

# 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 presences 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

reported earlier [1]. In 1850 Debus [2] reported the strong metal binding property of dithiocarbamic (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].

The chelating property of DTC arises from the  $\pi$ -electron flow from the nitrogen atom to the sulphur atom via a plane delocalized  $\pi$ -orbital system. The net effect of such an electron flow is strong donation to metal, resulting in a high electron density on the metal [8]. In 1956, Chatt [9] and his co-workers reported a detailed IR study of a number of dithiocarbamates complexes and conclude that the resonance form does indeed contribute to the structure to a considerable extent.

## I. INTRODUCTION

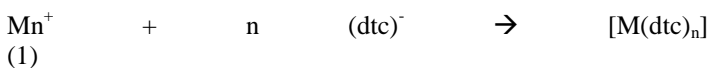
Co-ordination compounds that contain several donor atoms like oxygen, sulphur, nitrogen, and phosphorous were

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

S.No	Dithiocarbamate/complexes	Trade name	Applications
1	Disulfiram	DS [10]	Treatment of chronic alcoholism
2	Ferric dimethyl dithiocarbamate	Febam [11]	Fruit fungicide
3	Disodium ethylenebisdithiocarbamate	Nabam [12]	Filed fungicide
4	Sodium methyl dithiocarbamate	Vapam [13]	Insecticide, herbicide
5	Sodium dimethyl dithiocarbamate	Ziram [14]	Vegetable fungicide
6	Zinc ethylene bi Dithiocarbamate	Zineb [15]	Fungicide
7	Manganese ethylene bi Dithiocarbamate	Maneb [16]	Fungicide
8	Tetramethylthiuram disulfide	Thiram [17]	Seed treatment
9	Nickel(II) Dithiocarbamate	NBC [18]	Rubber industry
10	Bismuth(III) dimethyl dithiocarbamate	Bismate [19]	Vulcanization acceleration
11	Pyridine Dithiocarbamate	PDTC [20]	Antioxidant

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.



In the above scheme,  $M(dte)_n$  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 200-4000 $cm^{-1}$  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  $H_2O:H_2SO_4$  (25:75).

### 2.4 Preparation of Ethylenediamine Dithiocarbamate

M.M. Jones et al [21], reported the synthesis of Ethylenediamine 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 settled 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 equipped 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.

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

S.No	Complexes	Colour	Solubility	Melting point (°C)
1	[Pt(II)-(edadc) <sub>2</sub> ]	Yellow	Water	84-267 Melts with decomposition
2	[Pt(II)-(deadc) <sub>2</sub> ]	Brown	Water	85-359 Mels with decomposition

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

S.No	Ligands/Complex	Carbon %	Hydrogen %	Nitrogen %	Sulphur %	Oxygen %	Metal %	Molecular weight	Molecular formula
1	EDADTC	26.42* (26.45)	5.86* (5.92)	20.50* (20.56)	46.96* (47.07)	-	-	124.11* (136.24)	C <sub>3</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub>
2	DEADTC	32.90* (32.94)	7.71* (7.71)	14.36* (15.38)	34.98* (35.21)	6.26* (8.73)	-	178.52* (182.16)	C <sub>5</sub> H <sub>14</sub> N <sub>2</sub> S <sub>2</sub> O
3	Pt(II) edadc <sub>2</sub> ]	15.38* (15.40)	3.4* (3.45)	10.76* (11.98)	25.72* (27.43)	-	40.82* (41.72)	464.66* (467.56)	C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> S <sub>4</sub> Pt
4	Pt(II) deadc <sub>2</sub> ]	20.80* (21.45)	5.02* (5.04)	9.92* (10.01)	20.36* (22.93)	40.92* (5.68)	33.23* (34.87)	553.08* (559.4)	C <sub>10</sub> H <sub>28</sub> N <sub>4</sub> S <sub>4</sub> O <sub>2</sub> Pt

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

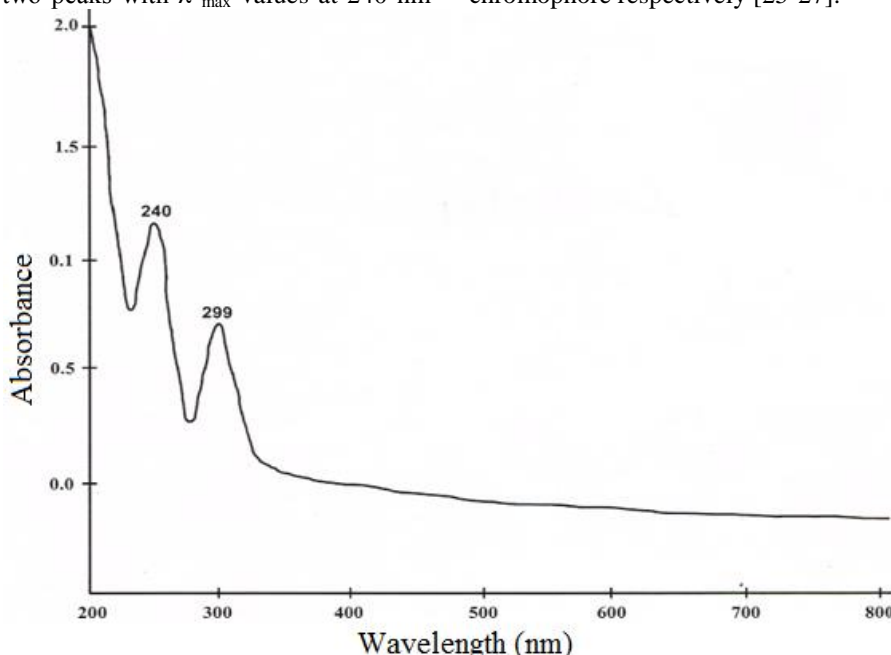
### 3.2 Spectral analysis

#### 3.2.1 Electronic spectral analysis

##### (i) [Pt<sup>(II)</sup>(edadc)<sub>2</sub>]

The yellow coloured Pt (II) complex of ethylenediamine dithiocarbamate showed two peaks with  $\lambda_{max}$  values at 240 nm

and 299 nm. The shift in  $\lambda_{max}$  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  $\pi-\pi^*$  transition of S-C-N and S-C-S chromophore respectively [25-27].



**Figure.1 Electrtonic Spectrum of Platinum (II) bisethylenediamine dithiocarbamate**

##### (ii) [Pt<sup>(II)</sup>(deadc)<sub>2</sub>]

The brown colored complex, Pt [(deadc) 2] showed two peaks with  $\lambda_{max}$  at 248 nm and 348 nm. These shift in  $\lambda_{max}$  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  $\pi-\pi^*$  transition of S-C-N and S-C-S chromophore in the complexes.

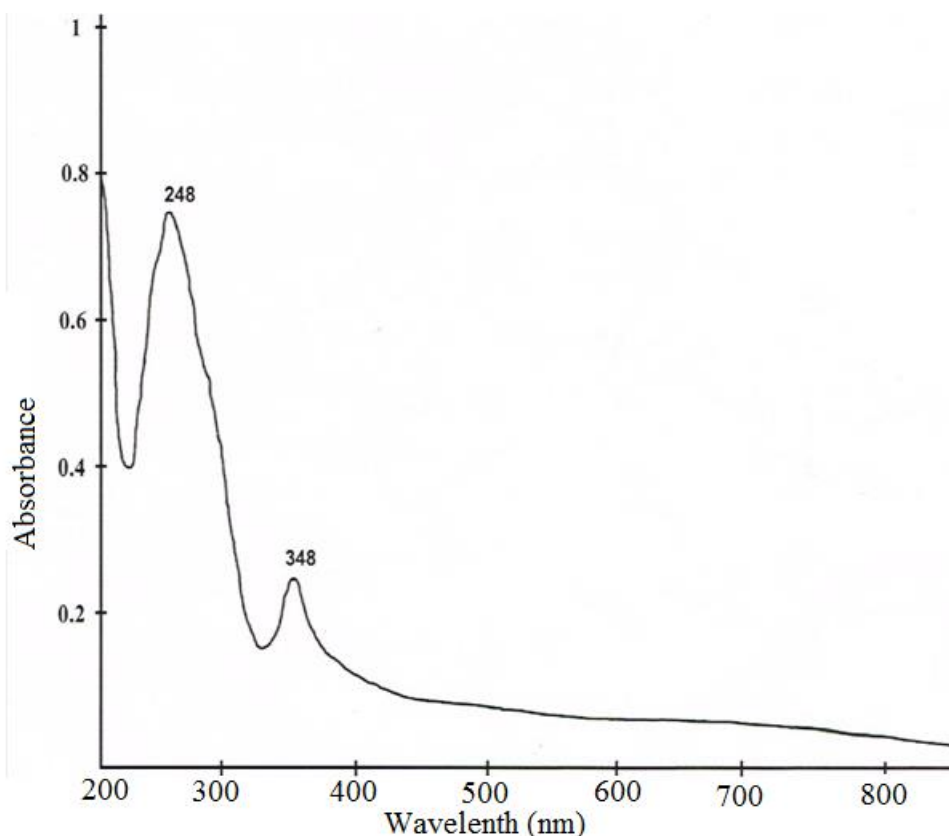


Figure.2 Electrtonic Spectrum of Platinum (II) bisdiethanolamine dithiocarbamate

Table.4 Characteristic IR Frequencies of  $[Pt^{(II)}(edadc)_2]$  complex

3.2.2 IR Spectral analysis

(i)  $[Pt^{(II)}(edadc)_2]$

Thioureide [28] exhibit a band in between  $1478.636\text{ cm}^{-1}$  and  $1541.876\text{ cm}^{-1}$  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  $994.837\text{ cm}^{-1}$  is due to the stretching vibration of c-s band. The stretching vibration of (C-S+  $\delta$  (S-C-S) are observed at  $722.929\text{ cm}^{-1}$  and  $675.428\text{ cm}^{-1}$ . A strong band at  $11\text{ cm}^{-1}$  indicates the formation of complex.

S.No	Frequency of bared observed ( $\text{cm}^{-1}$ )	Characteristic bared correspond to
1	311	$\gamma$ (M-S)
2	675.428,722.92	$\delta$ (SCS) +CS
3	994.837	$\gamma$ (C-S)
4	1478.636,1541.876	$\gamma$ (C-N)

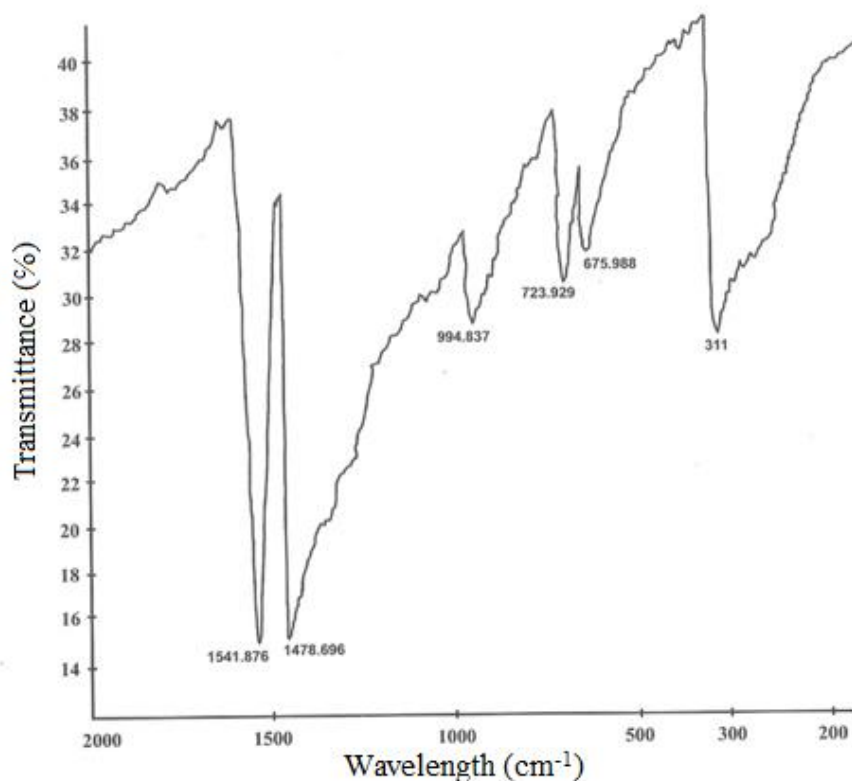


Figure.3 IR Spectrum of Platinum (II) bisethylenediamine dithiocarbamate

(ii) [Pt(II)(deadtc)<sub>2</sub>]

A partial double bond character between the carbon and nitrogen in thioureide is confirmed by the observation of a band in between 1435.602cm<sup>-1</sup> and 1514.711 cm<sup>-1</sup>. Bands correspond to δ C-S and (S-C-S) are observed at 710.51 cm<sup>-1</sup> and 790.12 cm<sup>-1</sup> respectively. A strong band of metal-sulphur linkage is seen at 382 cm<sup>-1</sup> and this confirms the formation of a complex.

S.No	Frequency of observed (cm <sup>-1</sup> )	Characteristic correspond to
1	382	γ (M-S)
2	710.51,790.12	δ (SCS) +CS
3	990.574	γ(C-S)
4	1435.602,1514.711	γ(C-N)

Table.5 Characteristic IR Frequencies of [Pt<sup>(II)</sup>(deadtc)<sub>2</sub>] complex

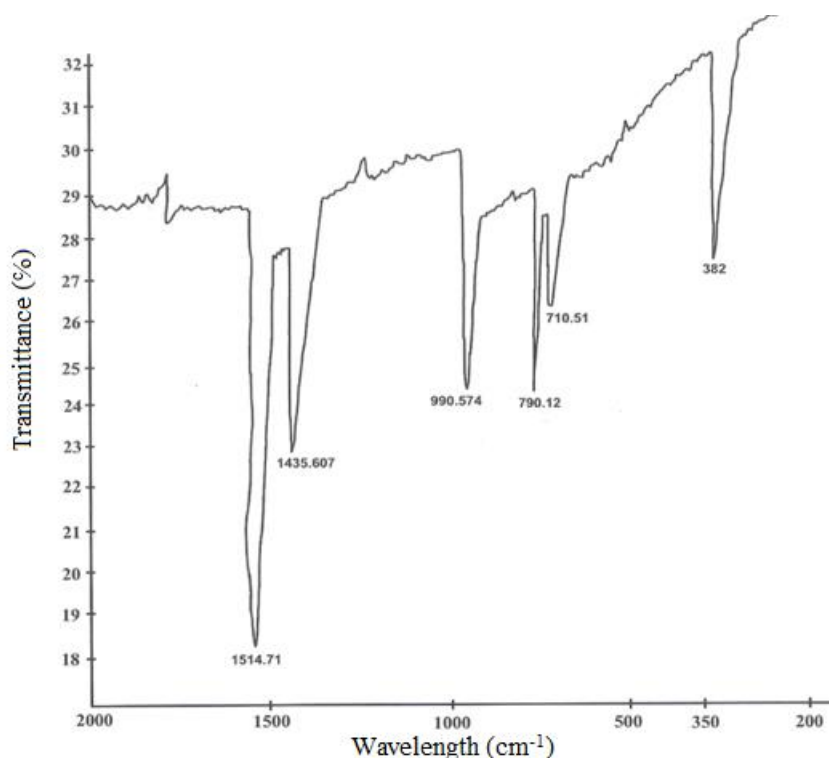


Figure.4 IR Spectrum of Platinum (II) bisdiethanolamine dithiocarbamate

### 3.3 Structure of complexes

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

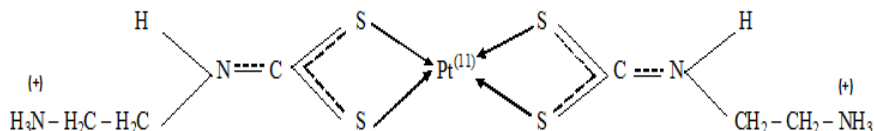


Figure.5 Structure of a bis-ethylenediamine dithiocarbamate complex of Platinum (II)

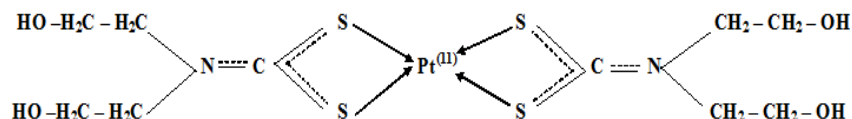


Figure.6 Structure of bis-diethanolamine dithiocarbamate complex of Platinum (II)

## IV. CONCLUSIONS

The molecular formula of the  $[Pt^{(II)}(edadc)_2]$  complex is  $C_6H_{16}N_4S_4Pt$ . It is yellow and the molecular weight of the complex has been found to be 467.56. The molecular formula of the  $[Pt^{(II)}(deadc)_2]$  complex is  $C_{10}H_{28}N_4S_4O_2Pt$ . 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.

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