Studies on stable Platinum (II) metal complexes of Ethylenediamine and Diethanolamine dithiocarbamates

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Abstract - This paper studies the structure and properties of platinum complexes of dithiocarbamate derivatives. Dithiocarbamate complexes are found to be very stable and are highly water soluble due to the presence of hydrophilic moiety in their structure. Such complexes have been used as metal complexing species for several decades. They form chelates with almost all metals ions in the Periodic table and have found numerous applications on biological, agricultural, electronics and act as stabilizing agents in electroless copper plating. In this work, ethylenediamine and diethanolamine dithiocarbamates are prepared and complexed with Pt(II) salts to form stable complexes. The complexes are characterized by Rapid Elemental Analysis. The structure of the stable complexes are confirmed with Electronic and I.R Spectral Analysis.

Index Terms - Dithiocarbamate; Platinum (II) Complexes; Ethylenediamine; Diethanolamine; Water soluble

I. INTRODUCTION

Co-ordination compounds that contain several donor atoms like oxygen, sulphur, nitrogen, and phosphorous were reported earlier [1]. In 1850 Debus [2] reported the strong metal binding property of dithiocarboxamic (DTC) acid and such chelates play an important role in biological, agricultural and Industrial fields were recognized earlier [3]. DTC act as effective stabilizing agents and are good corrosion inhibitors for copper in various electroless copper plating methods.[4,5] Substituted dithiocarbamates can be used to effectively treat both rinses and spent plating baths of electroless formulations. Studies show that DTC effectively precipitates copper from rinse water that contain complexing or chelating agents[6,7].

Dithiocarbamate is bidentate. The Dithiocarbamate ligands with “soft” sulphur donor atoms effectively complex with soft ions of transition element. It forms a four membered ring during chelations of “bis”, “tris” and “tetrakis” chelates. The metal complexation reaction is represented below.

Table.1 The trade name of some dithiocarbamate complexes and their application

<table>
<thead>
<tr>
<th>S.No</th>
<th>Dithiocarbamate/complexes</th>
<th>Trade name</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Disulfiram</td>
<td>DS [10]</td>
<td>Treatment of chronic alcoholism</td>
</tr>
<tr>
<td>3</td>
<td>Disodium ethylenebisdithiocarbamate</td>
<td>Nabam [12]</td>
<td>Filed fungicide</td>
</tr>
<tr>
<td>4</td>
<td>Sodium methylidithiocarbmate</td>
<td>Vapam [13]</td>
<td>Insecticide, herbicide</td>
</tr>
<tr>
<td>5</td>
<td>Sodium dimethyl dithiocarbamate</td>
<td>Ziram [14]</td>
<td>Vegetable fungicide</td>
</tr>
<tr>
<td>6</td>
<td>Zinc ethylene bi Dithiocarbamate</td>
<td>Zineb [15]</td>
<td>Fungicide</td>
</tr>
<tr>
<td>7</td>
<td>Manganese ethylene bi Dithiocarbamate</td>
<td>Maneb [16]</td>
<td>Fungicide</td>
</tr>
<tr>
<td>8</td>
<td>Tetrathiyulfuram disulfide</td>
<td>Thiram [17]</td>
<td>Seed treatment</td>
</tr>
<tr>
<td>9</td>
<td>Nickel(II) Dithiocarbamate</td>
<td>NBC [18]</td>
<td>Rubber industry</td>
</tr>
<tr>
<td>10</td>
<td>Bismuth(III) dimethyl dithiocarbamate</td>
<td>Bismate [19]</td>
<td>Vulcanization acceleration</td>
</tr>
<tr>
<td>11</td>
<td>Pyridine Dithiocarbamate</td>
<td>PDTC [20]</td>
<td>Antioxidant</td>
</tr>
</tbody>
</table>
In the above scheme, M \((\text{dtc})_n\) represents the metal complex of Dithiocarbamate in which the charge of metal ion is represented by “n”. The chelate ring system becomes more stable, owing to the resonance implicated in the –NCS\(_2\) of the ligand. The back donation from the metal having low energy “t” orbital to donor atoms stabilizes the chelate ring.

A partial double bond character between carbon and nitrogen is identified and this is attributed to the flow of electrons from the alkyl groups to nitrogen and then to the donor center via carbon by inductive effect (+I effect) and conjugation effect. Dithiocarbamate readily reacts with transition metals to form complexes and are colored in nature.

II. EXPERIMENTAL

2.1 Equipments

The molecular weights, of the complexes synthesized were determined using the Beckmann freezing point apparatus. The molecular formula of the complexes were ascertained using elemental analysis and molecular weights. HARAeus-CHN-O-RAPID ANALYSER (West Germany) was used for the estimation of carbon, hydrogen, sulphur and nitrogen contents present in the complexes. Electronic spectra data were obtained with (HITACHI 210 MODEL) using a regular quartz cuvette 10mm path length. Infrared spectra were recorded on a HITACHI 210 MODEL 200-4000cm\(^{-1}\) using KB, pellet.

The following chemicals were used to prepare the ligand and complexes:

2.2 Reagents

(i) Ethylenediamine (Qualigens)
(ii) Diethanolamine (Qualigens)
(iii) Ammonia solution (Fisher)
(iv) Carbon- disulphide (S.D. Fine Chem. Ltd)
(v) Absolute ethanol (Reid-de-Ham)
(vi) Dry ether (Qualigens)
(vii) Platinum (II) chloride (S.D. Fine Chem. Ltd)

2.3 Preparation of stock solutions

The 0.1 m stock solutions, Platinum (II) chloride were prepared by dissolving the required quantities of metal salts in H\(_2\)O:H\(_2\)SO\(_4\) (25:75).

2.4 Preparation of Ehtylenediamine Dithiocarbamate

M.M. Jones et al [21], reported the synthesis of Ehtylenediamine Dithiocarbamate in 1979. 45 ml of concentrated aqueous ammonia (28%) 20ml of Ethylene diamine (0.33 mole) and 42 ml of absolute ethanol were added to a beaker equipped with a magnetic stirrer. A mixture of 81 ml of carbon disulphide dissolved in 45 ml ethanol was added in drop wise to the reaction mixture with constant stirring such that the temperature did not rise above 48°C, while adding the mixture. The clear yellow reaction mixtures become turbid upon addition of about 23 ml of a mixture containing carbon disulphide and ethanol solution. The off white precipitate settle shortly after the addition was complete and the reaction mixture was treated with 150 ml of anhydrous ether and stirred for 1.5 hrs. The beaker was covered with a film and allowed to stand overnight. The crystal formed were collected on a filter paper and allowed to air dry.

2.5 Preparation of diethanolamine dithiocarbamate

Diethanolamine (0.81 moles) 78 ml and 200 ml of concentrated (28%) aqueous ammonia were added to a 500ml beaker equiied with a magnetic stirrer and thermometer. The reaction mixture was cooled in an ice bath to below 10°C then, 60 ml of ethanol containing 60 ml (0.99) moles of CS\(_2\) were added drop wise to the reaction mixture at such a rate that the temperature did not rise above 18°C. After the addition was complete the solution was stirred for 30 minutes and a yellowish precipitate formed. Then 100 ml of ethanol was added and stirred for additional 10 minutes. The precipitate was filtered washed with ether and dried in air. The yellow colour disappeared on drying.

2.6 Preparation of Pt (II) ethylenediamine dithiocarbamate

Pt (II) ethylenediamine dithiocarbamate (edadtc) was prepared by mixing an aqueous solution of platinum (II) chloride and EDADTC in the ratio of 1:2. EDADTC was added drop wise to the metal solution with constant stirring under hot conditions. The yield was found to be significant at pH 2.5. The reaction resulted in the formation of a yellow colored precipitate. This was filtered and dried.

2.7 Preparation of Pt (II) diethanolamine dithiocarbamate

Pt (II) diethanolamine dithiocarbamate (deadtc) chelate was prepared by mixing an aqueous solution of platinum (II) chloride and DEADTC in a ratio of 1:2. Pt (II) chloride was added drop wise to the DEADTC solution with hot and stirring. The pH of the above reaction was maintained at 2.5 since the yield was found to be better at this pH. The reaction resulted in the formation of a brown precipitate, which was filtered and dried.

III. RESULTS AND DISCUSSION

3.1 Physico-Chemical analysis

The ethylenediamine complex of Pt(II) was found to be green, but this Pt(II) complex of diethanolamine was brown. Both complexes were found to be soluble in water. The hydrophilic moieties in these complexes are responsible for their water solubility. In water, the conductance of 10\(^{-3}\)m solution of all the complexes prepared in deionised water was found to be < 10 m ohm\(^{-1}\). This shows that the complexes are covalent in nature [22]. These complexes decomposed on heating and a sharp melting was observed. Decomposition led to the formation of products such as thiocyanate, sulphides and non-stoichiometric sulphides of various compositions as reported earlier [23]. The elemental analysis of these complexes shows that the percentage composition of carbon, hydrogen, nitrogen, oxygen and sulphur corroborates with the theoretical value. The following results prove that the EDADTC and DEADTC complexes of platinum are bichelates.

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Table 2: Colour, solubility and melting point of the ethylenediamine and diethanolamine dithiocarbamates complexes of platinum (II).

<table>
<thead>
<tr>
<th>S.No</th>
<th>Complexes</th>
<th>Colour</th>
<th>Solubility</th>
<th>Melting point (˚C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Pt(II)-(edadtc)₂]</td>
<td>Yellow</td>
<td>Water</td>
<td>84-267 Melts with decomposition</td>
</tr>
<tr>
<td>2</td>
<td>[Pt(II)-(deadtc)₂]</td>
<td>Brown</td>
<td>Water</td>
<td>85-359 Melts with decomposition</td>
</tr>
</tbody>
</table>

Table 3: Elemental analysis, molecular weight and molecular formulae of the complexes in comparison with the ligands.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Ligands/Complex</th>
<th>Carbon %</th>
<th>Hydrogen %</th>
<th>Nitrogen %</th>
<th>Sulphur %</th>
<th>Oxygen %</th>
<th>Metal %</th>
<th>Molecular weight</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EDADTC</td>
<td>26.42*</td>
<td>5.86*</td>
<td>20.50*</td>
<td>46.96*</td>
<td>-</td>
<td>-</td>
<td>124.11*</td>
<td>C₆H₁₀N₂S₂</td>
</tr>
<tr>
<td>2</td>
<td>DEADTC</td>
<td>32.90*</td>
<td>7.71*</td>
<td>14.36*</td>
<td>34.98*</td>
<td>6.26*</td>
<td>-</td>
<td>178.52*</td>
<td>C₅H₁₄N₂S₂O</td>
</tr>
<tr>
<td>3</td>
<td>Pt(II)edadtc₂</td>
<td>15.38*</td>
<td>3.4*</td>
<td>10.76*</td>
<td>25.72*</td>
<td>-</td>
<td>40.82*</td>
<td>464.66*</td>
<td>C₆H₁₆N₄S₂Pt</td>
</tr>
<tr>
<td>4</td>
<td>Pt(II)deadtc₂</td>
<td>20.80*</td>
<td>5.02*</td>
<td>9.92*</td>
<td>20.36*</td>
<td>40.92*</td>
<td>33.23*</td>
<td>553.08*</td>
<td>C₁₀H₂₈N₄S₂O₂Pt</td>
</tr>
</tbody>
</table>

*Average of six determinations. The values in the Parenthesis indicate theoretical percentage of the elements.

3.2 Spectral analysis

3.2.1 Electronic spectral analysis

(i) [Pt(II)(edadtc)₂]

The yellow coloured Pt (II) complex of ethylenediamine dithiocarbamate showed two peaks with λ_max values at 240 nm and 299 nm. The shift in λ_max observed for the two peaks towards the UV region may be attributed to the complex formation as reported earlier [24]. The peaks at 240 nm and 299 nm in the UV region correspond to π-π* transition of S-C-N and S-C-S chromophore respectively [25-27].

(ii) [Pt(II)(deadtc)₂]

The brown colored complex, Pt [(deatc)₂] showed two peaks with λ_max at 248 nm and 348 nm. These shift in λ_max values in the UV region correspond to the ligand moiety and may be due to the effect of complex formation. The observed two peaks may be due to π-π* transition of S-C-N and S-C-S chromophore in the complexes.
3.2.2 IR Spectral analysis

(i) \([\text{Pt}^{\text{II}} (\text{edadtc})_2]\)

Thioureide [28] exhibit a band in between 1478.636 cm\(^{-1}\) and 1541.876 cm\(^{-1}\) which is due to the electron releasing tendency of nitrogen that leads to high electron density on sulphur atoms via the \(\pi\)-system. The strong band observed at 994.837 cm\(^{-1}\) is due to the stretching vibration of c-s band. The stretching vibration of \((\text{C-S} + \delta (\text{C-S}))\) are observed at 722.929 cm\(^{-1}\) and 675.428 cm\(^{-1}\). A strong band at 11 cm\(^{-1}\) indicates the formation of complex.

**Table 4: Characteristic IR Frequencies of \([\text{Pt}^{\text{II}} (\text{edadtc})_2]\) complex**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Frequency of observed (cm(^{-1}))</th>
<th>Characteristic correspond to</th>
<th>bared</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>311</td>
<td>(\gamma (\text{M-S}))</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>675.428, 722.92</td>
<td>(\delta (\text{SCS}) +\text{CS})</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>994.837</td>
<td>(\gamma (\text{C-S}))</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1478.636, 1541.876</td>
<td>(\gamma (\text{C-N}))</td>
<td></td>
</tr>
</tbody>
</table>
A partial double bond character between the carbon and nitrogen in thioureide is confirmed by the observation of a band in between 1435.602 cm\(^{-1}\) and 1514.711 cm\(^{-1}\). Bands correspond to \(\delta\) C-S and \((S-C-S)\) are observed at 710.51 cm\(^{-1}\) and 790.12 cm\(^{-1}\) respectively. A strong band of metal-sulphur linkage is seen at 382 cm\(^{-1}\) and this confirms the formation of a complex.

**Table 5 Characteristic IR Frequencies of \([\text{Pt}^{II}(\text{deadtc})_2]\) complex**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Frequency of bared observed (cm(^{-1}))</th>
<th>Characteristic bared correspond to</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>382</td>
<td>(\gamma) (M-S)</td>
</tr>
<tr>
<td>2</td>
<td>710.51,790.12</td>
<td>(\delta) (SCS) +CS</td>
</tr>
<tr>
<td>3</td>
<td>990.574</td>
<td>(\gamma) (C-S)</td>
</tr>
<tr>
<td>4</td>
<td>1435.602,1514.711</td>
<td>(\gamma) (C-N)</td>
</tr>
</tbody>
</table>
3.3 Structure of complexes

The structure of complexes of platinum (II) metal ion with ethylenediamine and diethanolamine dithiocarbamates are given below.

![Figure 5](image1.png)

**Figure 5** Structure of a bis-ethylenediamine dithiocarbamate complex of Platinum (II)

![Figure 6](image2.png)

**Figure 6** Structure of bis-diethanolamine dithiocarbamate complex of Platinum (II)

IV. CONCLUSIONS

The molecular formula of the [Pt(II)(edadtc)₂] complex is C₁₀H₂₈N₄S₄O₂Pt. It is brown and the molecular weight of the complex has been found to be 559.4. The molecular weight determination and rapid elemental analysis supports the fact that the complexes are water soluble and are bichelates. The electronic spectral analysis and IR Spectral analysis supports the fact that both complexes are covalent and are very stable.

REFERENCES


AUTHORS

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