CHAPTER III

PREPARATION AND CHARACTERIZATION OF METHYLENEBISTHIOACETIC ACID
WITH COBALT(II), NICKEL(II), COPPER(II) AND CADMIUM(II)
EXPERIMENTAL

Materials used and physical measurements

Methylenebisthioacetic acid (MBTAA) of 99.5 per cent purity was obtained from Evans Chemetics Inc., New York, U.S.A. and used without further purification. All other chemicals used were of analar grade or chemically pure grade. Double distilled water or absolute alcohol was used for preparing fresh solutions whenever required. The thermogravimetric analysis of Cu(II) complex was made on a station Redcroft Thermal Analyser 671b. For details of the methods and physical measurements please see in Chapter-II.

Preparation of complexes

Cobalt (II) - MBTAA Complex: 25 ml. of 0.25 M aqueous solution of cobalt chloride hexahydrate was added to an equimolar solution (75 ml.) of methylenebisthioacetic-acid in absolute alcohol. A few drops of concentrated NaOH solution were then added and the resulting mixture was refluxed for seven hours. The violet coloured solid was then separated out on cooling in ice cold water. It was filtered and washed several times with water,
ethanol and finally with ether and then dried in vacuum over calcium chloride. It was found to decompose at 270°C. It was slightly soluble in hot water and common organic solvents. Analysis: \( \text{Co(C}_5\text{H}_6\text{S}_2\text{O}_4 \), requires; Co, 23.28; C, 23.72; H, 2.39; S, 25.33 %. Found; Co, 23.34; C, 23.76; H, 2.35; S, 25.38 %.

**Nickel (II) - MBTAA complex:** A green solid complex was obtained by the same procedure as described above for Co(II), using nickel chloride hexahydrate. The complex decomposed at 265°C. It was slightly soluble in hot water and common organic solvents. Analysis: \( \text{Ni(C}_5\text{H}_6\text{S}_2\text{O}_4 \), requires; Ni, 23.21; C, 23.74; H, 2.93; S, 25.23 %. Found; Ni, 23.30; C, 23.71; H, 2.97; S, 25.16 %.

**Copper (II) - MBTAA complex:** A greenish-yellow solid complex was obtained by the same procedure reported above, using copper nitrate trihydrate. The complex decomposed at 160°C. It was slightly soluble in water and common organic solvents. Analysis: \( \text{Cu(C}_5\text{H}_6\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \), requires; Cu, 21.62; C, 20.44; H, 3.43; S, 21.82 %. Found; Cu, 21.64; C, 20.38; H, 3.34; S, 21.75 %.

**Cadmium (II) - MBTAA complex:** 50 ml of 0.2 M aqueous solution of cadmium acetate was added to an equimolar solution of methylenebisthioacetic acid (100 ml) in absolute alcohol. The white precipitate thus obtained was filtered and washed with water, alcohol and ether and then dried in vacuum over
calium chloride. It was found to decompose at $280^\circ$C. It was insoluble in water and most common organic solvents. Analysis: Cd(C$_5$H$_6$S$_2$O$_4$), requires; Cd, 40.93; C, 21.87; H, 2.20; S, 23.35%. Found; Cd, 40.61; C, 21.80; H, 2.12; S, 23.15%.
RESULTS AND DISCUSSION

The above reported decomposition temperatures which range between 160°C and 280°C indicate that the complexes are thermally quite stable. The molar conductance values in dimethylsulphoxide for Co(II), Ni(II), Cu(II) and Cd(II) as given in Table-4, are too low to account for any dissociation and lead to non-electrolytic nature of these complexes. The effective magnetic moment values are reported in Table-4.

**Cobalt (II) - MBTAA Complex:** The observed magnetic moment of 4.97 B.M., Table-4, is in agreement with the generally accepted values, 4.80 to 5.60 B.M.,(39) for high-spin octahedral Co(II)-complexes, suggests that the complex is octahedral.

The observed electronic spectra for Co(II)-complex is recorded in Fig.7 and the observed transitions are summarized in, Table-5. A perusal of, Table-5, shows that Co(II)-MBTAA electronic spectra consists of two main bands at 7.80 kK and 19.60 kK and a weak band at 16.00 kK consistent with the
Table 4 - Magnetic moment and Molar conductance measurements of MBTAA complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Temp. (°K)</th>
<th>$\chi_{M \text{uncorr.}} \times 10^5$</th>
<th>$\chi_{M \text{corr.}} \times 10^5$</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>Molar conductance (cm$^{-1}$ cm$^2$ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co($C_5H_6S_2O_4$)</td>
<td>Violet</td>
<td>298</td>
<td>10185.78</td>
<td>10276.30</td>
<td>4.97</td>
<td>2.1</td>
</tr>
<tr>
<td>Ni($C_5H_6S_2O_4$)</td>
<td>Green</td>
<td>298</td>
<td>4206.24</td>
<td>4297.26</td>
<td>3.21</td>
<td>2.2</td>
</tr>
<tr>
<td>Cu($C_5H_6S_2O_4$)$2H_2O</td>
<td>Greenish yellow</td>
<td>298</td>
<td>1413.16</td>
<td>1530.18</td>
<td>1.95</td>
<td>2.1</td>
</tr>
<tr>
<td>Cd($C_5H_6S_2O_4$)</td>
<td>White</td>
<td>298</td>
<td></td>
<td></td>
<td></td>
<td>Diamag</td>
</tr>
</tbody>
</table>

Calculated from $\mu_{\text{eff}} = 2.84 \left(\chi_{M \text{corr.}} \cdot T\right)^{\frac{1}{2}}$

34B
FIG. 7 DIFFUSE REFLECTANCE SPECTRA OF METHYLENEBISTHIOACETIC ACID COMPLEXES OF (a) COBALT (II) (b) NICKEL (II) AND (c) COPPER(II)
Table 5 - Diffuse reflectance spectra and ligand field parameters of Cobalt(II), Nickel(II) and Copper(II) complexes of MBTAA

| Complex       | Bands (kK) | Assignments | \( \frac{\text{Dq}}{\text{parameter}} \) \( \frac{\nu_2}{\nu_1} \) \( \frac{\beta}{\nu} \) \( \frac{\text{L.F.S.E.}}{\text{term}} \) | \( \frac{\text{Kcal/mol}}{\text{separa-}} \) \( \frac{1972 \times \text{B}^{2+} \text{(complex)}}{\text{cm}^{-1}} \) |
|---------------|------------|-------------|-----------------|-----------------|-----------------|-----------------|
| \( \text{Co(C_5H_5S_2O_4)} \) | 7.80       | \( 4_{1g}(F) \rightarrow 4_{2g}(\frac{\nu_1}{2}) \) | 848             | 858             | 2.05            | 0.883           | 12871           | 19.33           | 859             |
|               | 16.00      | \( 4_{1g}(\frac{\nu_2}{2}) \) | 19.60           | \( 4_{1g}(F)(\frac{\nu_3}{2}) \) | 840             | 920             | 1.66            | 0.884           | 13800           | 28.72           | -               |
| \( \text{Ni(C_5H_5S_2O_4)} \) | 8.40       | \( 3_{1g}(F) \rightarrow 3_{2g}(\frac{\nu_1}{2}) \) | 14.00           | \( 3_{1g}(F)(\frac{\nu_2}{2}) \) | 25.00           | \( 3_{1g}(F)(\frac{\nu_3}{2}) \) | 22.23           | -               | -               | -               |
| \( \text{Cu(C_5H_5S_2O_4)} \) \( 2\text{H}_2\text{O} \) | 13.00      | \( 2_{g} \rightarrow 2_{2g} \) | 1300            | -               | -               | -               | -               | -               | -               |

\* \( \beta = \frac{B}{B_0} \) where \( B_0 = \text{Racah's parameter for the gaseous ion; } \text{Co}^{2+} = 972 \text{ cm}^{-1}; \text{Ni}^{2+} = 1041 \text{ cm}^{-1} \) .
octahedral or tetragonal arrangement of the ligand. The observed transitions can, however, be interpreted in terms of metal ion surrounded by a weak ligand field of octahedral microsymmetry. The octahedral Co(II)-complexes, generally, exhibit three spin-allowed bands corresponding to the transitions $4T_{1g}^e(F) \rightarrow 4T_{2g}^e(F)(\nu_1)$, $4T_{1g}^e(F) \rightarrow 4A_{2g}^e(F)(\nu_2)$ and $4T_{1g}^e(F) \rightarrow 4T_{1g}^e(F)(\nu_3)$ in order of increasing energies in the absorption spectra. The transition $4T_{1g}^e(F) \rightarrow 4A_{2g}^e(F)(\nu_3)$ may or may not be observed because of the weakness and proximity to a strong $\nu_2$ transition (see chapter-II). The observed lowest energy band (Fig.7, Table-5) at 7.80 kK is, therefore, assigned as $\nu_1$ and the strong band at 19.60 kK as $\nu_2$. The weak band at 16.00 kK is, however, assumed as $\nu_3$ transition. These observed bands are quite similar to $\Sigma\text{Co(H}_2\text{O)}_6^{2+}$ (114) consisting of two main bands at 8.10 kK ($\nu_1$) and 19.40 kK ($\nu_2$) and a third weak band at 16.00 kK ($\nu_3$). To resolve the position of $\nu_3$ transition on the basis of octahedral symmetry, the ligand field parameters were calculated, by the use of semiempirical equations (91) and results are summarized in Table-5. The position of $\nu_3$ transition was then calculated using the relation (91), $\nu_3 = \nu_1 + 10 \text{Dq}$. The calculated value of $\nu_3$, 16.28 kK, is in good agreement with the observed band at 16.00 kK. Furthermore, Lever (92) has shown that in case of an octahedral Co(II)-complex the $\nu_3$ transition must have an energy approximately
twice but not greater than 2.2 times that of (ν₂) transition. The observed ratio \( \frac{\nu₂}{\nu₁} \) as 2.05 also supports the assignment of the band at 16.00 kK to (ν₂) corresponding to the transition \( ^4T_{1g} \longrightarrow ^4A_{2g} \).

Considering the above band positions for (ν₁), (ν₂) and (ν₃) the value of ligand field stabilization energy (L.F.S.E.) comes out to be 19.33 K.cal/mole. The calculated value, 0.883, of \( \beta \) indicates a low degree of covalency and the term separation, \( E(\ ^4P\ ) - E(\ ^4F\ ) \), of 12871 cm\(^{-1}\) corresponds to about 89 per cent of free ion value.

**Nickel (II) - MBTAA complex:** For high-spin octahedral Ni(II) complexes the available effective magnetic moment values lie in the range 3.20 to 3.40 B.M. (54). Our observed effective magnetic moment value of 3.21 B.M., Table-4, indicates clearly the octahedral nature of the complex.

The electronic spectra of Ni(II)-MBTAA complex is recorded in Fig.7 and Table-5. The electronic spectra in the range of 8.00 kK to 30.00 kK and the magnetic moment value of 3.21 B.M. are typically of octahedrally coordinated Ni(II)-complex. The observed energies of the spin-allowed transitions \( ^3A_{2g} \rightarrow ^3T_{2g} \), and \( ^3A_{2g} \rightarrow ^3T_{1g} \) at 8.40 kK, \( ^3A_{2g} \rightarrow ^3T_{1g} \) at 14.00 kK and \( ^3A_{2g} \rightarrow ^3T_{1g} \) at 25.00 kK agree well with those predicted from Leir and Ballhausen (115) energy level diagram for Ni(II) in a ligand field of octahedral
symmetry. These bands are also very similar to those of nickel aquate \[ \text{Ni(II)O}_6^{2+} \], (93).

The ligand field parameter, 10 Dq, was taken equal to the observed energy of the first triplet transition (\( \nu_1 \)) and the Racah parameter, B, was calculated by the substitution of (\( \nu_1 \)), (\( \nu_2 \)) and (\( \nu_3 \)) band energies in the secular equation \( 15B = \nu_2 + \nu_3 - 3\nu_1 \). The calculation includes the mutual interaction between the \( T_{1g} \) levels but ignores spin-orbit coupling. The observed separation, 11.00 kK, of (\( \nu_2 \)) and (\( \nu_3 \)) bands compared with the calculated value (94) of 11.04 kK, on the basis of octahedral symmetry, further confirms that the tetragonal distortion is rather small and the complex remains practically octahedral. Further more it has been reported that as Dq increases the interaction (95) between high-spin \( 3_{T_{1g}} \) (P) and \( 3_{T_{1g}} \) (F) excited states gradually lowers the ratio \( \frac{\nu_2}{\nu_1} \) from the theoretical value of 1.80 for the Ni(II)-complexes in octahedral symmetry. Our value of 1.66 for ratio \( \frac{\nu_2}{\nu_1} \) is in accord with the commonly reported value of 1.60 to 1.70 for Ni(II) - complex of octahedral symmetry and indicates a strong \( T_{1g} \) level interaction.

The ligand field stabilization energy calculated on the basis of octahedral symmetry comes out to be 28.72 K cal/mole. The calculated value, 0.884, of \( \beta \) indicates a low degree of covalency and the term-separation of 13800 cm\(^{-1}\) corresponds to about 87 per cent of free ion value. The
reduction of B after multiplying by \( \left( \frac{E_b \text{ Co}^{2+}}{E_b \text{ Ni}^{2+}} \right) \)gaseous (96),
the so called nephelauxetic effect, seems to be more effective
for Co(II) ion than for Ni(II) ion.

**Copper(II) - MBTA complex:** The majority of Cu(II)-
complexes show magnetic moment values of 1.75 to 2.20 B.M.
(97), near the spin only value of 1.73 B.M., indicating the
absence of any appreciable spin coupling between unpaired
electrons belonging to different copper atoms. The magnetic
moment of tetrahedral complexes are generally higher than the
square-planar or octahedral Cu(II) complexes (98). On the
other hand some complexes like copper (II) carboxylates
(99,100) and the so called tricoordinated Cu(II)-complexes
(101) show a subnormal magnetic moment < 1.73 B.M. but not
in all carboxyl group bridged polymers like Cu (II) benzoate
trihydrate (102) which has a magnetic moment of 1.87 B.M.
The observed magnetic moment value of 1.95 B.M., Table-4,
excludes strong spin-spin pairing but does not exclude a poly-
meric structure.

The electronic spectra of an octahedrally coordi-
nated Cu(II)- complex should normally exhibit one absorption
band due to \( ^2E_g \rightarrow ^2T_{2g} \) transition. State \( ^2E_g \) is highly sus-
ceptible to Jahn-Teller distortion and no Cu(II) - complex
should have a regular octahedral symmetry. The distortion
causes broadening or even splitting of the absorption band.
Therefore, all six coordinated Cu (II)-complexes are tetragonal with $D_{4h}$ or $C_{4v}$ symmetry or rhombic with $C_{2v}$ symmetry. In $D_{4h}$ symmetry the $E_g$ and $T_{2g}$ levels of the $^2D$ free ion term will further split into $E_{1g}$, $A_{1g}$ and $B_{2g}$, $E_g$ levels respectively and the energy level sequence will depend on the amount of the distortion (116). Hence three spin-allowed transitions are expected in the absorption spectra for a Cu (II) - complex in $D_{4h}$ or $C_{4v}$ symmetry. In $C_{2v}$ symmetry the $E_g$ level from $T_{2g}$ level splits further, however, only slightly and hence the splitting is difficult to detect. The observed spectrum shows only one broad band, Fig.7 and Table-5, at 16.00 kK. The complex being formally of $D_{4h}$ symmetry excludes a square-planar form because a square-planar Cu (II) shows two bands of nearly equal intensity at about 15.00 kK and 18.00 kK corresponding to the transitions $^2E_{1g} \rightarrow ^2A_{1g}$ and $^2E_{1g} \rightarrow ^2E_g$ (103-105) respectively. Therefore, the observed band is identified as d-d band $^2E_g \rightarrow ^2T_{2g}$ of octahedral Cu (II) ion.

**Cadmium (II) - MBTAA complex:** The Cd (II) forms stable tetrahedral complexes with sulphur containing ligands (106-108). Podlaha and coworkers (81a) have shown that Cd (II) complexes of thiopolycarboxylic acids are tetrahedral in nature and the sulphur in these complexes remains uncoordinated with the Cd (II).
The white solid Cd (II) - MBTAA complex was insoluble in water and was found to be diamagnetic, Table-4. The electronic spectra of the complex was practically identical with that of ligand, MBTAA. The following infrared measurements coupled with the diamagnetic nature and the insolubility of the complex in water as well as in organic solvents indicates that the cadmium ion is tetrahedrally coordinate and forms a polymeric net work.

**Infrared spectra:** The infrared spectra of the ligand and its complexes were recorded in the region 4000 - 400 cm\(^{-1}\) and are shown in Fig.8 to 12. The important bands and their tentative assignments, Table-6, were obtained with reference to the spectra of the other carboxylate complexes as well as those of thio and amino acid complexes (109-112). The C-S stretching band at 730 cm\(^{-1}\) of the ligand on complexation was found to shift to lower frequency indicating the coordination through sulphur. The symmetric COO\(^-\) stretching band in the ligand also shifted to lower frequency. The antisymmetric COO\(^-\) stretching band on complexation shifted to lower frequencies in the region 1580 - 1590 cm\(^{-1}\) for the complexes of Co (II), Ni (II) and Cu (II). These values correspond to those of glycinate and other amino acid complexes. The bridging carboxylic groups of metal carboxylate complexes also show an absorption in this region. Furthermore, the -OH deformation band at 810 cm\(^{-1}\) in the ligand disappear on
FIG. 8  INFRARED SPECTRUM OF METHYLENEBISTHIOACETIC ACID IN (a) PARAFFIN MULL AND (b) HALOCARBON MULL
FIG. 10 INFRARED SPECTRUM OF METHYLENEBISTHIOACETIC ACID COMPLEX OF NICKEL (II) IN (a) PARAFFIN MULL AND (b) HALOCARBON MULL
FIG. 11  INFRARED SPECTRUM OF METHYLENEBISTHIOACETIC ACID COMPLEX OF COPPER (II) IN (a) PARAFFIN MULL AND (b) HALOCARBON MULL
FIG. 12  INFRARED SPECTRUM OF METHYLENEBISTHIOACETIC ACID COMPLEX OF CADMIUM(II) IN PARAFFIN AND HALOCARBON MULLS
Table 6 - I.R. frequencies (cm⁻¹) of MBTAA and its complexes of Cobalt(II), Nickel(II), Copper(II) and Cadmium(II)

<table>
<thead>
<tr>
<th></th>
<th>$\tilde{\nu}_{-P}$</th>
<th>$\tilde{\nu}_{\text{Co(C}_5\text{H}_8\text{S}_2\text{O}_4)}$</th>
<th>$\tilde{\nu}_{\text{Ni(C}_5\text{H}_8\text{S}_2\text{O}_4)}$</th>
<th>$\tilde{\nu}_{\text{Cu(C}_5\text{H}_8\text{S}_2\text{O}_4) \cdot 2\text{H}_2\text{O}}$</th>
<th>$\tilde{\nu}_{\text{Cd(C}_5\text{H}_8\text{S}_2\text{O}_4)}$</th>
<th>Tentative assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>730 (S)</td>
<td>710 (S)</td>
<td>710 (m)</td>
<td>710 (S)</td>
<td>710 (S)</td>
<td>$\tilde{\nu}$ (C-S)</td>
<td></td>
</tr>
<tr>
<td>795 (S)</td>
<td>790 (S)</td>
<td>790 (w)</td>
<td>780 (m)</td>
<td>780 (m)</td>
<td>$\delta$ (C - C = O)</td>
<td></td>
</tr>
<tr>
<td>810 (m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$\delta$ (CH) deformation</td>
<td></td>
</tr>
<tr>
<td>1410 (S)</td>
<td>1400 (S)</td>
<td>1400 (S)</td>
<td>1400 (S)</td>
<td>1370 (m)</td>
<td>$\tilde{\nu}_{\text{sym}}$ (COO⁻)</td>
<td></td>
</tr>
<tr>
<td>1710 (S)</td>
<td>1590 (S)</td>
<td>1590 (S)</td>
<td>1580 (S)</td>
<td>1640 (S)</td>
<td>$\tilde{\nu}_{\text{assym}}$ (COO⁻)</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>190</td>
<td>190</td>
<td>180</td>
<td>270</td>
<td>$\Delta \tilde{\nu}$ (COO⁻)</td>
<td></td>
</tr>
</tbody>
</table>

S = strong,  m = medium,  w = weak
complexation as the ionization of the carboxylic group is envisaged in coordination. It is, therefore, concluded that coordination takes place through both sulphur and carboxylate groups. In case of Cd (II) – MBTAA complex the coordination sphere is formed besides the sulphur atoms by carboxylic oxygens. The position of the band of the antisymmetric COO\(^-\) stretching vibration as well as the difference of the wave numbers of the antisymmetric and symmetric COO\(^-\) vibrations higher than 220 cm\(^{-1}\) (Table-6) indicate the covalent character of the carboxyl metal bond (117,118). The observed strong band at 3340 cm\(^{-1}\) indicate the presence of water molecule in Cu (II) complex and the second observed band at 940 cm\(^{-1}\) was, however, assigned to coordinated water molecules which was further supported by thermogravimetric analysis (Fig.13) which indicated the loss of one molecule of water at 145°C (weight loss = 5.7 \%, theoretical 6.13 \%) and another at 160°C (weight loss = 12.60 \%, theoretical 12.26 \%). It is, therefore, concluded that Cu (II) complex is six coordinated and the two coordination positions are occupied by two water molecules.

On the other hand, in case of, anhydrous Co (II) and Ni (II) complexes, the magnetic and spectral data indicate that these complexes are octahedral, their coordination polyhedron must be completed by some intermolecular interaction, probably through free carboxyl oxygen as,
FIG. 13 THERMOGRAVIMETRIC ANALYSIS OF METHYLENEBISTHIOACETIC ACID COMPLEX OF COPPER (II)
where, $M = \text{Co(II)}$ and $\text{Ni(II)}$.

In the Cd(II)-MBTAA complex coordination number and the donating ability is saturated by two carboxylic oxygens and two sulphur atoms forming a tetrahedrally coordinated cadmium ion. The coordination of carboxylic oxygen further supported by the disappearance of $-OH$ deformation band in the complex. The insolubility of the complex seems to indicate a polymeric net work.

**Conclusion:** Methylenebisthioacetic acid, $\text{CH}_2(\text{S-}\text{CH}_2\cdot\text{COOH})_2$, forms stable complexes, with Co(II), Ni(II), Cu(II) and Cd(II) of the type $\text{ML}_X \cdot \text{H}_2\text{O}$ ($M = \text{metal}$, $L = \text{ligand}$, $X = 2$ for Cu(II) and $X = 0$ for Co(II), Ni(II) and Cd(II)). Their structures have been characterized on the basis of elemental analysis, magnetic moment, electronic and infrared spectral studies. The Co(II) and Ni(II) complexes are high-spin octahedral, the Cu(II) forms a distorted octahedral complex and the Cd(II) forms a tetrahedral polymeric structure. The coordination takes place through both sulphur and carboxylic oxygen groups. Relevant ligand field parameters have been calculated for these complexes.