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# Synthesis and characterization of cadmium and zinc dithiocarbamate complexes derived from α-aminoacid L-proline

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Dithocarbamate metal complexes have been used to prepare nanoparticles and nanowires of a variety of semiconducting metals including CdS, ZnS, PbS, and EuS. The two new cadmium (II) L-Proline Dithiocarbamate and zinc (II) L-proline dithiocarbamate complexes have been synthesized. Both of the metal complexes are able to produce semiconductor sulphides, nanoparticles which are applicable in the electronic industries. The amino acid L-proline has the unique property, it is the only DNA determined amino acid which has a secondary five membered cyclic amino group alpha to the carbonyl group in the biosystem. Metal dithiocarbamate which is derived from L-proline is able to produce the corresponding metal sulphides as nanoparticles and nanowire. This is very much applicable in Thin Film Technology. Besides, the Zinc complex is used as a drug in increasing the immune system of the body against bacteria and viruses. Zinc dithiocarbamate derived from alpha aminoacid is biocompatible so that it can be used as pharmaceutical products. The two complexes exhibit the important $NCS_2$ peak from 202.73-215 in $^{13}$C NMR, attributing to the presence of the dithiocarbamate ligand. A resonance signal around δ 4.92 is due to COOH-proton in $^{1}$H NMR. The complexes also shows the important IR frequencies, ν(CN), ν(CS) and ν(CO) in the ranges 1443-1430 cm$^{-1}$, 954-945 cm$^{-1}$ , and 1720-1712 cm$^{-1}$ , respectively. LMCT transitions have been observed at **λ** 214 nm for the Cd complex. Based on the thermo gram the complexes are stable up to 200°C, and fast decomposed to produce $M(SCN)_2$ at 400°C and finally MS(M= Cd), as residue at 600°C by slow steps. From FTIR, $^{1}$H, $^{13}$C NMR, only dithiocarbamate sulphurs are coordinated to metal and not the carboxylate oxygen in the two complexes.

**Keywords:** Cadmium, Dithiocarbamate, Insecticides, Zinc, L-Proline, Sensors, Nanoparticles

A number of metal dithiocarbamates have been synthesized and characterised in recent years. Special interest in the study of metal dithiocarbamates have aroused because of the striking structural features exhibited by this class of compound[1]. Dithiocarbamate complexes have received most attention in the previous decades because of their number of applications such as insecticides herbicides, fungicides in agriculture, accelerators in vulcanization, scavengers in wastewater treatment[2-5], supramolecular chemistry[6,7]. The metal dithiocarbamate complexes have been used to prepare nanoparticles and nanowires of a variety of semiconducting metals including CdS, ZnS, PbS and EuS[8-10]. Many reviews have appeared about the preparation, application and structural aspects of the dithiocarbamate complexes[11,12]. Preparation of amino acid dithiocarbamate complexes is a new avenue in dithiocarbamate chemistry[13-16]. Both of the metal complexes are able to produce semiconductor sulphides, nanoparticles which are applicable in the electronic industries. The amino acid L-Proline has a unique property where it is the only DNA determined amino acid which has a secondary five membered cyclic amino group alpha to the carbonyl group in the biosystem[27]. Metal dithiocarbamate derived from L-proline is able to produce the corresponding metal sulphides in nanoparticles and nanowire. This is very much applicable in Thin Film Technology. Besides, the Zinc complex is used as a drug in increasing the immune system of the body against bacteria and viruses. It has been noted that the dithiocarbamate formed with α–amino acid L-proline is able to provide tridentate dinegative binding sites from their two sulphurs and carboxylate oxygen for complexation. A perusal of the literature reveals that metal complexes with dithiocarbamate derived from amino acids are very few. Besides Cd (II) and Zn (II) dithiocarbamates have wide spectrum of application in smarter material synthesis as precursor. Present study focusses on the preparation of the ligand, L-proline dithiocarbamate and synthesis of Cd (II) and Zn(II)complexes of L-proline dithiocarbamate following the method of synthesis as described by

Schanabel, Deuten and Klar[17] with slight modification. The newly synthesized complexes were characterized by CHNS elemental analysis, ESI-Mass, UV-Visible, FTIR, $^1$H, $^{13}$C NMR spectra, TGA and DTG analysis to further establish their structures.

## Experimental Section

### Reagents, apparatus and synthetic procedure

All chemicals and solvents were purchased and used as received from suppliers. Sodium hydroxide and L-Proline (LOBA Chemicals India), carbon disulphide and hydrochloric acid (Merck, Germany), ethanol (Hayman England), Cadmium Nitrate and Zinc Sulphate (SD Fine Chem,India). Carbon, hydrogen, nitrogen and sulphur elemental analysis were performed at Department of Chemistry IIT, Chennai, India. Cadmium and Zinc were estimated by 8-hydroxyquinolate method[18]. The conductivity of the $10^{-3}$ M ethanolic solutions of the complexes were measured with Precision conductivity bridge model WER/JAV NTW, WEST Germany. FTIR Spectra were recorded in the range 4000-450 cm$^{-1}$ using a Bruker IFS 66 V E spectrophotometer on KBr disc. $^1$H NMR spectra were recorded on a Bruker A VIII 500 MHz spectrometer in MeOD. The $^{13}$C NMR spectra were recorded on a Bruker A VIII 50 MHz spectrometer in deuterated methanol. ESI–Mass spectra were obtained from a micro mass JEOL GC mass spectrometer. UV–Visible spectra were recorded on a UV–VIS– NEAR–IR – Varian Carry 5E spectrometer in methanol. The thermal analyser (model TGAQ 500 V20.10 Build 36) was used to study the thermal decomposition of dtc complexes. The data was analysed by Universal VA.5A.TA. Analysis computer program. Samples were placed in an alumina crucible and heated from 50°C to 830°C at a heating rate of 20°C / min in a nitrogen atmosphere.

### Synthesis of L – Proline dithiocarbamate ligand

L–proline (0.1 mol, 11.53 g ) dissolved in 50 mL of ethanol, was mixed with (0.2 mol, 8g) NaOH and kept in an ice bath. The reaction was conducted at very low temperature, the temperature of the reaction mixture was maintained < 4°C throughout the process at atmospheric pressure. To that cold $CS_2$ (0.1 mole, 6.2 mL) in 25 mL of ethanol was added drop wise and stirred continuously using a magnetic stirrer. After complete mixing, the solution was stirred for another half an hour and the temperature was maintained < 4°C. The disodium salt of the dithiocarbamate formed was highly hygroscopic. In addition to large excess of acetone, a small amount of the $Na_2$(L – Prodtc). Precipitated as a white salt when exposed to air the precipitated absorbed water and becomes pasty liquid. For the preparation of the complexes, a freshly prepared solution of the $Na_2$(L – Prodtc) was used. The synthesis of ligand is depicted in Scheme 1.

Reaction condition: Temperature < 4°C, atmospheric pressure.

### Synthesis of Cadmium (II) L – Proline dithiocarbonate (complex1) and Zinc (II) L– Proline dithiocarbonate (complex 2)

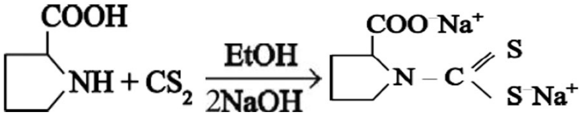
The metal salt (1 mmol – 0.308g $Cd(NO_3)_2 . 4H_20$, 0.2879 g $ZnSO_4 . 7H_20$) was dissolved completely in 25mL of cold water and 25ml of 4N HCl, was mixed with freshly prepared $Na_2$(L–Prodtc) (0.05 mol). A white coloured solid was precipitated. The precipitate was allowed to stand for an hour, filtered, washed. The complex was recrystallized from ethanol, dried in a desiccator. Both complexes were synthesized accordingly to the molar ratios of 2:1 for $Na_2$ (L–Prodtc): metal. The synthesis of complexes 1 and 2 is depicted in Scheme 2.

Reaction condition: Room temperature, atmospheric pressure.

## Results and Discussion

### Synthesis

The dithiocarbamate ligand was successfully synthesised via in situ method in equimolar amounts between α–amino acid, L – Proline and $CS_2$ in a basic condition at< 4°C. The complexes were successfully


Scheme 1 — Reaction mechanism of $Na_2$(L – Prodtc)ligand.

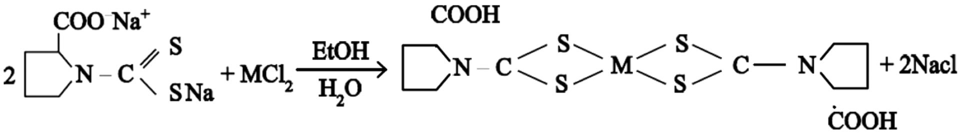

Scheme 2 — Reaction mechanism of complex 1 (M = Cd) and complex 2 (M = Zn).

Table 1 — Physical and Elemental analysis of complexes 1 and 2.

| Complex | Molecular formula | Yield (%) | Physical form | M.Wt. (g/mol) | Elemental analysis (%) Observed (Expected) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | S | M |
| 1 | $C_{12}H_{16}N_2S_4Cd$ | 74 | White powder | 429 | 29.57<br>(29.23) | 3.50<br>(3.27) | 4.45<br>(4.78) | 26.38<br>(26.0) | 22.54<br>(22.80) |
| 2 | $C_{12}H_{16}N_2S_4Zn$ | 68 | White powder | 382 | 32.59<br>(32.28) | 3.35<br>(3.61) | 5.98<br>(6.27) | 28.38<br>(28.73) | 14.45<br>(14.76) |

prepared from the reaction between respective metal (II) salts dissolved in cold water with freshly prepared ligand in a ratio1:2. Complexes 1 and 2 were produced with good yield approximately 70% which proves that the adopted method is a suitable method of synthesis[17]. Both complexes are white coloured powder and stable towards air at room temperature. They are insoluble in water and soluble in ethanol. The complexes were analyzed for metal and CHNS. The analytical data are given in Table 1. These data are consistent with four-fold coordination of the metal complexes.

### Fourier – Transform infrared spectroscopy (FTIR)

Spectral Studies: The FTIR Spectra of the complexes were recorded in KBr matrix as shown in the Fig 1A – 1B. The IR spectral data are present in Table 2

The stretching in region 1443–1430 $cm^{-1}$ are due to C – N groups of the $NCS_2$ moiety whose position correspond to a partial double bond character. The stretching observed in the region 954-945 $cm^{-1}$ corresponds to the C – S vibrations one typical of a bidentate bonding of the dithiocarbamate unit to the metal cation[19,20]. The ν (CO) band in the free carboxylic acid group occurs at 1720-1712 $cm–^{1}$ in the spectra of the complexes[13-20]. M-Sulfur signal are usually appeared below 300 wavenumber $cm^{-1}$ has not been observed, because of the spectrum has been recorded up to 450 $cm^{-1}$ The C-S stretching after coordination of metal has been shifted from 11-20 $cm^{-1}$ lower range. The C-N stretching after coordination of metal has been shifted from 20-33 $cm^{-1}$ higher range were observed. These data further confirm that although the free amino acids contains the carboxylate anion, in the complexes the amino acids are in the carboxylic (acidic) form, suggesting that coordination to metal (II) takes place through the sulphur atoms of the ligand molecule. The FTIR spectrum was recorded between the range 4000-450 wavenumber $cm^{-1}$, the stretching frequency for metal-sulphur (M-S) is below 300 wavenumber $cm^{-1}$ is not observed.

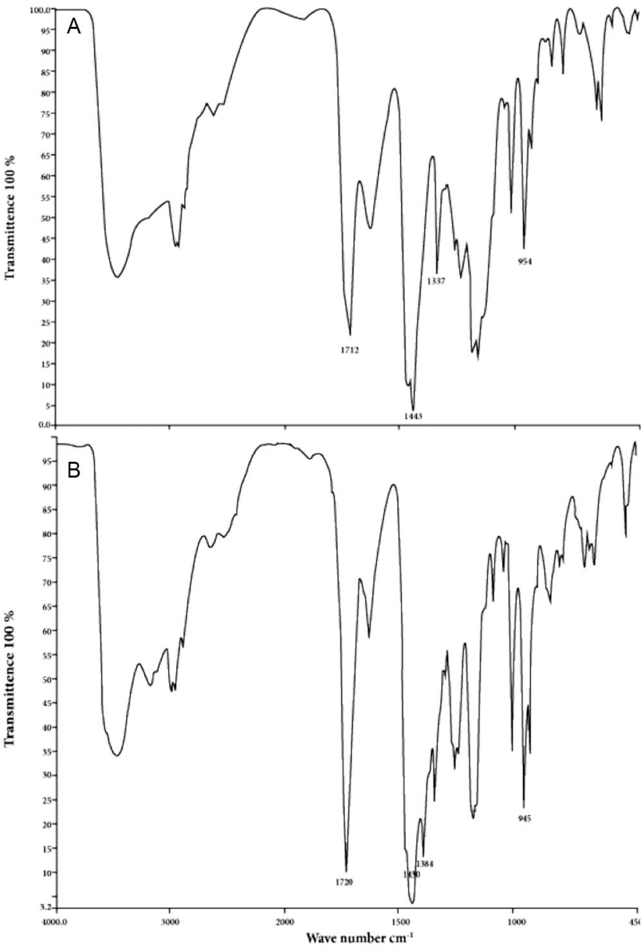


Fig. 1A — IR spectrum of Cd $(L\text{-}Prodtc)_2$ in KBr Matrix and (B) IR spectrum of Zn $(L\text{-}Prodtc)_2$ in KBr Matrix.

### Ultra Violet – Visible spectral studies

The electronic spectra of both the metal complex were recorded in methanol in the region 200–800 nm. The spectra of complex 1 , in addition to intra ligand bands, contains bands which are attributed to charge transfer (CT) transition of the types L→M. So the bands at λ 214nm for the Cd complex. The band at λ 262nm is due to intra ligand п→п* transitions located on the N—C—S. The other band located at λ 295nm arises from п→п* transitions, but within the S—C—S group. A tetrahedral geometry may be proposed for Cd (II) – L – Prodtc complex[21,22] (Fig. 2) .

Table 2 — Important FTIR observed frequencies (cm$^{-1}$) of complexes 1 and 2

| Observed Frequencies | ν(CN) | ν$_{as}$(CS) | ν$_{as}$(COO$^{-}$) | ν$_{s}$(COO$^{-}$) |
|---|---|---|---|---|
| Na$_2$(L-prodtc) Ligand | 1410 | 965 | 1610 | 1356 |
| Complex 1 | 1443 | 954 | 1712 | 1337 |
| Complex 2 | 1430 | 945 | 1720 | 1384 |

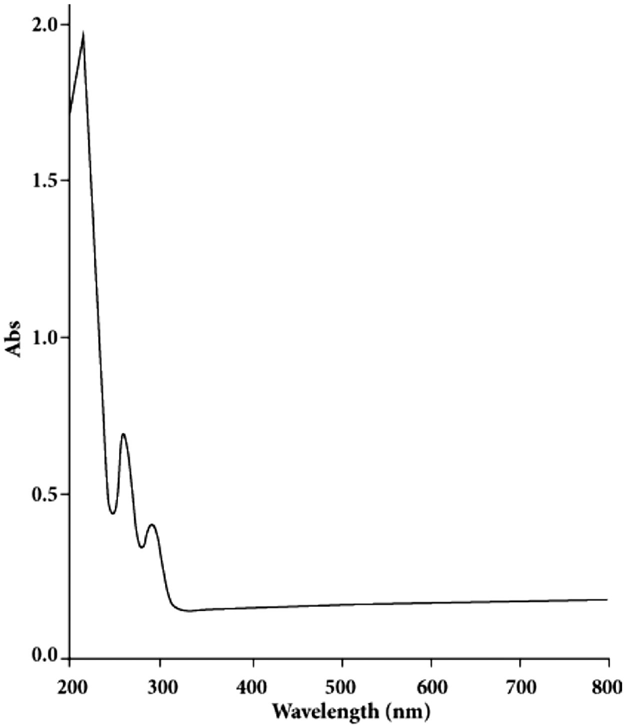


Fig. 2 — Absorption spectrum of Cd(L-Prodtc)$_2$ in methanol.

**Nuclear Magnetic Resonance Spectroscopy**

The $^{1}$H and $^{13}$C NMR spectra were recorded in MeOD at room temperature. The spectra depicted in Figs 3 and 4 and the spectral date are presented in Table 3.

The $^{1}$H NMR Chemical Shifts of both the complexes showed three multiplet resonance signals around δ 1.990-3.921 ppm is assigned to –CH$_2$ protons of 3CH$_2$, 2CH$_2$ and 4CH$_2$ respectively. The multiplet resonance signal around δ 4.058-4.846 ppm is assigned to –CH proton of 1CH position. The L – Prodtc ligand gives a resonance around δ 4.920 ppm is due to 5COOH proton[23,24].

In $^{13}$C NMR, the carboxylate carbon and 1CH carbon of the ligand appear as a singlet around δ 173.137 and δ 67.67 ppm. The carbon of pyrrolidine ring in ligand appears as a set of three resonance signals. The resonance signals around δ 24.633, δ 31.453 and δ 54.531 ppm are assigned to C3,C2 and C4 carbons of pyrrolidine ring of L–Prodtc respectively, the resonance peak around δ 202.732 ppm is assigned to the 6CSS carbon[25].

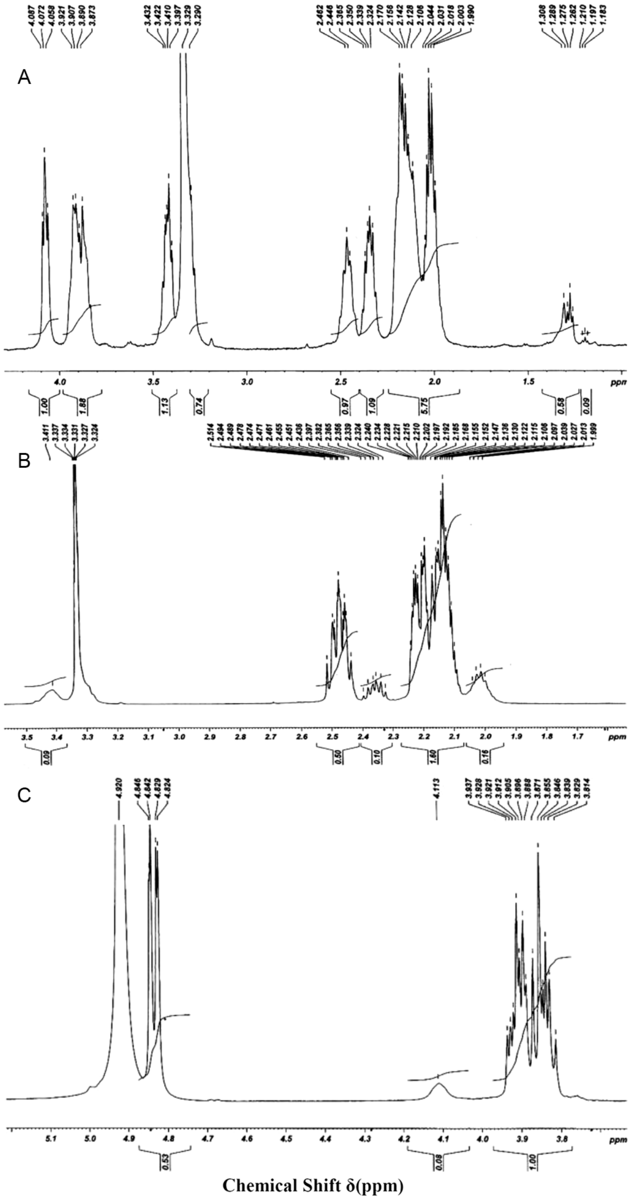


Fig. 3 — $^{1}$H NMR spectrum of (A) L-(Prodtc)$_2$ , (B) Cd (L-Prodtc)$_2$ and (C) Zn (L-Prodtc)$_2$ Chemical shift δ(ppm)

**Thermogravimetric analysis of Cd (II) (L- Prodtc)$_2$ Complex 1.**

The TGA and DTG curves of the complex 1 is shown in Fig 5A, 5B and the results are tabulated in Table 4.

Table 3 —$^1$H and $^{13}$C NMR spectral data of complexes 1 and 2. Chemical Shift (ppm)

| NMR | Complex 1 | Complex 2 |
|---|---|---|
| $^1$H | 1.990 - 2.170 (m,2H, $H_3$ –$CH_2$) | 1.999 - 2.039 (m,2.H, $H_3(CH_2)$ |
| | 2.324 - 2.462 (m,2H, $H_2$ –$CH_2$) | 2.097 - 2.397 (m,2H, $H_2$ –$CH_2$) |
| | 3.290 - 3.921 (m,2H, $H_4$ –$CH_2$) | 3.814 - 3.937 (m,2H, $H_4$ –$CH_2$) |
| | 4.058 - 4.087 (m,1H, $H_1$ – CH) | 4.824 - 4.846 (m,1H, $H_1$ – CH) |
| | 4.904 (S,1H, $H_5$ – COOH) | |
| $^{13}$C | 215 ($C_6$ – CSS), 179 ($C_5$ – COO) | 202.73 ($C_6$ – CSS) 173.13($C_5$ – COO) |
| | 67.69 ($C_1$ – CH), 55.713 ($C_4$ – $CH_2$) | 66.39 ($C_1$ – CH) 54.53($C_4$ – $CH_2$) |
| | 31.699 (S, $C_2$ – $CH_2$), 28.94($C_3$ – $CH_2$) | 31.45 ($C_2$ – $CH_2$), 24.63 ($C_3$ – $CH_2$) |

Table 4 —Thermogravimetric analysis of Cd (L- Prodtc)$_2$ Complex 1

| Temp°C | DTG Peak Temp °C | % Weight loss Observed (expected) | % Weight remaining Observed (expected) | Probable decomposition |
|---|---|---|---|---|
| 50–200 | 183 | 13.85<br>(14.26) | 86.15<br>(85.74) | $CdL_2.2H_2OEtOH$, →<br>$CdL_2$ |
| 200–400<br>(fast) | 243.9 | 45.26<br>(46.02) | 40.89<br>(39.72) | $CdL_2$→ $Cd(SCN)_2$ |
| 400–600 | 537 | _ | 20.51 | Cd $(SCN)_2$ |
| (slow) 600–830<br>(fast) | 812 | _ | (19.5) | ↓ CdS→Cd |

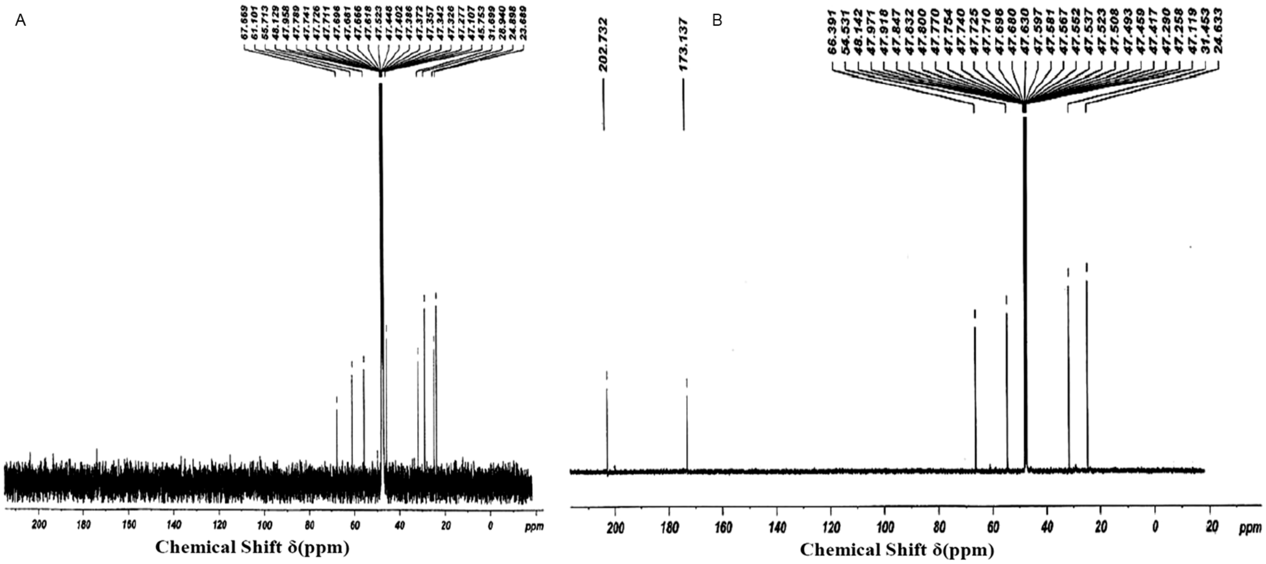


Fig. 4A — $^{13}$C NMR spectrum of Cd (L-Prodtc)$_2$ Chemical shift δ(ppm) and (B) $^{13}$C NMR spectrum of Zn (L-Prodtc)$_{22}$ Chemical shift δ(ppm)

Thermogravimetric studies show that the complex 1 was stable above 200°C which indicates complex formation. The complex 1 decomposes in four steps. The first weight loss stage has a decomposition loss of 13.85% with weight loss of two molecules of water and one molecule of ethanol (calcd: 14.26%). The fact that the water molecule and solvent ethanol were lost at a low temperature suggests that the water is crystal water. The second weight loss 200 and 400°C, with a weight loss of 45.26% which corresponds to the decomposition of isothiocyanate (calcd, 46.02%). This may be due to the complex formed with the ligand through the Sulpur coordination easily decomposed and rearranged to form isothiocyanate complex.The third and fourth stage indicated a continuous weight loss between 400 and 830°C, 20.51% of the original sample remained with its calculated weight percentage of 19.50%. The cadmium is the final product. The DTG peak around 537°C was attributed to decomposition of metal isothiocyanate in the third step (Cd $(SCN)_2$ → CdS) and the fourth step which was one decomposition

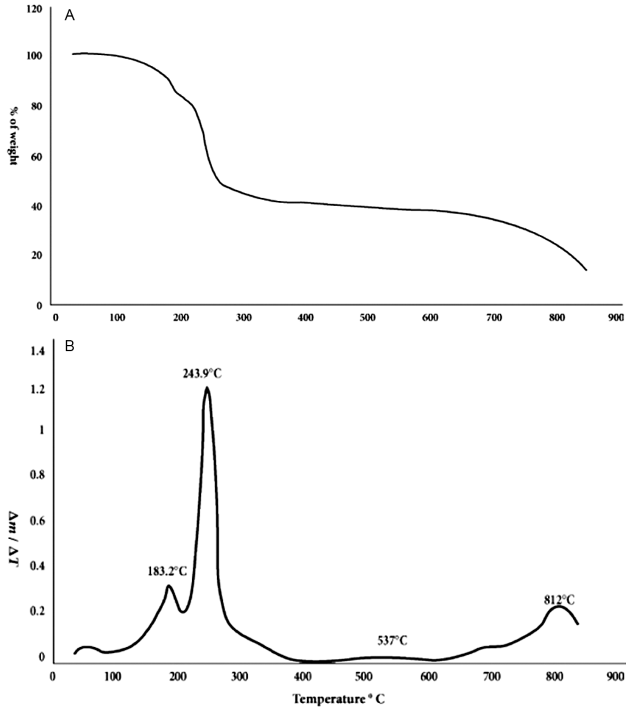


Fig. 5A — TG curve of Cd (L-Prodtc)$_2$ and (B) DTG curve of Cd (L-Prodtc)$_2$

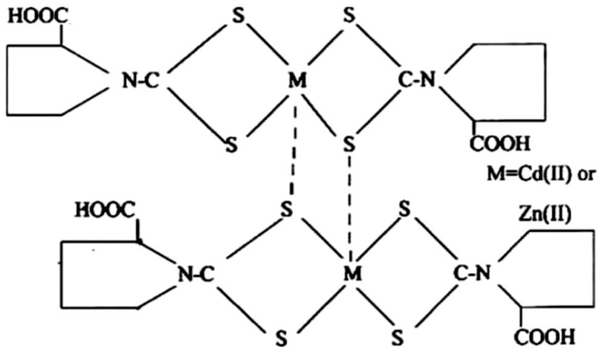


Fig. 6 — Structure of M (L-Prodtc)$_2$

around 812°C CdS→Cd. The third decomposition step was slow and overlapped with the fourth step decomposition.

The similar decomposition was observed for the decomposition of Cd (II) $(S_2CNRR1)_2$ complexes where R= $C_2H_5$, R1 = $C_6H_4$. $CH_3$[26]. Based on the observation, the thermal decomposition pattern of the complex 1 can be proposed as

$$Cd(L\text{–}Prodtc)_2 .2H_2O \rightarrow Cd(L\text{–}Prodtc)_2 \rightarrow Cd(SCN)_2 \rightarrow CdS \rightarrow Cd.$$

Based on the above facts and considering the reported structures of dithiocarbamate complexes the following distorted tetragonal pyramidal structures have been proposed for the L – Proline Dithiocarbamate metal (II) complexes (Fig. 6).

Each pair of centrosymmetrically related metal atoms share sulphur atoms, thus forming a dimeric unit in which each metal is coordinated with five sulphur atoms.

## Conclusion

The ligand was prepared in a single step. The α–amino acid containing secondary amine type nitrogen atom is L-Proline. The α–amino acid L–Proline, carbondisulfide and sodium hydroxide in ethanol react 1:1:2 molar ratio in exothermic condition to produce L-Proline Dithiocarbamate ligand. Dithiocarbamate complexes were prepared by freshly prepared L–Proline Dithiocarbamate reacting with metal (II) salts. All products were sparingly soluble in water and soluble in ethanol indicating the products may be in a monomeric or dimeric form. The coordination of Cd(II) and Zn(II) to ligand can be assigned as a bidentate mode.

The FTIR spectra of the complexes indicate that only dithiocarbamate sulphur are coordinating to metal and not the carboxylate oxygen.

The elemental analysis and thermo gravimetric analysis indicate the molecular formula of Cd(II) complex (1) to be $CdL_2$ ( where L=L – Prodtc). Thermo gram also showed that the Cd(II) complex contains two molecules of water of hydration, so the molecular formula was tentatively fixed as $CdL_2$. $2H_2O$. It is interesting to note that the Cd(L – Prodtc)$_2$ complex can be used as a single source precursor for the synthesis of semiconducting CdS with appropriate temperature to produce nanoparticles , nanowires and solid thin films.

The UV–Visible spectra are close to the values expected for the cadmium (II) dithiocarbamate complex. The observed data are in consistent with $d^{10}$ Configuration of the metal centre after complex formation with L–Prodtc ligand. L →M (LMCT) charge transitions at λ max 214 nm was observed indicating that they can be applicable in photochemical reactions.

The $^1H$ NMR spectra of the complexes show five proton environments and $^{13}C$ NMR spectra of the complexes exhibited six resonances. Their data are in accordance with the structure of the ligand L –Prodtc and also showed the carboxyl group is in the acidic form not being coordinated to the metal (II) cations.

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