TRANSITION METAL COMPLEXES
OF SULPHUR CONTAINING LIGANDS

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Certified that the work embodied in this thesis entitled "Transition metal complexes of sulphur containing ligands" is the result of the original researches carried out under my supervision by Mr. Dharmendra Kumar Varshney and is suitable for submission for the award of the Ph. D. degree of Aligarh Muslim University.

( S.A.A. Zaidi )

Reader in Chemistry
TO

MY PARENTS
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The nature of the complexes of 2,5-dimercapto-1,3,4-thiadiazole (Bismuthiol I) with Cu(I) and Cu(II),

ABSTRACT

The coordination chemistry of sulphur containing ligands has recently assumed greater importance in view of the fact that several of these compounds have been found to be biologically active and have found uses in medicine as well as in industry. Some sulphur compounds have been found to be useful as protective agents against hazardous radiations. Furthermore a knowledge of the nature of metal complexes of organic sulphur compounds is an important requirement for understanding the interaction of metal ions with proteins.

The present work is an attempt to gain some more information on the nature of the complexes of organic sulphur compounds. About forty five new complexes of three different sulphur containing ligands viz., 2,5-dimercapto-1,3,4-thiadiazole (Bismuthiol I), 2-aminothiazole and 2-amino-6-ethoxybenzothiazole with transition metals of first, second and third row have been synthesized, characterized and studied on the basis of elemental analysis, infrared, far infrared and electronic spectral studies and magnetic measurements.

Bismuthiol I has been shown by the help of infrared studies to be in an associated form and to exist predominantly in the thiono form in equilibrium with a small quantity of the
thiol form. Excepting for the complex formed by Cu(II) chloride where the ligand is suggested to be completely deprotonated, the complexed ligand has been shown to be in the following form.

Coordination has been shown to occur through either the nitrogen or the exocyclic sulphur atom or both. In no case has ring sulphur been found to coordinate. All the complexes are insoluble and seem to be polymeric in nature. In all the cases the magnetic moment values have been found to be substantially lower than expected due presumably to antiferromagnetic interactions.

Tentative geometries of the complexes of bismuthiol I have been suggested by the help of reflectance spectra. The geometry of the nickel complex seems to be unique in the sense that it has the nickel ions in both square planar and octahedral environments. The Cu(I) complex seems to have some Cu(II) ions and the Cu(II) complex is presumably a mixed valence Cu(I)-Cu(II) complex. The Ru(I) complex is feebly paramagnetic which suggests antiferromagnetic interactions through weak Ru-Ru bonds.

Complexes of 2-aminothiazole with different transition
Metal ions have been obtained having the general formula $[M(2\text{-aminothiazole})_{1-4}X_2]$ where $M$ stands for the metal ions and $X=\text{Cl}^-, \text{NO}_3^-$ or $1/2 \text{SO}_4^{2-}$. In all the cases coordination occurs through either the ring nitrogen or the amino nitrogen atom. In no case has the ring sulphur atom been found to coordinate. The possibility of bidentate coordination is ruled out in view of the requirements of the stoichiometry and stereochemistry of the complexes. These complexes seem to be polymeric in nature. Tentative geometries have been suggested for these complexes. Platinum and gold complexes having octahedral geometries are suggested to have one chloride ion outside the coordination sphere and must be ionic. The silver complex has a linear geometry. The vanadium and copper complexes are proposed to have a square planar geometry. A tetrahedral structure has been suggested for zinc, cadmium and mercury complexes while the complexes of cobalt, nickel, ruthenium, palladium and iridium have been proposed to have an octahedral geometry.

2-Amino-6-ethoxybenzothiazole, which exists in an associated form, has been found to form very stable and insoluble complexes with the transition metals. Coordination has been suggested in these complexes to occur through the aminonitrogen atom. The iridium, vanadium and copper complexes are proposed to have a square planar geometry whereas the silver, zinc, cadmium and mercury complexes are presumably tetrahedral. An octahedral geometry is proposed for the gold, ruthenium, palladium and platinum complexes.
CHAPTER I

GENERAL INTRODUCTION
GENERAL INTRODUCTION

A knowledge of the nature of metal complexes of organic sulphur compounds is an important requirement for understanding the interaction of metal ions with proteins. During the past few decades sulphur donor ligands have received greater attention because of the fact that some organic compounds containing sulphydryl and disulphide groups find important uses in medicine, biology and industry. Some sulphur containing organic compounds have been found to be useful as protective agents against hazardous radiations. Thiosalicylic acid has been found to be an analytically\(^1,^2\) and therapeutically\(^3,^4\) promising ligand. Thioacetic acid stimulates the respiratory activity\(^5\) of the brain cortex and is a preservative for food stuff\(^6\). The Keratin fibers, especially human hair\(^7\) are shaped by some of the thioacids viz., thioacetic acid, thiolactic acid and thiosalicylic acid etc. The use of metal salts\(^8,^9\) of thioacetic acid has been suggested to be an antidote in heavy metal poisoning. This acid has also been found to be active as a co-factor in enzymic oxidation of cystamine to hypotaurine\(^10\). Cobalt and sodium salts of thiolactic acid which are related to the hydrolysis products of vitamin B\(_{12}\) inhibit the effect of weight reduction in young animals by diet containing
thyroid powder. It has been claimed that thiolactic acid stabilizes the solutions of vitamin $B_1$ and $C$ and prevents the formation of a precipitate during the heating of such solutions. Thiolactic acid also prevents the occurrence of diabetes due to alloxan and dithizone. The use of some of the above mentioned acids has been claimed in the separation of ruthenium, zirconium and niobium from uranium. Such compounds have also been used in the preparation of photographic antiblooming agents. Lead, cadmium and nickel salts of these thioacids have been used in plasticization of natural rubber.

The formation of thiobridges, enhanced stability, anomalous magnetic behaviour and the spectra of many transition metal complexes of sulphur containing ligands have, in recent times, aroused keen interest regarding the metal sulphur linkage.

In view of the foregoing the metal complexes of sulphur containing ligands have attracted the attention of a lot of research workers in this area.

One of the common sulphur containing ligands whose interaction with metal ions has been examined in some detail, is thiol. The distinguishing property associated
with the mercapto group is its ability to form complexes containing sulphur bridge. Mercaptide ions RS⁻ being highly polarisable, form strong bonds with typical class b metal ions. The mercaptides Hg(RS)₂(where R is an alkyl group) are monomeric in benzene\textsuperscript{16}. With nickel(II) ion ethyl mercaptan forms the diamagnetic complex Ni(SEt)₂(where SEt = ethyl sulphide) for which the polymeric structure(I) has been suggested\textsuperscript{17}. The palladium(II) mercaptides Pd(RS)₂ (R = ethyl, n-propyl, n-butyl or n-amyl) are associated in ethylene dibromide and chloroform and probably have a similar polymeric structure\textsuperscript{16}.

\[ \text{Et} \quad \text{Et} \quad \text{Et} \]
\[ \text{Et} \quad \text{Et} \quad \text{Et} \]
\[ \text{Ni} \quad \text{Ni} \quad \text{Ni} \]
\[ \text{S} \quad \text{S} \quad \text{S} \]

\[ \text{Et} \quad \text{Et} \quad \text{Et} \]

\[ \text{S} \quad \text{S} \quad \text{S} \]

(I)

Thiophenol gives an intense colour with palladium(II) ion Pd(RS)₂ is bright vermilion but silver, gold, rhodium, iridium or platinum fail to produce any colour with thiophenol\textsuperscript{16}. The halogen bridged dimeric complexes of palladium(II) and platinum(II) are readily split by p-toluidine and other unidentate ligands but the corresponding alkyl
thiobridged complexes are not split by such ligands. Cis and trans isomers of the platinum(II) complexes \( \text{Pt}(\text{PPr}_3^n)-(\text{EtS})X_2(X = \text{Cl, SEM})(\text{where PPr}_3^n = n\text{-tripropyl phosphine}) \) (II) and (III) have been prepared.

However, the palladium(II) analogue \((X = \text{Cl})\) of the platinum(II) complex could be isolated only in the cis form. Another type of isomerism involving the bridging thiol, has been reported to occur in alkyl thiobridged platinum(II) complexes containing two different alkyl mercaptans. A pair of such isomers (IV and V) is shown below:

![Diagram](attachment:image.png)
Hexanethiol forms a cobalt(III) complex
Co(C₆H₁₃S)₃ for which the polymeric structure(VI) has been
tentatively suggested²¹.

Thioethers do not coordinate very strongly to
metals apart from Pt(II), Pd(II), Rh(III) and Hg(II). Sulphur
has a much lower affinity for Pt(IV) than Pt(II) and various
tries to prepare Pt(IV) complexes of thioethers have been
 unsuccessful. The Pd(II) complexes having the general formula
Pd(R₂S)₂Cl₂, where R₂S is the thioether, can be readily
formed but in the trans-form only²². Pd(Me₂S)₂Cl₂ is completely
isomorphus with the trans-Pt(Me₂S)₂Cl₂²³. With palladium
chloride yellow monomeric complexes of the type Pd(PhSR)₂Cl₂
(where R = alkyl and Ph = phenyl) are usually formed but
when R = tertiary butyl or tertiary amyl group, the red complexes of the general formula PhSR₂PdCl₂ are formed. These complexes have been suggested to have the tetrameric structure (VII) and are the only known palladium(II) complexes of this type.

\[
\begin{align*}
\text{Ph} & \quad \downarrow \quad \text{S} \\
\text{R} & \quad \text{Pd} \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} & \quad \text{Pd} \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} & \quad \text{Pd} \quad \text{Cl} \quad \text{Cl} \\
\text{S} & \quad \text{R} \\
\text{Ph} & \quad \uparrow
\end{align*}
\]

Chlorobridged Pt(II) compounds of general formula \( \text{L}_2\text{Pt}_2\text{Cl}_4 (\text{L} = \text{R}_2\text{S}, \text{R} = \text{alkyl}) \) have been prepared. Rhodium(III) gives complexes of the type \( \text{Rh(SEt}_2)_3\text{X}_3 (\text{X} = \text{Cl, Br, I}) \). The Ir(IV) chloro complex \( \text{Ir(Et}_2\text{S})_2\text{Cl}_4 \) has also been reported. Alkyl thioethers form at least three types of Hg(II) halogen complexes: (a) monomeric \( \text{R}_2\text{S}_2\text{HgX}_2 \) (b) halogen-bridged dimeric \( \text{R}_2\text{SHgX}_2)_2 \) (VIII) (c) complexes \( \text{R}_2\text{S}_2\text{HgX}_2 \) of uncertain structures. However, thioether complexes of Ti(III) are unstable and less well defined. The coordinating ability of \( \text{Et}_2\text{S} \) is greater than that of \( \text{Et}_2\text{O} \), since the dipole moment of \( \text{Et}_2\text{S}(1.58 \text{D}) \) is greater than that of \( \text{Et}_2\text{O}(1.15 \text{D}) \) while the
polarizability of sulphur in $\text{Et}_2\text{S}$ is much greater than that of oxygen in $\text{Et}_2\text{O}$.

Cyclopentadienyl complexes containing sulphur donor ligands $[(\text{C}_5\text{H}_5)\text{Fe(CO)SMe}]_2$, $[(\text{C}_5\text{H}_5)\text{CoSMe}]_2$, $[(\text{C}_5\text{H}_5)\text{Cr}_2(\text{MeS})_3]$ (Me=methyl group) etc. have been prepared$^{28,23b}$ King and Bisnette$^{29}$ have recently reported a new type of complex with a sulphur containing ligand coordinated through a $\text{C} = \text{S}$ bond. The postulated structures of two of these complexes (IX and X) are shown below:

Both these complexes may possibly be regarded as derivatives
of the unsaturated sulphonium ion $\text{H}_2\text{C}^\text{+}=\text{S}-\text{CH}_3$ where the carbon-sulphur double bond is π-bonded to the transition metal like a carbon-carbon double bond. Chelate ligands with two thioether groups give complexes which are similar to those formed by unidentate thioethers. Chelate ligands having a thioether sulphur and another donor atom often coordinate more strongly than dithioethers. The coordinating ability of some β-aminothioethers, $\text{RS.CO.CH}_2\text{CH}_2\text{NH}_2$ has been investigated by Douglas et al\textsuperscript{30}. 

The chelating tendencies of some κ-mercapto acetamides $\text{R.NH.CO.CH}_2\text{SH}(\text{R} = \text{aryl})$ have been examined by Martin\textsuperscript{31}. It has been shown that the chelates of Zn(II) and Pb(II) with o-aminobenzenthiothiol(XI) and 6-mercapto purine(XII) are more stable than the corresponding oxygen chelates\textsuperscript{32,32a} o-Aminobenzenethiol forms low-spin inner complexes with Co(II) and Ni(II)\textsuperscript{33,34}. 8-Mercapto-quinoline(XIII) forms strong chelates with class b metals\textsuperscript{35-37}.

\[
\begin{align*}
\text{(XI)} & \quad \text{(XII)} & \quad \text{(XIII)}
\end{align*}
\]
Dimethylamino ethanethiol\textsuperscript{38,40}(XIV) and diethyl amino ethanethiol\textsuperscript{39}(XV) have been shown to form coloured complexes with transition metal ions. An analogous compound -mercapto-ethyl amine(XVI) has been reported to form stable complex with a number of transition metal ions\textsuperscript{41-44}.

\begin{align*}
\text{N-(CH}_3\text{)}_2\text{-(CH}_2\text{)}_2\text{-SH} & \quad \text{N-(C}_2\text{H}_5\text{)}_2\text{-(CH}_2\text{)}_2\text{-SH} & \quad \text{CH}_3\text{-CH-NH}_2 \\
\text{(XIV)} & \quad \text{(XV)} & \quad \text{(XVI)}
\end{align*}

Complexes of neutral and deprotonated guanyl thiourea(XVII) have been reported\textsuperscript{45}. The crystal structure of dithio-oxamide(XVIII) has been recently determined\textsuperscript{46}. This ligand forms insoluble complexes which are probably polymeric in nature\textsuperscript{47,47a}.

\begin{align*}
\text{HN-C-NH-C-NH}_2 \\
\text{S \quad N}
\end{align*}

\begin{align*}
\text{HN-C-NH-C-NH}_2 \\
\text{S \quad N}
\end{align*}
Thiosemicarbazide exists in tautomeric forms (XIX) and (XX) and can act as a neutral or a charged chelate group. Its inner complexes of Ni(II), Pd(II) and Pt(II) have been obtained by Jensen in two forms which are assumed to be cis-trans isomers 48, 48a.

\[
\begin{align*}
\text{(XIX)} & \quad \text{(XX)} \\
\end{align*}
\]

Four membered chelate rings are formed by dialkyl dithiocarbamates (XXI) and dialkyl dithiophosphates (XXII). The i.r. spectra of dithiocarbamate complexes show that there is considerable double bond character in the C-N bond 49 (XXIII). The i.r. spectrum of the Pt(II) complex of N,N'-diethyl dithiocarbamate indicate single bond-order in the C-S bond, while Pt-S stretching mode occurs at 375 cm\(^{-1}\) 50. The M-S stretching frequencies of the Ni(II), Pd(II), Co(II) and Cr(III) chelates of diethyl dithiophosphates occur in the range 308-358 cm\(^{-1}\) 51.
Several \( \kappa \)-dithiols form strong complexes with Fe(III), Sn(II), Pb(II), As(III) and Bi(III) as well as with typical class b metals. The stability of the complexes of Zn(II), Cd(II), Hg(II) and Pb(II) with a number of \( \kappa \)-dithiols have been compared\(^{37,52}\). Carbonyl compounds containing bridging \( \kappa \)-dithiols viz., \([\text{Co}](\text{CO})_6\text{Fe}_2(\text{TDI})\] and \([\text{C}_{5}H_{5}]_2\text{M}_2\{\text{S}_2\text{C}_2(\text{CF}_3)_2\}_2\] (\(M=V, \text{Cr}, \text{Mo}\)) have been reported by King\(^{53}\) who suggested structure(XXIV) for the monomeric Co(III) complex (where TDI stands for toluene-3,4-dithiol).
Thiourea acts as a unidentate ligand forming strong complexes with class b metal ions, in particular Cu(I), Ag(I), Au(I) and Hg(II). Thiourea reduces Cu(II) to Cu(I), Au(III) to Au(I), Pt(IV) to Pt(II) and forms complexes with metals in lower oxidation states. Infrared studies have shown that thiourea coordinates through sulphur not only with class b metals, but also with Sn(IV), Pb(II) and Te(II). However, infrared spectral studies indicate that the ligand is coordinated through nitrogen in Ti(tu)₂Cl₄ (tu=thiourea). The compound Ni(tu)₂(NCS)₂ is octahedral and has a polymeric structure in which the sulphur atom of each thiourea molecule is bound to two nickel atoms. The complex Cd(tu)₂Cl₂ is tetrahedral but Pb(tu)₂Cl₂ has a polymeric structure in which the lead atom is seven-coordinate. Complexes of N,N'-substituted thioureas (XXV) (R=alkyl or aryl, R' = alkyl, aryl or H atom) have been extensively studied. Ethylene thiourea (etu; XXVI) reacts with Cu(I) and Ag(I) giving complexes which contain up to four molecules of ligand. However, its Au(I) complexes are formed having only one or two ligand molecules. Complexes of ethylene thiourea with Fe(II), Co(II) and Ni(II) have also been investigated. Cu(I) and Ag(I) complexes with other substituted thioureas are known, but their structures are often complex.
N,N'-Diethyl thiourea, N,N'-diphenyl thiourea and N,N'-diphenylthiourea behave as bidentate chelating agents, being bonded through both the nitrogen atoms in the complexes $2	ext{TiCl}_4\cdot L(L=$substituted thiourea$)^{58}$. S-Acetyl thiourea(Satu) forms only a 1:1 complex Cu(Satu)Cl with Cu(I)^{63}.

Thiazoles and imidazoles are of much interest mainly because of their importance in biological systems^{64}. Some of them have been shown to be antiparasitic in solution. Further, their complexes with metals like tin and mercury have recently been found to act as fungicides and insecticides^{65,66}. Infrared studies on thiazole and imidazole complexes of transition metal ions have established that the bonding of ligand to metal in these complexes occurs through the nitrogen atom. In a few instances, however, thiazoles have also been shown to act as bridging ligands^{67-70}. As imidazolethiol and thiazole derivatives have more than one donor sites, they present the possibility of formation of several interesting compounds. In view of the importance
of the thiazole group in biological systems, recently complexes of thiazole and 2-methyl benzothiazole have been studied and it has been suggested that the ligand is N-bonded, but there are some examples where the ligand is probably acting as a bridging ligand with coordination through both nitrogen and sulphur atoms.

Heterocyclic compounds containing sulphur and nitrogen have been used mainly in the preparation of biologically active complexes. Thiazoles and imidazolethiol in addition to acting as fungicides have in some cases been used as antioxidant and heat resistant materials. Bismuthiol I complex of tribuyl tin chloride has been used as corrosion inhibitor and in painting ships to prevent damage from marine organisms. In a few cases these heterocyclic compounds have been used in detection and identification of metals, by virtue of their specific interaction. More recently, the coordination compounds of thiazoles and imidazoles with transition metal ions have been synthesized. Their coordination behaviour and structure have been studied on the basis of infrared spectral data. A very large number of papers on transition metal complexes with sulphur containing ligands have recently appeared in the chemical literature.
In view of the foregoing discussion and the growing importance of sulphur compounds in medicine, biology and industry it was considered worthwhile to prepare and study new complexes of a few important sulphur containing ligands; viz.,

1. 2,5-dimercapto-1,3,4-thiadiazole (Bismuthiol I),
2. 2-aminothiazole,
3. 2-amino-6-ethoxybenzothiazole,

each of which are described in separate chapters.
CHAPTER II

EXPERIMENTAL METHODS
EXPERIMENTAL METHODS

Several physico-chemical methods are now a days available for structure elucidation of coordination compounds. The techniques most commonly available and used for the investigation of the structures of the compounds described in the present work are as follows:

1. Infrared spectra
2. Magnetic susceptibility
3. Electronic spectra

While information about these techniques is found in most modern text-books and in several books exclusively on these subjects, a brief description of these methods seems appropriate.

Infrared Spectra:

The infrared region of electromagnetic spectrum covers a wide range of wave lengths. The range 12500-4000 cm\(^{-1}\) is the near i.r. region, 4000-650 cm\(^{-1}\) is medium i.r. region and the region extending from 650-100 cm\(^{-1}\) is known as the far i.r. region. The infrared frequencies are determined
by the internal vibratory motions of the molecule while the intensities are related to its electrical properties.

For a non-linear molecule of \( n \) atoms possessing \( 3n \) degrees of freedom the fundamental modes of vibrational motion will be \( 3n-6 \). Sometimes the observed vibrational modes are less than the theoretically expected number.

Since the absorption of electromagnetic radiation in the i.r. region is possible only when there is a change in the dipole moment of the molecule, during the normal vibrations, if there is no such change, it will be 'Infrared inactive'. The occurrence or non-occurrence of an infrared band is governed by some 'Selection Rules' which state:

1. In order for molecules to absorb infrared radiation as vibrational excitation energy there must be a change in the dipole moment of the molecule as it vibrates.

2. In absorption of radiation only transitions for which change in the vibrational energy level i.e. \( \Delta v \) is + 1, can occur.

In view of the restriction due to dipole moment, infrared spectrum of a molecule is not its complete 'fingerprint' and 'Raman Spectroscopy' is used for the purpose. It is a complementary technique to i.r. spectroscopy and deals with the vibrations which may not be 'infrared active'.
In the Raman effect the light scattered by the molecule contains frequencies other than that of the incident monochromatic light and differences between these frequencies and the frequency of the incident light correspond to normal vibrations.

While the complete normal coordinate analysis of a given molecule is necessary for prediction of all the bands in its i.r. spectrum, it is at times enough to consider the frequencies of certain group of atoms called 'group frequencies'. These frequencies are characteristic of groups, no matter in what molecule they occur. The absence of any band in the appropriate region is a good indication of the absence of that particular grouping from the molecule. In this work, only those frequencies which are pertinent to the discussion of the newly synthesized complexes will be discussed.

**S-H Stretching**

The absorption due to SH stretching vibration has been found to be in the region of 2600 to 2400 cm$^{-1}$. Although it is a well defined bond, the SH peak is rather weak. The i.r. spectrum of mercapto compounds has been very helpful in deciding about the presence or the absence
of the mercapto group. Studies in the thio-region have been used, for example, to determine whether certain thiols of quinoline exist in the mercaptan or the thiol-ketoform, whilst the absence of any SH absorption in the spectrum of mercapto benzothiazole is one of the strongest pieces of evidence for the existence of this substance as a thio-ketone under normal conditions.

C-S Stretching:

The C-S stretching frequency generally appears as a band of weak or moderate intensity in the range 720-570 cm⁻¹. In the Raman spectra this band is very strong. There appears to be a progressive decrease in the frequency in the order: Primary, Secondary and Tertiary C-S. In aromatic derivatives the C-S frequency is found towards the top of this range and some difficulty is experienced in recognizing the C-S frequency due to the presence of the intense CH out-of-plane deformation band in this region. In phenyl sulphonyl halides the C-S vibration is found between 715 and 706 cm⁻¹. In organic thiocyanates it appears in the region 740-680 cm⁻¹. In thio ketals, broad bands with several maxima are found probably due to vibrational coupling.
\textbf{C=S Stretching:}

Frequencies ranging from 1570 to 850 cm\(^{-1}\) have been attributed to the C=S stretching mode in the literature but there seems to be no adequate correlation of the literature data\(^{95,96}\). A careful examination of the data reveals that the assignments of very high or low frequencies are always made in the nitrogen containing thiocarbonyl compounds. The C=S stretching frequency in thiofenone is found at around 1180 cm\(^{-1}\). There has been great indefiniteness with regard to the C=S stretching frequency in nitrogen containing compounds. The assignment in these compounds varies in the wide range of 850-1570 cm\(^{-1}\). Many of the earlier assignments of the C=S frequencies in compounds such as thioamides\(^{97}\), dithiooxamides\(^{98}\), thiadiazole\(^{99}\) etc., appear to be partial in the sense that these might have had some contribution from C=S stretching.

Mecke et al.\(^{100}\) assigned C=S stretching frequency in the region 1050-1200 cm\(^{-1}\) in some cyclic thioamides. As a result of the correlation of Rao and Venkataraman\(^{101}\) it is possible to assign the range 1025-1225 cm\(^{-1}\) to the C=S stretching vibration in simple derivatives where there are no appreciable coupling effects.
N-N Stretching:

Important information regarding the coordination of ligands containing two adjacent nitrogen is obtained from the shift in N-N stretching vibrations appearing in the form of medium intensity band in the region 1100-1000 cm\(^{-1}\). In the case of nitroamines absorptions corresponding to the N-N\(^-\) stretching have been identified to occur near 1050 cm\(^{-1}\)\(^{102}\). The presence of this absorption has also been confirmed by Haszeldine on some compounds\(^{103,104}\).

N-H Stretching:

The N-H stretching vibrations occur in the region 3500-3300 cm\(^{-1}\) in dilute solutions\(^{105}\). The N-H stretching band shifts to lower values in the solid state due to extensive hydrogen bonding. Primary amines in dilute solution in non-polar solvent give two absorption bands in the above mentioned region. The first of band arising from the symmetric stretch is usually found near 3500 cm\(^{-1}\) and the second which arises from the corresponding asymmetrical mode is found near 3400 cm\(^{-1}\). These bands are usually 125-150 cm\(^{-1}\) apart. Secondary amines show only a single N-H stretching absorption in dilute solution. The N-H band in pyrroles occurs at 3496 cm\(^{-1}\)\(^{106}\) and the frequency
range for substituted pyrroles has been found to be 3435-3400 cm$^{-1}$.

**N-H Deformation:**

For the deformation frequencies of the NH$_2$ group in primary amines four characteristic peaks should appear. But the only definite assignment has been done in the case of scissoring vibrations generally observed in the region 1650-1590 cm$^{-1}$ $^{107}$. The lower frequency deformation vibrations of the NH$_2$ group have not been investigated in detail. The NH$_2$ twisting, wagging and torsional vibrations in methylamine have, however, been assigned to 1455, 780 and 264 cm$^{-1}$ respectively.

**C-H Stretching:**

These frequencies are usually observed between 3100-3000 cm$^{-1}$ $^{105}$. Some aromatic compounds give rise to three bands near 3038 cm$^{-1}$. The spectra of several mono-substituted benzenes show a band around 2934 cm$^{-1}$ and two to five bands in the region 3100-3000 cm$^{-1}$, only one of which was assigned as a combination band. Pyridine shows C-H absorptions in the range 3070-3020 cm$^{-1}$ which appear as a series of multiple absorptions under high resolution $^{108}$. 
C-H in-plane and out-of-plane Deformation:

A number of characteristic absorption bands in the region 1250-1000 cm\(^{-1}\) are exhibited by most of the heterocyclic compounds, and are attributed to C-H in-plane deformation bands\(^{109}\). Bands appearing in the region 900-700 cm\(^{-1}\) have been attributed to the C-H out-of-plane deformation vibrations, and the position of these bands depend on the number of free hydrogen atoms adjacent to one another\(^{110}\).

C=C and C=N Stretching:

These frequencies occur at from 1700-1575 cm\(^{-1}\). In conjugated systems where both C=C and C=N linkages are present, identification of the C=N absorption band is rendered difficult due to its interaction with the C=C vibration\(^{111}\). Thus specific assignment of the C=N frequency has not been possible in heterocyclic compound such as the tetrazoles, benzothiazoles and thiazoles. The absorption bands in the region 1650-1500 cm\(^{-1}\) in such compounds can be associated with the entire ring skeleton. Pyridine, however, shows a C=N absorption band at 1580 cm\(^{-1}\). Imines (>C=NH) usually yield a moderate to strong absorption between 1690 and 1630 cm\(^{-1}\).
C-N Stretching :

The C-N stretching absorption gives rise to strong bands in the region 1350-1250 cm\(^{-1}\) in all the amines\(^{112}\). In aromatic primary amines there is one band in the region 1340-1250 cm\(^{-1}\) but in secondary amines two bands have been observed in the region 1350-1280 cm\(^{-1}\) and 1280-1230 cm\(^{-1}\).

M-S Stretching :

The metal-sulphur stretching frequency is of particular interest as it gives a direct evidence for coordination through the sulphur atom. It appears in the low frequency region. Generally this band occurs in the region 300-380 cm\(^{-1}\)\(^{51}\).

M-X Stretching :

The metal-halogen stretching vibrations generally occur in the far i.r. region (150-400 cm\(^{-1}\)) and are a good piece of evidence in support of the coordination of the halogens to the metal.

M-N Stretching :

The M-N stretching frequency is of particular interest since it provides direct information regarding the
coordinate bond. It appears in the far infrared region and could be anywhere from \(700-150\) cm\(^{-1}\). The M-N frequency depends on the following factors:

1. Mass of the metal and ligand
2. Oxidation number of metal ion
3. Coordination number of metal ion
4. Geometry of the complexes
5. Basicity of the ligand
6. Bridging or non-bridging anions
7. Ligand-field stabilization energy

**Magnetic Susceptibility**:

The most rewarding application of magnetochemistry has been the one which deals with coordination compounds. This is because the more important aspects of magnetochemistry are concerned with the effects arising from the incomplete shells of electrons, isolated from each other and these conditions are fulfilled by complex compounds of the transition elements. There are several kinds of magnetism in substances viz., paramagnetism, diamagnetism, ferromagnetism or anti-ferromagnetism. The magnetic effects arising from the spin angular momentum and orbital angular momentum
of the unpaired electrons give rise to paramagnetism. Most of the compounds of the transition elements are paramagnetic. Diamagnetism is attributable to the interaction of closed-shell electrons with an applied magnetic field. Ferromagnetism or anti-ferromagnetism arises as a result of interaction between dipoles of neighbouring atoms.

The possession of the spin and orbital angular momentum turns an atomic system into a micromagnetic dipole with a moment:

$$\vec{\mu} = (L+2S) \beta b$$

where $L$ and $S$ stand for total angular momentum and total spin angular momentum (in units of $\hbar/2\pi$) respectively and $\beta b$ is Bohr Magneton.

For the case when spin orbit coupling can be essentially neglected, that is, the multiplet splitting of the ground term is small compared with $kT (\lambda \ll kT$ where $\lambda$ is spin orbit coupling constant), the effective magnetic ($\mu_{\text{eff}}$) is given by

$$\mu_{\text{eff}} = \sqrt{[L(L+1)+4S(S+1)]/2} \text{ B.M.}$$
In another extreme case where $\lambda \gg KT$ and the multiplicity splitting is so great that virtually all ions are in the ground component of the multiplet for the usual temperature of measurement:

$$\mu_{\text{eff}} = g[J(J+1)]^{1/2} \text{ B.M.}$$

where $g$ is Lande factor and is given by the expression:

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

Here $J$, $S$, and $L$ are total angular momentum, total spin angular momentum and the total orbital angular momentum.

While this expression describes the value of $\mu_{\text{eff}}$ for the complexes of rare-earths, the equation often applied for the complexes of first series of transition metal is:

$$\mu_{\text{eff}} = [L(L+1)+4S(S+1)]^{1/2} \text{ B.M.}$$

It is however, only valid for complexes of Co$^{2+}$ and Ni$^{2+}$ and generally pure-spin formula given below is used:

$$\mu_{\text{eff}} = [4S(S+1)]^{1/2} \text{ B.M.}$$
i.e. the orbital angular momentum contribution is neglected. While spin-magnetic moment is insensitive to environment of metal ions, the orbital magnetic moment is not. In order for an electron to have an orbital angular momentum and thereby an orbital to transform the orbital into a fully-equivalent orbital by rotation about that axis.

Electrons in $d_{\pi}$ states can not contribute to the orbital moment because the $d_{x^2-y^2}$ and $d_{z^2}$ orbital can not be transformed into one another by a rotation about any axis. However, all $d_{\pi}$ states excepting $d_{\pi 3}$ and the $d_{\pi 6}$ contribute to the orbital moment.

No orbital contributions are expected for octahedral high-spin complexes of configurations $d^3(d\epsilon^3)$, $d^4(d\epsilon^3d\pi)$, $d^5(d\epsilon^3d\pi^2)$, $d^6(d\epsilon^6d\pi^2)$, $d^9(d\epsilon^6d\pi^3)$ while for $d^1(d\epsilon)$, $d^2(d\epsilon^2)$, $d^6(d\epsilon^4d\pi^2)$ and $d^7(d\epsilon^5d\pi^2)$ a non-zero orbital moment contribution is possible. For low-spin complexes of octahedral symmetry an orbital moment contribution is seen for $d^4(d\epsilon^4)$ and $d^5(d\epsilon^5)$ and none for $d^6(d\epsilon^6)$ and $d^7(d\epsilon^6d\pi)$.

In tetrahedral complexes due to term inversion it follows that where one does not expect orbital moment contribution in $O_h$ symmetry one expects it in $T_d$ symmetry. For high-spin tetrahedral complexes no orbital moment
contribution is therefore expected for \( d^{1}, d^{2}, d^{2} d^{3}, \)
\( d^{3} d^{3}, d^{4} d^{4} \) while for \( d^{2} d^{2}, d^{3} d^{2}, d^{2} d^{4}, \)
\( d^{4} d^{5} \) no orbital moment is expected. Low-spin tetrahedral complexes for central ion of first transition series are not generally known.

An orbital moment contribution is expected for tetrahedral and octahedral complexes when the ground state is split. However, the term splitting into a three-fold orbitally degenerate state \( T \) will contribute but that splitting, into a two-fold orbitally degenerate state \( E \) will not contribute as it is non-magnetic. The one-fold orbitally degenerate state \( A \) should give no orbital moment contribution.

Even when no splitting of the ground state appears in cases having no orbital moment contribution, an interaction with the higher states can appear, due to spin-orbit coupling, giving an orbital moment contribution. Hence in the first half of the transition metal series for the complexes, a decrease of the moment compared with the pure spin moment is expected, but in the second half of the series an increase should be seen. It has been found that for octahedral complexes there is appreciable orbital moment contribution and for tetrahedral complexes it is
comparatively lesser.

Practically the magnetic moment value of an unknown complex is obtained from the measured magnetic susceptibility which is defined as follows. If a magnetic field is applied to a substance, then the flux $B$ within the substance is given by a formula:

$$B = H + 4\pi I$$

where $H$ is the magnitude of the applied field and $I$ is known as the intensity of magnetization. The magnetic permeability is $B/H$ and is given by $B/H = 1 + 4\pi (I/H) = 1 + 4\pi K$, $K$ is called the volume susceptibility. Conventionally instead of volume susceptibility, gram susceptibility ($\chi_g$) is used where magnetic susceptibility is considered on weight basis. $\chi_g$ when multiplied by the molecular weight of the complex and corrected for diamagnetic values gives rise to $\chi_{mol}$. The $\mu_{eff}$ value is calculated from the $\chi_{mol}$ by the expression:

$$\mu_{eff} = 2.84 \left[ \chi_{mol} \times T \right]^{1/2} \text{B.M.}$$

$T$ is the absolute temperature at which the experiment is performed.
Magnetic susceptibility may or may not be dependent on temperature. A relationship for the paramagnetic susceptibility and temperature is given by Curie's law: $\chi_{\text{mol}} = C/T$

where $C$ and $T$ are Curie constant and absolute temperature. Magnetic moment should not depend on temperature for the complexes where this law is valid. In general, however, deviations are found and $\mu_{\text{eff}}$ values depend on temperature. Within a certain temperature range (20-40 K) the dependence of $\chi_{\text{mol}}$ upon $T$ is represented by:

$$\chi_{\text{mol}} = \frac{C}{T - \Theta} \quad (\Theta = \text{Curie - Weiss constant})$$

Ultra-violet and Visible (ligand-field) Spectra:

The transition metal complexes usually absorb light somewhere in the spectral region between 200-2000 nm. The transitions responsible for these absorptions correspond to the excitation of electrons of molecules from ground state to higher electronic states. While ultra-violet and visible spectra of organic molecules have been extensively studied, the application of ligand field spectra to coordination chemistry has come into fashion relatively recently. In a transition metal all the five 'd orbitals' viz., $d_{xy}$, $d_{yz}$, $d_{xz}$, $d_{x^2-y^2}$ and $d_{z^2}$ are degenerate. However, in coordination compounds due to the presence
of ligand, this degeneracy is lifted and d orbitals split into two groups, called $t_{2g}$ ($d_{xy}$, $d_{yz}$ and $d_{xz}$) and $e_g$ ($d_{z^2}$ and $d_{x^2-y^2}$). In an octahedral complex, the set of $t_{2g}$ orbitals goes below and the set of $e_g$ orbitals goes above the original level of the degenerate orbitals. In the case of the tetrahedral complexes, the position of the $t_{2g}$ and $e_g$ orbital is reversed.

When a molecule absorbs energy equal in magnitude to $h\nu$ (where $h$ is the Planck's constant and $\nu$ is the frequency of radiation) which is sufficient to cause electronic transitions, the electrons are excited from the ground to the excited state. In order to interpret the spectra of transition metal complexes, the device of energy level diagram based upon 'Russell Saunders scheme' must be introduced. This has the effect of splitting the highly degenerate configurations into groups of levels having lower degeneracies known as 'Term Symbols'.

The orbital angular momentum of electrons in a filled shell vectorially adds up to zero. The total orbital angular momentum of an incomplete d shell electrons is obtained by adding L values of the individual electrons; which are treated as a vector with the component $m_l$ in the direction of the applied field. Thus,
The total spin angular momentum $S = \sum_i S_i$ where $S_i$ is the value of spin angular momentum of the individual electrons. $S$ has a degeneracy $\gamma$ equal to $2S + 1$, which is also known as 'spin multiplicity'. Thus a term is finally denoted as "L". For example, if $S = 1$ and $L = 1$ the term will be $^3P$ and similarly if $S = 1\frac{1}{2}$ and $L = 3$ the term will be $^4F$.

In general the terms arising from a $d^4$ configuration are as follows:

$$d^{1d^9} \rightarrow 2D$$
$$d^{2d^8} \rightarrow 3F, 3P, 1G, 1D, 1S$$
$$d^{3d^7} \rightarrow 4F, 4P, 2H, 2G, 2F, 2D(2), 2P$$
$$d^{4d^6} \rightarrow 5D, 3H, 3G, 3F(2), 3D, 2P(2), 1I, 1G(2), 1F, 1D(2), 1S(2)$$
$$d^{5} \rightarrow 6S, 4G, 4F, 4D, 4P, 2I, 2H, 2G(2), 2F(2), 2D(3), 2P, 2S.$$  

Coupling of $L$ and $S$ also occurs, because both $L$ and $S$ if non-zero, generate magnetic fields and thus tend to orient their moments with respect to each other, in the direction where their interaction-energy is least. This coupling is known as "LS coupling" and gives rise to the
resultant angular momentum denoted by the quantum number 
\( J \) which may have quantized positive values from \(| L \pm S | \) upto 
\(| L - S | \) e.g. in cases of \( ^3P (L = 1, S = 1) \) and \( ^4F (L = 3, S = \frac{1}{2}) \) 
possible values of \( J \) representing states arising from term 
splitting are 2,1 and 0 and \( 4\frac{1}{2}, 3\frac{1}{2}, 2\frac{1}{2} \) and \( 1\frac{1}{2} \) respectively.
Each state specified by \( J \) is \( 2J + 1 \) fold degenerate. The 
total number of states obtained from a term is called the 
multiplet and each value of \( J \) associate with a given value 
of \( L \) is called a component. Spectral transition due to 
spin orbit coupling in atom or ion occur between the compo­
nents of two different multiplets. While LS coupling scheme 
is used for the elements having atomic number less than 30, 
in whose case spin orbital interactions are relatively 
small, another scheme called "jj coupling scheme" is used 
when spin orbital interaction are large and electron 
repulsion parameters decrease. The spin angular momentum 
of an individual electron couples with its orbital momentum 
to give an individual \( j \) for that electron. The individual 
\( j \)'s couple to produce a resultant \( jJ \) for the atom. The 
electronic transition taking place in an atom or ion are 
governed by certain "Selection Rules", which are as follows:

1. Transition between states of different multi­
plicity are forbidden.
2 Transition involving the excitation of more than one electron are forbidden.

3 In a molecule, which has a centre of symmetry, transition between two gerade or two ungerade states are forbidden.

The ground term of a $d^4$ system is the one which has the highest spin multiplicity and the highest $L$ value. All the terms of a given system further split in the presence of a ligand field. Inter-electronic repulsions within a configuration give the energies of the terms above the ground term. The energies are function of two parameters related to the electron repulsion. The two parameter may be chosen in either the way of Condon and Shortley ($F_2$ and $F_4$) or in that of Racah ($B$ and $C$) for $d$ orbital electrons. For the first transition series ions the value of $C/B$ is around 4.0 and $B$ is about $1000 \text{ cm}^{-1}$. It is possible to examine the effects of crystal field on a polyelectron configuration. The ligand-field splitting due to cubic-field can be obtained by considerations of group theory. It has been shown that an $S$ state remains unchanged, $P$ state does not split, a $D$ state split into two and $F$ state into three and a $G$ state into four states as tabulated below. This holds for an octahedral $O_h$ as well as for $T_d$ symmetry.
In weak crystal fields the interelectronic repulsions are larger. The crystal field may however, be of comparable magnitude (medium strength) or it may be larger than the inter-electronic repulsion.

Coorelation diagram for free ion (weak-field) strong-field configuration from $d^1 - d^9$ for both octahedral and tetrahedral cases are available. In addition to the qualitative aspects of transition from weak to strong crystal-fields it is also necessary to have quantitative results available for the interpretation of spectra. The so-called Tanabe Sugano diagrams make it possible. In these diagrams, the energies of the levels of a $d^n$ system as $E/B$ are plotted as the vertical coordinate and the crystal-field strength in the form of $D_q/B$ as the horizontal coordinate. This diagram requires two parameters B and C for the inter-electronic repulsions. It can be drawn only if the ratio $C/B$ is specified.
Transition from the ground state to the excited state occur according to selection rules described earlier. The energy-level order of the states arising from the splitting of a term state for a particular ion in an octahedral field is the reverse of that for this ion in a tetrahedral field.

Sometimes due to transfer of charge from ligand to metal or metal to ligand, bands appear in the ultraviolet region of the spectrum. Such spectra are known as "Charge Transfer Spectra". For metal complexes there are often possibilities that charge transfer spectra extend into the visible region to obscure d - d transition. However, these should be clearly discerned from the ligand band which might also occur in the same region.
CHAPTER III

COMPLEXES OF BISMUTHIOL I
INTRODUCTION

Thiadiazole is a five membered heterocyclic ring system having one sulphur and two nitrogen atoms. Depending on the position of the nitrogen atoms in the ring with reference to the sulphur atom numbered I, there are three different thiadiazoles mentioned below:

1. 1,2,3-thiadiazole (I)
2. 1,2,4-thiadiazole (II)
3. 1,3,4-thiadiazole (III)

\[
\begin{align*}
\text{(I)} & \quad \text{(II)} & \quad \text{(III)} \\
\text{N-CH} & \quad \text{HC-N} & \quad \text{N-N} \\
\text{N} & \quad \text{CH} & \quad \text{HC} & \quad \text{N} \\
\text{N} & \quad \text{CH} & \quad \text{N} & \quad \text{CH} \\
\text{S} & \quad \text{S} & \quad \text{S} &
\end{align*}
\]

2,5-Dimercapto-1,3,4-thiadiazole is thus a derivative of III in which the hydrogen atoms attached to the carbon atoms 2 and 5 are substituted by mercapto (-SH) groups. This compound is since long known to be a specific analytical reagent for bismuth\textsuperscript{113-125} and is also called bismuthiol I.
It is also used in the analysis of several other metals\(^{126-128}\).

Bismuthiol I exists in the form of a yellow powder having a melting point of 163°C. It was synthesized by Losanitch\(^{129}\) in 1922 and by Bambas\(^{130}\) in 1952. Badisch\(^{131}\) in 1956 prepared it by the interaction of carbon disulphide with hydrazine in the presence of sodium hydroxide. It is fairly soluble in hot alcohol and insoluble in water.

There seems to be no report of any structural study on bismuthiol I and Bambas\(^{130}\) had suggested the thiol structure for this compound on the basis of its chemical reactions. In the year 1960 Thorn\(^{99}\) suggested on the basis of ultraviolet studies that bismuthiol I could exist in three tautomeric forms (IV-VI) given below:

\[
\begin{align*}
\text{(IV)} & : \quad \text{HS-C} \quad \text{C-SH} \\
\text{(V)} & : \quad \text{S=C} \quad \text{C=S} \\
\text{(VI)} & : \quad \text{SH-C} \quad \text{C=S}
\end{align*}
\]

He suggested that while in CHCl\(_3\) the dithiol structure predominates, in alcohol it is mainly in the dithione form. We have recently confirmed\(^{132}\) the thione structure for the solid from infrared spectral studies.
Bismuthiol I has since long been known to interact with various metals and complex formation with Cu(II), Co(II), Ni(II) and Zn(II) has been noted. Amperometric titrations of copper and palladium and spectrophotometric determination of palladium with this ligand have been made. It is used in potentiometric titrations and solubility determination of silver salts. However, except for the complexes of bismuthiol I with rhodium, osmium and tellurium, no attempt seems to have been made either to determine the structure or in some cases even the composition of the complexes formed. Spectrophotometric studies showed that the composition of the osmium complex was $\text{H}_6\text{OsO}(\text{C}_2\text{N}_2\text{S}_3)_6$ and that of rhodium was $\text{H}_3\text{Rh}(\text{C}_2\text{N}_2\text{S}_3)_3$ and $\text{HRh}(\text{C}_2\text{N}_2\text{S}_3)_2$ in 3 N and N-HCl, respectively.

Bismuthiol I finds several industrial applications. Its zinc compound is used as an antioxidant for motor oil. The tributyl tin chloride compound of bismuthiol I is used as a protective agent against the attack of marine organisms on the bottom of the ships. The nickel compound is used as catalytic agent in the manufacture of acrylic acid, its Co(II), Cu(II) and Zn(II) compounds have been used as bactericides. It is also used in the manufacture of tetracycline, which is low in chlorotetracycline. The physiology, biochemistry and cytopathology of the cornea.
In relation to the injury by mustard gas and allied toxic agents has been examined. In this connection the effect of bismuthiol I on the rabbits was also examined but it was found to be very toxic due to its S-H groups\textsuperscript{141}. It has been tested for decontamination of lewisite on human skin but it was found to be unsatisfactory\textsuperscript{142}. It has also been used to form mercury derivatives which are intermediates in the manufacture of pharmaceuticals and insecticides\textsuperscript{143}. The disulphide of dimercapto thiadiazole restrains the digestion of photographic emulsion and has a distinct antifogging effect\textsuperscript{144}.

In view of the biological and industrial importance of the compounds of the bismuthiol I, it was of interest to undertake the preparation of its complexes and to systematically investigate their structure with a view to understanding and collecting evidence for ultimately correlating the same to their various activities.

**EXPERIMENTAL TECHNIQUES**

**Chemical Analysis**:  
The elemental analysis for carbon, hydrogen and
nitrogen were done in the micro-analytical laboratory of this department, at the Indian Institute of Technology, Kanpur, and at the micro-analytical services division, C.S.I.R.O., Melbourne, Australia. The anions and sulphur were estimated gravimetrically by standard methods\textsuperscript{145}. Zinc, cadmium, silver, thallium and platinum group metals were determined gravimetrically\textsuperscript{146}, and the rest of the metals were estimated by complexometric titration method with ethylenediaminetetraacetic acid (E.D.T.A.)\textsuperscript{147,148}. For this titration, it was necessary to decompose the complexes with a mixture of nitric, perchloric and sulphuric acid.

**Infrared Spectra**:

The infrared spectra were recorded in the range 4000-650 cm\(^{-1}\) in KBr discs on a Perkin-Elmer grating spectrophotometer model 521 and model 137 at the Indian Institute of Technology, Kanpur, on an infracord spectrophotometer at the Central Drug Research Institute, Lucknow and on a Hilger & Watts spectrophotometer (H 800.306) at the Indian Institute of Technology, Delhi. The far infrared spectra were also recorded in the range 650-250 cm\(^{-1}\) in nujol mull on a Perkin-Elmer grating spectrophotometer model 621.
Electronic Spectra:

The diffuse reflectance spectra were recorded in the range 230-1000 nm on a Carl-Zeiss VSU-2P spectrophotometer at the chemistry department, Guru Nanak University, Amritsar, India.

Magnetic Susceptibility:

These measurements were carried out by two methods:

1. Gouy Method (In the chemistry department at Roorkee University, Roorkee.)
2. Faraday Method (In the chemistry department at B.H.U. Varanasi.)

Gouy Method:

The solid complex was finely powdered and filled in the gouy tube very carefully. The tube containing the material under examination was suspended vertically between the poles of an electromagnet. The length of the tube was so adjusted that its lower end remained under the influence of magnetic field. The weight of the tube containing the sample was known with magnet on and off. The gouy tube was calibrated with a standard CuSO₄·5H₂O. The gram susceptibility was calculated by the following formula:
\[ \chi_g = \frac{\Delta W_{\text{unk.}} \times W_{\text{std.}} \times \chi_{\text{std.}}}{W_{\text{unk.}} \times \Delta W_{\text{std.}}} \]

\( W_{\text{corrected}} = \Delta W (\text{sample + tube}) - \Delta W (\text{empty tube}) \)

\[ \chi_g = \text{Gram susceptibility of unknown.} \]

\( \Delta W_{\text{unk.}} = \text{Change in the weight of unknown sample with magnet on and off.} \)

\( W_{\text{unk.}} = \text{Weight of unknown.} \)

\( \Delta W_{\text{std.}} = \text{Change in the weight of standard with magnet on and off.} \)

\( W_{\text{std.}} = \text{Weight of the standard.} \)

\( \chi_{\text{std.}} = \text{Gram susceptibility of the standard} \)

\[ (5.92 \times 10^{-6} \text{ for CuSO}_4 \cdot 5\text{H}_2\text{O}) \]

**Faraday Method:**

The method consists in measuring the forces on a given specimen placed in a non homogeneous magnetic field. In this method only a few milligrams of the sample is required, and a high degree of accuracy was observed in the measurement of gram susceptibilities. The sample was so small that the force was constant throughout its volume. The force was measured by direct weighing of the substance which was suspended from one arm of a sensitive balance. The weight of the sample and standard Hg \([\text{CO(CNS)}_4]\) was determined with and without the field. The gram susceptibility was calculated
using the formula:

\[ \chi_g = K \frac{\Delta m}{m} \]

Where \( \Delta m/m \) is the actual pull, \( K = \text{constant} \), and its value is determined by the formula:

\[ K = \chi_g \frac{m}{\Delta m} \]

\( \chi_g \text{ for } \text{Hg}[\text{CO(CNS)}_4] = 16.44 \times 10^{-6} \)

\( m \) was corrected for the diamagnetism of the sample tube.

The molar susceptibility \( (\chi_M) \) of the compound was calculated from the gram susceptibility by multiplying it with the molecular weight of the compound. The value of \( \chi_M \) after correcting for diamagnetism of the ligands was substituted in the following formula, and effective magnetic moment \( (\mu_{\text{eff}}) \) was calculated.

\[ \mu_{\text{eff}} = 2.84 \times \chi'_M \times T \]

where \( \chi'_M = \text{corrected molar susceptibility} \).
EXPERIMENTAL

Preparation and Purification of Reagents:

2,5-dimercapto-1,3,4-thiadiazole (Bismuthiol I) (Koch-Light) m.p. 163°C was used after recrystallisation from ethanol. All metal salts: FeSO$_4$.7H$_2$O, FeCl$_3$.5H$_2$O, CoCl$_2$.5H$_2$O, NiCl$_2$.5H$_2$O, CuCl$_2$.2H$_2$O, ZnCl$_2$.nH$_2$O, AgNO$_3$, CdCl$_2$.5H$_2$O, Hg$_2$(NO$_3$)$_2$, HgCl$_2$, TlCl.H$_2$O (B.D.H. reagents) and RuCl$_3$.3H$_2$O, PdCl$_2$, IrCl$_3$, H$_2$PtCl$_6$ and HAtfCl$_4$ (All J. M. England reagents) were used as such. Ethanol and methanol were distilled over KOH while acetone and ether were used as such.

Preparation of Cuprous Chloride:

About 2.5 gram of cupric chloride (A.R. grade) was dissolved in about 15 ml. of conc. HCl. 3.0 grams of metallic copper (cleaned and dried) were then added and the solution was warmed, until the dark colour disappeared. The resulting solution was poured into a litre of cold water. The pouring was done through a funnel whose neck was loosely plugged with a little glass wool. The cuprous chloride at once separated out and after stirring well, was allowed to settle and was washed twice with water containing a little HCl.
The precipitated product was filtered off and washed with absolute alcohol and finally with ether to remove the last traces of alcohol. The cuprous chloride after final washing was dissolved in 50 ml. of saturated potassium chloride solution.

Preparation of the Complexes:

**Bis (2,5-dimercapto-1,3,4-thiadiazolato) Iron(II):** 50 ml. of 0.1 M ethanolic solutions of the ligand was added to a 25 ml. of 0.1 M aqueous acidified ferrous sulphate solution. This mixture was kept for two days after concentrating the solution to half its volume on a water bath. The yellow crystalline solid obtained was filtered, washed several times with water, alcohol and ether and was dried in vacuo for about eight hours.

**Tris (2,5-dimercapto-1,3,4-thiadiazolato) Iron(III):** 50 ml. of the alcoholic ligand (0.75 g.) solution was added slowly to an acidified alcoholic solution of the 25 ml. (0.70 g.) of ferric chloride. A yellow solid was obtained after keeping the mixture for two days. This solid was digested on a water bath, filtered and washed as above. It was dried in an oven at 60°C.
Bis (2,5-dimercapto-1,3,4-thiadiazolato) Cobalt(II): An alcoholic solution of the ligand was added to an alcoholic cobalt chloride solution in 1:2 metal to ligand ratio. A black solid was obtained after stirring the mixture for 36 hours. It was then isolated and dried in the manner described above.

Bis (2,5-dimercapto-1,3,4-thiadiazolato) Nickel(II): Alcoholic solutions of nickel chloride and the ligand were mixed in a 1:2 metal to ligand ratio. A brown solid was obtained after stirring the solution for 36 hours. It was filtered, washed and dried as usual.

(2,5-dimercapto-1,3,4-thiadiazolato) Copper(I): An alcoholic solution of the ligand (0.75 g. in 50 ml.) was added to an excess of the aqueous solution of cuprous chloride in potassium chloride solution. Immediate precipitation occurred on mixing the two solutions. The solid was digested on a water-bath for about half an hour. It was then filtered, washed several times with water and alcohol to remove any excess of metal, ligand or KCl. It was finally washed with ether and dried in vacuo.

Bis (2,5-dimercapto-1,3,4-thiadiazolato) Copper(II): To an
ethanolic solution of cupric chloride (0.43 g. in ml.), an ethanolic solution of the ligand (0.75 g. in 50 ml.) was added. Immediate precipitation occurred on mixing the two solutions. The solid was isolated and dried in the same manner described above.

Bis (2,5-dimercapto-1,3,4-thiadiazolato) Zinc(II) : An alcoholic solution of the ligand (0.75 g. in 50 ml.) was added to an aqueous solution of the zinc chloride (0.56 g. in 25 ml.). The solid thus obtained immediately was isolated and dried as usual.

(2,5-dimercapto-1,3,4-thiadiazolato) Ruthenium(I) : A black solid was obtained on mixing 0.1 M alcoholic ligand and ruthenium(III) chloride solutions in 1:3 metal to ligand ratio. The metal ion seemed to undergo reduction to ruthenium(I). The solid was isolated and dried in the usual manner.

Bis (2,5-dimercapto-1,3,4-thiadiazolato) Palladium(II) : To an aqueous solution of the palladium chloride, an alcoholic solution of the ligand (0.75 g. in 50 ml.) was added in a 1:2 metal to ligand ratio. The solid thus obtained immediately was digested on a water bath, filtered and washed with water,
alcohol and ether. It was dried in an oven at 60°C.

(2,5-dimercapto-1,3,4-thiadiazolato) Silver(I) : An aqueous solution of the silver nitrate was added to an alcoholic ligand solution (0.75 g. in 50 ml.) in a 1:1 metal to ligand ratio when immediate precipitation occurred. The solid thus obtained was isolated and dried as above.

Bis (2,5-dimercapto-1,3,4-thiadiazolato) Cadmium(II) : 50 ml. of alcoholic ligand solution (0.75 g.) was added to 25 ml. of an aqueous cadmium chloride solution (0.57 g.). Immediate precipitation occurred on mixing the two solutions. The solid obtained was digested on a water bath, filtered, washed as above and dried in vacuo.

Hexakis (2,5-dimercapto-1,3,4-thiadiazolato) Iridium(VI) : A grey solid was obtained when alcoholic solutions of the ligand (0.75 g. in 50 ml.) and iridium(III) chloride were mixed in a 1:3 metal to ligand ratio. The metal ion seemed to undergo oxidation to Ir(VI). The solid obtained after heating on water bath for about one hour, was isolated and dried in the manner of other complexes described above.

Tetrakis (2,5-dimercapto-1,3,4-thiadiazolato) Platinum(IV): Alcoholic solutions of chloroplatinic acid and the ligand
(0.75 g. in 50 ml.) were mixed in a 1:4 metal to ligand ratio. The solid thus obtained immediately was filtered, washed thoroughly in the manner of other complexes and was dried in vacuo.

(2,5-dimercapto-1,3,4-thiadiazolato) Gold(I) : An alcoholic solution of the ligand (0.75 g. in 50 ml.) was added to an alcoholic solution of chloroauric acid in a 1:3 metal to ligand ratio. The metal ion seemed to undergo reduction to gold(I). The solid thus obtained was isolated and dried in the same manner as described above.

Bis (2,5-dimercapto-1,3,4-thiadiazolato) Mercury(II) : An alcoholic solution of the ligand (0.75 g. in 50 ml.) was added to an aqueous acidified mercurous nitrate solution (0.66 g. in 25 ml.) or to an alcoholic mercuric chloride solution (0.68 g. in 25 ml.). Immediate precipitation occurred on mixing in each case. Both of these solids obtained were isolated in the usual manner and were dried in vacuo.

Tris (2,5-dimercapto-1,3,4-thiadiazolato) Thallium(III) : To the excess of an aqueous solution of thallous chloride, an alcoholic ligand solution (0.75 g. in 50 ml.) was added. The metal ion seemed to undergo oxidation to thallium(III).
The solid thus obtained was isolated and dried in usual manner.

All the solids isolated were found to be insoluble in usual organic solvents. Most of the compounds decomposed over 250°C.

**RESULTS AND DISCUSSION**

2,5-Dimercapto-1,3,4-thiadiazole (Bismuthiol I) has been found to form complexes with different metals in varying ratios. The results of analysis of the complexes are in good agreement with the suggested stoichiometries (Table 1). These complexes have the general formula: \( M(2,5\text{-dimercapto-1,3,4-thiadiazolato})_{1-6} \). All of them are coloured and are very stable at room temperature. They are found to be insoluble in usual organic solvents and appear to be polymeric in nature.

The nature of coordination of the ligand in the above complexes has been determined with the help of infrared spectral study and tentative assignments have been made for their structures on the basis of electronic spectral study.
### Table 1

Analytical data, colour and melting points of bismuthiol I and its complexes.

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<td>(Obs.)</td>
<td>(Obs.)</td>
<td>(Obs.)</td>
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<td>19.01</td>
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<td>(13.13)</td>
<td>(1.10)</td>
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<td>(15.00)</td>
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<td>(13.59)</td>
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<td>(13.31)</td>
<td>(0.67)</td>
<td>(15.89)</td>
<td>(53.60)</td>
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<td>11.29</td>
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<td>13.17</td>
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<td>(12.12)</td>
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<td>(13.49)</td>
<td>(1.00)</td>
<td>(16.31)</td>
<td>(53.67)</td>
</tr>
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<td>200d</td>
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<td>9.60</td>
<td>0.40</td>
<td>11.20</td>
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<td>(0.74)</td>
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<td>(46.50)</td>
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<td>10.90</td>
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<td>(10.00)</td>
<td>(0.40)</td>
<td>(10.90)</td>
<td>(38.14)</td>
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<td>11.69</td>
<td>0.50</td>
<td>13.65</td>
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<td>(47.16)</td>
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<td>10⁻⁶ b (cm² mol⁻¹)</td>
<td>10⁻⁶ μ (cm² mol⁻¹)</td>
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<td>Ir⁶⁺(C₂H₇N₂S₃)⁺</td>
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<td>(47.80)</td>
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<td>6.93</td>
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<td>8.10</td>
<td>27.74</td>
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<td>(7.00)</td>
<td>(0.50)</td>
<td>(8.60)</td>
<td>(27.17)</td>
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<td>Hg²⁺(C₂H₇N₂S₃)₂⁻</td>
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<td>250d</td>
<td>40.23</td>
<td>9.63</td>
<td>0.40</td>
<td>11.23</td>
<td>38.01</td>
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<td>(40.29)</td>
<td>(10.46)</td>
<td>(1.07)</td>
<td>(11.13)</td>
<td>(38.53)</td>
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<td>Tl³⁺(C₂H₇N₂S₃)₃⁻</td>
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<td>180</td>
<td>31.37</td>
<td>11.05</td>
<td>0.45</td>
<td>12.89</td>
<td>43.20</td>
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<td>(31.35)</td>
<td>(11.70)</td>
<td>(0.50)</td>
<td>(13.20)</td>
<td>(43.58)</td>
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and magnetic measurements. With a view to obtaining information on the metal ligand bonding which could be either through the sulphur or the nitrogen atom or both, the far-infrared spectra of the ligand and its complexes were recorded. The assignments of various modes of vibration have been made by analogy with the spectra of similar heterocyclic compounds particularly benzothiazoles. Only significant spectral changes which provide information regarding coordination and the identification of the donor site in the complexes have been discussed in detail.

Bismuthiol I has two isomeric structures, the thiol form I and the thiono form II having five possible coordination sites, two involving the nitrogen atoms and the remaining three involving sulphur atoms.

\[
\begin{align*}
\text{(I)} & : \quad \text{HN} \quad \text{NH} \\
\text{(II)} & : \quad \text{HS-C} \quad \text{C-SH} \\
\text{(III)} & : \quad \text{HS-C} \quad \text{C-S} \\
\end{align*}
\]

As mentioned earlier excepting for the u.v. spectral studies of Thorn no other mention of the structural study of bismuthiol I appears in chemical literature. The infrared spectrum of this ligand has been recently reported.
The i.r. spectrum of the ligand has a very weak band at 2490 cm\(^{-1}\) characteristic of S-H stretching vibration\(^{132}\) (Table 2). The medium bands at 2875 and 3060 cm\(^{-1}\) must be due to the N-H stretching mode as it occurs in this region\(^{105}\). Even though an alternative structure (III) could be proposed which would account for the presence of both N-H and S-H groups, it is ruled out in view of the fact that the S-H band is very weak as compared to N-H bands. It is, therefore, suggested that bismuthiol I like 3,5-dimercapto-1,2,4-thiadiazole exists predominantly in the thionoform\(^{150}\), but may be having a small quantity of the thiol form in equilibrium with it. Examples of this kind of tautomerism and preferential existence of the compounds in thionoform are perthiocyanic acid\(^{150,151}\) and 2-mercapto-benzothiazole\(^{38}\). Excepting for the complex formed by the interaction of Cu(II) chloride where the ligand is suggested to be completely deprotonated the absence of S-H stretching frequency and the presence of N-H and C=N bands in the i.r. spectra of all the complexes suggests that the complexed ligand is in the following form,

\[
\begin{align*}
\text{N} & \quad \text{NH} \\
\text{S} & \quad \text{C} \quad \text{C=\_S} \quad \text{\textendash} \quad \text{S} & \quad \text{C} \quad \text{N} \quad \text{NH}
\end{align*}
\]
TABLE 2

Characteristic frequencies in cm\(^{-1}\) of bismuthiol I and its complexes.

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<th>Compound</th>
<th>S-H</th>
<th>N-H</th>
<th>C=N</th>
<th>C=S</th>
<th>C-N</th>
<th>C-S</th>
<th>M-N</th>
<th>M-S</th>
</tr>
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<tr>
<td>C(<em>{2})H(</em>{2})N(<em>{2})S(</em>{3})</td>
<td>2490m</td>
<td>3060s</td>
<td>1460s</td>
<td>1120s</td>
<td>1265s</td>
<td>715s</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(^{2+}) (C(<em>{2})HN(</em>{2})S(<em>{3}))(</em>{2})</td>
<td>-</td>
<td>3175s</td>
<td>1449s</td>
<td>1099s</td>
<td>1266w</td>
<td>720s</td>
<td>-</td>
<td>320m</td>
</tr>
<tr>
<td>Fe(^{3+}) (C(<em>{2})HN(</em>{2})S(<em>{3}))(</em>{3})</td>
<td>-</td>
<td>3247s</td>
<td>1466s</td>
<td>1111s</td>
<td>1235s</td>
<td>719s</td>
<td>-</td>
<td>324m</td>
</tr>
<tr>
<td>Cd(^{2+}) (C(<em>{2})HN(</em>{2})S(<em>{3}))(</em>{2})</td>
<td>-</td>
<td>3150b</td>
<td>1470s</td>
<td>1104m</td>
<td>1240m</td>
<td>712m</td>
<td>-</td>
<td>338s</td>
</tr>
<tr>
<td>Ni(^{2+}) (C(<em>{2})HN(</em>{2})S(<em>{3}))(</em>{2})</td>
<td>-</td>
<td>3279w</td>
<td>1449w</td>
<td>1111w</td>
<td>1242w</td>
<td>714b</td>
<td>-</td>
<td>330s</td>
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<td>Cu(^{+}) (C(<em>{2})HN(</em>{2})S(_{3}))</td>
<td>-</td>
<td>3135b</td>
<td>1465s</td>
<td>1122s</td>
<td>1260s</td>
<td>725s</td>
<td>540s</td>
<td>-</td>
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<td>Cu(^{+}).Cu(^{2+}) (C(<em>{2})HN(</em>{2})S(<em>{3}))(</em>{2})</td>
<td>-</td>
<td>3160s</td>
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<td>720m</td>
<td>540s</td>
<td>380m</td>
</tr>
<tr>
<td>Cu(^{+}).Cu(^{2+}) (C(<em>{2})HN(</em>{2})S(<em>{3}))(</em>{2})</td>
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<td>1055m</td>
<td></td>
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<td>Zn(^{2+}) (C(<em>{2})HN(</em>{2})S(<em>{3}))(</em>{2})</td>
<td>-</td>
<td>3226b</td>
<td>1471s</td>
<td>1111m</td>
<td>1235s</td>
<td>712w</td>
<td>539s</td>
<td>337s</td>
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<tr>
<td>Ru(^{+}) (C(<em>{2})HN(</em>{2})S(_{3}))</td>
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<td>1109s</td>
<td>1259s</td>
<td>695w</td>
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<td>1453m</td>
<td>1109s</td>
<td>1282m</td>
<td>716b</td>
<td>-</td>
<td>335s</td>
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<td>Ag(^{+}) (C(<em>{2})HN(</em>{2})S(_{3}))</td>
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<td>Cd(^{2+}) (C(<em>{2})HN(</em>{2})S(_{3}))</td>
<td>-</td>
<td>3226s</td>
<td>1460s</td>
<td>1110m</td>
<td>1282s</td>
<td>729s</td>
<td>542s</td>
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Table continued on next page
Table continued.

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<tr>
<th>Compound</th>
<th>Intensity</th>
<th>Wave Length (nm)</th>
<th>Lifetime (µs)</th>
<th>Other Observations</th>
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<td>3049w</td>
<td>1481m</td>
<td>1099s</td>
<td>1250s, 711s, -</td>
</tr>
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<td></td>
<td>2874w</td>
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<td>1031s</td>
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<tr>
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<td>3125w</td>
<td>1456w</td>
<td>1105s</td>
<td>1255w, 719s, -</td>
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<td>2907m</td>
<td></td>
<td>1046s</td>
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<tr>
<td></td>
<td>3068s</td>
<td>1451m</td>
<td>1101s</td>
<td>1250s, 711s, 540m</td>
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<tr>
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<td>2841m</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3125m</td>
<td>1445s</td>
<td>1092s</td>
<td>1250s, 713s, 545s</td>
</tr>
<tr>
<td></td>
<td>2817b</td>
<td></td>
<td>1026s</td>
<td></td>
</tr>
<tr>
<td>Tl$^{3+}$($C_2H_2S_3$)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3226w</td>
<td>1456s</td>
<td>1111s</td>
<td>1268s, 704s, 545s</td>
</tr>
<tr>
<td></td>
<td>2941w</td>
<td></td>
<td>1053s</td>
<td></td>
</tr>
</tbody>
</table>

s=strong, m=medium, w=weak and b=broad.
in which each site could be potentially coordination active. The N-H stretching frequency in all the complexes as compared with that in the free ligand is positively shifted. This is presumably due to the fact that the extensively hydrogen bonded ligand molecules are disassociated when complexed with the metal ions.

**NATURE OF BONDING AND STRUCTURE OF THE COMPLEXES**

Bis (2,5-dimercapto-1,3,4-thiadiazolato) Iron(II) and Tris (2,5-dimercapto-1,3,4-thiadiazolato) Iron(III) :

I. R. Spectra: There is no significant change in the C=N stretching frequency of the ligand after complex formation. Also there is practically no change in the C-S stretching frequency which occurs at 715 cm\(^{-1}\) in the spectrum of the ligand. However, the strong bands at 1120 and 1055 cm\(^{-1}\) in the spectrum of the ligand assigned to C=S stretching vibration are negatively shifted in both the complexes suggesting coordination through the exocyclic sulphur atom.

Far I. R. Spectra: A comparison of the far i.r. spectra of the above complexes with that of the free ligand reveals
that there is a new medium intensity band at 320 and 324 cm\(^{-1}\) in the Fe(II) and Fe(III) complexes respectively. This band is tentatively assigned to M-S stretching frequency. There is, however, no band attributable to M-N frequency. It, therefore, further suggests the coordination to be occurring through the sulphur atom.

Electronic Spectra: In the electronic spectrum of the Fe(II) complex the bands at 23,170 and 26,670 cm\(^{-1}\) must be attributed to charge transfer. While only one band at around 10,000 cm\(^{-1}\) should be expected\(^{152}\) for the \(^{5}E\_g \rightarrow ^{5}T\_2g\) transition for an Fe(II) ion having an octahedral geometry, the two very weak bands observed at 11,000 and 10,300 cm\(^{-1}\) must be due to a splitting of \(^{5}E\_g\) level because of Jahn-Teller effect. The low magnetic moment (2.3 B.M.) of this compound is presumably due to the antiferromagnetic interactions in the polymeric complex. It is, therefore, suggested that Fe(II) is in an octahedral environment with ligand bridging through the sulphur atoms and metal-metal bonds. In the case of Fe(III) complex which has a 1:3 metal:ligand stoichiometry an intense band is observed at 23,170 cm\(^{-1}\) which must be a charge transfer band. Two other very weak bands at 11,200 and 10,600 cm\(^{-1}\) are also observed but could not be assigned. The very low magnetic moment value of this
complex is presumably due to the antiferromagnetic interac-
tions in the polymeric compound. An octahedral geometry
is proposed for this complex also.

Bis (2,5-dimercapto-1,3,4-thiadiazolato) Cobalt(II) and
Bis (2,5-dimercapto-1,3,4-thiadiazolato) Nickel(II) :

spectra of the above complexes with that of free ligand
reveals that there is a new strong band at 338 and 330 cm$^{-1}$
in the cobalt and nickel complexes respectively, tentatively
assigned to the M-S stretching frequency. There is, however,
no band attributable to M-N frequency. It is, therefore,
suggested that coordination in these cases occurs only
through the sulphur atom. The strong C=S bands at 1120 and
1055 cm$^{-1}$ in the spectrum of the ligand are also negatively
shifted in the complexes confirming sulphur coordination.

Electronic Spectra : The electronic spectra rule out an
octahedral geometry for both the complexes. In the spectrum
of cobalt complex, there is a strong charge transfer band
at 27,030 cm$^{-1}$. A number of other bands observed have,
however, not been assigned and no definite conclusion
regarding the geometry of this complex could be drawn from
the electronic spectrum. However, the $u_{\text{eff}}$ value of 2.7 B.M. indicates a square planar geometry. Complexes of Co(II) with square planar geometry are reported to have magnetic moments in the range 2.1-2.9 B.M.\textsuperscript{153}. It is well known that disulphur ligands yield square planar Co(II) complexes\textsuperscript{154}.

The electronic spectrum of the nickel complex has a strong charge transfer band at 28,570 cm\textsuperscript{-1}. The absence of any absorption band in the region 16,600-10,000 cm\textsuperscript{-1} rules out a tetrahedral geometry for nickel complex\textsuperscript{155} which is, therefore, suggested to have a square planar structure. The band at 15,950 cm\textsuperscript{-1} indicates a square planar environment for the Ni(II) ion for which a band is expected at 22,000-16,600 cm\textsuperscript{-1}\textsuperscript{156}. The paramagnetism in this complex with an observed $u_{\text{eff}}$ value of 1.4 B.M., however, suggests that its magnetic behaviour is 'anomalous' and presumably the complex has some nickel ions also present in an octahedral environment\textsuperscript{157}. The additional coordination being achieved either through the ring sulphur atom of the ligand above and below the square plane of the molecule. It is well established that the magnetic moment values between zero and 3.2 are observed in the solid state for square planar Ni(II) complexes also having some of the nickel ions in octahedral environment e.g., Ni(2,3-butylene diamine)\textsubscript{2}Cl\textsubscript{2}\textsuperscript{157}. The presence of some nickel ions in octahedral environment may not
unequivocally be shown by the help of the optical spectrum as even if such ions are in sufficient enough concentration to show up in the spectrum, out of the three bands expected the band due to $^3\pi_{1g}(P) \leftarrow ^3\Lambda_{2g}(F)$ transition may have merged with the charge transfer at 28,570 cm$^{-1}$ and the band due to $^3\Pi_{2g}(F) \leftarrow ^3\Lambda_{2g}(F)$ transition is out of the range of the instrument. The remaining band $^3\pi_{1g}(P) \leftarrow ^3\Lambda_{2g}(F)$ which could have been discerned in the spectrum may have contributed to the breadth of the observed band at 16,950 cm$^{-1}$.

The following possible square planar structure having ligand bridges is tentatively proposed for the cobalt and nickel complexes, the latter also having some octahedrally coordinated nickel ions through additional bonds.

where $M = \text{Co(II)}$ or $\text{Ni(II)}$
## TABLE 3

Electronic bands and magnetic moments of some of the bismuthiol I complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electronic bands in cm(^{-1})</th>
<th>Magnetic moment (\mu_{\text{eff}}) in B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe}^{2+} (\text{C}_2\text{HN}_2\text{S}_3)_2^-)</td>
<td>28,170 26,670 11,110</td>
<td>2.296</td>
</tr>
<tr>
<td>(\text{Fe}^{3+} (\text{C}_2\text{HN}_2\text{S}_3)_3^-)</td>
<td>28,170</td>
<td>1.261</td>
</tr>
<tr>
<td>(\text{Co}^{2+} (\text{C}_2\text{HN}_2\text{S}_3)_2^-)</td>
<td>27,030 18,180 16,000 14,290 12,820</td>
<td>2.736</td>
</tr>
<tr>
<td>(\text{Ni}^{2+} (\text{C}_2\text{HN}_2\text{S}_3)_2^-)</td>
<td>28,670 16,950</td>
<td>1.395</td>
</tr>
<tr>
<td>(\text{Cu}^+ (\text{C}_2\text{HN}_2\text{S}_3)_2^-)</td>
<td>23,260</td>
<td>1.070</td>
</tr>
<tr>
<td>(\text{Cu}^+ \cdot \text{Cu}^{2+} (\text{C}_2\text{HN}_2\text{S}_3)_3^-)</td>
<td>25,970</td>
<td>0.912</td>
</tr>
<tr>
<td>(\text{Ru}^{2+} (\text{C}_2\text{HN}_2\text{S}_3)_2^-)</td>
<td>25,320 18,870 12,740 11,760 10,870</td>
<td>0.750</td>
</tr>
<tr>
<td>(\text{Pd}^{2+} (\text{C}_2\text{HN}_2\text{S}_3)_2^-)</td>
<td>27,030 22,730</td>
<td>Dia.</td>
</tr>
<tr>
<td>(\text{Ir}^{6+} (\text{C}_2\text{HN}_2\text{S}_3)_6^-)</td>
<td>40,000 27,780 26,315 13,000</td>
<td>Dia.</td>
</tr>
<tr>
<td>(\text{Pt}^{4+} (\text{C}_2\text{HN}_2\text{S}_3)_4^-)</td>
<td>43,480 26,670 17,390</td>
<td>Dia.</td>
</tr>
</tbody>
</table>
(2,5-dimercapto-1,3,4-thiadiazolato) Copper(I) and Bis (2,5-dimercapto-1,3,4-thiadiazolato) Copper(II) :

I. R. and far I. R. Spectra : The strong band at 1460 cm\(^{-1}\) in the spectrum of the ligand attributed to C=N stretching vibration is shifted in both the complexes suggesting coordination through the nitrogen atom. The C=S stretching vibration has been assigned mainly on the basis of Mecke and Mecke's work on cyclic thioamides\(^{158}\), who suggested it to occur in 1200-1050 cm\(^{-1}\) region. The strong band at 1265 cm\(^{-1}\) in the spectrum of the ligand is assigned to C-N stretching vibration and is also shifted in the complexes.

A comparison of far infrared spectrum of the ligand with that of both the complexes reveals that an absorption band at 540 cm\(^{-1}\) appears in both the complexes but is absent in the ligand and must presumably be due to the Cu-N stretching vibration suggesting coordination through nitrogen atom in both the complexes. In the Cu(II) complex of bismuthiol I coordination through sulphur atom is also indicated by the appearance of a strong new band at 380 cm\(^{-1}\) which is absent in both, the ligand and in copper(I) complex. This band could reasonably be assigned to the Cu-S stretching mode as it is in this region that the M-S stretching vibration is known to appear\(^{32}\).
It is important to note that both the complexes analyse for a 1:1 metal to deprotonated ligand ratio. It is also significant that the copper(I) complex is yellow, while the copper(II) complex is yellowish brown in colour. The ligand has several donor sites involving sulphur and nitrogen atoms available for coordination and a consideration of the foregoing discussion of the i.r. and far i.r. spectra of the ligand and the complexes leads the author to conclude that in copper(I) complex the ligand must be coordinating only through the nitrogen atom in view of the absence of any copper sulphur band. The charge balance requires that there should be the loss of only one hydrogen consistent with the appearance of the N-H frequency. The copper(I) complex, therefore, must have the empirical formula \( \text{Cu}^+\left(\text{C}_2\text{HN}_2\text{S}_3\right)^- \). Its magnetic moment value of 1.07 B.M., however, suggests some conversion of Cu(I) to Cu(II). Such a conversion of Cu(I) to Cu(II) in a mercapto complex is shown by the reaction of Cu(I) with 8-mercapto-quinoline and has been ascribed to a greater stability of the Cu(II) complex.

In the case of Cu(II) complex the i.r. and far i.r. spectral evidence shows the presence of both the Cu-N and Cu-S bands. A consideration of the 1:1 metal to deprotonated ligand ratio and charge balance would have required
the formulation of this compound as $\text{Cu}^{2+}(C_2N_2S_3)^2^-$ in which the N-H band should have disappeared. However, the appearance of NH absorption band indicates some conversion of Cu(II) to Cu(I) as only Cu(I) may combine in a 1:1 ratio with $(C_2HN_2S_3)^-$ having N-H band. It is thus concluded that in the case of Cu(II) complex we are encountering either a mixture of 1:1 Cu(I) : $(C_2HN_2S_3)^-$ and 1:1 Cu(II) : $(C_2N_2S_3)^2^-$ or as we are tempted to suggest a mixed valence complex Cu(I). Cu(II).$(C_2HN_2S_3)^-\cdot(C_2N_2S_3)^2^-$. The magnetic moment value of 0.912 B.M., also seems to be consistent with this formula.

Electronic Spectra: There is an intense band at 25,975 cm$^{-1}$ attributable to charge transfer. There is no band at 12,000 cm$^{-1}$ ruling out the possibility of an octahedral geometry. However, since the reflectance spectrum could not be run below 10,000 cm$^{-1}$, it is not possible to comment on the geometry of this molecule which could be either tetrahedral or square planar.

Bis (2,5-dimercapto-1,3,4-thiadiazolato) Zinc(II),
Bis (2,5-dimercapto-1,3,4-thiadiazolato) Cadmium(II) and
Bis (2,5-dimercapto-1,3,4-thiadiazolato) Mercury(II).

I. R. Spectra: There is a negative shift in the C$\equiv$N
stretching vibration in all the above complexes (except for the zinc complex in which case, there is a positive shift) indicating coordination through the nitrogen atom. The strong C-N stretching band at 1265 cm\(^{-1}\) in the ligand is also shifted by 17 to 30 cm\(^{-1}\) in the complexes. Sulphur coordination is suggested by a lowering of the C=S stretching vibration frequency which occurs at 1111 and 1052 cm\(^{-1}\) in the zinc complex, at 1110 and 1033 cm\(^{-1}\) in the cadmium complex and at 1052 and 1026 cm\(^{-1}\) in the mercury complex.

Far I. R. Spectra: A comparison of the far i.r. spectra of the ligand and the above complexes reveals that a new band not present in the ligand appears at 539, 542 and 545 cm\(^{-1}\) for Zn(II), Cd(II) and Hg(II) complexes respectively. These must presumably be due to the M-N stretching vibration suggesting coordination through the nitrogen. A new strong band at 337, 330 and 332 cm\(^{-1}\) in zinc, cadmium and mercury complexes respectively is attributed to M-S stretching vibration and confirms sulphur coordination. All these complexes are diamagnetic.

In view of the above discussion we propose a polymeric tetrahedral structure for these complexes.
Tetrakis (2,5-dimercapto-1,3,4-thiadiazolato) Platinum(IV), Bis (2,5-dimercapto-1,3,4-thiadiazolato) Palladium(II), (2,5-dimercapto-1,3,4-thiadiazolato) Ruthenium(I) and Hexakis (2,5-dimercapto-1,3,4-thiadiazolato) Iridium(VI).

I. R. Spectra: There is no significant change in the C=N stretching frequency of the ligand after complex formation. The C=S stretching frequency of the ligand observed at 715 cm\(^{-1}\) is also practically unchanged. However, the C=S stretching frequencies of the ligand at 1120 and 1056 cm\(^{-1}\) are negatively shifted in all the above complexes. It is, therefore, proposed that in all these complexes the coordination occurs through the mercapto sulphur atoms at position 2 and 5 of the ring.

Far I. R. Spectra: A comparison of the far i.r. spectra of these complexes with that of the spectrum of the free ligand reveals that there is a new strong band at about 335 cm\(^{-1}\) in all the complexes tentatively assigned to M-S stretching frequency. There is, however, no band attributable to M-N frequency. It is, therefore, suggested that coordination occurs only through the sulphur atom.

Electronic Spectra: In the case of platinum(IV) complex
bands have been observed at 43,480, 28,670 and 17,390 cm\(^{-1}\) and these are assigned to \(^1\)\(T_{2g} \leftarrow \^1\)\(A_{1g}\), \(^1\)\(T_{1g} \leftarrow \^1\)\(A_{1g}\) and \(^3\)\(T_{1g} \leftarrow \^1\)\(A_{1g}\) (forbidden) respectively. The spin forbidden band for \(^3\)\(T_{2g} \leftarrow \^1\)\(A_{1g}\) is not observed, however, this suggests an octahedral geometry for the Pt(IV) complex. This is in accordance with the strong tendency of Pt(IV) to be hexacoordinated in its complexes. It is, therefore, suggested that this complex is a polymeric octahedral one where coordination occurs through the sulphur atoms with ligand bridging. This complex is diamagnetic in nature. The following structure is tentatively suggested for this complex.

\[ \text{where } L^- = (\text{C}_2\text{HN}_2\text{S}_3)^- \]

In the case of the palladium complex two strong bands observed at 27,030 and 22,730 cm\(^{-1}\) are similar to the two strong bands also observed in the case of nickel complex:
which was suggested to have a square planar structure. Pd(II) is known to prefer a square planar geometry and is, therefore, suggested to have such a polymeric ligand bridged structure. It has been found to be diamagnetic as expected.

In the iridium complex which has a 1:6 stoichiometry the ligand seems to be monodentate for an octahedral coordination of the metal ion. It has an intense absorption band at 26,315 cm\(^{-1}\) which should be a charge transfer band. However, very weak bands merging into the charge transfer and appearing as a hump are also visible at 40,000 and 27,780 cm\(^{-1}\) and may be assigned to \(4T_{1g}(F) \leftrightarrow 4A_{2g}(F)\) and \(4T_{1g}(F) \leftrightarrow 4A_{2g}(F)\) transitions in the \(O_h\) symmetry for d\(^3\) ion. A very weak band at 13,000 cm\(^{-1}\) is assignable to the \(4T_{2g}(F) \leftrightarrow 4A_{2g}(F)\) transition. The diamagnetism of this complex must be due to antiferromagnetic interactions.

In the ruthenium complex which has a 1:1 stoichiometry, bands are observed at 25,320, 18,870, 12,740, 11,760 and 10,870 cm\(^{-1}\). The band at 25,320 cm\(^{-1}\) is attributed to charge transfer. The other bands could not be assigned. The complex is feebly paramagnetic (\(\mu_{\text{eff}} = 0.75\ T\)) and suggests antiferromagnetic interactions through weak Ru-Ru bonds as has been noted in several Ru(I) diamagnetic complexes\(^{160,161}\).
(2,5-dimercapto-1,3,4-thiadiazolato) Silver(I),
(2,5-dimercapto-1,3,4-thiadiazolato) Gold(I) and
Tris (2,5-dimercapto-1,3,4-thiadiazolato) Thallium(III).

I. R. Spectra: There is a negative shift in the C=N
stretching vibrations in all the above complexes indicating
coordination to be occurring through the nitrogen atom. The
strong C-N stretching band at 1265 cm\(^{-1}\) in the spectrum of
the ligand is also shifted by up to 15 cm\(^{-1}\) in the complexes.
Sulphur coordination is indicated by a lowering of the C=S
stretching vibration frequency in the complexes.

Far I. R. Spectra: A comparison of the far i.r. spectra
of the complexes with that of the free ligand reveals that
a new band appears at 532, 540 and 545 cm\(^{-1}\) in Ag(I), Au(I)
and Tl(III) complexes respectively. These bands must
presumably be due to the M-N stretching vibration. The
M-N bands in the case of copper complexes also have been
reported in this region. A new strong band at 330, 335 and
340 cm\(^{-1}\) in silver, gold and thallium complexes respectively
is attributed to M-S stretching vibration. All these complexes
are diamagnetic. Since the ligand is bidentate and has
sulphur as one of the donor sites, it seems more likely
that silver should have a coordination number three or
four and the complex be polymeric in nature. It is well known that Ag(I) forms polymeric and polynuclear complexes with such ligands. The gold and thallium complexes also seem to be polymeric in nature. An octahedral geometry is tentatively suggested for the thallium complex.
CHAPTER IV

COMPLEXES OF 2-AMINOTHIAZOLE
INTRODUCTION

Thiazole is a five membered heterocyclic ring system and is formally derived from imidazole by replacement of the NH group by sulphur atom at position 1, which makes thiazole a better π-accepter due to the availability of empty d-orbitals on sulphur atom.

\[
\begin{align*}
\text{(Imidazole)} & \quad \text{(Thiazole)} \\
HC & \quad HC \\
\| & \quad \| \\
HC & \quad NC \\
\| & \quad \| \\
N & \quad CH \\
H & \quad S
\end{align*}
\]

2-aminothiazole is a derivative of thiazole in which the hydrogen atom attached to the carbon atom on position 2 is substituted by amino group.

2-aminothiazole exists in the form of a brown powder having a melting point of 91°C. It was synthesized by Natradze in 1947 by condensation of chlorinated vinyl acetate with thiourea\textsuperscript{163}, the chlorination being carried out without any solvent by adding to the vinyl acetate a small quantity of pyridine or pyridine bases. It was also
It is fairly soluble in alcohol and hot water. Ultraviolet and n.m.r. spectral studies have been made on this compound indicating that 2-aminothiazole is protonated almost completely even in acetic acid. N.M.R. studies have shown that 2-aminothiazole reacts with its hydrochloride to yield a dimer.

It was considered that this compound might have some tuberculostatic effect and was tested for this activity but it was found that it has little or no effect on the growth of the bacterium. It has also been used as a nicotine antagonist.

The complexing ability of 2-aminothiazole has not been exploited much but recently Duff and coworkers have prepared the complexes of cobalt, nickel and copper in varying metal-ligand ratios. Recently Singh and coworker have also reported the formation of cobalt complexes of 2-aminothiazole. It is significant that while the former authors have reported the formation of two complexes of cobalt with 2-aminothiazole, one having a 1:2 stoichiometry and a tetrahedral structure and the other having a 1:4 stoichiometry and an octahedral structure, the latter authors have reported only a 1:2 complex with cobalt chloride having a tetrahedral structure. Duff et al found
an increase in industry and a shift to lower frequencies of the -NH bands in the cobalt complexes. They suggested that this phenomenon may have resulted from the coordination of the amino group, but it might also be due to electronic effects resulting from ring nitrogen coordination. They deduced ring nitrogen coordination for 2-aminothiazole. They also obtained two complexes of 2-aminothiazole with nickel, one having 1:4 and the other a 1:1 stoichiometry. The 1:1 complex was obtained on heating the 1:4 complex at 200°C under vacuum for one hour. These workers also obtained two complexes with CuCl₂ one having a 1:2 and the other a 1:4 stoichiometry and proposed an octahedral structure for both.

In all these complexes coordination has been suggested by Duff et al to occur through the ring nitrogen. Singh and coworker have, on the other hand, argued in favour of coordination occurring through the amino nitrogen in the case of the 1:2 cobalt complex that they obtained, by emphasizing that the lone pair of electrons available on the amino nitrogen is more exposed in comparison to that on the ring nitrogen which is sterically hindered. In no case has sulphur coordination been found to occur.

In view of the fact that the coordinating ability of 2-aminothiazole has not been fully exploited, and that not much is known about the structure of its complexes, it
was considered worth-while to prepare and characterize some new complexes of 2-aminothiazole with VO(IV), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(I), Hg(II), Ag(I), Au(III), Ru(III), Pd(II), Ir(III) and Pt(IV).

**EXPERIMENTAL**

**Preparation and Purification of Reagents:**

2-aminothiazole (E. Merck) m.p. 91°C was used without further purification. All the metal salts viz., VO\(_4\)\(\cdot\)nH\(_2\)O, CoCl\(_2\)•5H\(_2\)O, NiCl\(_2\)•5H\(_2\)O, CuCl\(_2\)•2H\(_2\)O, ZnCl\(_2\)•nH\(_2\)O, AgNO\(_3\), CdCl\(_2\)•5H\(_2\)O, H\(_2\)AuCl\(_4\), Hg\(_2\)(NO\(_3\))\(_2\), HgCl\(_2\)(B.D.H. reagents) and RuCl\(_3\)•3H\(_2\)O, PdCl\(_2\), IrCl\(_3\)•3H\(_2\)O and H\(_2\)PtCl\(_6\)(J.M. England reagents) were used as such.

**Preparation of the Complexes:**

Sulphato (2-aminothiazole) Oxovanadium(IV): An ethanolic solution of the ligand (1 g. in 25 ml.) was added to an aqueous solution of vanadyl sulphate (1.8 g. in 25 ml.). Immediate precipitation occurred on mixing the two solutions. The solid thus obtained was digested on a water bath for half an hour and then filtered and washed with water, alcohol
and ether. It was dried in vacuo.

Dichlorotetrakis (2-aminothiazole) Cobalt(II) : Ethanolic solutions of the ligand (1 g. in 25 ml.) and cobalt chloride (1.2 g. in 25 ml.) were stirred together for 12 hours when a solid appeared. This solid was filtered and washed with alcohol and ether. It was dried in vacuo.

Dichlorotetrakis (2-aminothiazole) Nickel(II) : This complex was prepared and isolated in the manner of cobalt complex described above.

Dichloro (2-aminothiazole) Copper(II) : A green coloured solid was obtained upon mixing the ethanolic solutions of the ligand (1 g. in 25 ml.) and copper(II) chloride (1.7 g. in 25 ml.). The solid thus obtained was digested on a water bath and isolated in the above described manner.

Nitrate (2-aminothiazole) Silver(I) : An ethanolic solution of the ligand (1 g. in 25 ml.) was added to an aqueous solution of silver nitrate (1.7 g. in 25 ml.). The solid which was obtained almost immediately was digested on a water bath and isolated in the manner of the vanadium complex described above.
Trichlorotetrakis (2-aminothiazole) Gold(III): An ethanolic solution of the ligand (1 g. in 25 ml.) was added to an ethanolic solution of the chloroauric acid (0.85 g. in 25 ml.). The appearance of a solid was noted immediately on mixing the two solutions. The solid obtained was purified and isolated in the usual manner.

Dichlorobis (2-aminothiazole) Zinc(II): Upon addition of an alcoholic solution of the ligand (1 g. in 25 ml.) to an aqueous solution of the hydrated zinc chloride (2.3 g. in 25 ml.) and mixing the two together, precipitation occurred. The solid obtained was isolated in the usual manner.

Dichloro (2-aminothiazole) Cadmium(II): A cream coloured solid was obtained upon mixing ethanolic solutions of the ligand (1 g. in 25 ml.) and cadmium chloride (2.2 g. in 25 ml.). The solid was isolated by washing with alcohol and ether and drying in vacuo.

Nitrato (2-aminothiazole) Mercury(I): An aqueous solution of mercurous nitrate (2.6 g. in 25 ml.) to which a few drops of nitric acid was added to get a clear solution was mixed with an alcoholic solution of the ligand (1 g. in 25 ml.).
This yielded a solid which was purified and isolated by washing it with water, alcohol and ether and drying in vacuo.

Dichloro (2-aminothiazole) Mercury(II) : Ethanolic solutions of the ligand (1 g. in 25 ml.) and mercuric chloride (1.4 g. in 25 ml.) were mixed together when an immediate precipitation occurred. The solid was isolated in the manner of the cadmium complex described above.

Trichlorotris (2-aminothiazole) Ruthenium(III) : A black solid was obtained upon mixing the ethanolic solutions of the ligand (1 g. in 25 ml.) and ruthenium chloride (0.7 g. in 25 ml.) in the 1:3 metal to ligand ratio. The solid obtained was digested on a water bath and isolated in the usual manner.

Dichlorotetrakis (2-aminothiazole) Palladium(II) : An ethanolic solution of the ligand (1 g. in 25 ml.) was added to an aqueous solution of palladium chloride (0.9 g. in 25 ml.). The appearance of a solid was noted immediately. This solid was isolated by washing with water, alcohol and ether. It was dried in vacuo.
Trichloro (2-aminothiazole) Iridium(III): To an ethanolic solution of the ligand (1 g. in 25 ml.) was added to an ethanolic solution of iridium chloride (1 g. 25 ml.). This yielded a solid which was isolated and purified in the usual manner.

Tetrachlorotrietyl (2-aminothiazole) Platinum(IV): Upon mixing together the ethanolic solutions of the ligand (1 g. in 25 ml.) and chloroplatinic acid (0.85 g. in 25 ml.), precipitation occurred. The solid obtained was digested on water bath, filtered and washed with alcohol and ether. It was finally dried in vacuo.

None of the complexes dissolve in usual organic solvents and most of them did not show a sharp melting point but decomposed above 200°C.

RESULTS AND DISCUSSION

2-Aminothiazole has been found to form complexes with different metals in varying ratios. The results of analysis of the complexes, are in good agreement with the suggested stoichiometries (Table 4). These complexes have
### TABLE 4

Analytical data, colour and melting points of 2-aminothiazole and its complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M.P.</th>
<th>%M</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%S</th>
<th>%Cl</th>
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<td>C(<em>{4})H(</em>{4})N(_{4})S</td>
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<td>4.00</td>
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<td>200d</td>
<td>19.38</td>
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<td>12.16</td>
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<td>11.13</td>
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<td>(2.95)</td>
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<td>27.17</td>
<td>3.02</td>
<td>21.15</td>
<td>24.15</td>
<td>30.87</td>
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<td>27.08</td>
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<td>12.16</td>
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<td>(13.36)</td>
<td>(1.25)</td>
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<td>(12.10)</td>
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<td>28.00</td>
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<td>310d</td>
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<td>215d</td>
<td>55.17</td>
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<td>1.10</td>
<td>11.55</td>
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<td>(9.73)</td>
<td>(1.74)</td>
<td>(11.33)</td>
<td>(8.50)</td>
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<td>7.53</td>
<td>8.60</td>
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<td>(0.70)</td>
<td>(7.32)</td>
<td>(9.10)</td>
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<td>300d</td>
<td>19.90</td>
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<td>16.55</td>
<td>18.92</td>
<td>20.93</td>
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<td>(19.87)</td>
<td>(20.93)</td>
<td>(3.15)</td>
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<td>(19.10)</td>
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<td>270d</td>
<td>18.43</td>
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<td>22.17</td>
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<td>(18.50)</td>
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<td>2.02</td>
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<td>(38.54)</td>
<td>(13.87)</td>
<td>(2.26)</td>
<td>(10.90)</td>
<td>(13.05)</td>
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<td>Brown</td>
<td>250d</td>
<td>36.31</td>
<td>16.95</td>
<td>1.88</td>
<td>13.19</td>
<td>15.08</td>
<td>26.44</td>
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<td></td>
<td></td>
<td>(36.46)</td>
<td>(17.12)</td>
<td>(2.20)</td>
<td>(13.20)</td>
<td>(15.20)</td>
</tr>
</tbody>
</table>
the general formula \( M(2\text{-}\text{aminothiazole})_{1-4}X_2 \) (where \( M \) stands for metal ions and \( X = \text{Cl}^-, \text{NO}_3^- \text{ or } 1/2 \text{SO}_4^- \)). All the complexes are coloured, stable at room temperature and insoluble in usual organic solvents.

The nature of coordination of the ligand in the above complexes has been determined and a tentative assignments have been made for their structures on the basis of infrared spectral studies. With a view to obtaining information on the metal ligand bonding which could be either through the sulphur or the nitrogen atom or both, far infrared spectra were also recorded. The assignments of various modes of vibration have been made by analogy with the spectra of similar heterocyclic compounds particularly of thiazoles\(^{170,171} \). Only significant spectral changes which provide information regarding coordination and the identification of the donor site in the complexes have been discussed in some detail.

The i.r. spectrum of the solid ligand in KBr shows two bands at 3460 and 3360 cm\(^{-1} \) which must be due to the asymmetric and symmetric N-H stretching frequencies respectively. The spectrum of 2-aminothiazole in KBr recorded in this work does not show a marked difference in the N-H stretching vibration observed in chloroform\(^{172} \) (Table 5). This shows that the ligand is not in an associated form.
**TABLE 5**

Characteristic frequencies in cm⁻¹ of 2-aminothiazole and its complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>N-H Symm</th>
<th>N-H Asymm</th>
<th>C=N</th>
<th>C-N</th>
<th>C-S</th>
<th>M-N</th>
<th>M-X</th>
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<td>C₃H₄N₂S</td>
<td>3460s</td>
<td>3360w</td>
<td>1440m</td>
<td>1330w</td>
<td>675s</td>
<td>-</td>
<td>-</td>
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<tr>
<td>VO(C₃H₄N₂S)SO₄</td>
<td>3390b</td>
<td>3125b</td>
<td>1481w</td>
<td>1351w</td>
<td>694w</td>
<td>390m</td>
<td>-</td>
</tr>
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<td>3145w</td>
<td>1418w</td>
<td>1333w</td>
<td>704b</td>
<td>390s</td>
<td>357m</td>
</tr>
<tr>
<td>Ni(C₃H₄N₂S)₂Cl₂</td>
<td>3509m</td>
<td>3030m</td>
<td>1418w</td>
<td>1316w</td>
<td>717b</td>
<td>392s</td>
<td>360w</td>
</tr>
<tr>
<td>Cu(C₃H₄N₂S)Cl₂</td>
<td>3480b</td>
<td>3270b</td>
<td>1415m</td>
<td>1330w</td>
<td>692m</td>
<td>385s</td>
<td>365s</td>
</tr>
<tr>
<td>Ag(C₃H₄N₂S)NO₃</td>
<td>3509w</td>
<td>3205w</td>
<td>1429w</td>
<td>1321w</td>
<td>690w</td>
<td>390s</td>
<td>-</td>
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<tr>
<td>Au(C₃H₄N₂S)₂Cl₃</td>
<td>3390b</td>
<td>3200b</td>
<td>1420m</td>
<td>1315w</td>
<td>650w</td>
<td>392s</td>
<td>360m</td>
</tr>
<tr>
<td>Zn(C₃H₄N₂S)₂Cl₂</td>
<td>3509s</td>
<td>3289s</td>
<td>1431w</td>
<td>1331s</td>
<td>694s</td>
<td>390m</td>
<td>360b</td>
</tr>
<tr>
<td>Cd(C₃H₄N₂S)Cl₂</td>
<td>3460s</td>
<td>3360s</td>
<td>1440m</td>
<td>1315s</td>
<td>710w</td>
<td>385s</td>
<td>362s</td>
</tr>
<tr>
<td>Hg(C₃H₄N₂S)NO₃</td>
<td>3460m</td>
<td>3030w</td>
<td>1408w</td>
<td>1307m</td>
<td>694w</td>
<td>397w</td>
<td>-</td>
</tr>
<tr>
<td>Hg(C₃H₄N₂S)Cl₂</td>
<td>3400s</td>
<td>3220s</td>
<td>1492m</td>
<td>1380s</td>
<td>707w</td>
<td>378s</td>
<td>352s</td>
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<tr>
<td>Ru(C₃H₄N₂S)₃Cl₃</td>
<td>3420w</td>
<td>3260b</td>
<td>1505m</td>
<td>1415m</td>
<td>680w</td>
<td>392s</td>
<td>360s</td>
</tr>
<tr>
<td>Pd(C₃H₄N₂S)₂Cl₂</td>
<td>3390w</td>
<td>3290s</td>
<td>1440w</td>
<td>1315m</td>
<td>700s</td>
<td>392s</td>
<td>360s</td>
</tr>
<tr>
<td>Ir(C₃H₄N₂S)₂Cl₃</td>
<td>3330b</td>
<td>3200b</td>
<td>1505m</td>
<td>1360w</td>
<td>700w</td>
<td>390s</td>
<td>353s</td>
</tr>
<tr>
<td>Pt(C₃H₄N₂S)₃Cl₄</td>
<td>3400w</td>
<td>3310m</td>
<td>1500s</td>
<td>1365m</td>
<td>700w</td>
<td>385s</td>
<td>370b</td>
</tr>
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</table>

s=strong, m=medium, w=weak, b=broad and X=Cl¹
A few complexes of thiazoles and 2-substituted thiazoles having the amino and bromo group in the 2 position have been prepared and studied by some workers. In addition to these compounds they have also examined the complexes of 2-amino, 2-chloro and 2-methylbenzothiazole with several metals. In all the cases the authors have found either the ring or the amino nitrogen (in case of amino derivatives) to coordinate with the metal ions. In no case has the ring sulphur atom been reported to coordinate. It appears that the basisity of the nitrogen atom is much greater than that of the sulphur atom. It was the aim of this work to examine if in some cases sulphur coordination also occurred.

Upon coordination through either the ring sulphur or the ring nitrogen atom, the C=S stretching frequency should increase. It should, however, decrease on coordination through the amino nitrogen atom. In the case of sulphur coordination the C=N stretching frequency should remain almost unaltered or increase slightly. This frequency should, however, decrease in the case of nitrogen coordination. Coordination in various complexes has been proposed by a close examination of the C=N and C=S bands and the far i.r. spectra of these complexes.

The infrared spectra of the complexed 2-aminothiazole
show a number of differences from that of the free ligand, principally in the regions associated with $\text{NH}_2$ group. There is a shift, to lower frequencies of the N-H bands in the complexes. This phenomenon may have resulted from the coordination of the amino group, but could also be due to electronic effects resulting from ring nitrogen coordination as has been suggested by Duff.\textsuperscript{170}

There is a negative shift in the C=N stretching vibration frequency of the ligand in all the complexes (excepting in those of vanadium, mercury, ruthenium, iridium and platinum) suggesting coordination to be occurring through the ring nitrogen atom of 2-aminothiazole.

The positive shift in the C=N stretching frequency observed in the case of vanadium, mercury, ruthenium, iridium and platinum complexes would suggest sulphur coordination. However, in these complexes, there is also a positive shift in the exocyclic C-N stretching frequency suggesting the coordination to be occurring through the amino nitrogen. Thus although it can not be said unequivocally on the basis of the present evidences whether coordination in these complexes is occurring through the sulphur atom it would appear in view of the known behaviour of such ligands described earlier (page 85) that coordination is more likely
occurring through the amino nitrogen atom in the above mentioned complexes and hence it is tentatively suggested that the amino nitrogen is coordinated to the metal ions in these complexes. The possibility of the bidentate coordinate of the ligand through both the nitrogen and sulphur atoms has been excluded in view of the requirements of the stieichiometry and stereochemistry of these complexes.

This seems reasonable as after coordination the polarization of the $\tilde{n}$-electrons from the aminothiazole ring towards nitrogen of the amino group would increase the double bond character of $\text{N-H}$ in $\text{C-NH}_2$ group giving a positive shift.

A comparison of the far infrared spectra of the complexes of 2-aminothiazole with that of the free ligand reveals that there is a new strong band at about 390 cm$^{-1}$ in all these complexes. It is tentatively assigned to the $\text{M-N}$ stretching frequency. Another medium intensity band not present in the free ligand is also observed at about 360 cm$^{-1}$ in all the chloro complexes and is tentatively assigned to the $\text{M-Cl}$ stretching vibrations.
PROPOSED STRUCTURE FOR THE COMPLEXES

The complexes of 2-aminothiazole have been obtained with different metals in various stoichiometry and their structures are discussed below:

The oxovanadium complex has a 1:1 metal-ligand stoichiometry. The i.r. spectrum of this complex shows a strong band at 961 cm\(^{-1}\). All oxovanadium(IV) compounds are expected to have i.r. bands in the region 900-1100 cm\(^{-1}\) [173]. The bands at 1150 and 1105 cm\(^{-1}\) are ascribed to a bidentate bridging sulphato group. The simplest structure for this complex should then be a dimeric square planar one with SO\(_4\)\(^{2-}\) bridges having terminal oxygen and aminothiazole as shown below:

\[
\begin{array}{c}
\text{V} \quad \text{SO}_4 \quad \text{V} \\
\text{L} \quad \text{SO}_4 \quad \text{L}
\end{array}
\]

\(L = 2\text{-Aminothiazole}\)
The complexes of cobalt and nickel both having 1:4 stoichiometries appear to have an octahedral structure. Both these complexes have also been studied by Duff and coworkers\textsuperscript{170}. They have suggested an octahedral geometry for these complexes on the basis of magnetic measurements and electronic spectral studies. As during the course of this work Duff et al published their work on these complexes, only their synthesis and i.r. spectra are reported here.

A dimeric square planar structure with chloride bridges and terminal chlorides and ligand is proposed for the 1:1 copper(II) complex.

\[
\text{L} \quad \text{Cl} \quad \text{Cu} \quad \text{Cl} \\
\text{Cl} \quad \text{Cu} \quad \text{Cl} \quad \text{L}
\]

The silver nitrate complex shows a band at 1376 cm\textsuperscript{-1} which is ascribable to the nitrate group. Unsplit nitrate band at 1376 cm\textsuperscript{-1} indicates a monodentate nitrate coordination. Thus this complex is proposed to have linear geometry.

The gold chloride complex has a 1:4 stoichiometry, and seems to have an octahedral geometry having one chloride ion outside the coordination sphere. This fact could not be
verified by conductance measurements owing to the insolubility of this compound in usual organic solvents.

The zinc complex, having a 1:2 stoichiometry, apparently has a tetrahedral structure.

The 1:1 complexes obtained with Cd(II) and Hg(II) have the general formula \( M(L)X_2 \). Both of these complexes seem to have a tetrahedral geometry. The 1:1 Hg(I) complex shows an intense band at 1376 \( \text{cm}^{-1} \) tentatively assigned to monocoordinated nitrato group. A linear geometry is therefore proposed for this complex.

An octahedral geometry is proposed for the 1:3 ruthenium complex.

In the case of the palladium complex the Pd(II) ion seems to be in an octahedral environment. Although no direct evidence in its favour could be obtained, it is tentatively suggested that the two chlorine atoms should be in transposition to each other.

The iridium complex has a 1:2 metal to ligand ratio. An octahedral geometry with chlorine bridges is proposed for this complex.

The 1:3 Pt(IV) complex appears to have an octahedral
structure which is the preferred geometry for the Pt(IV) ion. It must have one chloride ion outside the coordination sphere, the remaining three being coordinated to the metal atom. The ionic nature of this complex could not be confirmed by conductivity studies as the complex was insoluble in usual organic solvents. The following structure is tentatively proposed for this complex.

\[
\begin{array}{c}
\text{L} \\
\text{L} \quad \text{Cl} \\
\text{Pt} \\
\text{Cl} \quad \text{Cl} \\
\text{L} \\
\end{array}
\]

Concluding Paragraph:

It could not be possible to get the diffuse reflectance spectra of the cobalt, nickel, copper, ruthenium, palladium, iridium and platinum complexes which may provide more structural evidences and that further work is necessary to completely unravel the structures of these compounds. All the suggestions are only tentative based on the evidences collected from the experimental facilities available to this author.
CHAPTER V

COMPLEXES OF 2-AMINO-6-ETHOXYBENZOTHIAZOLE
INTRODUCTION

2-amino-6-ethoxybenzothiazole is a derivative of benzothiazole in which the hydrogen atoms attached to the carbon atoms at position 2 and 6, are substituted by amino and ethoxy groups respectively. It exists in brown crystalline form having a melting point of 161°C. It was synthesized by Mdzhoyan and coworkers in 1967 by the hydrogenation of p-alkoxy-nitrobenzene over Ni-Cr$_2$O$_3$ when p-alkoxy aniline was obtained. This compound was treated with KSCN and bromine to yield 2-amino-6-ethoxybenzothiazole. It is fairly soluble in alcohol and hot water.

Benzothiazole derivatives have been investigated for antiviral activity against various influenza A$_2$ strains in mice and it has been noted that 2-aminobenzothiazole had a better effect compared to other benzothiazole derivatives. However, significant antiviral effect could not be demonstrated for any compound in vitro. It was also tested for tuberculostatic activity. Several benzothiazole derivatives were synthesized with the help of this compound. 2-Aminobenzothiazoles are used in the manufacture of papers for legal documents to prevent forgery through ink eradicators which cause the formation of bright colours on the paper.
The complexing tendency of benzothiazole and 2-aminobenzothiazole has been determined by Duff and coworkers\(^{70,179}\). They suggested that the ligand is N-bonded. In case of 2-aminobenzothiazole, it was suggested that the coordination in few cases may be through the amino-nitrogen. Recently Dash and coworkers\(^{180}\) have also reported a few complexes of benzothiazoles and 2-aminobenzothiazoles and have suggested that in 2-aminobenzothiazole complexes the amino group is not involved in coordination.

2-Amino-6-ethoxybenzothiazole has an additional coordination site and offers itself as an interesting ligand for the formation of complexes. Several complexes of this ligand with transition metals have, therefore, been prepared and studied.

**EXPERIMENTAL**

Preparation and Purification of the Reagents:

2-Amino-6-ethoxybenzothiazole was used after recrystallization from ethanol (m.p. 161\(^{\circ}\)C) and all the metal salts viz., \(\text{VOSO}_4\cdot\text{nH}_2\text{O}\), \(\text{CuCl}_2\cdot\text{2H}_2\text{O}\), \(\text{AgNO}_3\), \(\text{HAuCl}_4\), \(\text{ZnCl}_2\cdot\text{nH}_2\text{O}\), \(\text{CdCl}_2\cdot\text{5H}_2\text{O}\), \(\text{Hg}_2(\text{NO}_3)_2\), \(\text{HgCl}_2\) (B.D.H. reagents)
and RuCl₃·3H₂O, PdCl₂, IrCl₃·3H₂O and H₂PtCl₆ (J.M. England reagents) were used as such.

Preparation of the Complexes:

The complexes were prepared by mixing together in appropriate ratios the alcoholic solution of the ligand and an aqueous or alcoholic solution of the metal salt. All the complexes when formed were digested in a water bath, filtered and washed with water, alcohol and ether. They were dried in an oven at 60°C for a few hours and were kept in an evacuated desiccator.

Sulphato (2-amino-6-ethoxybenzothiazole) Oxovanadium(IV): An alcoholic solution of the ligand (0.97 g. in 25 ml.) was added to an aqueous solution of vanadyl sulphate (0.45 g. in 25 ml.). Immediate precipitation occurred on mixing the two solutions together. The solid was finally isolated and dried as above.

Dichlorobis (2-amino-6-ethoxybenzothiazole) Copper(II): A green coloured solid obtained upon mixing the ethanolic solutions of the ligand (0.97 g. in 25 ml.) and cupric chloride (0.43 g. in 25 ml.). The solid was isolated and dried.
Nitrato-bis (2-amino-6-ethoxybenzothiazole) Silver(I) :
To an aqueous silver nitrate (0.43 g. in 25 ml.), an
ethanolic solution of the ligand (0.97 g. in 25 ml.) was
added when the precipitation occurred. The solid obtained
was isolated and dried in vacuo.

Trichlorotris (2-amino-6-ethoxybenzothiazole) Gold(III) :
Ethanolic solutions of the ligand (0.97 g. in 25 ml.) and
chloroauroic acid (0.85 g. in 25 ml.) were mixed together
to yield a precipitate. This solid was isolated and dried
in vacuo.

Dichlorobis (2-amino-6-ethoxybenzothiazole) Zinc(II) :
An ethanolic solution of the ligand (0.97 g. in 25 ml.)
was added to an aqueous solution of hydrated zinc chloride
in 1:2 metal to ligand ratio. The solid obtained was
isolated and dried in vacuo.

Dichlorobis (2-amino-6-ethoxybenzothiazole) Cadmium(II) :
Upon mixing the ethanolic solutions of the ligand (0.97 g.
in 25 ml.) and cadmium chloride (0.58 g. in 25 ml.) precip­
itation occurred immediately. This compound was isolated
and dried as usual.

Nitrato-bis (2-amino-6-ethoxybenzothiazole) Mercury(I) :
To
an aqueous solution of the mercurous nitrate (1.31 g. in 25 ml.), to which a few drops of nitric acid was added to get a clear solution, an ethanolic solution of the ligand (0.97 g. in 25 ml.) was added when precipitation occurred. This solid was isolated and dried as usual.

Dichlorobis (2-amino-6-ethoxybenzothiazole) Mercury(II) :
This complex was prepared by mixing the ethanolic solutions of ligand and mercuric chloride in 1:2 metal to ligand ratio and was isolated and dried as above.

Trichlorotris (2-amino-6-ethoxybenzothiazole) Ruthenium(III) :
A black coloured solid was obtained upon mixing the ethanolic solutions of the ligand (0.97 g. in 25 ml.) and ruthenium chloride (0.99 in 25 ml.). This solid was isolated and dried.

Dichloro (2-amino-6-ethoxybenzothiazole) Palladium(II) :
An ethanolic solution of the ligand (0.97 g. in 25 ml.) was added to an aqueous palladium chloride (0.8 g. in 25 ml.) solution. Appearance of a solid was noted immediately which was isolated and finally dried as usual.

Trichloro (2-amino-6-ethoxybenzothiazole) Iridium(III) :
Ethanolic solutions of the ligand (0.97 g. in 25 ml.) and
iridium chloride (0.8 g. in 25 ml.) were mixed together when the solid was obtained. The solid obtained was isolated and dried.

Tetrachlorobis (2-amino-6-ethoxybenzothiazole) Platinum(IV) : An ethanolic solution of the ligand (0.97 g. in 25 ml.) was added to an ethanolic solution of the platinum chloride (0.9 g. in 25 ml.). Immediate precipitation occurred on mixing the two solutions together. The solid was isolated and dried as usual.

RESULTS AND DISCUSSION

The results of analysis of the complexes of 2-amino-6-ethoxybenzothiazole are quite satisfactory and agree with the suggested stoichiometries (Table 6). These complexes have the general formula $M(2\text{-amino}-6\text{-ethoxybenzothiazole})_1 3^\frac{X}{2}$ where $M$ stands for the metal ion and $X = Cl^-$, $NO_3^-$ or $1/2 SO_4^-$ . All the complexes are coloured, stable at room temperature and insoluble in usual organic solvents. They all decomposed above 200°C.

The nature of the coordination of the ligand and tentative assignments of the structures of the complexes
## TABLE 6

Analytical data, colour and melting points of 2-amino-6-ethoxybenzothiazole and its complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>M.P.  °C</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
<th>S (%)</th>
<th>Cl (%)</th>
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<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Brown</td>
<td>161</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>VO(C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;)SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Green</td>
<td>210d</td>
<td>15.40</td>
<td>30.25</td>
<td>2.80</td>
<td>8.50</td>
<td>19.50</td>
<td>-</td>
</tr>
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<td>Cu(C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;)Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Green</td>
<td>250d</td>
<td>12.15</td>
<td>41.34</td>
<td>3.84</td>
<td>10.72</td>
<td>12.25</td>
<td>13.59</td>
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<td>Murkey</td>
<td>220</td>
<td>19.30</td>
<td>38.72</td>
<td>3.58</td>
<td>12.50</td>
<td>11.50</td>
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<td>Brown</td>
<td>190</td>
<td>22.25</td>
<td>36.17</td>
<td>3.38</td>
<td>9.48</td>
<td>10.84</td>
<td>12.03</td>
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<td>White</td>
<td>268</td>
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<td>41.23</td>
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<td>12.40</td>
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<td>9.71</td>
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<td>Brown</td>
<td>250d</td>
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<td>2.18</td>
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<td>7.10</td>
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<td>Yellow</td>
<td>225d</td>
<td>30.40</td>
<td>32.78</td>
<td>3.03</td>
<td>8.40</td>
<td>9.70</td>
<td>10.70</td>
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<td>Black</td>
<td>300d</td>
<td>9.26</td>
<td>40.88</td>
<td>3.78</td>
<td>10.00</td>
<td>12.12</td>
<td>9.77</td>
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<td>Brown</td>
<td>295</td>
<td>28.61</td>
<td>29.07</td>
<td>2.69</td>
<td>7.54</td>
<td>8.61</td>
<td>19.09</td>
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<tr>
<td>Ir(C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;)Cl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Black</td>
<td>300d</td>
<td>38.85</td>
<td>21.93</td>
<td>2.03</td>
<td>5.68</td>
<td>6.49</td>
<td>21.60</td>
</tr>
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<td>Pt(C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;)Cl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Green</td>
<td>255</td>
<td>26.89</td>
<td>30.49</td>
<td>2.76</td>
<td>7.73</td>
<td>8.83</td>
<td>19.59</td>
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*d* = decomposed.
have been suggested on the basis of infrared spectral studies. Far infrared spectra were also recorded with a view to obtaining information on the metal ligand bonding which could be through any of the potential donor sites viz., the sulphur atom, the oxygen atom or the nitrogen atom. The assignments of various modes of the vibration have been made by analogy with the spectra of similar heterocyclic compounds. Only significant spectral changes which provide information regarding coordination and the identification of the donor site in the complexes have been discussed in detail.

The i.r. spectrum of the ligand shows a strong band at 1260 cm$^{-1}$ tentatively assigned to the ethoxy group of the ligand which remains almost unaltered or is slightly increased suggesting the non-involvement of oxygen atom in complex formation.

The i.r. spectrum of the solid ligand in KBr shows two bands at 3330 and 3200 cm$^{-1}$ which must be due to the asymmetric and symmetric N-H stretching frequencies respectively. Sartori et al. have recorded the spectrum of 2-aminobenzothiazole in carbon tetrachloride and have assigned the two N-H stretching frequencies at 3480 (asymmetric) and 3412 cm$^{-1}$ (symmetric). It is clear from the above that there is a marked difference in the NH
band positions observed for 2-amino-6-ethoxybenzothiazole in the solid phase and for 2-aminobenzothiazole in CCl₄. Assuming that there should not be any effect on the NH band position by introduction of the ethoxy group at position 6 of the ring it appears that the ligand is associated in the solid phase.

The infrared spectra of 2-amino-6-ethoxybenzothiazole and its complexes have been compared and showed a number of differences in the region associated with -NH₂ group and in C-S band position. A shift to lower frequencies in the case of NH₂ bands has been observed (Table 7). This may have resulted from the coordination of the amino group. The coordination through the nitrogen atom of the amino group in 2-aminobenzothiazole has also been suggested by Duff. A positive shift in the exocyclic C-N stretching frequency observed in all the complexes is further evidence in favour of bonding through amino-nitrogen. The C=N stretching vibration is, however, almost unaltered in all the complexes indicating the non-involvement of ring nitrogen in coordination. The C-S stretching frequency observed at 685 cm⁻¹ in the ligand is lowered in all the complexes ruling out the sulphur coordination through the sulphur atom.

A comparison of far i.r. spectra of the complexes and the ligand reveals a new strong band at about 380 cm⁻¹ in all the complexes which is tentatively assigned to M-N stretching vibration. This further confirms coordination
<table>
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<tr>
<th>Compound</th>
<th>N-H Asym.</th>
<th>N-H Symm.</th>
<th>RO-C=C_6H_5</th>
<th>C=N</th>
<th>C-N</th>
<th>M-N</th>
<th>M-Cl</th>
<th>C-S</th>
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<tr>
<td>C_{9}H_{10}N_{10}O_{5}S</td>
<td>3330s</td>
<td>3200s</td>
<td>1260m</td>
<td>1623s</td>
<td>1380s</td>
<td>-</td>
<td>-</td>
<td>685w</td>
</tr>
<tr>
<td>VO(C_{9}H_{10}N_{2}O_{5})SO_4</td>
<td>3320w</td>
<td>3200m</td>
<td>1265s</td>
<td>1620m</td>
<td>1375m</td>
<td>375w</td>
<td>-</td>
<td>665w</td>
</tr>
<tr>
<td>Cu(C_{9}H_{10}N_{2}O_{5})_2Cl_2</td>
<td>3340s</td>
<td>3220s</td>
<td>1265m</td>
<td>1620w</td>
<td>1375s</td>
<td>382s</td>
<td>330s</td>
<td>666m</td>
</tr>
<tr>
<td>Ag(C_{9}H_{10}N_{2}O_{5})_2NO_3</td>
<td>3500w</td>
<td>3200s</td>
<td>1257m</td>
<td>1613s</td>
<td>1378s</td>
<td>380s</td>
<td>-</td>
<td>666m</td>
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<td>Au(C_{9}H_{10}N_{2}O_{5})_3Cl_3</td>
<td>3275w</td>
<td>3125w</td>
<td>1265w</td>
<td>1620w</td>
<td>1389w</td>
<td>380m</td>
<td>328s</td>
<td>665w</td>
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<td>Zn(C_{9}H_{10}N_{2}O_{5})_2Cl_2</td>
<td>3260s</td>
<td>3180s</td>
<td>1260s</td>
<td>1628w</td>
<td>1385s</td>
<td>378s</td>
<td>325w</td>
<td>685w</td>
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<td>3200s</td>
<td>1270s</td>
<td>1628w</td>
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<td>380s</td>
<td>325s</td>
<td>665m</td>
</tr>
<tr>
<td>Hg(C_{9}H_{10}N_{2}O_{5})_2NO_3</td>
<td>3320w</td>
<td>3200w</td>
<td>1271w</td>
<td>1622w</td>
<td>1374s</td>
<td>382s</td>
<td>-</td>
<td>655m</td>
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<td>Hg(C_{9}H_{10}N_{2}O_{5})_2Cl_2</td>
<td>3310m</td>
<td>3200s</td>
<td>1262s</td>
<td>1630m</td>
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<td>665m</td>
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<td>Ru(C_{9}H_{10}N_{2}O_{5})_3Cl_3</td>
<td>3300b</td>
<td>3160w</td>
<td>1265s</td>
<td>1600s</td>
<td>1395s</td>
<td>380m</td>
<td>325w</td>
<td>650s</td>
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<tr>
<td>Pd(C_{9}H_{10}N_{2}O_{5})_2Cl_2</td>
<td>3300s</td>
<td>3200m</td>
<td>1280s</td>
<td>1625s</td>
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<td>385s</td>
<td>325w</td>
<td>665</td>
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<tr>
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<td>3380m</td>
<td>3200s</td>
<td>1265s</td>
<td>1630m</td>
<td>1381s</td>
<td>385s</td>
<td>330m</td>
<td>655w</td>
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<td>3208w</td>
<td>1275s</td>
<td>1615m</td>
<td>1360m</td>
<td>278s</td>
<td>322m</td>
<td>685s</td>
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s=strong, m=medium, w=weak, b=broad.
through the amino-nitrogen. Another band at about 325 cm\(^{-1}\) also appears in all the chloro-complexes and is tentatively assigned to M-Cl stretching vibrations.

**PROPOSED STRUCTURE FOR THE COMPLEXES**

The oxovanadium complex of this ligand having a 1:1 stoichiometry shows two strong bands at 970 and 1050 cm\(^{-1}\). All oxovanadium(IV) complexes are expected to have the i.r. bands in the region 900-1100 cm\(^{-1}\). Two other bands at 1147 and 1102 cm\(^{-1}\) are ascribed to a bidentate bridging sulphato group. The possible structure for this complex should then be a dimeric square planar one with sulphate bridges as shown below:

\[
\begin{align*}
\text{L} & \quad \text{SO}_4^{-} & \quad \text{V} & \quad \text{SO}_4^{-} & \quad \text{O} \\
\text{O} & \quad \text{V} & \quad \text{SO}_4^{-} & \quad \text{L}
\end{align*}
\]

The copper complex also seems to be a square planar one with two chlorine and two ligand molecules. The structure is tentatively suggested for this complex.
The silver complex shows two bands at 1378 and 1340 cm\(^{-1}\) which are ascribable to the coordinated nitrate group. The presence of two bands indicates a bidentate nitrate coordination. This complex is, therefore, proposed to have a tetrahedral structure with nitrate bridges.

The gold complex, which has 1:3 stoichiometry seems to have an octahedral geometry. The following structure may be proposed for this complex.

The zinc and cadmium complexes have a 1:2 stoichiometry. A tetrahedral structure may be proposed for these complexes. It is in conformity with the fact that these ions generally prefer to have a tetrahedral structure.
The complex obtained by the interaction of the ligand with mercurous nitrate has a 1:2 stoichiometry and shows two bands at 1374 and 1330 cm\(^{-1}\) tentatively assigned to the nitrate bands. These two bands are ascribed as in silver complex to a bidentate nitrate coordination. A tetrahedral structure may be proposed for this complex involving nitrate bridges. The mercury(II) complex also seems to have a tetrahedral structure.

An octahedral geometry may be proposed for the complex formed with ruthenium chloride having a 1:3 stoichiometry.

For the palladium complex which has a 1:1 stoichiometry, the following dimeric square planar structure having chloride bridges may be proposed.

\[
\begin{align*}
\text{L} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Pd} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{L}
\end{align*}
\]

A square planar structure is also proposed for the iridium complex. The possible structure is shown below:
The Pt(IV) complex appears to have an octahedral geometry which is generally preferred by this ion. The following structure having trans-ligands may be proposed for this complex.

Concluding Paragraph:

It could not be possible to obtain the diffuse reflectance spectra of these complexes. Further work is necessary for completely elucidating the structures of these compounds which have only tentatively been proposed, with the help of the data obtained in this work.
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