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)

\[ \begin{align*}
&\text{(I)} \\
&\text{(II)} \\
&\text{(III)}
\end{align*} \]

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.\textsuperscript{126-128}

Bismuthiol I exists in the form of a yellow powder having a melting point of 163°C. It was synthesized by Losanitch\textsuperscript{129} in 1922 and by Bambas\textsuperscript{130} in 1952. Badisch\textsuperscript{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\textsuperscript{130} had suggested the thiol structure for this compound on the basis of its chemical reactions. In the year 1960 Thorn\textsuperscript{99} suggested on the basis of ultraviolet studies that bismuthiol I could exist in three tautomeric forms (IV-VI) given below:

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

He suggested that while in CHCl\textsubscript{3} the dithiol structure predominates, in alcohol it is mainly in the dithione form. We have recently confirmed\textsuperscript{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\(^7\). Amperometric titrations of copper and palladium and spectrophotometric determination of palladium with this ligand have been made\(^13\),\(^15\). It is used in potentiometric titrations and solubility determination of silver salts\(^1\). However, except for the complexes of bismuthiol I with rhodium, osmium and tellurium\(^7\),\(^8\),\(^12\), 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 \(H_6OsO(C_2N_2S_3)_6\) and that of rhodium was \(H_3Rh(C_2N_2S_3)_3\) and \(HRh(C_2N_2S_3)\) in \(3\) \(N\) and \(N-HCl\), respectively.

Bismuthiol I finds several industrial applications. Its zinc compound is used as an antioxidant for motor oil\(^13\). 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\(^6\). The nickel compound is used as catalytic agent in the manufacture of acrylic acid\(^13\), its Co(II), Cu(II) and Zn(II) compounds have been used as bactericides\(^7\). It is also used in the manufacture of tetracycline\(^13\),\(^9\),\(^14\) 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. Zinc, cadmium, silver, thallium and platinum group metals were determined gravimetrically, and the rest of the metals were estimated by complexometric titration method with ethylenediaminetetraacetic acid (E.D.T.A.)

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 the off. The gouy tube was calibrated with a standard CuSO$_4$$\cdot$5H$_2$O. The gram susceptibility was calculated by the following formula:
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, \( K \) = constant, and its value is determined by the formula:

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

\( \chi_g \) for Hg \( [\text{CO(CNS)}_4] \) = 16.44 x 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 \( \chi_M' \) = corrected molar susceptibility.
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: FeSO₄·7H₂O, FeCl₃·5H₂O, CoCl₂·5H₂O, NiCl₂·5H₂O, CuCl₂·2H₂O, ZnCl₂·nH₂O, AgNO₃, CdCl₂·5H₂O, Hg₂(NO₃)₂, HgCl₂, TlCl·H₂O (B.D.H. reagents) and RuCl₃·3H₂O, PdCl₂, IrCl₃, H₂PtCl₆ and HAuCl₄ (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.

**Bis (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-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.

<table>
<thead>
<tr>
<th></th>
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</tr>
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<tbody>
<tr>
<td>C₂H₂N₂S₃</td>
<td>Yellow</td>
<td>163</td>
<td>-</td>
<td>16.00</td>
<td>1.30</td>
<td>19.01</td>
<td>64.00</td>
<td>(16.38)</td>
<td>(1.37)</td>
</tr>
<tr>
<td>Fe²⁺(C₂H₂N₂S₃)₂</td>
<td>Yellow</td>
<td>175</td>
<td></td>
<td>15.79</td>
<td>13.56</td>
<td>0.57</td>
<td>15.83</td>
<td>43.10</td>
<td>(14.89)</td>
</tr>
<tr>
<td>Fe³⁺(C₂H₂N₂S₃)³</td>
<td>Yellow</td>
<td>160</td>
<td></td>
<td>11.11</td>
<td>14.32</td>
<td>0.60</td>
<td>16.71</td>
<td>57.28</td>
<td>(11.95)</td>
</tr>
<tr>
<td>Co²⁺(C₂H₂N₂S₃)₂</td>
<td>Black</td>
<td>300d</td>
<td>16.15</td>
<td>13.44</td>
<td>0.56</td>
<td>15.68</td>
<td>53.78</td>
<td>(16.61)</td>
<td>(13.59)</td>
</tr>
<tr>
<td>Ni²⁺(C₂H₂N₂S₃)₂</td>
<td>Brown</td>
<td>320d</td>
<td>16.15</td>
<td>13.44</td>
<td>0.56</td>
<td>15.68</td>
<td>53.78</td>
<td>(16.12)</td>
<td>(13.31)</td>
</tr>
<tr>
<td>Cu⁺(C₂H₂N₂S₃)⁻</td>
<td>Yellow</td>
<td>300d</td>
<td>29.89</td>
<td>11.29</td>
<td>0.47</td>
<td>13.17</td>
<td>45.12</td>
<td>(30.68)</td>
<td>(12.12)</td>
</tr>
<tr>
<td>Cu⁺Cu²⁺(C₂H₂N₂S₃)⁺(C₂N₂S₃)²⁻</td>
<td>Brownish</td>
<td>250d</td>
<td>29.96</td>
<td>11.29</td>
<td>0.23</td>
<td>13.20</td>
<td>45.27</td>
<td>(29.31)</td>
<td>(11.37)</td>
</tr>
<tr>
<td>Zn²⁺(C₂H₂N₂S₃)₂⁻</td>
<td>Yellow</td>
<td>195</td>
<td>17.99</td>
<td>13.20</td>
<td>0.85</td>
<td>15.41</td>
<td>52.80</td>
<td>(18.17)</td>
<td>(13.49)</td>
</tr>
<tr>
<td>Ru⁺(C₂H₂N₂S₃)⁻</td>
<td>Black</td>
<td>200d</td>
<td>40.40</td>
<td>9.60</td>
<td>0.40</td>
<td>11.20</td>
<td>38.40</td>
<td>(41.05)</td>
<td>(9.77)</td>
</tr>
<tr>
<td>Pd²⁺(C₂H₂N₂S₃)₂⁻</td>
<td>Red</td>
<td>240d</td>
<td>26.31</td>
<td>11.87</td>
<td>0.49</td>
<td>13.84</td>
<td>47.47</td>
<td>(26.30)</td>
<td>(12.17)</td>
</tr>
<tr>
<td>Ag⁺(C₂H₂N₂S₃)⁻</td>
<td>Yellow</td>
<td>275d</td>
<td>42.00</td>
<td>9.34</td>
<td>0.40</td>
<td>10.90</td>
<td>37.38</td>
<td>(42.06)</td>
<td>(10.00)</td>
</tr>
<tr>
<td>Cd²⁺(C₂H₂N₂S₃)₂⁻</td>
<td>Yellow</td>
<td>300</td>
<td>27.39</td>
<td>11.69</td>
<td>0.50</td>
<td>13.65</td>
<td>46.78</td>
<td>(28.20)</td>
<td>(12.40)</td>
</tr>
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</table>

continued on next page.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>λ (nm)</th>
<th>λ (µm)</th>
<th>λ (Å)</th>
<th>δ (°)</th>
<th>²θ (°)</th>
<th>λ (°)</th>
<th>²θ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(^{6+})(C(_2)HN(_2)S(_3))(^-)</td>
<td>Brown</td>
<td>210</td>
<td>17.68</td>
<td>13.26</td>
<td>0.55</td>
<td>15.47</td>
<td>53.04</td>
<td></td>
</tr>
<tr>
<td>Pt(^{4+})(C(_2)HN(_2)S(_3))(^-)</td>
<td>Brown</td>
<td>200d</td>
<td>24.65</td>
<td>12.13</td>
<td>0.50</td>
<td>14.16</td>
<td>48.54</td>
<td></td>
</tr>
<tr>
<td>Au(^{+})(C(_2)HN(_2)S(_3))(^-)</td>
<td>Yellow</td>
<td>260d</td>
<td>56.93</td>
<td>6.93</td>
<td>0.29</td>
<td>8.10</td>
<td>27.74</td>
<td></td>
</tr>
<tr>
<td>Hg(^{2+})(C(_2)HN(_2)S(_3))(^-)</td>
<td>Yellow</td>
<td>250d</td>
<td>40.23</td>
<td>9.63</td>
<td>0.40</td>
<td>11.23</td>
<td>38.01</td>
<td></td>
</tr>
<tr>
<td>Tl(^{3+})(C(_2)HN(_2)S(_3))(^-)</td>
<td>Yellow</td>
<td>180</td>
<td>31.37</td>
<td>11.05</td>
<td>0.45</td>
<td>12.89</td>
<td>43.20</td>
<td></td>
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</table>
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.

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\(^{88}\) (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\(^{88}\).

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,

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

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

<table>
<thead>
<tr>
<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>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)</td>
<td>2490w</td>
<td>3060s</td>
<td>1460s</td>
<td>1120s</td>
<td>1265s</td>
<td>715s</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Fe}^{2+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2)</td>
<td>3175s</td>
<td>1449s</td>
<td>1099s</td>
<td>1266w</td>
<td>720s</td>
<td>-</td>
<td>320m</td>
<td></td>
</tr>
<tr>
<td>(\text{Fe}^{3+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_3)</td>
<td>3247s</td>
<td>1466s</td>
<td>1111s</td>
<td>1235s</td>
<td>719s</td>
<td>-</td>
<td>324m</td>
<td></td>
</tr>
<tr>
<td>(\text{Co}^{2+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2)</td>
<td>3150b</td>
<td>1470s</td>
<td>1104m</td>
<td>1240m</td>
<td>712m</td>
<td>-</td>
<td>338s</td>
<td></td>
</tr>
<tr>
<td>(\text{Ni}^{2+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2)</td>
<td>3279w</td>
<td>1449w</td>
<td>1111w</td>
<td>1242w</td>
<td>714b</td>
<td>-</td>
<td>330s</td>
<td></td>
</tr>
<tr>
<td>(\text{Cu}^{+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2)</td>
<td>3135b</td>
<td>1465s</td>
<td>1122s</td>
<td>1260s</td>
<td>725s</td>
<td>540s</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(\text{Cu}^{+}\cdot\text{Cu}^{2+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2)</td>
<td>3160s</td>
<td>1465w</td>
<td>1122m</td>
<td>1270m</td>
<td>720m</td>
<td>540s</td>
<td>380m</td>
<td></td>
</tr>
<tr>
<td>(\text{Zn}^{2+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2)</td>
<td>3226b</td>
<td>1471s</td>
<td>1111m</td>
<td>1235s</td>
<td>712w</td>
<td>539s</td>
<td>337s</td>
<td></td>
</tr>
<tr>
<td>(\text{Ru}^{2+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2)</td>
<td>3175s</td>
<td>1468s</td>
<td>1109s</td>
<td>1259s</td>
<td>695w</td>
<td>-</td>
<td>340s</td>
<td></td>
</tr>
<tr>
<td>(\text{Pd}^{2+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2)</td>
<td>3125m</td>
<td>1453m</td>
<td>1109s</td>
<td>1282m</td>
<td>716b</td>
<td>-</td>
<td>335s</td>
<td></td>
</tr>
<tr>
<td>(\text{Ag}^{+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2)</td>
<td>3125m</td>
<td>1458s</td>
<td>1111s</td>
<td>1258s</td>
<td>717s</td>
<td>532s</td>
<td>330s</td>
<td></td>
</tr>
<tr>
<td>(\text{Cd}^{2+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)_2)</td>
<td>3226s</td>
<td>1460s</td>
<td>1110m</td>
<td>1282s</td>
<td>729s</td>
<td>542s</td>
<td>330s</td>
<td></td>
</tr>
</tbody>
</table>

Table continued on next page
Table continued.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Wave (nm)</th>
<th>Intensity</th>
<th>Temp (°C)</th>
<th>Lifetime (μs)</th>
<th>Width (μs)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir$^{6+}$($C_2H_2N_3S_3$)$_6$</td>
<td>3049w, 2874w</td>
<td>1481m</td>
<td>1099s</td>
<td>1250s</td>
<td>711s</td>
<td>335 s</td>
</tr>
<tr>
<td>Pt$^{4+}$($C_2H_2N_3S_3$)$_4$</td>
<td>3125w, 2907m</td>
<td>1456w</td>
<td>1105s</td>
<td>1255w</td>
<td>719s</td>
<td>335 s</td>
</tr>
<tr>
<td>Au$^+$($C_2H_2N_3S_3$)$_-$</td>
<td>3068s, 2841m</td>
<td>1451m</td>
<td>1101s</td>
<td>1250s</td>
<td>711s</td>
<td>540m, 335 s</td>
</tr>
<tr>
<td>Hg$^{2+}$($C_2H_2N_3S_3$)$_2$</td>
<td>3125m, 2817b</td>
<td>1445s</td>
<td>1092s</td>
<td>1250s</td>
<td>713s</td>
<td>545s, 332s</td>
</tr>
<tr>
<td>Tl$^{3+}$($C_2H_2N_3S_3$)$_3$</td>
<td>3226w, 2941w</td>
<td>1456s</td>
<td>1111s</td>
<td>1268s</td>
<td>704s</td>
<td>545s, 340w</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 28,170 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 $5_{\text{Eg}} \leftrightarrow 5_{\text{T}_{2g}}$ 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 $5_{\text{Eg}}$ 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 28,170 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\(^{-1}\). The absence of any absorption band in the region 16,600-10,000 cm\(^{-1}\) 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\(^{-1}\) indicates a square planar environment for the Ni(II) ion for which a band is expected at 22,000-16,600 cm\(^{-1}\)\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)\(_2\)Cl\(_2\)\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 $^3_{7/2} \rightarrow ^3_{1/2}$ transition may have merged with the charge transfer at 28,570 cm$^{-1}$ and the band due to $^3_{7/2} \rightarrow ^3_{1/2}$ transition is out of the range of the instrument. The remaining band $^3_{7/2} \rightarrow ^3_{1/2}$ 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.

![Diagram](image)

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+} \left( \text{C}_2\text{HN}_2\text{S}_3 \right)_2^- )</td>
<td>28,170, 26,970, 11,110</td>
<td>2.296</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} \left( \text{C}_2\text{HN}_2\text{S}_3 \right)_3^- )</td>
<td>28,170</td>
<td>1.261</td>
</tr>
<tr>
<td>( \text{Co}^{2+} \left( \text{C}_2\text{HN}_2\text{S}_3 \right)_2^- )</td>
<td>27,030, 18,180, 16,000, 14,290, 12,320</td>
<td>2.736</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} \left( \text{C}_2\text{HN}_2\text{S}_3 \right)_2^- )</td>
<td>28,570, 16,950</td>
<td>1.395</td>
</tr>
<tr>
<td>( \text{Cu}^+ \left( \text{C}_2\text{HN}_2\text{S}_3 \right)_3^- )</td>
<td>23,260</td>
<td>1.070</td>
</tr>
<tr>
<td>( \text{Cu}^+.\text{Cu}^{2+} \left( \text{C}_2\text{HN}_2\text{S}_3 \right)_3^- )</td>
<td>25,970</td>
<td>0.912</td>
</tr>
<tr>
<td>( \text{Ru}^+ \left( \text{C}_2\text{HN}_2\text{S}_3 \right)_3^- )</td>
<td>25,320, 18,970, 12,740, 11,760, 10,870</td>
<td>0.750</td>
</tr>
<tr>
<td>( \text{Pd}^{2+} \left( \text{C}_2\text{HN}_2\text{S}_3 \right)_2^- )</td>
<td>27,030, 22,730</td>
<td>Dia.</td>
</tr>
<tr>
<td>( \text{Ir}^{6+} \left( \text{C}_2\text{HN}_2\text{S}_3 \right)_6^- )</td>
<td>40,000, 27,780, 26,315, 13,000</td>
<td>Dia.</td>
</tr>
<tr>
<td>( \text{Pt}^{4+} \left( \text{C}_2\text{HN}_2\text{S}_3 \right)_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\(^{159} \) 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 \( \text{Cu}^{2+}(\text{C}_2\text{H}_2\text{N}_2\text{S}_3)^{2-} \) 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 \( (\text{C}_2\text{H}_2\text{N}_2\text{S}_3)^{-} \) 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) : \( (\text{C}_2\text{H}_2\text{N}_2\text{S}_3)^{-} \) and 1:1 Cu(II) : \( (\text{C}_2\text{H}_2\text{N}_2\text{S}_3)^{2-} \) or as we are tempted to suggest a mixed valence complex Cu(I). Cu(II). \( (\text{C}_2\text{H}_2\text{N}_2\text{S}_3)^{-} \).\( (\text{C}_2\text{N}_2\text{S}_3)^{2-} \). 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=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 forma­
tion. 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 coordi­
nation 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 coordi­
nation 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 \(^1T_{2g} \leftrightarrow ^1A_{1g}\), \(^1T_{1g} \leftrightarrow ^1A_{1g}\) and \(^3T_{1g} \leftrightarrow ^1A_{1g}\) (forbidden) respectively. The spin forbidden band for \(^3T_{2g} \leftrightarrow ^1A_{1g}\) 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.

\[
\begin{array}{c}
\text{N} \quad \text{NH} \\
\text{L}^- \quad \text{L}^- \quad \text{S-C} \quad \text{C=S} \quad \text{L}^- \quad \text{L}^- \\
\text{Pt} \quad \text{Pt} \\
\text{L}^- \quad \text{L}^- \quad \text{S=C} \quad \text{C-S} \quad \text{L}^- \quad \text{L}^- \\
\text{HN} \quad \text{N}
\end{array}
\]

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 (\(\mu_{\text{eff}} = 0.75\) B.M.) 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 upto 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.