



## Synthesis and Characterization of bis 3-phenyldithiocarbazato Cadmium(II): a new single-source precursor for preparation of CdS nanocompounds

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### ABSTRACT

*Metal complex of the type  $ML_2$  [ $M = Cd$ ;  $L = 3$ -phenyldithiocarbazate] have been successfully synthesized through reaction between potassium 3-phenyldithiocarbazate with cadmium nitrate in 2:1 ratio and characterized by UV-vis and FT-IR spectroscopy. The complex is formulated as four coordinate species with the dithiocarbazate acting as bidentate chelating ligand. The complex is thermolysed at  $100^\circ C$  in ethylene glycol and used as single-source precursors for the synthesis of CdS nanocompounds without using any surfactant and/or additives at mild reaction condition.*

**KEYWORDS :** Metal complex; Solvothermal; CdS; Nanocompound.

### 1. Introduction

Coordination compounds containing ligands with sulfur atoms as donors have received much attention [1]. Among these sulfur containing ligands, the dithiocarbazate species  $[RC(S)S]$  form an important family of classical anionic ligands [2] and are very relevant to the chemistry of disulfides. This anion, derived from primary amine, is versatile chelating agents. The strong chelating property is utilized in their extensive use as separating agents in gas chromatography [3] and liquid-liquid extraction [4], in purification [5], as fungicides in agriculture [6] and antidotes to fight metal poisoning [7]. The anions are three-electron donors [8] and have a small bite angle ( $2.8$ – $2.9 \text{ \AA}$ ) [9]. Hence, they are able to delocalize the positive charge from the metal toward the periphery of the complex and this stabilizes the metal ions [8, 10]. These ligands, apart from their vast technological applications, are of interest as a potential source of novel structures [11] as well as good source of sulfur. Dithiocarbazato complex of group 12 represent a large and interesting class of inorganic compounds [12] and they have been widely use as single-source precursors for synthesis of semiconductor nanocompounds.

The use of single-source molecular precursors in which a metal-chalcogenide bond is available has proven to be a very efficient route to high-quality nanoparticles [13]. Since the introduction of a single source precursor as an alternative and most convenient approach to the synthesis of semiconductor nanoparticles, the compounds that have found the greatest dissemination as precursors for II–VI semiconductors are the dithiocarbamate complexes [14]. Dialkyldithiocarbamate complexes  $[M(S_2CNR_2)_2]$  ( $M = Zn(II)$ ) have been used as single-source precursor to prepare nanoparticles and to deposit ZnS thin films by metal-organic chemical vapour deposition (MOCVD) [15]. A verity of techniques have been developed for the synthesis of nanocompounds including self promoting high temperature synthesis, solid state reaction, solvothermal synthesis, sonochemical method, microwave techniques and so on [16, 17, 18, 19, 20, 21]. Among the mention techniques, the solvothermal route has been extensively useful to achieve different morphological patterns of nanocompounds using different solvents. Generally most of these techniques involve high temperature or surfactants and/or additives in the reaction mixture which may cause of complicated purification steps and environmental pollution. Solvothermal route having single source precursor offers potential advantages like mildness, safety and simplification of the synthesis of nanocompounds and it also avoid complicated purification steps and environmental pollution.

Therefore, in this study we have introduce a facile root to

synthesis of bis-(3-phenyl dithiocarbazato)cadmium(II) where 3-phenyldithiocarbazate initially acting as a structure directing ligand and consequently use as precursors for growth of CdS nanocompounds which are composed of crystalline CdS nanomaterials, via Solvothermal method without using any surfactants or additives at relatively low temperature.

### 2. Experimental Section:

#### 2.1. Materials

Ethanol, methanol, chloroform, ethylene glycol, carbondisulphide, phenylhydrazine, potassium hydroxide and cadmium nitrate (analytical grade) were purchased from Mark, India. All the reagents were used as purchased without further purification.

#### 2.2. Physical measurements

Infrared spectra were recorded on a PERKIN ELMER FT-IR model RXI spectrophotometer with sample prepared by KBr pellets. Optical measurements were recorded on a SHIMAZDU UV 1800 spectrophotometer in the wavelength range of  $200$ – $1200 \text{ nm}$  at room temperature. The samples were placed in glass cuvettes ( $1 \text{ cm}$  path length) using DMSO as a reference solvents for all measurements. A Perkin-Elmer LS 45 Fluorimeter was used to measure the photoluminescence of the nanoparticles by dissolving them in DMF and placing the samples in glass cuvettes ( $1 \text{ cm}$  path length) for analysis.

#### 2.3. Synthesis of potassium 3-phenyldithiocarbazate (KL)

Potassium hydroxide ( $5.61 \text{ gms}$ ;  $100 \text{ mmol}$ ) were taken in a  $100 \text{ ml}$  beaker. ETOH ( $30 \text{ ml}$ ) was added to it, followed by  $9.91 \text{ ml}$  of  $PhNHNH_2$  ( $101 \text{ mmol}$ ). A magnetic bar was placed into the mixture, The beaker was placed on an ice-bath and the resulting solution was stirring at a moderate speed till the complete dissolution of KOH. After that the chilled  $CS_2$  ( $6.05 \text{ ml}$ ;  $100 \text{ mmol}$ ) was added drop by drop during a period of about  $45$  minutes with vigorous stirring. During the stirring, a pale yellow precipitation was obtained. The stirring was continued for another  $30$  minutes. The precipitation was filtered and washed with ( $4:6 \text{ v/v}$ ) cold ETOH. The pure product was obtained by recrystallization, keeping ethanolic solution in refrigerator, overnight. The yield was  $4.68 \text{ gms}$  ( $43 \%$ ). m.p.  $63 \text{ C}$ . UV-Vis:  $\lambda_{max}$   $489 \text{ nm}$  ( $\epsilon$   $8.84$ );  $\lambda_{max}$   $457 \text{ nm}$  ( $\epsilon$   $8.58$ ). FT-IR:  $\nu$  (C-N)  $1462 \text{ cm}^{-1}$ ;  $\nu$  (C-S)  $1002 \text{ cm}^{-1}$  (symm) and  $995 \text{ cm}^{-1}$  (asym); (O-H)  $3467 \text{ cm}^{-1}$ .

#### 2.4. Synthesis of complex

Potassium 3-phenyldithiocarbazate ( $2.1 \text{ gm}$ ;  $10.0 \text{ mmol}$ ) was dissolved in  $40 \text{ ml}$  EtOH and taken in a  $250 \text{ ml}$  beaker. Ethanolic solution ( $40 \text{ ml}$ ) of Cadmium nitrate ( $1.5 \text{ gm}$ ;  $5.0 \text{ mmol}$ ) was added drop-wise in to the beaker with vigorous stirring. During stirring, pale-yellow coloured precipitation was formed. Stirring was

continued for 30 minutes. The precipitation was filtered-off and the residue was washed with cold water & hot ethanol respectively for a number of times for purification. The solid product was obtained by drying under vacuum. The yield was 1.502 gm (81 %). UV-Vis:  $\lambda_{\text{max}}$  496nm ( $\epsilon$ 44). FT-IR: (C-N) 1494  $\text{cm}^{-1}$ ;  $\nu(\text{C}=\text{S})$  976  $\text{cm}^{-1}$ ,  $\nu(\text{Cd}-\text{S})$  469  $\text{cm}^{-1}$ .

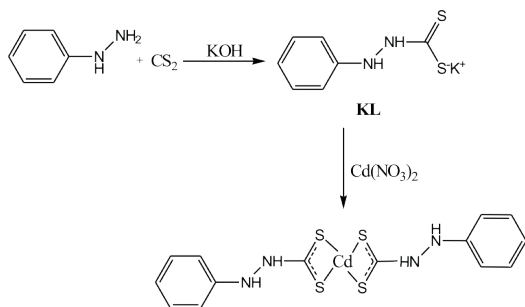
### 2.5. Synthesis of CdS compounds

Cadmium complex (209 mg; 0.4 mmol), was taken in 5 ml of Glycerol. Now this solution was injected into a three-neck round bottom flask with standard joint containing glycerol at 100 C. During addition, the solution inside the round bottom flask becoming yellow. The reaction was allowed for another 10 minutes. After that the solution was cooled to room temperature. After cooling, the solid mass was separated through centrifuge. The product was washed with water and ethanol for several times and dried in a vacuum for 2 hr. The obtained powders were then used for characterization with FL spectral analysis.

## 3. Results and discussion

### 3.1. Synthesis

Potassium salt of the ligand (KL) was obtained by the reaction of phenyl hydrazine with  $\text{CS}_2$  and potassium hydroxide in aqueous medium at low temperature, adapting the literature procedure [22]. The white solids so formed were stable at room temperature. The metal complex was conveniently obtained in high yield at room temperature by the reaction of KL and the metal salt in 2:1 molar ratio in ethanol (Scheme 1). The complex was air-stable and was poor soluble in inorganic and organic solvents. The poor solubility of the cadmium complex in both organic and inorganic solvents could be attributed to the possibility of the complex existing in the polymeric form. The formation of polymers might be due to the fact that dithioacid complexes of the  $\text{CdL}_2$  type are coordinatively unsaturated [23].



### 3.2. UV-vis spectral studies

Absorption spectrum of ligand [Fig. 1(a)] in DMSO has displayed a peak at about 490 nm and that of metal complex [Fig. 1(b)] at absorption tail reached about 700 nm. The slight absorption for the complex was occurred at lower energy region may be attributed to the electronic transition in the sulfur group and may slightly metal-ligand charge transfer transition occur in the complex.

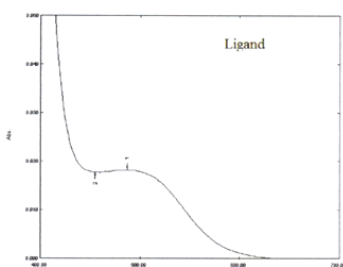


Fig. 1(a): UV-vis spectrum of ligand KL in DMSO

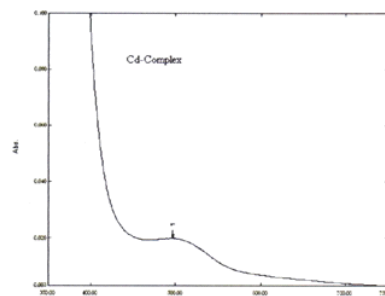


Fig.1(b):UV-VIS spectrum of CdL2 in DMSO

### 3.3. Infrared spectral studies

Infrared spectra of the ligand [Fig. 2(a)] and the complex [Fig. 2(b)] were compared and assigned on careful comparison. In ligand, the broad peak was observed around 3467  $\text{cm}^{-1}$  due to (O-H) vibration of water molecule in the sodium salt of the dithiocarbazates [24]. This peak was absent in the complex, indicating the loss of the water molecule upon coordination to the metal ions. An observed feature of the spectra of the complex is the CN bond at 1494  $\text{cm}^{-1}$ . This (C-N) band is shifted to higher energy relative to the ligand (ca. 1462  $\text{cm}^{-1}$ ). The shift is a reflection of increased bond strength. This strengthening of the CN bond is ascribed to the increase in the double bond character, which is observed upon coordination to the metal centre [25,26]. The difference in the electron releasing ability of the organic groups affects the electron density on the sulfur atom via the electron system and therefore influences the double bond character of the C=N bond [25]. This observed peak for the complex was fall within the stretching frequencies of (C-N) 1250–1350  $\text{cm}^{-1}$  and (C-N) 1640–1690  $\text{cm}^{-1}$  [27]. In the above region, a single sharp band implies a symmetrical bidentate coordination, while the splitting of this band into a doublet may indicate a monodentate unsymmetrical coordination of the dithiocarbato group. The synthesized complex shows a single peak within this region which implies the presence of symmetrically bonded bidentate dithiocarbazates. A prominent peak found at 469  $\text{cm}^{-1}$  for the complex, which is absent in the free ligand, indicated the formation of Cd-S bond in the complex. This peak is usually depends on the nature of the substituent attached to the nitrogen atom [28].

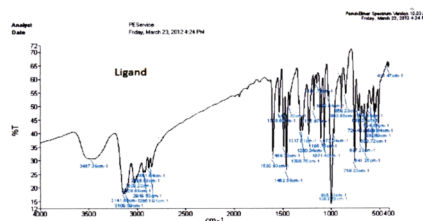


Fig. 2(a): FT-IR spectrum of ligand KL in KBr

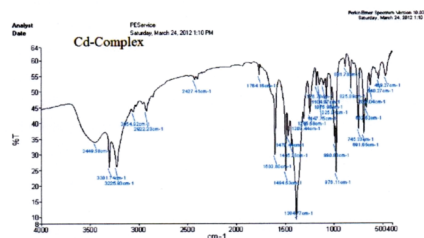


Fig. 2(b): FT-IR spectrum of CdL2 in KBr

### 3.4. Synthesis and characterization of CdS compound

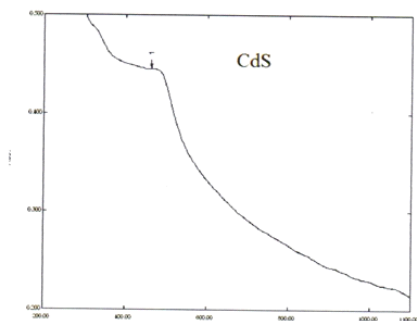
The cadmium complex was used for the preparation of nanocompounds from ethylene glycol media at 100 C temperature.

The compound crystallizes into yellow precipitates in relatively good yield.

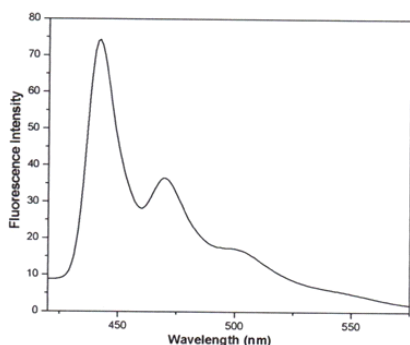
### 3.4.1. Optical property of CdS compound

Semiconductor nanoparticles CdS prepared from their single source precursor shows a excitonic feature at 478 nm [Fig. 3. (a)] with tailing. The tailing of absorption feature results from the particle sizes ranging from significantly small to large.

The emission maximum peak positions are 442, 470, 500 nm ( $\lambda_{exc}$  330 nm and  $\lambda_{emi}$  380-600 nm) [Fig. 3. (b)]. Previous reports suggest that the emission arises from the recombination of an electron trapped in a sulfur vacancy with a hole in the valence band of CdS [29]. The electrons generated by the absorption of photons can be trapped into sulfur vacancies through a radiation-less decay followed by the recombination with holes in the valence band. It is argued that creation of sulfur vacancies in CdS nanocrystallites prepared by reacting  $Cd^{2+}$  with a  $S^{2-}$  source is due to the formation of non-stoichiometric CdS consequent to the slow generation of  $S^{2-}$  ions in the reaction medium which is insufficient to form a stoichiometric CdS crystallite [30]. Studies on CdS nanoparticles also show emission spectrum due to the vacancies of the chalcogenide ions. Hence it should be concluded that creation of chalcogenide ion vacancies is extraneous to the effect of its availability in the reaction medium, rather it is governed by the intrinsic growth mechanism of the crystallites under the reaction conditions.



**Fig.3(a):**Optical absorption spectrum of CdS nanocompounds synthesized in ethylene glycol at 100°C



**Fig. 3(b):** Fluorescence spectrum of as prepared CdS nanocompounds at 100°C.

## 4. Conclusions

*Bis*-(3-phenyldithiocarbazato)cadmium(II) have been prepared and characterized by spectroscopic techniques. Four coordinate geometries are proposed for the complex. The complex was used as a single precursor for preparation of nanosize CdS through a rapid and eco-friendly solvothermal route under mild reaction condition. The nanocompounds showed a blue shift in their absorption band edges, and emissions which are red shifted. The present synthetic route is also expected to provide an alternative method for the ease of preparation of CdS nanocompounds with unique technique. Similar methods may be effective in the synthesis of other metal

chelcohenides.

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