CHAPTER V

Stereo chemical studies on octahedral and square planar complexes of copper (II), Manganese (II) and Uranyl (II) with 2:5-Dimethoxy phenyl glyoxal thiosemicarbazone and 4-p-methoxy phenyl thiosemicarbazone of 2:5 Dimethoxy phenyl glyoxal.

Introduction: Preparation and characterisation of molecules containing polynuclear copper has evoked much interest in recent years (1-6). Binuclear complexes being the simplest of such polynuclear centres there has been a steady increase in the number and variety of such compounds studied. The magnetic moments of five coordinate copper (II) complexes are generally in the range reported for d9 system in four or six coordinate complexes (7-8) i.e. 1.85-2.10 B.M. The magnetic properties of copper (II) complexes have been reviewed. (9-11). In general, these complexes have been found to obey the Curie-Weiss law, but in some cases variation of magnetic moment with temperature has been observed (12). The lowering of \( \mu_{\text{eff}} \) value has been attributed to exchange coupling.

Diverse biological activities have been found in compounds having the phenyl glyoxal moiety. Electronic configuration (3d5) has the possibility of existing in three possible spin states (S= 5/2, 3/2, and 1/2). Complexes with spin sextet and doublet ground states give rise to magnetic moment corresponding to five unpaired electrons in the range 5.80-6.0 B.M. Several high spin manganese (II) complexes are known to have normal values of \( \mu_{\text{eff}} \). The stability constants of the chelates of 4-(o-methoxy phenyl) thiosemicarbazide (16) have been studied by Saxena et.al. Here we wish to present the result
of our studies on copper (II), Manganese (II) and uranyl complexes with 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone and 4-p- methoxy phenyl thio semicarbazone of 2:5 Dimethoxy phenyl glyoxal. The transition metal ions used in the present investigations are also of biological importance (18).

Experimental:

1. [Cu (C₁₁ H₁₃ N₃ O₃ S)₃] Cl₂ Dark greenish colour precipitate was obtained by mixing ethanolic solution of CuCl₂ and 8555 gm. 0.05M) 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone (0.025 M) dissolved in ethanol in 1:2 ratio. The mixture was refluxed for about two hours over water bath and on subsequent cooling greenish mass was prepared. It was filtered, washed with water ethanol and dried in an air oven.

2. [Cu(C₁₁ H₁₃ N₃ O₃ S)₂]Cl₂ - Alcoholic solution of liquid ammonia (d = 0.88) was dropped to attain pH 6.5 into the reaction mixture obtained by mixing 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone and cupric chloride dissolved in ethanol in a ratio of 1:2 when Buff green colour mass was obtained, after refluxing the contents over water bath for about an hour. It was filtered, washed and dried as before.

3. Cu₂ (C₁₉ H₁₉ N₃ O₄ S)₂ Cl₄ - Greenish coloured reaction mixture was obtained by mixing hot ethanolic solution of cupric chloride dihydrate (0.85 g, 0.005 M) and ligand (4p-methoxy phenyl thiosemicarbazone of 2:5 dimethoxy phenyl glyoxal) (0.005M) dissolved in the same solvent, and heated over a water bath for two hours. The greenish solid obtained was collected on a filter paper under suction washed with water ethanol mixture as usual.
4. [Mn(C11 H13 N3 O3 S)2Cl2] — Solution of 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone (0.005M) in ethanol and MnCl₂. 4 H₂O (0.98 g, 0.005 M) in ethanol water (25 ml) were mixed together and content was refluxed for about an hour, on a water bath. The pinkish solid obtained was collected on a filter paper under suction, washed with water ethanol mixture and dried.

5. [Mn(C11 H13 N3 O3 S)2 (NH₂)₂] — To a 1:2 ethanolic solution of MnCl₂. 4 H₂O and the 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone few ml. of alcoholic solution of ammonia was added to attain 6.5 pH. The reaction mixture was stirred and refluxed for 1 hr. A pinkish mass was obtained, filtered and washed with water, and dried under vacuum over P₄O₁₀ to form the desired compound.

6. [Mn₂(C19 H₁₂ N₅ O₄ S)₂ Cl₄] — Light pink colour metal complex was isolated by refluxing ethanolic solution of the MnCl₂. 4 H₂O and 4-p-Methoxy phenyl thiosemicarbazone of 2:5 Dimethoxy phenyl glyoxal in 1:1 molar ratio for two hours. The insoluble complex was filtered, washed with water, dried in vacuum and analysed for the percentage of the metal, C, H, and N, micro analytically.

7. [UO₂ (C₁₀ H₈ O₂ N₃ O₄ S) Cl (SC)₂] — Alcoholic solution of uranyl acetate (2.180 g, 0.005 M) and 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone was mixed together in 1:1 molar ratio. The content was refluxed for about an hour and then concentrated and cooled to obtain the yellow colour mass.

8. [U₂(C₁₁ H₁₂ N₃ O₃ S)₂Cl₂(NH₂)₂] — Yellow coloured solid was obtained by reacting uranyl nitrate hexahydrate (2.516 g, 0.01 M)
and 2:5 Dimethoxy phenyl glyoxal thiosemicarbazone (M=L ; 1:2) in ethanol solution, after refluxing the mixture for about an hour.

9. $[\text{UO}_2\text{L}_2\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_4\text{S}_2\text{N}_0\text{O}_3]_4^{--}$ Brownish yellow coloured precipitate forms after refluxing the mixture containing uranyl nitrate hexahydrate and 4-p-methoxy phenyl-thiosemicarbazone of 2:5 Dimethoxy phenyl glyoxal in 1:1 molar ratio for 2 hours. The product was filtered off, washed with water and finally dried in a desiccator over fused calcium chloride.
Table 5.1: Analytical and magnetic data of Copper (II) Complexes.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound (Colour)</th>
<th>Chemical analysis calcd/ (Found)</th>
<th>Magnetic Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>1</td>
<td>Cu(C11H13N3O3S)3Cl2 (Green)</td>
<td>4.73</td>
<td>4.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(42.07)</td>
<td>(3.72)</td>
</tr>
<tr>
<td>2</td>
<td>Cu(C11H13N3O3S)2Cl2 (Buff green)</td>
<td>3.48</td>
<td>3.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(59.06)</td>
<td>(3.28)</td>
</tr>
<tr>
<td>3</td>
<td>Cu2(C19H17N3O4S)2Cl4 (Greenish)</td>
<td>4.35</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(43.13)</td>
<td>(3.15)</td>
</tr>
</tbody>
</table>
### Table (5.2) Analytical and magnetic date of Manganese (II) Complexes.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound Colour</th>
<th>Chemical analysis calcd/ (Found)</th>
<th>Metal $X_1 m\times 10^{-6} M_{eff}$</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C  H  N  S  Cl</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Mn (C 11 H13 N3 O3 S )2 ] cl2 (Pink)</td>
<td>40.00 3.93 12.72 9.69 10.75 8.32</td>
<td>14289.93 5.84</td>
<td>High spin octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(39.62) (3.22) (11.88) (9.38) (10.02) (8.00)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Mn (C 11 H13 N3 O3 S )2 (NH3)2 ] (Pink)</td>
<td>44.37 5.13 17.99 10.27</td>
<td>8.82 14100.34 5.8</td>
<td>High spin octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(41.80) (4.83) (17.17) (9.65)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Mn2 (C19 H19 N4 O3 S )2 cl4 ] (Light Pink)</td>
<td>44.62 3.71 8.22 6.26 13.89 10.75</td>
<td>14943.03 5.75</td>
<td>High spin octahedral</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(44.00) (3.12) (8.05) (5.95) (12.65) (9.85)</td>
<td></td>
<td></td>
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### Table (5.3) Analytical and magnetic data of uranyl—Complexes.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound Colour)</th>
<th>Chemical analysis calcd/ (Found)</th>
<th>Metal Anion</th>
<th>$\chi_{1 \text{max}}$ (B.M.)</th>
<th>Stereo chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C  H  N</td>
<td>X 1 mx -*f</td>
<td>T0 (B.M.)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>33.83 3.47 9.11 24.94 12.79 161.05</td>
<td>(32.75) (3.07) (9.35) (23.55) (11.80)</td>
<td></td>
<td>0.62 High spin octahedral</td>
</tr>
<tr>
<td>1</td>
<td>CuO2(C11 H13 N3 O3 S)2J(CH3COO)2 (Yellow)</td>
<td>28.44 2.80 15.08 25.64 13.36 229.55</td>
<td>(27.67) (2.15) (14.73) (24.17) (12.65)</td>
<td></td>
<td>0.75 High spin octahedral</td>
</tr>
<tr>
<td>2</td>
<td>CuO2(C11 H13 N3 O3 S)2J(NO3)2 (Yellow)</td>
<td>29.26 2.48 8.98 30.55 15.91 310</td>
<td>(28.85) (2.30) (8.01) (27.87) (14.80)</td>
<td></td>
<td>0.86 High spin octahedral</td>
</tr>
<tr>
<td>3</td>
<td>CuO2(C19 H19 N3 O4 S)2J(NO3)4 (Brownish yellow)</td>
<td></td>
<td></td>
<td></td>
<td>0.86 High spin octahedral</td>
</tr>
<tr>
<td>No.</td>
<td>Compound</td>
<td>Absorption bands CM-1</td>
<td>Tentative assignments</td>
<td>Relevent Ligand field parameters</td>
<td></td>
</tr>
<tr>
<td>-----</td>
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<td>-----------------------</td>
<td>---------------------------------</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>[Mn(C11 H13 N3 O3 S)2 Cl2]</td>
<td>18300, 22640, 25170, 28830, 34760</td>
<td>6A1g \rightarrow 4 T1g(G) ---4 T2g(G) ---4 A1g(G) \cdot 4Eg(G) ---4 T2g(D) ---4 T1g(P)</td>
<td>762.5, 8380, 58.71, 38.43, 0.794, 2.807, 1.47</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>[Mn(C11 H13 N3 O3 S)2 (NH3)2]</td>
<td>19000, 23200, 25180, 29070, 35300</td>
<td>6A1g \rightarrow 4 T1g(G) ---4 T2g(G) ---4 A1g(G) \cdot 4Eg(G) ---4 T2g(D) ---4 T1g(P)</td>
<td>791.66, 8704, 60.92, 39.89, 0.824, 2.837, 1.50</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[Mn2(C19 H19 N3 O4 S)2 Cl4]</td>
<td>18000, 22100, 25030, 28800, 34900</td>
<td>6A1g \rightarrow 4 T1g(G) ---4 T2g(G) ---4 A1g(G) \cdot 4Eg(G) ---4 T2g(D) ---4 T1g(P)</td>
<td>750, 8250, 57.74, 37.8, 0.756, 2.769, 1.53</td>
<td></td>
</tr>
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</table>

**Table (5.4) Electronic spectralabsorption bands, Tentative assignments and relevent ligand field parameters for Mn (II) complexes**
Table (5.5) Electronic spectral absorption bands, and their assignments for Cu (II) / UO2 (II) complexes.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>observed bands in cm⁻¹</th>
<th>charge-Transfer bands</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(C11 H13 N3 O3 S)3C12</td>
<td>15300 20600 23200</td>
<td>2B1g→E 2A1g (γ1) 2Eg (γ2) 2B2g</td>
<td>Distorted Square planar</td>
</tr>
<tr>
<td>2</td>
<td>Cu(C11 H13 N3 O3 S)2C12</td>
<td>7300 17450</td>
<td>2A1→E 2E→E</td>
<td>Distorted Octahedral</td>
</tr>
<tr>
<td>3</td>
<td>Cu2(C19 H19 N3 O4 S)2C14</td>
<td>7200 16890</td>
<td></td>
<td>Distorted Octahedral</td>
</tr>
</tbody>
</table>

(1) (4) (2) (7) (3) (5) (8) (6)

| 4 | Cu2(C11 H13 N3 O3 S)2(C3H3COO) | 19900 1.1933 | 36400 830 44200 Cm⁻¹ 36400 870 | Octahedral m.dynes/A 900 6.57552 |
| 5 | Cu2(C11 H13 N3 O3 S)2(NO3)2 | 20200 1.17746 | 36700 810 | Octahedral 6.42243 |
| 6 | Cu2(C19 H19 N3 O4 S)2(NO3)4 | 20010 1.178 | 36600 800 | Octahedral 6.42266 |
Table (5.6) Thermo-analytical data of copper (II) complexes.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Complex</th>
<th>Sample wt. (mg)</th>
<th>Residual wt. (mg)</th>
<th>Mass loss %</th>
<th>Residual %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CCu(C11H13N3O3S)3Cl2</td>
<td>85</td>
<td>53.64</td>
<td>10.35</td>
<td>61.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.14</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CCu(C11H13N3O3S)2Cl2</td>
<td>110</td>
<td>64.72</td>
<td>9.39</td>
<td>83.10</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>10.22</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CCu2(C19H19N3O4S)3Cl4</td>
<td>60</td>
<td>38.78</td>
<td>7.72</td>
<td>36.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.15</td>
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Table (5.7) Thermo-analytical data of Mn (II) complexes.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Complex</th>
<th>Sample wt. (mg)</th>
<th>Residual wt. (mg)</th>
<th>Mass loss % 40 - 180</th>
<th>Residual % 210-380</th>
<th>Residual % 400-630</th>
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<tbody>
<tr>
<td>1</td>
<td>[Mn(C11 H13 N3 O3 S)3]Cl2</td>
<td>75</td>
<td>30.31</td>
<td>NIL</td>
<td>9.20 10.01 12.20</td>
<td>13.33</td>
</tr>
<tr>
<td>2</td>
<td>[Mn(C11 H13 N3 O3 S)2(NH3)2]</td>
<td>125</td>
<td>65.48</td>
<td>NIL</td>
<td>8.11 9.77 98.77</td>
<td>99.02</td>
</tr>
<tr>
<td>3</td>
<td>[Mn2C19 H19 N3 O4 S]2Cl4</td>
<td>135</td>
<td>82.75</td>
<td>NIL</td>
<td>20.46 22.14 93.69</td>
<td>94.22</td>
</tr>
<tr>
<td>No</td>
<td>Complex</td>
<td>Sample wt. (mg)</td>
<td>Residual wt. (mg)</td>
<td>40 - 170</td>
<td>170 - 300</td>
<td>330 - 620</td>
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</tr>
<tr>
<td>1</td>
<td>[UO₂(C₁₁H₁₃N₃O₃S)₂(CH₃COO)]₂</td>
<td>85</td>
<td>35.58</td>
<td>NIL</td>
<td>11.77</td>
<td>12.87</td>
</tr>
<tr>
<td>2</td>
<td>[UO₂(C₁₁H₁₃N₃O₃S)₃(NO₃)]₂</td>
<td>120</td>
<td>64.77</td>
<td>NIL</td>
<td>15.34</td>
<td>16.60</td>
</tr>
<tr>
<td>3</td>
<td>[(UO₂)₂(C₁₉H₁₉N₃O₄S)₂(NO₃)]₄</td>
<td>60</td>
<td>31.12</td>
<td>NIL</td>
<td>10.61</td>
<td>11.88</td>
</tr>
</tbody>
</table>
Result and discussion:

(a) Magnetic measurement studies:

**Distorted Square planar with tetragonal distortions**

The magnetic moment value for copper (II) complexes should be close to 1.78 B.M. irrespective of the nature of bonding involved however these values seldom provide much information about the stereochemistry. Therefore the low effective magnetic moment found for [Cu(C11 H13 N3 O3 S2)Cl2 (1.37 B.M) can be considered due to the formation of dimeric/polymeric molecules which lead to the presence of exchange coupled antiferromagnetism in the complex either (19-22) through (Cu+2 – Cu+2) interaction or through ligand participation.

(b) **Distorted octahedral compound:** The room temperature magnetic moment observed for [Cu (C11 H13 N3 O3 S)3]Cl2 (1.91) and [Cu2(C19 H19 N3 O4 S)2]Cl4 (2.10 B.M). The value is slightly higher than that expected for metal ion containing one unpaired electron. This difference in magnetic moment is attributed to orbital contribution forming distorted octahedral symmetry. (23).

Electronic spectral studies:

(a) **Distorted square planar with Tetragonal distortions:** In tetragonal geometry three transitions of the position dx2-y2—> dxy; dx2-y2—> dz2 and dx2-y2—> dxy.dyz, are observable but generally these transitions overlap each other giving rise to one broad absorptions band. (24) [Cu (C11 H13 N3 O3 S)2] Cl2 exhibit three (d-d) transitions along with one charge transfer transition, in the visible region and tentatively assigned as given below—
15300 cm⁻¹  2 B²g ⟷ 2 A¹g (ν¹); (dx²−y² → dx²)
17750 cm⁻¹  2 B¹g ⟷ 2 E₂g (ν²); (dx²−y² → dx₂−y₂)
20600 cm⁻¹  2 B¹g ⟷ 2 B₂g (ν₃); (dx²−y₂ → dxy)
23200 cm⁻¹  ⟷ charge transfer band.

The intensity of the ν¹ band was found to be low as compared to other two transition (ν² and ν₃). It is reported (25) that distorted Cu(II) complexes exhibit one broad absorption band around 14.5 - 15.3 KK regions (26-27). In the above complexes transitions similar to distorted octahedral copper(II) complexes are observed, suggesting distortion in octahedral geometry.

(b) **Distorted octahedral complexes:**

The complexes [Cu(C₁₁H₁₃N₃O₃S)₃]Cl₂ and [Cu₂(C₁₉H₁₉N₃O₄S)₂]Cl₄ exhibit two bands in the region 7000 - 7500 and 16000 - 18000 cm⁻¹, tentatively assigned to 2 A¹ → 2 E and 2 E₂ → 2 E transition respectively as certaining distorted octahedral microsymmetry of the organic compounds around Cu(II) ion. 2 E₂ state is highly susceptible to Jahn-Teller distortion. Third band which appear as 103 a shoulder around 26000 cm⁻¹ is believed to be a charge transfer band. These bands have been assigned to dxz, dyz → dx²−y² and dxy → dx²−y₂ transitions respectively as reported earlier (28-30) Tsuchida (31) and coworkers indicated that all the copper complexes in which the paramagnetism is partially or completely quenched absorb around 26000 cm⁻¹. From the above studies it may be concluded that in copper(II) complexes, bands correspond to octahedral geometry, Further the results are consistent with an octahedral d⁹ system with considerable Jahn-Teller distortion. It is also reported that green or blue Cu(II) complexes are tetra-gonally distorted.
(1) Electronic spectra studies: The spectra of Mn(II) complexes show very broad or poorly resolved bands. The Mn(II) octahedral complex, which are assigned as 

\[ \text{6 lig} \rightarrow 4 \text{Tig} \ (\pi^*) \sim 12400-10500 \text{ cm}^{-1} \]
\[ \text{6 lig} \rightarrow 4 \text{Tig} \ (\pi^*) \sim 10000-1000 \text{ cm}^{-1} \]
\[ \text{6 lig} \rightarrow 4 \text{Tig} \ (\pi^*) \sim 22000-2000 \text{ cm}^{-1} \]
\[ \text{6 lig} \rightarrow 4 \text{Tig} \ (\pi^*) \sim 20000-18000 \text{ cm}^{-1} \]

The 6 lig \( \rightarrow \) 4 Tig electronic transition energy can be estimated as \( \text{6 lig} \rightarrow \text{4 Tig} \), separation energy.

For 2 d transition metal ions, the variation of orbital interaction electronic repulsion parameters with the cationic charge (z+) and the number 'q' of electrons in the partially filled d-subshell is expressed by the relation (32,34).

\[ B = 384 + 50q + 124 \ (z^+ + 1) - \frac{540}{(z^+ + 1)} \]

where B is in cm\(^{-1}\). Lower value of B show the reduction in effective positive charge with cation and with an increased tendency to be reduced to lower oxidation state. The effective cationic charge (z+) for the [Mn(C11H13N3O3S)2 Cl2]; [Mn(C11H13N3O3S)2 (NH3)2] and [Mn2(C19H19N3O4S)2Cl4] complexes
are found to be 1.4732; 1.5011; and 1.5312 respectively, which is considerably lower than the formal +2 oxidation state of the metal. The values of \( Dq \) and \( B \) have been calculated by the linear relation

\[
6 \text{ A1g} \rightarrow 4 \text{ T1g (G)} \quad \frac{\text{------------------------}}{B} = 24.00; \quad \frac{\text{Dq}}{B} = 1.1
\]

Slater - condon shortley repulsion parameters \( F_2 \) and \( F_4 \) are also evaluated by the relation.

\[
\frac{F_2}{49} = \text{----} \quad \frac{5 \ F_4}{441} \quad \text{and} \quad \frac{35 \ F_4}{441} \quad \text{and} \quad C = 4 \ B
\]

and found to be 58.71; 38.43 complex I; 60.92; 39.89 complex II; 57.74; 37.80 complex III respectively which are in agreement with the previous work(35-36). Decreased value of \( B \) is considered due to an increased distance between electrons and thus an effective increase in the size of the orbitals.

**Uranyl complexes, Magnetic and Electronic spectral studies:** The uranyl complexes \([UO_2(C11H13N3O3S)_2](CH_3COO)_2; UO_2(C11H13N3O3S)_2(NO_3)_2 \) and \([UO_2(C19H19N3O4S)_2](NO_3)_4 \) possess magnetic moment value of 0.62, 0.74 and 0.86 B.M. respectively indicate that the complexes are diamagnetic as expected for 5 FO system, although a totally symmetric ground state has been ascribed to the orbital contribution due to the involvement of uranium -5f- electrons in coordination(37).

Diffused reflectance spectra of the uranyl complexes exhibits three bands which are tentatively assigned(38) to 19000-21000 cm \(^{-1}\) \((\gamma_1)\); Transition with in the Uranyl ions 36000-38000 cm \(^{-1}\) \((\gamma_2)\); Ligand \(\rightarrow\) uranyl(II) charge transfer transitions. 43000-45000 cm \(^{-1}\) \((\gamma_3)\); Intra ligand transitions of the organic molecule or \(\pi \rightarrow\) in the organic molecule.
The electronic spectral band around 2000 cm\(^{-1}\) is due to \(1\text{ Eg} \rightarrow 3\text{ A}^2\) transition typical of OUD symmetric stretch frequency for the first excited state(39).

The complexes exhibit a strong band at 880-900 cm\(^{-1}\) characteristic of \((\text{O=U=O})\). The force constant \((f)\) values for \(\nu\text{ as (O=U=O)}\) agree well with the values reported by earlier workers(41). The \((\text{U-O})\) bond length has been calculated with the help of the equation(42). \(R(\text{U-O}) = 1.17 + 1.08 f^{-1/3}\).

The \(R(\text{U-O})\) in the complexes is in the range \((1.17\text{ to }1.19\text{ A})\) and the values are comparable to those \((1.60-1.92\text{ A})\) observed for some other Dioxouranium complexes(43). The \(\nu\text{ s (O=U=O)}\) stretch occurs in the region 800-830 cm\(^{-1}\). The complex \(\text{UO}_2\text{ L}_2\) exhibited a strong absorption at 260 cm\(^{-1}\) attributable to \((\text{UO}_2)\) bending mode. The formation of \((\text{M-N})\) and \((\text{M-O})\) bonds was further supported by the appearance of \(\nu(\text{M-N})\) and \(\nu(\text{M-O})\) in the regions 460-540 and 350-440 cm\(^{-1}\) respectively in metal complexes.

**Thermo Gravimetric Analysis:**

Thermo gravimetric analysis has widely been used in the determination of structures of various metallic salts and complexes(44-45). By this method stability of the complex and hydration of the complex is determined.

**Schematic representation of pyrolysis of copper(II) complexes:**

(a) \((\text{1}) \text{ [Cu(C11H13N3O3S)]Cl}_2 \) \((\text{2}) \text{ [Cu(C11H13N3O3S)]}_2 \text{Cl}_2\) and \([\text{Cu}_2(\text{C19H19N3O4S})\text{Cl}_2] \text{Cl}_4\).

\[\begin{align*}
\text{(1)} \text{ [Cu(C11H13N3O3S)]}_2 \text{Cl}_2 \quad &\longrightarrow \quad [\text{Cu(C11H13N3O3S)]}_2 \text{Cl}\quad 210-340^\circ C \\
\text{430 - 610}^\circ C \quad &\longrightarrow \quad \text{Cu} \quad \longrightarrow \quad \text{CuO} \\
\quad - 2 \text{ L}
\end{align*}\]
From thermogravimetric curves the horizontal lines indicates thermal stability of the complexes upto ~ 210 °C with no loss in weight, above this temperature a small weight loss was observed in the temperature range 220-340 °C. This may be due to the loss of chlorine molecules. By further raising the temperature no loss in weight is noticed, this shows thermal stability of the complex and strong coordination sites of the organic molecules. However by raising the temperature beyond 430 °C a heavy loss in weight is observed which indicate the oxidation of the organic part of the compound into carbon dioxide and water, with the formation of metal oxide cupric oxide at the end of the reaction, and no loss in mass was noticed beyond 610 °C.

DTA curves show medium endothermic peaks at 270 and 410 °C (complex I); 270 and 390 °C complex (II) and 230 and 430 °C complex (III) and very strong exothermic peaks at (490 and 520; 470, 520 °C and 490 and 530 °C) for compounds 1, 2, and 3.
respectively. These exothermic peaks may account the formation of SO₂, CO₂, and Nitrogen oxide while endothermic peaks at around ~ 24 can be considered due to the loss of chlorine as well as HCL molecule, while second peak observed in the range ~ 340 C may be subsequently represent the abrupt decomposition of organic compound.

1. [Cu(C₁₁H₁₃N₃O₃S)₃] Cl₂ Amount taken = 85 mg. Endopeaks = 270 and 410 C; Exopeaks = 490 and 530 C.
2. [Cu(C₁₁H₁₃N₃O₃S)₂] Cl₂ Amount taken = 110 mg. Endopeaks = 270 and 390 C. Exopeaks = 470 and 520 C.
3. [Cu₂(C₁₉H₁₉N₃O₄S)₂] Cl₄ Amount taken = 60 mg. Endopeaks = 230 and 430 C; Exopeaks = 490 and 530 C.

Manganese (II) complexes:

(b) (1). [Mn(C₁₁H₁₃N₃O₃S)₂. Cl₂] (2). [Mn₂(C₁₁H₁₃N₃O₃S)₂ (NH₃)₂] (3). [Mn₂(C₁₉H₁₉N₃O₄S)₂ Cl₄]

The horizontal line on (TG) came upto 180 C shows the thermal stability of the complexes. Poor thermal stability of the complexes is due to weak coordination sphere. This also suggest the absence of bridging of halogen moieties between the manganese ions in a single complex molecule. Small weight loss are observed in the temperature range 140-300 C, indicate the liberation of ammonia and chlorine molecules. Further heavy loss in weight was reported above 415 C, showing combustion of the organic part of
the molecule in presence of oxygen to form the oxide Mn2O3. This may be contaminated with higher oxide Mn3O4 also.

DTA curves show endothermal effect at 160, 205 and 435 C, showing liberation of ammonia, chlorine molecules and decomposition of organic compound. At higher temperature some exothermal peaks are observed in the range 410-580 C, exhibiting the combustion of the complex organic part, with the formation of CO2, H2O etc.

Schematically thermal decomposition is given below:—

\[\text{40-1800^\circ}C\]

1. \[\text{[Mn(C11H13N3O3S)]}_2 \text{Cl}_2 \rightarrow \text{[Mn(C11H13N3O3S)]}_2 \text{Cl}_2\]

\[\text{140-370 C}\]

\[\text{[Mn(C11H13N3O3S)]}_2 \text{Cl}_2 \rightarrow \text{[Mn(C11H13N3O3S)]}_2 \text{Cl} \rightarrow \text{[Mn(C11H13N3O3S)]}_2 \rightarrow \text{Mn}_2\text{O}_3 \]

Mn \rightarrow Mn2O3.

2. \[\text{[Mn(C11H13N3O3S)]}_2 (\text{NH}_3)_2 \rightarrow \text{[Mn(C11H13N3O3S)]}_2 (\text{NH}_3)_2\]

\[\text{210-370 C}\]

\[\text{[Mn(C11H13N3O3S)]}_2 \rightarrow \text{Mn(C11H13N3O3S)]}_2 \rightarrow \text{Mn}_2\text{O}_3 \]

\[\text{40-620 C}\]

\[\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_2\text{O}_3\]

\[\text{2NH}_3\]

\[\text{[Mn(C11H13N3O3S)]}_2 \rightarrow \text{Mn}_2\text{O}_3\]

\[\text{140-160 C}\]

3. \[\text{[Mn}_2\text{(C19H19N3O4S)]}_2 \text{Cl}_4\], \[\text{[Mn}_2\text{(C19H19N3O4S)]}_2 \text{Cl}_4\]

\[\text{210-370 C}\]

\[\text{[Mn}_2\text{(C19H19N3O4S)]}_2 \text{Cl}_4\]

\[\text{40-620 C}\]

\[\text{[Mn}_2\text{(C19H19N3O4S)]}_2 \text{Cl}_4\]

\[\text{430-600 C}\]

\[\text{Mn}_2\text{O}_3 \leftarrow \text{Mn}_2\text{O}_3\]

(c) \textbf{Uranyl (II) complexes:—}

1. \[\text{[UO}_2\text{(C11H13N3O3S)]}_2 \text{(CH}_3\text{COO)}_2\] (2). \[\text{[UO}_2\text{(C11H13N3O3S)]}_2 \text{(NO}_3)_2\]

3. \[\text{[UO}_2\text{(C19H19N3O4S)]}_2 \text{(NO}_3)_4\]
From TG curve the thermal stability of the uranyl(II) complexes is shown to be up to 180 °C. Then some weight started losing up to 315 °C, may be due to liberation of gas molecules like Cl₂, NO₂, etc. The horizontal plateaus in the temperature range 220-380 °C clearly show the thermal stability of the complexes. The heavy loss in weight between 430-640 °C indicates the decomposition of coordination sphere to form CO₂, H₂O, and ultimately U₃O₈ uranium sesqui-oxide, which is most stable oxide of uranium.

DTA curves of the complexes show endothermic peaks at 230 and 460 °C (complex I) and 210 and 440 °C complex (II) and 210 and 410 °C complex (III) respectively, whereas exothermic peaks are observed at around 400, 460, 520 (l), 400, 470, 500 °C (II) and 400, 520, 540 (III) shows the decomposition of organic part with the formation of U₃O₈. Schematically representation of Pyrolytic behaviour of uranyl complexes given below:

1. \[ \text{[UO}_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_3\text{S})_2\text{]} \text{(CH}_3\text{COO)}_2 \longrightarrow \text{[UO}_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_3\text{S})_2\]} \]
   \[ \text{170-300}\]
   \[ \text{(CH}_3\text{COO)}_2 \longrightarrow \text{UO}_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_3\text{S})_2 \longrightarrow \text{UO}_3 \longrightarrow \text{U}_3\text{O}_8. \]
   \[ \text{- 2L} \]

2. \[ \text{[UO}_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_3\text{S})_2\text{(NO}_3)_2 \longrightarrow \text{[UO}_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_3\text{S})_2\text{(NO}_3)_2 \.HandlerFunc[170-300]
   \[ \text{330-620}^\circ \text{C} \]
   \[ \text{[O]} \]
   \[ \text{[UO}_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_3\text{S})_2 \longrightarrow \text{UO}_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_3\text{S})_2 \longrightarrow \text{UO}_3 \longrightarrow \text{U}_3\text{O}_8 \]
   \[ \text{- 2NO}_3 \]
   \[ \text{- 2L} \]

3. \[ \text{[(UO}_2)_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_4\text{S})_2\text{(NO}_3)_4 \longrightarrow \text{[(UO}_2)_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_4\text{S})_2\text{(NO}_3)_4 \.HandlerFunc[170-300]
   \[ \text{330-620}^\circ \text{C} \]
   \[ \text{[O]} \]
   \[ \text{[(UO}_2)_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_4\text{S})_2 \longrightarrow \text{[(UO}_2)_2\text{(C}_1\text{H}_1\text{N}_3\text{O}_4\text{S})_2 \longrightarrow \text{UO}_3 \longrightarrow \text{U}_3\text{O}_8 \]

The complexes exhibit high thermal stability and get decomposes only above 180 °C, indicating absence of absorbed
moisture or lattice water.(46). Exothermic peak at higher temperature may be due to decomposition of the organic ligand and subsequent slow oxidation.(47).

**Infra red spectral studies:-**

(i) **Cu(II) complexes** - [Cu (C11H13N3O3S)3] Cl2 and [Cu (C11H13N3O3S)2 Cl] Cl2 The coordination sites of the ligand involved in coordination with metal ion have been ascertained by comparing the spectra of the complexes with parent compounds. Some important frequencies diagnostic of chelation with the metal ion have been discussed here. Phenyl glyoxal thiosemicarbazone show intense absorptions at 3400, 1635, 1350, 1690 and 810 cm⁻¹ which may respectively assigned to (NH) stretch, \(\nu(C=\text{N})\) and \(\nu(N-H)\) bonding, \(\nu(C=S) + \nu(C-N) > C=O\), and \(\nu(C=S)\), the corresponding bands are observed in the spectra of Cu complex at 1600 cm⁻¹ and 1630 cm⁻¹. Thus the negative shift in \(\nu(CH=\text{N})\) and \(\nu(C=O)\) suggest coordination through the azomethine nitrogen(48-49) and ketonic oxygen. Further the band at 810 cm⁻¹ due to \(\nu(C=S)\) remain unaltered in chelation suggesting non participation of Thiol group.

Therefore phenyl glyoxal thiosemicarbazone seems to behave as bidentate ligand and the coordination sites are azomethine nitrogen and ketonic oxygen atoms. Lowering in the frequencies of \(-CH=\text{N}\) and \(\nu(C=O)\) are due to the drainage of electron from Nitrogen and oxygen atom in chelation, which in turn weaken the bonds.

The non ligand bands appearing in far IR region in the spectra of the complexes, have been assigned to \(\nu(M-O)\) and \(\nu(M-N)\) modes(50-51).
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<th>NH-stretch</th>
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<th>N-H Bend-</th>
<th>Benzene $\sqrt[n]{(C=O)}$</th>
<th>C=O</th>
<th>$\sqrt[n]{(C=S)}$ of plane</th>
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<td>805 s</td>
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<td>1600 (w)</td>
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</table>
Fig. (5.1): I. R. Spectra of Cu(II) complexes.
(ii) Cu₂(C₁₉H₁₉N₃O₄S)₂ Cu₄ – 4-p- methoxy phenyl thiosemicarbazone of phenyl glyoxal behave as Tetridentate ligand, and the coordinating sites are >C=O, –CH=N, >C=S and –CH=NH. A sharp band at 1630 cm⁻¹ (CH=N) of the compound indicate the coordination because this frequency considerably reduces on complexation(52-53). The sharp to medium broad absorption bands observed in the region 3200-3400 cm⁻¹ due to (NH) remain unaltered in complex spectra. A single >C=O band observed at 1700 cm⁻¹ in the spectra of the ligand suffered a negative shift of 60 cm⁻¹ in the spectra of the complex, indicating coordination, through ketonic oxygen atom. Satapathy and Sahoo(54) reported two (C=N) bands at 1613 and 1595 cm⁻¹ in case of Fe(II) complex but we observed one band at 1600 cm⁻¹ which suggest coordination of both the (CH=N) group. The coordination through both the azomethine group is further supported by shifting in the frequency of (N⁻N) in complexes(55).

The band appearing at 1420 and 615 cm⁻¹ assigned to (C=S) stretching vibration is susceptible to coordination. In metal complex it shifts to lower frequency at 1170 cm⁻¹ showing coordination of sulphur atom with metal(56).

Other bands noticed in the spectra of ligands at 720, 740 cm⁻¹ shift in an irregular way in the metal complexes, which probably arises due to out of plane CH-bonding absorption of the benzene ring(57).

Absorption observed in the far infrared region have been assigned to ν(M-O) 490 cm⁻¹, ν(M-N) 560 cm⁻¹ and 630 cm⁻¹ ν(M-S) bonds. Such assignments have also been reported by earlier workers(58).
In some cases high frequencies for (M-S) may also be expected(59).

The (NH3) stretching frequency observed at 3205 and 3140 cm\(^{-1}\) can be assigned to symmetrical stretching vibrations of NH3 molecule.

Thus on the basis of IR studies it may be concluded that the ligand act as tetradentate and the coordinating sites are two azomethine group, one \(\text{C=O} \) and one \(\text{C=S} \) group.

Manganese (II) complexes: \([\text{Mn (C11H13N303S)Z C1Z]}; [\text{Mn (C11H13N303S)Z (NH3)Z}]; [\text{Mn (C19H19N304S)Z C14}]\) The tentative assignments for IR absorption bands in the range (4000-400 cm\(^{-1}\)) for Mn(II) complexes are based on the corresponding compounds (60-62).

In (C9H9N305)-Mn(II) complexes the sharp band at 1635 cm\(^{-1}\) (-CH=N) shifts to lower frequencies at \(\sim 1600 \text{ cm}\(^{-1}\) in the complexes showing the coordination through nitrogen atom, similar observations are reported earlier(53).

Further a band at 1690 cm\(^{-1}\) due to \(\text{C=O} \) is shifted downward in their complexes by 20-30 cm\(^{-1}\) indicating that the oxygen atom of ketonic group involved in coordination.

The bands at 1280 and 810 cm\(^{-1}\) in free ligand are probably due to \(\nu(C=S) \). Besides these bands a weak band 2500 cm\(^{-1}\) due to \(\text{SH} \) is also noticed in the spectra of free ligand. This is probably due to the presence of Thioenolic form in the ligand which on complexation does not shift either upward or downward, showing it does not take part in chelation(64).

In (C19H19N304S) -Mn(II) complexes the band at 1635, 1360; 1700; 805(1280) have been assigned to \(\nu(C=N) ; \nu(C=S+C\text{N}) \);
Fig. (5.2): I.R. Spectra of Mn(II) complexes.
$\textit{C=O}$ and $\textit{C=S}$ grouping on complexation the frequencies of $\textit{C=O}$, $\textit{-CH=N}$ and $\textit{C=S}$ grouping changes considerably. It is observed that coordination of sulphur considerably lower ($\textit{C=S}$) stretching frequency due to the drainage of electrons from the sulphur in chelation which in turn weaken the ($\textit{C=S}$) band (66–67), suggest coordination of the metal ion through sulphur atom of the $\textit{C=S}$ group.

All the ligands show two $\nu$(N–H) bands at 3400 and 670 cm$^{-1}$ which do not undergo any appreciable shift on complex formation, indicating non coordination of (NH$_2$) group.

In the far infra red region, the complex show new bands located in the range 480–400 cm$^{-1}$ are tentatively assigned to $\nu$(M–N) and $\nu$(M–S) stretching vibrations (68–70).

Brown and Kubota (71) reported different regions of $\nu$(M–X), where X=Cl/Br, depending upon the stereochemistry around coordinated metal ion. In octahedral and tetrahedral complexes $\nu$(M–Cl), frequency found around 250–200 cm$^{-1}$ and 350–280 cm$^{-1}$ as reported in literature (72–73). It is observed (74–75) that the complexes having only one coordinated halogen the stretching frequencies (M–Cl) are intermediate between those found in tetrahedral and octahedral complexes. The complexes show one weak broad band at about 400 cm$^{-1}$ which is assigned to (M–Cl) bonds.

$\textbf{Uranyl Complexes}$ – [UD$_2$(C$_{11}$H$_{13}$N$_3$O$_3$)$_2$] (CH$_3$COO)$_2$; [UD$_2$(C$_{11}$H$_{13}$N$_3$O$_3$)$_2$] (NO$_3$)$_2$; [UD$_2$(C$_{19}$H$_{19}$N$_3$O$_4$)$_2$] (NO$_3$)$_4$ On comparing the spectra of free ligands and the complexes, considerably reduction in the frequencies of $\textit{C=O}$, $\textit{-CH=N}$; and
Fig. (5.2): I.R. Spectra of Uranium Complexes

- $[\text{UO}_2(\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_3\text{S})_2](\text{CH}_3\text{COO})_2$
- $[\text{UO}_2(\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_3\text{S})_2](\text{NO}_3)_2$
- $[\text{UO}_2(\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_6\text{S})_2](\text{NO}_3)_4$
>C=S have been noticed. This shows these are the active sites of participation in complexation(76-77). Further the directions of the shift in the positions of all the bands in the spectra of the complexes are same, suggesting similar stoichiometry.

New bands appears in the far infrared region in the spectra of the complexes, assigned to $\sqrt{(M-N)}$, $\sqrt{(M-O)}$ and $\sqrt{(M-S)}$ vibrations(78).
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