula $\text{RuX}_2(\text{CO})_2(\text{L})_n$; most of which have the CO groups in cis position^{38,39}.

A series of octahedral complexes containing nitrogen, sulphur and tin as donor ligands have been

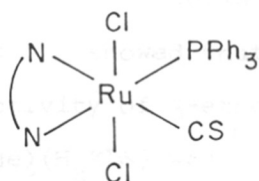
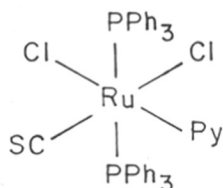
prepared from ruthenium red carbonyl solution. The complexes prepared include $\text{RuX}_2(\text{CO})_2(\text{C}_6\text{H}_5\text{NH}_2)_2$, $\text{RuX}_2(\text{CO})_2[\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2]_2$, $\text{RuX}_2(\text{CO})_2(\text{Phenan})$, $\text{Ru}(\text{CO})_2(\text{Py})_2(\text{SnX}_3)_2$, etc. Many of these complexes show in their spectra three bands in the carbonyl region indicating a cis-trans mixture, and attempts to isolate them have failed⁴⁰.

$\text{RuCl}_2(\text{PPh}_3)_3$ reacts with carbon disulphide giving two products⁴¹.



The compound I has a thiocarbonyl group and is dimer through chlorine bridges, II has a π CS_2 group. The chlorine bridges in I can be cleaved by reaction with CO, pyridine, 2,2'-bipyridyl and 1,10-phenanthroline

giving the corresponding hexa-coordinated complexes. Thus when pyridine or 1,10-phenanthroline reacts with I in benzene or carbon disulphide, compounds with monomeric structure as shown below are obtained.



Pyridine or
1,10-phenanthroline

$\text{RuCl}_2(\text{PPh}_3)_3$ reacts with the sodium salt of Schiff bases⁴² to give compounds of the type $\text{trans Ru}(\text{PPh}_3)_2(\text{L})$ (for quadridentate bifunctional ligands) and $\text{Ru}(\text{PPh}_3)_2(\text{L})_2$ (for bidentate monofunctional ligands). However, $\text{N,N}'$ -ethylenebis-salicylidineimine [Salen-H_2] reacts with red carbonyl solution to give $\text{cis-Ru}(\text{CO})_2(\text{Salen})$.

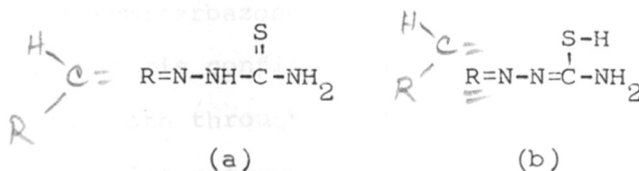
A cationic complex $[\text{RuCl}(\text{CO})(\text{Bipy})_2]\text{Cl}$ is formed when ruthenium trichloride and 2,2'-bipyridyl are refluxed in a CO releasing solvent like dimethyl formamide for a number of days⁴³.

E. Literature survey

1) Thiosemicarbazones and their metal complexes

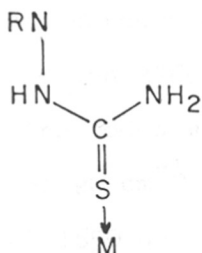
The first report on the antitubercular activity of thiosemicarbazones by Domagk⁴⁴ has initiated an interesting branch in which numerous papers have been published to date. Thiosemicarbazones have been found to be active against certain kinds of tumour⁴⁵ and also have been suggested as possible pesticides⁴⁶ and fungicides⁴⁷. Their activity has been mainly thought to be due to their ability to chelate trace metals. Petering and coworkers⁴⁸ showed that the active intermediate in the antitumour activity of 3-ethoxy-2-oxobutylaldehyde bis(thiosemicarbazone) (H_2KTS) was the chelate $Cu(KTS)$. These findings have led to an increased interest in the chemistry of transition metal chelates of thiosemicarbazones.

It has been observed by infrared spectral studies⁴⁹ that in solution thiosemicarbazones exist as an equilibrium mixture of thione (a) and thiol (b) tautomers

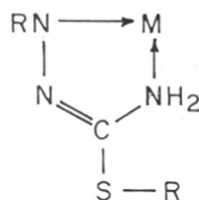


in which (a) acts as a neutral bidentate ligand, while

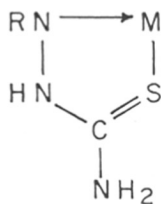
the loss of the thiol proton from (b) yields a singly charged bidentate ligand. Therefore, depending upon preparative methods, the complex unit can be cationic, neutral or anionic. However, most investigations of metal thiosemicarbazone complexes have involved ligands in the uncharged form (a), while definitive data on the complexes containing thiosemicarbazone in the thiol (b) form are generally lacking. It has been shown^{50,51} that the thiosemicarbazide molecule itself exist in the trans configuration (c), and while complexing in this configuration, it behaves as a monodentate ligand, bonding only through the sulphur atom. Gerbeleu et al.⁵² have shown that bonding may also occur through the hydrazine nitrogen and the amide nitrogen (d) if the sulphur center is substituted. On reinvestigating the crystal structure of thiosemicarbazide hydrochloride, Coghi et al.⁵³ explained these conformational changes on the basis of protonated/deprotonated isomeric forms and steric effects. In most of the complexes studied the thiosemicarbazone function coordinates to the metal ion in the cis configuration (e), as a bidentate ligand bonding, both through the thione/thiol sulphur atom and the hydrazine nitrogen atom.



(c)



(d)



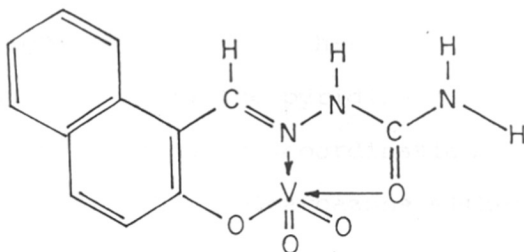
(e)

Relevant to the bonding in thiosemicarbazone complexes is the ability to locate various group frequencies corresponding to typical linkages. Although there have been many attempts to assign a few infrared bands of metal complexes of thiosemicarbazone ligands, no complete assignment of their infrared spectra had been available. However, Geetharani and Sathyanarayana⁵⁴ have made a fairly reliable assignment of infrared frequencies for thiosemicarbazide and its $\text{Ni}(\text{Htsc})_2\text{Cl}_2$ and $\text{Ni}(\text{tsc})_2$

complexes through normal coordinate analysis. The bands in the region $3360-2970\text{ cm}^{-1}$ are easily assigned to NH stretching modes and these bands shift on deuteration to $2530-2190\text{ cm}^{-1}$ in case of $\text{Ni}(\text{Htsc})_2\text{Cl}_2$. The strong bands at 1650 and 1618 cm^{-1} are due to the bonding of the planar NH_2 group coupled with CN stretching and NH bending modes. On coordination of a thioamide molecule through sulphur usually the C=S stretching frequency decreases by $30-50\text{ cm}^{-1}$ and the C-N stretching frequency increases by $50-60\text{ cm}^{-1}$ due to the decrease in the C=S bond order and consequent increase in the C-N bond order⁵⁵. The strong band at 808 cm^{-1} of Htsc is due to $\nu(\text{C}=\text{S})$ coupled with NH_2 wagging and NCN bending. In the metal complexes, as in $\text{Ni}(\text{Htsc})_2\text{Cl}_2$, the C=S stretching is almost localized and occurs around 700 cm^{-1} , which shifts to 665 cm^{-1} on deuteration.

After Campbell's review⁵⁶ on thiosemicarbazone complexes upto 1975, a considerable amount of work has been reported in this field. Samus and coworkers⁵⁷ isolated the compound $\text{NH}_4^+[\text{VO}_2\text{L}]$ (L = the monoanion of 2-hydroxynaphthaldehyde semicarbazone) in which vanadium is in the pentavalent state. The formation of such a complex is attributed to the fixation of oxygen from the air giving a diamagnetic complex. X-ray crystallographic studies⁵⁸ of $[\text{VO}_2\text{L}]$ revealed the vanadium atom to possess

a distorted tetragonal pyramidal geometry in the complex.



Monomeric oxovanadium(IV) complexes of cyclohexanone thiosemicarbazone of the type $[\text{VOL}_2\text{X}]\text{X}$ (L = the ligand and X = Cl, Br or $1/2 \text{SO}_4$), which have tetragonal structures with anions interacting trans to the oxygen have been reported by Chandra and Pandeya⁵⁸. The complexes exhibit magnetic moments in the usual 1.67-1.73 B.M. range, corresponding to one unpaired electron. Jain et al.⁵⁹ have described dimeric vanadyl(IV) complexes of α -pyridyl thiosemicarbazone of the type $[\text{LVO}(\mu\text{-X})_2\text{VOL}]\text{X}'_2$ (L = the ligand, X = OH, Cl, or CN, and $\text{X}' = \text{H}_2\text{O}$, Cl or CN respectively). The vanadyl ions have square pyramidal geometry with oxygen at the apex, and with the bidentate ligand coordinating

via the pyridine nitrogen and the thione sulphur atoms. The $V=O$ frequency is observed between $996-980\text{ cm}^{-1}$, while the bridging $V-OH$ frequency is observed at 975 cm^{-1} . The non-participation of the hydrazino nitrogen atom, however, implies that sterically it is unavailable for coordination. On the other hand Pino and coworkers⁶⁰ have shown that it is the pyridine nitrogen atom that either moves in or out of coordination making the ligand α -pyridyl thiosemicarbazone either tridentate or bidentate, respectively.

Paramagnetic, octahedral complexes of the type $[CrL_3]$ are also obtained with *p*-substituted benzaldehyde thiosemicarbazone where the ligand is found to be bidentate⁶¹. Formation of complexes of the type $[Cr(HL)L]$ (where $L =$ the dianion of diacetyl monoxime thiosemicarbazone) from the interaction of $[Cr(H_2O)_6]Cl_3$ with the corresponding ligand derivatives has been reported by Zelentsov and coworkers⁶².

Jain et al.⁶³ have synthesised and studied Mn(III) complexes of 1-salicyl-4-benzyl amidothiosemicarbazone and 1-phenyl-4-benzylamidothiosemicarbazone. The former ligand yields an octahedral complex of the type $[ML_2]^+$ while the latter leads to the pseudooctahedral compounds of the type $[ML_2(OH)_2]^+$. The complex structures are supported by I.R. and magnetic data.

Zelentsov and coworkers⁶⁴ have reported structural features and magnetic properties of iron(III) complexes of substituted salicylaldehyde thiosemicarbazone ligands of the type $M[Fe(R-L)_2] \cdot n H_2O$ (where $M = \underline{CS}$, NH_4 or K ; $R = H, 5-Cl, 5-Br, 3,5-di-Cl, \text{ or } 3,5-di-Br$; $n = 0 \text{ or } 1.5$ and $L = \text{salicylaldehyde thiosemicarbazone}$).

Iron(III) complexes N^+ , N^+ -disubstituted 2-acetylpyridine thiosemicarbazone and 2-hydroxy-1-naphthaldehyde thiosemicarbazone have been described by Bhoon et al.^{65,66} in which they have assigned a square pyramidal structure to these complexes based on the magnetic measurements data.

Spingarn and Sartorelli⁶⁷ have synthesised several tridentate ligands of the 2-pyrazine carboxaldehyde thiosemicarbazone class and evaluated their potential for removing excess iron from iron-loaded mice. These ligands seem to be very potent for removing excess iron accumulated in patients suffering from Cooley's anemia. Similarly, 2-acetylpyridine thiosemicarbazone derivatives have been found to possess inhibitory activity for the RNA-polymerases of the influenza virus, which is thought to be mediated through chelation. In view of this, Raina and Srivastava⁶⁸ have characterised low spin iron(III) complexes of 2-acetylpyridine thiosemicarbazone

of the type $\text{Fe}(\text{APTSC})_2\text{X}$ (where APTSC = the monoanion of 2-acetylpyridine thiosemicarbazone, and $\text{X} = \text{NO}_3^-$, OH , Cl , N_3 , NCS , or NO_2).

Cobalt(III), nickel(II) and copper(II) complexes of 5(3)-methylpyrazole-3(5)-aldehydthiosemicarbazone (MePzATSH) have been isolated for the first time and their structures have been characterised by IR and PMR spectral data⁶⁹. It has been concluded from the data that the ligand behaves as a neutral (NNS) tridentate in its thioketo form when complexed with nickel(II) and copper(II), giving respectively bis- and mono-species, while with cobalt(III), the deprotonated ligand in its thiol form exhibits a monoacidic (NNS) tridentate function, yielding bis-species. Pradhan and Rao⁷⁰ have described octahedral complexes of Mn(II) ions with thiosemicarbazide and acetone thiosemicarbazone ligands. Reactions of MnCl_2 with another class of N^4 , N^4 -disubstituted thiosemicarbazones of acetylpyridine also gives a bis-ligand complex with octahedral geometry.

The X-ray crystal structural determination of the thiosemicarbazide complex of $\text{Fe}(\text{II})$ ⁷¹ shows that $[\text{Fe}^{\text{II}}(\text{H}_2\text{TSC})_2\text{SO}_4]$ is a sulphato-bridged polymer consisting of alternating $\text{FeS}_2\text{N}_2\text{O}_2$ octahedra with different spatial orientations in a monoclinic unit cell.

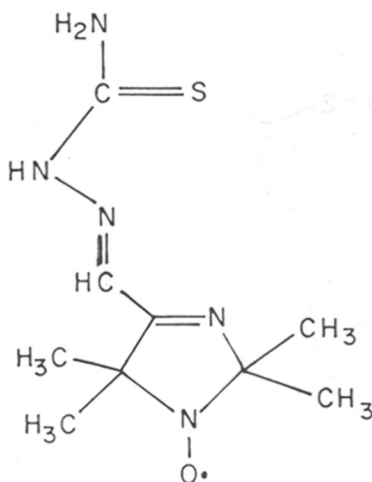
The crystal structure of the chloro complex of iron(II) with acetone thiosemicarbazone $[\text{Fe}(\text{AcTSC})_2]\text{Cl}\cdot\text{H}_2\text{O}$ was determined by Malinovskii and coworkers⁷² who confirmed a pentacoordination for this compound.

Sahni et al.^{73,74} have studied the diamagnetic octahedral Ru(II) complexes of thiosemicarbazide derivatives of 4-nicotinamide and 4-benzamide ligands and also the paramagnetic octahedral Ru(III) complexes of thiosemicarbazides and thiosemicarbazones.

Crystal structure data⁷⁵ on $[\text{CoL}_2(\text{CH}_3\text{COO})]\text{I}$ where L = acetone-5-methylthiosemicarbazone shows that the coordination around cobalt is trigonal bipyramidal formed by four nitrogen atoms and one oxygen atom of the acetyl group. Square planar Co(II) complex of 2-furaldehyde thiosemicarbazone was reported by Nair et al.⁷⁶ where the complexation through imine nitrogen and thiocarbonyl sulphur atoms (shifts in the bands at 1570 cm^{-1} and 850 cm^{-1}) was quite evident in infrared spectra.

Paramagnetic octahedral nickel(II) complexes of acetone and cyclohexanone thiosemicarbazones⁷⁷ and planar diamagnetic nickel(II) complexes with 3-hydroxy-2-naphthaldehyde thiosemicarbazone, 2-hydroxyacetophenone and its substituted derivatives^{78,79} have been reported.

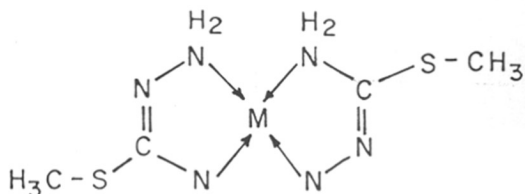
Ni(II), Pd(II) and Pt(II) complexes of 4-formyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl thiosemicarbazone have been synthesised and characterised by Ovcharenko and Larionov⁸⁰ for which the following structure has been proposed.



The thiosemicarbazone ligand acts as a tridentate ligand in Ni(II) complexes, coordinating through imine nitrogen in addition to the usual sulphur and nitrogen centres. Palladium(II) and platinum(II) complexes of these ligands are essentially planar with bidentate coordination.

Nickel complexes of thiosemicarbazone ligands also provide rare examples of complexes in which the

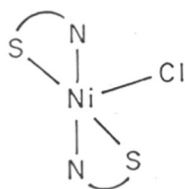
sulphur atom is not involved in the coordination⁸¹.
 The complexation thus takes place through the hydrazinic nitrogen atom and the amide nitrogen atom, resulting in a square planar geometry as shown below.



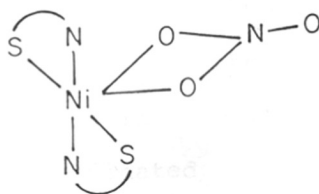
Similar results are observed in the case of acetone thiosemicarbazone methylated at sulphur atom. However, the salicylaldehyde thiosemicarbazone ligand when methylated at the sulphur atom does not undergo complexation with metals⁸².

The interaction of Ni(II) salts with thiosemicarbazone derivatives of acetone and cyclohexanone give complexes of the type $[\text{NiL}_2\text{X}_2] \cdot [\text{H}_2\text{O}]_n$,
 (where L = the neutral thiosemicarbazone ligand and

X = Cl, Br, NO₃ or ClO₄) which were initially thought to be high spin octahedral complexes. X-ray diffraction studies⁸³, however, revealed the attachment of only one chlorine atom to the central nickel ion, indicating an essentially five coordinate complex as shown below.



On the other hand, when X = NO₃, the resulting complex is found to be octahedral with resulting polyhedron greatly distorted to a geometry close to trigonal bipyramidal as shown.



Binding of the anticancer agent, 2-formylpyridine thiosemicarbazone copper(II) with Ehrlich ascites tumour cells has been described by Petering and coworkers⁸⁴. This is found to inhibit cellular DNA formation at low concentrations, but the RNA formation is seen to be less sensitive.

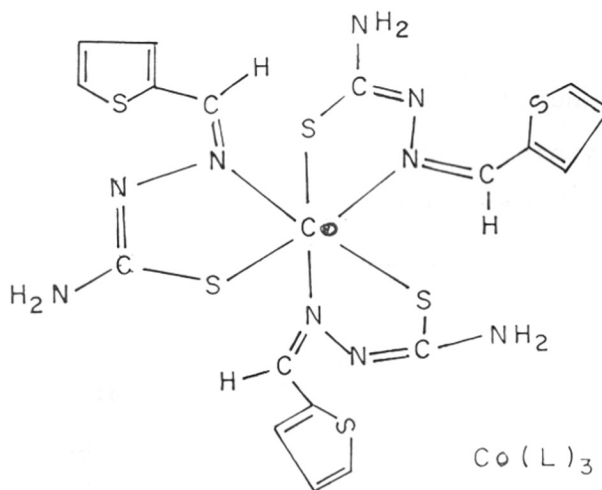
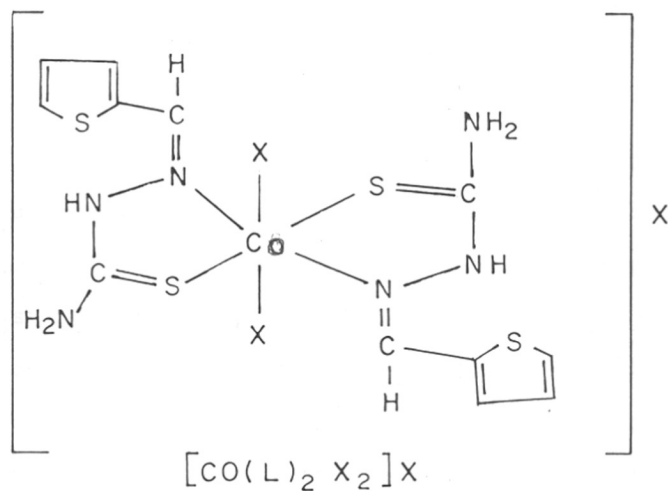
Campbell et al.⁸⁵ studied the ESR spectrum and covalency parameters of the antitumour agent 3-ethoxy-2-oxobutyraldehyde thiosemicarbazone copper(II), commonly referred to as the 'Cu(KTS)-complex' and found the bonding parameters to be similar to those of bis(thiosemicarbazido)copper(II) sulphate. It has been established that inhibition of RNA-directed DNA-polymerase in the viron by thiosemicarbazone copper(II) complexes prevent malignant transformation by Rous Sarcomavirus⁸⁶.

Sharma and others⁸⁷ have synthesised Ni(II) complexes of benzylmethylketone thiosemicarbazone with the general formula NiL_2X_2 where L = thiosemicarbazone and $X = Cl^-$, Br^- , I^- , CH_3COO^- , SCN^- and $1/2 SO_4^{2-}$. The stereochemistry of these complexes is dependent upon the anion involved. The thiocyanato complex possesses six coordinated octahedral geometry

whereas the chloro, bromo and iodo complexes possess five-coordinated trigonal bipyramidal configuration. The acetato and sulphato complexes are four coordinated square planar and tetrahedral respectively.

Raina and Srivastava⁸⁸ have isolated and studied the low-spin iron(III) complexes of 2-pyridine-carboxaldehyde thiosemicarbazone of the type $\text{Fe}(\text{PT-H})_2\text{X}$ where PT-H = 2-pyridinecarboxaldehyde thiosemicarbazone and X = Cl, NO_3 and CNS where the ligand acts as a tridentate donor.

Cobalt(III) complexes of thiophene-2-carboxaldehyde thiosemicarbazone (L) of general formulae, $\text{Co}(\text{L})_2\text{X}_3$, $\text{Co}(\text{L})\text{X}_3 \cdot \text{H}_2\text{O}$ (where X = NO_3^- , Cl^- , Br^- , I^- and CH_3COO^-) and $\text{Co}(\text{L})_3$ have been prepared and characterised⁸⁹. I.R. spectra show that the ligand acts as a bidentate. All the complexes are diamagnetic with octahedral geometry with the following structures.



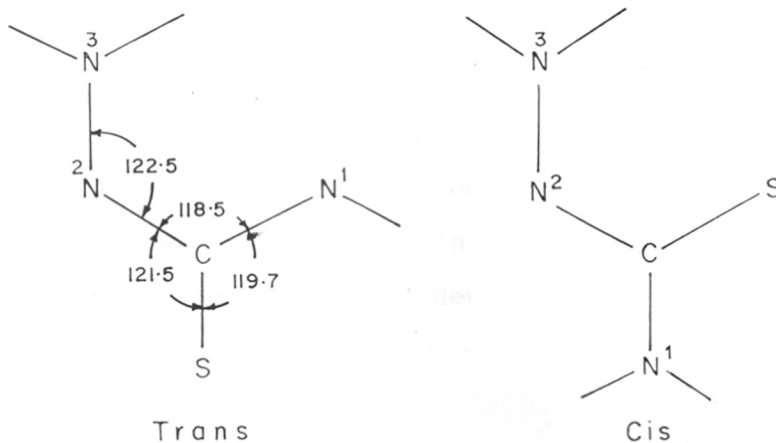
Metal complexes derived from 1-isatin-4-phenyl-3-thiosemicarbazone (IPTS) and 1-(α -)furyl-4-phenyl-3-thiosemicarbazone (FPTS) with nickel(II), cobalt(II), copper(II) and cadmium(II) have been synthesised and characterised⁹⁰. I.R. spectra show that IPTS coordinates in a tridentate manner via CN, CO and CS groups, while FPTS acts as a bidentate ligand coordinating via CN and CO

groups. Magnetic and spectral studies suggest a square-planar structure for the copper(II) and nickel(II) complexes derived from FPTs and a low-spin octahedral structure for $[\text{Co}(\text{FPTS-H})_3] \cdot 2\text{H}_2\text{O}$. On the other hand, octahedral structures are proposed for the complexes of nickel(II) and copper(II) that are derived from IPTS and low-spin octahedral structure for $[\text{Co}(\text{IPTS-H})_2]$.

Tricoordinated tin(II) complexes with semi-carbazones and thiosemicarbazones of the type SnL (where L = the semicarbazone or thiosemicarbazone of salicylaldehyde, o-hydroxyacetophenone, 2-hydroxy-1-naphthaldehyde and benzoin) have been reported⁹¹ and characterised by IR and NMR techniques.

X-ray crystallographic work

The thiosemicarbazide (TSC) molecule is known to exist in trans and cis forms⁹² as shown.

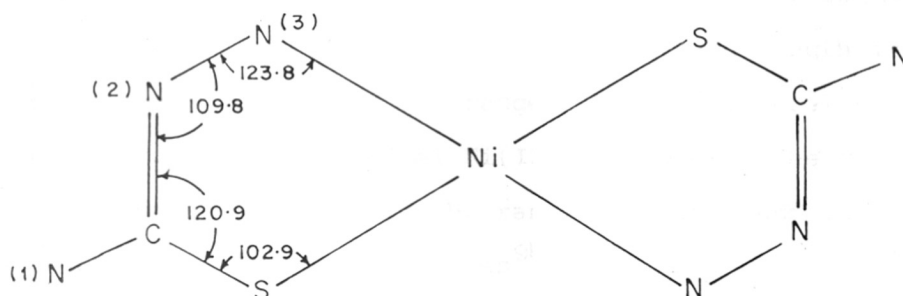


In the polymeric complex, $\text{Ag}(\text{TSC})\text{Cl}$, two kinds of silver atoms are present, both being tetrahedrally coordinated but having environments which are both crystallographically and chemically distinct. $\text{Ag}(\text{I})$ is coordinated to two S atoms and two Cl atoms with one of the Ag-Cl bonds longer than the other, while $\text{Ag}(\text{II})$ is coordinated to three S atoms and one Cl atom, with one of the Ag-S bonds being markedly longer than the other two.

In all other known TSC complexes the TSC molecule is in the cis configuration and is bidentate, bonding through sulphur and hydrazinic nitrogen. $\text{Ni}(\text{TSC})_2\text{SO}_4$, $\text{Ni}(\text{TSC})_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{TSC-H})_2$ are all square planar and diamagnetic, and Ni-N and Ni-S bond distances are very similar in all three compounds. The Ni-S bond distances are considerably shorter than the sum of the radii of the Ni(II) ion and the sulphur atom ($2.4\text{-}2.5 \text{ \AA}$) and also shorter than the sum of the Pauling covalent radii (2.25 \AA). The most interesting feature in the compound $\text{Ni}(\text{TSC})_2\text{SO}_4$ is the presence of both cis and trans isomers of $\text{Ni}(\text{TSC})_2^{2+}$ cation.

Although the Ni-N and Ni-S bond distances in $\text{Ni}(\text{TSC-H})_2$ are similar to those in the two sulphate complexes, bond angles about Ni deviate appreciably from

90° and there are marked changes in the geometry of the ligand⁹³. The short C-N(2) distance shows this to be essentially a localized double bond, implying that the ligand is in the thiol form which has been deprotonated. There is other evidence that this is the form involved in complex formation under alkaline conditions. The thiol form of the ligand is seen in the figure.



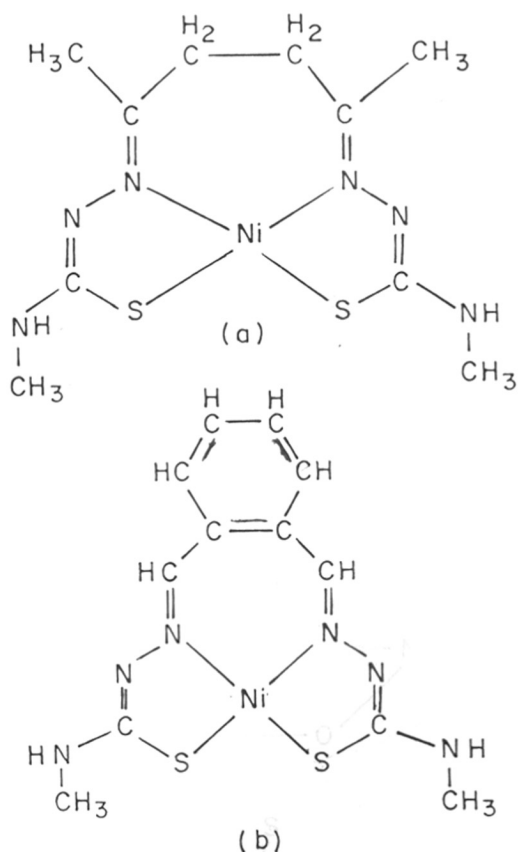
The Molecular Structure of
Ni(TSC-H)₂ (Hydrogen atoms are not shown)

Nardelli and coworkers⁹² have pointed out that in TSC itself the C-S and C-N(1) bond distances are intermediate between the usual values for single and double bonds. It is therefore interesting to note that in Ni(TSC-H)₂ these bonds and also the N(2)-N(3) bond are markedly longer than in TSC while, the C-N(2) bond is appreciably shorter. In the nickel sulphate complexes the C-N(1)

and C-N(2) bond distances are not very different from those in TSC itself while the C-S and N(2)-N(3) distances are longer as might be expected for bonds involving donor atoms.

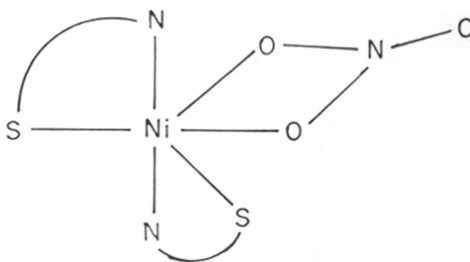
In the paramagnetic six coordinate complex $[\text{Ni}(\text{TSC})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ the coordination about Ni is approximately octahedral with two O, two N and two S atoms in trans positions relative to each other. The Ni-N and Ni-S bonds are much longer than in the diamagnetic complexes but the ligand geometry is much the same as in TSC itself. The Ni-S bond length is in the lower end of the range 2.4-2.6 Å generally accepted for octahedral Ni(II) molecules. The Ni-N distances also lie in the range usually found for octahedral Ni(II) complexes⁹⁴.

McCleverty and coworkers⁹⁵ have determined the structures of the two square planar diamagnetic complexes formed with the bis-thiosemicarbazones of hexene-2,5-dione (TSC-2,5-D) and phthaldehyde (TSC PHAL). Both of the complexes contain a seven-membered chelate ring as well as the two five-membered rings involving the TSC moieties as shown below. The C-S and N(2)-N(3) as well as the Ni-N and Ni-S bond lengths are similar to those found in the square planar nickel(II) complexes of TSC.



In the complex $\text{Ni}(\text{TSCAc})_2\text{Cl}_2$, the Ni atom is penta-coordinated with the donor atom set $\text{N}_2\text{S}_2\text{Cl}$, the two S atoms being in the axial positions of an approximately trigonal bipyramidal coordination polyhedron. The geometries of the two TSCAc ligands are not identical but apart from the longer C-S bond lengths they are not very different from that of the free ligand. The Ni-S bond lengths are intermediate between those found for four- and six-coordinated nickel(II) complexes of thiosemicarbazones, as might have been expected, but

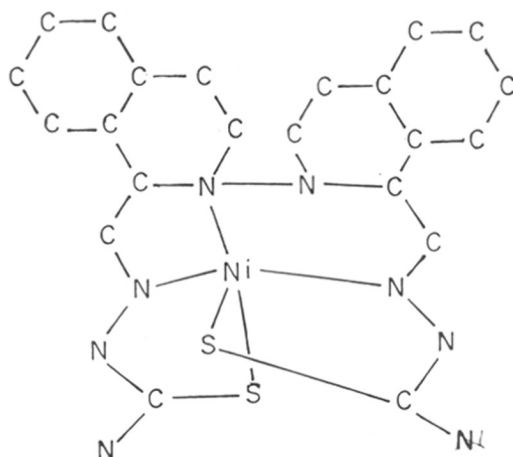
the Ni-N distances are longer than those in both four- and six-coordinated species. In the corresponding nitrate complex, $\text{Ni}(\text{TSCAc})_2(\text{NO}_3)_2$, the Ni atom is six-coordinate with the donor atom set $\text{N}_2\text{S}_2\text{O}_2$ but only one of the NO_3 groups is coordinated and is therefore necessarily bidentate⁹⁶.



Schematic molecular structure of the nitrate bis(acetone thiosemicarbazone)nickel(II) cation (only the N and S donor atoms of the thiosemicarbazone ligand are shown).

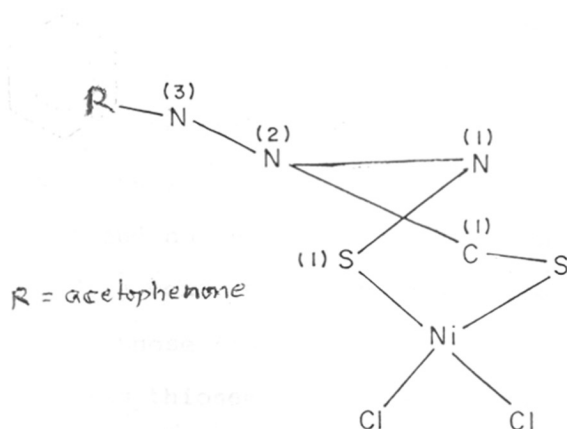
The structures of two six-coordinate complexes of Ni(II) with thiosemicarbazones of 1-formaldehyde isoquinoline and 2-formaldehyde pyridine have been

determined⁹⁷. Both the ligands are tridentate, the third donor atom being the heterocyclic nitrogen and the complexes are paramagnetic. The Ni-S bond lengths are appreciably longer than those in the four and five coordinate complexes and are similar to the values found for the paramagnetic six coordinate nickel(II) complexes of TSC. The Ni-N (hydrazinic N) bond lengths are intermediate between those in the four- and the five-coordinate species and are appreciably shorter than the Ni-N (heterocyclic N) bond lengths as shown below.

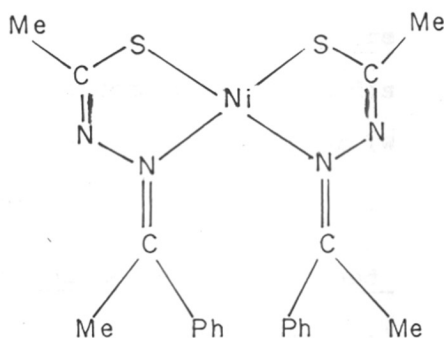


Molecular Structure of
bis(isoquinoline-1-carboxaldehyde
thiosemicarbazonato)nickel(II)
monohydrate (hydrogen atoms not shown)

X-ray crystallographic studies⁹⁸ on dichlorobis(acetophenone thiosemicarbazone)nickel(II) shows that the nickel(II) coordinates to the sulphur atoms of the ligand alone forming NiS_2Cl_2 chromophore. The Ni-S bond length of $2.280(1) \text{ \AA}$ may be compared with the sum of the single bond covalent radii, 2.43 \AA ⁹⁹. As expected, it is significantly shorter than that in octahedral nickel (diisopropylthiourea)₆ClO₄ ($2.481\text{--}2.514 \text{ \AA}$)¹⁰⁰ and longer than Ni-S in the square planar nickel (dimethylthiourea)₄Br₂ ($2.23\text{--}2.204$)¹⁰¹. There is little difference when compared with Ni-S (2.290 \AA) in trigonal bipyramidal $[\text{Ni}(\text{acetone thiosemicarbazone})_2\text{Cl}]\cdot\text{Cl}\cdot\text{H}_2\text{O}$ ¹⁰². The Ni-Cl bond length is as expected for tetrahedral coordination. The bond distances and the molecular structure for the dichlorobis(acetophenone thiosemicarbazone)nickel(II) are as follows: Ni-S, $2.280(1)$; S-C(1), $1.710(4)$, C(1)-N(1), $1.310(5)$, N(2)-N(3), $1.313(4)$, N(3)-C(2), $1.285(5)$.



The molecular structure of bis(acetophenone thioacetylhydrazonato)nickel(II) has been confirmed¹⁰³ to be a cis-syn configuration out of the six possible isomers indicating that the sulphur atoms are cis and that phenyl groups are syn. The structure is illustrated by schematic drawing as follows.



Although from this drawing, the structure would appear like least possible due to the bulkiness of the phenyl groups, however, the ORTEP¹⁰⁴ plot of the molecule viewed down the two fold axis shows it to be possible for this diamagnetic inner complex to have the cis-syn configuration and not to have any close contacts. The Ni-S and Ni-N(1) bond lengths of 2.150 Å and 1.935 Å are similar to those found in other planar nickel complexes having thiosemicarbazide or its derivatives

as ligands¹⁰⁵⁻¹⁰⁸. Bond lengths in this molecular structure are observed to be as follows: Ni-S, 2.155; C-N (double bond), 1.28; N-N 1.428 and C-S, 1.73 Å.

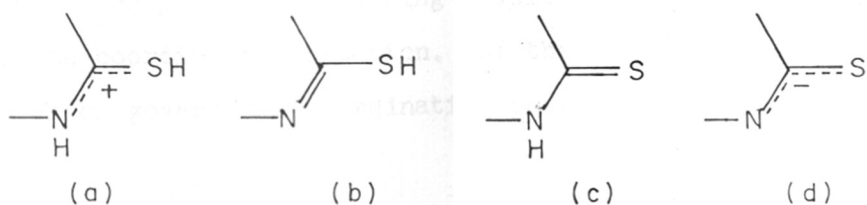
Bis(acetone-4-phenylthiosemicarbazone)bromocobalt(II) bromide (green form) was separated from its blue isomer mechanically. The blue crystals were found to contain the solvent molecule and the isomer was found to assume the stable green form after about one month. The crystal structure data¹⁰⁹ on the green form concludes the structure of the complex to be a distorted trigonal bipyramid with the formula $[\text{CoL}_2\text{Br}]\text{Br}$ (where L = acetone-4-phenylthiosemicarbazone).

2) Heterocyclic thione derivatives and their metal complexes

Thiocarbonyl compounds are formal analogues of carbonyl compounds and are as such structurally characterised by the C=S linkage, in which bivalent sulphur is multiple bonded to carbon by overlap of a carbon 2p-orbital and a sulphur 3p-orbital. Owing to differences in spatial symmetry and electron density distribution between the orbitals involved, this overlap is less efficient than the 2p-2p overlap of the C=O link. On this background it is understandable that thiocarbonyl compounds in general are more reactive, less stable, and to a higher degree influenced by stabilizing effects of incorporated

neighbouring atoms or groups than are their oxygen analogues. Furthermore, although thiocarbonyl compounds in many respects in their reactions behave like the corresponding carbonyl compounds, the comparatively 'softer' character and lower electronegativity of sulphur, as well as the higher polarisability of the C=S bonding, give rise to important differences in reactivity. As a third-period element, sulphur has empty 3d-orbitals, the role of which as a stabilizing factor for many types of compounds not having their counterpart among the carbonyl compounds is a special feature of thiocarbonyl compounds.

Derivatives of thiazoline thiones, 1,3,4-thiadiazole and 1,2,4-triazoline thiones form a class of heterocyclic thione type ligands. The combination of an exocyclic thione (thioketo) group and a heterocyclic molecule, which may contain nitrogen, oxygen, sulphur or a combination of these represents a novel group of ligands with a good coordination ability with various metal ions. A common feature of all nitrogen-containing heterocyclic thiones is 'thione' - 'thiol' tautomerism as shown below.

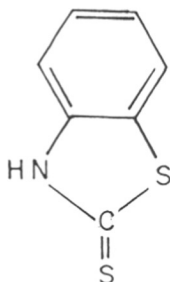


X-ray crystallographic studies¹¹⁰⁻¹¹⁴ on several heterocyclic thiones indicate a tendency for the thione form to dominate in the solid state. The C-S bond length ranging from 1.629 to 1.722 Å and the corresponding π -character ranging between 37.7 to 73.5 percent clearly indicates the predominance of 'thione' structures in these molecules. Infrared spectra of these ligand molecules support the dominance of the thione form in the solid with the presence of ν (NH) bands (ca 3100 cm^{-1}), and the absence of ν (SH) (ca 2500 cm^{-1}). X-ray photoelectron spectroscopy provides further evidence of thione dominance with the nitrogen (1S) spectra of benz-1,3-imidazoline-2-thione consisting of a single peak and with electron core binding energies (ca 400 eV) consistent with the presence of imido (NH) groups. Proton NMR measurements¹¹⁵ usually support the presence of thione tautomers in solution with chemical shifts consistent with imido (NH) (δ , ppm, 8-11). Both thione and thiol forms are occasionally reported for the same molecule, e.g. tetrahydropyrimidine-2-thione^{116,117}.

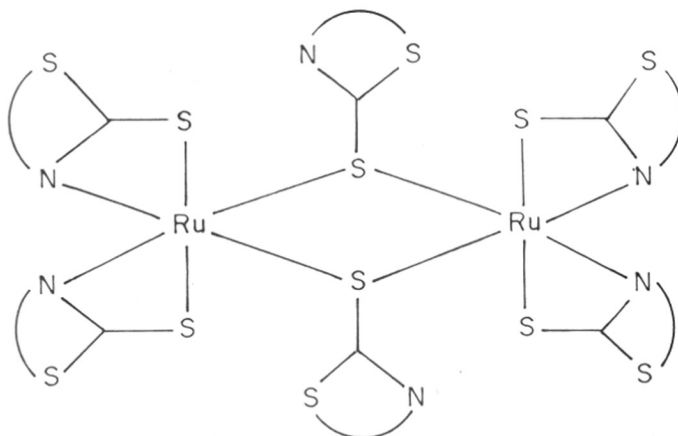
Heterocyclic thiones generally are found to retain their identity during chemical reactions with metal salts; only rarely does ring fission or fusion disrupt the coordination reaction. Of the various factors which govern the coordination phenomena of

heterocyclic thiones, the role of the metal atom appears to be insignificant as far as the oxidation states I-III are concerned. One exception to this generalisation is copper(I) which shows an affinity for thione sulphur. In general, molecular and electronic structure of a heterocyclic thione plays the most vital role in the coordination process.

1,3-Thiazoline-2-thione forms $M(LH)_2Cl_2$ complexes with nickel and mercury and $M(LH)Cl_2$ type complexes with copper and cadmium. On the basis of IR spectral shifts in $\nu(NH)$ monodentate nitrogen donation is proposed for cadmium and sulphur donation for the remaining metals¹¹⁸. The thione nature of benzo-thiazoline-2-thione in solid state has been established by X-ray crystallographic data¹¹⁹ and X-ray photoelectron spectroscopy¹²⁰. The bond length of C-S bond (1.662 Å) and the predominant π character (60.7%) of this bond supports the thione structure and the presence of two different types of sulphur atoms in the ligand with electron core binding energies for $2p_{3/2}$ electrons of 164.5 eV (thione) and 162.3 eV (thioether) further supports the structure shown below.

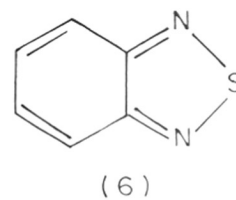
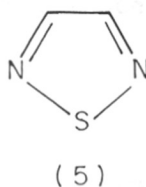
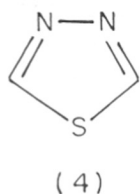
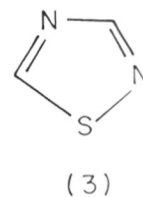
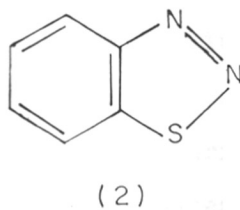
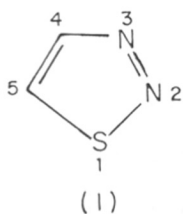


The presence of thiol-(SH) δ (1.95 ppm) and imido (NH) nitrogen δ (10.2 ppm) for benzothiazoline-2-thione has been reported by ^1H NMR studies. In acid media complexes of type $\text{M}(\text{LH})_2\text{X}_2$ ($\text{M} = \text{Pd}, \text{Pt}, \text{X} = \text{Cl}, \text{I}$) are formed. Location of thiol (SH) groups δ (2.10 ppm) in the complexed molecules suggests nitrogen donation by proton migration. In basic media ML_2 ($\text{M} = \text{Pd}, \text{Pt}$) complexes are formed as polymeric species with thiolate anions bridging¹²¹. Nickel complexes NiL_2 , are either diamagnetic and square ^{planar} or paramagnetic (2.75 B.M.) and octahedral¹²³. The complex $\text{Ru}(\text{L})_3$ is dimeric in chloroform, contains weakly paramagnetic octahedral and metal-metal bonded ruthenium(III) together with both S,N-chelating and sulphur bridging ligands as shown.



The thione predominance in 1,3-thiadiazolidine-2-thione (tzdtH) has been established by X-ray crystallography (C-S \AA , 1.676 and π -character %, 55.4)¹²⁴.

The thiadiazole system contains the following members: the 1,2,3-thiadiazoles (1) and their benz derivatives (2), the 1,2,4-thiadiazoles (3), the 1,3,4-thiadiazoles (4), and the 1,2,5-thiadiazoles (5) and their benzo derivatives (6).



1,3,4-Thiadiazoles were first described in 1882 by Fischer and further developed by Busch and coworkers. The advent of sulphur drugs greatly accelerated the rate of progress in the field of thiadiazoles. Thiadiazoles carrying mercapto, hydroxy and amino substituents can exist in many tautomeric forms.

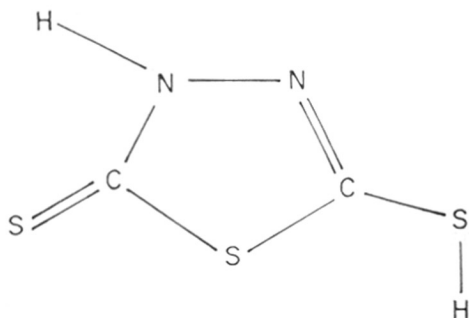
The structural features of many 1,3,4-thiadiazoles have been determined by X-ray diffraction techniques. 1,3,4-Thiadiazole in the vapour phase is a planar molecule having C_{2v} symmetry¹²⁵. 5-Amino-1,3,4-thiadiazole-2-thiol is also planar. Bond lengths suggest that the compound exists in the solid state in the thione rather than the thiol form. The ring is aromatic with a localized C(1) = N(1) double bond of length 1.305 Å. Other C-N bond lengths are 1.334 and 1.339 Å and the N-N- bond length is 1.382 Å. The cyclic C-S distances are 1.746 and 1.748 Å and the exocyclic C-S bond length is 1.678 Å. Hydrogen bonding of the type N-H...S is also present¹²⁶.

The crystal structure of 5-amino-2-thiol-1,3,4-thiadiazole ($C_2H_3N_3S_2$) has been determined¹²⁷ by three dimensional Patterson and Fourier methods and refined by block-matrix least squares calculations. The crystals are monoclinic, space group $P2_1/c$ with four

molecules in a unit cell of dimensions $a = 6.167$, $b = 10.048$, $c = 9.007 \text{ \AA}$, $\beta = 116.8^\circ$. The final R index is 0.106 for 796 observed reflections, collected with Cu K α radiation. (The molecule may be regarded as being rather planar since the deviations of the atoms from the mean plane of the molecule are all less than 0.02 \AA). Bond lengths indicate that the compound exists in the thione rather than the thiol form. The 1,3,4-thiadiazole ring possesses a fair degree of aromaticity with a localized C(1) = N(1) double bond of length $1.305 (6) \text{ \AA}$. Other C-N bond lengths are 1.334 and 1.339 \AA . The N-N bond length is $1.382(8) \text{ \AA}$. The cyclic C-S distances are 1.746 and 1.748 \AA and the exocyclic C-S bond length is 1.678 \AA . Of particular interest is the short S-S intramolecular contact of 3.008 \AA which is approximately 0.5 \AA shorter than the sum of the Pauling Van der Waals radii. There is a reasonable probability that hydrogen bonds of type N-H...S and length 3.32 \AA exist, joining pairs of molecules across centres of symmetry.

The crystal structure of 2,5-dimercaptothiadiazole ($C_2H_2N_2S_3$) has been determined¹²⁸. The compound has the space group $P2_1/c$ with $a = 6.225 (1)$, $b = 10.593 (3)$, $c = 9.248 (3) \text{ \AA}$ and $\beta = 113.65(2)^\circ$.

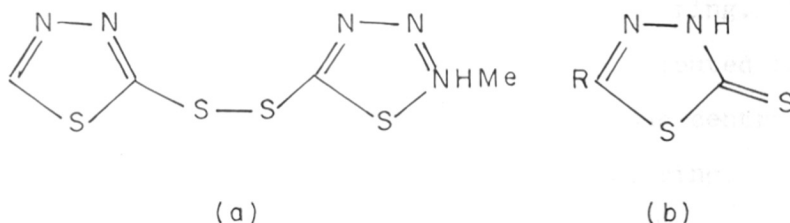
The compound crystallises as thiadiazole-2-thiol-5-thione, as a result of proton transfer in one of the two S-H---N hydrogen bonds. The measurement of bond lengths shows that 2,5-dimercaptothiadiazole in the crystalline state exists predominantly in the thione form.



The molecular packing of 2,5-dimercaptothiadiazole is similar to that found in 5-aminothiadiazole-2-thiol and the compound crystallises as a thione as suggested by Downie et al¹²⁷. The molecule with the exception of H(2), is almost planar. Both H atoms are involved in a SH---N hydrogen bond.

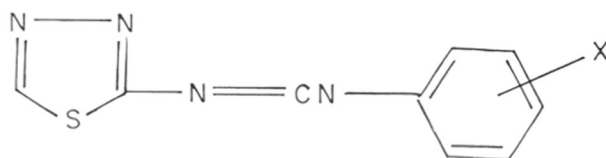
The NMR spectra of thiadiazoles are solvent dependent. When the substituent in the 5-position is H or Me the signals are shifted towards higher fields

on changing from CCl_4 to benzene, suggesting the formation of a π type complex between the thiadiazole and the benzene molecule with the 5-substituent placed in the shielding area of diamagnetic anisotropy of the benzene molecule. The signals from the NH group exhibit a shift towards higher fields on dilution with CDCl_3 , suggesting intermolecular hydrogen bonding (solute-solute). In DMSO, however, the shifts of the NH protons are concentration independent, but are shifted towards higher fields with increasing temperature¹²⁹. Bartels-Keith and others¹³⁰ have measured ^{13}C NMR chemical shifts for (a) and (b) ^{and} used the technique to distinguish between thione and thiol tautomers.



Compound	C-2	C-5	Others
(a)	146.6	173.0	31.2 (Me)
(b)			
R = MeNH	180.6	161.6	29.9 (Me)
R = Thiophene ring	187.2	154.2	-

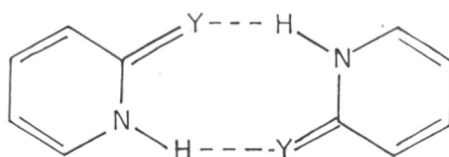
Unconjugated 1,3,4-thiadiazoles have no selective absorption above 220 nm. Substituents with lone pairs cause bathchromic shifts, the effect of an alkylthio group is greater than that of an amino group. The UV spectrum of 2-aminoarylidine-1,3,4-thiadiazole derivative shows four bands¹³⁰.



Two of these are in the 204-265 nm region and are due to the $\pi-\pi^*$ transition state of the benzene ring. The third band in the 265-305 nm region is attributed to the excitation of the π electrons within the central C=N and that within C=N bond of the hetero ring. The fourth band is due to a transition within the whole molecule and its position is sensitive to the nature of X.

The chemical shift of the SH (or NH) proton appears at 13.43 ppm, i.e. close to the corresponding shift of 2-hydroxypyridine (13.23 ppm), which suggests that 2-mercaptopyridine, like 2-hydroxypyridine, mainly

occurs in the thioamide form as hydrogen bonded dimers as shown below (Y = O,S).



The IR spectra of 2-hydroxypyridine and 2-mercaptopyridine in 10 mol % acetone solutions were recorded using acetone as reference. Both compounds displayed a broad absorption band near 3200 cm^{-1} , which is presumably due to hydrogen bonded N-H stretching. The S-H stretching band was not observed for 2-mercaptopyridine, while a weak and broad band at ca 3250 cm^{-1} in the 2-hydroxypyridine spectrum may indicate hydrogen bonded OH. In the former compound a strong band measured at 1155 cm^{-1} can be attributed to C=S stretching.

Thione tautomer is the only detectable form in solution and is clearly shown by ^1H , ^{13}C and ^{15}N NMR spectroscopic studies^{131,132}. The dominance of the

thione form over the thiol form arises from the differences in the π -electron energies of solvation between the two forms¹³³⁻¹³⁶.

¹H NMR measurements of chemical shifts of 1,3-thiazolidine-2-thione suggests the presence of both thione and thiol forms in solution (imido NH, 10.0 ppm and thiol (SH) at 1.8 ppm). Several metal complexes of 1,3-thiazolidine-2-thione have been synthesised and characterised by various techniques. Diamagnetic nickel(II) complexes¹³⁷ of 1,3-thiazolidine-2-thione with square planar geometry have been reported. Tetrahedral, octahedral or polymeric Ni(II) complexes^{138,139} also have been isolated with 3.15-3.50 B.M. values.

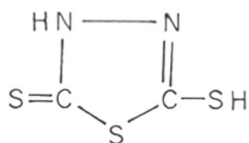
PMR measurements show the presence of (NH) in both the free ligand (10.05 ppm) and the octahedral (Ru, Os, Ir, Rh) complexes with low-field shift (12.00 ppm) upon complexation¹⁴⁰. Nitrogen coordination in case of some of these complexes is supported by the absence of (NH) in I.R. spectra of the complexes and by the appearance of (SH) (ca 2.0 ppm) in the ¹H NMR spectra¹⁴¹.

Coordination of 1,3-thiazolidine-2-thione, tzdth, by means of its thione sulphur with various metal ions has been identified from the IR spectra of the complexes

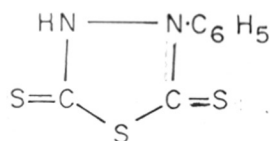
in which the ν (NH) band usually occurs between 3100 and 3170 cm^{-1} ; the ν (CS) band in the 600-700 cm^{-1} region is lowered by 40-50 cm^{-1} and ν (M-S) bands occur between 300 and 400 cm^{-1} ^{142,143}.

In alkaline media the deprotonated thiolate anion, tzdt^- , forms complexes of formulae ML_2 [M(II) = Zn, Cd, Hg, Co, Ni, Pd, Pt, Mn], ML [M(I)] = Cu, Ag]. The involvement of both the thiolate sulphur and heterocyclic nitrogen in coordination is evident by the presence of ν (M-S) and ν (M-N) in their respective regions; 185-313 and 240-380 cm^{-1} ¹⁴⁴.

1,3,4-Thiadiazole-2,5-dithione (Bismuthiol I)
and 1,3-phenyl-4-thiadiazole-2,5-dithione (Bismuthiol II)



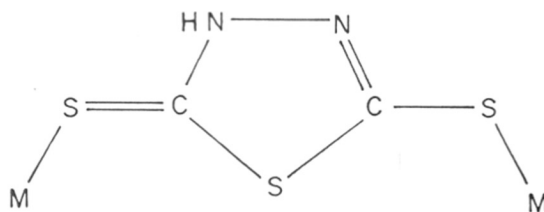
Bismuthiol I



Bismuthiol II

are well known ligands due to their use as analytical reagents. The presence of both ν (NH) (2860-3060 cm^{-1}) and ν (SH) (2470 cm^{-1}) in the infrared spectra suggests the above structures to be the most likely combination in the solid state ^{145,146}.

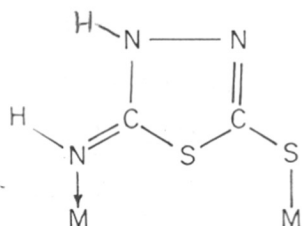
Complexes of formula $M(LH_2)_2(PPh_3)_2$ [$M(O) = Pd, Pt$] are prepared from 1,3,4-thiadiazole-2,5-dithione and the appropriate metal phosphine in benzene. The presence of $\nu(M-N)$ in the region of 400 cm^{-1} suggests the molecule to be monodentate nitrogen donor. The readily deprotonated Bismuthiol I molecule reacts with a wide range of metal ions either as the free molecule or its mono-potassium salt producing insoluble polymeric species. The monoanion (LH^-) is present in these complexes and is characterised in the infrared spectra by the absence of $\nu(SH)$ and the presence of $\nu(CN)$ ($1440-1470\text{ cm}^{-1}$), $\nu(CS)$ ($1020-1050\text{ cm}^{-1}$) and $\nu(NH)$ ($2800-3300\text{ cm}^{-1}$)¹⁴⁷. The anion normally uses both of its exocyclic thione sulphur atoms in the formation of S,S-bridges as shown below, which are characterised



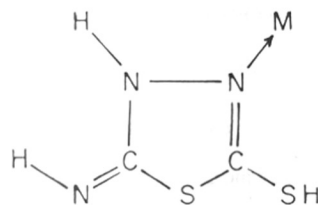
by a combination of negative shifts to the $\nu(CS)$ bands and the production of $\nu(M-S)$ bands ($330-390\text{ cm}^{-1}$).

S,N-bridging has been proposed for the zinc, cadmium and mercury complexes on the basis of the presence of $\nu(M-N)$ and $\nu(M-S)$.

Gajendragad and Agarwala¹⁴⁸ have reported several metal complexes of 5-amino-2-thiol-1,3,4-thiadiazole. The complexes of Zn(II), Cd(II), Pb(II), Cu(I), Ag(I) and Tl(I) have been proposed the structure (a) on the basis of their infrared spectral data. The band due to $\nu(SH)$ is absent in the spectra of all these complexes suggesting the involvement of exocyclic sulphur atom in coordination. The positions of $\nu(NH)$ bands shift towards lower wave-number, indicating that one of the NH groups in the ligand takes part in bond formation. Since the N-H group present in the ring system is less basic than the imino group, bonding through the N atom of the imino group is favoured and the structure (a) is proposed for these complexes.



(a)

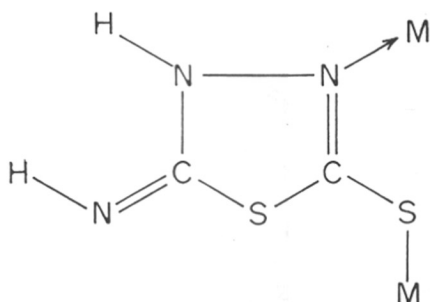


(b)

On the other hand the band due to ν (S-H) is present in the infrared spectra of Pd(O) and Pt(O) complexes suggesting that the S-H group of the ligand is not involved. There is no shift in the positions of the bands due to ν (N-H) indicating that the bonding is not through the imino group of the ligand. The band due to ν (C=N) from the N=C-SH group of the ligand, however, was found to shift to lower wave number and a lowering in the ν (C=S) band was also observed. On the basis of the IR data the structure (b) was proposed to these complexes. The same structure was assigned to Cu(I), Ag(I) and Tl(I) on the basis of the fact that these metal ions are ~~to~~ class^b_A metals from the Periodic Table having great affinity for highly polarizable sulphur as compared to nitrogen, although ionic structures involving bonding through the thiocarbonyl sulphur cannot be ruled out. A tetrahedral structure is proposed to Zn(II), Cd(II) and Pb(II) complexes.

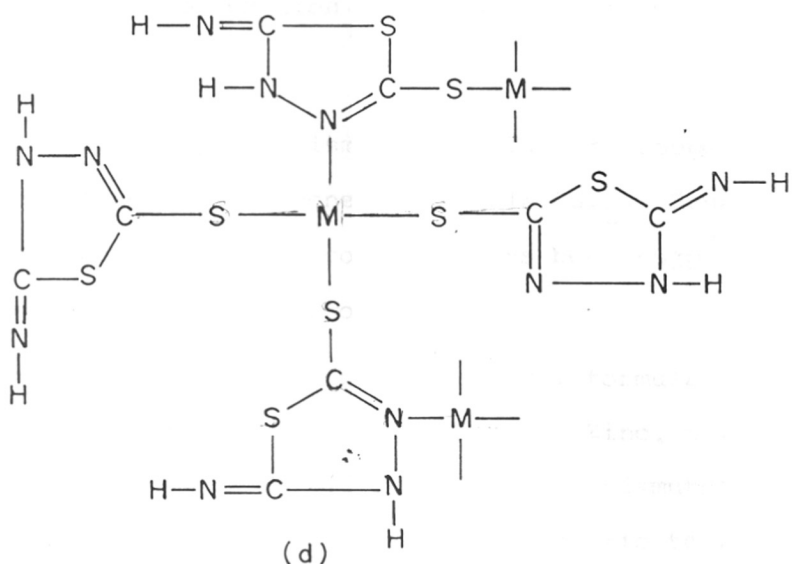
Complexing behaviour of 5-amino-1,3,4-thiadiazole-2-thiol has been studied by Gajendragad and Agarwala^{149,150} by synthesizing and characterising the Ni(II), Pd(II), Pt(II), Cu(II), Rh(I), Au(III), Fe(II), Co(II), Ru(II), Ru(III), Rh(III), Ir(III), Pd(IV) and Pt(IV) complexes of the ligand.

The lowering in $\nu(\text{C}=\text{S})$ and $\nu(\text{C}=\text{N})$ bands in the infrared spectra of Ni(II) and Co(II) complexes indicates the involvement of both thiolate sulphur and the nitrogen atom from N=C-SH group and the following structure (c) has been proposed.



Fe(II), Ru(II), Pd(II), Pt(II), Cu(II), Ru(III), Ir(III), Rh(III), Pd(IV) and Pt(IV)_{complexes} have been proposed structure (a) on the basis of their infrared spectral shifts.

Appearance of a new band in the vicinity of 400 cm^{-1} region_{due to $\nu(\text{Rh}-\text{N})$} in the IR spectrum of Rh(I)_{complex} and also the presence of $\nu(\text{SH})$ band in the complex favours the structure (b). The infrared spectrum of Au(III) complex is complicated because most of the bands are either split or broadened, however, the careful analysis of the spectrum and the diamagnetic nature of the complex suggests that two of the ligand molecules act as monodentate whereas the third one as bidentate as shown in structure (d).



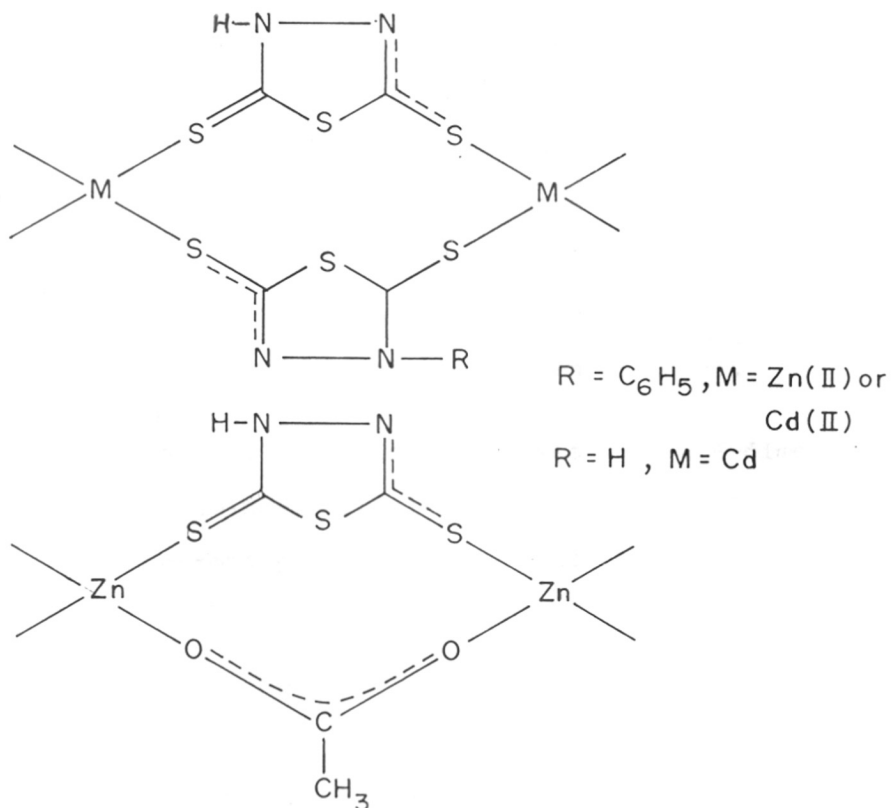
Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

complexes of 1,3,4-thiadiazoline-2,5-dithione (Bismethiol I) and 5-mercapto-3-phenyl-1,3,4-thiadiazoline-2-thione (Bismuthiol II) have been isolated and characterised by Osman and others¹⁵¹. The electronic spectra and magnetic data of the cobalt complexes suggest a tetrahedral environment. The electronic and infrared spectral data of the nickel complexes indicate that the nickel atom is four coordinate. The paramagnetic nature of these complexes (μ_{eff} 3.2-3.5 B.M.) is attributed to the expansion of coordination number from 4 to 6 due to molecular association through an additional weak coordination being achieved through the hetero sulphur

atom. However, no definite conclusion for participation of this atom in complexation could be drawn from infrared spectral data.

Bismuthiol (I) and Bismuthiol (II) form copper(II) acetate complexes of the general formula CuL_2 . Square planar structure for these complexes has been suggested on the basis of their electronic spectra.

Cadmium(II) complexes of the general formula CdL_2 have been isolated with both Bismuthiols. Zinc, however, forms ZnL_2 with Bismuthiol (II), while with Bismuthiol (I) $\text{ZnL}(\text{OAc})$ was isolated. The following polymeric tetrahedral structures are proposed for zinc and cadmium complexes.



Fabretti and others¹⁵² have synthesized SnX_4 (X = Cl, Br) complexes of 2,5-dimethyl(dtz), 2-amino-5-methyl(matz), 2-mercapto-5-methyl(mttz) and 2,5-dimethylmercapto-1,3,4-thiadiazole(dmttz) and studied by conductometric, infrared and Raman spectra methods. In $\text{SnBr}_4(\text{matz})_3$, one ligand molecule is uncoordinated, the other two being NH_2 -bonded to the metal. In SnX_4L_2 (L = dtz, mttz; X = Cl, Br), dtz acts as monodentate ligand bonded through a ring nitrogen atom to the metal in a trans-octahedral coordination. The ligand mttz was found to exist in thioketo form by infrared spectral studies.

Zinc(II), Cadmium(II) and mercury(II) complexes of 2-methyl-5-mercapto-1,3,4-thiadiazole(mttz) have been prepared¹⁵³. The ligand is bonded to the metal atom through its thiocarbonylic sulphur atom with terminal M-X bonds (M = Zn, Cd, Hg and (X = Cl, Br, I) for Zn and Hg and with bridging halide ions for cadmium complexes. For these polymeric complexes S_2N_2^- , S_2N_4^- or S_3N_3^- coordination has been proposed.

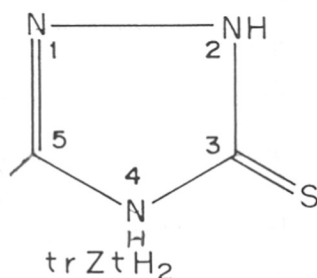
Palladium(II) halide complexes with 2,5-dimethyl-2-amino-, 2-amino-5-methyl-, 2-ethylamino- and 2-mercapto-5-methyl-1,3,4-thiadiazole have been synthesised

and characterised¹⁵⁴. The involvement of ring N or ring N and exocyclic sulphur atom has been proposed on the basis of IR spectral data.

Two types of copper complexes with Cu(I) (LH^-) and Cu(I), Cu(II) (LH^-) (LH^{2-0}) ($\text{LH} = 1,3,4\text{-thiadiazoline-2,5-dithione}$) have been prepared¹⁵⁵ and only N coordination is proposed for the former complex on the basis of the infrared data [(M-N), 540 cm^{-1}] and the appearance of two new bands due to $\nu(\text{M-N})$ and $\nu(\text{M-S})$ at 540 cm^{-1} and 380 cm^{-1} respectively in the infrared spectrum of the latter complex indicates the involvement of both N and S atoms in complexation.

$\text{MH}_2(\text{CO})(\text{PPh}_3)_3$ ($\text{M} = \text{Ru}$ or Os), $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, $\text{OsH}_2(\text{CO})_2(\text{PPh}_3)_2$ and $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ react with 1,3,4-thiadiazolidine-2,5-dithione (LH_2) in boiling toluene to afford the 1,3,4-thiadiazole-2,5-dithiolato complexes $\text{M}(\text{LH})_2\text{CO}(\text{PPh}_3)_2$, $\text{M}(\text{LH})_2(\text{CO})_2(\text{PPh}_3)_2$ and $\text{IrH}(\text{LH})_2(\text{CO})(\text{PPh}_3)_2$ respectively. The molecular structure has been determined by X-ray diffraction methods¹⁵⁶. The structure contains octahedral ruthenium(II) with monodentate (S-coordinated) and bidentate (N,S-coordinated) ligands, a carbonyl group and a trans pair of triphenylphosphine molecules.

The 1,2,4-triazoline-3(5)thione molecule, trzth_2 ,



is di-protic and may coordinate in the neutral (LH_2) or anionic (LH^- , L^{2-} , L = ligand) forms. The presence of $\nu(\text{NH})$ at 3050 cm^{-1} , as well as four thioamide bands ($1580, 1275, 1080, 650 \text{ cm}^{-1}$)^{155,156} suggests the thione form to be predominant in the solid state.

Coordination of trzth_2 occurs with a range of metals producing mostly polymeric and insoluble products. The most commonly coordinated form of the molecule is the monoanion, LH^- , which is invariably S,N-bridging. This is suggested by IR spectra which indicate an increase in bond order of the $\nu(\text{CN})$ containing vibrations and by low frequency $\nu(\text{M-L})$ activity.

The electronic spectrum of the nickel(II) complex (Dq 1016 cm^{-1} , β 0.74), suggests both fairly strong ligand fields and a moderate degree of covalency in the metal-ligand bonds. The parent molecule is monodentate

sulphur donating with platinum(II) in $\text{Pt}(\text{trzth}_2)_4\text{Cl}_2$ and the dianion, L^{2-} , forms a highly distorted octahedral complex with cobalt(II), $\text{CoL}\cdot 3\text{H}_2\text{O}$. The copper complex contains both +1 and +2 oxidation states of the metal as well as LH_2 and LH^- forms of the ligand and rhodium(III) coordinates with both the free molecule (LH_2) and the monoanion.

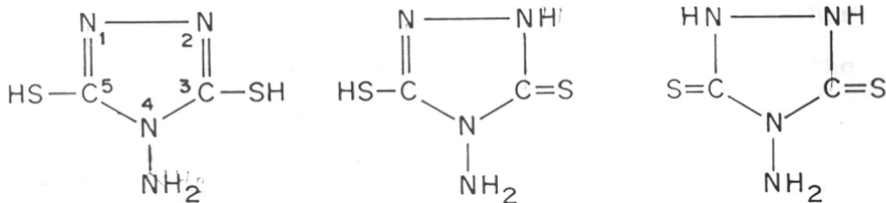
Infrared spectra of the N(4)- and C(5)-alkyl substituted derivatives of trzth_2 suggest that thione forms are present in the solid state and the coordination to silver(I) occurs through the sulphur¹⁵⁷.

Metal complexes have been reported^{158,159} of the 3-alkyl substituted derivatives of 1,2,4-triazoline-4-amino-5-thione. The IR spectrum of the molecule contains both $\nu(\text{SH})$ (2500 cm^{-1}) and $\nu(\text{CS})$ (750 cm^{-1}) and suggest that both the thiol and thione forms as shown above exist in the solid, the complexes however do not contain $\nu(\text{SH})$. Incidentally the crystal structure of 1,2,4-triazoline-3-hydrazino-4-amino-5-thione shows the thione tautomer to be dominant in the solid state with C(5)-S distance of $1.681(5)\text{ \AA}$ ¹⁶⁰, Coordination of this ligand occurs with deprotonation of the ligand in ammonia. Cobalt(II) and nickel(II) form hydrated octahedral chelates.¹⁵⁸

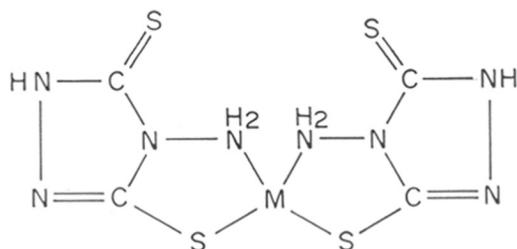
Zinc(II) and cadmium(II) produce tetrahedral (ML_2) chelates; copper(I), silver(I) and thallium(I) produce polymeric (ML) products¹⁵⁹ with λ (M-S) at 360 cm^{-1} and λ (M-N) at 400 cm^{-1} suggesting S,N coordination involving thiolate sulphur and amino nitrogen.

The \odot (5-pyridyl) derivative of $trztH_2$ is readily deprotonated at the N(4) position with the production of S,N chelates [Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Pt(II), Rh(III)] or S,N-bridged polymers [Cu(II), Pt(IV)]¹⁶¹⁻¹⁶³. The parent molecule monodentate sulphur donates to rhodium(I)¹⁶¹. All the complexes have 1:2 (metal:ligand) stoichiometry; the rhodium (I and III) complexes are dinuclear with chlorine bridging.

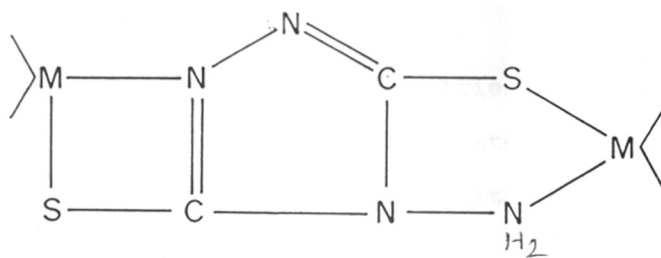
At least three forms of 1,2,4-triazoline-4-amino-3,5-dithione are possible.



The molecule is diprotic and is capable of coordinating in LH_2 , LH^- and L^{2-} forms. Two types of complexes are reported: $M(LH)_2(H_2O)_n$ [$M(II) = Co$ or Ni , $n = 2$; $M(II) = Zn, Cd, Pb$, $n = 0$] and $M(L)(H_2O)_n$ [$M(II) = Ni, Co$, $n = 4$; $M(II) = Cu, Zn$, $n = 2$; $M(II) = Pd, Cd$, $n = 1$]¹⁶⁴. Electronic spectra suggest octahedral cobalt ($Dq = 952\text{ cm}^{-1}$, $\beta = 0.92$), octahedral or tetragonal nickel and copper, as well as square ^{plane} palladium; zinc and cadmium are presumed to be tetrahedral. Infrared spectra suggest that the complexes of the mono-anion involve thiolate sulphur and amino nitrogen in S.N-chelation, whereas those of the



dianion involve both thiolate sulphur atoms together with amino nitrogen and heterocyclic nitrogen in the formation of S.N-bridged polymers.



The latter complexes are insoluble in common organic solvents. Most of the complexes also contain coordinated water.

Bridging of pairs of N(4)-phenyl substituted trzth_2 molecules at the C(5) and C(5) positions has been achieved by using ethylene glycol¹⁶⁵ and propyl¹⁶⁶ groups. Complexes of this molecule have a 1:1 (metal:ligand) stoichiometry when R = ethylene glycol. The nickel(II) and iron(III) complexes are octahedral and paramagnetic. The remaining complexes are diamagnetic with either tetrahedral [Zn(II), Hg(II)] or tetragonal [Cu(II)] structures. The diamagnetism of the copper(II) complex suggest the metal-metal interaction in the solid. Coordination occurs by means of thione sulphur donation in these polymeric species.

Complexes formed by the above ligand have a 1:2 (metal:ligand) stoichiometry when R = propyl. The nickel and zinc complexes are diamagnetic, the former is square^{planar} and the latter tetrahedral. The remaining complexes are paramagnetic with tetragonal [Cu(II)] or

octahedral [Co(II), Fe(III)] geometries. Coordination involves both of the thione sulphur atoms or a combination of thione sulphur and heterocyclic nitrogen.

3) Ruthenium Hydrido Complexes

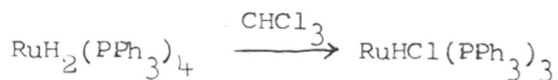
The first series of ruthenium hydrides with the general formula RuHCl(L)_2 (L = ligand) was prepared by reduction of $\text{RuCl}_2(\text{L})_2$ with lithium aluminium hydride¹⁶⁷; further reduction of the monohydrido complex with lithium aluminium hydride gave the dihydrido complex, $\text{RuH}_2(\text{L})_2$. The triphenylphosphine analogue, $\text{RuH}_2(\text{PPh}_3)_4$, is prepared by the reduction of ruthenium trichloride with sodium borohydride in presence of triphenylphosphine in boiling ethanol. The hydrido complexes are fairly stable substances with Ru-H stretching bands appearing between 1978 and 1804 cm^{-1} . They react with carbon monoxide, ligands containing nitrogen, oxygen and sulphur etc. with the elimination of hydrogen as well as triphenylphosphine groups.

Salts like $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$ reacted with ethanol in presence of potassium hydroxide to give a hydrido complex, $\text{RuHCl(CO)(PEt}_2\text{Ph)}_3$. PMR spectrum of the complex showed that the resonances due to hydridic

hydrogen is split into two triplets by coupling with the phosphorus nuclei¹⁶⁸. It was observed that $2J(\text{PH})_{\text{cis}}$ has a value of about 820 and $2J(\text{PH})_{\text{trans}}$, about 811.0. This observation has been widely used to ascertain the stereochemistry of similar complexes.

Many hydrido carbonyl complexes are obtained by decarbonylation of alcohols. Thus ruthenium trichloride reacts with triphenylphosphine in 2-methoxyethanol to yield $\text{RuHClCO}(\text{PPh}_3)_3$ ¹⁶⁹.

Many ruthenium hydrides react with halocarbon solvents to yield metal halide derivatives¹⁷⁰.

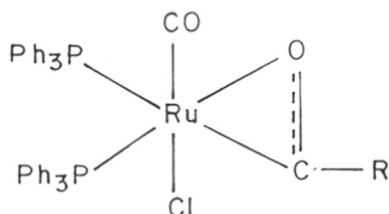


The hydrido ligand causes strong trans labilizing effect in $\text{RuHClCO}(\text{PR}_2\text{Ph})_3$ ($\text{R} = \text{Et}, \text{n-Pr}, \text{n-Bu}$)¹⁷¹. On adding tertiary phosphines, arsines, phosphites, etc. which are more strongly bonding than PR_2Ph , the phosphine trans to the hydride is displaced; the relative affinities of various ligands have been studied.

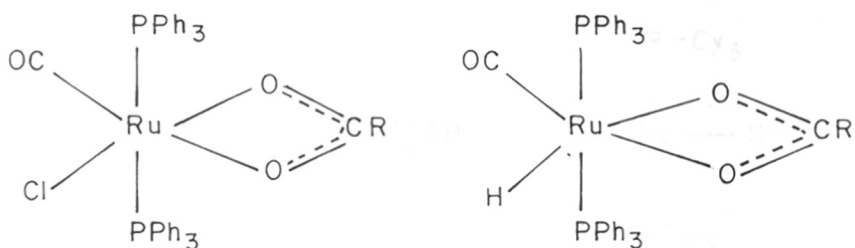
$\text{RuHX}(\text{PPh}_3)_3$ reacts with an excess of triphenylphosphite forming a Ru-C bond with the elimination of hydrogen and formation of $\text{RuX}[\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\text{P}(\text{OPh})_3]_3$.

$\text{RuHClCO}(\text{PPh}_3)_3$ reacts with aliphatic aldehydes

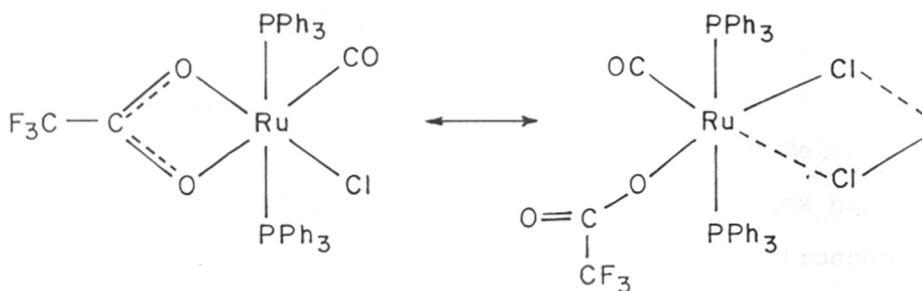
giving complexes with π bonded acyl groups¹⁷².



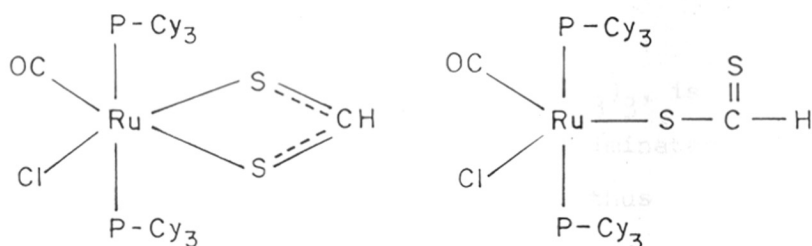
The carbonyl hydrido complex $\text{RuHClCO}(\text{PPh}_3)_3$ reacts with carboxylic acids in boiling 2-methoxyethanol forming a carboxylate eliminating hydrogen and one triphenylphosphine group; the dihydrido ruthenium complex also yields a similar product¹⁷³.



Perfluorocarboxylic acids¹⁷⁴ react with $\text{RuHClCO}(\text{PPh}_3)_3$ forming complexes where the carboxylate group functions as monodentate or bidentate. Spectral evidences suggest an equilibrium between a monomer and a dimer with chlorine bridges:

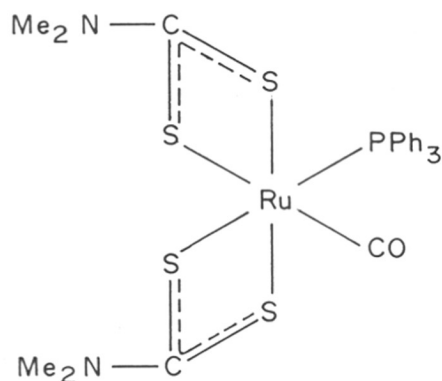


Hydrated ruthenium trichloride reacts with tricyclohexyl phosphine in 2-methoxyethanol¹⁷⁵ to give the hydrido complex $\text{RuHClCO}(\text{P-Cy}_3)_3$. Carbon disulphide reacts with the above complex forming $\text{RuClCO}(\text{P-Cy}_3)(\text{HCS}_2)$. Two structures have been proposed for this product.



A large number of dithiocarbamato and *o*-alkyl dithiocarbamato derivatives of the type $\text{M}(\text{S-S})_2(\text{PPh}_3)_2$, $\text{M}(\text{S-S})_2(\text{CO})(\text{PPh}_3)$, $\text{MH}(\text{S-S})\text{CO}(\text{PPh}_3)_2$ [$\text{M} = \text{Ru}$ or Os , $\text{S-S} = \text{R}_2\text{NCS}_2^-$, RCOS_2^- , $\text{R} = \text{Me}$ or Et] have been prepared by treating the appropriate chloro or carboxylato

complexes with sodium salt of the ligand¹⁷⁶. For example, the complex $\text{Ru}(\text{S}_2\text{CNMe}_2)_2\text{CO}(\text{PPh}_3)$ was obtained by vigorous and prolonged treatment of $\text{RuCl}(\text{OCOME})\text{CO}(\text{PPh}_3)_2$ with sodium dimethyldithiocarbamate. The complex has been assigned the following structure from spectroscopic evidences.



The chloro hydrido complex, $\text{RuHClCO}(\text{PPh}_3)_3$, is photosensitive. On UV/IR radiation, CO is eliminated giving $\text{RuHCl}(\text{PPh}_3)_3$ ¹⁷⁷. The carbon monoxide thus eliminated reacts with parent compound giving $\text{RuHCl}(\text{CO})_2(\text{PPh}_3)_2$.

The complexes $\text{Ru}(\text{OCOCF}_3)_2\text{CO}(\text{PPh}_3)$ and $\text{RuH}(\text{OCOCF}_3)\text{CO}(\text{PPh}_3)_2$ take up CO to form the dicarbonyl derivatives, the hydride adds to one PPh_3 group to form the tris-triphenylphosphine complex¹⁷⁸. $\text{Ru}(\text{OCOCF}_3)_2\text{CO}(\text{PPh}_3)_2$ reacts with β -diketones in presence of alcoholic KOH

to give $\text{RuH}(\text{acac})\text{CO}(\text{PPh}_3)_2$ where acac is a diketone.

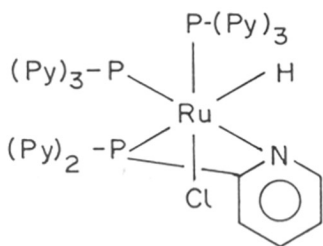
Insertion of CS_2 into Ru-H bond resulted in a series of complexes such as $\text{RuX}(\text{S}_2\text{CH})\text{CO}(\text{PPh}_3)_2$, $\text{Ru}(\text{S}_2\text{CH})_2(\text{PPh}_3)_2$, etc¹⁷⁹. Similar insertion reactions have been reported between hydrido complexes and alkyl and aryl isothiocyanates (RNCS) ¹⁸⁰ yielding complexes of the type $\text{RuX}(\text{RN}-\text{CH}=\text{S})\text{CO}(\text{PPh}_3)_2$. Similarly N,N'-di-p-tolylcarbodiimide ($\text{TOIN} = \text{C}=\text{N Tol}$) reacts with ruthenium hydrido complexes yielding isomers¹⁸¹.

Substituted olefins such as dimethyl fumarate, 2-vinyl pyridine and acrylonitrile insert into the Ru-H bond of $\text{RuClH}(\text{CO})(\text{PPh}_3)_3$ to yield substituted alkyl ruthenium(II) complexes¹⁸².

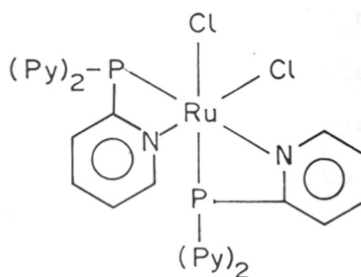
β -Diketones react with ruthenium hydrido compounds giving a series of complexes¹⁸³. Thus acetylacetone and $\text{RuHClCO}(\text{PPh}_3)_3$ give $\text{RuCl}(\text{acac})(\text{CO})(\text{PPh}_3)_2$. In presence of a chlorine acceptor the product is $\text{RuH}(\text{acac})(\text{CO})(\text{PPh}_3)_2$. $\text{RuH}_2(\text{PPh}_3)_4$ and acetylacetone give $\text{Ru}(\text{acac})_2(\text{PPh}_3)_2$. All these compounds show o,o'-coordination in the β -diketonato group. Similar results have been reported by Natrajan¹⁸⁴ from diketones such as dibenzoylmethane and benzoylacetone.

A five coordinated hydrido complex namely, $\text{RuHCl}(\text{CO})(\text{p-But-t-Me})_2$ is obtained when ruthenium trichloride and $\text{pBu}_2\text{t-R}$ ($\text{R} = \text{Me}$ or Et) are reacted in boiling 2-methoxyethanol¹⁸⁵. It takes up small molecules such as, CO , MeCN etc. giving hexa-coordinated complexes.

$\text{RuHCl}(\text{PPh}_3)_3$ reacts with tripyridylphosphine¹⁸⁶ to yield a complex (I) where one of the pyridylphosphine groups acts as a bidentate ligand. $\text{RuCl}_2(\text{PPh}_3)_3$ reacts with tripyridylphosphine to give a complex (II) where both the pyridylphosphine groups are bidentate.



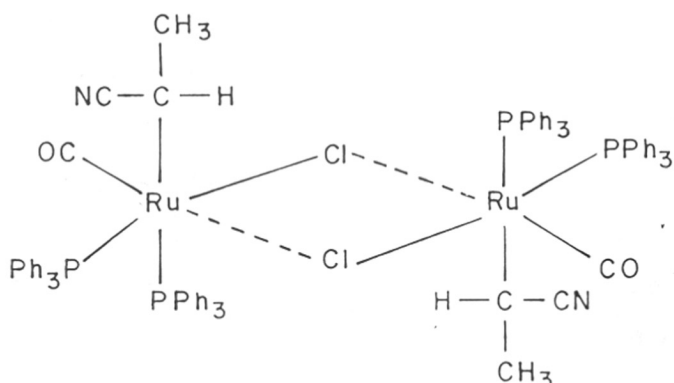
(I)



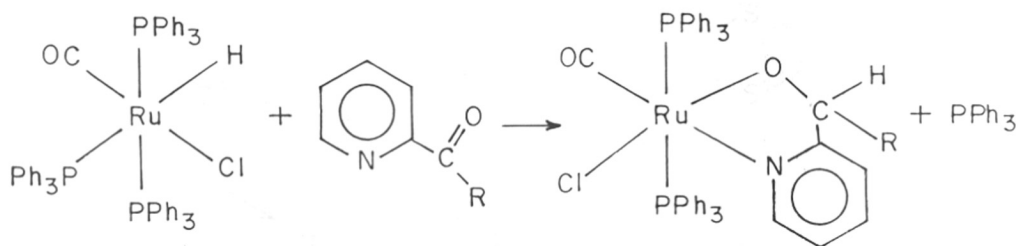
(II)

$\text{RuH}_2\text{CO}(\text{PPh}_3)_3$ reacts with palladium hexa-fluoroacetylacetonone¹⁸⁷ giving two complexes, $\text{RuHCO}(\text{Hfacac})(\text{PPh}_3)_2$ and $\text{RuCO}(\text{Hfacac})_2(\text{PPh}_3)$.

Acrylonitrile reacts with $\text{RuHClCO}(\text{PPh}_3)_3$ forming a metal carbon bonded compound¹⁸⁸.

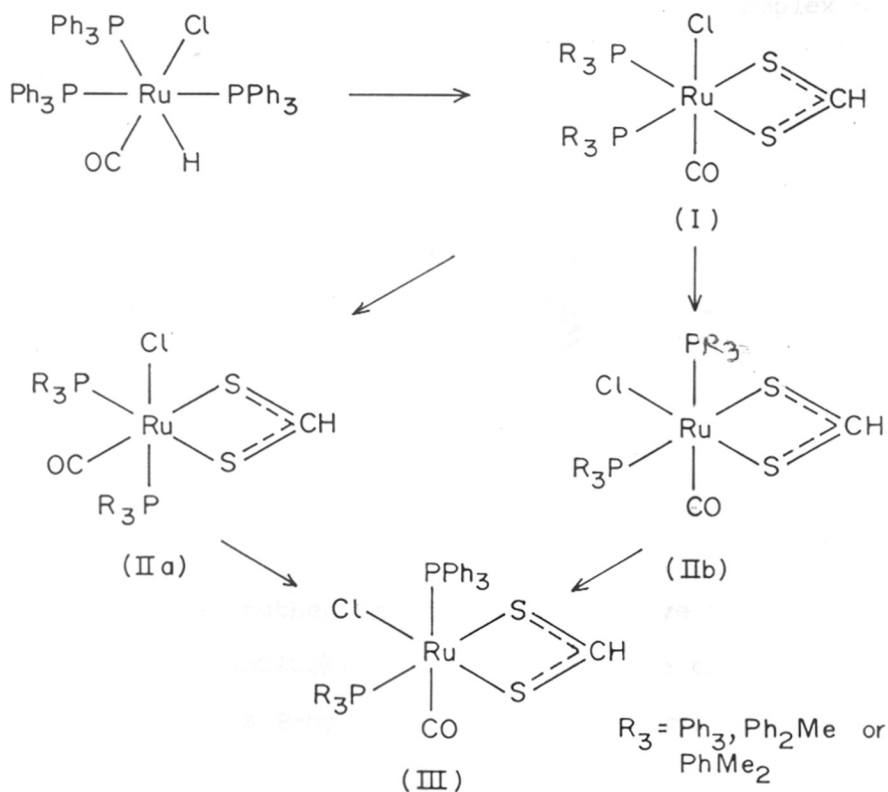


The chlorine bridges in the dimer complex can be cleaved with ligands like α -picoline. Similar reactions have been reported with fumaronitrile also. $\text{RuHClCO}(\text{PPh}_3)_3$ reacts with formylpyridine¹⁸⁹ in THF at room temperature to give $\text{cis-RuCl}(\text{OCH}_2\text{C}_6\text{H}_4\text{N})\text{CO}(\text{PPh}_3)_2$. The cis-complex isomerises to the trans complex in refluxing benzene. 2-Acetyl and 2-benzoyl-pyridines also react with the chloro hydrido complex to afford insertion products.



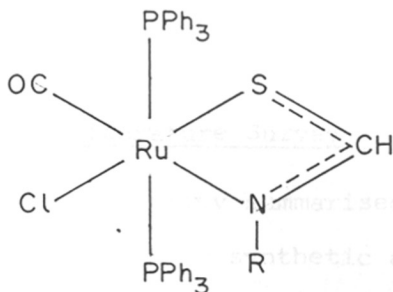
The isocyanide complexes of the type $[\text{RuHCl}(\text{CO})(\text{CNR})(\text{PPh}_3)_2]$ ($\text{R} = \text{Pr}^i, \text{Bu}^t, \text{or } p\text{-ClC}_6\text{H}_4$) were obtained by reacting $\text{RuHClCO}(\text{PPh}_3)_3$ with $(\text{CNR})_2$. The metal hydride stretching frequency could not be conclusively identified in the IR spectra of these compounds, since it is probably weak and occurred close to or under ν_{CN}^{190} .

$[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ reacts with carbon disulphide in boiling benzene to yield $[\text{RuCl}(\text{S}_2\text{CH})(\text{CO})(\text{PPh}_3)_2]$ (I)¹⁹¹ as air stable yellow crystalline solid. On further heating in benzene or toluene solution isomer(III) is formed.



The isomerisation process (I \rightarrow III) is thought to involve an intermediate isomer (IIa or IIb) for which no experimental evidence has been obtained.

Robinson et al¹⁹² has further found that alkyl and aryl isothiocyanates parallel carbon disulphide in their ability to insert into metal-hydrogen bonds and that the products contain the novel N-alkyl or N-arylthioformamide (RN---CH---S) chelate ligands with the general formula $[\text{RuCl}(\text{RN---CH---S})(\text{CO})(\text{PPh}_3)_2]$. The bidentate N,S-donor character of the thioformamide ligands has been established by infrared and NMR spectroscopy and following structure to the complex has been postulated.

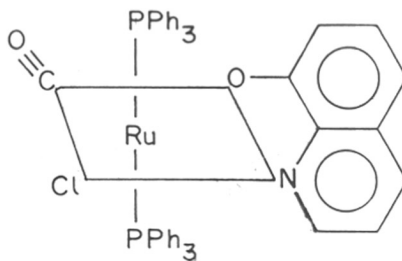


Several ruthenium(II) complexes have been prepared¹⁹³ by reacting $\text{HRuCl}(\text{CO})(\text{PPh}_3)_3$ with bidentate chelating ligands such as 8-hydroxyquinoline, salicylaldehyde-

hydrazone and β -diketones in 2-methoxyethanol.



The proton decoupled spectra of these complexes show a singlet for ^{31}P around 31.3 δ , ppm suggesting trans-disposition of phosphine groups around ruthenium and the following structure is suggested for these type of complexes:



Conclusions from Literature Survey

The literature survey summarised above reveals that many areas of work in synthetic and structural chemistry of metal complexes of thiosemicarbazones, 1,3,4-thiadiazol^{ine} thiones, 1,2,4-triazol^{ine}-thiones and thiazolidine thiones have remained unexplored.

Several thiosemicarbazones with aliphatic and aromatic aldehydes and ketones and their metal complexes have been synthesised and reported, however, less attention has been given to the class of α -heterocyclic thiosemicarbazones and their metal complexes.

2,5-Dimercapto-1,3,4-thiadiazole (Bismuthiol I) and 5-mercapto-3-phenyl-1,3,4-thiadiazoline-2-thione (Bismuthiol II) have been well known as analytical reagents for bismuth, palladium and copper. Most of their transition metal complexes have been reported. The chemistry of 5-alkylthio-1,3,4-thiadiazole^{ine}-2-thiones and their metal complexes has not been studied in detail. Similarly 1,2,4-triazole^{ine}-3-thione-4-phenyl-5-methyl and 1,2,4-triazole^{ine}-3-thione-4-phenyl-5-phenylethyl ligands and their metal complexes have not been characterised.

Hydridoruthenium complexes are known to undergo acidolysis with mild acids eliminating molecular hydrogen. Many organic ligands with potential hydroxyl groups like 8-hydroxyquinoline, salicylaldehyde hydrazone and β -diketones have been reacted with $\text{HRuClCO}(\text{PPh}_3)_3$ to yield stable hexa-coordinated ruthenium(II) complexes. However, hexa-coordinated ruthenium(II) complexes of nitrogen, sulphur containing heterocyclic ligands such

as, substituted 1,3,4-thiadiazoles^{ine}, 1,2,4-triazoles^{ine} and thiazolidine thiones have not been synthesised and characterised.

These observations prompted us to work in the unexplored areas and the investigations have been reported and discussed in the following chapters.

SUMMARY

Thiosemicarbazones and nitrogen, sulphur containing ligands like substituted 1,3,4-thiadiazoles, 1,2,4-triazoles and thiazolidine-2-thione have attracted much attention in recent years due to their pharmacological properties and donor capacity to form complexes with certain metal ions. While remarkable progress in understanding the activity of these compounds has been made by biological methods, the chemistry remains obscure in detail.

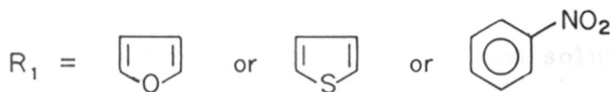
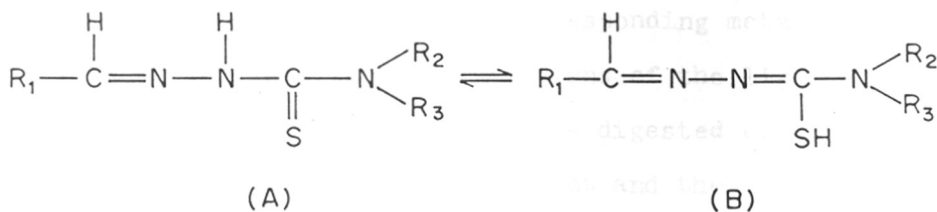
This thesis describes the synthesis and characterisation of square planar ³schiff base complexes of the type ML_2 where $M = Ni(II), Pd(II)$ and $Pt(II)$ and $HL =$ thiosemicarbazone, or 4-phenyl or 4-methyl thiosemicarbazone of 2-furaldehyde or thiophene-2-carboxaldehyde or 2-nitrobenzaldehyde. Metal complexes of 5-alkylthio-1,3,4-thiadiazoline-2-thiones of the type ML_2 where $M = Ni(II), Pd(II)$ and $Cd(II)$ and $HL =$ 5-alkylthio-1,3,4-thiadiazoline-2-thione (alkyl = methyl isopropyl or n-butyl) have been synthesised and characterised by elemental analysis and spectral measurements. Several new $Ru(II)$ complexes of the type $RuH(L)CO(PPh_3)_2$, $RuCl(L)CO(PPh_3)_2$ and $Ru(L)(CH_3CHCN)CO(PPh_3)_2$ $HL =$ 5-alkylthio-1,3,4-thiadiazoline-2-thione (alkyl = methyl, isopropyl or n-butyl), or 5-R'-4-R-1,3,4-triazoline-3-thiones (where R = phenyl, R = methyl and R = methyl,

R = phenethyl) or thiazolidine-2-thione have been prepared and characterised, and the data presented.

The thesis consists of four chapters. The first chapter gives a general introduction relevant to the literature on the topic of the research.

The second chapter describes the preparation and characterisation of thiosemicarbazone, 4-phenylthiosemicarbazone and 4-methylthiosemicarbazone of 2-furaldehyde, thiophene-2-carboxaldehyde and 2-nitrobenzaldehyde and their square planar metal complexes having Ni(II), Pd(II) and Pt(II) as the metal ions.

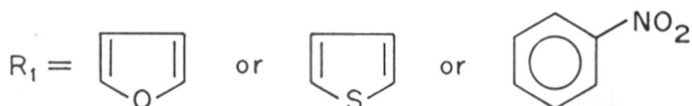
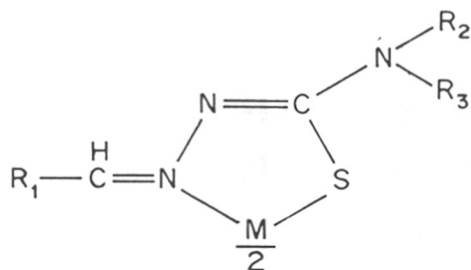
Thiosemicarbazones studied here exist in the thioketo form in solid state as observed in their infrared spectra.



$\text{R}_2 = \text{H}$ and

$\text{R}_3 = \text{Phenyl, Methyl or H}$

In the enolised form (B) they are potentially monobasic bidentate ligands coordinating through nitrogen (1) and the thiolate sulphur atom forming five membered chelate rings with metal ions.



$M = \text{Ni(II)} \text{ or } \text{Pd(II)} \text{ or } \text{Pt(II)}$

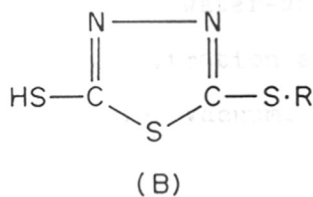
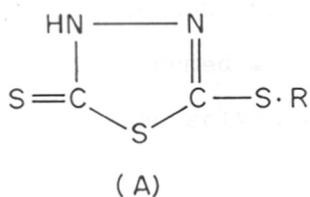
The metal complexes were prepared by mixing hot aqueous or alcoholic solutions of corresponding metal salts with aqueous or alcoholic solutions of the ligands in 1:2 molar ratios. The contents were digested on water-bath, filtered, washed with same solvent and the solids obtained were dried under vacuum.

The infrared spectra in chloroform solution of 2-furaldehyde thiosemicarbazone, 2-furaldehyde-4-phenylthiosemicarbazone and thiophene-2-carboxaldehyde-thiosemicarbazone show medium to weak absorption bands in the $2564\text{-}2538\text{ cm}^{-1}$ region due to $\nu(\text{SH})$.

The X-ray crystallographic data on bis(2-furaldehyde-thiosemicarbazonato)nickel(II), a greenish brown micro-crystalline diamagnetic compound has been presented. The data confirms the square planar geometry for this metal chelate with Ni-S = 2.149 Å and Ni-N = 1.92 Å and the coordination of the nickel ion through N and S donor atoms.

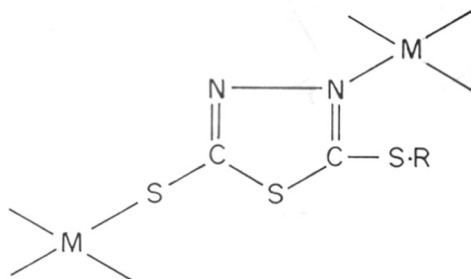
The third chapter describes synthesis and characterisation of 5-alkylthio-1,3,4-thiadiazoline-2-thiones (alkyl = methyl, isopropyl or n-butyl) and their Ni(II), Pd(II) and Cd(II) complexes by infrared and n.m.r. techniques.

5-Alkylthio-1,3,4-thiadiazoline-2-thiones studied here exist in thione form in solid state as evidenced from infrared spectral data. Bands attributable to ν (SH) in the region 2600-2550 cm^{-1} are absent in the spectra. However, in chloroform solution, weak absorptions at 2560 cm^{-1} due to ν (SH) along with medium to strong absorptions at 3400 cm^{-1} due to ν (NH) were observed. This confirms the existence of both thione (A) and thiol (B) forms of these ligands.



R = methyl, isopropyl or n-butyl.

^{13}C n.m.r. chemical shift data on 5-alkylthio-1,3,4-thiadiazoline-2-thiones indicate that these compounds exist predominantly in thione form in dimethyl sulphoxide solutions. On the basis of these results and infrared spectral assignments of the metal complexes following polymeric structure has been suggested for the metal complexes of these ligands.

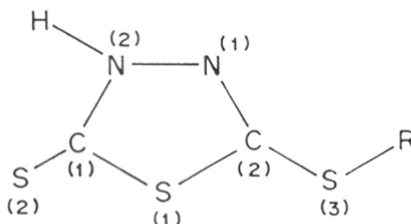


M = Ni(II), Pd(II) or Cd(II)

R = Methyl, isopropyl or n-butyl.

The metal complexes were synthesised by mixing hot aqueous alcoholic solutions of corresponding metal salts with the alcoholic solutions of the ligands in 1:2 molar ratios. The contents were refluxed on water-bath and the solids formed were isolated by filtration and washing with the same solvent and drying under vacuum.

The thione structure of 5-methyl-thio-1,3,4-thiadiazoline-2-thione has been confirmed by its X-ray crystallographic studies and the data are presented. The bond lengths S(2)-C(1) and C(1)-N(2) 1.665 Å and 1.330 Å respectively indicate partial double bond character, while C(2)-N(1) 1.282 Å is a pure double bond.



R = methyl, isopropyl or n-butyl.

The fourth chapter presents synthesis and spectral data on ruthenium(II) phosphine complexes of nitrogen, sulphur containing heterocyclic ligands.

Several hexacoordinated ruthenium(II) phosphine complexes containing bidentate chelating ligands with N, O or O, O donor atoms have been reported in ^{the} literature. However, comparatively less attention has been given towards the chemistry of ruthenium(II) phosphine complexes with N, S containing heterocyclic ligands.

Triphenylphosphine stabilized ruthenium(II) complexes are found to be selective towards hydrogenation of alkenes under mild conditions like room temperature and atmospheric pressure. Chlorohydridotris(triphenylphosphine)ruthenium(II) is known to be a specific hydrogenation catalyst for alkenes under mild conditions. $\text{RuHClCO}(\text{PPh}_3)_3$ is a well known catalyst for the reduction of aldehydes and ketones.

To study the bonding nature of N-S containing heterocyclic ligands with ruthenium(II) metal ion, several new ruthenium(II) phosphine complexes of the ligands 5-phenyl-4-methyl-1,2,4-triazoline-3-thione, 5-methyl-4-phenethyl-1,2,4-triazoline-3-thione, thiazolidine-2-thione and 5-alkylthio-1,3,4-thiadiazoline-2-thiones (alkyl = methyl, isopropyl or n-butyl) have been synthesised and characterised by elemental analyses, ^1H n.m.r. and infrared spectral data.

The intermediate ruthenium complexes $\text{RuHClCO}(\text{PPh}_3)_3$ and $[\text{Ru}(\text{CH}_3\text{CHCN})\text{ClCO}(\text{PPh}_3)_2]_2$ were prepared by reported methods. The reactions were carried out under dry nitrogen atmosphere using freshly dried, distilled and degassed solvents.

Sodium derivatives of ligands were prepared by stirring the corresponding ligands and sodium hydride in equimolar ratios in diethyl ether. The ether was

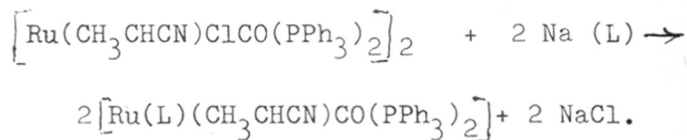
removed and the solid was suspended in THF. The suspensions of the sodium salts of the ligands were used for their reactions with the intermediate ruthenium complexes.

Sodium derivatives of the ligands (HL) react with $\text{RuHClCO}(\text{PPh}_3)_3$ in THF at room temperature when mixed in equimolar ratios and stirred for 16 hrs to furnish chlorine free chelated Ru(II) complexes.



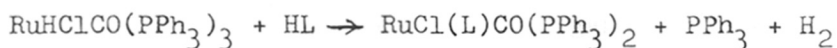
These complexes are light yellow, microcrystalline solids, stable towards air and sparingly soluble in common organic solvents.

Similarly the dimer $\left[\text{Ru}(\text{CH}_3\text{CHCN})\text{ClCO}(\text{PPh}_3)_2\right]_2$ reacts with the sodium derivatives of the ligands (HL) in 1:2 molar ratio to give mononuclear complexes of the type $\text{Ru(L)}(\text{CH}_3\text{CHCN})\text{CO}(\text{PPh}_3)_2$.



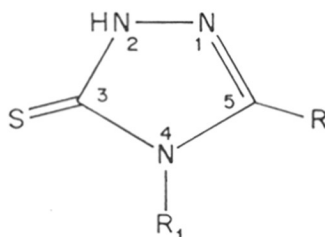
The products are yellow solids, stable towards air and slightly soluble in common organic solvents.

(L) chlorocarbonylbis(triphenylphosphine)ruthenium(II) complexes were isolated from 2-methoxyethanol by refluxing $\text{RuHClCO}(\text{PPh}_3)_3$ and the ligands (HL) in 2-methoxyethanol in equimolar ratios.



The complexes are cream yellow, stable towards air and slightly soluble in common organic solvents.

The infrared spectra of 1,2,4-triazoline-3-thione-5-methyl-4-R (R = phenyl or phenylethyl) do not show any absorption in the region $2600\text{--}2550\text{ cm}^{-1}$ due to $\nu(\text{SH})$ favouring the thione structure of the ligands in solid state. In chloroform solution, 1,2,4-triazole ligands show strong absorption at 3420 cm^{-1} due to $\nu(\text{NH})$ indicating that they exist in thione form in chloroform solution.

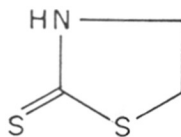


R = phenyl, R₁ = methyl .

R = methyl, R₁ = phenethyl .

The infrared spectra of thiazolidine-2-thione in solid state and in chloroform solution show absorption at 3100 cm^{-1} and 3400 cm^{-1} respectively. No absorption

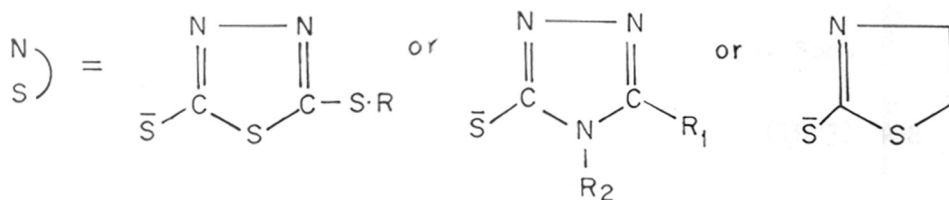
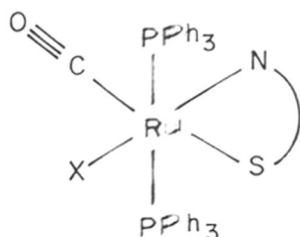
due to $\nu(\text{SH})$ around $2600\text{-}2550\text{ cm}^{-1}$ has been observed in these spectra. ^1H n.m.r. of the ligand in CDCl_3 gives a broad weak signal at 8.1 ppm due to NH. These results clearly support the thione structure of the ligand.



The bidentate coordination of these ligands has been evidenced by the disappearance of $\nu(\text{NH})$ (3100 cm^{-1} and $\nu(\text{C-N})$ ($1285\text{-}1260\text{ cm}^{-1}$) frequencies and the appearance of the new bands in the region $600\text{-}700\text{ cm}^{-1}$ and $400\text{-}300\text{ cm}^{-1}$ regions due to (C-S) and (M-N), (M-S) stretching vibrational modes in the infrared spectra of all the ruthenium complexes. The complexes of the type $\text{RuH(L)CO(PPh}_3)_2$ show an absorption at 2020 cm^{-1} of weak intensity ascribable to $\nu(\text{Ru-H})$.

The chemical shift due to Ru-H resonance in ^1H n.m.r. of $\text{RuH(L)CO(PPh}_3)_2$ type complexes is observed at $\overset{\pm 0}{-13.0\text{-}13.3}$ ppm. The resonances due to $-\text{CH}_3$, $-\text{CH}_2$ and $-\text{CH}$ protons of the complexes were observed at 2.7-1.27, 1.5-1.4 and 3.7-2.4 ppm respectively.

From these data the following hexacoordinated structure to the complexes has been proposed.



R = Methyl, isopropyl or n-butyl .

R₁ = phenyl, R₂ = methyl .

R₁ = methyl, R₂ = phenethyl .

The above mentioned aspects of the chemistry of sulphur and nitrogen containing ligands and the coordination and organometallic chemistry of their complexes with some metals, mainly from the Group VIII, form the basis of this thesis.

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**CHAPTER II : SYNTHESIS AND SPECTRAL STUDIES OF
SOME HETEROCYCLIC CARBOXALDEHYDE
THIOSEMICARBAZONES AND THEIR METAL
COMPLEXES**

Introduction

The α -(N)-heterocyclic carboxaldehyde thiosemicarbazones constitute a class of chelating agents which possess both antineoplastic and antiviral activity¹. The first compound to be examined for biological activity, 2-formyl pyridine thiosemicarbazone, was shown to possess mild antileukemic activity against L-1210 tumour in mice at levels of drug which produced significant toxicity^{2,3}. The biological activity of this class of compounds is associated with chelation and direct correlation between antitumour activity and chelating ability of several of these compounds was shown by Michaud and Sartorelli⁴. Similarly the mode of antiviral action of methisazone (1-methylisatin- β -thiosemicarbazone) - the first synthetic antiviral drug - is initially thought to be metal chelation⁵. More recently coprecipitation of copper ion, methisazone and nucleic acids has been observed and was suggested to be important for the in vivo antiviral action of methisazone⁶. There are many thiosemicarbazone-copper(II) complexes which have significant antitumour activity⁷⁻⁹.

While remarkable progress in understanding the activity of these compounds has been made by biological methods, the chemistry remains obscure in detail.

Furthermore, pyridine and isoquinoline are the two heterocyclic ring systems which have been more extensively investigated^{3,10} for structure activity relationships. Thiosemicarbazones of other available ring systems have not been to any extent explored. In an attempt to gain more insight into the nature of bonding and stereochemistry present in this class of compounds, metal chelates of ligands with carboxaldehyde thiosemicarbazone side chain \rightarrow to an unencumbered ring oxygen (sulphur) of heteroaromatic carboxaldehyde thiosemicarbazones have been synthesised and studied. Infrared, UV-visible, ^1H and ^{13}C n.m.r. spectra and polarographic techniques have been used to characterise free ligands and their metal chelates.

X-ray crystallographic data on bis(2-furaldehyde-thiosemicarbazonato)nickel(II) clearly supports square planar structure of the chelate with $\text{Ni-S} = 2.149(1) \text{ \AA}$ and $\text{Ni-N}(2) = 1.921(2) \text{ \AA}$.

Experimental

2-Furaldehyde, thiophene-2-carboxaldehyde, 2-nitrobenzaldehyde, thiosemicarbazide, 4-methyl thiosemicarbazide and 4-phenyl thiosemicarbazide and DMSO-d_6 were purchased from Fluka AG, Switzerland or from Aldrich Chemical Company, Inc., U.S.A. All other chemicals used were of A.R. grade. Solvents were purified and dried prior to use.

K_2PtCl_4 and Na_2PdCl_4 were prepared by reported methods¹¹.

Thiosemicarbazones used here were prepared by a general method¹². A thiosemicarbazide is condensed with an aldehyde in alcoholic medium in equimolar quantities in presence of glacial acetic acid (1-2 ml). The crude products obtained were purified by repeated crystallization from chloroform or alcohol.

The deuterio analogues were prepared by either refluxing with D_2O (99.8%, Atomic Energy Commission, Bombay) or with acetonitrile and D_2O under N_2 atmosphere, followed by evaporation of the solvent under vacuum.

Nickel chelates were synthesised by mixing aqueous alcoholic solutions of nickel chloride hexahydrate, $NiCl_2 \cdot 6H_2O$, and the corresponding aldehyde thiosemicarbazone in alcohol. The pH of the resulting solution was adjusted to 7.0-7.5 with dilute ammonia (1:3). The mixture was heated on a waterbath for 1 hr and the solid products (green to brown) were collected on a filter under suction, washed with water (2x5 ml) followed by ethanol (2x5 ml) and dried under vacuum.

Platinum(II) and palladium(II) chelates (yellow to orange) were prepared by reacting aqueous solutions of K_2PtCl_4 or Na_2PdCl_4 with aqueous or alcoholic solutions

of the thiosemicarbazones at pH 7.0-7.5 and heating the mixture on waterbath for 1 hr. The solid products obtained were isolated and dried under vacuum.

Preparation of thiosemicarbazones

1. 2-Furaldehyde thiosemicarbazone, 2-fur-tsc

Thiosemicarbazide (9.1 g, 0.1 mole) was dissolved in warm water (250 ml) and the alcoholic solution (100 ml) of 2-furaldehyde (9.6 g, 0.1 mole) was added to it followed by 1-2 ml of glacial acetic acid. The clear light yellow solution was refluxed on waterbath for 5 hrs. The yellow crystalline product obtained after filtration was recrystallised from alcohol.

Yield 12 g (71%). M.p. 156°C.

Analysis: Found C, 43.26; H, 4.63; N, 22.54; S, 19.46%.

Calculated for $C_6H_7N_3OS$: C, 42.60; H, 4.14; N, 24.85; S, 18.93%.

Infrared spectrum shows the following absorption frequencies (cm^{-1}) in nujol: 3400s, 3220s,b, 3140sb, 1605s, 1580s, 1520s, 1340s, 1280sb, 1220m, 1150m, 1095sb, 1060m, 1020s, 930s, 920m, 880m, 840s, 820m, 760s, 715m, 610mb, 600m, 555mb, 430s, 380m.

2. Deuterated 2-furaldehyde thiosemicarbazone, d-2-fur-tsc

2-fur-tsc (0.5 g) was dissolved in hot acetonitrile (5 ml) and D_2O (10 ml) was added to it. The clear

solution was refluxed under N_2 stream for 5 hrs. The cream white solid product was filtered under N_2 and dried under vacuum. Yield 0.4 g (80%).

Infrared absorption frequencies (cm^{-1}) in nujol: 2560m, 2400s, 1620m, 1500w, 1400s, 1330m, 1280w, 1245w, 1140m, 1085w, 1065w, 1010s, 930m, 900m, 880w, 840w, 820m, 750m, 725m, 630w, 590m, 550w, 410sb, 390sb.

3. Bis(2-furaldehydethiosemicarbazonato)nickel(II),
Ni(2-fur-tsc)₂

This compound was prepared by heating solutions of 2-fur-tsc (0.338 g, 0.002 mole) in alcohol (10 ml) and nickel chloride hexahydrate, $NiCl_2 \cdot 6H_2O$, in alcohol (10 ml) and adjusting the pH of the clear light greenish solution to 7.05 with dilute ammonia (1:3). The mixture was heated on waterbath for 1 hr. The green compound formed was isolated by filtration and dried under vacuum.

Yield 0.35 g (89%). M.p. $250^{\circ}C$ (decomp.).

Analysis: Found C, 36.60; H, 3.26; N, 20.05; S, 15.97; Ni, 15.07%. Calculated for $C_{12}H_{12}N_6O_2S_2Ni$: C, 36.49; H, 3.04; N, 21.28; S, 16.21; Ni, 14.87%.

Infrared absorption frequencies (cm^{-1}) observed in nujol: 3360m, 3260m, 3150m, 1590s, 1510sb, 1330s, 1230m, 1140s, 1090s, 1005s, 940m, 885m, 820s, 760s, 715m, 670s, 590m, 460s, 320m.

4. Bis-(2-furaldehydethiosemicarbazonato)palladium(II)
Pd(2-fur-tsc)₂

2-Fur-tsc (0.676 g, 0.004 mole) was dissolved in hot alcohol (70 ml) and added to the solution of Na₂PdCl₄ (0.588 g, 0.002 mole) in water (25 ml) with stirring. The pH of the mixture was adjusted to 7.05 with the addition of dilute NaOH solution (0.1 N) and the mixture was heated on waterbath for 30 minutes. The orange compound formed was filtered and washed with water (3x5 ml) and alcohol (2x5 ml) and dried under vacuum. Yield 0.5 g (62%). M.p. 251°C (decomp.).

Analysis: Found C, 32.51; H, 3.08; N, 18.43; S, 13.17; Pd, 24.25%. Calculated for C₁₂H₁₂N₆O₂S₂Pd: C, 32.68; H, 2.72; N, 18.98; S, 14.46; Pd, 24.10%.

Infrared absorption maxima (cm⁻¹) in nujol are: 3470w, 3290m, 3150w, 1590s, 1510s, 1320s, 1240w, 1140m, 1090s, 1020m, 940m, 900w, 885w, 830s, 765s, 710w, 665s, 600m, 440m, 320w.

5. Bis(2-furaldehydethiosemicarbazonato)platinum(II)
Pt(2-fur-tsc)₂

This compound was prepared by mixing hot solutions of 2-fur-tsc (0.338 g, 0.002 mole) in water (50 ml) and K₂PtCl₄ (0.415 g, 0.001 mole) in water (5 ml). The mixture was adjusted to pH 7.0 with the addition of dilute NaOH solution (0.1 N) and heated on waterbath

for 30 minutes. The yellow compound formed was collected on filter, washed with hot water (3x5 ml) and dried under vacuum. Yield 0.4 g (75%). M.p. 247°C (decomp.). Analysis: Found C, 27.69; H, 2.78; N, 15.50; S, 13.27%, Pt, 36.11%. Calculated for $C_{12}H_{12}N_6O_2S_2Pt$: C, 27.11; H, 2.26; N, 15.81; S, 12.05; Pt, 36.74%.

Infrared absorption frequencies (cm^{-1}) observed in nujol: 3390w, 3240m, 3160w, 1590s, 1495s, 1330s, 1230m, 1135s, 1090s, 1005s, 940m, 885w, 820s, 755s, 720s, 660s, 590m, 450m, 320m.

6. 2-Furaldehyde-4-methylthiosemicarbazone, 2-furmethylsc

4-Methyl thiosemicarbazide (2.1 g, 0.02 mole) was dissolved in hot alcohol (50 ml) and 2-furaldehyde (1.92 g, 0.02 mole) was added to it followed by addition of glacial acetic acid (1 ml). The clear solution was refluxed for 4 hrs and concentrated to half of its original volume to yield a yellow product (3 g). This was recrystallised from alcohol. Yield 2 g (55%). M.p. 163°C.

Analysis: Found C, 45.72; H, 5.21; N, 22.00; S, 16.25%. Calculated for $C_7H_9N_3OS$: C, 45.90; H, 4.92; N, 22.95; S, 17.49%.

Infrared spectrum in nujol shows the following absorption frequencies (cm^{-1}): 3370m, 3155m, 1535s, 1330w, 1285s, 1220s, 1080w, 1070m, 1020m, 925m, 885m, 805m, 755m, 700s, 550w, 510m, 410m.

7. Bis(2-furaldehyde-4-methylthiosemicarbazonato)nickel(II)

2-fur-methyltsc (0.336 g, 0.002 mole) was dissolved in hot alcohol (30 ml) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (90.238 g, 0.001 mole) dissolved in water (5 ml) was added to it. The pH of clear solution was adjusted to 7.05 with the addition of dilute ammonia (1:3) and the green compound formed was isolated by filtration and washing with water (2x5 ml) and alcohol (2x5 ml). The compound was dried under vacuum. Yield 0.3 g (72%). M.p. 255°C (decomp.). Analysis: Found C, 39.21; H, 4.08; N, 19.00; S, 15.72; Ni, 14.07%. Calculated for $\text{C}_{14}\text{H}_{16}\text{N}_6\text{O}_2\text{S}_2\text{Ni}$: C, 39.74; H, 3.79; N, 19.87; S, 15.14; Ni, 13.89%.

Infrared absorption frequencies (cm^{-1}) in nujol: 3380w, 1530m, 1320w, 1280s, 1200s, 1070w, 1060w, 1005m, 920w, 875m, 800w, 750m, 705s, 695m, 540m, 520m, 415w, 360w.

8. 2-Furaldehyde-4-phenyl-thiosemicarbazone, 2-fur-4-phenytsc

This ligand was prepared by refluxing the solutions of 4-phenytsc (4.1 g, 0.04 mole) in alcohol (120 ml) and 2-furaldehyde (2.4 g, 0.04 mole) for 5 hrs in presence of 1 ml glacial acetic acid. The crude product was isolated by filtration and recrystallised from alcohol. Yield 4.1 g (67%). M.p. 181°C . Analysis: Found C, 58.88; H, 4.90; N, 16.12; S, 12.35%. Calculated for $\text{C}_{12}\text{H}_{11}\text{N}_3\text{OS}$: C, 58.78; H, 4.49; N, 17.14; S, 13.06%.

Infrared spectrum in nujol shows following

absorption maxima (cm^{-1}): 3280m, 3120mb, 1620w, 1595w, 1515s, 1320w, 1275s, 1210s, 1090w, 1070m, 1020m, 925m, 885w, 800m, 750m, 735s, 690s, 540w, 500m.

9. Deuterated 2-furaldehyde-4-phenylthiosemicarbazone,
d-2-furtsc

2-furphenytsc (0.4 g) was dissolved in 4 ml hot acetonitrile and 10 ml D_2O was added to it. The resulting clear solution was refluxed under N_2 atmosphere for 4 hrs. The cream coloured product was filtered and dried under vacuum. Yield 0.3 g (75%).

Infrared absorption maxima (cm^{-1}) observed in nujol: 3290w, 3120w, 2440m, 2300m, 1615w, 1495w, 1330s, 1240m, 1220w, 1100m, 1060m, 1000s, 930m, 880m, 790m, 760s, 730s, 690m, 560w, 490w.

10. Bis(2-furaldehyde-4-phenyl-thiosemicarbazonato)-
nickel(II)

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g, 0.001 mole) dissolved in alcohol (5 ml) was added to 2-fur-4-phenytsc (0.49 g, 0.002 mole) dissolved in hot alcohol (35 ml). The pH of the deep brown clear solution was adjusted to 7.0 with the addition of dilute ammonia (1:3) and the mixture was heated on waterbath for 30 minutes. The greenish brown compound was isolated by filtration and washing it with alcohol (2x5 ml) and drying under vacuum. Yield 0.42 g (77%). M.p. 254°C (decomp.).

Analysis: Found C, 52.48; H, 3.85; N, 14.60; S, 10.40; Ni, 11.05%. Calculated for $C_{24}H_{20}N_6O_2S_2Ni$:
C, 52.68; H, 3.66; N, 15.36; S, 11.71; Ni, 10.74%.

Infrared absorption frequencies (cm^{-1}) observed in nujol: 3110w, 1600m, 1595w, 1505w, 1320m, 1255m, 1200w, 1090m, 1045w, 1020m, 950w, 870w, 755m, 745s, 695s, 600m, 525w, 500m, 430m, 395w.

11. Bis(2-furaldehyde-4-phenyl-thiosemicarbazonato)-palladium(II)

Na_2PdCl_4 (0.294 g, 0.001 mole) in water (25 ml) was added to 2-fur-phenytsc (0.49 g, 0.002 mole) dissolved in hot alcohol (40 ml) and the pH of mixture was adjusted to 7.05 with dilute NaOH solution (0.1 N) and heated on waterbath for 1 hr. The orange yellow product formed was filtered and washed with hot water (2x5 ml) and alcohol (2x5 ml) and dried under vacuum. Yield 0.4 g (67%). M.p. 265°C (decomp.).

Analysis: Found C, 48.35; H, 3.54; N, 13.60; S, 11.33; Pd, 18.27%. Calculated for $C_{24}H_{20}N_6O_2S_2Pd$: C, 48.45; H, 3.36; N, 14.13; S, 10.77; Pd, 17.90%.

Infrared absorption maxima in nujol were as follows:
3110w, 1600m, 1500m, 1330s, 1255s, 1200m, 1080m, 1050s, 1020m, 950m, 870m, 760s, 740m, 695s, 600w, 520m, 500s, 405m, 370m.

12. Bis(2-furaldehyde-4-phenyl-thiosemicarbazonato)
platinum(II)

2-Fur-4-phenytsc (0.49 g, 0.002 mole) was dissolved in hot water (50 ml) and K_2PtCl_4 (0.415 g, 0.001 mole) in water (5 ml) was added to it. The pH of mixture was adjusted to 7.05 with the addition of dilute NaOH (0.1 N) and heated on waterbath for 1 hr. The yellow compound formed was filtered and washed with hot water (3x10 ml) and dried under vacuum. Yield 0.4 g (59%). M.p. 235°C (decomp.).

Analysis: Found C, 43.24; H, 3.42; N, 11.75; Pt, 29.13%. Calculated for $C_{24}H_{20}N_6O_2S_2$: C, 42.16; H, 2.93; N, 12.30; Pt, 28.56%.

Infrared absorption spectrum in nujol shows following maxima (cm^{-1}): 3400w, 3230w, 3150m, 1505m, 1330s, 1250s, 1200m, 1085m, 1060s, 1010m, 940m, 880w, 760s, 725s, 695s, 600m, 525m, 500m, 415m, 375w.

13. Thiophene-2-carboxaldehyde-thiosemicarbazone, Thiophtsc

Thiophene-2-carboxaldehyde (2.8 g, 0.025 mole) in alcohol (5 ml) was added to 4-phenyl thiosemicarbazide (4.17 g, 0.025 mole) dissolved in hot alcohol (150 ml) followed by addition of glacial acetic acid (2 ml). The clear solution was refluxed for 5 hrs and cooled to room temperature (28°C) overnight. The light yellow crude product was collected on filter and recrystallised from

alcohol and chloroform mixture (1:1). Yield 4.0 g (62%).

M.p. 191°C.

Analysis: Found C, 39.10; H, 4.11; N, 21.66; S, 33.29%.

Calculated for $C_6H_7N_3S_2$: C, 38.92; H, 3.78; N, 22.70; S, 34.59%.

Infrared absorption spectrum in nujol shows following maxima (cm^{-1}): 3400s, 3220w, 3120m, 1615s, 1570m, 1530s, 1425m, 1320s, 1275m, 1220m, 1100s, 1060m, 1040m, 940m, 920s, 830s, 740s, 720s, 610s, 550s, 410s.

14. Deuterated thiophene-2-carboxaldehyde-thiosemi-carbazone-d-thiophtsc

Thiophtsc (0.5 g) was dissolved in hot acetonitrile (10 ml) and D_2O (10 ml) was added to it. The mixture was refluxed under N_2 atmosphere for 5 hrs. The solid obtained was filtered under N_2 and dried under vacuum. Yield 0.38 g (76%).

Infrared absorption frequencies (cm^{-1}) observed in nujol are: 3400vw, 3220vw, 3140w, 2530s, 2320bs, 1590m, 1490bs, 1430m, 1320s, 1255m, 1220m, 1080m, 1040w, 1015s, 940m, 830m, 720m, 700m, 610m, 500m, 390bs.

15. Bis(thiophene-2-carboxaldehyde thiosemicarbazonato)-nickel(II)

This compound was prepared by adding solution of $NiCl_2 \cdot 6H_2O$ (0.47 g, 0.002 mole) in water (10 ml) to the hot solution of the ligand thiophtsc (0.74 g, 0.004 mole)

in alcohol (75 ml). The clear green solution was stirred and its pH was adjusted to 7.0 with the addition of dilute ammonia (1:3). The greenish brown precipitate formed was heated on waterbath for 40 minutes and isolated by filtration and washing with alcohol (3x5 ml). It was dried under vacuum. Yield 0.58 g (68%). M.p. 257°C (decomp.). Analysis: Found C, 34.05; H, 3.10; N, 18.33; Ni, 12.32%. Calculated for $C_{12}H_{12}N_6S_4Ni$: C, 33.75; H, 2.81; N, 19.69; Ni, 13.76%.

Infrared spectrum in nujol shows following absorption maxima (cm^{-1}): 3390m, 3280m, 3170w, 1610m, 1570w, 1510s, 1410s, 1320s, 1220s, 1055s, 1020m, 940m, 920m, 815s, 735m, 710s, 640s, 390m, 315w.

16. Bis(thiophène-2-carboxaldehyde thiosemicarbazonato) palladium(II)

Hot solutions of Na_2PdCl_4 (0.294 g, 0.001 mole) in water (50 ml) and thiophtsc (0.37 g, 0.002 mole) in water (150 ml) were mixed and heated on waterbath by adjusting the pH of the mixture to 7.05 with the addition of dilute NaOH (0.1 N). The yellow compound formed was isolated by filtration and washed with hot water (3x5 ml) and dried under vacuum. Yield 0.3 g (63%). M.p. 278° (decomp.).

Analysis: Found C, 30.74; H, 2.86; N, 16.33; S, 25.55; Pd, 23.41%. Calculated for $C_{12}H_{12}N_6S_4Pd$: C, 30.35; H, 2.53; N, 17.71; S, 26.98; Pd, 22.43%.

Infrared absorption maxima (cm^{-1}): observed in nujol 3370m, 3270m, 3160w, 1590m, 1570w, 1500s, 1410s, 1330s, 1250m, 1220s, 1060m, 940m, 810s, 715s, 625s, 380w, 300w.

17. Bis(thiophene-2-carboxaldehyde thiosemicarbazonato) platinum(II)

Thiophthsc (0.37 g, 0.002 mole) dissolved in hot water (10 ml) was added to K_2PtCl_4 (0.415 g, 0.001 mole) in water (5 ml) and the pH of the mixture was adjusted to 7.05 with dilute NaOH (0.1 N). The yellow compound formed was heated on waterbath for 40 minutes and collected on filter. It was washed with hot water (3x50 ml) and dried under vacuum. Yield 0.42 g (75%). M.p. 276°C (decomp.).

Analysis: Found C, 26.03; H, 2.89; N, 13.69; Pt, 34.96%. Calculated for $C_{12}H_{12}N_6S_4Pt$: C, 25.57; H, 2.13; N, 14.92; Pt, 34.65%.

Infrared absorption frequencies (cm^{-1}) observed in nujol: 3365m, 3260m, 3160w, 1585m, 1560w, 1500s, 1405s, 1330s, 1250m, 1220s, 1060m, 940m, 805s, 710s, 620s, 375w, 305w.

18. Thiophene-2-carboxaldehyde-4-methyl thiosemicarbazone,
Thioph-4-methyltsc

Solutions of 4-methylthiosemicarbazide (2.278 g, 0.0217 mole) in hot alcohol (120 ml) and thiophene-2-carboxaldehyde (2.43 g, 0.0217 mole) in alcohol (2 ml) were refluxed in presence of glacial acetic acid (1.5 ml) for 3 hrs. The reaction mixture was cooled overnight at room temperature (28°C). The white crystalline solid settled at the bottom of the container was collected on filter and dried. It was recrystallised from alcohol. Yield 3.2 g (80%). M.p. 159°C.

Analysis: Found C, 43.74; H, 4.55; N, 19.98; S, 31.24%.
Calculated for $C_7H_9N_3S_2$: C, 42.21; H, 4.52; N, 21.10; S, 32.16%.

Infrared spectrum in nujol shows following absorption maxima (cm^{-1}): 3380w, 3340w, 3160m, 1590w, 1540s, 1415w, 1350w, 1270s, 1240w, 1220w, 1155w, 1090m, 1040w, 1030w, 935w, 920m, 880m, 810w, 750s, 720s, 695w, 655w, 610w, 540m.

19. Bis(thiophene-2-carboxaldehyde-4-methyl-
thiosemicarbazonato)nickel(II)

This compound was prepared by mixing solutions of thioph-4-methyltsc (0.398 g, 0.002 mole) in hot alcohol (25 ml) and $NiCl_2 \cdot 6H_2O$ (0.237 g, 0.001 mole) in alcohol (5 ml). The pH of the clear greenish brown solution was adjusted to 7.0 with dilute ammonia (1:3) and the

mixture was heated on waterbath for 40 minutes. The greenish brown compound was filtered washed with alcohol (3x5 ml) and dried under vacuum. Yield 0.3 g (66%).

M.p. 231°C (decomp.).

Analysis: Found C, 37.90; H, 3.92; N, 17.67; Ni, 12.54%.

Calculated for $C_{14}H_{16}N_6S_4Ni$: C, 36.94; H, 3.52; N, 18.47; Ni, 12.91%.

Infrared absorption frequencies (cm^{-1}) observed in nujol: 3380s, 1580w, 1530s, 1420s, 1345w, 1285s, 1260s, 1225s, 1180s, 1100w, 1080w, 1070m, 945w, 920w, 855s, 820w, 745s, 720s, 690w, 540m, 410w, 360w.

20. Thiophene-2-carboxaldehyde-4-phenylthiosemicarbazone,
Thioph-4-phenyltsc

Thiophene-2-carboxaldehyde (2.8 g, 0.025 mole) in alcohol (5 ml) was added to 4-phenylthiosemicarbazide (4.17 g, 0.025 mole) dissolved in hot alcohol (150 ml) followed by the addition of glacial acetic acid (2 ml). The mixture was refluxed for 5 hrs and cooled to room temperature (27°C) overnight. The crystalline cream white product was filtered and dried. It was recrystallised from alcohol. Yield 4.0 g (62%). M.p. 198°C.

Analysis: Found C, 55.64; H, 4.51; N, 15.13; S, 23.11%.

Calculated for $C_{12}H_{11}N_3S_2$: C, 55.17; H, 4.21; N, 16.09; S, 24.52%.

Infrared absorption maxima (cm^{-1}) observed in nujol are: 3390m, 3220w, 3110w, 1610s, 1570m, 1530s, 1425m, 1310s, 1275s, 1100m, 1050m, 945w, 840s, 750s, 620s, 565s, 405s.

21. Bis(thiophene-2-carboxaldehyde-4-phenylthiosemicarbazonato)nickel(II)

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g, 0.001 mole) dissolved in alcohol (5 ml) was added to solution of thioph-4-phenytsc (0.522 g, 0.002 mole) in hot alcohol (120 ml). The pH of the clear solution was adjusted to 7.05 with dilute ammonia (1:3) and the greenish brown compound precipitated was heated on waterbath for 30 minutes. It was collected on filter, washed with alcohol (3x5 ml) and dried under vacuum. Yield 0.5 g (87%). M.p. 220°C (decomp.). Analysis: Found C, 48.98; H, 4.05; N, 14.37; Ni, 9.40%. Calculated for $\text{C}_{24}\text{H}_{20}\text{N}_6\text{S}_4\text{Ni}$: 49.77; H, 3.46; N, 14.52; Ni, 10.04%.

Infrared absorption frequencies observed in nujol: 3380m, 3270m, 3150w, 1620m, 1580w, 1515s, 1420s, 1310s, 1225s, 1060s, 1025w, 950m, 820s, 745m, 715s, 650s, 395m, 310w.

22. Bis(thiophene-2-carboxaldehyde-4-phenylthiosemicarbazonato)palladium(II)

Na_2PdCl_4 (0.294 g, 0.001 mole) dissolved in water (25 ml) was added to the solution of thioph-4-phenytsc

(0.522 g, 0.002 mole) in hot alcohol (125 ml). An orange compound formed on addition of dilute NaOH (0.1 N) for adjustment of pH to 7.05 was heated on waterbath for 40 minutes. It was isolated by filtration and washing with alcohol (3x5 ml). The compound was dried under vacuum. Yield, 0.4 g (64%). M.p. 215°C (decomp.).

Analysis: Found C, 46.09; H, 3.70; N, 12.64; Pd, 16.31%.
 Calculated for $C_{24}H_{20}N_6S_4Pd$: C, 45.98; H, 3.19; N, 13.41; Pd, 16.99%.

IR absorption frequencies (cm^{-1}) in nujol: 3375w, 3245m, 3155w, 1580m, 1550w, 1505s, 1415s, 1340m, 1250s, 1235m, 1075m, 1000w, 950w, 930m, 810s, 715s, 625s, 550m, 370w, 310m.

23. Bis(thiophene-2-carboxaldehyde-4-phenylthiosemi-carbazonato)platinum(II)

K_2PtCl_4 (0.415 g, 0.001 mole) dissolved in water (5 ml) was added to solution of thioph-4-phenyltsc (0.522 g, 0.002 mole) in hot water (25 ml). The pH of the solution was adjusted to 7.05 with the addition of dilute NaOH (0.1 N) and the yellow solid formed was heated on waterbath for 30 minutes. It was filtered, washed with water (2x5 ml) and dried under vacuum. Yield 0.4 g (56%). M.p. 267°C (decomp.).

Analysis: Found C, 39.58; H, 3.08; Pt, 28.34%.

Calculated for $C_{24}H_{20}N_6S_4Pt$: C, 40.27; H, 2.80; Pt, 27.28%.

Infrared absorption spectrum in nujol shown following maxima (cm^{-1}): 3370w, 3250m, 3155w, 1580m, 1560w, 1505s, 1410s, 1340s, 1255m, 1230s, 1070m, 1010w, 950w, 925m, 800s, 710s, 625s, 555m, 375m, 305w.

24. o-Nitrobenzaldehyde-thiosemicarbazone, o-nitrobenzaltsc

Solutions of o-nitrobenzaldehyde (3.77 g, 0.025 mole) in hot alcohol (25 ml) and thiosemicarbazide (2.27 g, 0.025 mole) in hot water (60 ml) were mixed and refluxed in presence of glacial acetic acid (1 ml) for 5 hrs. A bright yellow crystalline solid was yielded on cooling the container at room temperature ($27^{\circ}C$) for 16 hrs. This was filtered and recrystallised from alcohol.

Yield 5.0 g (89%). M.p. $245^{\circ}C$.

Analysis: Found C, 42.31; H, 3.77; N, 24.05; S, 13.62%.

Calculated for $C_8H_8N_4SO_2$: C, 42.86; H, 3.57; N, 25.00; S, 14.28%.

Infrared absorption frequencies (cm^{-1}) in nujol:

3420s, 3220m, 3140m, 3100m, 1600s, 1535s, 1510s, 1330m, 1310m, 1270m, 1250w, 1220w, 1110s, 1080s, 950m, 930s, 880m, 850m, 820m, 780w, 725s, 625m, 570s, 520m, 460m, 370w.

25. Bis(o-nitrobenzaldehyde-thiosemicarbazonato)nickel(II)

o-Nitrobenzaldehyde (0.448 g, 0.002 mole) was dissolved in hot methanol (300 ml) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g, 0.001 mole) in methanol (10 ml) was added to it. The pH of the mixture was adjusted to 7.0 with dilute ammonia (1:3) and the resulting red brown compound was heated on waterbath for 45 minutes. It was filtered and washed with methanol (3x5 ml) and dried under vacuum. Yield 0.4 g (79%). M.p. 250°C (decomp.).

Analysis: Found C, 38.97; H, 3.17; N, 21.94; S, 11.11; Ni, 11.62%. Calculated for $\text{C}_{16}\text{H}_{14}\text{N}_8\text{S}_2\text{O}_4\text{Ni}$: C, 38.04; H, 2.77; N, 22.19; S, 12.68; Ni, 11.63%.

Infrared spectral frequencies (cm^{-1}) observed in nujol: 3420m, 3300s, 3150w, 1595s, 1510s, 1490s, 1350s, 1310w, 1270s, 1250w, 1210w, 1110w, 1070m, 950w, 920s, 870w, 840m, 810m, 770w, 730s, 690s, 570w, 520m, 480w, 440s, 370m, 320m.

26. Bis(o-nitrobenzaldehyde-thiosemicarbazonato)-palladium(II)

This compound was prepared by mixing solutions of o-nitrobenzaldehyde (0.448 g, 0.002 mole) in hot methanol (300 ml) and Na_2PdCl_4 (0.294 g, 0.001 mole) in water (25 ml), adjusting the pH to 6.5 with diluted NaOH (0.1 N) and heating it on waterbath for 1 hr. The golden yellow compound was collected on filter,

washed with methanol (3x5 ml) and dried under vacuum.

Yield 0.42 g (76%). M.p. 252°C (decomp.).

Analysis: Found C, 35.28; H, 3.13; S, 10.55; Pd, 19.71%.

Calculated for $C_{16}H_{14}N_8S_2O_4Pd$: C, 34.76; H, 2.53;

S, 11.59; Pd, 19.26%.

Infrared absorption band frequencies (cm^{-1}) observed in
 nujol: 3420w, 3310s, 3145w, 1590s, 1510s, 1480s, 1350m,
 1310m, 1265m, 1250m, 1210w, 1105w, 1060m, 950w, 920m,
 870w, 840w, 810m, 770m, 730s, 690s, 560w, 520m, 485m,
 435m, 370m, 310w.

27. o-Nitrobenzaldehyde-4-phenylthiosemicarbazone:

o-nitrobenzal-4-phenytsc

4-Phenylthiosemicarbazide (4.17 g, 0.025 mole)
 was dissolved in hot alcohol (120 ml) and hot solution
 of o-nitrobenzaldehyde (3.77 g, 0.025 mole) in alcohol
 (30 ml) was added to it followed by the addition of
 glacial acetic acid (1.5 ml). The clear yellow
 solution was refluxed on waterbath for 5 hrs. The
 yellow crystalline solid yielded on cooling was filtered,
 dried and recrystallised from alcohol. Yield 5 g (67%).
 M.p. 212°C.

Analysis: Found C, 56.28; H, 4.29; N, 18.25; S, 9.33%.

Calculated for $C_{14}H_{12}N_4O_2S$: C, 56.00; H, 4.00; N, 18.66;

S, 10.66%.

Infrared absorption maxima (cm^{-1}) observed in nujol:
 3340m, 3120m, 1600s, 1510s, 1340s, 1280m, 1260m, 1220m,
 1160w, 1090m, 1070m, 930s, 870m, 850s, 790s, 750s,
 700s, 650s, 630m, 610m, 580w, 530s, 510s, 480m, 400w, 370w.

28. Bis(o-nitrobenzaldehyde-4-phenylthiosemi-
carbazonato)nickel(II)

This compound was prepared by adding hot solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g, 0.001 mole) in methanol (10 ml) to the hot solution of o-nitrobenzal-4-phenylthio (0.60 g, 0.002 mole) in methanol (300 ml). The pH of the resulting clear light greenish yellow solution was adjusted to 7.05 with dilute ammonia (1:3) and it was heated on waterbath for 1 hr. The brown compound formed was filtered hot and washed with hot methanol (3x5 ml) and dried under vacuum. Yield 0.5 g.

M.p. 253°C (decomp.).

Analysis: Found C, 51.79; H, 3.68; N, 16.46; S, 8.28; Ni, 9.01%. Calculated for $\text{C}_{28}\text{H}_{22}\text{N}_8\text{O}_4\text{S}_2\text{Ni}$: C, 51.16; H, 3.35; N, 17.05; S, 9.75; Ni, 8.94%.

Infrared absorption frequencies (cm^{-1}) observed in nujol: 3380m, 1600s, 1490s, 1330s, 1270w, 1250s, 1200s, 1140w, 1070w, 1050s, 940w, 850m, 840w, 780s, 745s, 695s, 590w, 560s, 470m, 310m.

29. Bis(o-nitrobenzaldehyde-4-phenylthiosemicarbazonato)palladium(II)

Solutions of Na_2PdCl_4 (0.294 g, 0.001 mole) in water (25 ml) and o-nitrobenzal-4-phenyltsc (0.60 g, 0.002 mole) in hot methanol (300 ml) were mixed and the pH of the resulting mixture was adjusted 7.0 with dilute NaOH (0.1 N). An orange compound formed was heated on waterbath for 1 hr. It was filtered and washed with hot methanol (3x5 ml) and dried under vacuum. Yield 0.6 g. M.p. 258°C (decomp.).

Analysis: Found C, 48.40; H, 3.78; N, 15.52; S, 8.54; Pd, 15.98%. Calculated for $\text{C}_{28}\text{H}_{22}\text{N}_8\text{O}_4\text{S}_2\text{Pd}$: C, 47.70; H, 3.12; N, 15.90; S, 9.08; Pd, 15.11%.

Infrared absorption maxima (cm^{-1}) in nujol observed: 3370w, 1595s, 1485s, 1330s, 1265w, 1250m, 1210s, 1145m, 1060m, 1050m, 950m, 840m, 830w, 775s, 740s, 690s, 580w, 550s, 465m, 305w.

30. Bis-(o-nitrobenzaldehyde-4-phenylthiosemicarbazonato)platinum(II)

This compound was synthesised by adding solution of K_2PtCl_4 (0.415 g, 0.001 mole) in water (5 ml) to the hot solution of o-nitrobenzal-4-phenyltsc (0.60 g, 0.002 mole) in water (300 ml). The pH of the resulting mixture was adjusted to 7.05 with dilute NaOH (0.1 N) and the brown compound formed was heated on waterbath

for 1 hr. It was filtered and washed with hot water (3x5 ml) and dried under vacuum. Yield 0.5 g.
M.p. 288°C (decomp.).

Analysis: Found C, 42.11; H, 3.23; Pt, 25.05%.

Calculated for $C_{28}H_{22}N_8O_4S_2Pt$: C, 42.37; H, 2.77; Pt, 24.60%.

Infrared absorption frequencies (cm^{-1}) observed in nujol: 3360m, 1595s, 1470s, 1335s, 1260w, 1240w, 1205w, 1145w, 1060m, 1040w, 940w, 840w, 835w, 770s, 740s, 690s, 580w, 550s, 460w, 305w.

X-ray crystallographic work on the structure of bis(2-furaldehyde-thiosemicarbazonato)nickel(II)

The compound bis(2-furaldehydethiosemicarbazonato)-nickel(II) was repeatedly crystallised from absolute alcohol and crystals of approximate dimensions 0.15 x 0.25 x 0.4 m were selected. CAD-4F-11M diffractometer graphite monochromated $MoK\alpha$ radiation, $w/2 \theta$ scan mode, scan speed 1° min^{-1} ; $\theta < 23.5^\circ$, h 0 to 12, k -12 to 12, l -12 to 12, 3472 reflections collected, 929 judged significant ($|F_0| \geq 3\sigma |F_0|$). Lattice parameters from 25 reflections ($12 < 2\theta < 36^\circ$) three standard reflections (-5, -1, -2, -4, 0, -2 and -1, 1, -5) every 1000, with 3% variation in intensity. No correction for absorption was applied. Structure

was solved by direct methods, MULTAN-78¹³ using a modified procedure¹⁴. Full-matrix least squares refinement¹⁵ of scale factor was applied. Atomic scattering factors from International Tables for X-ray crystallography¹⁶ were chosen.

Crystal Data

$C_{12}H_{12}N_6O_2S_2Ni$, MW = 395, rhombohedral,
 $R\bar{3}$, $G = 10.689(2) \text{ \AA}$, $\alpha = 82.04(2)^\circ$, $V = 119.0 \text{ \AA}^3$,
 $Z = 3$, $D_m = 1.65(7)$, $D_x = 1.655 \text{ Mg m}^{-3}$, $(MoK\alpha) =$
 0.7107 \AA , $\mu(MoK\alpha) = 14.92 \text{ cm}^{-1}$, $F(000) = 336.0$,
 $T = 293 \text{ K}$, $R = 0.028$ for 929 observed reflections.

Instruments used for characterisation of the ligands
and their metal complexes

IR spectra of the compounds were recorded on a Perkin Elmer 221 or Perkin Elmer 599 infrared spectrophotometer provided with CsI optics. UV-Visible spectra were run on a Pye Unicam SP8-100 UV-VIS Spectrophotometer.

PMR spectra were recorded on a Varian FT-80A at 80 MHz and ^{13}C NMR spectra on a Bruker WH-90 FT Spectrophotometer at 90 MHz.

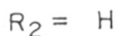
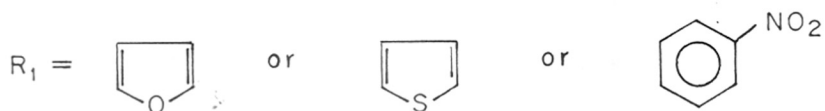
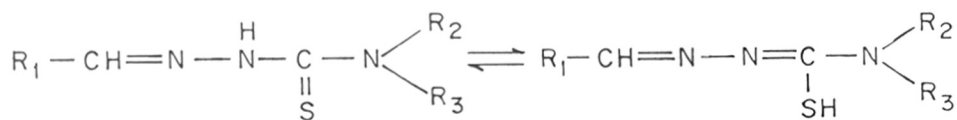
Polarograms were recorded on a 174A (PAR) Polarographic analyser Model in combination with PAR 303 static mercury drop electrode.

X-ray crystallographic data was collected on Enraf-Nonius CAD-4F-11M diffractometer.

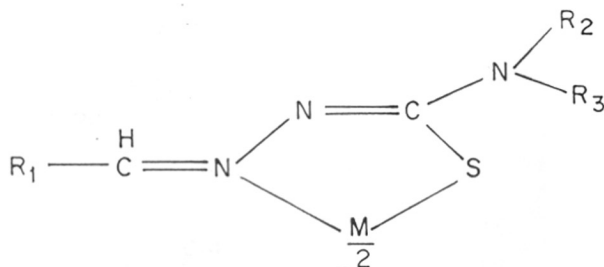
Elemental analyses were carried out in the microanalysis section of this laboratory.

Results and Discussion

2-Furaldehyde thiosemicarbazone and other heterocyclic thiosemicarbazones studied here, exist in the thioketo form in the solid state as evidenced from the infrared spectral data given in Table 1. Bands attributable to SH vibrations in the region 2650-2500 cm^{-1} are absent. All the compounds showed N-H stretching modes of vibration in the region 3400-3100 cm^{-1} and strong bands in the region 1570-1395 cm^{-1} , 1420-1260 cm^{-1} and 1140-700 cm^{-1} assignable to C=S stretching vibration. Various authors¹⁷⁻²⁰ assigned C=S stretching vibration to frequencies ranging from 700 cm^{-1} to 1570 cm^{-1} depending on the type of compound in which this group occurs. The lack of consistency in their position confirms the view that in the compounds in which the thiocarbonyl group is linked to nitrogen, strong vibrational coupling effects are possible. In solution, however, thiosemicarbazones can exist in the thioketone (A) and thioenol (B) forms, the latter being favoured in alkaline solution.

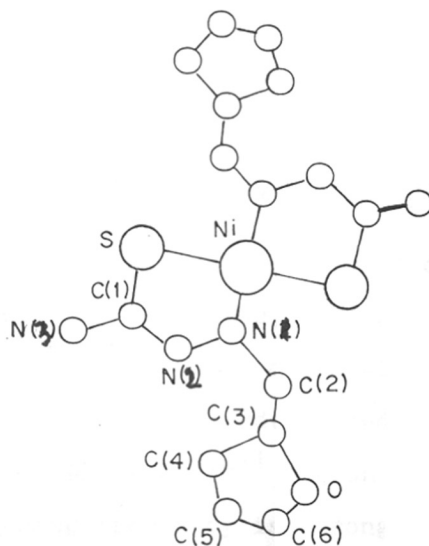


Ni(II) is found to be in a square planar ligand field of the N_2S_2 chromophore as in case of bis(hexane-2,5-dione-4-phenylthiosemicarbazonato)Ni(II)²², bis(diiminosuccinonitrilo)Ni(II)²³ and bis(butane-dione-diphenyl acetylthiohydrazonato)Ni(II)²⁴. In the deprotonated form they are potentially bidentate ligands coordinating through 1-nitrogen and the thiolate sulphur atom forming five membered chelate rings²⁵.



M = Divalent metal ion

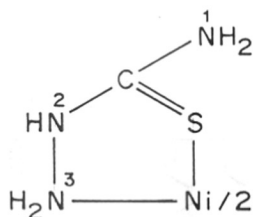
X-ray crystallographic data on bis(2-furaldehyde-thiosemicarbazonato)nickel(II) shows that the thiosemicarbazone group is planar with $\text{Ni-S} = 2.149(1) \text{ \AA}$ and $\text{Ni-N}(2) = 1.921(2) \text{ \AA}$. The coordination around nickel is transplanar with respect to the two sulphur and two nitrogen atoms. A similar coordination is observed in bis-thiosemicarbazidato nickel(II)²¹ in which the furaldehyde ring is disposed at an angle of $3(1)^\circ$ with respect to the 'coordination plane'. Bond lengths and bond angles involving non-H atoms are given in Table 2. A perspective view of the molecule along with the numbering of atoms is given below.



The infrared spectra in chloroform solution of 2-furtsc, 2-fur⁴phentsc and thiophtsc show medium to weak/weak-broad absorption bands in the 2564-2538 cm^{-1} region due to $\nu(\text{SH})$. Confirmation of this assignment was forthcoming from the weak absorption bands observed in the region 5180-5019 cm^{-1} ascribable to its first overtone band²⁶. In the spectra of the corresponding deuterated compounds the bands either disappeared or shifted. The observed shift for the $\nu(\text{SH})$ frequency in these compounds from the usual $\nu(\text{SH})$ assignment²⁷ (2600-2550 cm^{-1}) is rather small and is due to inter/intra molecularly bonded SH present in solutions. The spectra of 2-furtsc, 2-fur-4-phentsc, 2-fur-4-methytsc, thioph-4-methytsc, thiophtsc, o-nitrobenztsc in DMSO (dried over CaH_2) show medium/weak and broad absorptions in the range 2550-2580 cm^{-1} Table 3. These observations indicate the presence of enolised species (thioenol form B) in the solutions of the thiosemicarbazones.

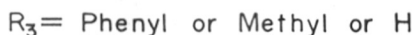
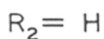
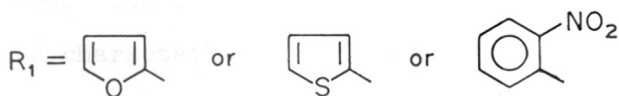
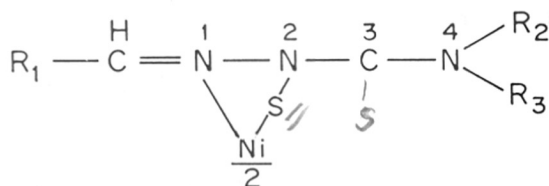
The infrared absorption spectra of 2-furtsc, 2-furphenytsc, 2-furmethytsc, thiophtsc, thioph-4-methytsc, and some of their deuterated analogues and metal chelates of Ni(II), Pd(II) and Pt(II) were recorded in the 4000-200 cm^{-1} region (Figs. 1-4), (Table-1). (C=S) stretching frequency is strongly coupled in

nearly all the compounds in which the carbon is directly linked to nitrogen. In the spectra of all the ligands studied, strong absorption bands appearing in the two regions $840-800\text{ cm}^{-1}$ (shifted slightly on deuteration) and at $1100-1040\text{ cm}^{-1}$ attributable respectively to nearly pure $\nu(\text{C}=\text{S})$ and to $\nu(\text{C}=\text{S})$ coupled with N-C-N stretching²⁸. An interesting feature of the infrared spectra of all the metal chelates studied here is the appearance of a strong band at $900-1000\text{ cm}^{-1}$ region assignable to N-N stretching vibration. Strictly speaking, in a symmetrical molecule the N-N vibration is infrared forbidden by symmetry arguments. In the ligand and ionic complexes it should be allowed but is probably very weak. For the neutral chelates, however, the vibration becomes more intense²⁹. This is explained by the X-ray study³⁰ which shows that the C=N double bond is almost completely localized in C-N² region in thiosemicarbazide complexes and hence the N² and N³ atoms are different.



The position of the band at lower energy is also consistent with the observed lengthening of the N^2-N^3 bond.

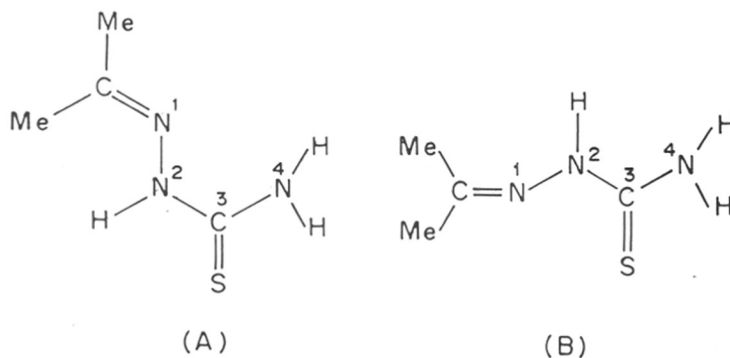
In the spectra of all thiosemicarbazones well defined bands in the region $3500-3000\text{ cm}^{-1}$ and at $\sim 1600\text{ cm}^{-1}$ were observed. The medium intense bands at $\sim 3400\text{ cm}^{-1}$, $\sim 3220\text{ cm}^{-1}$ and at $\sim 3140\text{ cm}^{-1}$ on deuteration shifted (isotope ratio 1:3). The band observed in the vicinity of 3400 cm^{-1} can be ascribed to $\nu(\text{NH}_2)$ and the one near 3170 cm^{-1} to $\nu(\text{NH})$ on the basis of previous assignments³¹. The strong absorption near 1600 cm^{-1} ascribable to $\delta(\text{NH}_2)$ also shifted on deuteration. A medium to strong band for C=N stretching appears in the $1550-1595\text{ cm}^{-1}$ region of the spectra of all thiosemicarbazones which shifts to lower frequencies on coordination with metal ion, by about $10-15\text{ cm}^{-1}$, indicating the involvement of N^1 in chelate formation.



The infrared spectra of Ni(II), Pd(II) and Pt(II) chelates and some of their deuterated analogues in the region $600-200\text{ cm}^{-1}$ (Figs. 5-8) showed absorptions which are absent in the spectra of the corresponding ligands. The medium intense bands at $\sim 300-320\text{ cm}^{-1}$ which are least sensitive to deuteration could arise predominantly due to metal sulphur stretching modes. In the region $400-470\text{ cm}^{-1}$ two medium intense absorptions were observed. The bands in the higher frequency region are sensitive to deuteration and accordingly the bands at $430-460\text{ cm}^{-1}$ are tentatively assigned to $\nu(\text{M-N})$ frequencies³²⁻³⁴.

The ^1H NMR spectra of heterocyclic carboxaldehyde thiosemicarbazones and some of their corresponding metal chelates were recorded in DMSO, DMSO- d_6 or CDCl_3 solutions (Figs. 9-11). The data are reported in Table 4. Solubility problems precluded study of other ligands and chelates. In DMSO- d_6 / CDCl_3 the spectra of the ligands, 2-furtsc, 2-fur-4-phenytsc and thioph-4-phenytsc exhibited two resonances (sometimes obscured by that of aromatic protons as in the case of thiophytsc) for the $\text{N}(4)\text{H}_2$ protons indicating hindered rotation about the $\text{C}(\text{S})-\text{NH}_2$ bond due to its partial double bond character²⁴. The NMR spectra of 2-furtsc

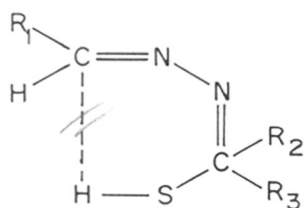
and 2-fur-4-phenyltsc measured in DMSO- d_6 /DMSO at various concentrations show, in addition, a sharp singlet at 11.22 δ and 11.77 δ . The peak observed for 2-fur-4-phenyltsc showed marked concentration dependence (moved upfield by 1.20 δ with higher concentration). The concentration dependence and upfield shift are typical of a thiol group^{35,36}. This signal disappeared either on deuteration or on chelate formation. The presence of a hydrogen bonded chelate ring can be inferred from the downfield position of the signal. However, this could arise also due to a bonded proton attached to a nitrogen atom. In their variable temperature ^1H NMR study, Bellitto et al³⁷ observed two resonances for the N(4)H₂ protons in the spectrum of acetone thiosemicarbazone in chloroform solution and that one of the signals is almost independent of temperature, suggesting that one conformer (A) exists in solution since it is the only one allowing formation of an intramolecular hydrogen bond between N(1) and one of the protons of the NH₂ group.



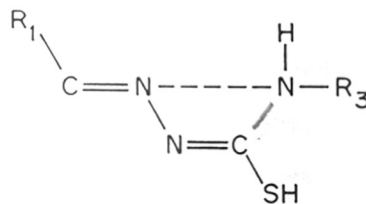
In acetone solution the presence of an equilibrium between (A) and (B), fast on NMR time scale even at low temperature is also suggested. The rather broad NH resonance became sharper at low temperatures and exhibited a downfield shift which indicates the absence of intramolecular bonds.

X-ray crystallographic data for several thiosemicarbazones and semicarbazones show that both C(3)-N(2) and C(3)-N(4) bonds are shorter than single bonds, the latter having the larger double bond character³⁸. Restricted rotation about these two bonds can result in several different conformations. In solution, particularly in DMSO-d₆ the heterocyclic carboxaldehyde thiosemicarbazones can assume modifications containing bonded or free SH (D-E, F) in addition to thio-ketone forms. Confirmation of the existence of 2-furtsc in thiol form in solution (DMSO) is obtained from

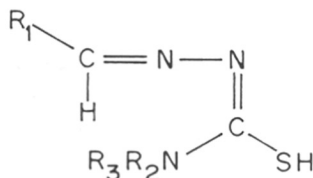
polarographic and ^{13}C NMR spectral data. The NH_2 signals in ^1H NMR spectra of the neutral chelates studied showed shielding effects probably due to the absence of hydrogen bonding³⁹.



(D)



(E)



(F)

The ^{13}C NMR chemical shift data of 2-furaldehyde-thiosemicarbazone and its neutral nickel and palladium chelates are presented in Table 5 (Fig 12, 13). The carbon resonance assignments for C₂, C₃, C₄, C₅ and for C(a) are in agreement with those reported in literature⁴⁰. The replacement of a carbonyl group by a thiocarbonyl group results in a downfield shift. In compounds containing the thio functional group such as in $\text{CH}_3-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$

and others containing $\begin{array}{c} \text{N} \\ \diagdown \\ \text{C}=\text{S} \\ \diagup \\ \text{N} \end{array}$ and $\text{>N}\text{-C}=\text{S}$ group, the carbon resonances are reported at 207.2, 192.8 and 200 ppm respectively^{41,42}. In the monothio- β -diketones the thio carbonyl carbon resonance $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ | \\ \text{S-H} \end{array}$ is observed at 182.4 ppm⁴³. The sharp signal at 178.49 ppm in the spectrum of 2-furtsc which on deuteration is reduced considerably with slight upfield shift (178.05 ppm) and on chelate formation shifted upfield, could reasonably be assigned to the carbon attached to the thiol function (C-SH) rather than to thione carbon (C=S). The significant upfield shift in the neutral Pd and Ni chelate indicates binding to the metal atom through thiolate sulphur (the other binding site being N(1)). It is noted that the carbon atoms (aldehydic, a) in the chelates are more shielded than the corresponding carbon of the ligand.

Differential pulse polarograms of thiosemi-carbazide and 2-furaldehyde thiosemicarbazone in alcohol/isopropanol/DMSO solvents buffered with LiCl/Phosphate/NaOAc + CH₃COOH were recorded. In anodic dissolution polarography the current obtained is actually due to the reaction of $\text{Hg}^0 \rightarrow \text{Hg}_2^{++} + 2e$. The concentration of mercurous ions produced is a function of the mercaptide concentration. The irreversible dissolution

peak for 2-furaldehyde thiosemicarbazone has an $E_{1/2}$ at -0.16 V vs Ag/AgCl in an electrolyte consisting of 0.15 M ($\text{Na}_2\text{HPO}_4 + \text{KH}_2\text{PO}_4$) in 40% isopropanol solvent. The half wave potential for thiosemicarbazide in the same solvent and buffer is at -0.25 V (Figs. 14, 15). The half wave potentials for several thiols are reported at -0.30 V vs S.C.E⁴⁴. The observed increase in the negative direction for 2-furaldehyde thiosemicarbazone in the $E_{1/2}$ value is attributable to the insolubility of its mercury salt in the organic solvent. No peak corresponding to the presence of C=S in the solution in the range 0.05 - 0.12 V or near 0.00 V, however, could be observed^{45,46}.

The polarographic reduction of thiosemicarbazide and 2-furaldehyde thiosemicarbazone in 75% alcohol + 0.1 M LiCl/75% alcohol + 0.2 M ($\text{NaOAc} + \text{CH}_3\text{COOH}$) gave two well defined diffusion controlled reduction peaks. Differential pulse polarogram for thiosemicarbazide showed peaks with $E_{1/2}$ at -0.25 V and at -0.65 to -0.61 V. In DMSO + 0.1 M LiCl, thiosemicarbazide showed two peaks with $E_{1/2}$ at 0.58 V and at -0.79 V, while 2-furaldehyde thiosemicarbazone showed only one peak with $E_{1/2}$ at -0.59 V. The absence of the peak with $E_{1/2}$ at -0.79 V suggest the absence of the thioketone

form of 2-furaldehyde thiosemicarbazone in this solvent. However, in view of the $E_{1/2}$ values reported⁴⁷ for several thiobenzophenones and other compounds containing C=S group at -0.82 - 0.95 V, one could not unequivocally assign the peak with $E_{1/2}$ in both these compounds at -0.79 V to a C=S group.

The UV visible spectra of 2-furtsc, 2-fur-4-phenytsc, 2-fur-4-methytsc and thiotsc were recorded in different solvents ^{Table G.} In alcohol/chloroform solutions, the heterocyclic thiosemicarbazones showed a single broad absorption band with maxima at \sim 320-325 nm (12,800-13,000 cm^{-1}). The alkaline solutions of the corresponding thiosemicarbazones also showed a single absorption (broad with a marked shift, with maxima at 335-365 nm (13,400-14,600 cm^{-1}). Of the two (thioketone, thioenol) forms, the thioenol form may be assumed to be favoured in alkaline solution.

It may be concluded that the thioketone and thioenol forms predominate in alcohol solutions and alkaline solutions respectively. Stern⁴⁸ in his study of thiol-thione tautomerism of 5-amino and 5-acetamido-2-mercapto thiazoles observed that in alcohol solutions the thione form predominates and the predominant form in alkaline solutions is the thiol form.

The electronic spectra of nickel(II) chelates

with 2-furtsc, 2-fur-4-methytsc, 2-fur-4-phenytsc, thiophtsc, thioph-4-phenytsc, and Pt(II) and Pd(II) chelates of 2-furtsc have been recorded in chloroform solution. The spectra of nickel chelates exhibit two absorptions in the region at $17,500\text{ cm}^{-1}$ and at $21,500\text{ cm}^{-1}$ due to ν_2 and ν_3 transitions respectively which may suggest square planar configuration around Ni(II) ions⁴⁹⁻⁵². Generally ν_3 and ν_2 are tentatively assigned to ${}^1A_{1g} \rightarrow {}^1B_{3g}$ and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transitions respectively. Above $20,000\text{ cm}^{-1}$ region there are two very intense bands. The lowest energy band can be assigned to L \rightarrow M charge transfer transition while the highest energy band at $32,000\text{ cm}^{-1}$ is probably due to $\pi - \pi^*$ of the ligand. Due to limited solubility, the spectra of Pd(II) and Pt(II) chelates with 2-furtsc were not well resolved in the visible region. The bands at $41,500\text{ cm}^{-1}$ in $\text{Pd}(2\text{-furtsc})_2$ and at $42,000\text{ cm}^{-1}$ in $\text{Pt}(2\text{-furtsc})_2$ could be assigned to internal ligand transitions, $L(\pi) \rightarrow L(\pi^*)$. The intense band observed at $31,500\text{ cm}^{-1}$ in both the chelates are L \rightarrow M charge transfer bands⁴². The d \rightarrow d bands are obscured by the more intense charge transfer bands. The spectra of the chelates do not show any absorption in the near infrared region.

From the similarity in the spectral characteristics with reported square planar complexes^{53,54} it may be inferred that Ni(II), Pd(II) and Pt(II) chelates with heterocyclic carboxaldehyde thiosemicarbazones possess square planar geometry.

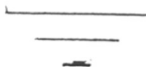


Table 1. Principal Infrared Absorption Frequencies (cm^{-1}) of some Thiosemicarbazones and Their Metal Complexes

Compound	(NH)	(C=N)	(N-N)	(C-S)	(M-N)	(M-S)
2-furtsc	3400s 3220s 3140s	1535s	930m			
Ni(2-furtsc) ₂	3360m 3260m 3150m	1510s	940m	670s	460s	320m
Pd(2-furtsc) ₂	3470w 3290m 3150w	1510s	940m	665s	440m	320w
Pt(2-furtsc) ₂	3390w 3240m 3160w	1495s	940m	660s	450m	320m
Thioptsc	3400s 3220w 3120m	1530s	940m	610s		
Ni(thioptsc) ₂	3390m 3280m 3170w	1510s	940m	640s	390m	315w
Pd(thioptsc) ₂	3370m 3270w 3160w	1500s	940m	625s	380w	300w
Pt(thioptsc) ₂	3365m 3260m 3160w	1500s	940m	620s	375w	305w

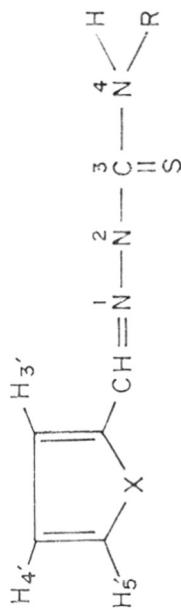
Table 2. Bond distances (Å) and Bond angles (°) with E.S.D.S. in Parentheses

		<u>Bond lengths</u>	<u>Bond angles</u>	
Ni	S	2.149(1)		
Ni	N(2)	1.922(2)		
S	C(1)	1.724(3)		
O	C(3)	1.386(4)		
O	C(6)	1.357(5)	C(3)	O C(6) 106.5(3)
N(1)	N(2)	1.395(3)		
N(1)	C(1)	1.310(4)	N(2)	N(1) C(1) 111.6(3)
N(2)	C(2)	1.289(4)	NI	N(2) N(1) 121.0(2)
N(3)	C(1)	1.342(5)	NI	N(2) C(2) 125.1(2)
			N(1)	N(2) C(2) 113.9(2)
			S	C(1) N(1) 123.7(3)
			S	C(1) N(3) 116.8(3)
			N(1)	C(1) N(3) 119.6(3)
C(2)	C(3)	1.439(4)	N(2)	C(2) C(3) 129.2(3)
C(3)	C(4)	1.340(5)	O	C(3) C(2) 110.7(3)
			O	C(3) C(4) 109.1(3)
			C(2)	C(3) C(4) 140.1(3)
C(4)	C(5)	1.429(5)	C(3)	C(4) C(5) 107.4(3)
C(5)	C(6)	1.341(6)	C(4)	C(5) C(6) 106.0(3)

Table 3. Infrared Absorption Frequencies (cm^{-1}) of Thiosemicarbazones

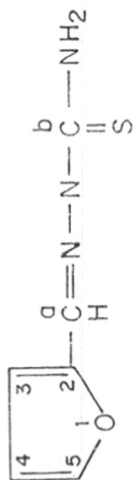
No.	Compound	ν (SH)		First overtone of ν (SH) in CHCl_3
		DMSO	(CHCl_3)	
1.	2-Furaldehyde thiosemicarbazone	2550b,m	2540b,w	5180w
2.	2-Furaldehyde-4-methylthiosemicarbazone	2545b,w	2545b,w	5075b,w
3.	2-Furaldehyde-4-phenyl thiosemicarbazone	2550m,w	2560b,w	5180w
4.	Thiophene-2-carboxaldehyde thiosemicarbazone	2540w	2545w	
5.	Thiophene-2-carboxaldehyde-4- methyl thiosemicarbazone	2560m,w	2560w	5180w
6.	Thiophene-2-carboxaldehyde-4- phenylthiosemicarbazone	2540m,w	2570b,w	

Table 4. ^1H NMR spectral data of heterocyclic carboxaldehyde thiosemicarbazones and their metal chelates



Sl. No.	X	R	Solvent	Metal	Heterocyclic ring protons/phenyl					-CH= (ppm)	N(2)H	N(4)H
					3	4	5	phenyl	phenyl			
1.	0	H	DMSO-d ₆	-	7.08	6.74	7.89			8.09	11.54	7.73
					7.05	6.72						
2.	0	H	DMSO	-	6.9	6.6	7.7			8.0	11.0	7.5
3.	0	C ₆ H ₅	DMSO	-	7.1	6.6	7.3			8.1	11.77	9.8
4.	0	C ₆ H ₅	CDCl ₃	-	6.72	6.47	6.94	7.3-		7.2	10.62	9.12
					6.78	6.53		7.69				
5.	S	H	DMSO	-	-	-	-	-		8.0	11.12	7.85
6.	S	C ₆ H ₅	CDCl ₃	-	6.69	6.45	6.94	7.25-		7.2	10.03	8.03
								7.63				
7.	0	H	DMSO	Ni(II)	-	-	-	-		7.2	-	7.1
8.	0	C ₆ H ₅	DMSO	Ni(II)	-	-	-	-		7.4	-	9.6

and its nickel and palladium chelates



Sl. No.	Compound	Solvent	C ₂	C ₃	C ₄	C ₅	a	b
1.	2-furtsc	DMSO-d ₆	145.35	113.18	112.66	133.13	149.83	178.49
2.	2-furtsc (deuterated)	DMSO-d ₆	145.4	113.86	112.79	133.49	149.51	178.05
3.	Ni(2-furtsc) ₂	DMSO-d ₆	145.13	120.49	112.94	140.85	147.67	174.97
4.	Pd(2-furtsc) ₂	DMSO-d ₆	146.0	121.22	113.75	140.9	147.18	174.63

Table 6. Electronic Spectral Data of some Thiosemicarbazones and Their Metal Complexes

Compound	Maxima, λ_{\max} (nm)
2-fur-tsc	320
2-fur-4-ph-tsc	325
2-fur-4-methy-tsc	325
Thiophtsc	325
Thioph-4-ph-tsc	325
Thioph-4-methy-tsc	325
2-fur-tsc (alkaline pH, 8.0)	335
F-4-ph-tsc (alkaline pH, 8.0)	360
Thioph-tsc (alkaline pH, 8.0)	365
Ni(2-fur-tsc) ₂	520, 425, 322
Ni(2-fur-4-ph-tsc) ₂	518, 440, 360
Ni(2-fur-4-methy-tsc) ₂	520, 432, 332
Ni(Thioph-tsc) ₂	518, 432, 324
Ni(Thioph-4-ph-tsc) ₂	518, 440, 332
Pd(2-fur-tsc) ₂	520, 392, 326
Pt(2-fur-tsc) ₂	434, 356, 334

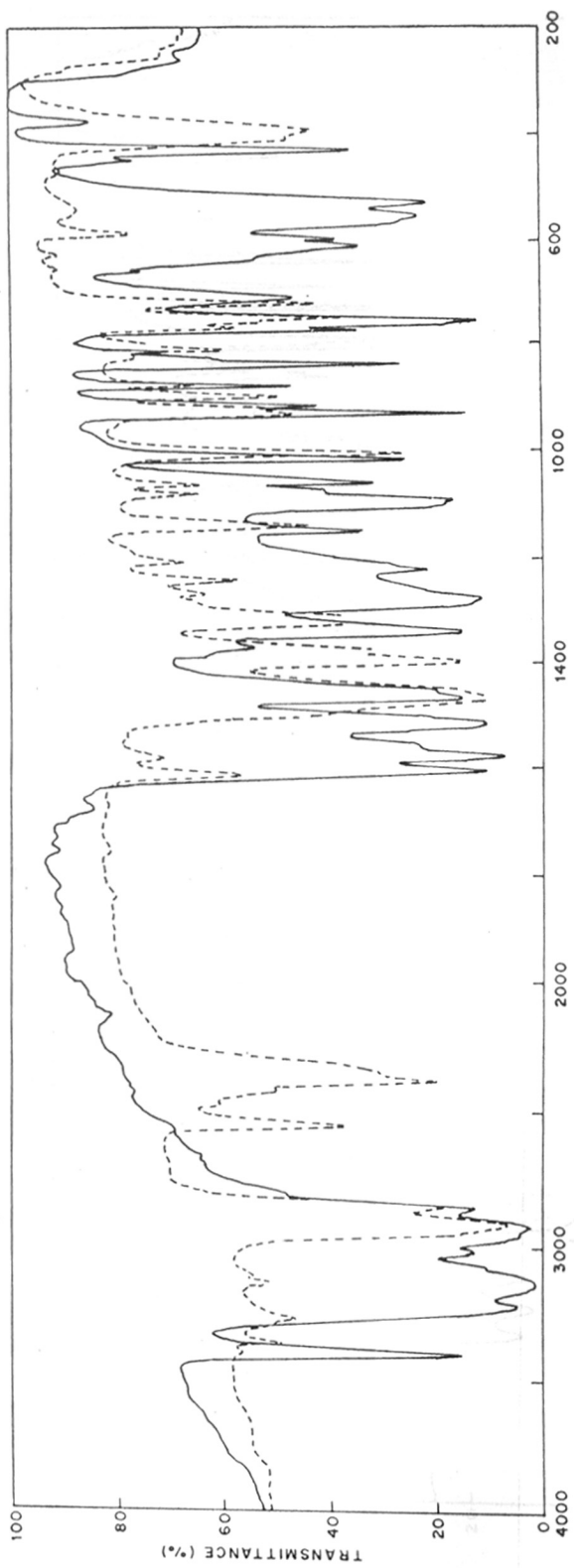


FIG. 1 INFRARED SPECTRA OF 2-FURALDEHYDE-THIOSEMICARBAZONE, (—) AND DEUTERATED 2-FURALDEHYDE-THIOSEMICARBAZONE, (---) IN NUJOL

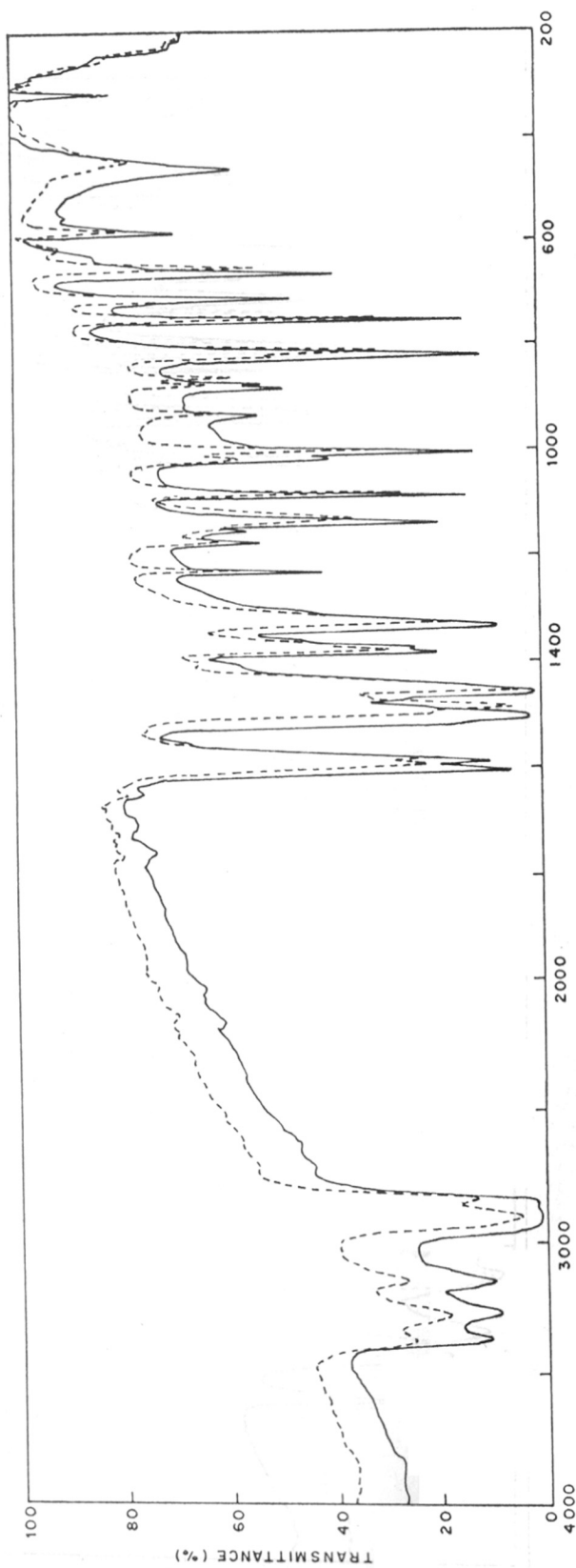


FIG. 2 INFRARED SPECTRA OF BIS (2-FURALDEHYDE - THIOSEMICARBAZONATO) NICKEL(II) (—) AND BIS (2-FURALDEHYDE - THIOSEMICARBAZONATO) PLATINUM(II) (-----) IN NUJOL

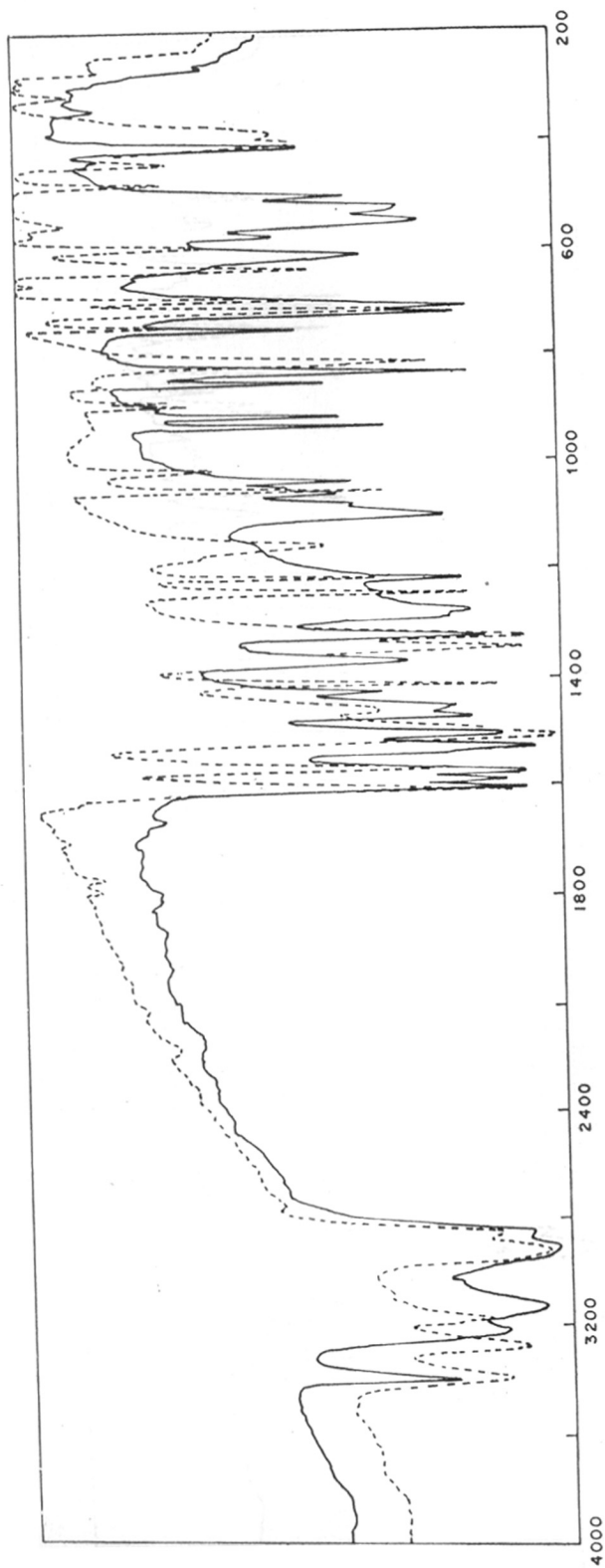


FIG. 3 INFRARED SPECTRA OF THIOPHENE - 2 - CARBOXYALDEHYDE THIOSEMICARBAZONE (—) AND BIS (THIOPHENE - 2 - CARBOXYALDEHYDE THIOSEMICARBAZONATO) NICKEL (II) (- - -) IN NUJOL

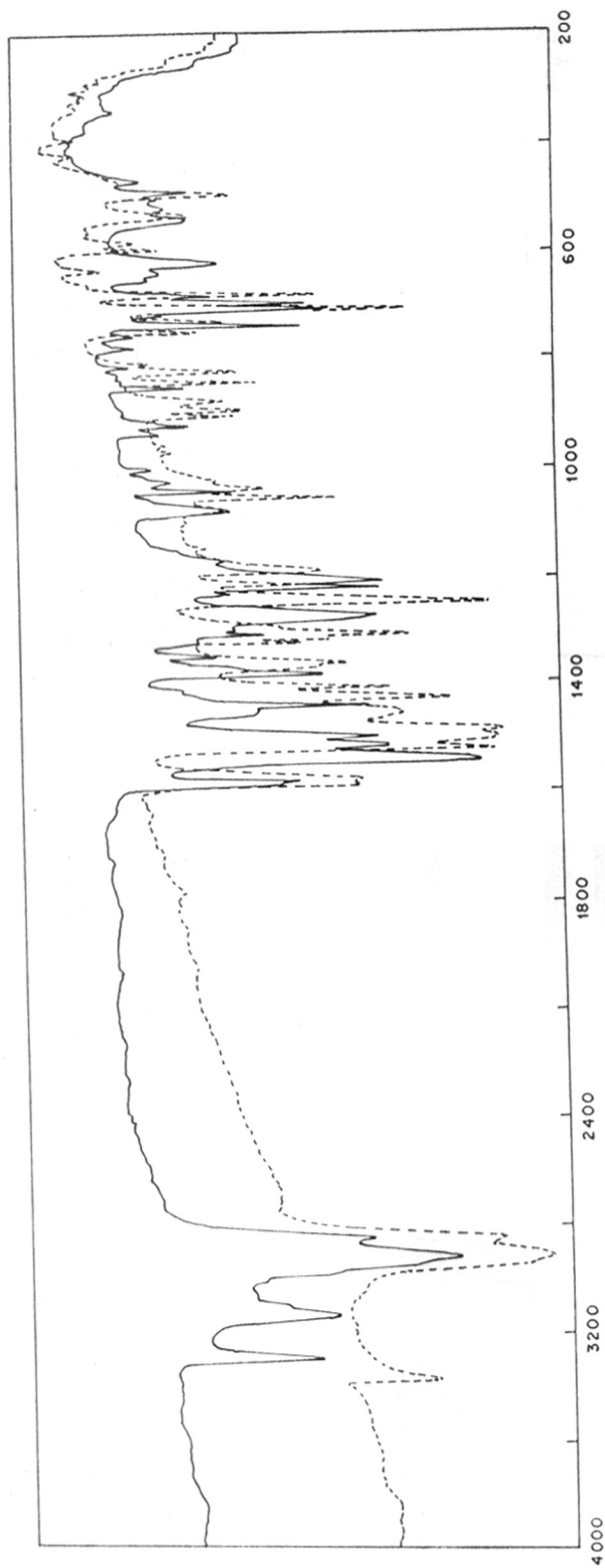


FIG. 4 INFRARED SPECTRA OF THIOPHENE-2-CARBOXALDEHYDE-4-PHENYLTHIOSEMICARBAZONE (—) AND BIS (THIOPHENE-2-CARBOXALDEHYDE-4-PHENYL THIOSEMICARBAZONATO) NICKEL (II) (---) IN NUJOL

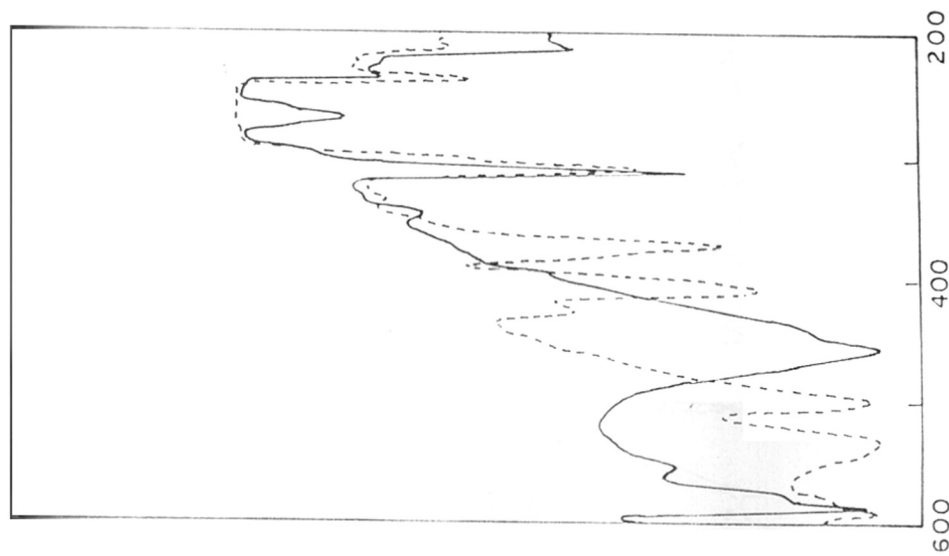


FIG. 5 INFRARED SPECTRA OF BIS (2-FURALDEHYDE THIOSEMICARBAZONATO)NICKEL (II) (----) AND DEUTERATED BIS(2-FURALDEHYDE THIOSEMICARBAZONATO) NICKEL (II) (——) IN NUJOL

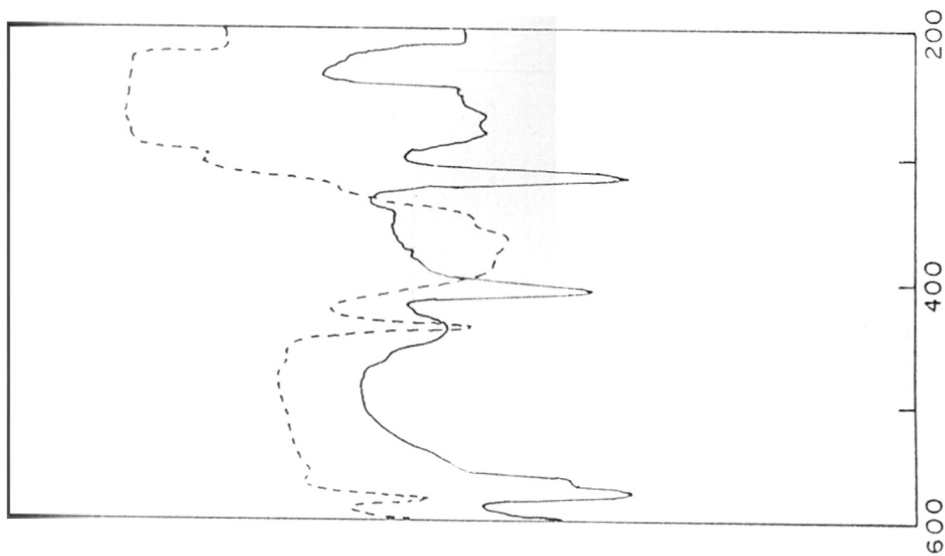


FIG. 6 INFRARED SPECTRA OF BIS (2-FURALDEHYDE THIOSEMICARBAZONATO) PALLADIUM (II) (----) AND DEUTERATED 2-FURALDEHYDE THIOSEMICARBAZONATO) PALLADIUM (II) (——) IN NUJOL

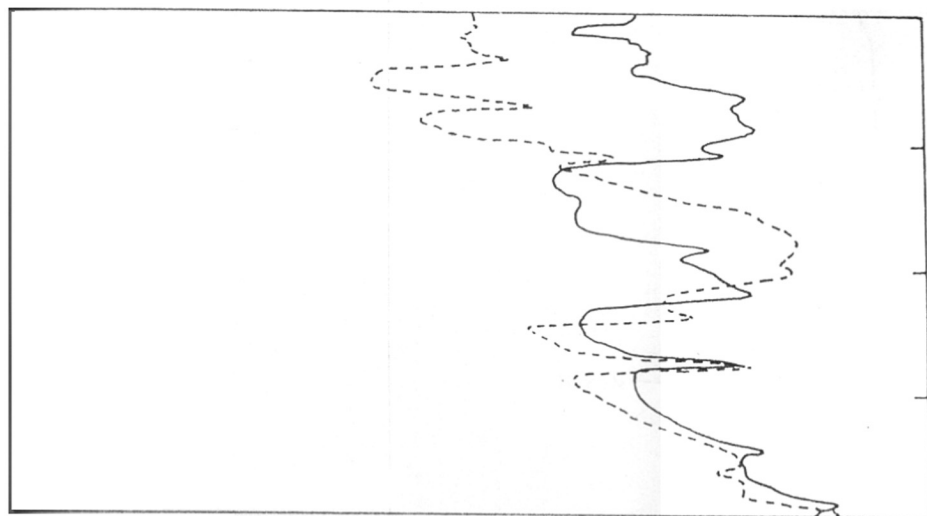


FIG. 7 INFRARED SPECTRA OF BIS
 (THIOPHENE-2-CARBOXALDEHYDE
 THIOSEMICARBAZONATO) NICKEL(II), (----)
 AND DEUTERATED BIS(THIOPHENE-2-
 CARBOXALDEHYDE THIOSEMICARBAZONATO)
 NICKEL(II), (——) IN NUJOL

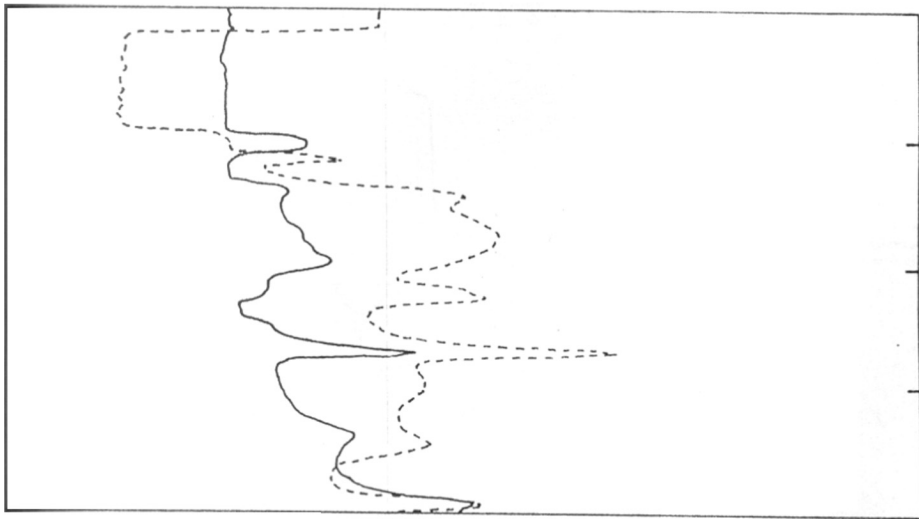


FIG. 8 INFRARED SPECTRA OF BIS (THIOPHENE-
 2-CARBOXALDEHYDE THIOSEMICARBAZONATO)
 PALLADIUM(II), (----) AND DEUTERATED BIS
 (THIOPHENE-2-CARBOXALDEHYDE
 THIOSEMICARBAZONATO)
 PALLADIUM(II), (——) IN NUJOL

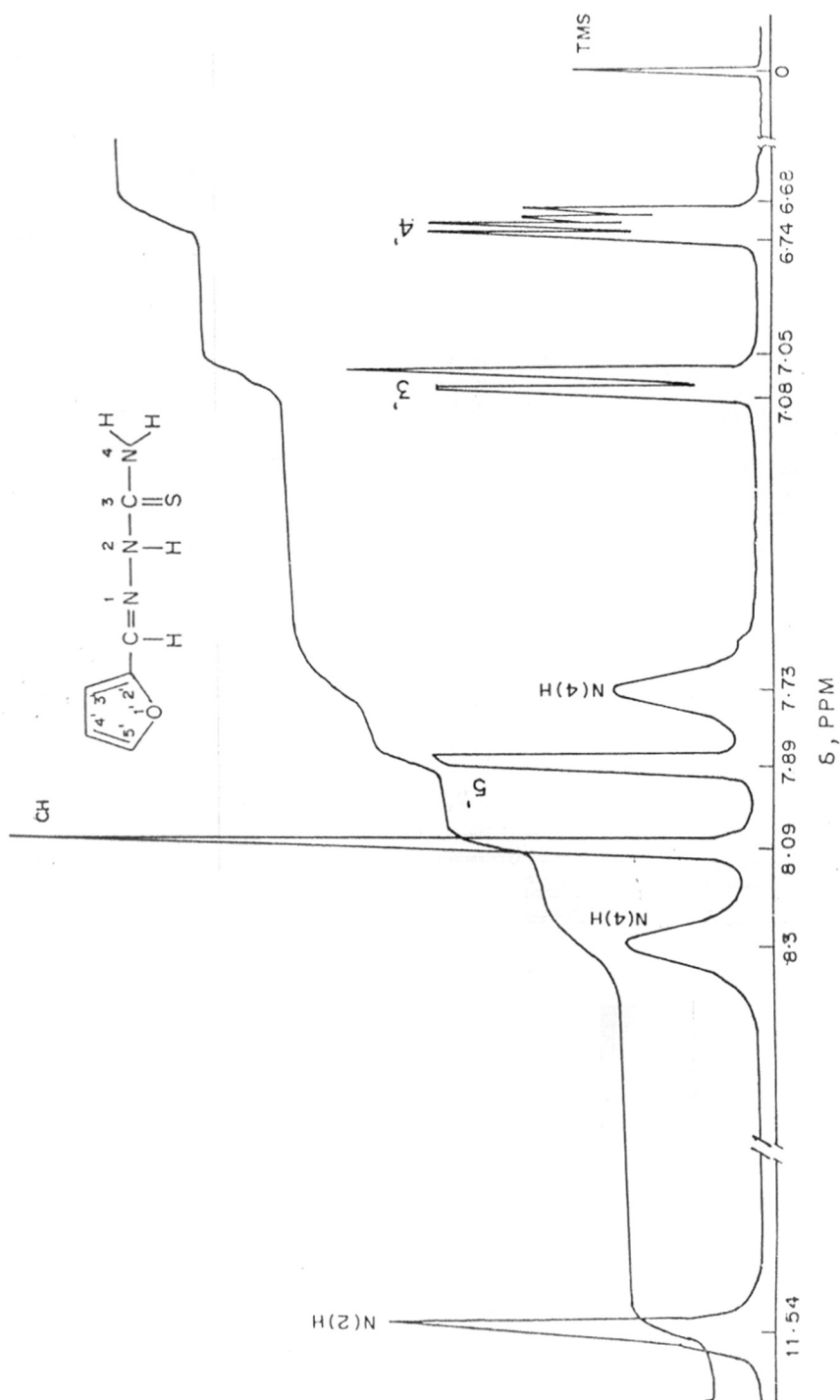


FIG. 9 : P.M.R. SPECTRUM OF 2-FURALDEHYDE THIO-SEMICARBAZONE IN DMSO - d₆

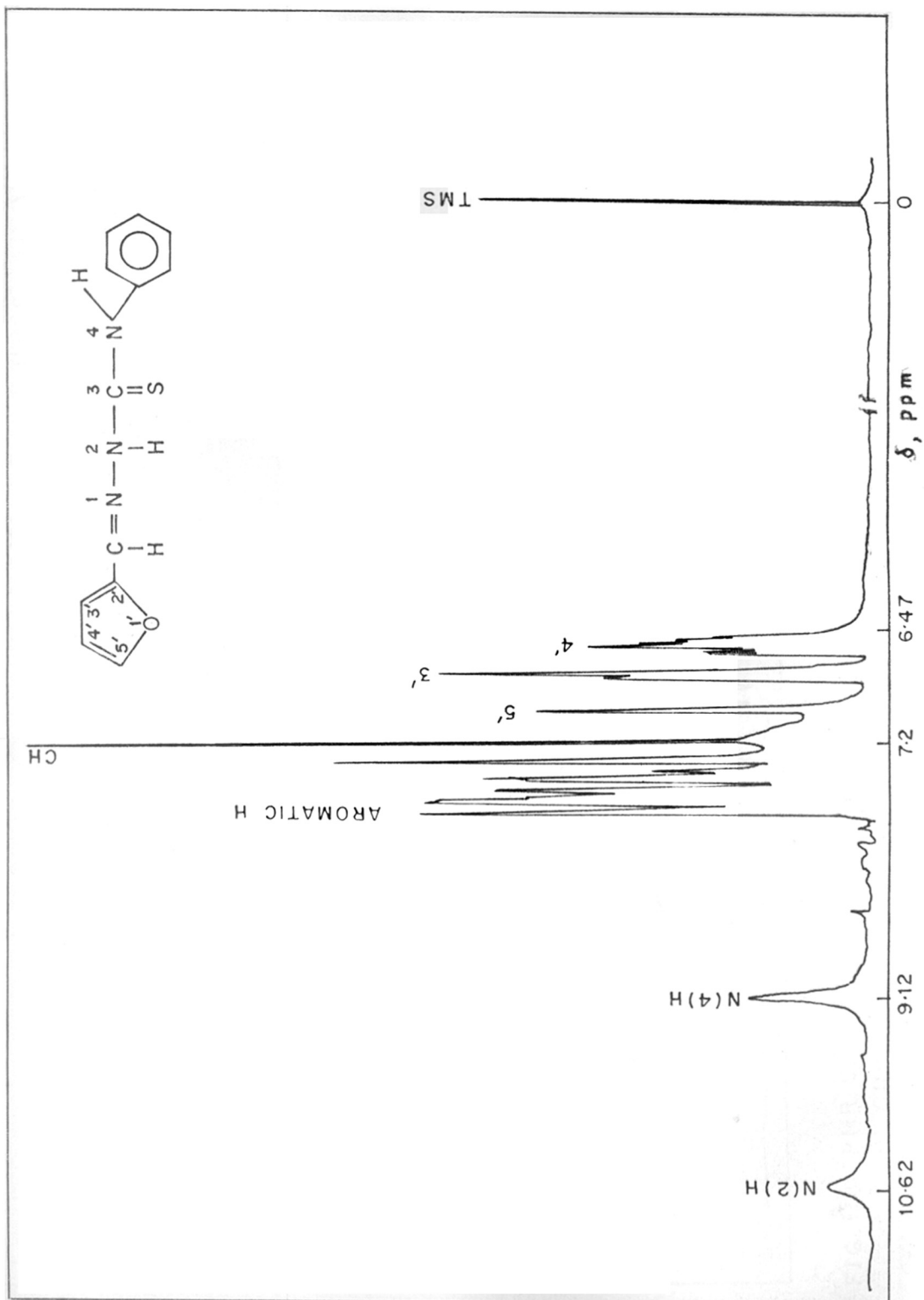


FIG. 10 PMR SPECTRUM OF 2-FURALDEHYDE-4-PHENYL THIOSEMICARBAZONE IN CDCl_3

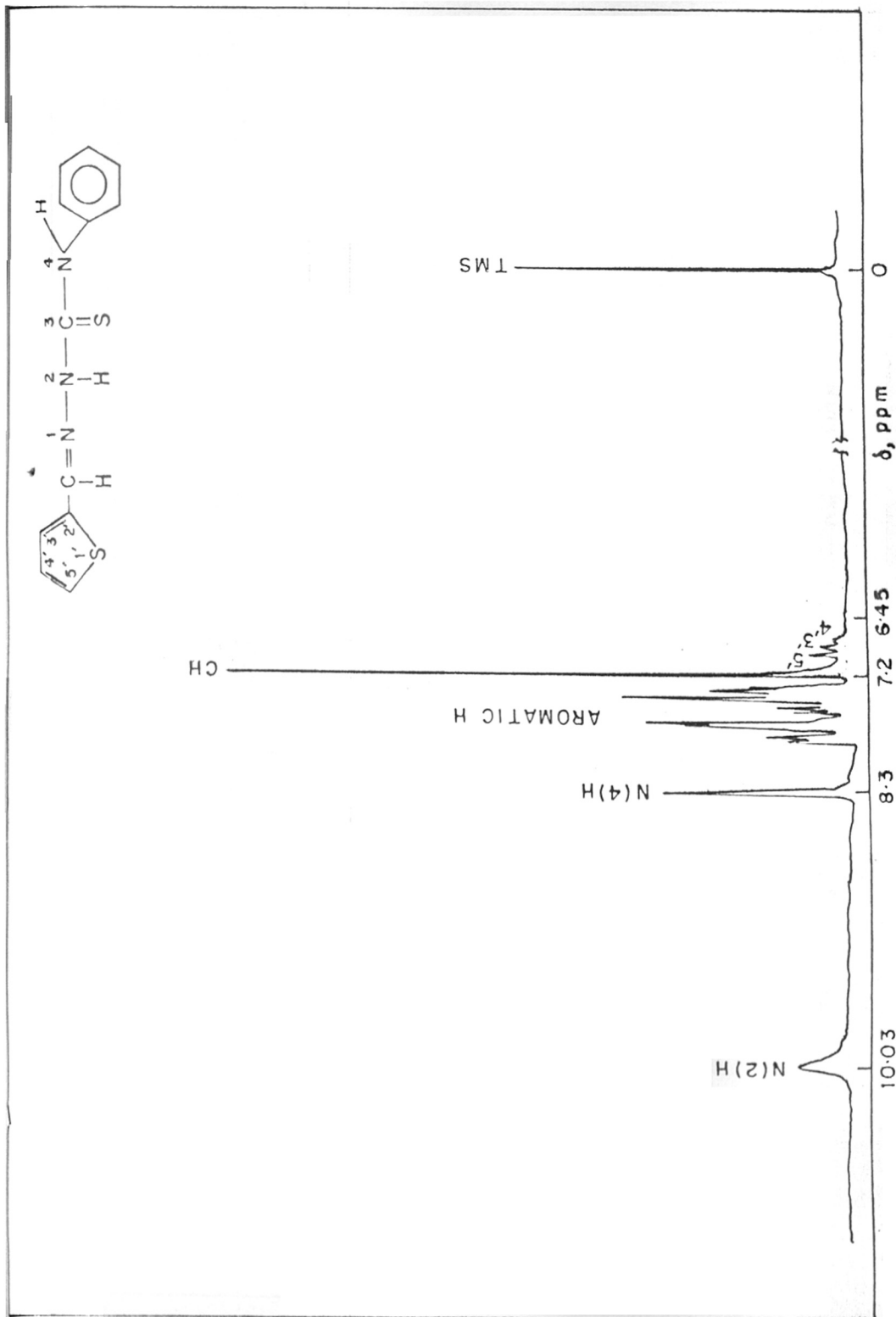


FIG. 10a. PMR SPECTRUM OF THIOPHENE-2-CARBOXALDEHYDE-4-PHENYLTHIOSEMICARBAZONE IN CDCl_3 172

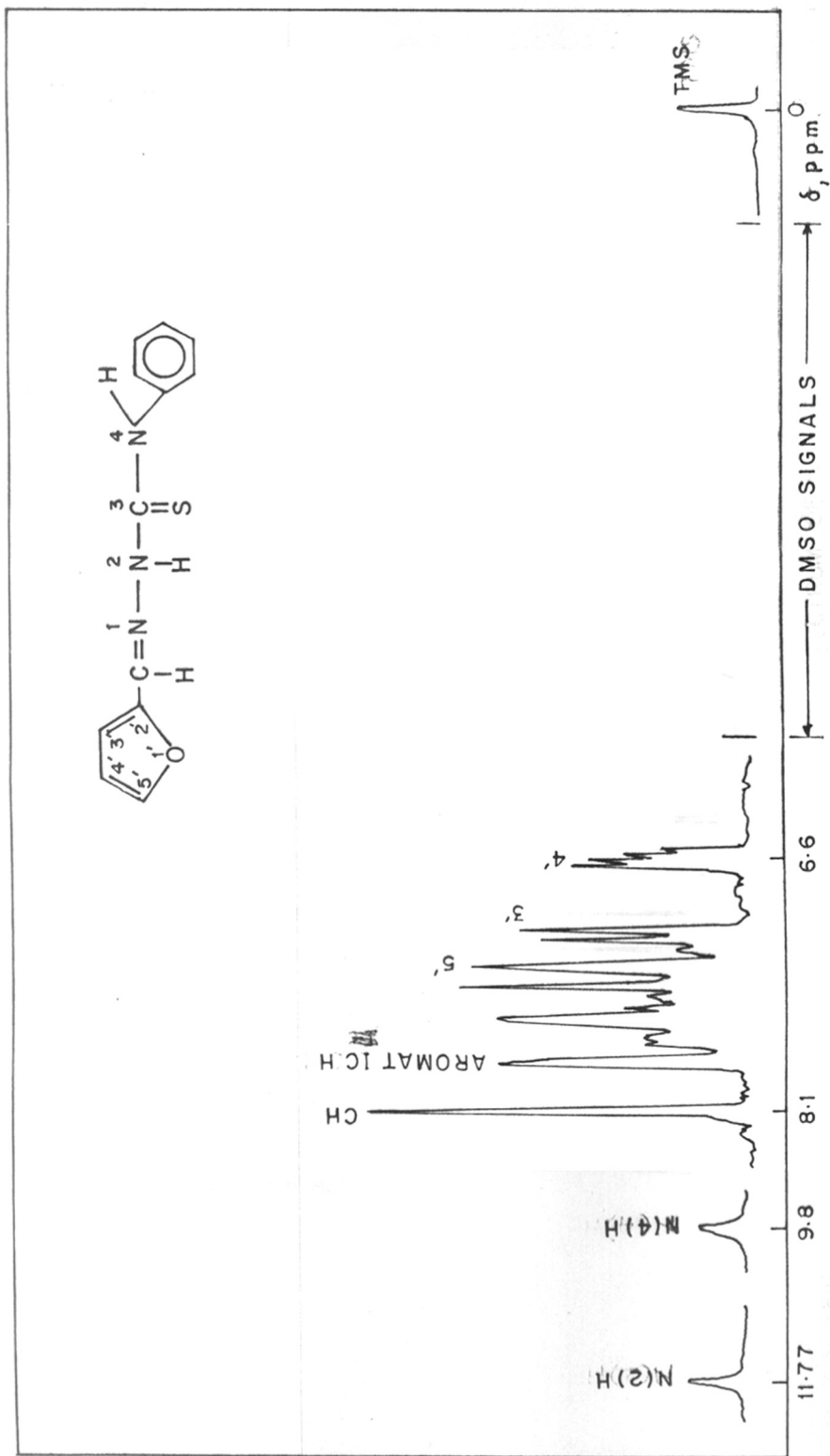


FIG. 11 PMR SPECTRUM OF 2-FURALDEHYDE-4-PHENYL-THIOSEMICARBAZONE IN DMSO

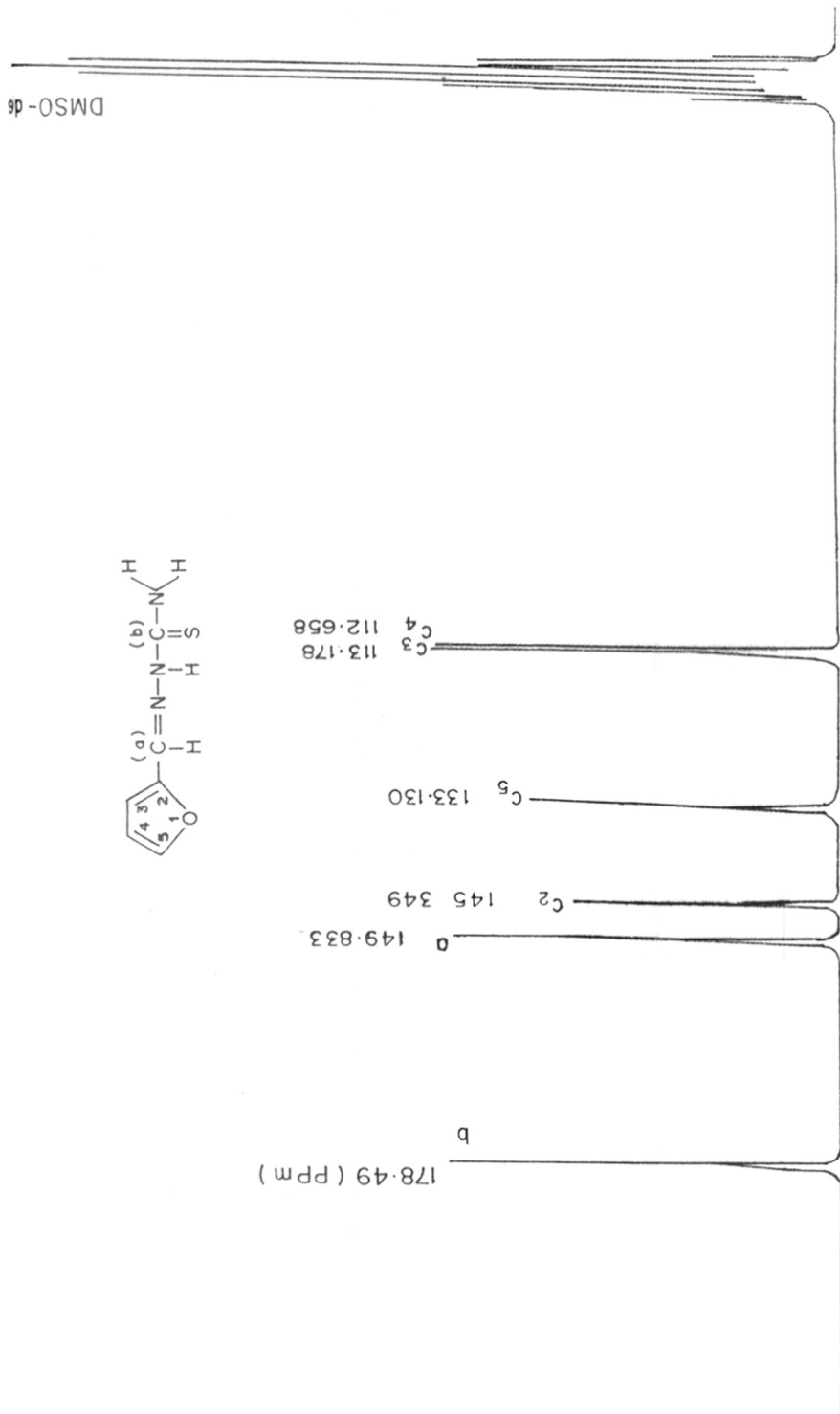


FIG. 12 PROTON NOISE DECOUPLED ¹³C N.M.R. SPECTRUM OF 2-FURALDEHYDE THIOSEMICARBAZONE IN DMSO - d₆

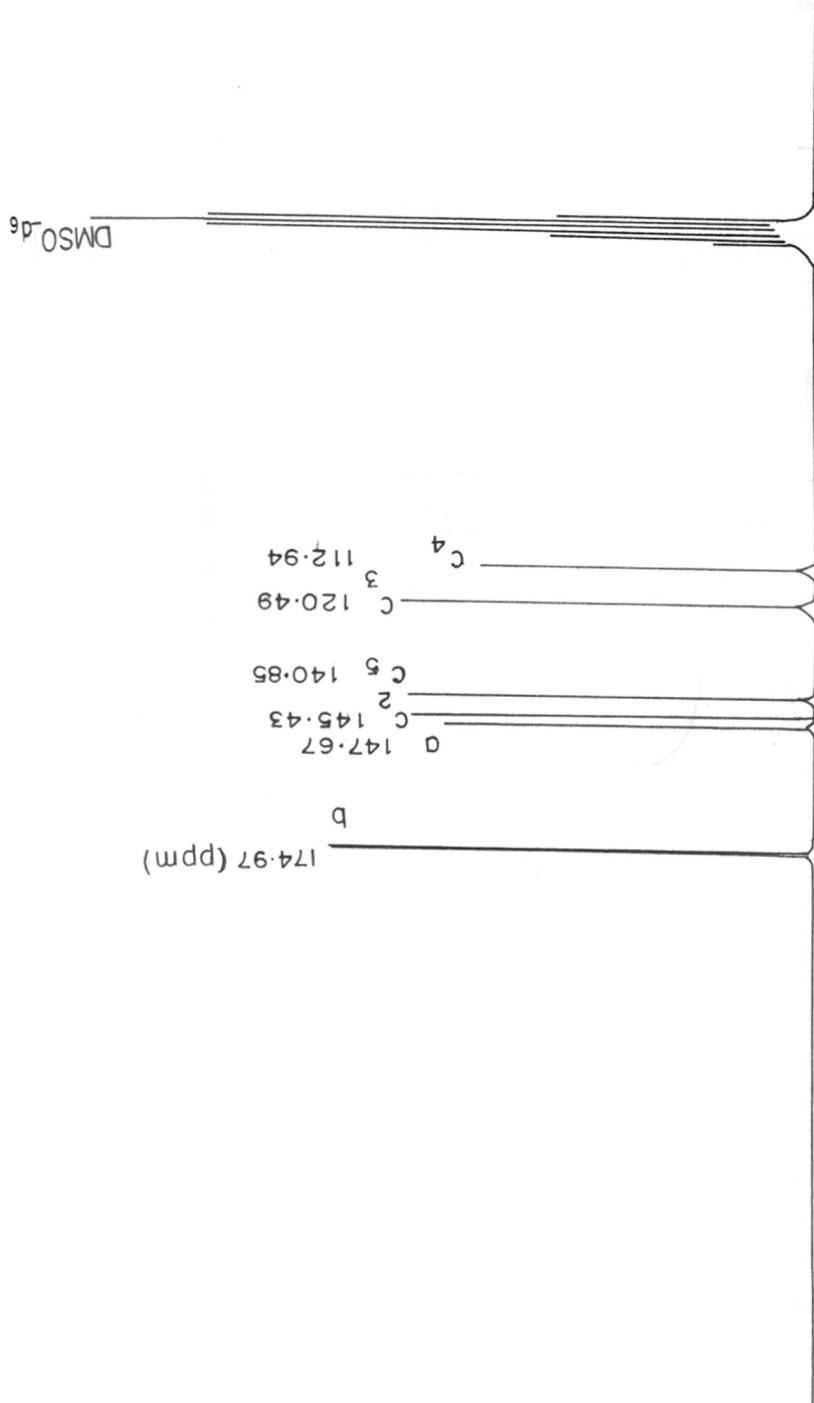


FIG. 13 ^{13}C NMR SPECTRUM OF BIS(2-FURALDEHYDE THIOSEMICARBAZONATO) NICKEL (II) IN $\text{DMSO-}d_6$

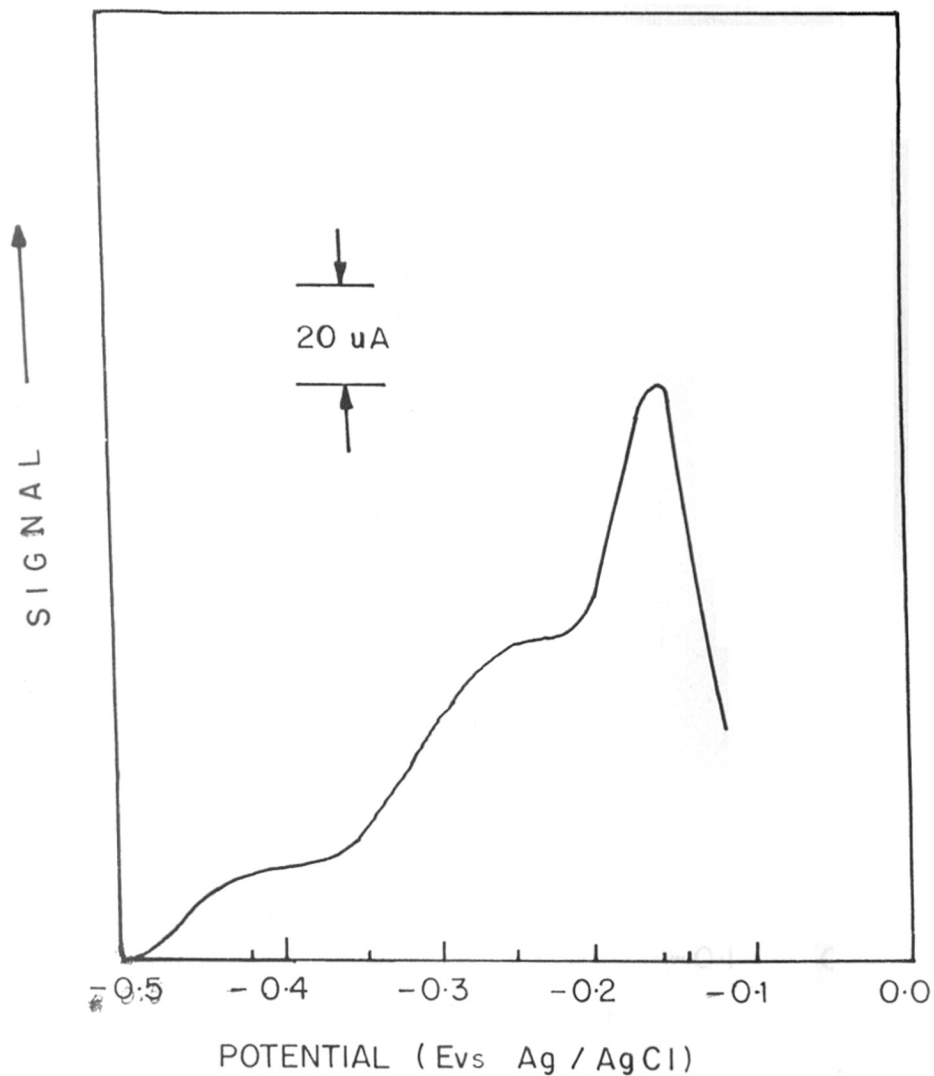


FIG. 14 DIFFERENTIAL PULSE POLAROGRAM OF
2-FURALDEHYDE THIOSEMICARBAZONE IN 40%
ISOPROPANOL PHOSPHATE BUFFER (PH=7.7)

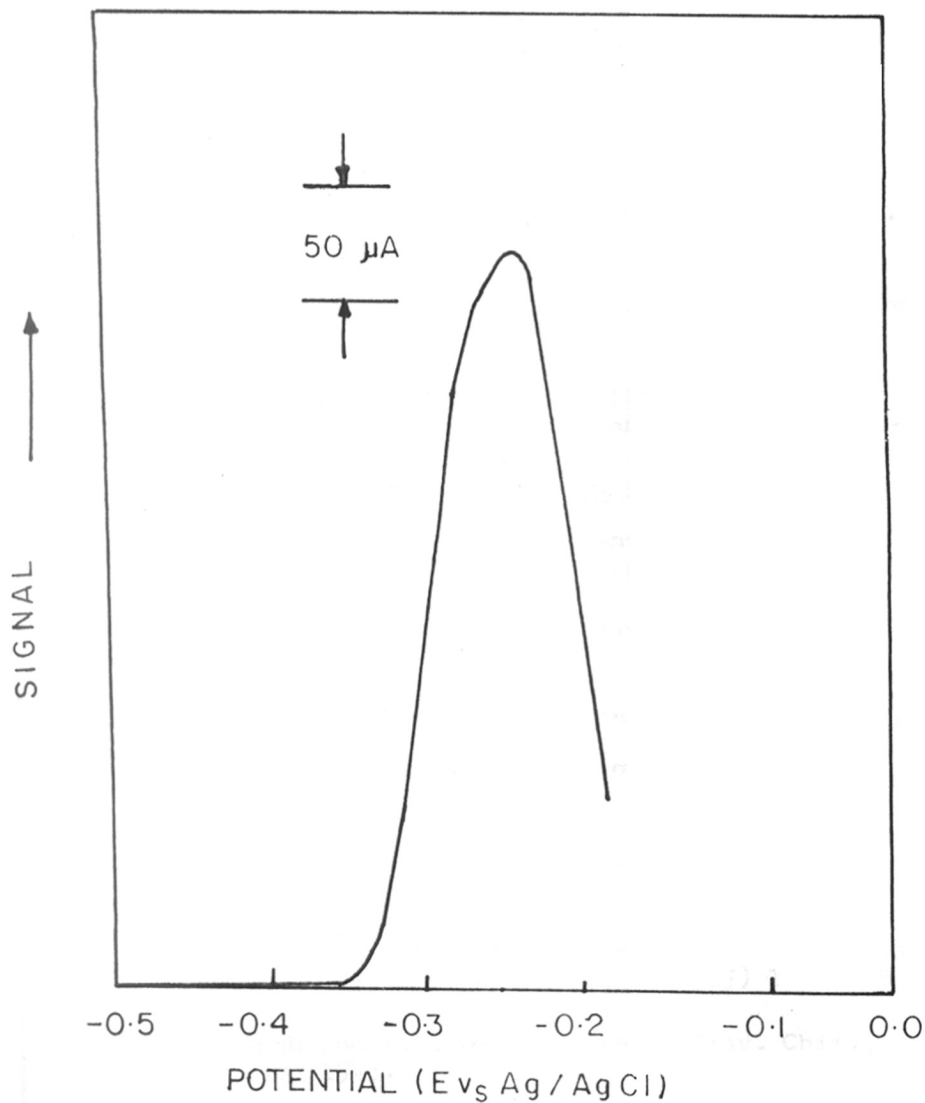


FIG. 15 DIFFERENTIAL PULSE POLAROGRAM OF THIOSEMI-CARBAZIDE IN 40% ISOPROPANOL-PHOSPHATE BUFFER (PH=7.7)

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**CHAPTER III : SYNTHESIS AND SPECTRAL STUDIES ON METAL
COMPLEXES OF 5-ALKYLTHIO-1,3,4-THIADIAZOLINE-2-
THIONES**

Introduction

The mono- and di-substituted 1,3,4-thiadiazoles have pharmacological properties¹ and are potential coordinating agents. These multi-functional molecules complex with a wide variety of metals, and the structural and stereochemical aspects of the metal complexes of 1,3,4-thiadiazole-2,5-dithiol and other substituted thiadiazoles have been extensively investigated²⁻⁶. However, the metal complexes of 5-alkylthio-1,3,4-thiadiazoline-2-thiones (alkyl = methyl, isopropyl or n-butyl) have not been studied. In order to elucidate the tautomeric forms and bonding modes adopted by these multidentate ligands, Ni(II), Pd(II) and/or Cd(II) complexes of 5-methylthio-1,3,4-thiadiazoline-2-thiones, 5-isopropylthio-1,3,4-thiadiazoline-2-thione and 5-butylthio-1,3,4-thiadiazoline-2-thione were synthesised and studied. The infrared, ¹³C NMR spectral and magnetic susceptibility data for the complexes are presented and discussed. X-ray crystallographic data on the structure of 5-methylthio-1,3,4-thiadiazoline-2-thione has been collected and its molecular structure established. The crystal of the compound, C₃H₄N₂S₃ is monoclinic, space group P2₁ n, a = 4.126(1), b = 9.507(1), c = 16.701(2) Å, β = 92.12(1)°, v = 654.7 Å³, z = 4,

$D_m = 1.68$, $D_x = 1.67 \text{ Mgm}^{-3}$, Mo $K\alpha$ $\lambda = 0.7107 \text{ \AA}$,
 $\mu = 0.98 \text{ mm}^{-1}$, $F(000) = 336.0$, $T = 293 \text{ K}$, $R = 0.037$
 for 900 observed reflections. The thiadiazole ring
 is planar with S-C(2) and C(2)-N(3) partial double
 bonds. The compound crystallises as 5-methylthio-
 1,3,4-thiadiazoline-2-thione due to proton transfer in
 an N-H...S hydrogen bond. The crystal structure is
 also stabilized by two short S-S interactions.

Experimental

Methyl iodide, n-butyl iodide and isopropyl
 bromide were of C.P. grade. 2,5-Dimercapto-1,3,4-
 thiadiazole (DMTD) was prepared according to the method
 described by Sandström⁷. DMSO- d_6 was purchased from
 Sigma Chemical Co., U.S.A. and palladium metal powder
 (chemically precipitated) was purchased from Arora-
 Matthey Ltd. All other chemicals were of C.P. grade.
 Solvents were purified and dried prior to use. Disodium
 tetrachloropalladate Na_2PdCl_4 , was prepared by the
 reported method⁸.

Preparation of derivatives of DMTD

The organic compounds, 5-methylthio-1,3,4-
 thiadiazoline-2-thione (Me-TD), 5-isopropylthio-
 1,3,4-thiadiazoline-2-thione (Isopr-TD) and 5-butylthio-
 1,3,4-thiadiazoline-2-thione (Bu-TD) were prepared by
 a slight modification of the general procedure described
 in the literature⁹.

a) 2,5-Dimercapto-1,3,4-thiadiazole, DMTD

The starting material for the substituted ligands was prepared by refluxing hydrazine hydrate (80%, 18 ml) in 150 ml pyridine (distilled and dried over NaOH) and carbon disulphide (54.6 g) initially at room temperature and finally on a water-bath for 1 hr. The bright yellow crystalline pyridinium salt (Yield, 48 g, 70%) obtained on concentration of the refluxed solution was dissolved in 500 ml water. The solution was filtered and the filtrate was acidified with 5-6 ml of concentrated hydrochloric acid. The white product formed was filtered, washed with 5 ml water and sucked dry and further dried under vacuum. Yield 38 g (97%), m.p. 169°C. Analysis: Found C, 16.13; H, 1.60; N, 17.06; S, 63.59%. Calculated for $C_2H_2N_2S_3$: C, 16.00; H, 1.33; N, 18.67; S, 64.00%.

b) 5-Methylthio-1,3,4-thiadiazoline-2-thione (Me-TD)

Me-TD was prepared by refluxing a mixture of 2,5-dimercapto-1,3,4-thiadiazole (6.0 g, 0.04 mole) in alcohol (70 ml), potassium hydroxide (2.24 g; 0.04 mole) in alcohol (50 ml) and methyl iodide (5.68 g, 0.04 mole) on a water-bath for 5 hrs. The solvent was removed under reduced pressure and the crude product was recrystallised from benzene. Yield 3.3 g (50%). M.p. 137°C. Elemental analysis: Found C, 22.03; H, 2.73; N, 16.78; S, 58.15%. Calculated for $C_3H_4N_2S_3$: C, 21.95; H, 2.44; N, 17.07; S, 58.54%.

The infrared spectrum in nujol shows the following absorption maxima (in cm^{-1}): 3240m, 3100m,b, 2900m,b, 2790w, 1500s, 1270s, 1130s, 1070s, 985w, 970w, 865w, 755w, 725s, 675m, 570w, 565w.

c) 5-Butylthio-1,3,4-thiadiazoline-2-thione, (Bu-TD)

Bu-TD was prepared by refluxing 2,5-dimercapto-1,3,4-thiadiazole (6.0 g, 0.04 mole) in alcohol (70 ml), potassium hydroxide (2.24 g, 0.04 mole) in alcohol (50 ml) and methyl iodide (5.68 g, 0.04 mole) on a water-bath for five hours. The solvent was removed under vacuum and the crude cream coloured product was recrystallised from benzene. Yield 3.19 g (50%). M.p. 85°C .
 Analysis: Found C, 35.76; H, 5.22; N, 13.60; S, 47.00%.
 Calculated for $\text{C}_6\text{H}_{10}\text{N}_2\text{S}_3$: C, 34.95; H, 4.85; N, 13.59; S, 46.60%.

The infrared spectrum in nujol shows the following absorption maxima (in cm^{-1}): 3230m, 3100mb, 3080mb, 2900mb, 2800w, 1500s, 1270s, 1115s, 1045s, 895w, 865w, 755w, 705s, 675m

d) 5-Isopropylthio-1,3,4-thiadiazoline-2-thione, Isopr-TD

This ligand was prepared by the same method as described for Me-TD and Bu-TD ligands. The quantities used were as follows: 2,5-dimercapto-1,3,4-thiadiazole (4.5 g, 0.03 mole), alcohol (60 ml), potassium hydroxide (1.68 g, 0.03 mole), in alcohol (30 ml) and isopropyl bromide (3.69 g, 0.03 mole). Yield 3.0 g (52%), m.p. 112°C .

Analysis: Found C, 31.10; H, 4.38; N, 15.45; S, 49.60%.
 Calculated for $C_5H_8N_2S_3$: C, 31.25; H, 4.17; N, 14.58;
 S, 50.00%.

The infrared absorption maxima (in cm^{-1}) observed in nujol are: 3240w, 3100mb, 2930mb, 2790w, 1500s, 1280s, 1125s, 1075s, 950w, 890w, 865w, 765m, 720s, 675m, 645w, 580w, 550w

The deuterated derivative of 5-methylthio-1,3,4-thiadiazoline-2-thione was prepared by refluxing 0.1 g of the compound in 10 ml D_2O (99.8%, Atomic Energy Commission, Bombay) under N_2 atmosphere followed by evaporation of the solvent under reduced pressure. The compound was dried under vacuum.

Preparation of Metal Complexes

1. Mono(5-methylthio-1,3,4-thiadiazoline-2-thiolato) potassium(I), K(Me-TD)

This compound was prepared by mixing solutions of 5-methylthio-1,3,4-thiadiazoline-2-thione (0.82 g, 0.005 mole) in alcohol (10 ml) and potassium hydroxide (0.28 g, 0.005 mole) in alcohol (5 ml) and heating the mixture on a waterbath for 1 hr. The product obtained was collected on a filter, washed with alcohol (2 ml) and dried under vacuum.

Yield: 0.35 g (35%). M.p. $205^{\circ}C$ (decomp.).

Analysis: Found C, 16.99; H, 0.64; N, 13.01; S, 46.92%.

Calculated for $C_3H_3N_2S_3K$: C, 17.82; H, 1.48; N, 13.86; S, 47.52%.

I.R. frequencies (cm^{-1}) in nujol: 1460m, 1140w, 1030s, 970w, 885w, 710w, 650m, 545w

2. Bis(5-methylthio-1,3,4-thiadiazoline-2-thiolato)
palladium(II), Pd(Me-TD)₂

Pd(Me-TD)₂ was prepared by mixing aqueous solution (40 ml) of disodium tetrachloropalladate, Na_2PdCl_4 , (0.441 g, 0.0015 mole) with an alcoholic solution (15 ml) of 5-methylthio-1,3,4-thiadiazoline-2-thione (0.492 g, 0.003 mole). The mixture was heated on a waterbath for 1 hr and the brown product obtained was collected on a filter, washed with water (5 ml) and alcohol (2x5 ml) and dried under vacuum. Yield 0.56 g (85%). M.p. 285°C (decomp.).

Analysis: Found C, 17.10; H, 1.93; N, 13.98; S, 43.86; Pd, 24.81%. Calculated for $C_6H_6N_4S_6Pd$: C, 16.65; H, 1.38; N, 12.95; S, 44.40; Pd, 24.61%.

Infrared frequencies (cm^{-1}) in nujol observed were 2920w, 1410s, 1090s, 1045s, 1010m, 962s, 885w, 780s, 720w, 665s, 395m, 370w.

3. Bis(5-butylthio-1,3,4-thiadiazoline-2-thiolato)
palladium(II), Pd(Bu-TD)₂

An aqueous solution (50 ml) of disodium tetrachloropalladate, Na_2PdCl_4 (0.588 g, 0.002 mole) was added to

an alcoholic solution (20 ml) of 5-butylthio-1,3,4-thiadiazoline-2-thione (0.82 g, 0.004 mole) with stirring and the mixture was heated on waterbath for 1 hr. The red brown product obtained was collected on filter, washed with water (5 ml) and alcohol (2x5 ml) and dried under vacuum. Yield: 0.90 g (87%). M.p. 245°C (decomp.).

Analysis: Found C, 28.98, H, 4.41; N, 11.19; S, 36.25; Pd, 20.62%. Calculated for $C_{12}H_{18}N_4S_6Pd$: C, 27.89; H, 3.49; N, 10.84; S, 37.18; Pd, 20.60%.

Infrared spectrum in nujol shows the following absorption maxima (cm^{-1}): 2880w, 1455s, 1230w, 1090m, 1035m, 910w, 870w, 775m, 660m, 395w, 370m.

4. Bis(5-isopropylthio-1,3,4-thiadiazoline-2-thiolato) palladium(II), Pd(Isopr-TD)₂

Disodium tetrachloropalladate, Na_2PdCl_4 (0.588 g, 0.002 mole) was dissolved in 50 ml water and added to an alcoholic solution (25 ml) of 5-isopropylthio-1,3,4-thiadiazoline-2-thione (0.768 g, 0.004 mole). The resultant mixture was heated on waterbath for 1 hr. The deep brown product formed was collected on a filter, washed with water (5 ml) and alcohol (2x5 ml) and dried under vacuum. Yield 0.42 g (87%). M.p. 183°C (decomp.). Analysis: Found C, 25.99; H, 2.79; N, 10.87; S, 40.70; Pd, 21.60%. Calculated for $C_{10}H_{14}N_4S_6Pd$: C, 24.57; H, 2.87; N, 11.47; S, 39.31; Pd, 21.78%.

I.R. frequencies (cm^{-1}) observed: 2910m, 2740w, 1420s, 1240w, 1152w, 1095s, 1040s, 925w, 875w, 775s, 670m, 615w, 560w, 540w, 380m, 300w.

5. Bis(5-methylthio-1,3,4-thiadiazoline-2-thiolato) nickel(II), Ni(Me-TD)₂

Ni(Me-TD)₂ was prepared by mixing solutions of nickel chloride hexahydrate, NiCl₂·6H₂O (0.476 g, 0.002 mole) in alcohol (10 ml) with 5-methylthio-1,3,4-thiadiazoline-2-thione (0.656 g, 0.004 mole) in alcohol (10 ml). The pH of the resulting mixture was adjusted to 7.0-7.5 with the addition of dilute ammonia (1:3) and heated on a waterbath for 1 hr. The green compound obtained was collected on filter, washed with alcohol (3x5 ml) and dried under vacuum. Yield 0.66 g (85%). M.p. 255°C (decomp.). Analysis: Found C, 19.83; H, 2.85; N, 14.47; S, 48.54; Ni, 15.05%. Calculated for C₆H₆N₄S₆Ni: C, 18.72; H, 1.56; N, 14.56; S, 49.91; Ni, 15.26.

μ_{eff} . (B.M.) observed: 2.27.

I.R. frequencies (cm^{-1}) observed: 2940m, 1440s, 1140s, 1088s, 1040s, 978w, 880w, 765s, 670w, 545w, 415w, 360w.

6. Bis(5-butylthio-1,3,4-thiadiazoline-2-thiolato) nickel(II), Ni(Bu-TD)₂

Nickel chloride hexahydrate, NiCl₂·6H₂O (0.476 g, 0.002 mole) in alcohol (10 ml) was added to Bu-TD

(0.824 g, 0.004 mole) in alcohol (5 ml). The pH of the resulting mixture was adjusted to 7.5 with the addition of dilute ammonia solution (1:3) and heated on a waterbath for 1 hr. The light green compound obtained was filtered, washed with alcohol (3x5 ml) and dried under vacuum. Yield 0.80 g (86%). M.p. 238°C (decomp.). Analysis: Found C, 30.80; H, 4.58; N, 12.15; S, 39.30; Ni, 12.06%. Calculated for $C_{12}H_{18}N_4S_6Ni$: C, 30.72; H, 3.84; N, 11.95; S, 40.96; Ni, 12.53%.

μ_{eff} . (B.M.) observed: 2.26.

Infrared spectrum in nujol shows the following absorption maxima (cm^{-1}): 2880w, 1465s, 1240w, 1085s, 1035s, 895w, 865w, 755s, 670w, 390w, 365w.

7. Bis(5-isopropyl-1,3,4-thiadiazoline-2-thiolato) nickel(II), Ni(Isopr-TD)₂

This compound was prepared by mixing solutions of nickel chloride hexahydrate, $NiCl_2 \cdot 6H_2O$ (0.476 g, 0.002 mole) in alcohol (10 ml) with Isopr-TD (0.768 g, 0.004 mole) in alcohol (10 ml). The pH of the mixture was maintained at 7.0-7.5 by adding dilute ammonia solution (1:3) and heated on waterbath for 1 hr. The green complex obtained was collected on a filter, washed with alcohol (3x5 ml) and dried under vacuum. Yield 0.75 g (85%). M.p. 178°C (decomp.).

Analysis: Found C, 27.70; H, 4.45; N, 13.55; S, 43.73; Ni, 13.06%. Calculated for $C_{10}H_{14}N_4S_6Ni$: C, 27.23; H, 3.18; N, 12.71; S, 43.56; Ni, 13.32%.

μ_{eff} . (B.M.) observed: 2.42.

I.R. frequencies (cm^{-1}) observed in nujol spectrum: 2925m, 2800w, 1455s, 1240w, 1155s, 1075s, 840w, 885w, 760m, 670w, 625w, 440m, 310w.

8. Bis(5-methylthio-1,3,4-thiadiazoline-2-thiolato) cadmium(II), $Cd(Me-TD)_2$

This compound was prepared by the same method as described for the Ni(II) complexes using $CdCl_2 \cdot 2.5H_2O$ (0.228 g, 0.001 mole) in alcohol (15 ml) and Me-TD (0.328 g, 0.002 mole) in alcohol (5 ml). The pH of the mixture was adjusted to 7.0 with dilute ammonia (1:3) addition and the cream coloured compound formed was filtered, washed with alcohol (2x5 ml) and dried *in vacuo*. Yield 0.36 g (81%). M.p. 228°C (decomp.). Analysis: Found C, 15.96; H, 2.73; N, 12.73; S, 42.08; Cd, 25.03%. Calculated for $C_6H_6N_4S_6Cd$: C, 16.42; H, 1.37; N, 12.77; S, 43.79; Cd, 25.64%.

Infrared spectrum in nujol shows the following absorption frequencies (cm^{-1}): 2940w, 1440m, 1155m, 1080s, 1055s, 1022s, 975m, 965m, 895w, 765s, 660m, 540w, 330w.

9. Bis(5-butylthio-1,3,4-thiadiazoline-2-thiolato)
cadmium(II), Cd(Bu-TD)₂

Cd(Bu-TD)₂ was prepared by following essentially the same method as described for Cd(Me-TD)₂. The following quantities were used. CdCl₂·2.5H₂O, (0.228 g, 0.001 mole), in alcohol (15 ml), Bu-TD (0.412 g, 0.002 mole) in alcohol (5 ml). Yield 0.83 g (80%). M.p. 182°C (decomp.).

Analysis: Found C, 28.42; H, 3.83; N, 11.39; S, 37.75; Cd, 22.24%. Calculated for C₁₂H₁₈N₄S₆Cd: C, 27.57; H, 3.45; N, 10.72; S, 36.75; Cd, 21.52%.

I.R. frequencies (cm⁻¹) observed in nujol: 2840w, 1435s, 1220w, 1085m, 1025s, 910w, 870w, 765m, 655m, 544w, 355w.

Crystal structure determination of 5-methyl-thio-1,3,4-thiadiazoline-2-thione¹⁰

Transparent yellow, needle shaped crystals of 5-methylthio-1,3,4-thiadiazoline-2-thione (Me-TD) were obtained by slow evaporation of an alcoholic solution. Single crystal of an approximate dimensions 0.35 x 0.25 x 0.48 mm was used for data collection; lattice parameters from 22 reflections ($22 \leq 2\theta \leq 38^\circ$); Enraf-Nonius CAD-4F-11M diffractometer, graphite-monochromated MoK_α radiation, three standard reflections ($\bar{1}$, 5, $\bar{11}$, 075, 24 $\bar{7}$). 5% intensity variation; w/2 scan mode; scan speed 1° min⁻¹; $\theta \leq 23.5^\circ$; 1203 reflections

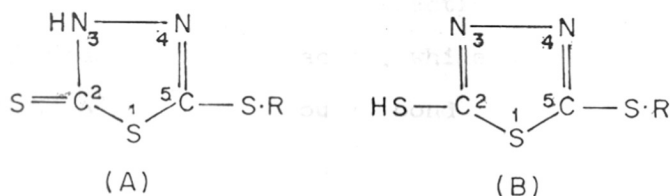
measured, 900 significant ($|FO| < 3\sigma|FO|$); index range h 0-4, k 0-10, l \pm 18; no correction for absorption. Structure solved by direct methods using MULTAN 78¹¹.

Crystal data

$C_3H_4N_2S_3$, $M = 164.3$, monoclinic, $P2_1/n$
 $a = 4.126(1)$, $b = 9.507(1)$, $c = 16.701(2)$ Å,
 $\beta = 92.12(1)^\circ$, $V = 654.7$ Å³, $Z = 4$, $D_m = 1.68$,
 $D_x = 1.67$ Mg m⁻³, $MoK\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.98$ mm⁻¹,
 $F(000) = 336.0$, $T = 293$ K, $R = 0.037$ for 900 observed reflections.

Results and Discussion

Thione-thiol tautomerism is possible in the 1,3,4-thiadiazole ring system when certain substituents, such as mercapto, hydroxy or amino are present¹. 5-Alkylthio-1,3,4-thiadiazoline-2-thiones studied here exist in the thione form in the solid state as evidenced from infrared spectral data. Bands attributable to $\nu(\text{SH})$ in the region $2600\text{--}2550\text{ cm}^{-1}$ are absent in the spectra. These compounds showed N-H stretching modes of vibration (ca 3100 cm^{-1}) and strong characteristic thioamide bands^{12,13} due to extensive coupling of (NH), (CN) and (CS) vibrational activity with the regions $1500\text{--}1395\text{ cm}^{-1}$, $1420\text{--}1260\text{ cm}^{-1}$, $1140\text{--}940\text{ cm}^{-1}$ and $850\text{--}700\text{ cm}^{-1}$. In compounds where a thiocarbonyl group is linked to nitrogen atoms, strong vibrational coupling effects are possible and C=S vibration is not localised. However, in chloroform solution, weak absorptions at $\sim 2560\text{ cm}^{-1}$ due to $\nu(\text{SH})$ along with medium to strong absorptions at $\sim 3400\text{ cm}^{-1}$ due to $\nu(\text{NH})$ were observed. Postulate may be advanced that in chloroform solution both thione (A) and thiol B) forms may be present.



R = methyl isopropyl or n-butyl

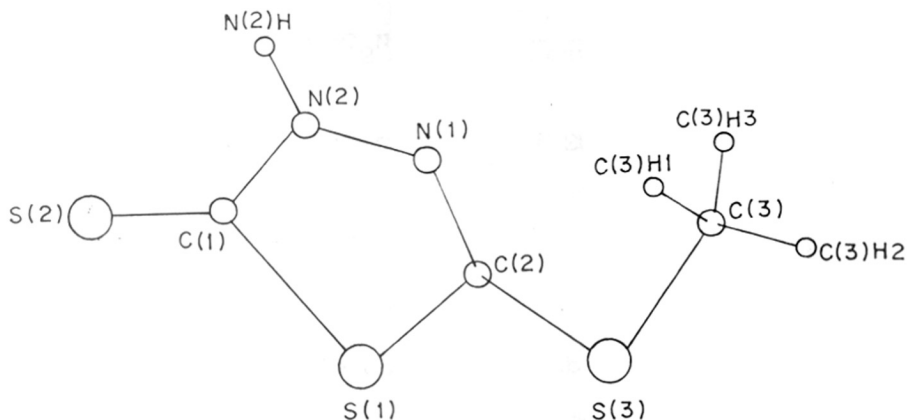
The U.V. absorption spectra of 5-alkylthio-1,3,4-thiadiazoline-2-thiones in ethanol solution show two absorption bands with λ_{\max} at 325-314 nm and at 245-224 nm. The absorption bands are nearly in identical position with those reported for 2-methylthio-4-methyl-5-thione-1,3,4-thiadiazole and other derivatives in ethanol by Thorn¹⁴. It may be inferred that in alcohol solutions, 5-alkylthio-1,3,4-thiadiazoline-2-thiones exist predominantly in the thione form. Spinner¹⁵ has studied infrared spectra of 2- and 4-mercaptopyridine, pyrimidine and quinoline of 2-mercaptopyrazine and quinoxaline of 1-mercaptoisquinoline of their N-methyl and S-methyl derivatives, of 3-mercaptopyridine and 8-mercaptoquinoline and their S-methyl derivatives and concluded that in systems of this type the compounds exist predominantly in thione form in solid state as well as in solvents of low polarity.

Bond lengths and bond angles in 5-methylthio-1,3,4-thiadiazoline-2-thione molecule are given in Table 7. Bond lengths S(2) - C(1) and C(1) - N(2) [1.665 (4) and 1.330(5) Å] respectively indicate partial double bond character, while C(2) - N(1) [1.282(5) Å] is a pure double bond. This type of

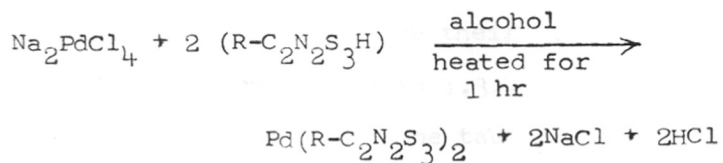
resonance structure also occurs in 5-mercapto-1,3,4-thiadiazole-2-thione¹⁵. The molecule, with the exception of the side groups, is essentially planar. The largest torsion angle within the five membered ring is $-1.0(4)^\circ$, N(2) is protonated as in 5-mercapto-1,3,4-thiadiazole-2-thione¹⁶, which makes the ring system asymmetric compared to 2,5-dimethylthiadiazole¹⁷ and 1,3,4-thiadiazole¹⁸ which both have approximate C_{2v} symmetry. The molecules are held together by an intermolecular N(2)...S(2) hydrogen bond [S(2)...N(2) = $3.299(6) \text{ \AA}$, S(2)...H[N(2)] = $2.29(16) \text{ \AA}$ and S(2) ...H[N(2)]-N(2) = $174(1)^\circ$].

There are two short S...S interactions [S(1) ...S(3) = $3.520(5) \text{ \AA}$, S(1) ...S(3) = $3.489(5) \text{ \AA}$]. These are attributed as being due to orbital interactions around sulphur and are also responsible for intermolecular interactions¹⁹.

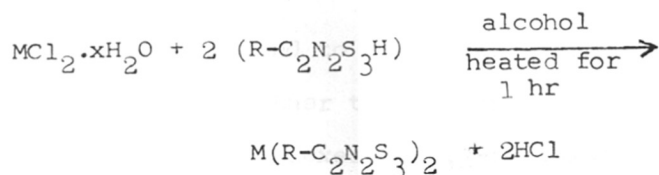
A perspective view of the molecule and the numbering of the atoms is given below.



Bis(5-alkylthio-1,3,4-thiadiazoline-2-thiolato) palladium(II) complexes were prepared by mixing aqueous solutions of sodium tetrachloropalladate(II) and the corresponding alkylthio compound in alcohol in 1:2 mole ratios. The reaction may be represented by the equation



Nickel(II) and cadmium(II) complexes were synthesised by reacting the nickel or cadmium chloride hydrated salts with the corresponding alkylthio ligands in 1:2 mole ratios in alcohol medium at pH 7.0-7.5.



where M = Ni(II), x = 6

and M = Cd(II), x = 2.5

All the complexes are insoluble in the usual organic solvents and appear to be polymeric in nature. Cadmium(II) complexes however, are fairly soluble in DMSO.

The ^{13}C NMR chemical shift data for 5-alkylthio-1,3,4-thiadiazoline-2-thiones and their cadmium complexes are presented in Table 8 (Figs. 16-18). The values of the chemical shift for C-2 indicates that in dimethyl sulphoxide solution, these compounds exist in the thione form. This is in agreement with the findings that certain alkylamino-, arylamino-1,2,3-thiadiazoline-thiones have their thione carbon resonance near 185 ppm²⁰, and in 1,3,4-thiadiazole derivatives at 188 ppm²¹. Thione tautomers have been observed as predominant species in several structurally related 4-thiazoline-2-thiones in which the thione carbon resonance appears in the 185-190 ppm range²². The significant upfield shift of the C-2 carbon resonance in cadmium complexes (175-176 ppm) suggests

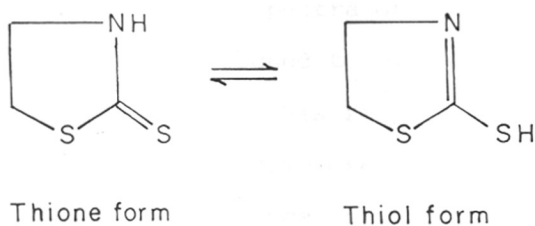
binding of the ligand to the metal atom through thiolate sulphur rather than thione-sulphur. A ^{13}C NMR study of copper complexes of 1,3-imidazoline-2-thione $\text{Cu}(\text{LH})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) involving thione-sulphur donation shows chemical shifts for the thione carbon atom at 184.5 ppm in the free molecule and 180.8 ppm in both the reported complexes²³. ^{13}C NMR measurements of 2-furaldehyde thiosemicarbazone and its neutral palladium(II) and nickel(II) chelate complexes also show chemical shifts for the thiolate carbon at 178.2 ppm in the free ligand and at 174.4 ppm in the chelates²⁴. The C-5 as well as alkyl carbon resonances in cadmium complexes however, are shifted downfield. As a result of complexation, there seems to be greater participation of the lone pair of electrons of the alkyl sulphur atom in the delocalization of the π -electron cloud of the parent heterocyclic ring system.

The infrared spectra of ligands and their metal complexes in Nujol are given in Figs. (19-21) and their possible assignments are given in Table 9.

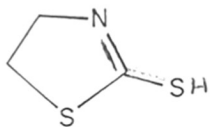
Of the ligand (5-methylthio-1,3,4-thiadiazoline-2-thione) absorptions at 3200(w), 3100(m,b), 2900(m), 2790(w) cm^{-1} , one is still present in the deuterated form

at $2895(w) \text{ cm}^{-1}$ and may be assigned to the $\nu(\text{CH})$ mode, while a new strong and broad band centered at $2280 \text{ cm}^{-1}(s,b)$ is assignable to the $\nu(\text{ND})$ mode, the corresponding $\nu(\text{NH})$ band at 3200 cm^{-1} disappears giving a $\nu(\text{NH}) : \nu(\text{ND})$ ratio of 1:4.

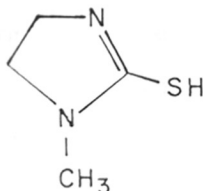
After reaction with metal salts, the ligands appear entirely to assume the thiol form as is evident from the absence of $\nu(\text{NH})$ vibrations around $3100\text{-}3180 \text{ cm}^{-1}$; the absorption bands due to the thioketo form initially at $\sim 1270 \text{ cm}^{-1}$ ascribable to the coupled CN vibration in the ligands have also disappeared. Basson et al.²⁵ have proposed that thiazolidine-2-thione changes into thiol form in solution and then bonds to Cu(II).



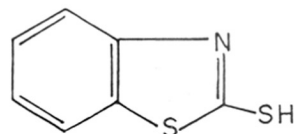
via the mercaptide sulphur and either the N or S heteroatom of the ligand. Similarly, the mercapto-substituted ligands, 2-mercaptothiazoline (SHth) 1-methyl-2-mercaptoimidazole (SHMe) and 2-mercapto-benzothiazole (SH-btz) exist in thioketo form in



SHth



SHme

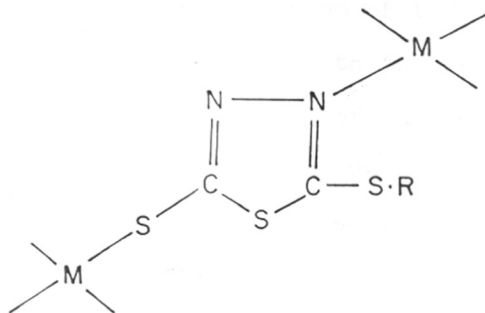


SHbtz

solid state and after reaction with the metal salt they entirely take the thiol form as is evidenced by the infrared and NMR spectra of these ligands and their platinum group metal complexes^{23,26}. The absorption band at $\sim 720 \text{ cm}^{-1}$ (at 710 cm^{-1} in the deuterio derivative) which contains a major contribution from $\nu(\text{C}=\text{S})$, is reduced considerably or absent in the spectra of the corresponding complexes. The intense band present in the $600\text{-}700 \text{ cm}^{-1}$ region in the spectra of the complexes could not be unequivocally assigned to $\nu(\text{C}-\text{S})$ due to the ligand $\nu(\text{C}-\text{S})$ vibrations in this region. A comparison of the far i.r. spectra of the complexes with those of the ligands reveals the presence of (medium to weak intensity) new bands in the region at $\sim 360 \text{ cm}^{-1}$ and at $\sim 415 \text{ cm}^{-1}$, ascribable to $\nu(\text{M}-\text{S})$ and $\nu(\text{M}-\text{N})$ vibrations²⁷. The infrared bands in the spectra of the potassium salt of 5-methylthio-1,3,4-thiadiazoline-2-thione and other metal complexes in the region $1460\text{-}1420 \text{ cm}^{-1}$

may be assigned to vibrational modes containing a high ν (C=N) contribution³. In the ligands ν (C=N) is observed²⁸ at ca 1500 cm^{-1} . The shift ($\sim 60\text{ cm}^{-1}$) of this band to lower frequencies suggests that nitrogen is involved in metal coordination. Thus, the i.r. frequency shifts show involvement of both N and S in bonding with metal atoms.

The following structure²⁹ involving a bridged configuration through the ligands is proposed for the metal complexes of 5-alkylthio-1,3,4-thiadiazoline-2-thione.



The complexes of nickel(II) studied here are paramagnetic (μ_{eff} 2.2-2.4 B.M.) whereas those of palladium are diamagnetic. The diamagnetism of the palladium complexes suggests a square planar arrangement of the ligand molecules around the central metal atom. The stoichiometry and i.r. investigations indicate that the nickel atom has a 4-coordinate square planar geometry. For the vast majority of four coordinate nickel(II) complexes planar geometry is preferred. The paramagnetism in the complexes suggests that the complex has some nickel atoms in octahedral environment. The additional coordination may be achieved through the hetero sulphur atom of the ligand. No definite conclusion for the participation of this atom could be drawn from i.r. studies due to the occurrence of the ligand bands in the region of interest. It is well known that magnetic moment values between 0 and 3.2 B.M. are observed³⁰ in the solid state for square planar Ni(II) complexes having some nickel atoms in octahedral environments, e.g. Ni(2,3-butylenediamine)Cl₂.

Table 7. Bond Distances (\AA) and Bond Angles ($^\circ$)
with their e.s.d's. in parantheses.

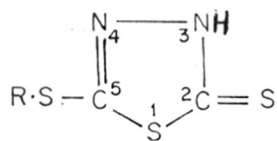
Bond lengths

S(1)-C(1)	1.738(4)
S(1)-C(2)	1.744(4)
S(2)-C(1)	1.665(4)
S(3)-C(2)	1.730(4)
S(3)-C(3)	1.794(5)
N(1)-N(2)	1.381(4)
N(1)-C(2)	1.282(5)
N(2)-C(1)	1.330(4)

Bond angles

C(1)-S(1)-C(2)	89.4(2)
C(2)-S(3)-C(3)	100.1(2)
N(2)-N(1)-C(2)	109.3(3)
N(1)-N(2)-C(1)	118.9(3)
S(1)-C(1)-S(2)	125.5(2)
S(1)-C(1)-N(2)	107.6(3)
S(2)-C(1)-N(2)	126.9(3)
S(1)-C(2)-S(3)	120.0(2)
S(1)-C(2)-N(1)	114.8(3)
S(3)-C(2)-N(1)	125.2(3)

Table 8 ^{13}C NMR chemical shifts of 5-alkylthio-2-mercapto-1,3,4-thiadiazoles and their cadmium complexes in DMSO-d_6



R = methyl, isopropyl or butyl

Compound	Chemical shifts (ppm)		
	C-5	C-2	Other carbon atoms
Me-TD	159.8	188.2	16.02
Isopr-TD	157.1	188.4	40.12, 23.16
Bu-TD	158.4	188.4	33.37, 31.16, 21.48, 13.61.
$\text{Cd}(\text{Me-TD})_2$	162.5	175.6	16.67
$\text{Cd}(\text{Bu-TD})_2$	161.5	176.3	34.15, 31.55, 21.61, 13.87

Table 9. Principal Infrared Absorption Frequencies (cm^{-1}) of 2-Alkylthio-5-mercapto-1,3,4-thiadiazoles and Their Metal complexes

Compound	(NH)	(C=N)	(C-N)	(C=S)	(C-S)	(M-N)	(M-S)
Me-TD	3200w 3100m, b	1500s	1270s	725s	675m	-	-
K-(Me-TD)	-	1450m	-	-	650m	-	385w
Ni(Me-TD) ₂	-	1440s	-	-	670m	445w	360w
Pd(Me-TD) ₂	-	1410s	-	720vw	665s	395m	370w
Cd(Me-TD) ₂	-	1440m	-	-	660m	540w	330w
Isopr-TD	3100w 3080m, b	1500s	1280s	720s	675m	-	-
Ni(Isopr-TD) ₂	-	1455s	1280vw	-	670w	440w	335m
Pd(Isopr-TD) ₂	-	1445s	-	720vw	660m	395w	370m
Bu-TD	3100w 3080m, b	1500s	1270s	705s	675m	-	-
Ni(Bu-TD) ₂	-	1465s	1270vw	-	670w	390w	365m
Pd(Bu-TD) ₂	-	1455s	-	-	660m	395w	370m
Cd(Bu-TD) ₂	-	1435s	1270vw	-	655m	545w	355w

Table 10. Principal Infrared Absorption Frequencies (in cm^{-1}) of
Heterocyclic Thione Derivatives and Their Ruthenium(II)
Carbonyl Complexes

Sl.No.*	NH	(C \equiv N)	(Ru-H)	(C \equiv O)	(C=N)	(C-N)	(C=S)	(C-S)	(Ru-N)	(Ru-S)
1.				1920	1485			695	415	315
2.				1920	1485			690	410	310
3.				1920	1480			700	410	330
4.			2020	1920	1480			695	415	330
5.			2005	1920	1480			695	415	320
6.			1990	1905	1480			690	410	330
7.		2180		1920	1480			690	410	330
8.		2180		1920	1480			690	410	310
9.		2190		1910	1480			690	410	340
10.				1920	1480			690	410	340
11.			2020	1900	1480			695	410	320
12.		2180		1905	1480			695	410	315
13.				1920	1480			695	410	310
14.			1990	1910	1480			695	410	320
15.		2180		1910	1480			690	415	315
16.				1900	1480			690	410	340
17.			1995	1900	1480			695	415	330
18.		2180		1900	1485			695	410	320
19.	3100m				1500	1270	725			
20.	3100w				1500	1280	720			

Table 10 (contd.)

Sl.No.	NH	(C≡N)	(Ru-H)	(C≡O)	(C=N)	(C-N)	(C-S)	(C-S)	(Ru-N)	(Ru-S)
21.	3100w				1500	1270	720			
22.	3100m				1500	1285	720			
23.	3100w				1500	1275	725			
24.	3120m				1500	1280	715			

* Compounds with numbers 1-24 are same as listed in Table 12.

Table 16. PMR Spectral Data (in ppm) on the Heterocyclic Thiones and Their Ru(II) Complexes in CDCl_3

Sl.No.*	Ru-H	CH_3	CH_2	CH	Aromatic H	NH
1.		2.33			6.6-7.6	
2.		1.35		3.7 qt	6.7-7.9	
3.		0.8 d	1.44m	3.52m	7.2-7.8	
4.	-13.0 t	2.27			6.9-7.7	
5.	-13.0 t	1.1, 1.27 d		3.22m	6.7-8.2	
6.	-13.0 t	0.88 d	1.55m	2.72m	6.9-8.33	
7.		0.84, 0.89 d 3.4	1.57m		7.1.8.0	
8.		1.1, 1.0 d 1.45, 1.5 d	2.4d, 3.6qt		7.0-7.6	
9.		1.06 m	1.57m	2.4qt, 3.06t	7.15-8.04	
10.		2.5			7.02-8.0	
11.	-13.3 t	2.66			6.60-8.3	
12.		0.82, 0.89 d 2.64		2.22m	6.93-8.0	
13.			2.25, 2.85 t		6.75-8.0	

Table II (contd.)

Sl.No.*	Ru-H	CH ₃	CH ₂	CH	Aromatic H	NH
14.	-13.t	1.78	2.25, 3.0 t		6.6-8.3	
15.		1.01d, 1.7, 1.9s	2.45, 2.95 t		6.6-8.0	
16.						
17.	-13.2t		1.65m, 2.1m		6.75-8.25	
18.						
19.		2.7 (2.6)				(14.4)
20.		1.27, 1.42 d (1.36, 1.43) d		3.67 qt (3.72 qt)		(14.54)
21.		0.9t, (0.83, 0.9t)	1.0, 1.5m, 3.75t			(14.5)
22.		1.75		3.05, 4.1 t		11.4
23.		3.66				10.91
24.				3.5m, 3.95m		8.1

* Compounds with numbers 1-24 are same as listed in Table 12. Values in brackets are observed in DMSO-d₆ solutions.

Table 12. Electronic Spectral Data on the Heterocyclic Thiones and Their Ru(II) Complexes

Sl. No.	Compound	λ_{max} (in nm)
1.	$\text{RuClCO}[\text{P}(\text{Ph}_3)]_2\text{Me-TD}$	340, 282
2.	$\text{RuClCO}[\text{P}(\text{Ph}_3)]_2\text{Isopr-TD}$	450, 340, 262, 240
3.	$\text{RuClCO}[\text{P}(\text{Ph}_3)]_2\text{-Bu-TD}$	480, 328, 260, 240
4.	$\text{RuHCO}[\text{P}(\text{Ph}_3)]_2\text{ Me-TD}$	338, 240.
5.	$\text{RuHCO}[\text{P}(\text{Ph}_3)]_2\text{Isopr-TD}$	450, 350, 278, 240
6.	$\text{RuHCO}[\text{P}(\text{Ph}_3)]_2\text{Bu-TD}$	320, 260, 240
7.	$\text{Ru}(\text{CH}_3\text{CHCN})\text{CO}[\text{P}(\text{Ph}_3)]_2\text{Me-TD}$	476, 340, 270, 240
8.	$\text{Ru}(\text{CH}_3\text{CHCN})\text{CO}[\text{P}(\text{Ph}_3)]_2\text{Isopr-TD}$	340, 240
9.	$\text{Ru}(\text{CH}_3\text{CHCN})\text{CO}[\text{P}(\text{Ph}_3)]_2\text{Bu-TD}$	344, 240
10.	$\text{RuClCO}[\text{P}(\text{Ph}_3)]_2\text{-Methyl-TD}$	460, 270, 240
11.	$\text{RuHCO}[\text{P}(\text{Ph}_3)]_2\text{-Methyl-TD}$	440, 310, 240
12.	$\text{Ru}(\text{CH}_3\text{CHCN})[\text{P}(\text{Ph}_3)]_2\text{-Methyl-TD}$	490, 280, 240
13.	$\text{RuClCO}[\text{P}(\text{Ph}_3)]_2\text{-Phenethyl-TD}$	260, 240
14.	$\text{RuHCO}[\text{P}(\text{Ph}_3)]_2\text{-Phenethyl-TD}$	350, 240
15.	$\text{Ru}(\text{CH}_3\text{CHCN})\text{CO}[\text{P}(\text{Ph}_3)]_2\text{-Phenethyl-TD}$	400, 340, 240
16.	$\text{RuClCO}[\text{P}(\text{Ph}_3)]_2\text{-Thiazolidine-2-thione}$	450, 309
17.	$\text{RuHCO}[\text{P}(\text{Ph}_3)]_2\text{-Thiazolidine-2-thione}$	350, 310

Table 12 (contd.)

Sl. No.	Compound	λ_{max} (in nm)
18.	$\text{Ru}(\text{CH}_3\text{CHCN})\text{CO}[\text{P}(\text{Ph}_3)]_2$ -Thiazolidine-2-thione	340, 316
19.	Me-TD	320, 240
20.	Isopr-TD	320, 239
21.	Bu-TD	320, 252
22.	Phenethyl-Tr	260, 225, 280sh
23.	Methyl-Tr	260, 220, 280sh
24.	Thiazolidine-2-thione	340, 300, 276

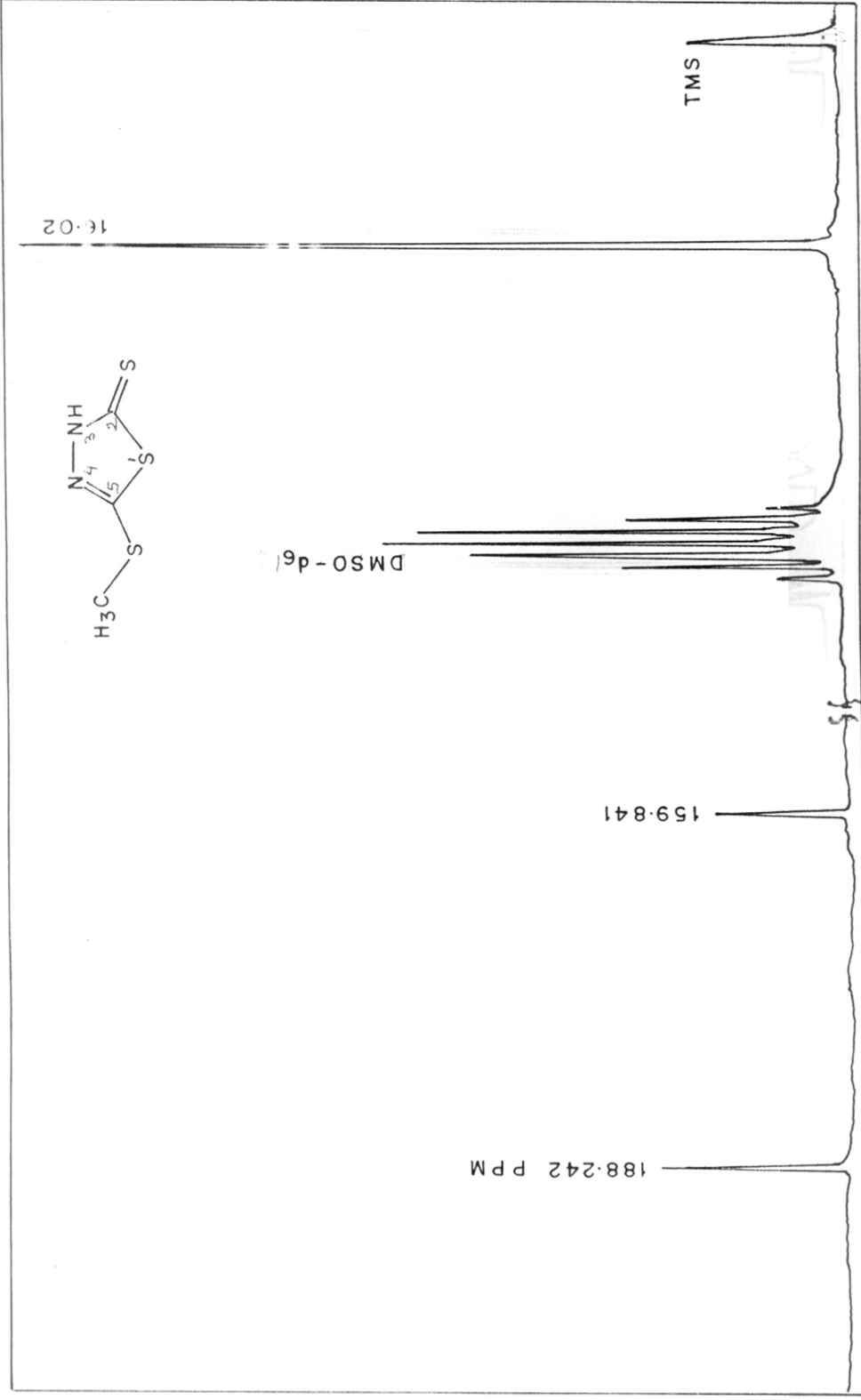
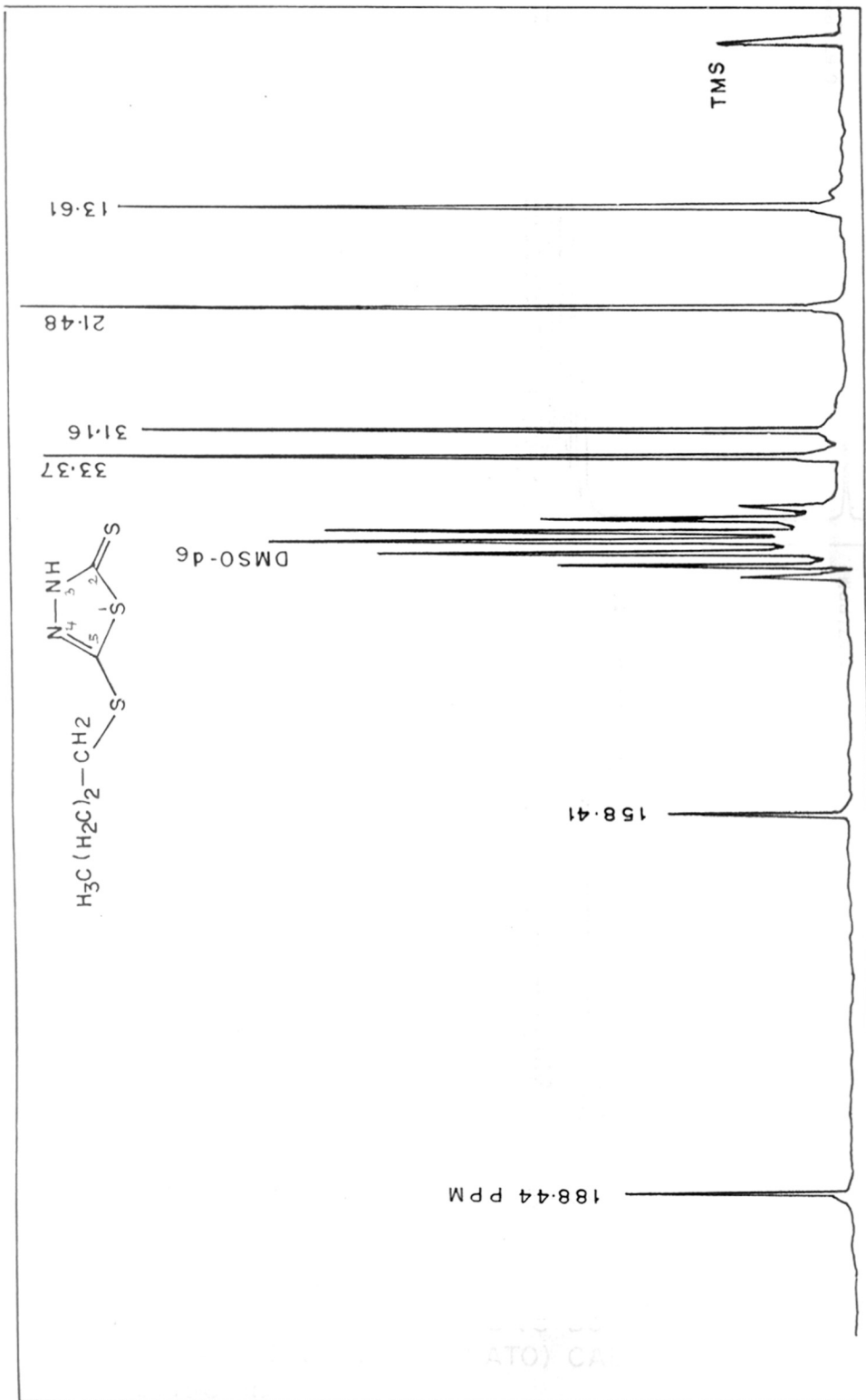


FIG.16 ^{13}C N.M.R. SPECTRUM OF 5-METHYLTHIO-1,3,4-THIADIAZOLINE-2-THIONE IN DMSO - d₆

FIG.17 ¹³C N.M.R. SPECTRUM OF 5-BUTYLTHIO-1,3,4-THIAZOLINE-2-THIONE IN DMSO - d₆

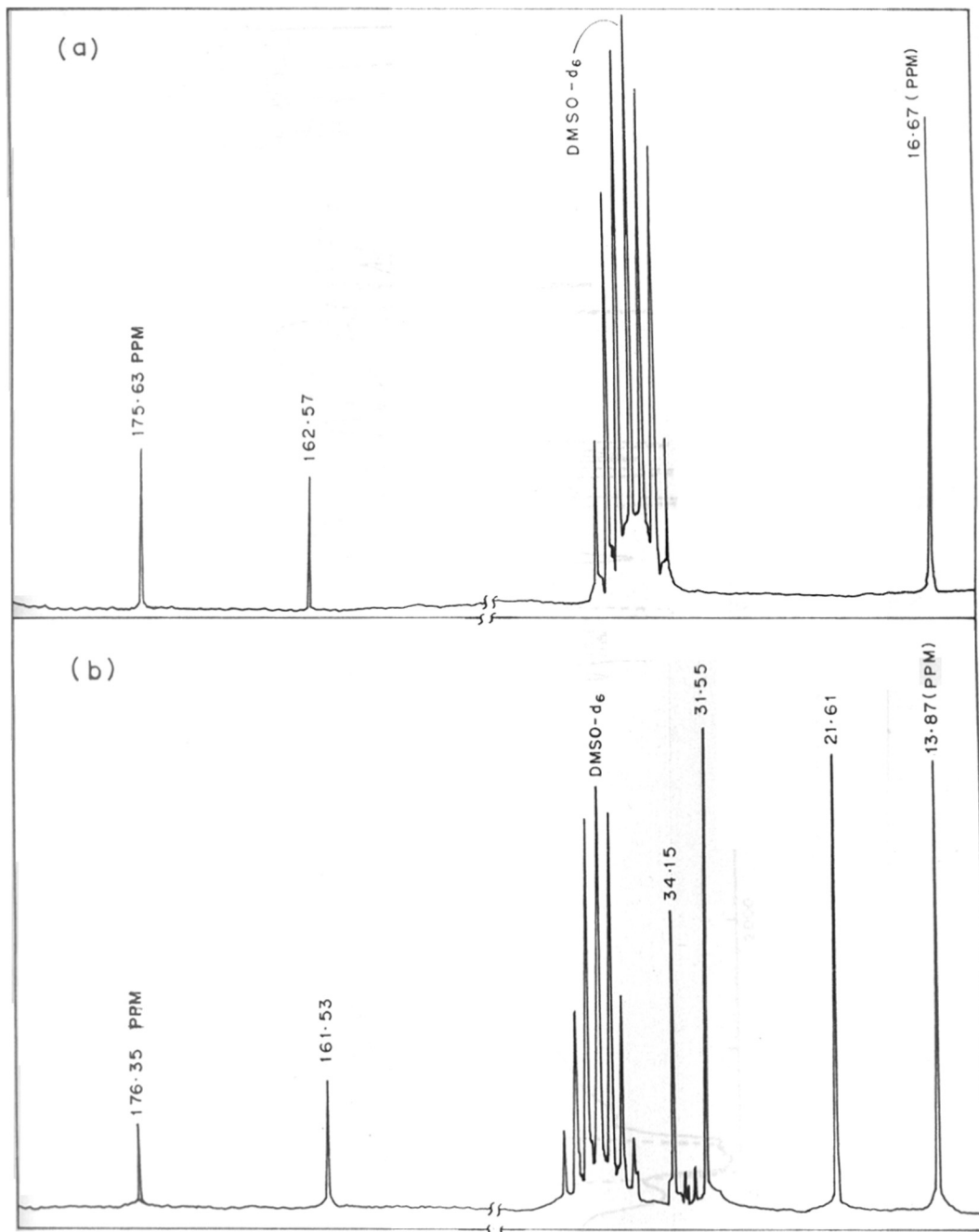


FIG. 18 a): ^{13}C NMR SPECTRUM OF BIS (5-METHYLTHIO-1,3,4-THIADIAZOLE-2-THIALATO) CADMIUM (II) IN DMSO-d_6

b): ^{13}C NMR SPECTRUM OF BIS (5-BUTYLTHIO-1,3,4-THIADIAZOLE-2-THIALATO) CADMIUM (II) IN DMSO-d_6

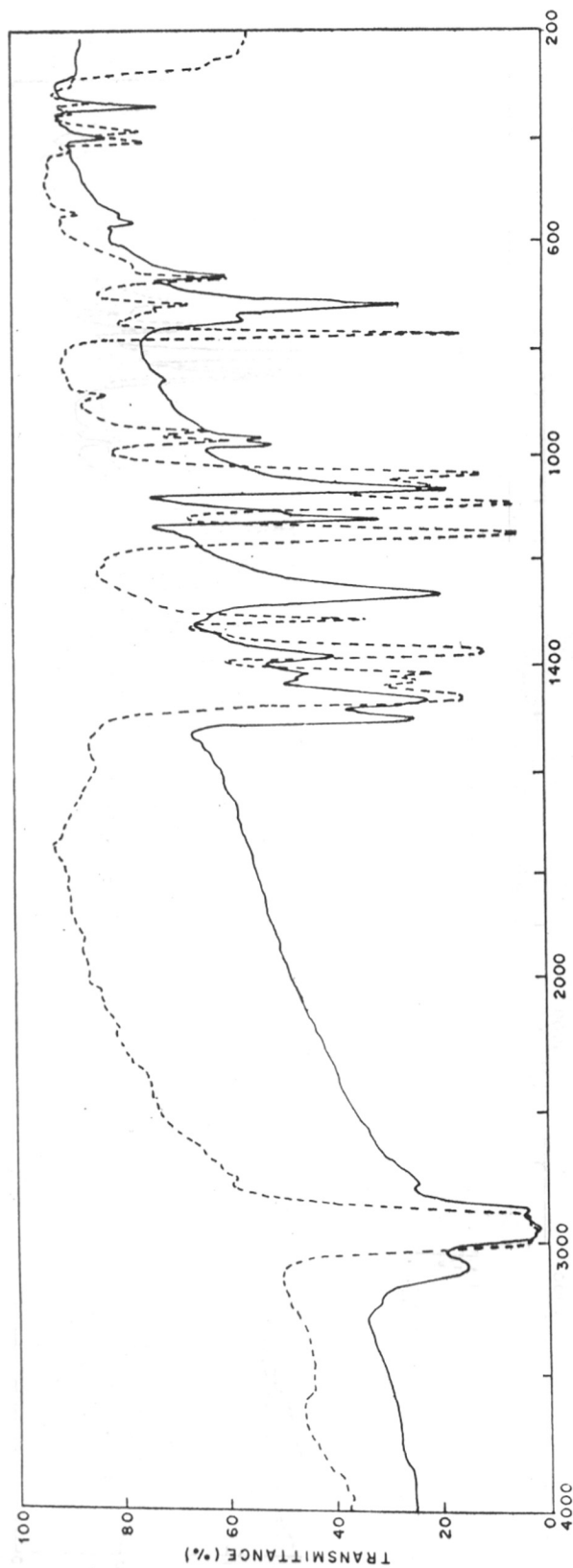


FIG. 19 INFRARED SPECTRA OF 5-METHYLTHIO-1,3,4-THIADIAZOLINE-2-THIONE Me-TD (—) AND BIS(5-METHYLTHIO-1,3,4-THIADIAZOLINE-2-THIOLATO) NICKEL (II) (---) IN NUJOL

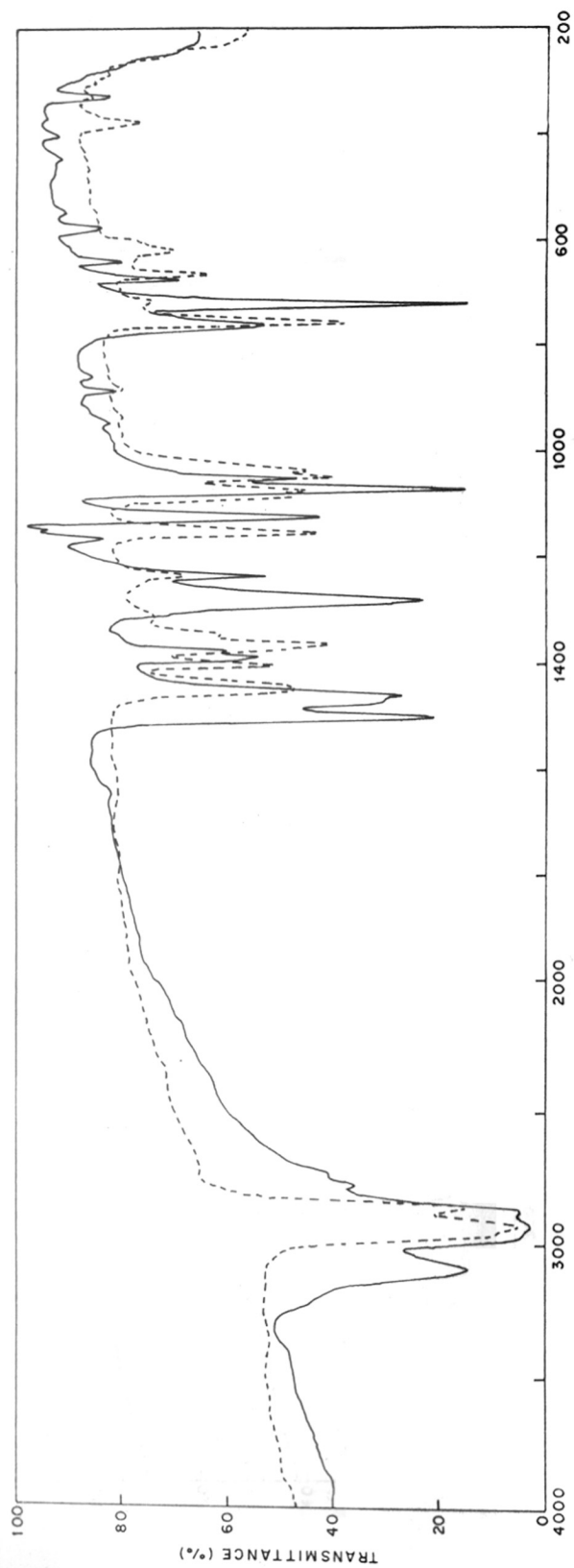


FIG. 20 INFRARED SPECTRA OF 5-ISOPROPYLTHIO-1,3,4-THIADIAZOLINE-2-THIONE-IPr-TD (—) AND BIS(5-ISOPROPYL-
-THIO-1,3,4-THIADIAZOLINE-2-THIOLATO)NICKEL(II) (---) IN NUJOL

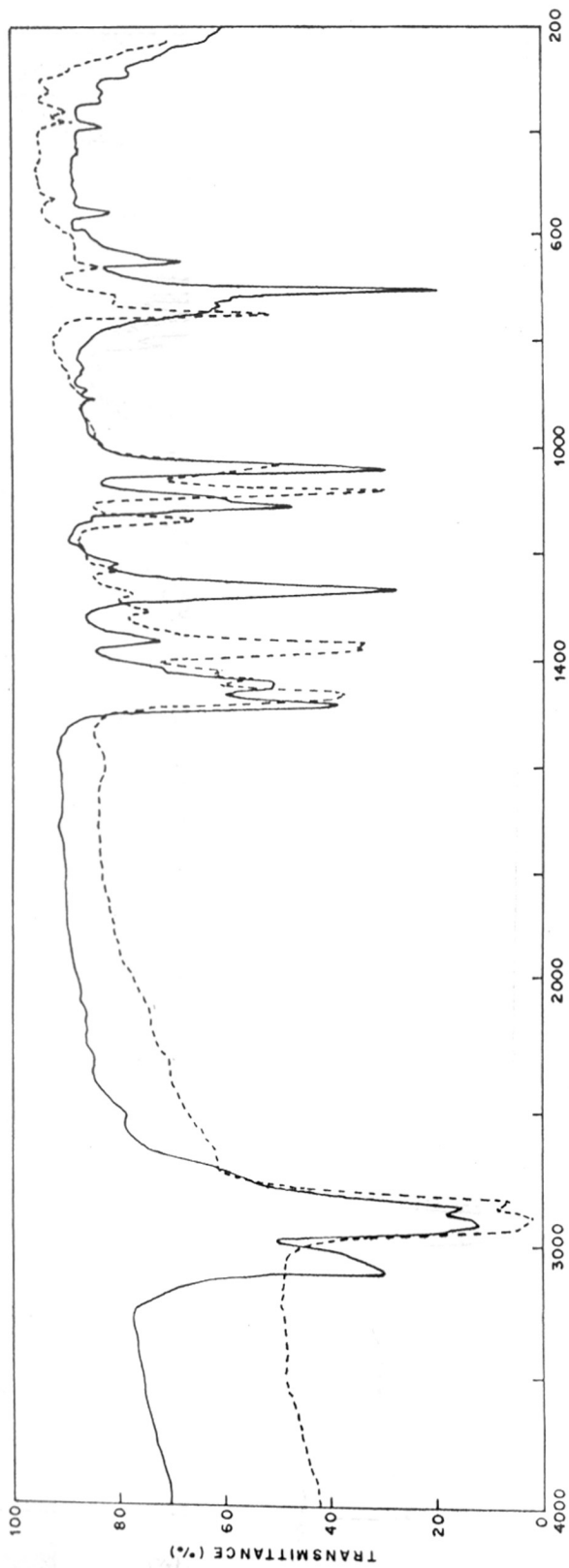


FIG. 21 INFRARED SPECTRA OF 5-BUTYLTHIO-1,3,4-THIADIAZOLINE-2-THIONE-Bu·TD (—) AND BIS(5-BUTYLTHIO-1,3,4-THIADIAZOLINE-2-THIOLATO)NICKEL(II) (-----) IN NUJOL

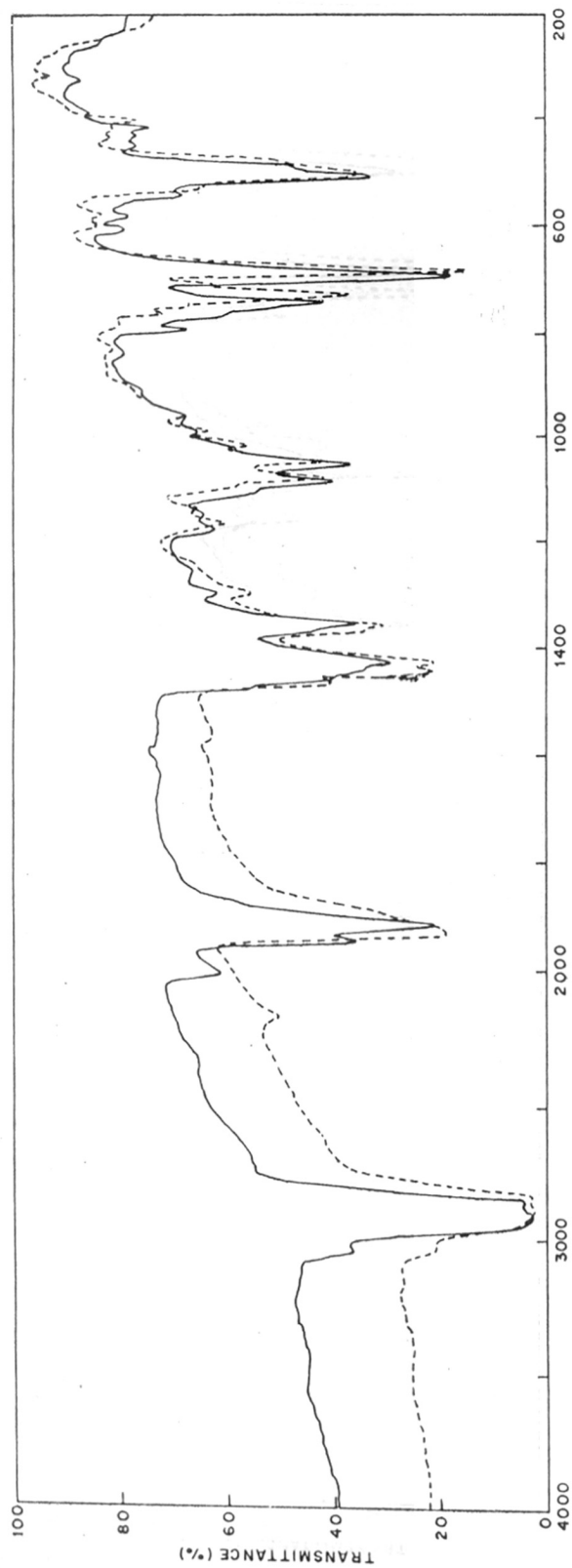


FIG. 22 INFRARED SPECTRA OF $\text{RuH}(\text{CO})(\text{PPh}_3)_2\text{-Me-TD}$ (—) AND $\text{Ru}(\text{CH}_3\text{CHCN})(\text{CO})(\text{PPh}_3)_2\text{-Me-TD}$ (---) IN NUJOL

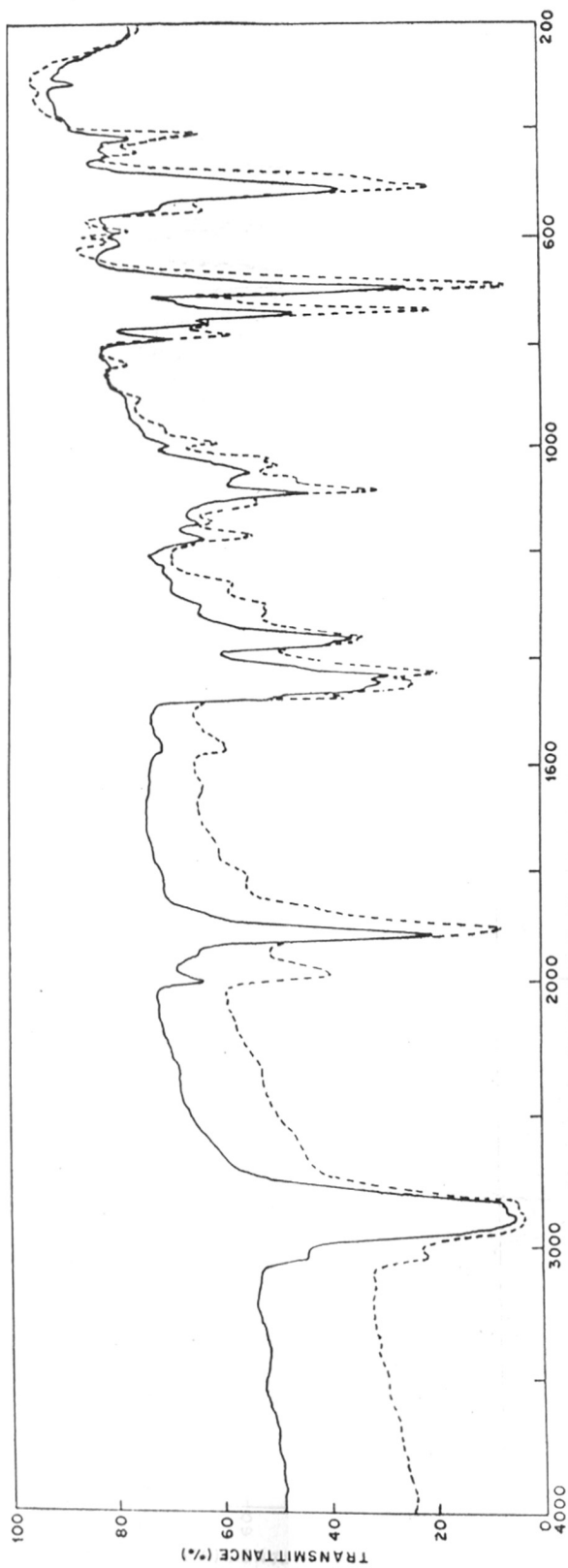


FIG. 23 INFRARED SPECTRA OF $\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{ISOP}_t\text{-TD})$ (—) AND $\text{RuH}(\text{CO})(\text{PPh}_3)_2(\text{Bu-TD})$ (----) IN NUJOL

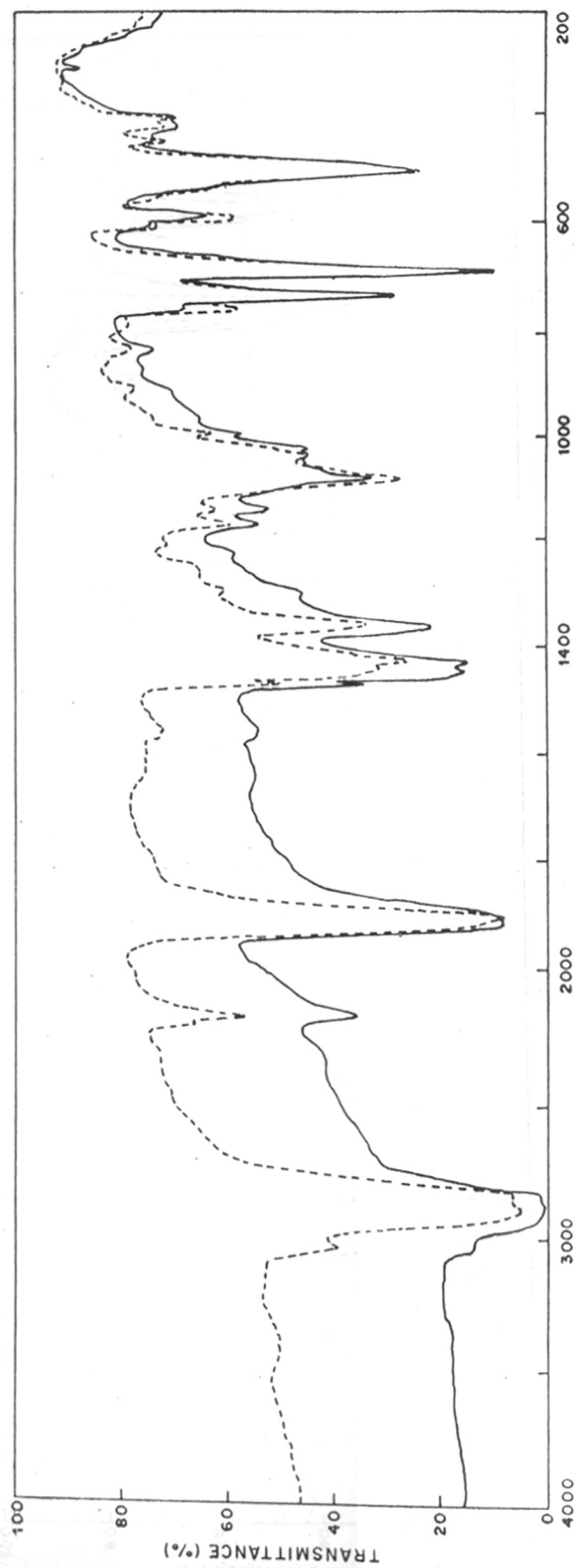


FIG. 24 INFRARED SPECTRA OF $\text{Ru}(\text{CH}_3\text{CHCN})(\text{CO})(\text{PPh}_3)_2$ -ISOPR - TD (—) AND $\text{Ru}(\text{CH}_3\text{CHCN})(\text{CO})(\text{PPh}_3)_2$ -
-BU-TD (---) IN NUJOL

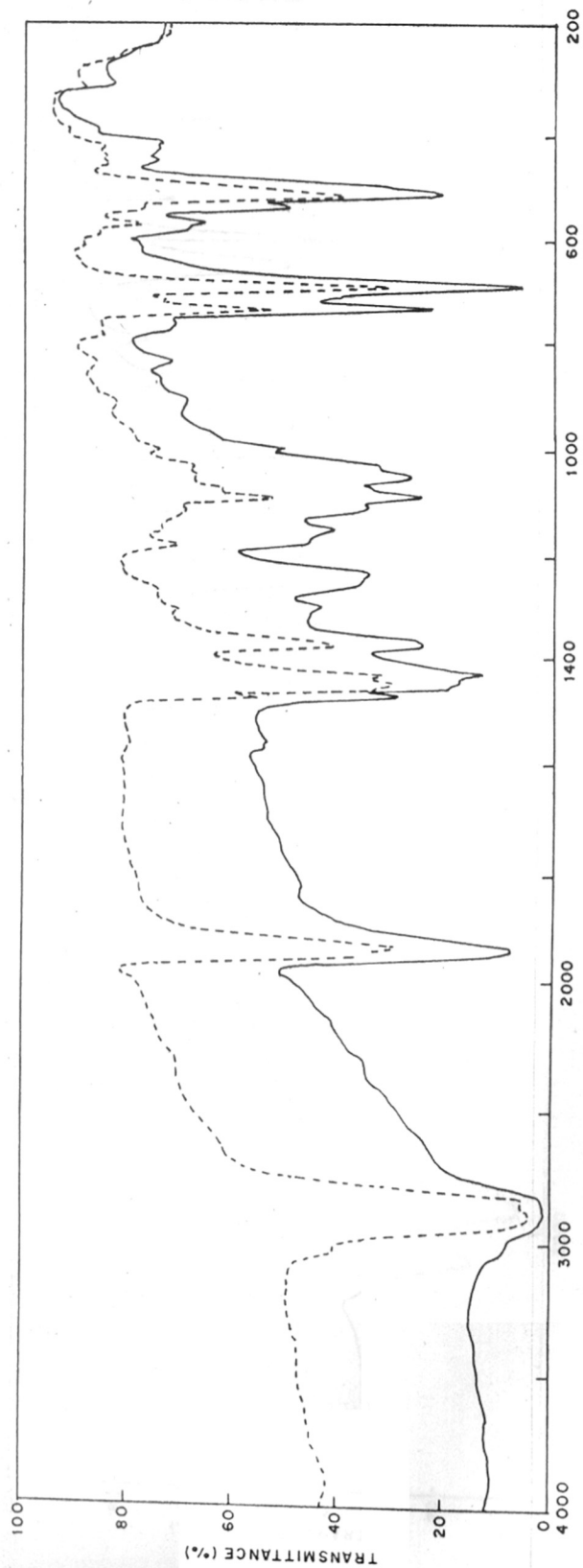


FIG. 25 INFRARED SPECTRA OF $\text{RuCl}(\text{CO})(\text{PPh}_3)_2 - \text{ISOPr} - \text{TD}$ (—) AND $\text{RuCl}(\text{CO})(\text{PPh}_3)_2 - \text{Bu-TD}$ (---) IN NUJOL

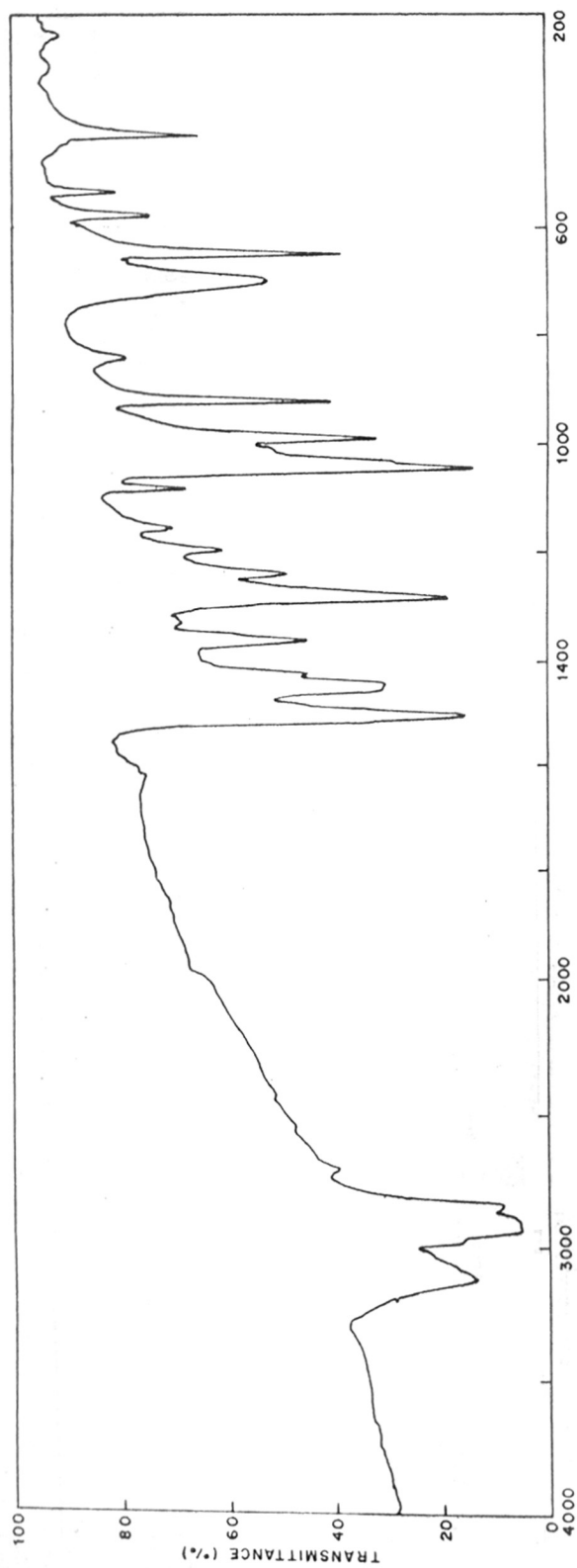


FIG. 26 INFRARED SPECTRUM OF THIAZOLIDINE-2-THIONE IN NUJOL

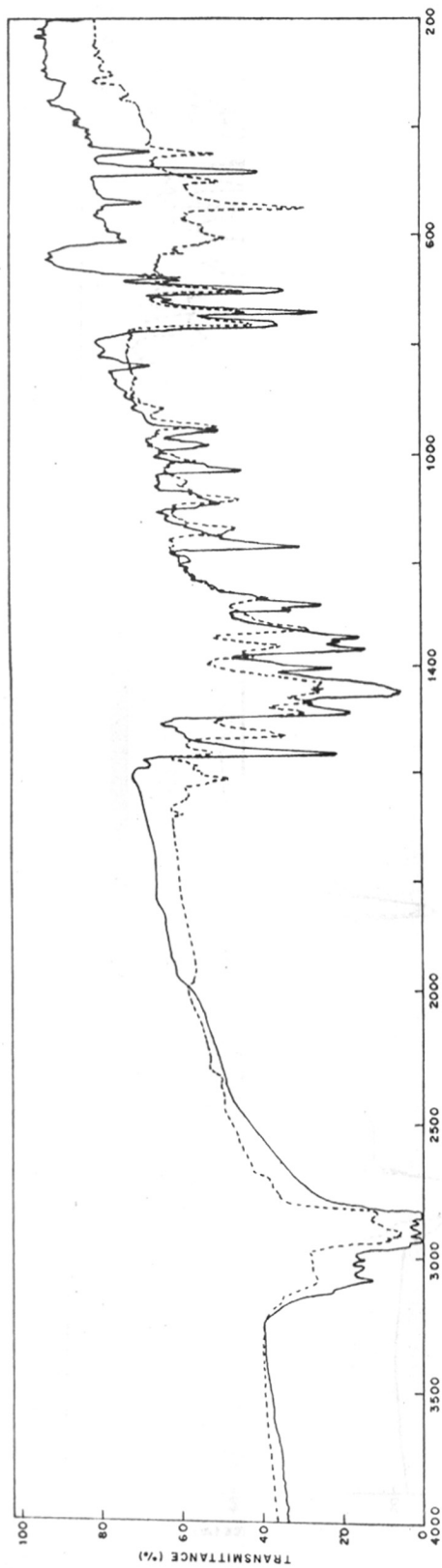


FIG. 27 INFRARED SPECTRA OF 5-METHYL 4-PHENETHYL-1,2,4-TRIAZOLINE-3-THIONE (PHENETHYL-TRJ) (——) AND 5-PHENYL-4-METHYL-1,2,4-TRIAZOLINE-3-THIONE (METHYL-TRJ) (----) IN NUJOL

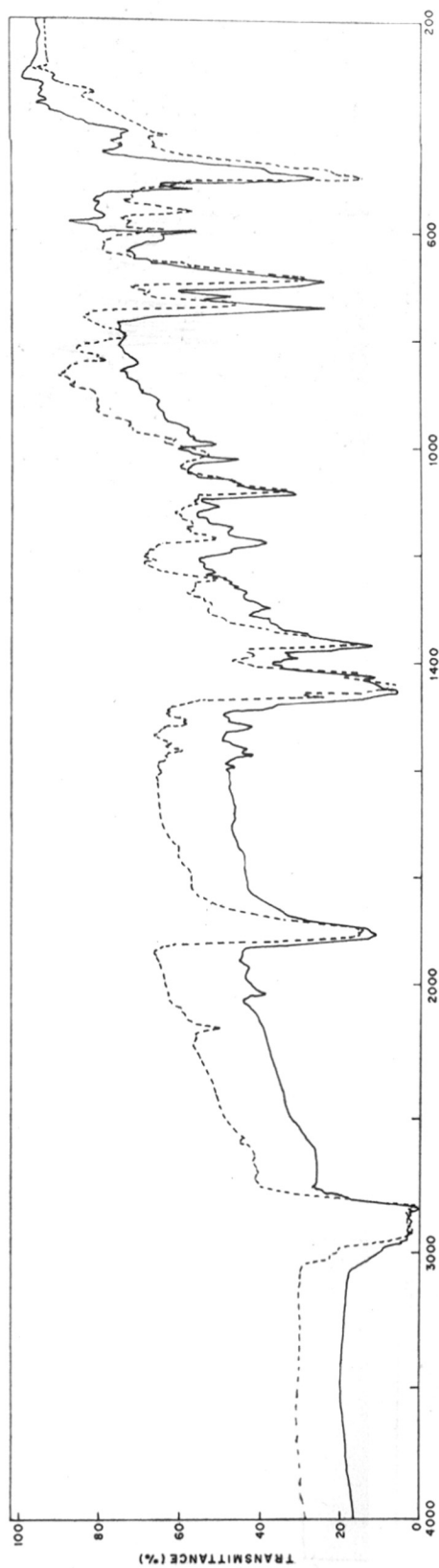


FIG. 28 INFRARED SPECTRA OF RuH(CO)(PPh₃)₂ (5-METHYL-4-PHENETHYL-1,2,4-TRIAZOLINE-3-THIONE) (——) AND Ru(CH₃CHCN)(CO)(PPh₃)₂ (5-METHYL-4-PHENETHYL-1,2,4-TRIAZOLINE-3-THIONE) (----) IN NUJOL

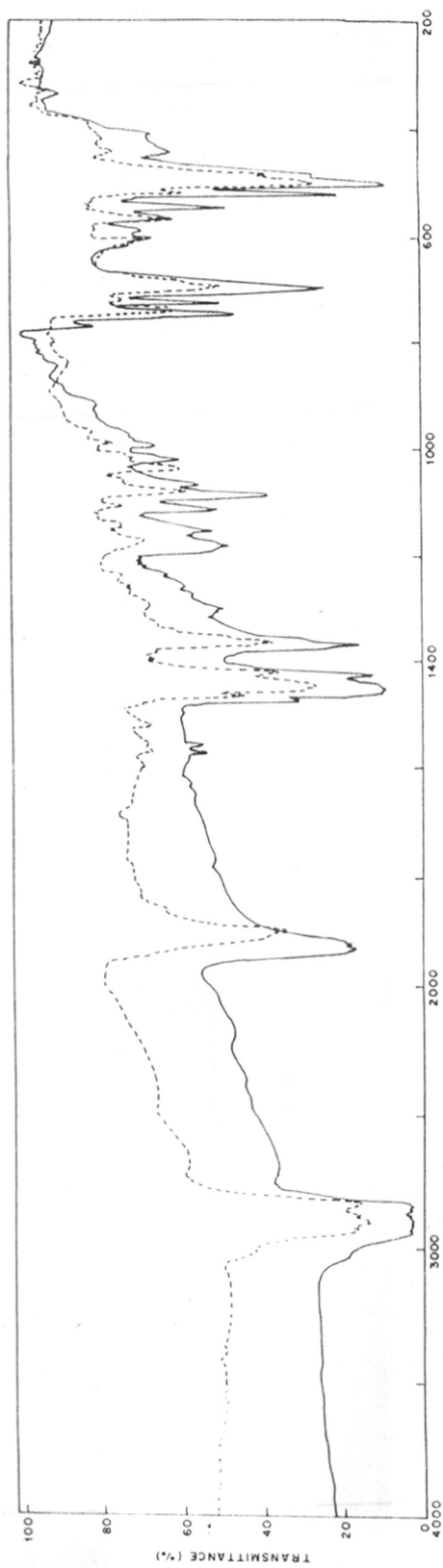


FIG. 29 INFRARED SPECTRA OF $\text{RuCl(CO)(PPH}_3)_2$ (5-PHENYL-4-METHYL-1,2,4-TRIAZOLINE-3-THIONE (—)) AND $\text{RuCl(CO)(PPH}_3)_2$ (THIAZOLIDINE-2-THIONE) (---)

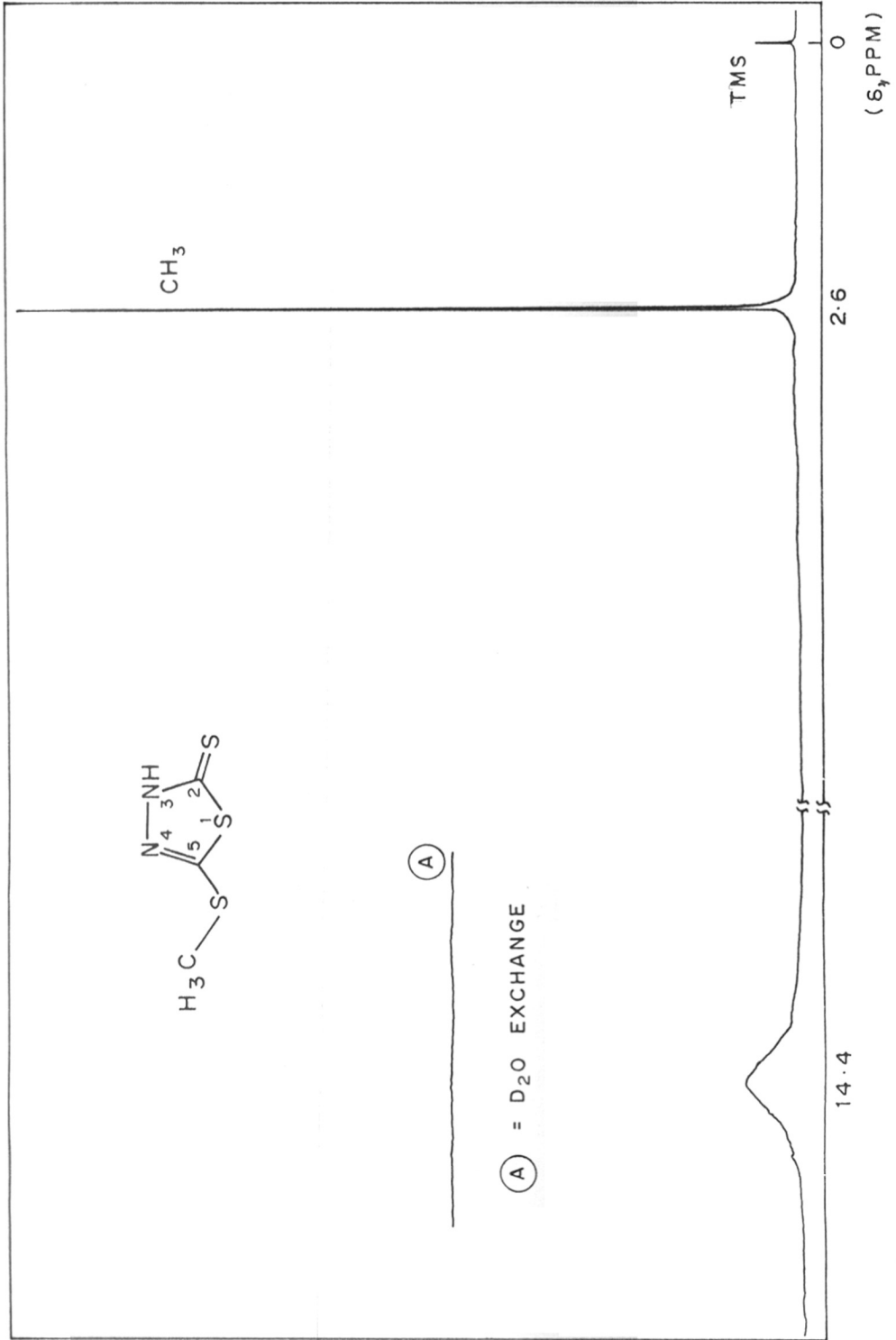


FIG. 30: PMR SPECTRUM OF 5-METHYLTHIO-1,3,4-THIADIAZOLINE-2-THIONE, Me-TD, IN DMSO-d_6

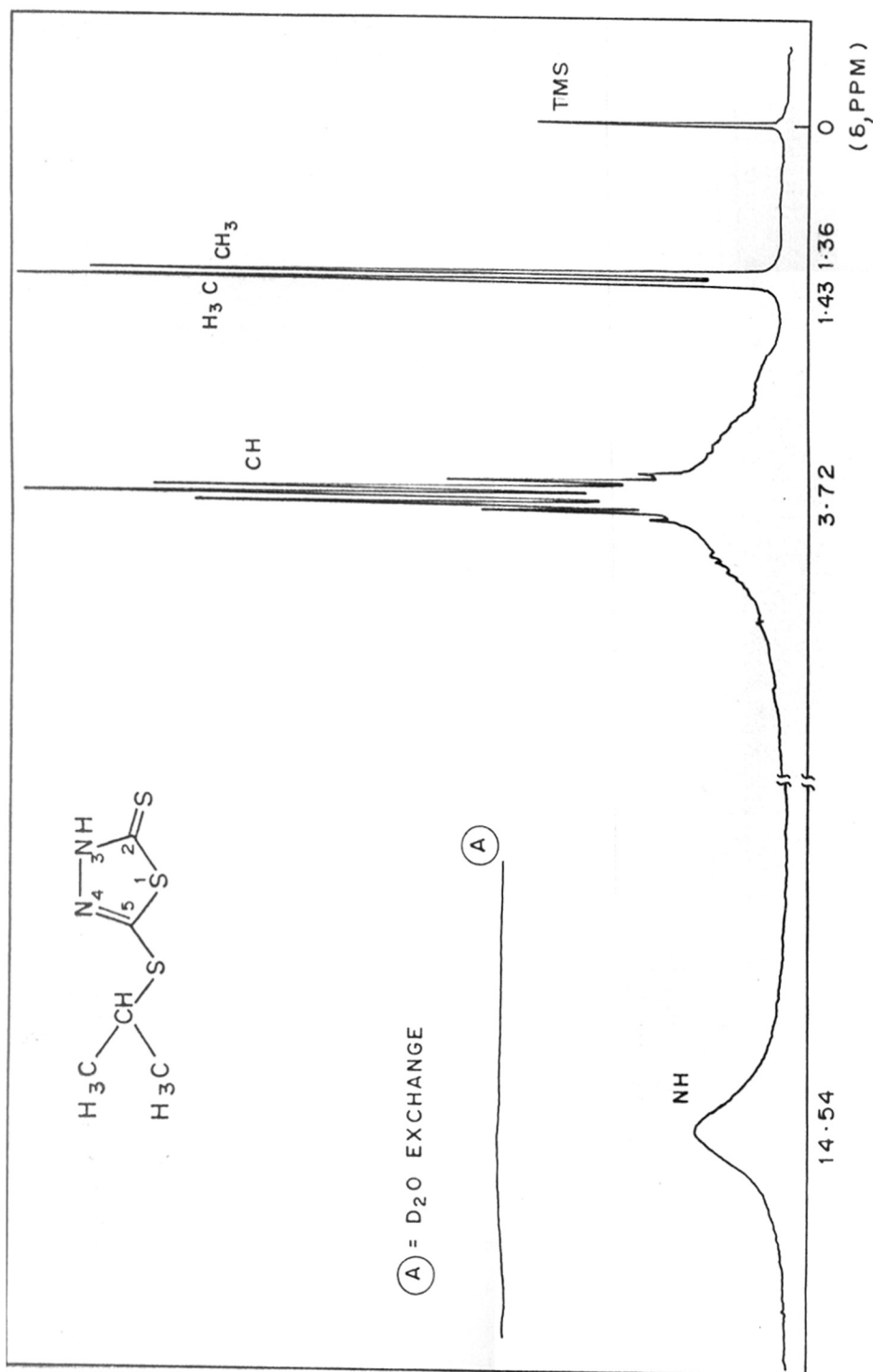


FIG. 31 : PMR SPECTRUM OF 5-ISOPROPYLTHIO-1,3,4-THIADIAZOLINE-2-THIONE, ISOPr-TD, IN DMSO-d₆

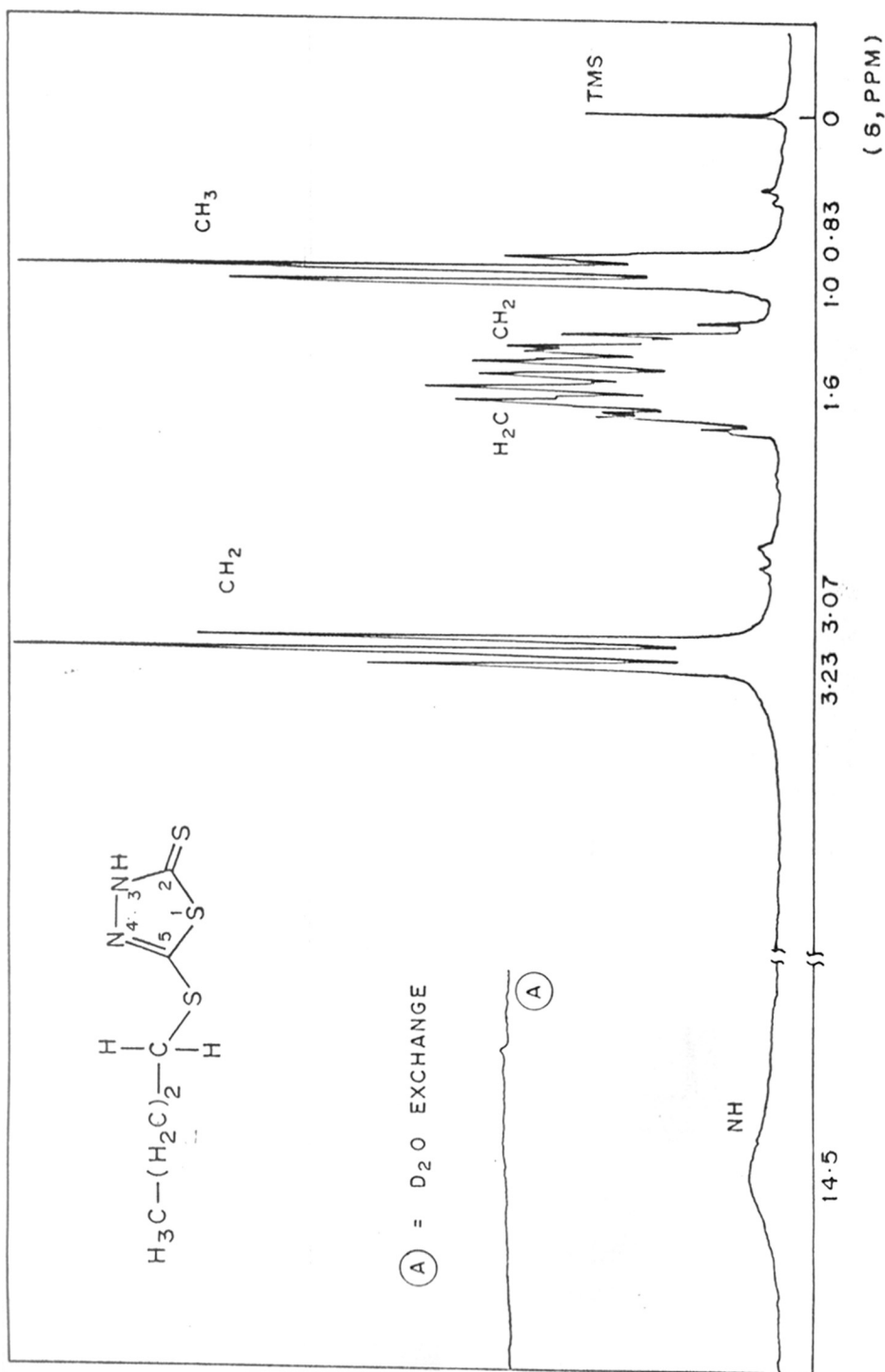


FIG. 32: PMR SPECTRUM OF 5-BUTYLTHIO-1,3,4-THIAZOLINE-2-THIONE, Bu-TD, IN DMSO-d₆

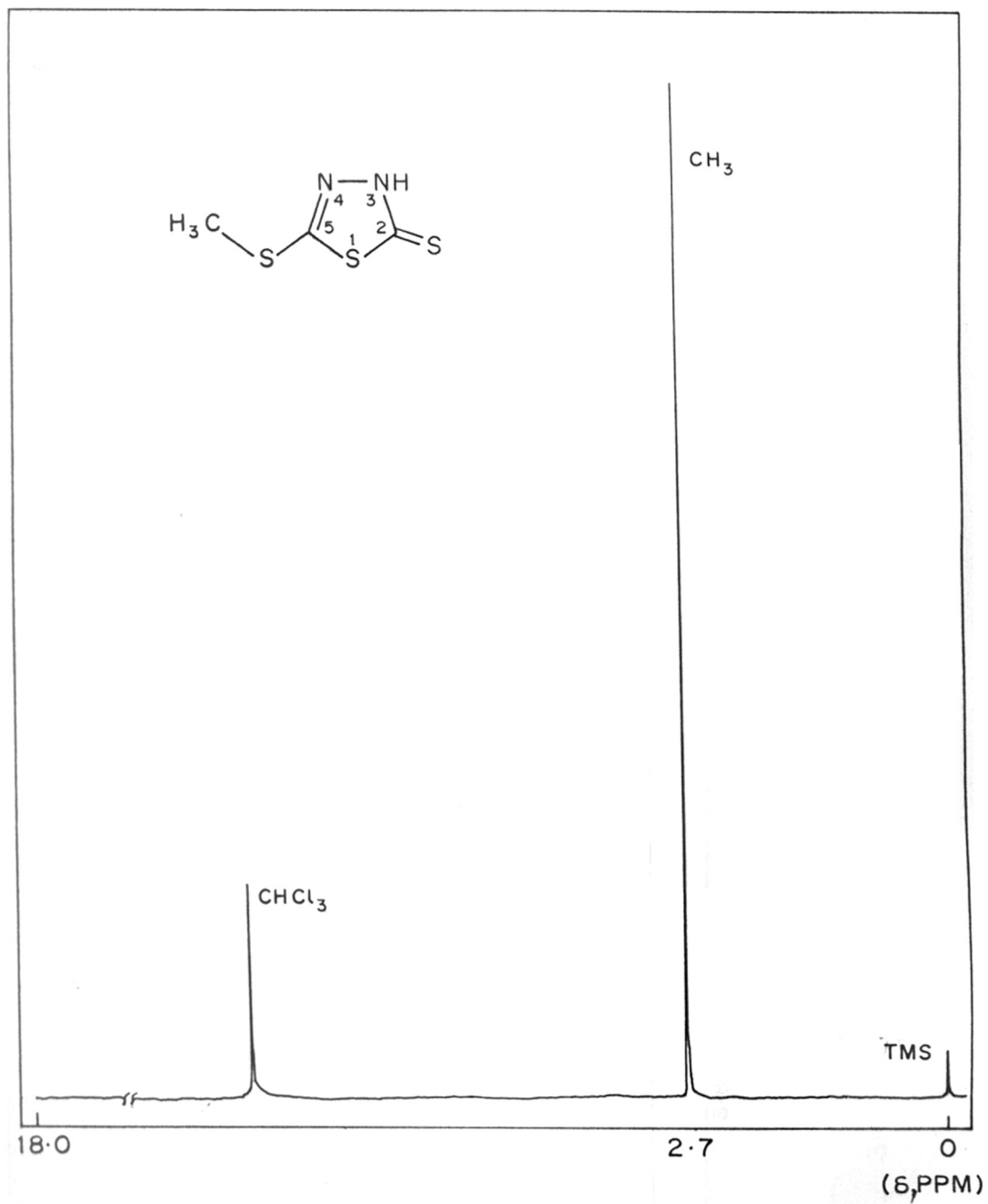


FIG. 33: PMR SPECTRUM OF 5-METHYLTHIO-1,3,4-THIADIAZOLINE-2-THIONE (Me-TD) IN CDCl₃

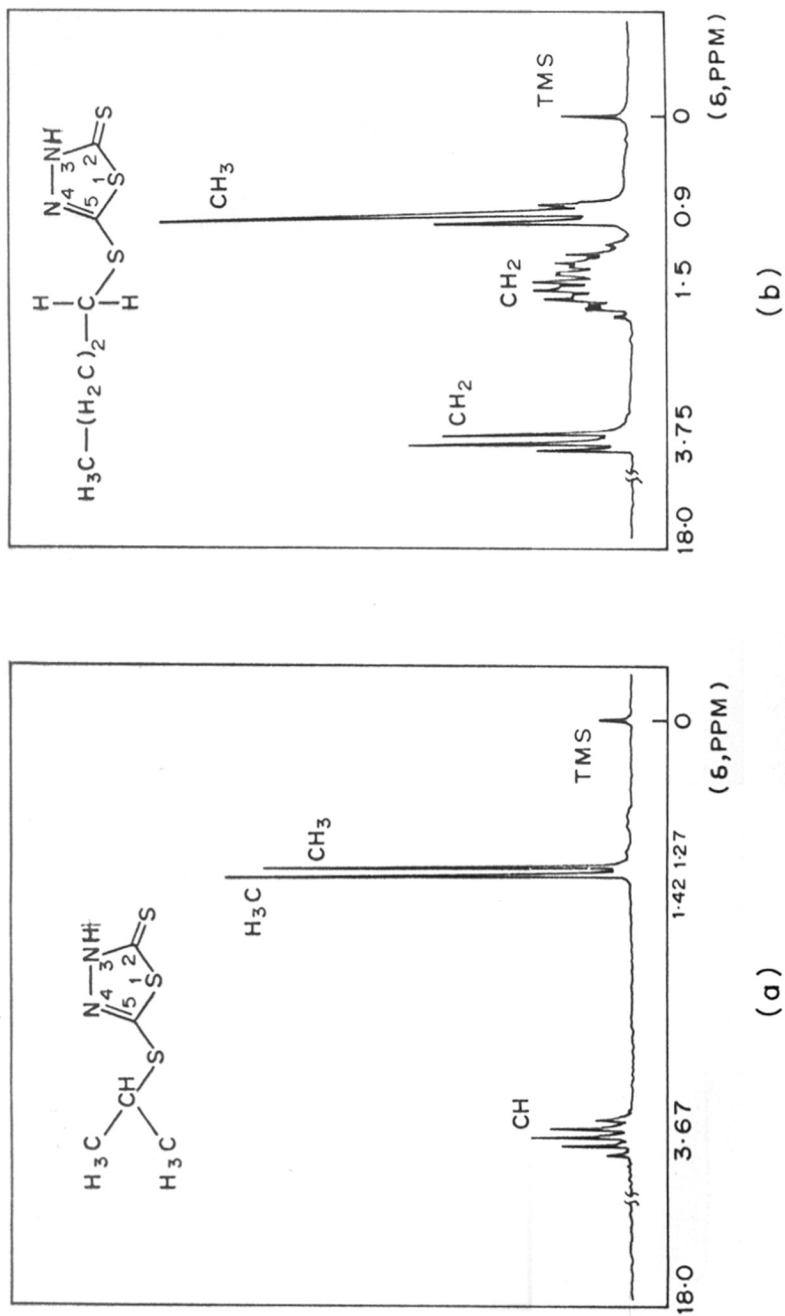


FIG. 34 (a): PMR SPECTRUM OF 5-ISOPROPYLTHIO-1,3,4-THIADIAZOLINE-2-THIONE, (ISOPR-TD) IN CDCl_3

(b): PMR SPECTRUM OF 5-BUTYLTHIO-1,3,4-THIADIAZOLINE-2-THIONE (Bu-TD) IN CDCl_3

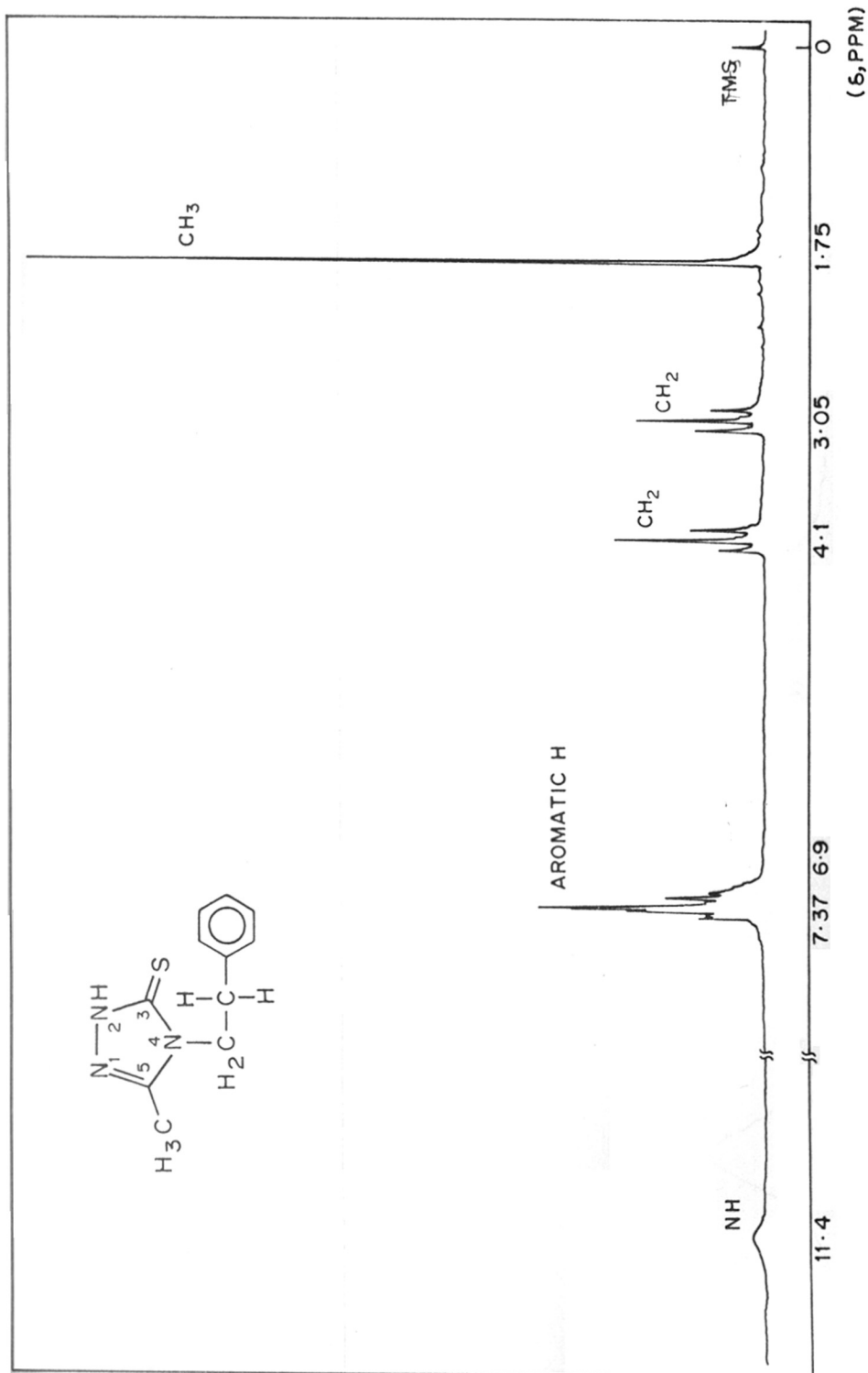


FIG. 35: PMR SPECTRUM OF 1,2,4-TRIAZOLINE-5-METHYL-4-PHENETHYL-3-
THIONE (PHENETHYL TRIAZOLE) IN CDCl₃

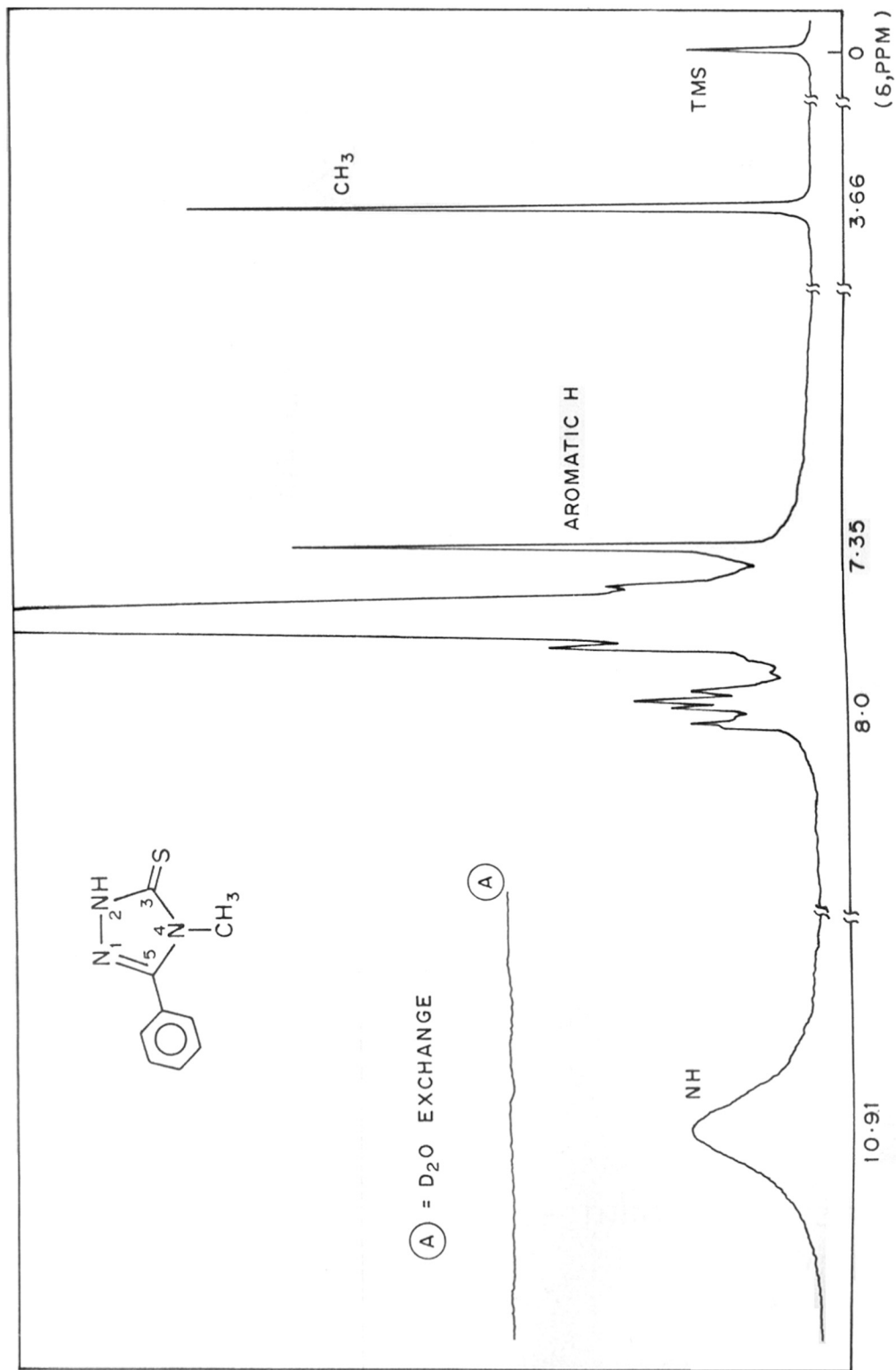


FIG. 36 : PMR SPECTRUM OF 1,2,4-TRIAZOLINE-5-PHENYL-4-METHYL-3-THIONE
(METHYL TRIAZOLE) IN CDCl₃

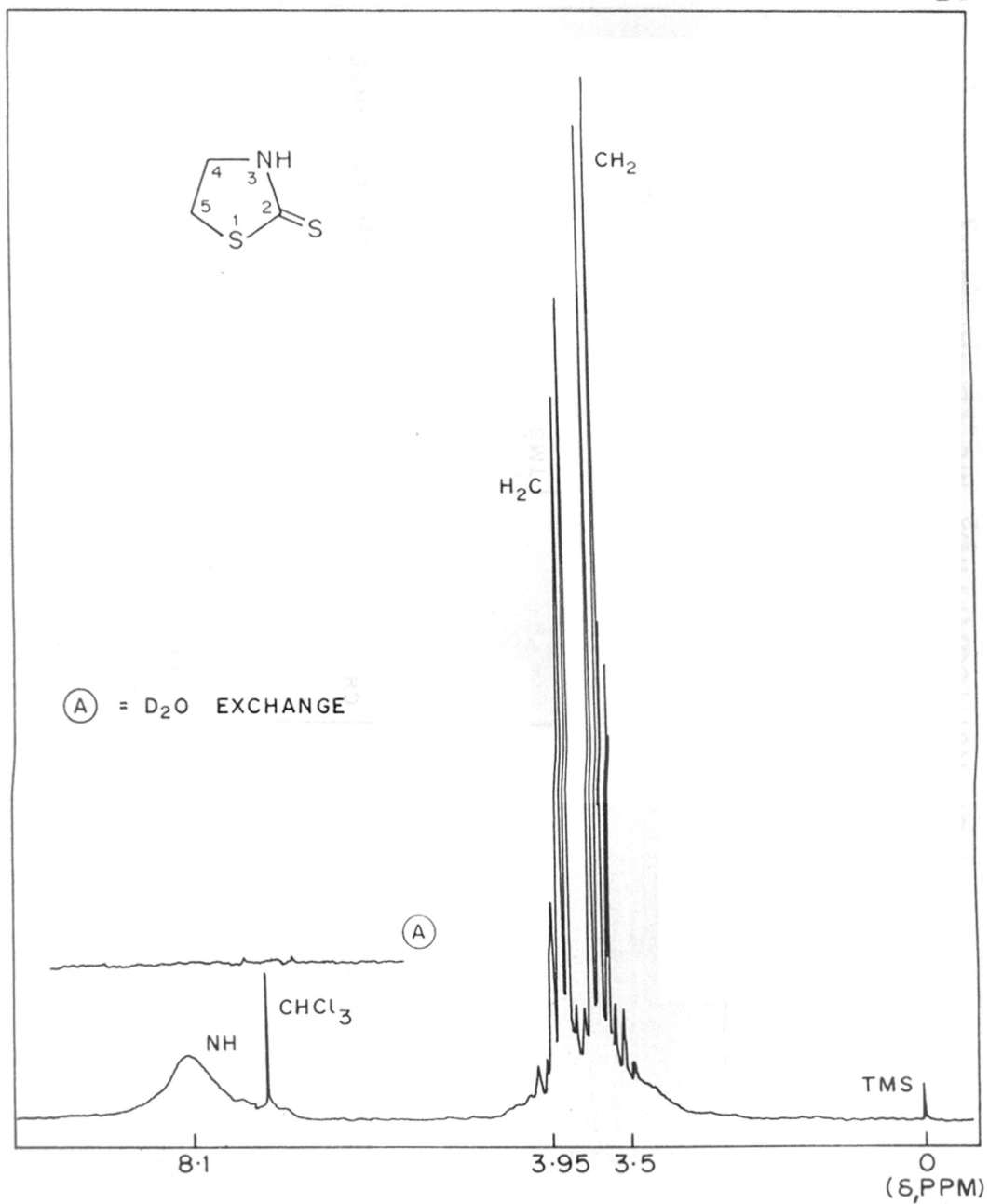


FIG. 37: PMR SPECTRUM OF THIAZOLIDINE-2-THIONE
IN CDCl_3

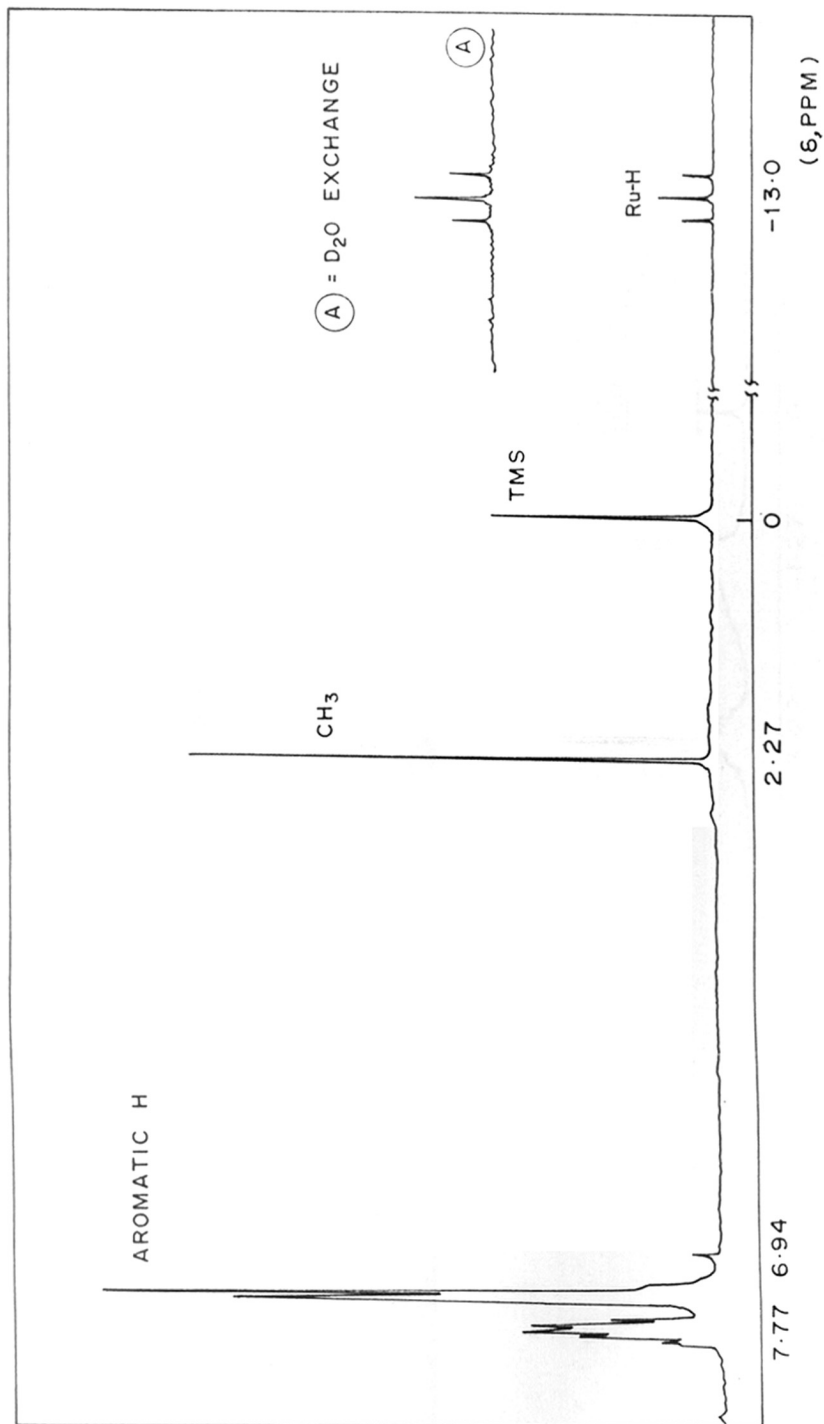
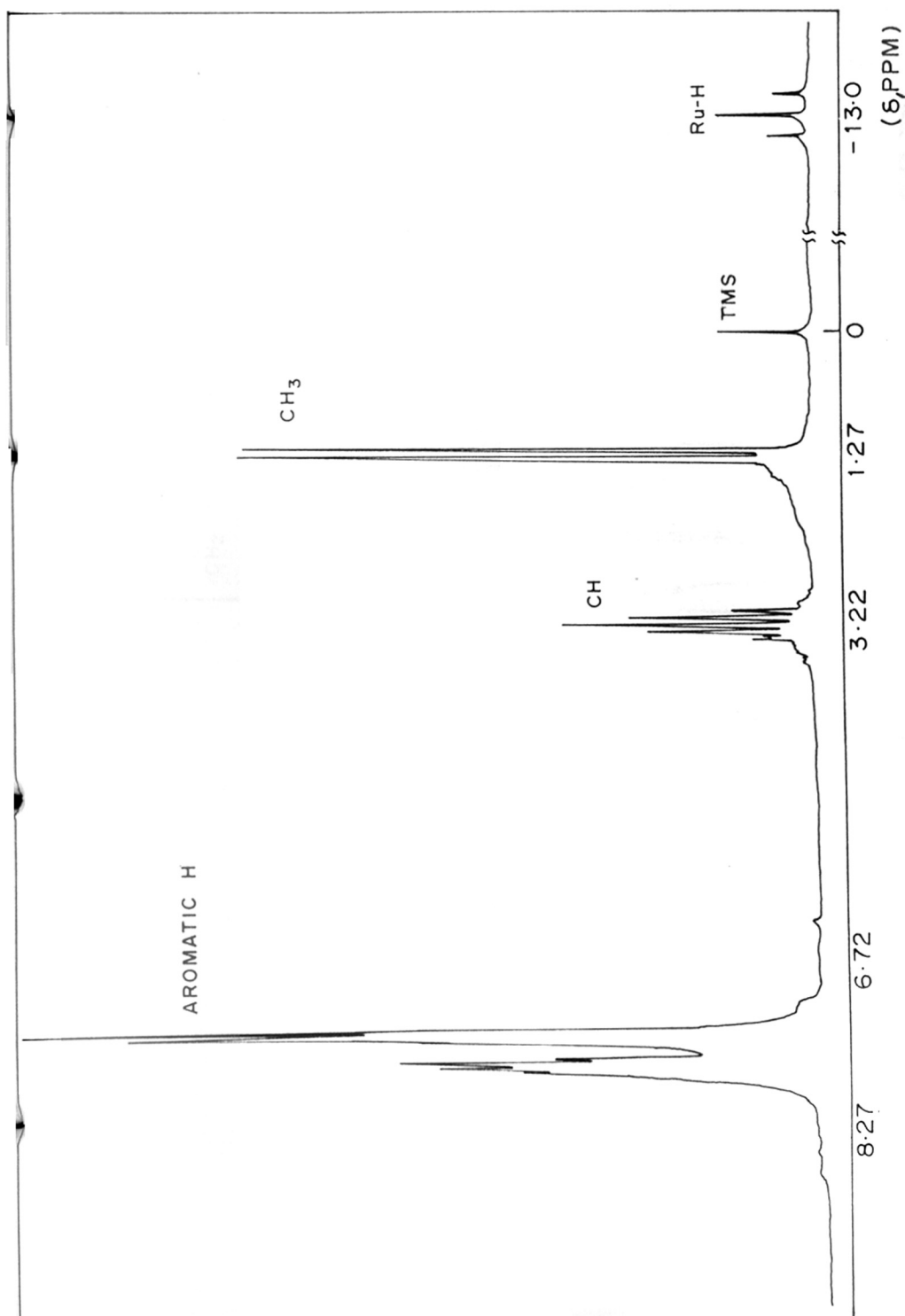
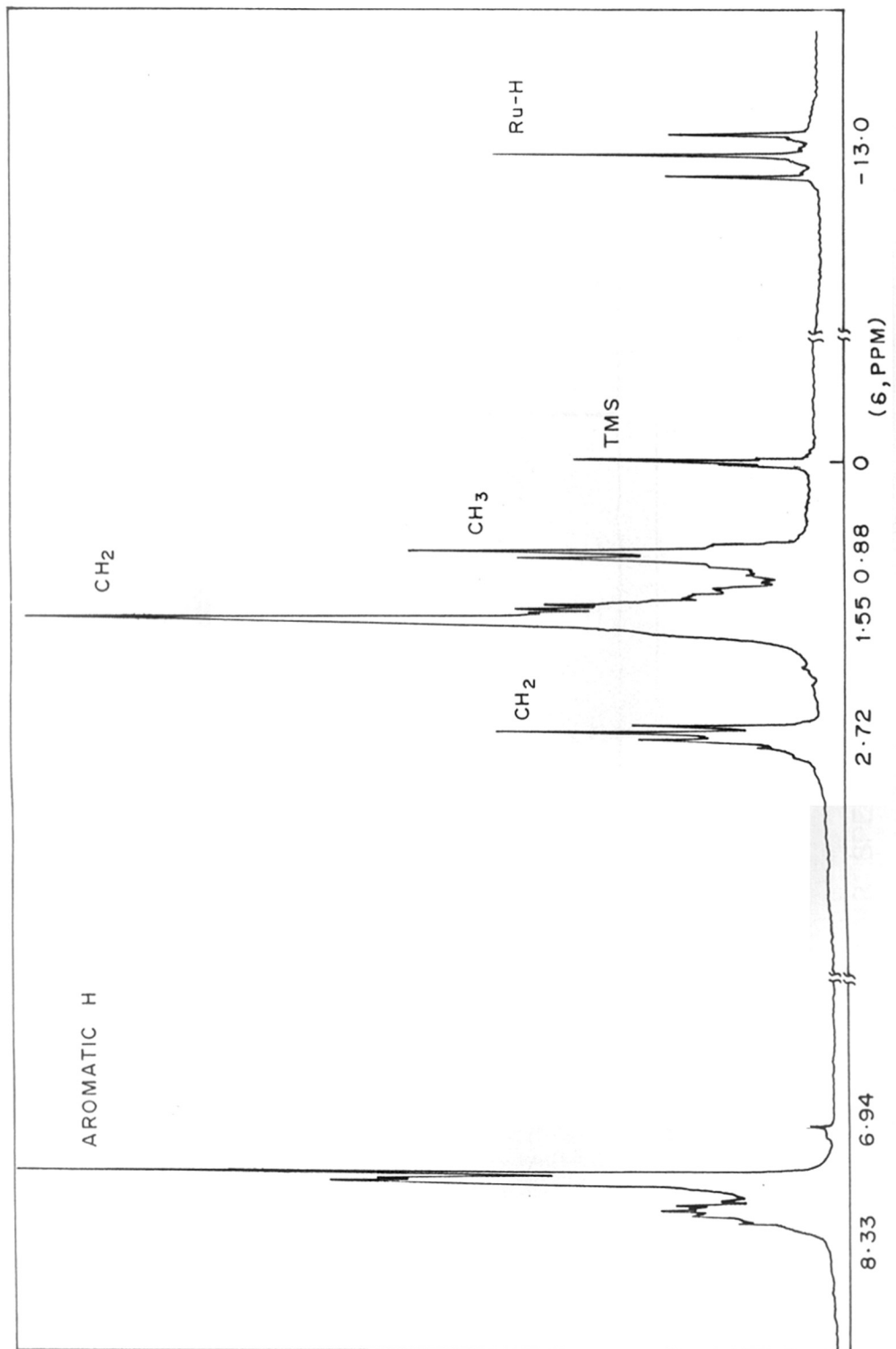


FIG. 38: PMR SPECTRUM OF $\text{RuH(CO)(PPh}_3)_2$ Me-TD IN CDCl_3

FIG. 39: PMR SPECTRUM OF $\text{RuH}(\text{CO})(\text{PPh}_3)_2 \text{ ISOPr-TD}$ IN CDCl_3

FIG. 40: PMR SPECTRUM OF RuH(CO)(PPh₃)₂ Bu-TD IN CDCl₃

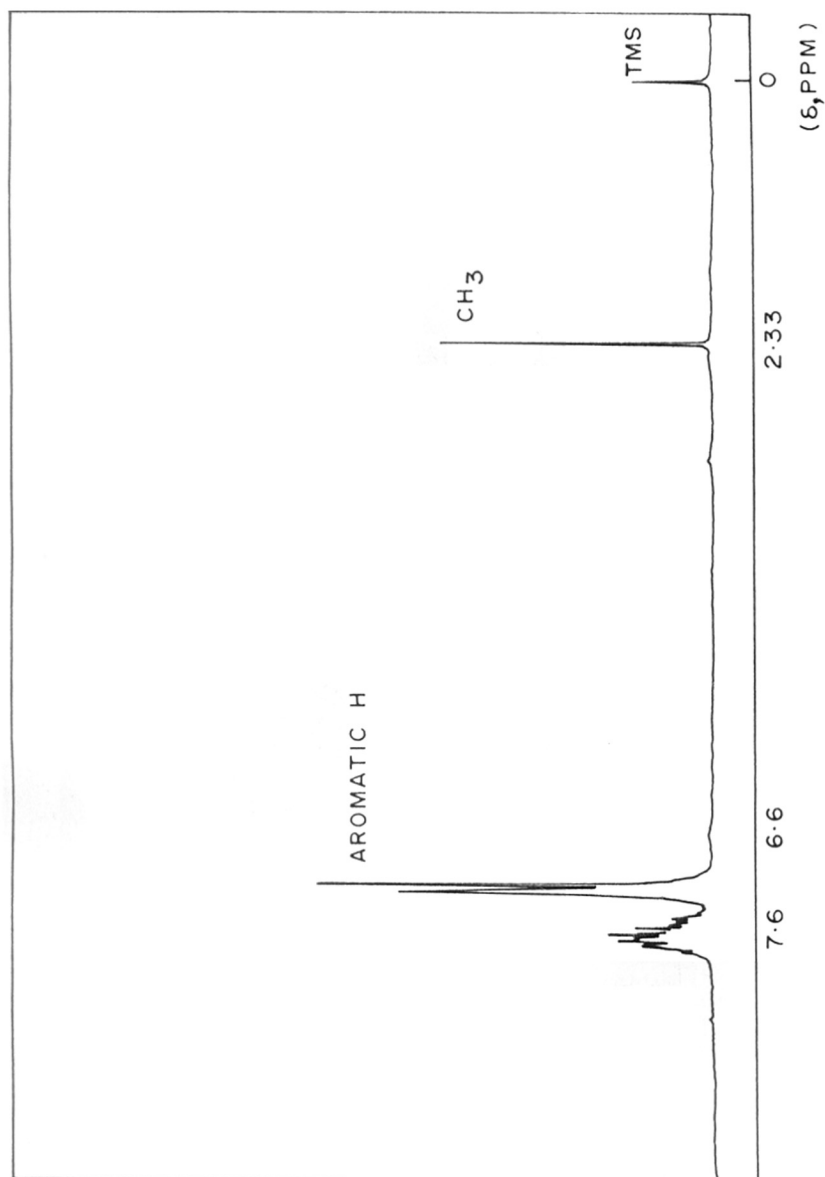


FIG. 41: PMR SPECTRUM OF $\text{RuCl}(\text{CO})(\text{PPh}_3)_2$ Me-TD IN CDCl_3

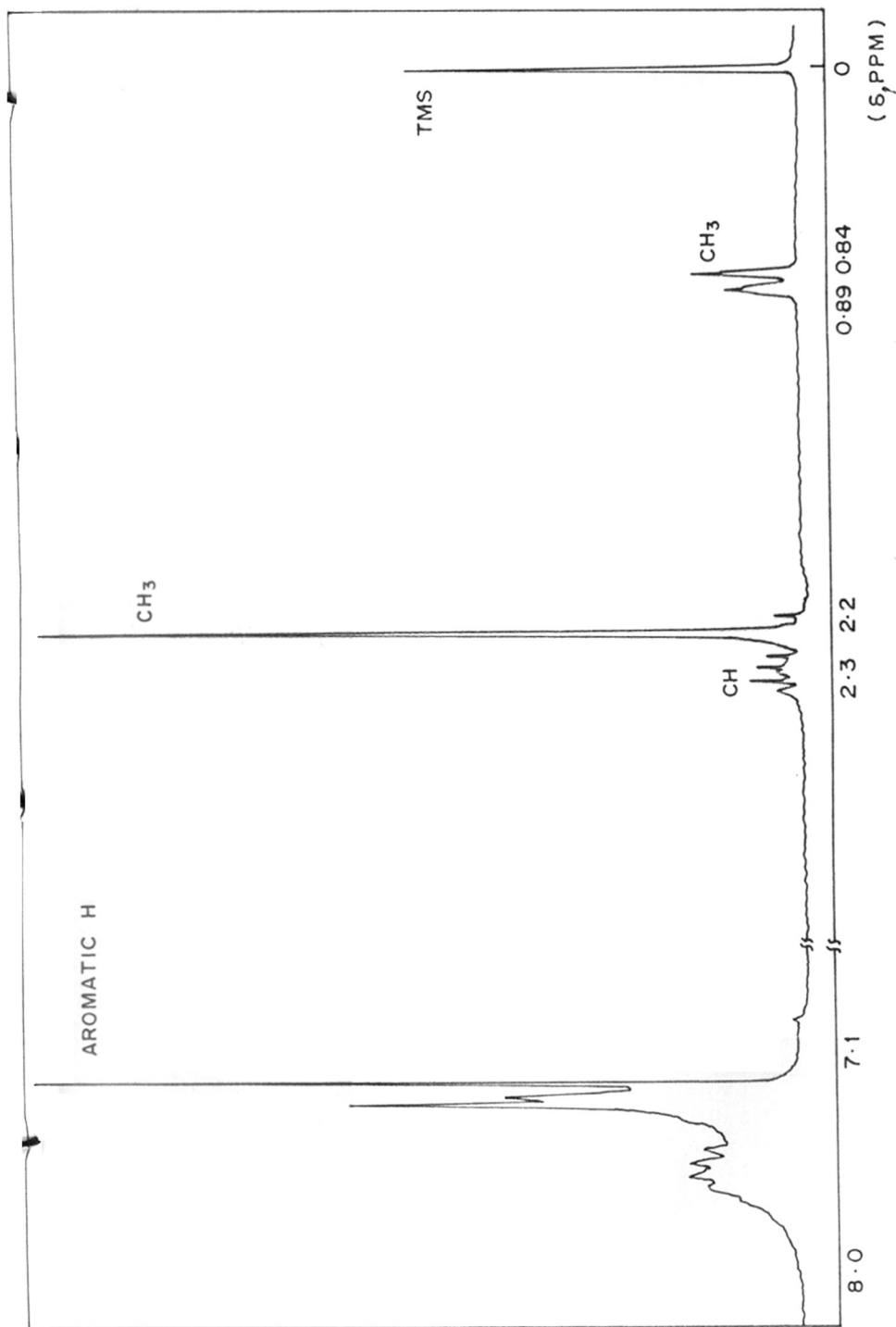


FIG. 42: PMR SPECTRUM OF $\text{Ru}(\text{CH}_3\text{CHCN})(\text{CO})(\text{PPh}_3)_2$ Me - TD IN CDCl_3

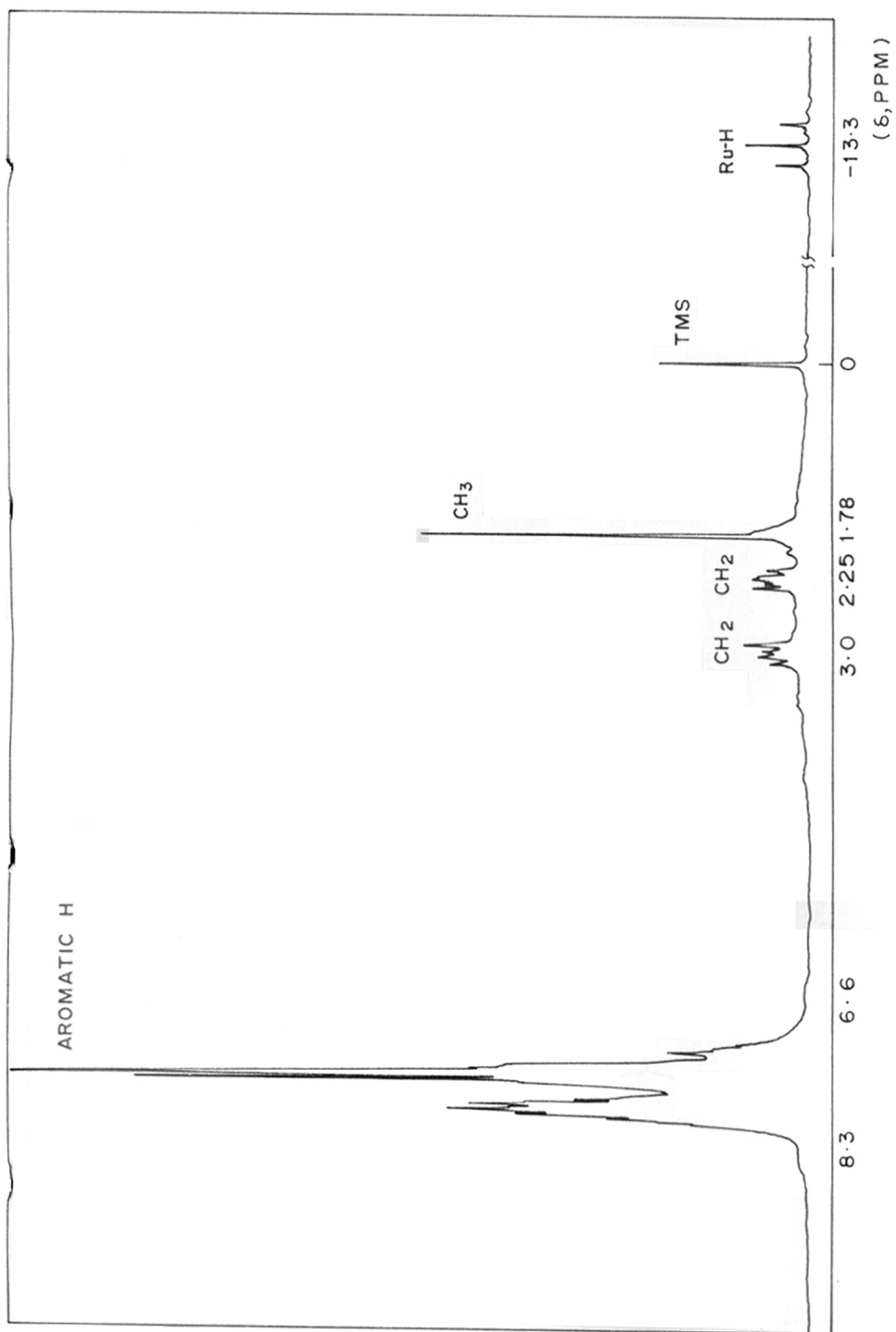


FIG. 43: PMR SPECTRUM OF $\text{Ru-H}(\text{CO})(\text{PPh}_3)_2$ PHENETHYL TRIAZOLE IN CDCl_3

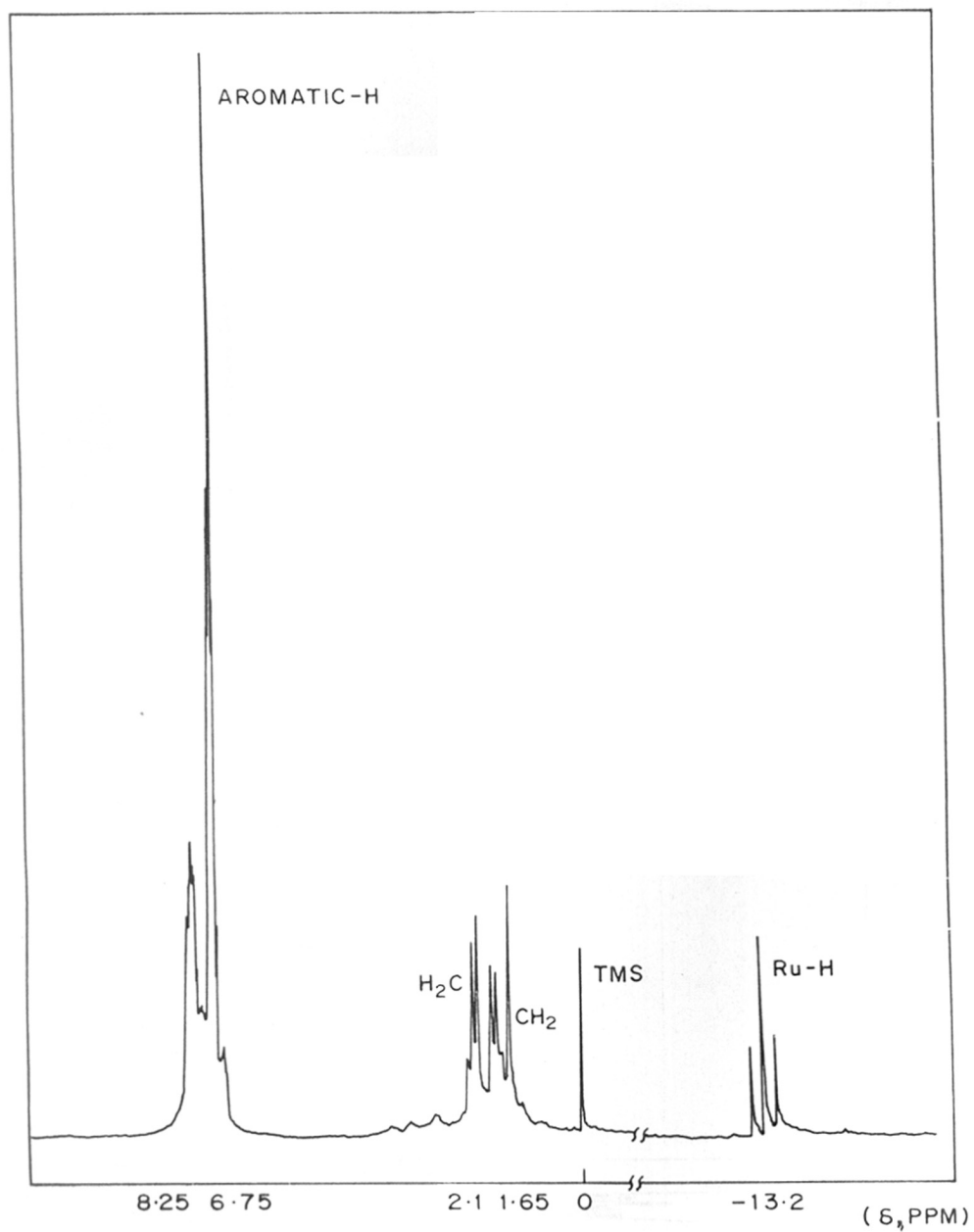
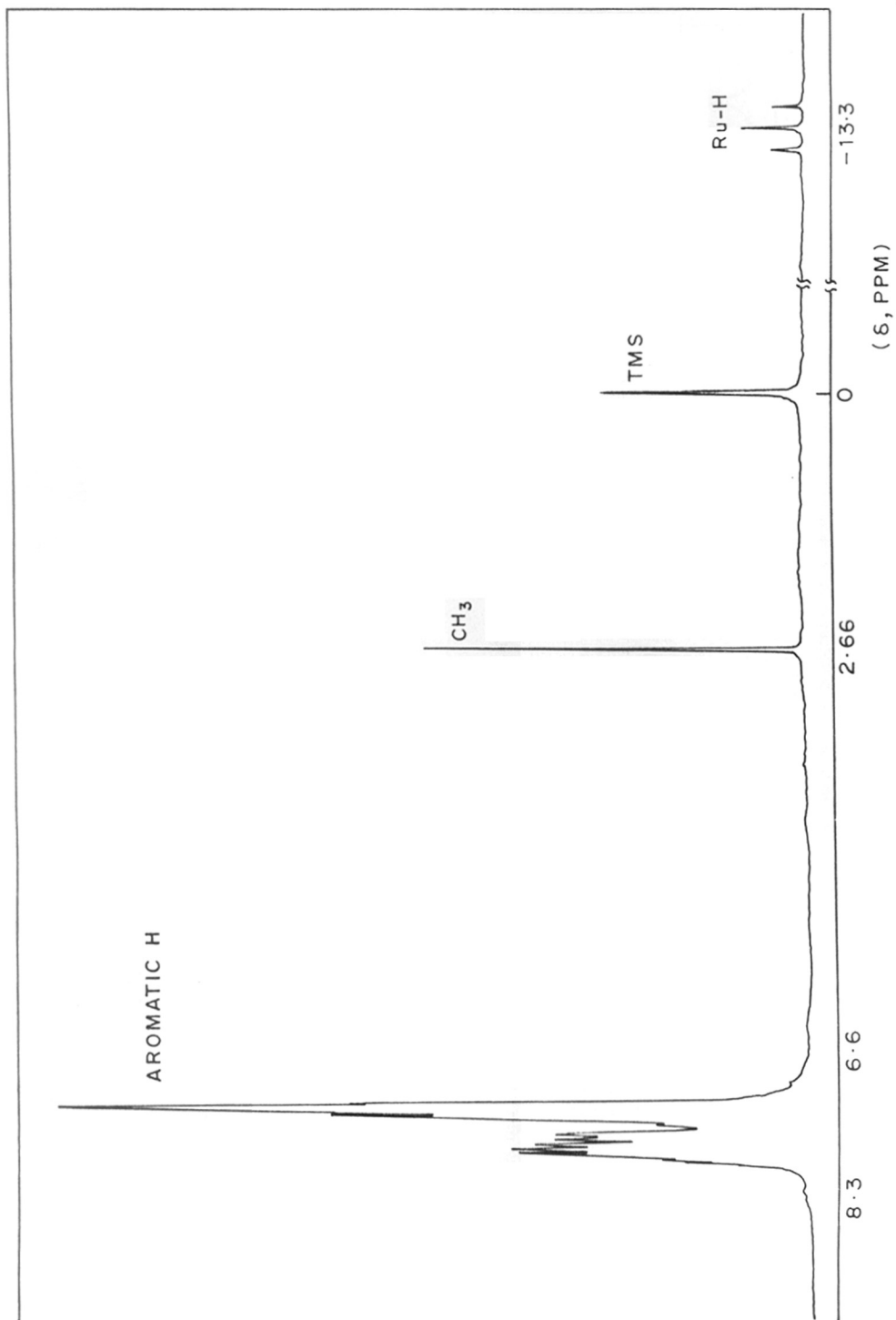


FIG. 44 : PPM SPECTRUM OF $\text{RuH}(\text{CO})(\text{PPh}_3)_2$
THIAZOLIDINE-2-THIONE IN CDCl_3

FIG. 45: PMR SPECTRUM OF RuH(CO)(PPh₃)₂ METHYL TRIAZOLE IN CDCl₃

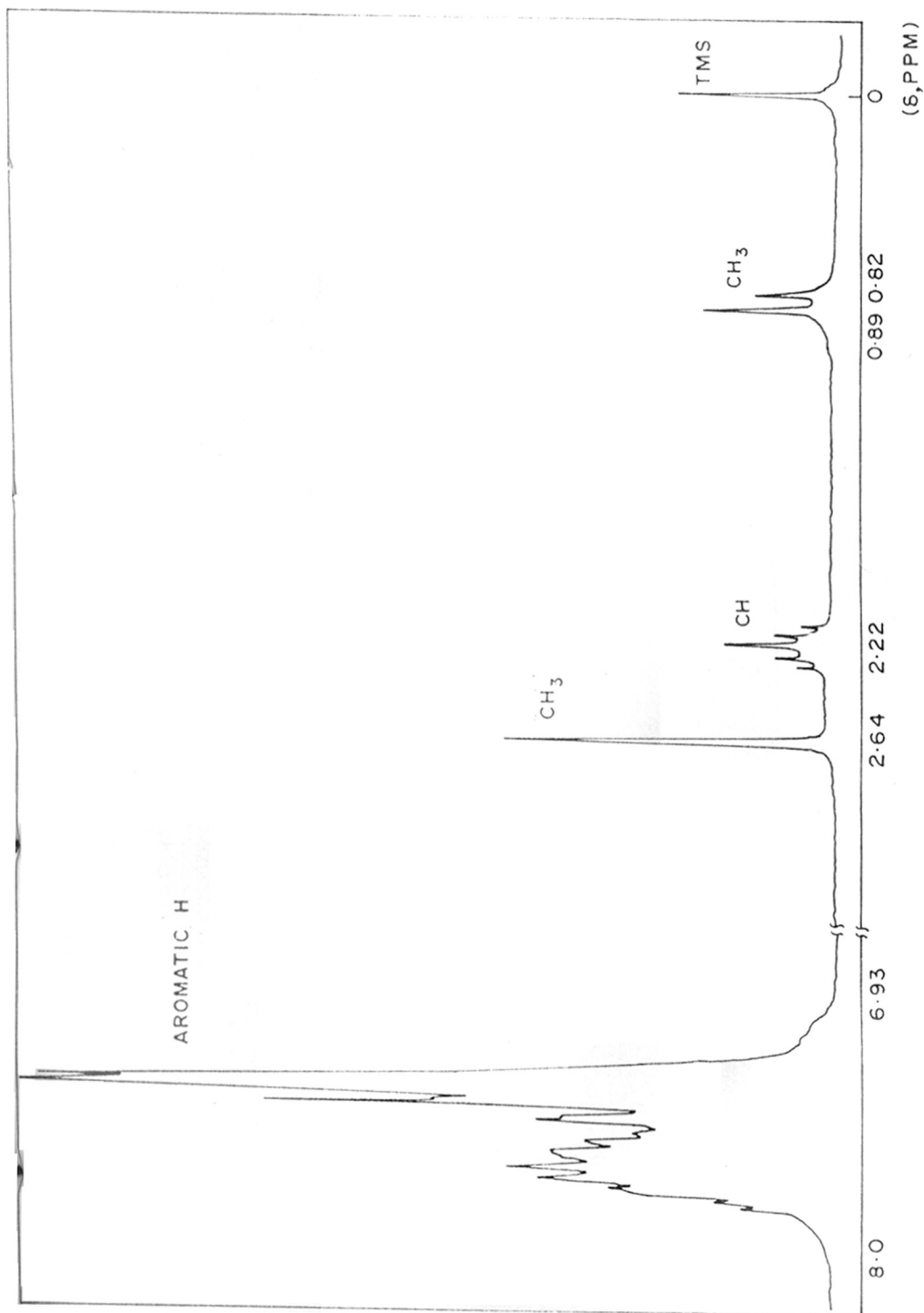


FIG. 46: PMR SPECTRUM OF $\text{Ru}(\text{CH}_3\text{CHCN})(\text{CO})(\text{PPh}_3)_2$ METHYL TRIAZOLE IN CDCl_3

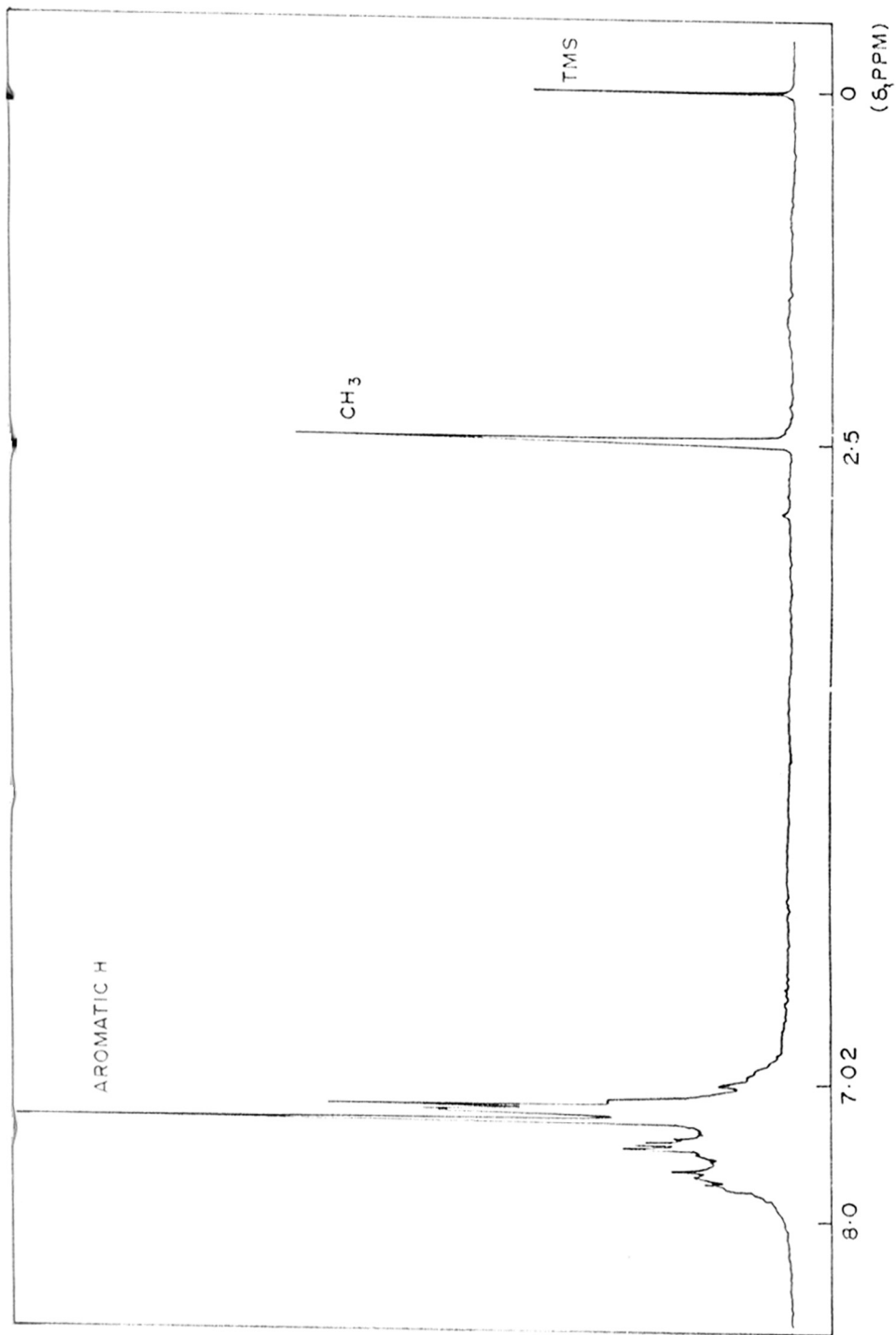


FIG. 47 : PMR SPECTRUM OF $\text{RuCl}(\text{CO})(\text{PPh}_3)_2$ METHYL TRIAZOLE IN CDCl_3

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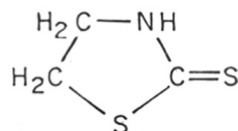
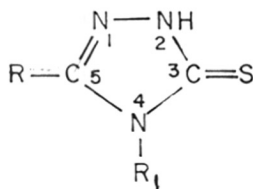
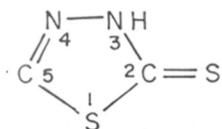
**CHAPTER IV : SYNTHESIS AND CHARACTERISATION OF
MONONUCLEAR RUTHENIUM(II) CARBONYL
COMPLEXES OF SOME HETEROCYCLIC THIONE
DERIVATIVES**

Introduction

The multifunctional N, S-donor ligand, 1,2,4-thiadiazole-2,5-dithiol, complexes with a wide range of class b metals ^{and} has been used as an analytical reagent for the detection, separation, gravimetric *and* spectrophotometric determination of metal ions like palladium, platinum, osmium and bismuth¹⁻⁶.

The free ligand crystallises as 1,3,4-thiadiazole-2-thiol-5-thione⁷. The substitution of 5-position by methyl group in the molecule shows an increase in bond length of the bond N(1)-N(2) [1.381(4) Å]⁸, as compared to the respective bond length in 1,3,4-thiadiazole-2-thiol-5-thione [1.366(2) Å]⁸. The 5-substituted ligands, 5-alkylthio-1,3,4-thiadiazoline-2-thiones (alkyl = methyl, isopropyl or butyl) have been studied and the existence of their thione form in solid state has been confirmed⁹ by NMR and IR data of the ligands and their nickel(II), palladium(II) and cadmium(II) complexes.

In this chapter, carbonyl ruthenium(II) complexes of the heterocyclic thiones with the following structures have been characterised by ¹H NMR, IR and UV spectral data *are* presented here:



-Alkylthio-
 ,3,4-thiadiazoline-
 -thione (R = methyl,
 isopropyl or
 -butyl)

Substituted
 1,2,4-triazoline-3-
 thione
 R = methyl,
 R₁ = phenethyl and
 R = phenyl,
 R₁ = methyl

Thiazolidine-2-
 thione

5-Methylthio-1,3,4-thiadiazoline-2-thione (Me-TD),
 isopropylthio-1,3,4-thiadiazoline-2-thione (Isopr-TD)
 and 5-butylthio-1,3,4-thiadiazoline-2-thione (Bu-TD) were
 prepared by a slight modification of the general procedure
 described by Thorn and Ludwig¹⁰ and details are given in
 the experimental section of the chapter III of the thesis.

Thiazolidine-2-thione was purchased from
 a Chemie, West Germany.

5-Methyl-4-phenethyl-1,2,4-triazoline-3-thione
 phenethyl-Tr) and 5-phenyl-4-methyl-1,2,4-triazoline-3-
 thione (Methyl-Tr) were prepared by the reported method¹¹.

The intermediate ruthenium complexes $\text{RuClCO}(\text{PPh}_3)_3$
 and $[\text{Ru}(\text{CH}_3\text{CHCN})\text{ClCO}(\text{PPh}_3)_2]_2$ were prepared by the methods
 described in literature^{12,13}.

The purities of the organic ligands and the intermediate ruthenium complexes used were checked prior to use. All the reactions were carried out under dry nitrogen atmosphere using freshly dried and distilled solvents.

Experimental

Preparation of 5-methyl-4-phenethyl-1,2,4-triazoline-3-thione, (Phenethyl-Tr)

Phenethyl-isothiocyanate (1.63 g) and hydrazine hydrate (0.5 g) were stirred in absolute alcohol (50 ml) for 30 minutes to yield 4-phenylthiosemicarbazide. The thiosemicarbazide (1.95 g) was cyclised by refluxing with ethyl orthoacetate (1.62 g) for 5 hrs and extracted with an alkali to get colourless crystals of 5-methyl-4-phenethyl-1,2,4-triazoline-3-thione.

Yield 1.1 g (50%). M.p. 160°C.

Analysis: Found C, 59.98; H, 5.19; S, 14.01; N, 19.81%.

Calculated for $C_{11}H_{13}N_3S$: C, 60.27; H, 5.94; S, 14.61; N, 19.18%.

IR frequencies (cm^{-1}) in nujol: 3100m, 3040m, 1570s, 1500s, 1285s, 1175s, 1095m, 1035m, 770m, 740s, 720m, 700s, 545m, 485s, 450m.

Preparation of 5-phenyl-4-methyl-1,2,4-triazoline-3-thione, Methyl-Tr

Methyl isothiocyanate (0.73 g) and benzoyl hydrazide (1.49 g) were stirred in absolute alcohol (30 ml) for 1 hr to yield the 1-benzoyl-4-methyl-thiosemicarbazide. The thiosemicarbazide was dehydrated by refluxing it with an alkali and neutralized with dil. HCl to yield 5-phenyl-4-methyl-1,2,4-triazole-3-thione. Yield 1.05 g (55%), M.p. 166°C.

Analysis: Found C, 56.01; H, 4.12; S, 16.01; N, 21.11%.

Calculated for $C_9H_9N_3S$: C, 56.54; H, 4.71; S, 16.75;

N, 21.99%.

I.R. absorption frequencies (cm^{-1}) in nujol: 3100m, 3020w, 1625m, 1575m, 1540s, 1500s, 1275s, 1140m, 1090m, 1020w, 760m, 720m, 700m, 600w, 555s, 510m, 460s.

Preparation of hydridochlorocarbonyl-tris-(triphenylphosphine)ruthenium(II):

A solution of $RuCl_3 \cdot 3H_2O$ (2.61 g, 10 mmol) in 2-methoxyethanol (200 ml) and aqueous formaldehyde (200 ml, 40% w/v) were added rapidly and successively to a vigorously stirred boiling solution of PPh_3 (15.8 g, 60 mmol) in the same solvent (300 ml). The mixture was heated under reflux for 10 minutes, allowed to cool, filtered through sintered disc, washed with

ethanol and hexane successively, and dried in vacuo.

Yield 9.1 g (95%). M.p. 209°C.

Principal IR frequencies (cm^{-1}) in nujol: 2020(m)-(Ru-H), 1920s ($\text{C}\equiv\text{O}$).

Preparation of (1-cyanoethyl)chlorocarbonyl bis-(triphenylphosphine)ruthenium(II) dimer

A THF suspension (60 ml) containing $\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3$ (0.951 g, 1 mmol) and acrylonitrile (0.265 g, 5 mmol) was stirred at an ambient temperature for 20 hrs to yield a green solution. The solution was concentrated and further diluted with hexane to give

$[\text{Ru}(\text{CH}_3\text{CHCN})\text{ClCO}(\text{PPh}_3)_2]_2$, sparingly soluble in usual organic solvents. Yield 1.2 g (83%). M.p. 155°C.

Principal IR frequencies (cm^{-1}) in nujol: 1920s ($\text{C}\equiv\text{O}$), 2220s ($\text{C}\equiv\text{N}$).

1. Preparation of (5-methylthio-1,3,4-thiadiazoline-2-thione)hydrido carbonyl bis(triphenylphosphine)ruthenium(II), $\text{RuH}(\text{CO})(\text{PPh}_3)_2$ -Me-TD

The sodium salt of Me-TD was prepared by stirring the ligand (0.18 g, 1.1 mmol) and sodium hydride (0.026 g, 1.1 mmol) in ether (30 ml) for 4 hrs. Ether was removed and the solid was suspended in tetrahydrofuran (25 ml). To this suspension $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.951 g, 1 mmol) was added and the contents were stirred for 16 hrs. THF was removed under reduced pressure and the solid was

extracted with benzene by centrifuging. The clear benzene solution upon concentration gave yellow coloured crystals, which were washed with hexane and dried under vacuum. Yield 0.57 g (70%). M.p. 225°C.

Analysis: Found C, 58.92; H, 4.27; P, 7.51; N, 3.51%.

Calculated for $\text{RuP}_2\text{N}_2\text{S}_3\text{C}_{40}\text{H}_{34}\text{O}$: C, 58.75; H, 4.16;

P, 7.58; N, 3.42%.

Infrared absorption spectrum in nujol shows following absorption bands (in cm^{-1}): 3050w, 2020m, 1920s, 1480m, 1260vw, 1090m, 1060m, 740m, 695m, 695s, 510s, 415m, 330w.

2. Preparation of (5-methylthio-1,3,4-thiadiazoline-2-thione)chlorocarbonyl bis(triphenylphosphine)ruthenium(II), $\text{RuCl}(\text{CO})(\text{PPh}_3)_2$ -Me-TD

(0.164 g, 1 mmol) of Me-TD was dissolved in 20 ml of methoxy ethanol and $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.951 g, 1 mmol) added to it. The mixture was refluxed for 5 hrs and cooled to room temperature for 16 hrs. The solvent removed under reduced pressure and the yellow solid was collected on filter, washed with n-hexane and dried under vacuum. Yield 0.55 g (64%). M.p. 250°C.

Analysis: Found C, 56.59; H, 3.91; P, 7.42; N, 3.13%.

Calculated for $\text{RuP}_2\text{N}_2\text{S}_3\text{ClC}_{40}\text{H}_{33}\text{O}$: C, 56.37; H, 3.87;

P, 7.28; N, 3.28%.

Infrared absorption frequencies (cm^{-1}) observed in nujol:

3060w, 1980s, 1930s, 1485m, 1180m, 1130m, 1090s, 1060m, 790m, 740s, 690s, 570s, 510s, 415m, 315s.

3. Preparation of (5-methylthio-1,3,4-thiadiazoline) (1-cyanoethyl)carbonyl bis(triphenylphosphine)-ruthenium(II), $\text{Ru}(\text{CH}_3\text{CHCN})(\text{CO})(\text{PPh}_3)_2$ - Me-TD

The sodium salt of Me-TD was prepared from the ligand (0.36 g, 2.2 mmol) and sodium hydride (0.052 g, 2.2 mmol) by stirring them in ether (25 ml) for 4 hrs. Ether was removed and the solid was suspended in THF (20 ml). To this suspension $[\text{Ru}(\text{CH}_3\text{CHCN})\text{ClCO}(\text{PPh}_3)_2]_2$ (1.485 g, 1 mmol) was added and the contents were stirred for 16 hrs. THF was removed under reduced pressure and the solid was extracted with benzene by centrifuging. The clear benzene solution upon concentration gave light yellow crystals, which were washed with n-hexane and dried under vacuum. Yield 1.2 g (70%). M.p. 200°C.

Analysis: Found C, 59.59; H, 4.47; P, 7.37; N, 4.90
 Calculated for $\text{RuP}_2\text{S}_3\text{N}_3\text{C}_4\text{H}_3\text{O}$: C, 59.31; H, 4.25; P, 7.12; N, 4.82.

Infrared absorption maxima observed in nujol were (in cm^{-1}): 3040w, 2185m, 1930s, 1475m, 1180m, 1150m, 1085m, 1055m, 730s, 690s, 590w, 510s, 410w, 330w.

4. Preparation of (5-isopropylthio-1,3,4-thiadiazoline-2-thione)hydridocarbonyl bis(triphenylphosphine)-ruthenium(II), $\text{RuH}(\text{CO})(\text{PPh}_3)_2$ - Isopr-TD

The sodium salt of Isopr-TD was prepared by stirring the ligand (0.21 g, 1.1 mmol) and sodium hydride (0.026 g, 1.1 mmol) in ether (30 ml) for 4 hrs. Ether was removed and the solid was suspended in tetrahydrofuran (25 ml). To this suspension $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.951 g, 1 mmol) was added and the contents were stirred for 16 hrs. THF was removed under reduced pressure and the solid was extracted with benzene by centrifuging. The clear benzene solution upon concentration gave yellow crystalline product. It was washed with hexane and dried under vacuum. Yield 0.48 g (54%). M.p. 235°C . Analysis: Found C, 59.02; H, 4.12; N, 3.12; P, 7.01%; Mol. wt., 750.

Calculated for $\text{RuC}_{42}\text{H}_{38}\text{N}_2\text{P}_2\text{S}_3\text{O}$: C, 59.64; H, 4.49; N, 3.36; P, 7.33%; Mol. wt., 845.

Infrared absorption maxima (in cm^{-1}) in nujol were located at: 3050w, 2010m, 1920s, 1480m, 1180m, 1050w, 1090m, 1050w, 790m, 740m, 695s, 510s, 415m, 320m.

5. Preparation of (5-isopropylthio-1,3,4-thiadiazoline-2-thione)chlorocarbonyl bis(triphenylphosphine)-ruthenium(II). $\text{RuCl}(\text{CO})(\text{PPh}_3)_2$ - Isopr-TD

$\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3$ (0.951 g, 1 mmol) was added to

Isopropyl-TD (0.192 g, 1 mmol) dissolved in methoxy ethanol (20 ml) and the mixture was refluxed for 5 hrs and cooled to room temperature overnight. The solvent was removed under reduced pressure and light yellow solid was filtered, washed with hexane and dried under vacuum. Yield 0.52 (60%). M.p. 250°C.

Analysis: Found C, 57.77; H, 4.44; P, 7.32; N, 3.43%.

Calculated for $\text{RuP}_2\text{S}_3\text{N}_2\text{ClC}_{42}\text{H}_{37}\text{O}$: C, 57.30; H, 4.20; P, 7.05; N, 3.18%.

Infrared absorption frequencies (in cm^{-1}) in nujol: 3050w, 1940s, 1485m, 1180m, 1150m, 1090m, 1050m, 740m, 690s, 510s, 410m, 310m.

6. (5-Isopropylthio-1,3,4-thiadiazoline-2-thione)
(1-cyanoethyl)carbonyl bis(triphenylphosphine)-
ruthenium(II), $\text{Ru}(\text{CH}_3\text{CHCN})(\text{CO})(\text{PPh}_3)_2$ - Isopr-TD.

The sodium salt of Isopr-TD was prepared from the ligand (0.42 g, 2.2 mmol) and sodium hydride (0.052 g, 2.2 mmol) by stirring them in ether (25 ml) for 4 hrs. Ether was removed and the solid was suspended in THF (20 ml). To this suspension $[\text{Ru}(\text{CH}_3\text{CHCN})\text{ClCO}(\text{PPh}_3)_2]_2$, (1.485 g, 1 mmol) was added and the contents were stirred for 16 hrs. THF was removed under vacuum and the solid was extracted with benzene by centrifuging. The clear benzene solution gave light yellow crystals on concentration. The crystals were washed with n-hexane

and dried under reduced pressure. Yield 1.06 g (60%).

M.p. 170°C.

Analysis: Found, C, 60.72; H, 4.14; P, 6.87; N, 3.72%.

Calculated for $\text{RuP}_2\text{N}_2\text{S}_3\text{C}_{45}\text{H}_{41}\text{O}$: C, 61.08; H, 4.63;

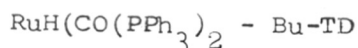
P, 7.01; N, 3.16%.

IR absorption maxima (in cm^{-1}) observed in nujol:

3050w, 2180m, 1920s, 1480m, 1180w, 1150w, 1090m, 1050w,

730s, 690s, 590m, 510s, 410m, 310w.

7. (5-Butylthio-1,3,4-thiadiazoline-2-thione)hydrido
carbonyl bis(triphenylphosphine)ruthenium(II),

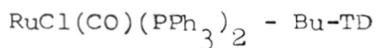


The sodium salt of Bu-TD was prepared by stirring the ligand (0.23 g, 1.1 mmol) and sodium hydride (0.026 g, 1.1 mmol) in ether (30 ml) for 4 hrs. Ether was removed and the solid was suspended in tetrahydrofuran (20 ml). To this suspension $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.951 g, 1 mmol) was added and the contents were stirred for 16 hrs. THF was removed under reduced pressure and the solid was extracted with benzene by centrifuging. The clear benzene solution on concentration gave yellow microcrystals of the product. The product was washed with hexane and dried under vacuum. Yield 0.47 g (55%). M.p. 175°C. Analysis: Found C, 60.61; H, 4.53; P, 7.47; N, 3.67%.

Calculated for $\text{RuP}_2\text{N}_2\text{S}_3\text{C}_4\text{H}_4\text{O}$: C, 60.06; H, 4.65; P, 7.21; N, 3.25%.

IR frequencies (cm^{-1}) in nujol: 3040w, 1990m, 1910s, 1480m, 1260w, 1170m, 1145w, 1085s, 1065w, 730s, 685s, 510s, 410s, 330w.

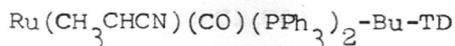
8. (5-Butylthio-1,3,4-thiadiazoline-2-thione)chloro carbonyl bis(triphenylphosphine)ruthenium(II),



Bu-TD (0.206 g, 1 mmol) was dissolved in methoxy ethanol (5 ml) and $\text{RuHClCO}(\text{PPh}_3)_3$ (0.951 g, 1 mmol) was added to it. The mixture was refluxed for 5 hrs and cooled overnight. The solvent was removed under vacuum and yellow solid was filtered, washed with hexane and dried under vacuum. Yield 0.53 g (60%). M.p. 205°C. Analysis: Found C, 57.99; H, 4.63; P, 6.82; N, 3.34%. Calculated for $\text{RuP}_2\text{S}_3\text{N}_2\text{ClC}_4\text{H}_4\text{O}$: C, 57.75; H, 4.36; P, 6.93; N, 3.13%.

IR frequencies (cm^{-1}) in nujol: 3040w, 1990m, 1910s, 1480m, 1260w, 1170m, 1150w, 1085s, 1040w, 730s, 690s, 510s, 410s, 330w.

9. (5-Butylthio-1,3,4-thiadiazoline-2-thione)(1-cyanoethyl) carbonyl bis(triphenylphosphine)ruthenium(II),



The sodium salt of Bu-TD was prepared from the

ligand (0.46 g, 2.2 mmol) and sodium hydride (0.052 g, 2.2 mmol) by stirring them in ether (25 ml) for 4 hrs. Ether was removed and the solid was suspended in THF (20 ml). To this suspension $[\text{Ru}(\text{CH}_3\text{CHCN})\text{ClCO}(\text{PPh}_3)_2]_2$, (1.485 g, 1 mmol) was added and the contents were stirred for 15 hrs. THF was removed under vacuum and the solid was extracted with benzene. The extract was concentrated and the light yellow crystals obtained were filtered, washed with n-hexane and dried under vacuum. Yield 1.08 g (60%). M.p. 185°C.

Analysis: Found C, 60.61; H, 4.81; P, 6.99; N, 4.25%.

Calculated for $\text{RuP}_2\text{N}_3\text{S}_3\text{C}_{46}\text{H}_{43}\text{O}$: C, 60.52; H, 4.71;

P, 6.79; N, 4.60%.

IR frequencies (cm^{-1}) in nujol: 3050w, 2190m, 1910s, 1480m, 1150w, 1090s, 1040w, 735s, 690s, 590m, 510s, 410m, 340w.

10. (5-Methyl-4-phenethyl-1,3,4-triazoline-3-thione) hydrido carbonyl bis(triphenylphosphine)ruthenium(II), $\text{RuH}(\text{CO})(\text{PPh}_3)_2$ - Phenethyl-Tr

Phenethyl-Tr (0.24 g, 1.1 mmol) and sodium hydride (0.026 g, 1.1 mmol) were stirred together in ether (25 ml) for 3 hrs. Ether was removed and the sodium salt of the ligand was suspended in THF (20 ml). To the suspension $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.951 g, 1 mmol) was added and the contents were stirred for 20 hrs. THF was removed under vacuum and the compound was extracted

with benzene. The extract was concentrated to yield yellow microcrystalline product. It was washed with hexane and dried under vacuum. Yield 0.54 g (60%).

M.p. 186°C.

Analysis: Found C, 66.72; H, 4.71; P, 7.53; N, 4.46%.

Calculated for $\text{RuP}_2\text{N}_3\text{SC}_{48}\text{H}_{43}\text{O}$: C, 66.05; H, 4.93;

P, 7.11; N, 4.82%.

IR frequencies (cm^{-1}) observed in nujol: 3040w, 1990m, 1910s, 1480m, 1180m, 1150w, 1090m, 1025m, 740s, 695s, 500s, 410m, 320m.

11. (5-Methyl-4-phenethyl-1,2,4-triazoline-3-thione) chlorocarbonyl bis(triphenylphosphine)ruthenium(II), $\text{RuCl}(\text{CO})(\text{PPh}_3)_2$ - Phenethyl-Tr

$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.951 g, 1 mmol) was added to Phenethyl-Tr (0.219 g, 1 mmol) dissolved in benzene and ethanol (20 ml, 1:1 mixture). The solution was refluxed for 4 hrs and cooled overnight at room temperature. The solvent was removed under reduced pressure and the light yellow compound was collected on filter, washed with hexane and dried under vacuum. Yield 0.59 g (65%). M.p. 219°C.

Analysis: Found: C, 63.32; H, 4.36; P, 6.77; N, 4.22%.

Calculated for $\text{RuP}_2\text{N}_3\text{SClC}_{48}\text{H}_{42}\text{O}$: C, 63.54; H, 4.63;

P, 6.84; N, 4.63%.

IR absorption bands (cm^{-1}) observed in nujol: 3040w, 1930s, 1480m, 1180m, 1155w, 1090s, 1030m, 1000m, 745s, 690s, 500s, 410w, 310m.

12. (5-Methyl-4-phenethyl-1,2,4-triazoline-3-thione)
(1-cyanoethyl)carbonyl bis(triphenylphosphine)-
ruthenium(II), $\text{Ru}(\text{CH}_3\text{CHCN})(\text{CO})(\text{PPh}_3)_2$ - Phenethyl-Tr

Sodium hydride (0.052 g, 2.2 mmol) and phenethyl-Tr (0.48 g, 2.2 mmol) were stirred in ether (20 ml) for 4 hrs. Ether was removed and the resulting sodium derivative was suspended in THF (20 ml). To this suspension $[\text{Ru}(\text{CH}_3\text{CHCN})\text{Cl}(\text{CO})(\text{PPh}_3)_2]_2$ (1.485 g, 1 mmol) was added and the mixture was stirred for 20 hrs. THF was removed under vacuum and the product was extracted with benzene. The extract was concentrated and the yellow crystalline product was collected on filter, washed with n-hexane and dried under vacuum. Yield 1.29 g, (65%). M.p. 205°C ; Mol. wt., 805.

Analysis: Found C, 66.86; H, 14.44; P, 16.33; N, 6.54%.

Calculated for $\text{RuP}_2\text{N}_4\text{SC}_5\text{H}_{14}\text{O}$: C, 66.16; H, 4.97; P, 6.70; N, 6.05%; Mol. wt., 925.

IR absorption frequencies (cm^{-1}) observed in nujol: 3040w, 2180m, 1910s, 1480m, 1250w, 1180w, 1150w, 1080s, 1020w, 740m, 690s, 515m, 495s, 415m, 315w.

13. (5-Phenyl-4-methyl-1,2,4-triazoline-3-thione)-
hydrido carbonyl bis(triphenylphosphine)ruthenium(II),
RuH(CO)(PPh₃)₂ - Methyl-Tr

Methyl-Tr (0.21 g, 1.1 mmol) and sodium hydride (0.026 g, 1.1 mmol) were stirred together in ether (30 ml) for 3 hrs. Ether was removed and the sodium salt of the ligand was suspended in THF (20 ml). To the suspension RuHCl(CO)(PPh₃)₃ was added and the contents were stirred for 15 hrs. THF was removed under vacuum and the compound was extracted with benzene. The extract upon concentration gave light yellow microcrystalline product. It was filtered and washed with hexane and dried under vacuum. Yield 0.55 g (65%). M.p. 192°C.

Analysis: Found C, 65.85; H, 4.11; P, 7.01; N, 4.85%.

Calculated for RuP₂SC₄₆H₃₉N₃O: C, 65.40; H, 4.62;

P, 7.34; N, 4.97.

IR frequencies (cm⁻¹) in nujol: 3040w, 1910s, 1480m, 1180m, 1150w, 1090m, 1020w, 745m, 695s, 520m, 500s, 410m, 320w.

14. (5-Phenyl-4-methyl-1,2,4-triazoline-3-thione)chloro
carbonyl bis(triphenylphosphine)ruthenium(II),
RuCl(CO)(PPh₃)₂ - Methyl-Tr

RuHCl(CO)(PPh₃)₃ (0.951 g, 1 mmol) and Methyl-Tr (0.19 g, 1 mmol) were refluxed in benzene and ethanol (25 ml, 1:1 mixture) for 4 hrs and cooled overnight at

room temperature. The solvent was removed under reduced pressure and the yellow compound was filtered, washed with hexane and dried under vacuum. Yield 0.53 g, (60%). M.p. 112°C.

Analysis: Found: C, 62.57; H, 4.08; P, 7.57; N, 4.67. Calculated for $\text{RuP}_2\text{SN}_3\text{ClC}_{46}\text{H}_{38}\text{O}$: C, 62.83; H, 4.32; P, 7.05; N, 4.78.

IR frequencies (cm^{-1}) observed in nujol: 3020w, 1925s, 1480m, 1180w, 1050w, 1090m, 1020w, 740m, 690s, 500s, 410m, 340m.

15. 5-Phenyl-4-methyl-1,2,4-triazoline-3-thione
(1-cyanoethyl)carbonyl bis(triphenylphosphine)
ruthenium(II), $\text{Ru}(\text{CH}_3\text{CHCN})(\text{CO})(\text{PPh}_3)_2$ - Methyl-Tr

Methyl-Tr (0.42 g, 2.2 mmol) and sodium hydride (0.052 g, 2.2 mmol) were stirred in ether (25 ml) for 4 hrs. The ether was removed and the resulting sodio derivative was suspended in THF (25 ml).

$[\text{Ru}(\text{CH}_3\text{CHCN})\text{Cl}(\text{CO})(\text{PPh}_3)_2]_2$ (1.485 g, 1 mmol) was added to the suspension and the mixture was stirred for 20 hrs. THF was removed under reduced pressure and the product was extracted with benzene. The extract upon concentration gave yellow microcrystalline compound. It was filtered and washed with hexane and dried under vacuum. Yield 1.05 g, (60%). M.p. 164°C, Mol. wt., 730.

Analysis: Found C, 65.37; H, 4.43; P, 6.51; N, 6.31.

Calculated for $\text{RuP}_2\text{N}_3\text{SC}_4\text{H}_9\text{O}$: C, 65.55; H, 4.68;

P, 6.91; N, 6.24; Mol. wt., 878.45.

IR frequencies (cm^{-1}) observed in nujol: 3040w, 2180m, 1910s, 1480m, 1180w, 1160w, 1040m, 1020w, 740m, 690s, 500s, 410m, 315w.

16. (Thiazolidine-2-thione)hydrido chlorocarbonyl
bis(triphenylphosphine)ruthenium(II), $\text{RuH}(\text{CO})(\text{PPh}_3)_2$ -
Thiazolidine-2-thione

Sodio derivative of the ligand was prepared by stirring sodium hydride (0.026 g, 1.1 mmol) and thiazolidine-2-thione (0.139 g, 1.1 mmol) in ether (25 ml) for 4 hrs. Ether was removed and the sodio derivative of the ligand was suspended in THF (20 ml). $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ was added to the suspension and the contents were stirred for 15 hrs. THF was removed under vacuum and the compound was extracted with benzene. The extract was concentrated and the light yellow product was collected on filter, washed with hexane and dried under vacuum. Yield 0.46 g (60%). M.p. 187°C.

Analysis: Found C, 62.71; H, 4.44; P, 8.37; N, 1.36%.

Calculated for $\text{RuP}_2\text{C}_4\text{H}_9\text{S}_2\text{NO}$: C, 62.17; H, 4.53;

P, 8.03; N, 1.81.

IR absorption maxima (cm^{-1}) in nujol observed were:
 3020w, 1995m, 1900s, 1480m, 1180m, 1150w, 1085s,
 1045s, 740m, 695s, 575m, 500s, 415s, 330w.

17. (Thiazolidine-2-thione)chlorocarbonyl bis(triphenyl-
phosphine)ruthenium(II), $\text{RuCl}(\text{CO})(\text{PPh}_3)_2$ -
Thiazolidine-2-thione

Thiazolidine-2-thione (0.119 g, 1 mmol) and
 $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.951 g, 1 mmol) were refluxed in
 benzene and alcohol (30 ml, 1:1 mixture) for 4 hrs and
 cooled overnight at room temperature. The solvent
 was removed under vacuum and the light yellow product
 was filtered, washed with hexane and dried under vacuum.
 Yield 0.48 g (60%). M.p. 208°C ; Mol. wt., 705.

Analysis: Found C, 59.31; H, 4.56; N, 1.47; P, 7.81.
 Calculated for $\text{RuP}_2\text{C}_{40}\text{H}_{34}\text{S}_2\text{NClO}$: C, 59.52; H, 4.22;
 N, 1.74; P, 7.69; Mol. wt., 806.45.

IR absorption spectral frequencies (cm^{-1}) observed in
 nujol: 3040w, 1920s, 1480m, 1185m, 1155w, 1090m,
 1070w, 745m, 690s, 550m, 500s, 410m, 340w.

18. (Thiazolidine-2-thione)(1-cyanoethyl)carbonyl
bis(triphenylphosphine)ruthenium(II),
 $\text{Ru}(\text{CH}_3\text{CHCN})(\text{CO})(\text{PPh}_3)_2$ - Thiazolidine-2-thione

Sodio derivative of thiazolidine-2-thione was
 prepared by stirring sodium hydride (0.052 g, 2.2 mmol)

and thiazolidine-2-thione (0.26 g, 2.2 mmol) in ether (25 ml) for 4 hrs. Ether was removed and the sodium salt obtained was suspended in tetrahydrofuran (25 ml). To the suspension, $[\text{Ru}(\text{CH}_3\text{CHCN})\text{Cl}(\text{CO})(\text{PPh}_3)_2]_2$, (1.485 g, 1 mmol) was added and the mixture was stirred for 20 hrs. THF was removed under reduced pressure and the product was extracted with benzene. The benzene extract upon concentration yielded a microcrystalline compound. It was collected on filter, washed with hexane and dried under vacuum. Yield 0.98 g (60%). M.p. 210°C.

Analysis: Found C, 62.12; H, 4.26; P, 7.02; N, 3.67%.

Calculated for $\text{RuP}_2\text{N}_2\text{S}_2\text{C}_{43}\text{H}_{38}\text{O}$: C, 62.54; H, 4.60; P, 7.51; N, 3.39%.

Infrared absorption bands (cm^{-1}) located in nujol spectrum of the compound are: 3040w, 2200m, 1900s, 1485m, 1180m, 1140w, 1085m, 1040m, 740m, 690s, 500s, 410m, 320w.

Results and Discussion

5-Alkylthio-1,3,4-thiadiazoline-2-thiones (alkyl = methyl, isopropyl or n-butyl) exist in thione form as evidenced by their UV, IR and ^1H NMR spectral data. The UV absorption spectra in ethanol show two absorption bands with λ_{max} at 325-314 nm and 245-224 nm. These bands are similar to those described by Thorn¹⁰ for 2-methylthio-4-methyl-1,3,4-thiadiazoline-5-thione and other derivatives in ethanol.

Infrared spectra of these ligands (Figs. 19-21) in solid state show a medium intensity band at ca 3100 cm^{-1} due to $\nu(\text{NH})$ which appears at ca 3420 cm^{-1} in chloroform solutions indicating the intermolecular hydrogen bonding and the presence of the ligands in the thione form in the solid state.

^1H NMR spectra of 5-alkylthio-1,3,4-thiadiazoline-2-thiones were recorded in CDCl_3 and DMSO-d_6 . The spectra in DMSO-d_6 show a broad signal at 14.4-14.5 ppm due to NH proton in all the ligands, which disappears on deuteration (Figs. 30-32). The same signal however, could not be observed in the ^1H NMR spectra of these ligand recorded in CDCl_3 , probably due to their low solubility in CDCl_3 and the concentration dependence of NH proton in it. (Figs. 33, 34). The typical concentration effects of

1,3,4-thiadiazoline-2-thione in CDCl_3 and DMSO-d_6 have been studied¹⁴ and NH proton has been found to be independent of its concentration in DMSO-d_6 and concentration dependent in CDCl_3 . The NH proton in the PMR spectra of substituted 1,2,4-triazoline-thiones with similar environment of thione-thiol tautomerism was located at ca 14.0 ppm in DMSO-d_6 .

The signal due to NH proton in PMR spectra of 5-methyl-4-phenethyl-1,2,4-triazoline-3-thione (Phenethyl-Tr) and 5-phenyl-4-methyl-1,2,4-triazoline-3-thione (Methyl-Tr) in CDCl_3 has been located at

11.4 and 10.91 ppm respectively. It was found to exchange with D_2O in the spectra of both the ligands (Figs. 35, 36). Two medium intensity bands at 220-225 nm and 260 nm with a weak shoulder at 280 nm were observed in the UV spectra of Phenethyl-Tr and Methyl-Tr in ethanol. The shoulder around 280 nm in triazoline ligands has been characterised as the absorption due to thiocarbonyl groups¹⁵.

The presence of thione form in the triazoline-thione ligands has been further evidenced by the IR spectral data. The IR spectra of Phenethyl-Tr and Methyl-Tr in solid state (Fig. 27) show a broad, intense band at 3100 cm^{-1} due to $\nu(\text{NH})$ which appears

at 3450 cm^{-1} in the IR spectra of these ligands in chloroform solutions. This indicates the extensive intermolecular hydrogen bonding confirming the predominance of thione form in these ligands.

Thiazolidine-2-thione exhibits thione-thiol tautomerism involving -N=C-SH and -NH-C=S groups in a thiol-thione equilibrium¹⁶. A medium intensity band has been located at 3125 cm^{-1} in solid state IR of thiazoline-2-thione (Fig. 26.), which appears at 3400 cm^{-1} in chloroform solution confirming the presence of $\nu(\text{NH})$ in solid state and the intermolecular hydrogen bonding. The bond distance¹⁷ (C-S , 1.680 \AA) further establishes the partial double ^{bond} character, typical of the thione-thiol tautomerism.

A broad intense band at 276 nm was observed in the UV spectrum of thiazolidine-2-thione in ethanol as reported by Lukens and Sisler¹⁸. The chloroform solution of the ligand, however, shows two medium intensity bands at 340 and 300 nm .

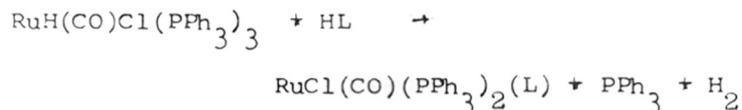
A broad signal in the PMR spectrum of thiazolidine-2-thione (Fig. 37.) due to NH proton at 8.1 ppm was found to be absent after D_2O exchange.

The absence of $\nu(\text{SH})$ around $2600\text{-}2550\text{ cm}^{-1}$ in the IR spectra of Me-TD, Isopr-TD, Bu-TD, Phenethyl-Tr,

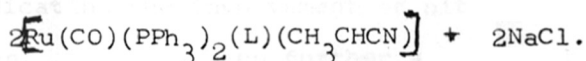
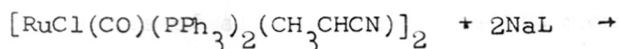
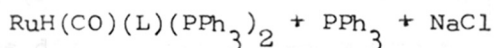
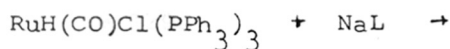
Methyl-Tr and Thiazolidine-2-thione in nujol unequivocally concludes the predominance of thione form of all these heterocyclic thione derivatives in solid state. IR spectra of Me-TD, Isopr-TD and Bu-TD in chloroform solution show a weak absorption band around 2600-2550 cm^{-1} along with a strong absorption band at ca 3420 cm^{-1} respectively due to $\nu(\text{SH})$ and $\nu(\text{NH})$ indicating that these ligands exist in solution in thione and thiol forms. The absorption band due to $\nu(\text{SH})$ in the chloroform solutions of Phenethyl-Tr, Methyl-Tr and Thiazolidine-2-thione could not be located due to the concentration dependence of the thiol group in solution.

The mononuclear ruthenium(II) complexes of these ligands (HL) have been prepared by the reaction of $[\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3]$, (A) or $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3\text{CHCN})]_2$, (B), with corresponding ligands in appropriate stoichiometric ratios.

5-Alkylthio-1,3,4-thiadiazoline-2-thiones (alkyl = methyl, isopropyl or n-butyl) react with (A) in 2-methoxy ethanol or benzene-alcohol medium to give mononuclear ruthenium(II) complexes with the elimination of a hydrogen molecule and a triphenylphosphine.



Sodio derivatives of the ligands have been prepared by the reaction of sodium hydride in anhydrous ether at an ambient temperature. When sodio derivative of the ligand (NaL) reacts with (A) or (B) in tetrahydrofuran at room temperature, chlorine free products are obtained.



Ru(II) derivatives of Phenethyl-Tr, Methyl-Tr and thiazolidine-2-thione have been prepared similarly.

The products isolated are stable yellow microcrystalline solids which are moderately soluble in chloroform and methylene chloride and insoluble in petroleum ether (40-60°). *Molecular weight determinations by vapour pressure osmometry indicates the mononuclear nature of these complexes.*

Electronic spectra of all the ligands and their ruthenium(II) complexes in chloroform/ethanol have been recorded and the data are presented in Table 12. Two bands with λ_{max} at 320 and 240 nm in the ruthenium(II) complexes of 1,3,4-thiazolidine-2-thione ligands are due to $\pi-\pi^*$ transitions. Additional band at higher wavelength (480-450 nm) could be tentatively assigned to the metal ligand charge transfer absorptions¹⁹.

Similar results have been obtained for the ruthenium(II) complexes of 1,2,4-triazoline-3-thione ligands and thiazolidine-2-thione.

An interesting feature of these heterocyclic thione derivatives is the appearance of a prominent band at ca $1290-1270\text{ cm}^{-1}$ mainly due to (C-N) vibrations coupled with (C=S) vibrations²⁰. This characteristic frequency has disappeared or reduced considerably in the IR spectra of all the ruthenium(II) complexes of these ligands indicating the involvement of nitrogen atom in coordination. This has been further supported by the absence of the stretching frequency at ca 3100 cm^{-1} due to NH (located in the IR spectra of all the ligands). This also indicates the complexation of the ligands with ruthenium(II) atom after deprotonation of NH proton via thiolate sulphur²¹.

An intense band appearing at ca 1500 cm^{-1} in the IR spectra of all the ligands is assigned to the stretching mode of (C=N) vibrations²² having a partial double bond character due to the presence of thione-thiol tautomerism. This band was found to be lowered by $\sim 20\text{ cm}^{-1}$ and was located at ca 1480 cm^{-1} in the IR spectra of all the ruthenium(II) carbonyl complexes (Figs. 22-25 and 28, 29).

Another intense band located at ca 720 cm^{-1} in the IR spectra of the ligands has been attributed to

$\nu(\text{C}=\text{S})$ on the basis of previous assignments²³. This band is absent in the spectra of the ruthenium(II) complexes and a new band of medium intensity at ca $690\text{-}680\text{ cm}^{-1}$ due to $\nu(\text{C}-\text{S})$ has been located. Two new bands of medium to weak intensity located at 415 cm^{-1} and 330 cm^{-1} are ascribed to $\nu(\text{Ru}-\text{N})$ and $\nu(\text{Ru}-\text{S})$ vibrations²⁴.

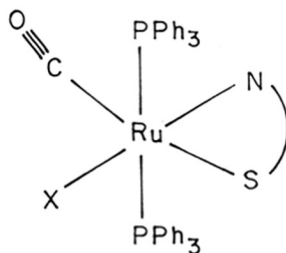
A strong band at 1925 cm^{-1} in the IR spectrum of $\text{RuHClCO}(\text{PPh}_3)_2$ has been shifted to a lower frequency ($1905\text{-}1920\text{ cm}^{-1}$) in the ruthenium(II) complexes of the thione ligands indicating increased $d\pi\text{-}p\pi$ backbonding in $\text{Ru}-\text{C}\equiv\text{O}$ bond.

The complex $\text{RuHClCO}(\text{PPh}_3)_2$ has a medium intensity band at 2020 cm^{-1} due to $\nu(\text{Ru}-\text{H})$, which has shifted to a lower frequency (1990 cm^{-1}) in the ruthenium(II) complexes of the thione ligands indicating the reduction in the metal hydrogen bond order as a result of increased electron density at the central metal atom, probably due to the presence of various substituent groups in the ligand molecules.

The IR spectrum of the binuclear complex $[\text{Ru}(\text{CH}_3\text{CHCN})\text{ClCO}(\text{PPh}_3)_2]_2$ shows $\nu(\text{C}\equiv\text{N})$ at 2220 cm^{-1} and $\nu(\text{C}\equiv\text{O})$ at 1930 cm^{-1} . In the mononuclear ruthenium(II) complexes, $\text{Ru}(\text{CH}_3\text{CHCN})\text{ClCO}(\text{PPh}_3)_2(\text{L})$ ($\text{L} = \text{thione ligand}$), the $\nu(\text{C}\equiv\text{N})$ is observed at $2200\text{-}2180\text{ cm}^{-1}$. The observed reduction of the carbon-nitrogen bond order could be

attributed to the increased charge on the nitrile carbon as a result of chelate formation. Principal IR frequencies (cm^{-1}) of ruthenium(II) complexes of the heterocyclic thiones with assignments have been shown in Table 10.

On the basis of these results the following hexa-coordinated structure with bidentate N,S coordination has been postulated to the mononuclear ruthenium(II) complexes of the thiadiazoline, triazoline and thiazolidine thione ligands:



X = H or Cl or CH_3CHCN

$\begin{matrix} \text{N} \\ \text{S} \end{matrix}$) = Me-TD or Isopr-TD or Bu-TD or Phenethyl-Tr
or Methyl-Tr or Thiazolidine-2-thione.

The δ resonance due to NH proton appearing at 11.4-8.1 δ , ppm in CDCl_3 solutions of all the ligands was absent in the PMR spectra of all the ruthenium(II)

(Figs. 38-47)
 complexes indicating the complex formation by deprotonation.

An upfield shift has been observed for the methyl protons of the 5-methylthio-1,3,4-thiadiazoline-2-thioato ruthenium(II) complex in its PMR spectrum. Similar upfield shifts have been noted in the case of Bu-TD and Isopr-TD complexes of ruthenium(II). Similarly upfield shifts of methyl protons in the case of ruthenium(II) complexes of Phenethyl-Tr and Methyl-Tr and that of CH_2 protons in the case of the thiazolidine-2-thione-ruthenium(II) complexes have been observed. The high field ^1H NMR spectrum of the hydridoruthenium(II) complexes show a triplet at -13.3 to -13.0 δ , ppm due to Ru-H with $^2\text{J}(\text{PH})$ cis ~ 20 Hz which suggest that the two phosphine groups are trans to each other²⁵ as shown in the structure of the complexes. The data is presented with assignments in Table II.

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