

Synthesis and Characterization of *bis*(3-phenyldithio carbazato) lead(II): A New Single-source Precursor, Designed for Growth of PbS Nanocompounds

Nilkamal Maiti

Assistant professor, Department of Chemistry, Midnapore College (Autonomous), Midnapore 721101, email: nkmaiti@gmail.com

ABSTRACT

Metal complex of the type ML_2 [M = Pb; L = 3-phenyldithiocarbazate] have been synthesized and characterized by UV-vis and FT-IR spectroscopy. The complex is formulated as four coordinate species where dithiocarbazate acting as bidentate chelating ligand. The complex, which is used as precursors, thermolysed in ethylene glycol to achieved single crystalline PbS nanocompounds without using any surfactant and additives under mild reaction condition. The nanocompounds are confirmed by TEM and FL spectroscopic analysis.

1. Introduction

Coordination compounds containing ligands with sulphur atoms as donors have received much attention [1]. Among these sulphur 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 Å) [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 sulphur. Dithiocarbazato complex of group 14 metals 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–chelcogenides 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]. A verity of techniques have been developed for the synthesis of nanocompounds including self promoting high temperature synthesis, solid state reaction, solvothermal synthesis, sonochemical methode, microwave techniques and so on [15, 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.

In this study we report the synthesis and characterization of *bis*-(3-phenyl dithiocarbazato)Pb(II) where 3-phenyldithiocarbazate initially acting as a structure directing ligand and therefore use as single molecular precursors for synthesis of PbS nanocompounds without using any surfactants and additives at relatively low temperature.

2. Experimental

2.1. Materials

Ethanol, methanol, chloroform, carbon disulphide, phenyl hydrazine, potassium hydroxide and lead 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 Bruker EQUINOX 55 FT-IR spectrophotometer with sample prepared by KBr pellets. Optical measurements were recorded on a shimadzu UV 1800 spectrophotometer in the wavelength range of 200-1200 nm at room temperature. The samples were placed in glass cuvettes (1 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 nanocompounds by dispersion in DMF and placing the samples in glass cuvette (1 cm path length) for analysis.

2.3. Synthesis of potassium 3-phenyldithiocarbazate (KL)

Potassium hydroxide (5.61 gms; 100 mmol) were taken in a 100 ml beaker. EtOH (30 ml) was added to it, followed by 9.91 ml of PhNHNH₂ (101 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 CS₂ (6.05 ml; 100 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 v/v) cold EtOH. The pure product was obtained by recrystallization, keeping ethanolic solution in refrigerator, overnight. The yield was 4.68 gms (43 %). M.P. 63 °C. UV-Vis: λ_{max} 489 nm (ϵ 8.84); λ_{max} 457 nm (ϵ 8.58). FT-IR: $\nu(\text{C-N})$ 1462 cm⁻¹; $\nu(\text{C-S})$ 1002 cm⁻¹(symm) and 995 cm⁻¹(asym); $\nu(\text{O-H})$ 3467 cm⁻¹.

2.4. Synthesis of complex (single precursor)

Potassium 3-phenyldithiocarbazate (2.080 gm; 9.0 mmol) was dissolved in 40 ml EtOH and taken in a 250 ml beaker. Water solution (40 ml) of lead nitrate (1.506 gm; 5.0 mmol) was added drop-wise in to the beaker with vigorous stirring. During stirring, orange-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 EtOH respectively for a number of times for purification. The solid product was obtained by drying under vacuum. The yield was 1.498 gm (99 %). UV-Vis: λ_{\max} 519 nm (ϵ 682). FT-IR: $\nu(\text{C-N})$ 1466 cm^{-1} ; $\nu(\text{C=S})$ 984 cm^{-1} , $\nu(\text{Pb-S})$ 468 cm^{-1} .

2.5. Synthesis of PbS

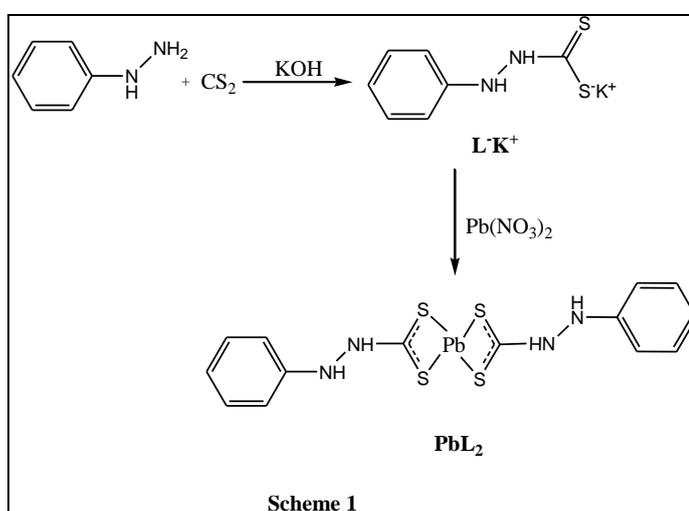
A two necked round bottom flask containing 80 ml of ethylene glycol was heated at 100 °C. The flask was degassed for 10 minutes and filled with nitrogen. *bis*-(3-phenyl dithiocarbazato)Pb(II) (230 mg; 0.4 mmol), was disperse in 5 ml of ethylene glycol and injected into the flask with constant starring. During addition, a yellow precipitation was observed in the flask. The reaction was then allowed for another 10 minutes. The flask was then cooled to room temperature and products were collected by centrifugation, wash with ethanol and water for several times and dried in a vacuum at 60 °C for 3 hr. The obtained powders were then used for characterization with TEM and 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 CS₂ and potassium hydroxide in ethanol at low temperature adapting the literature procedure [22]. The white solids so obtained were stable at room temperature. The metal complex was conveniently obtained in high yield at room temperature by the reaction of KL and the lead nitrate in 2:1 molar ratio in ethanol (**Scheme 1**). The obtained 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 complex of ML_2 type, are of 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 sulphur group and may slightly metal-ligand charge transfer transition occur in the complex.

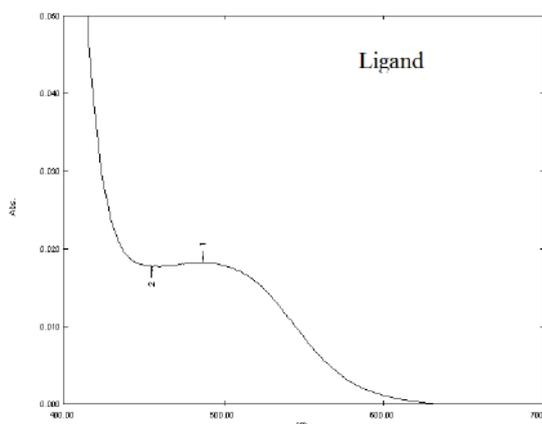


Fig. 1: (a) UV-vis spectrum of ligand KL in DMSO

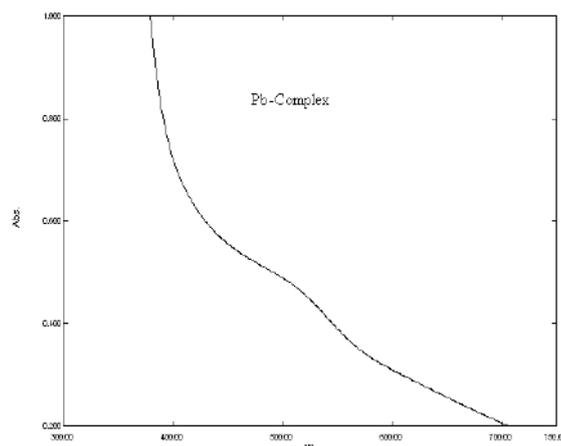


Fig. 1 (b): UV-Vis spectrum of PbL_2 in DMSO

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. For ligand, the broad peak was observed around 3467 cm^{-1} due to $\nu(\text{O-H})$ 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 1466 cm^{-1} . This $\nu(\text{C-N})$ band is shifted to higher energy relative to the ligand (ca. 1462 cm^{-1}). The shift is a reflection of increased bond strength. This strengthening of the CN bond is ascribed to 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 sulphur atom via the π 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 $\nu(\text{C-N})$ $1250\text{--}1350\text{ cm}^{-1}$ and $\nu(\text{C-N})$ $1640\text{--}1690\text{ cm}^{-1}$ [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 dithiocarbazato 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 525 cm^{-1} for the complex, which is absent in the free ligand, indicated the formation of Pb-S bond in the complex. This peak is usually depends on the nature of the substituent attached to the nitrogen atom [28].

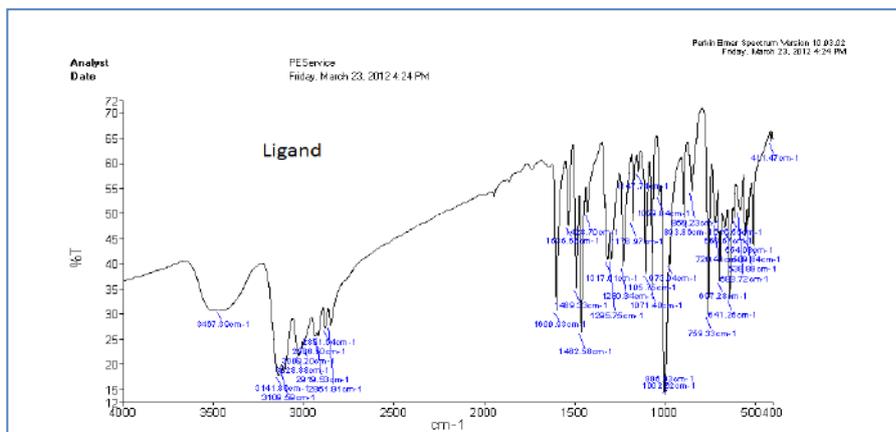


Fig. 2(a): FT-IR spectrum of ligand KL in KBr

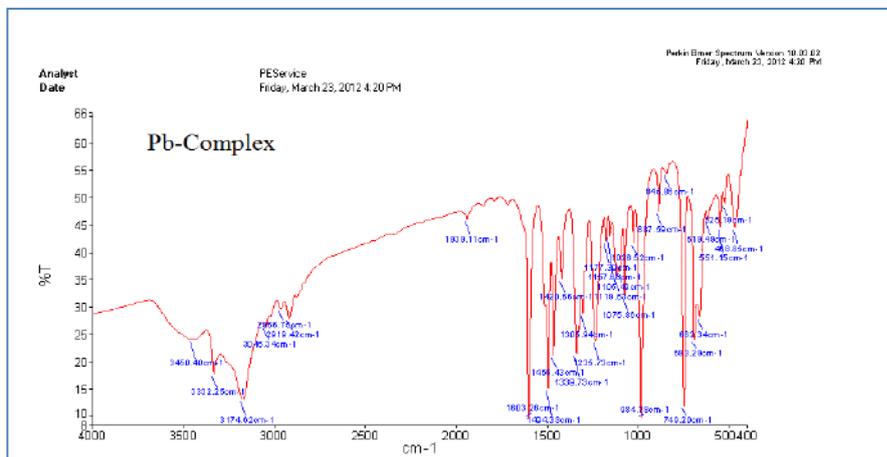


Fig. 2(b): FT-IR spectrum of Pb₂L₂ in KBr

3.4. Characterization of PbS

Fig. 3(a) represents the TEM image of nanocompounds. Fig. 3(b) represents a high resolution TEM (HRTEM) image of PbS nanoparticles in which crystal lattice fringes are clearly visible which indicated that the PbS nanoparticles are crystalline in nature. The electron diffraction

pattern [Fig 3(c)] was taken from a selected area of a PbS nanoparticles. The spotty pattern indicates that the as-prepared samples are single crystalline.

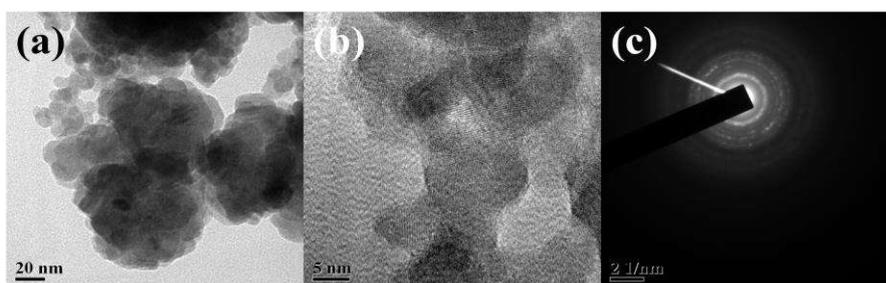


Fig. 3. TEM images of PbS at 100 °C (a) nanocompounds obtain by solvothermal process (b) HRTEM image of the nanocrystals and (c) SAED pattern of the nanocrystals.

Semiconductor nanoparticles PbS prepared from their single source precursor shows a excitonic feature at 675 nm [Fig. 4. (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 337, 372 nm (λ_{exc} 280 nm and λ_{emi} 300-500 nm) [Fig. 4. (b)]. Previous reports suggest that the emission arises from the recombination of an electron trapped in a sulphur vacancy with a hole in the valence band of PbS [29]. The electrons generated by the absorption of photons can be trapped into sulphur vacancies through a radiation-less decay followed by the recombination with holes in the valence band. It is argued that creation of sulphur vacancies in PbS nanocrystallites prepared by reacting Pb^{2+} with a S^{2-} source is due to the formation of non-stoichiometric PbS consequent to the slow generation of S^{2-} ions in the reaction medium which is insufficient to form a stoichiometric PbS crystallite [30]. Studies on PbS nanoparticles also shows 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.

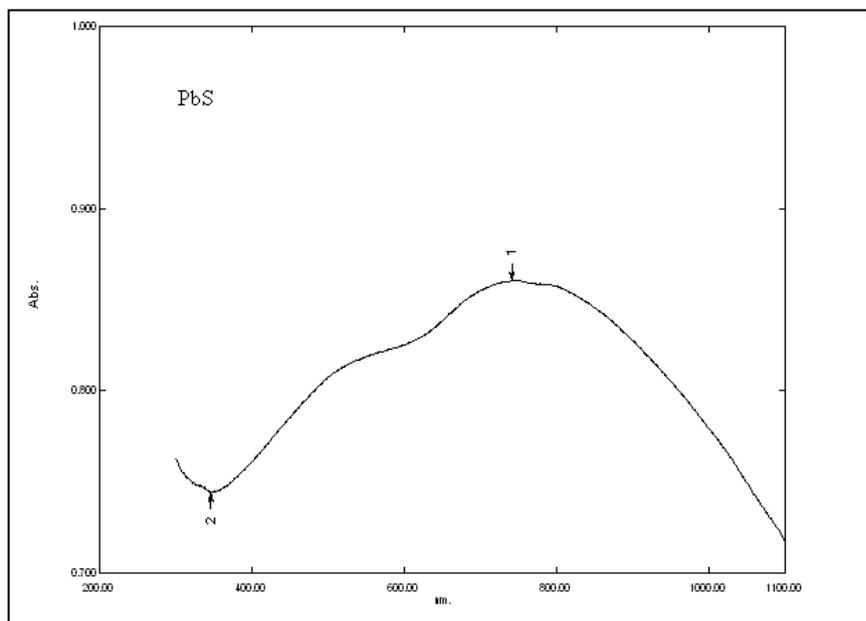


Fig. 4(a): Optical absorption spectrum of PbS nano compounds synthesized in ethylene glycol at 100 °C

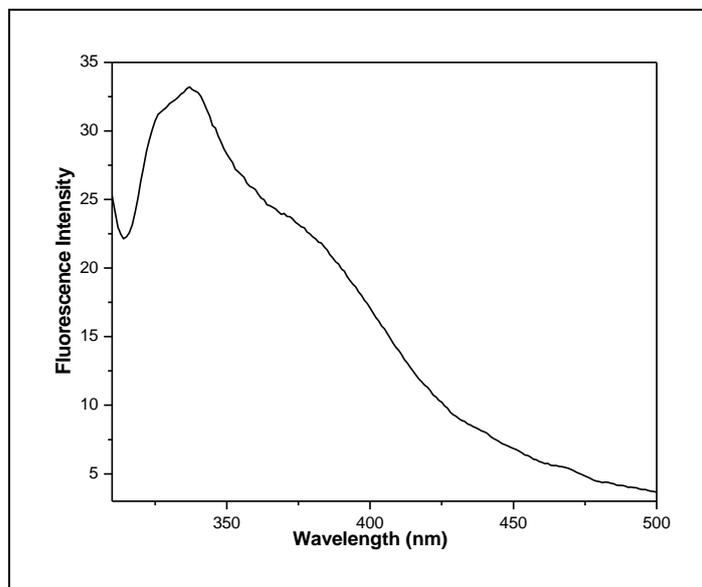


Fig. 4(b): Fluorescence spectrum of PbS nano compounds synthesized in ethylene glycol at 100 °C (PbS in DMF (λ_{exc} 280 nm and λ_{emi} 300-500 nm exsl 5, 5-dil-ascii peak position= 337, 372 nm)

4. Conclusion

The Complex, *bis*(3-phenyl dithiocarbazato)Pb(II) have been prepared and characterized by spectroscopic techniques. Four coordinate geometries are proposed for the complex. The complex was used as a single source precursor to synthesis of PbS nano compounds through a rapid and solvothermal route under mild reaction condition. The nanocompounds are single crystalline in nature and 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 PbS nanocompounds with unique technique. Similar methods may also be effective for the synthesis of other metal chelcogenides of one-dimensional structure.

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