1. Introduction

Substituted thiourea ligands are of interest because they possess various donor sites for metal ions and their application in separation of metal ions and as antimicrobial agents. The coordination of the sulfur donor atom led to interest in them as precursor for semiconductor nanoparticles. In this study, cadmium(II) complex of diethylthiourea was synthesized and characterized by elemental analysis, FTIR, and X-ray crystallography. Single crystal X-ray structure of the complex showed that the octahedral geometry around the Cd ion consists of two molecules of diethylthiourea acting as monodentate ligands and two chelating acetate ions. The thermal decomposition of the compound showed that it decomposed to give CdS. The compound was thermolysed in hexadecylamine (HDA) to prepare HDA-capped CdS nanoparticles. The absorption spectrum showed blue shifts in its absorption band edges which clearly indicated quantum confinement effect, and the emission spectrum showed characteristic band edge luminescence. The broad diffraction peaks of the XRD pattern showed the materials to be of the nanometric size.

2. Experimental Section

2.1. Materials and Instrumentation.

All the reagents and solvents used were of analytical grades and used without further purification. IR spectrum was obtained as KBr discs on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer equipped with CsI window (4000–250 cm⁻¹). Thermogravimetric analysis was performed on a Perkin Elmer thermogravimetric analyzer (TGA 7) fitted with a thermal analysis controller (TAC 7/DX). A flow of N₂ was maintained with a heating rate of 10°C/min between ambient temperature and 800°C. 10–12 mg of the sample was loaded into an alumina cup, and weight changes were recorded as a function of temperature.

2.2. Synthesis of the [Cd(detu)₂(OOCCH₃)₂]·H₂O. The complex was prepared by addition of 2 mmol (0.533 g) of Cd
of arbitrary radius. Displacement ellipsoids are drawn at 50% probability level. H atoms are represented by circles showing the atom-labeling scheme. 

2.4. Synthesis of CdS Nanoparticles. About 0.5 g of (CH$_3$COO)$_2$Cd dissolved in 50 mL of absolute ethanol to a stirring 4 mmol of diethylthiourea (0.529 g) in 50 mL of absolute ethanol. The mixture was refluxed for 6 h and filtered and left to evaporate slowly at room temperature. White crystals suitable for X-ray analysis were obtained after few days. Anal. Calc. For C$_{14}$H$_{32}$CdN$_2$O$_5$S$_2$: C, 32.78; N, 10.92; H, 6.29, S, 12.50. Found: C, 33.01; N, 10.64; H, 6.03; S, 12.79%.

2.3. Single Crystal X-Ray Crystallography. Single crystals suitable for X-ray analysis for [Cd(detu)$_2$(OOCCH$_3$)$_2$]CdS were obtained after few days by slow evaporation of ethanolic solution of the complex. The data sets for the single crystal X-ray studies were collected with Mo Kα radiation (k = 0.71073) at 100(2) K on a Bruker SMART APEX [16, 17] CCD diffractometer equipped with an Oxford Cryosystems low temperature device. Unit cell dimensions were obtained by least-squares refinement based on the setting angles of 925 reflections with theta ($\theta$) angles ranging from 2.50 to 26.50. The structure was solved by direct methods and refined by full-matrix least squares on SHELX97 [18, 19].

2.4. Synthesis of CdS Nanoparticles. About 0.5 g of [Cd(detu)$_2$(CH$_3$COO)$_2$]CdS was dissolved in 10 mL of tri$n$octylphosphine and injected into 6 g of hot hexadecylamine (HDA) at 150°C. A subsequent decrease in temperature of 20–30°C was observed. The solution was heated to 150°C and stabilized at this temperature for 1 h. The solution was then allowed to cool to 70°C, an excess of methanol was added, and a flocculants precipitate was formed. The solid was separated by centrifugation and re-dispersed in toluene. The toluene was removed under vacuum to give HDA-capped CdS nanoparticles.

2.5. Characterization of Nanoparticles. XRD patterns were recorded by a Bruker D8 Advance X-ray diffractometer equipped with a proportional counter, using Ni-filtered Cu Kα radiation ($\lambda$ = 1.5405 Å). Transmission electron microscopy (TEM) images were obtained on a Philips CM200 transmission electron microscope with an accelerating voltage of 200 kV. The electronic spectra of the complexes were taken on a Perkin Elmer Lambda 250 UV-vis spectrometer. A Perkin Elmer LS 45 Fluorimeter was used to measure the photoluminescence of the nanoparticles. The SEM image was obtained in a Jeol, JSM-6390 LV apparatus, using an accelerating voltage between 15–20 kV at different magnifications. Composition and energy dispersive spectrum was processed using energy dispersive X-ray analysis (EDX) attached to the SEM with Noran System six software.

3. Results and Discussion

3.1. Molecular Structure of [Cd(detu)$_2$(OOCCH$_3$)$_2$]CdS. The molecular structure of the complex with atom numbering scheme is shown in Figure 1. The crystal data and structure refinement are presented in Table 1, and selected bond lengths and angles are given in Table 2. The cadmium in the molecular structure is a six-coordinate CdS$_2$O$_4$ form in which the Cd ion is coordinated to two monodentate diethylthioureas and two chelating acetate ions. The coordination polyhedral around Cd(II) is a distorted octahedron which might be due to the small bite angles of the acetate ions: O(2)–Cd(1)–O(1) [54.51(6)°] and O(4)–Cd(1)–O(3) [54.20(6)°]. This also led to deviation of trans O(4)–Cd(1)–O(1), O(2)–Cd(1)–S(1) and O(3)–Cd(1)–S(2) bond angles significantly from 180° (ranges from 141.21(6)° to 151.48(4)°). The diethylthiourea ligands are cis to each other, and S–Cd(1)–S bond angle around the cadmium ion is 102.83(3)° which deviates considerably from 90°. This may be ascribed to the steric interaction between the substituents on the diethylthiourea. The C–S–Cd bond angles of 108.82(8)° and 111.59(8)° are slightly greater than the tetrahedral value.

The S–C–N and N–C–N bond angles ranges from 118.51(17)° to 121.62(17)° and are within the expected range of tetrahedral. The C–N bonds (1.327(3) Å to 1.458(3) Å) and C–S bonds 1.727(2) Å to 1.730(2) Å are intermediate between single and double bonds. This may be attributed to the delocalization of electron in the thioamide bonds [20, 21]. The hydrogen bonding network within the molecule is between the acetate oxygen atom and NH and acetate oxygen atom and the hydrogen atoms of water within the crystal lattice (Table 3). Each water molecule within the crystal lattice is linked to three cadmium complex units via intermolecular hydrogen bonds. The other intermolecular hydrogen bonding is between the acetate oxygen atom and the NH of the
3.2. Infrared Spectra Studies. The IR spectra of the ligand and complex were compared and assigned on careful comparison. The absorption band in the 3430–3200 cm\(^{-1}\) region was observed as multiple bands in the region 1554–1562 cm\(^{-1}\), and the thioamide bond is experienced only very slight changes in the complex. The N–H band occurs at 3275 cm\(^{-1}\) and the acetate ions with C–N stretching vibrations. The presence of multiple bands might be due to the overlap of the acetate ions with C–N bond stretching vibrations. The presence of multiple bands in the region 552–672 cm\(^{-1}\) can be attributed to the S–Cd–O interactions.

3.3. Thermogravimetric Studies. Thermogravimetric analysis of the compound, \([\text{Cd(detu)}_2(\text{OOCCH}_3)_2]\_\text{H}_2\text{O}\), has been carried out to study the pyrolysis pattern in the temperature range 20–800 \(^\circ\)C. From the thermogram (TGA/DTG) in Figure 3, the complex undergoes two decomposition stages. The first decomposition occurs between 24 \(^\circ\)C and 78 \(^\circ\)C with a mass loss of 3.5%; and the second decomposition starts at 114 \(^\circ\)C and ends at 233 \(^\circ\)C with a 71% mass loss. This huge mass loss corresponds to the loss of the ligands and formation of CdS. The DTG peak temperature, for each of the decomposition stages are 61 \(^\circ\)C and 186 \(^\circ\)C, respectively.
Considering the DTG peak temperatures, the first decomposition stage is due to entrapped solvent molecule. Thermal decomposition of related thiourea complexes reported in the literature has indicated that the residue formed corresponds to the formation of CdS [22]. Here, the weight of the residue calculated for CdS (3.68 mg) agrees favourably with the expected (3.65 mg). The DTA curve shows two pronounced endothermic peaks. The first and sharp peak is due to the melting of the complex at a temperature of 145°C. The second broad endothermic minimum which occurs at 182°C represents the decomposition of the complex. Comparing the TG curve with the DTA, it could be inferred that the second decomposition which gave CdS commenced in the liquid phase after the melting of the sample.

3.4. Synthesis and Characterization of Nanoparticles. HDA-capped CdS nanoparticles were synthesized at 150°C using the cadmium complex. Optical properties of the nanoparticles were investigated by UV-vis and photoluminescence spectroscopy at room temperature (Figure 4) and show CdS nanoparticles with excitonic features at 420 nm and emission at 559 nm. The CdS nanoparticles showed quantum size effect...
which is manifested as a blue shift in their absorption band edges in comparison to that of the bulk.

The cadmium complex produced particles in the hexagonal phase with XRD patterns (Figure 5) indexed to 111, 200, 220, 311, and 331 for peaks with 2θ values of 26.4, 35.8, 43.9, 51.6, and 70.5, respectively. The peaks are generally broad, indicative of nanoscale particles. The TEM image of the CdS nanoparticles is presented in Figure 6. The nanoparticles are almost spherical in shape. A little aggregation is observed which could be ascribed to the effect of the small dimensions and high surface energy associated with nanodimensional particles. The sizes of the nanoparticles ranged between 5 and 19 nm. The SEM image of the prepared CdS nanoparticles is shown in Figure 7. The CdS nanoparticles have spherical morphology and show an average agglomerate size. The agglomeration of the nanoparticles may arise from their small dimension and high surface energy.

4. Conclusions

The reaction of cadmium acetate with diethylthiourea yielded the coordination complexes, $[\text{Cd(detu)}_2(OOCH}_3)_2\cdot\text{H}_2\text{O}$. Recrystallization of the complex yielded well-defined crystals characterized by FTIR, elemental analysis, and single-crystal X-ray diffraction. Single crystal X-ray structure of the compound revealed that the coordination geometry around the Cd(II) is octahedron comprising of two diethylthiourea ligands and two acetate ions acting as bidentate chelating ligands. The single-source precursor route has been used for the preparation of CdS nanoparticles by thermolysis of the complex in hexadecylamine (HDA) to prepared HDA-capped nanoparticles. The absorption spectrum showed blue shifts in their absorption band edges which clearly indicated quantum confinement effect, and the emission spectrum showed characteristic band edge luminescence. The broad diffraction peaks of the XRD pattern showed the materials to be of the nanometric size with predominantly hexagonal phase. The TEM micrographs showed the CdS morphology to be almost spherical shape with particle sizes ranging between 5 and 19 nm.

Conflict of Interests

The authors declare no conflict of interest.

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