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Group 12 dithiocarbamate complexes: Synthesis, characterization and X-ray crystal structures of Zn(II) and Hg(II) complexes and their use as precursors for metal sulfide nanoparticles Peter A. Ajibade^{*,a}, Johannes Z. Mbese^a, Bernard Omondi^b

^aDepartment of Chemistry, University of Fort Hare, Private Bag X1314, Alice 5700, South Africa

^bSchool of Chemistry, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa

*Corresponding author. E-Mail: pajibade@ufh.ac.za

Abstract

Zn(II), Cd(II) and Hg(II) dithiocarbamate complexes were synthesize and characterized by elemental analysis, thermogravimetric analysis, UV-Vis, FTIR, ¹H- and ¹³C-NMR spectroscopy. Single crystal X-ray crystallography revealed that the Zn complex has a centrosymmetric dimeric structure while the Hg complex crystallizes with two monomeric molecules of the mercury complex and two molecules of toluene solvent in the asymmetric unit. The compounds were used as single molecule precursors to synthesize HDA capped metal sulfides nanoparticles with average crystallite size ranging from 7-22 nm. The optical properties of the nanoparticles showed evidence of quantum confinement.

Keywords

Dithiocarbamates; crystal structures; metal sulfides; chalcogenides; nanoparticles.

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INTRODUCTION

Semiconductor nanoparticles have been of particular interest because of their size-dependent properties as compared to those of bulk materials [1-5]. Metal sulfide nanoparticles are important compound semiconductor with wide ranging properties and applications [6, 7]. For example, ZnS is a group II–VI semiconductor with a wide direct band gap of about 3.65 eV depending on the crystalline phase (cubic or wurtzite). They have found practical applications in optoelectronic devices operating in the region from visible to near infrared such as optical coatings, solar cells, lasers, electro-optic modulators, photoconductors, field effect transistors, sensors, transductors and photonic crystal devices [8-18].

Among group II–VI semiconductor, CdS has been widely studied and has a direct band gap of 2.42 eV [19-22]. It has potential technological applications similar to those of ZnS [23, 24]. HgS is a technologically important nanocrystalline which has pronounced dichorism, photoelectric, acousto-optic properties and electrostatic image properties. Despite these applications of HgS nanoparticles, relatively scarce studies are available due to difficulty in synthesis and being extremely toxic. In this study, we present the synthesis and characterization of Zn(II), Cd(II) and Hg(II) dithiocarbamate complexes and their use as single source precursors [25-28] to synthesize ZnS, CdS and HgS nanoparticles. The complexes were characterized by analytical and spectroscopy techniques and the Zn(II) and Cd(II) complexes were characterized by single crystals X-ray crystallography. The optical and structural properties of the resulting nanocrystals were studied with optical absorption and emission spectroscopy, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

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EXPERIMENTAL

Materials and physical measurements

All chemicals and reagents were of analytical grade and used as obtained without further purification. The ammonium salt of the ligands, N-phenyldithiocarbamate (L¹) and N-ethyl-N-phenyldithiocarbamate (L²) were prepared using modified literature method [29]. Elemental analysis was carried out on Fission elemental analyser. FTIR on Bruker Tensor 27 and NMR spectra were recorded on Bruker ultrasheild 400 NMR spectrometer operating at frequencies of 400.1 MHz for ¹H and 100.6 MHz for ¹³C nuclei. The thermogravimetric analysis was performed using on Perkin Elmer thermogravimetric analyzer (TGA 7) fitted with a thermal analysis controller (TAC 7/DX). A flow of nitrogen was maintained with a heating rate of 10 °C min⁻¹ between ambient temperature and 900 °C using about 10-16 mg mass of each samples.

Perkin Elmer Lambda 25 UV–Vis spectrophotometer and LS 45 fluorimeter was used to measure the optical properties. Powder X-ray diffraction patterns were recorded on Bruker-D8 advance powder X-Ray diffractometer instrument operating at a voltage of 40 kV and a current of 30 mA with Cu Kα radiation. The X-ray diffraction data were analysed using EVA (evaluation curve fitting) software and the phase identification was done with standard in JCPDS database. The transmission electron microscopy (TEM) images were obtained using a ZEISS Libra 120 electron microscope operated at 120 kV. The samples were prepared by placing a drop of a solution of the sample in toluene on a carbon coated copper grid (300 mesh, agar). Images were recorded on a mega view G2 camera using iTEM Olympus software. The scanning electron microscopy (SEM) images were obtained on a Joel, JSM-6390 LV apparatus, using an accelerating voltage between 15-20 kV at different magnifications. Energy dispersive spectra

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were processed using energy dispersive X-ray analysis (EDS) attached to a Joel, JSM-6390 LV SEM with Noran system Six software.

Synthesis of ammonium N-phenyldithiocarbamate, NH_4 [$C_6H_5(H)NCS_2$], L^1

This compound was prepared by a modified literature method [29]. In a typical experiment, 30 mL concentrated ammonium hydroxide was added slowly to 9.13 mL (0.1 mol) aniline in an ice cold mixture at 0-5°C. To this mixture, 6.04 mL (0.1 mol) of carbon disulfide was added drop-wise with constant stirring for 1 hour in an ice bath and another 1 hour at room temperature. The resulting yellowish solid obtained was filtered by suction and rinsed three times with cold ethanol. The product is air and thermally unstable.

Synthesis of ammonium N-ethyl-N-phenyldithiocarbamate, NH_4 [$C_6H_5(C_2H_5)NCS_2$], L^2

The ligand was prepared according to a reported procedure [29]. To a mixture of 12.88 mL (0.1mol) of N-ethyl aniline and concentrated aqueous ammonia (30 mL) in ice, was added 6.00 mL (0.1 mol) of ice cold carbon disulfide. The yellowish green liquid mixture was stirred for 6-7 h given yellowish white solid product which was filtered by suction and rinsed three times with cold ethanol given thermally unstable, moisture and air-sensitive, ammonium salt of N-ethyl-N-phenyldithiocarbamate which was stored in the refrigerator.

Synthesis of metal dithiocarbamate complexes

Equimolar (1.25 mmol) concentration of ligands L^1 and L^2 dissolved in 30 mL of water was added to 1.25 mmol of the metal salt, MCl₂ [M = Zn, Cd, Hg] in 25 mL of water. The reaction mixture was stirred for 1 h at room temperature and the products filtered, washed with water and dried in vacuo.

ZnL¹L². Complex was obtained as white solid. Yield: 1.90 g (90 %), m.p. 190-210 °C.

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¹H NMR (DMSO) δ 7.45–7.25 (m, 8H, –C₆H₅), 3.36 (s, 2H, –CH₂), 1.15, 1.13, 1.12 (3H, – CH₃).¹³C NMR (DMSO) δ 144.93, 129.22, 128.48, 127.85, 126.96 (–C₆H₅), 53.46 (–CH₂), 12.12 (–CH₃), 206.33 (–CS₂)Selected IR, (cm⁻¹): 1500 v(C=N), 1248 (C₂–N), 900, 1020, 1063 (C=S). *Anal.* Calc. for C₁₆H₁₆N₂S₄Zn (427.95): C, 44.87; H, 3.77; N, 6.54; S, 29.88. Found: C, 44.85; H, 3.76; N, 6.52. Recrystallization of complex, **ZnL¹L²**, in toluene solvent gave colourless single crystals suitable for X-ray analysis.

CdL¹L². Complex was obtained as yellow solid. Yield: 2.43 g (98 %), m.p. 200-210 °C.

¹H NMR (DMSO) δ 7.43–7.23 (m, 8H, -C₆H₅), 3.35 (s, 2H, -CH₂), 1.17, 1.15, 1.14 (3H, -CH₃).¹³C NMR (DMSO) δ 146.02, 129.15, 127.58, 126.88 (-C₆H₅), 54.69 (-CH₂), 12.13 (-CH₃), 207.60 (-CS₂). Selected IR, (cm⁻¹): 1467 v(C=N), 1189 (C₂-N), 980, 995, 1001 (C=S).

Anal. Calc. for $C_{16}H_{16}N_2S_4Cd$ (476.97): C, 40.17; H, 3.37; N, 5.86; S, 26.76. Found: C, 40.24; H, 3.74; N, 5.70. Recrystallization of complex, CdL^1L^2 , in toluene solvent gave colourless single crystals suitable for X-ray analysis.

HgL¹L². Complex was obtained as black solid. Yield: 2.63 g (93 %), m.p. 150-160 °C. ¹H NMR (DMSO) δ 7.46–7.22 (m, 10H, $-C_6H_5$), 3.35 (s, $-CH_3$). ¹³C NMR (DMSO) δ 129.55, 128.65, 127.78, 126.57 ($-C_6H_5$), 54.69 ($-CH_2$), 11.89 ($-CH_3$), 208.30 ($-CS_2$) Selected IR, (cm⁻¹): 1432 v(C=N), 1289 (C₂–N), 909, 1009, 1012, 1020, 1080 (C=S) *Anal.* Calc. for C₁₆H₁₆N₂S₄Hg (565.17): C, 39.92; H, 2.85; N, 4.95; S, 22.60. Found: C, 33.90; H, 2.85; N, 4.93. Recrystallization of complex, **HgL**¹L², in toluene solvent gave colourless single crystals suitable for X-ray analysis.

X-ray crystallography

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Crystals of $bis(\mu_2-N-\text{ethyl-}N-\text{phenyldithiocarbamato-}S,S:S')-bis(N-\text{Ethyl-}N-\text{phenyldithiocarbamato-}S,S')-di-zinc(II) suitable for single crystal X-ray diffraction studies were grown by slow evaporation of the solutions of the compounds in dry CH₂Cl₂ were layered with a fourfold of excess diethyl ether and allowed to stand undisturbed in the dark at room temperature for 24 h. Crystals of the two polymorphs were selected and glued on to the tip of glass fibers. The crystals were then mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.$

The crystal evaluation and data collection were performed on a Bruker Smart APEXII diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). The diffractometer to crystal distance was set at 4.00 cm. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range about with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite [30]. The final cell constants were calculated from a set of 6460 strong reflections from the actual data collection. Data collection method involved ω scans of width 0.5°. Data reduction was carried using the program SAINT plus [30]. The structure was solved by direct methods using SHELXS [30] and refined. All structures were checked for solvent-accessible cavities using *PLATON* [31] and the graphics were performed with the DIAMOND [32] visual crystal structure information system software. Non-H atoms were first refined isotropically and then by anisotropic refinement with full-matrix least-squares calculations based on F^2 using SHELXS. All H atoms were positioned geometrically and allowed to ride on their respective parent atoms. The carboxyl H atoms were located from the difference map and allowed to ride on their parent atoms. All H atoms were

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refined isotropically. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [32]. Crystal data and structure refinement information for Complexes **1** (**Hg**) and **2** (**Zn**) are summarized in Table 1. Crystal data and structure refinement information for Complexes **3**, a polymorph of complex **2**, are included for comparison purposes.

Synthesis of metal sulfide nanoparticles

Synthesis of the metal sulfide nanoparticles, chemically passivated with hexadecylamine was carried out as follows: 0.7 g of each metal complex was dissolved in TOP (15 mL). This solution was then injected into 7.5 g of hot HDA at a temperature of 180 °C. A subsequent decrease in temperature of about 30 °C was observed. The solution was then allowed to attain 180 °C and then heated for a further 60 mins. The solution was then allowed to cool to 70 °C, and methanol was added to remove any excess HDA. The as-synthesized flocculent precipitate was separated by centrifugation and was redispersed in toluene. The solvent was then removed by evaporation under reduced pressure to give HDA-capped ZnS nanoparticles. The particles were again washed with methanol and redispersed in toluene for spectroscopic measurements.

RESULTS AND DISCUSSION

Synthesis

In this study, the synthesis of dithiocarbamate complexes was done by mixing equimolar concentrations of two different ligands and metal salts solutions and stirred thoroughly. Ammonium N-phenyldithiocarbamate (L^1) and ammonium N-ethyl-N-phenyldithiocarbamate (L^2) were mixed stoichiometrically with the respective metal salts to form *N*- phenyl-*N*, *N*-

methyl phenyl dithiocarbamato)M(II) complexes, where M = Zn, Cd or Hg. The formation of the complexes can be represented as shown below [33].

 $MCl_2 + NH_4L^1 + NH_4L^2 ML^1L^2 + 2NH_4Cl$

Where M = Zn, Cd and Hg

Electronic spectra of the metal complexes

The electronic spectra of the ligands show bands at 286 nm, 300 nm and 339 nm due to intraligand $\pi \to \pi^*$ transitions located on the N-C=S group, $\pi \to \pi^*$ transitions within the S-C=S group and $n \to \pi^*$ electronic transitions located on the sulfur atoms respectively [34, 35]. In electronic spectra of Zn(II), Cd(II) and Hg(II) complexes, the bands are below 350 nm confirming the presence of intra ligand π - π^* transitions, mainly associated with N-C=S and S-C = S groups [36].

Infrared spectra studies of the metal complexes

The dithiocarbamate ligands (\mathbf{L}^1 and \mathbf{L}^2) show two diagnostic bands in the infrared spectra. First is the band due to v(C–N) thiouride vibration which is observed in the region 1498–1548 cm⁻¹ [37]. The special feature of dithiocarbamate ligands is an additional n-electron flow from nitrogen to sulfur *via* a planar delocalized π -orbital system [38]. The high vibrational frequencies of this band in the complexes indicate a partial double bond character of the CN group arising from mesomeric drift of electrons from the dithiocarbamate moiety towards the M(II) ion centre [38] and the contribution of resonance structure of the dithiocarbamate ligands in the thiouride form. The second single band which appears in the region 964–973 cm⁻¹ corresponds to v(C–S) and indicates that the dithiocarbamate coordinate the metal ions through the sulfur atoms [38].

The v(C=S) appeared as single sharp band at 755-758 cm⁻¹ and this confirm that the ligands acted as bidentate chelating modes. The M-S bond stretching vibrations appeared in the range 325-384 cm⁻¹ [39]. The band observed at about 3436 cm⁻¹ is assigned to the N-H stretching frequency for the complexes. This simply indicates that the nitrogen to metal bonds is not present and therefore the bonding in this complex is between the sulfur and metal ions. The bonding of sulfur to metal ion is expected to increase the contribution of the highly polar structure to the dithiocarbamates, resulting in a greater double bond character for the nitrogen to carbon bond and a greater single bond character for the carbon to sulfur bond. The bands observed in between 1635-1028 cm⁻¹ are due to v(C-N) stretching, the v(C=S) was observed at 757 cm⁻¹ in the ligands. These bands shifted to lower frequency by 1 cm⁻¹ and 6 cm⁻¹ in the complex respectively. This behaviour signify a decrease in the double bond character of the C=S bond which confirms the metal ions are coordinated to sulfur [40].

NMR spectra studies

The ¹H NMR for the methylene carbon bonded directly to N atom of L^2 (N-CH₂) were observed in the range of 4.25-4.31 ppm and the ethyl protons appeared between 2.96-3.01 ppm. The aromatic protons showed multiplex peaks appearing from 7.29-6.46 ppm [41] and the peak due to solvent was found at 2.49 ppm. The ¹³C NMR of L^2 reveal the signal due to α -carbon of the – CH₃ group was found at 37.28 ppm and the –CH₂- carbon signal at 50.96 ppm. The six signals for aromatic carbons were found in the region between 112-129 ppm. The signal due to –CS₂ appeared at 214.53 ppm. The Zn complex showed a quartet signals at δ 4.09, 4.10, 4.12 and 4.14 ppm, corresponding to ethyl group protons. The multiplex peaks for aromatic rings protons appeared at 7.25-7.45 (8H, m, –C₆H₅) ppm. A sharp peak of one proton at 3.36 ppm (1H, s)

ascribed to (N - H) proton of L¹ ligand. The pick at δ 2.49 ppm was observed for DMSO. The Cd complex showed a quartet signals at δ 4.09, 4.10, 4.12 and 4.14 ppm, corresponding to ethyl group protons.

The multiplex peaks for aromatic rings protons appeared at 7.23-7.43 (8H, m, $-C_6H_5$) ppm. A sharp peak of one proton at 3.35 ppm (1H, s) ascribed to (N – H) proton of L¹ ligand. The peak at δ 2.49 ppm was observed for DMSO. The Hg complex showed a multiplex signals at δ 4.07 – 4.17(8H, m, $-C_2H_5$) ppm assigned to ethyl group protons. The multiplex peaks for aromatic rings protons appeared at 7.22 –7.46 (8H, m, $-C_6H_5$) ppm. A sharp peak of one proton at 3.35 ppm (1H, s) ascribed to (N – H) proton of L¹ ligand. The pick at δ 2.49 ppm was observed for DMSO. The ¹³C NMR signals of Zn, Cd and Hg dithiocarbamate complexes revealed the multiplex peaks for aromatic rings carbon appeared at 126.96 – 129.22 ppm. The peak corresponding to ethyl group carbons bonded to N atom appeared at 53.46 ppm. The primary methyl carbon in ethyl was assign to the peak that appear at 12.12 ppm.

Thermal decomposition studies

The thermal decomposition of the metal complexes was investigated by thermogravimetric analysis and the superimposed TG profiles results is presented in Figure 1. The thermal decomposition patterns of the Zn(II) complex show two steps that is equivalent to about 70 % weight loss associated with the decomposition of the dithiocarbamate ligands. This decomposition led to the formation of zinc sulfide (ZnS) with about 30 % residue, which was 7 % more than calculated value of 23 %. In the thermal decomposition profile of the Cd complex, three main decomposition steps with a total weight loss of about 80 % were observed. The first decomposition step below 100 $^{\circ}$ C is due to the loss of entrap solvent molecules within the

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complex crystallite lattice. The last two steps are associated with the decomposition of the ligands. The residue (CdS) of 20 % was obtained at the end of analysis and is 10% less than the expected value of 30 % [42-47]. Three main decomposition steps with a total weight loss of about 95 % corresponding to the formation of the HgS were observed in the TG curve of the mercury complex. The TG/DTG reveals the high volatility of the sample at the temperature range of 280-460 °C but the complex can still be used as a precursor for the synthesis of HgS [42, 44, 45].

Molecular structure of Zn and Hg Complexes

The **Hg** compound is a pseudo-polymorph of a previously reported $bis(\mu_2-N-ethyl-N-phenyldithiocarbamato-S,S')-bis-$ *N* $-phenyldithiocarbamato-S,S')-di-mercury(II) (1) [48] that crystallizes in <math>P2_1/c$ space group as centrosymmetric dimeric structure, The **Hg** complex in this paper crystallizes in *P*-1 space group with two monomeric molecules of the Hg(II) compound and two molecules of toluene solvent in the asymmetric unit. One of the toluene solvent molecules is located in a general position, while the second one is disordered about an inversion centre. In both Hg molecules, the Hg centre is strongly coordinated by two S atoms with two short Hg—S bond distances of 2.3834(6) and 2.3985(6) for molecule **1** and 2.3848(6) and 2.4091(6) Å for molecule **2** and interact with the other two S atoms through two long Hg…S interactions 2.8139(6) and 2.8850(6) for molecule **1** and 2.7880(6) and 2.9348(6) Å for molecule **2** showing the tendency of Hg to prefer linear coordination geometry. The long Hg…S interactions in both molecules are possibly responsible for the deviation from ideal linear geometry as seen in the S5—Hg1—S8 and S1—Hg2—S4 angles of 166. 58(2) and 165.47(2)° respectively. Comparatively all bond distances and angles are similar to those of previously

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reported related complexes. Figure 6 shows the root mean square deviation overlay of the two cations. The root mean square deviation for the two cations is 0.0678. This value is relatively low and is probably due to the difference in the orientation of mainly the ethyl and phenyl moieties.

The **Zn** compound, **2** is a polymorph of another Zn complex, **3** [29] and is similar to a number of similar dithiocarbamates in literature such as diisopropyldithiocarbamate zinc [49] and diethyldithiocarbamate zinc [50]. The molecular structure is shown in Fig. 4 while important bond distances and angles are shown in Table 2. Compound **Zn** has a centrosymmetric dimeric structure in which the Zn atom symmetrically chelated by one terminal bidentate dithiocarbamate anion and non-symmetrically coordinated by the other dithiocarbamate anion. The coordinated dithiocarbamate uses the second S atom to bridge the two Zn(II) centers resulting in a binuclear dimeric complex. The two Zn—S chelating and the coordinating bond distances are 2.3333(11), 2.4647(11) and 2.3200(10) Å. The chelation and coordination behaviour of these ligands can also be confirmed by Δd and θ which are 0.1 Å and 3.6° respectively for the chelating ligand and 0.5 Å and 17.3° for the monodentate ligand.

The bridging S atom interacts with the next Zn atom across an inversion center, forming a short Zn—S bond length of 2.3927(11) Å [symmetry code: 1-x, -y, 1-z] and this results in an eightmember symmetric metallacycle containing the two Zn(II) centers and the coordinating dithiocarbamate S and C atoms. Another Zn—S interaction is longer, 2.8539(11) Å and is comparable to corresponding values found in similar zinc dithiocarbamates [29, 51]. The Zn(II) centre shows a strongly distorted tetrahedral geometry, but if the long Zn—S bond distance is taken into account, then the Zn(II) center shows a distorted square pyramidal geometry, in which

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the square base is made up of CS_2 —Zn— S_2C ; the dihedral angle between the N— CS_2Zn planes is 39.3(3)°. The analogous Zn—S interaction in **3** is slightly shorter, 2.7513(6) Å while the dihedral angle is 41.8(2)°. Two of the tetrahedral angles deviate significantly (76.02(3)° and 137.33(4)° from the ideal 109°.

Optical properties of the HDA-capped ZnS, CdS and HgS nanoparticles

The absorption and emission spectra of the HDA-capped ZnS, CdS and HgS nanoparticles are shown in Figure 7. The energy bands and their corresponding parameters are tabulated in Table 4. The UV-Vis spectra exhibited blue-shift with respect to that of the bulk samples due to the quantum confinement [52]. The photoluminescence spectra showed narrow emission curves with the emission maximum at 385, 393 and 399 nm, for ZnS, CdS and HgS nanoparticles respectively. ZnS emission maximum is blue shifted to the absorption band edges while CdS and HgS gave emission maxima that are red shifted to the absorption band edges [53].

XRD studies of HDA-capped metal sulfide nanoparticles

The XRD patterns of the nanoparticles are shown in Figure 8. The ZnS nanoparticles (Figure 8A), shows three important peaks at 28.5°, 47.6° and 56.4° respectively corresponding to the (111), (220) and (311) planes indicates characteristic peaks of cubic crystal structure of ZnS nanoparticles [54]. The peaks observed in the XRD patterns correspond well with those of the β -ZnS (cubic) reported in the JCPDS 01-07921. The calculated average crystallite size from these peaks using Scherer's formula is 5.3 nm. The XRD pattern of CdS nanoparticles (Figure 8B) exhibited narrow peaks at 26.79, 29.72, 44.02, 48.58 and 52.20° assignable to the (111), (220), (311) and (400) Miller indices respectively, suggesting small crystallite sizes CdS nanoparticles in hexagonal phase. The XRD pattern of HgS nanoparticles (Figure 8C) exhibits diffraction

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peaks which correspond to the (111), (220), (311), (222), and (400) planes of HgS (metacinnabar, syn), and are in good agreement with the pattern JCPDS 00-006-0261. All the peaks with the (*) are due to HDA.

TEM studies of HDA-capped ZnS, CdS and HgS nanoparticles

The TEM micrograph of the ZnS nanoparticles (Figure 9A) shows well-defined nanoparticles having a diameter of about 9 nm. Generally the shape of nanoparticles are mainly close-to-spherical and some are elongated with some crystalline and others agglomerate [55]. The TEM image of the CdS nanoparticles showed nanoparticles with different shapes ranging from spherical to hexagonal with particle size diameter range of 7 to 14 nm. The particles have some aggregation due to the attraction between the spherical nanoparticles as a result of dipole-dipole interactions between their surfaces. One of the advantages of using single source precursor's methods is that it can give nanoparticles with increased size control, dramatic decreases in reaction times, improved product crystallinity, reactions exhibiting good reproducibility and high yields [56]. The TEM micrograph of the HgS nanoparticles (Figure 9C) showed highly agglomerated nanoparticles with nearly spherical and triangular shapes. The average size of the HgS nanoparticles is a challenge due to high degree of agglomeration observed [57].

SEM and EDX studies of the nanoparticles

The surfaces of the particles in Figure 9 ((a) and (b)) showed cluster of particles which are nearly spherical and agglomerated due to high surface energy of the particles as a results of their small crystallite sizes [58]. The EDS spectrum of the ZnS nanoparticles (Figure 9 A) reveals predominant peaks of Zn and S. The morphologies of the as-prepared CdS nanoparticles from

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the SEM micrograph reveal that the particles are porous with uniform particle dimension. This porosity may be due to the fact that the sample was completely dry and the uniformity of particles is due to the method of synthesis used. The porous and rough surface morphology is evident which makes it difficult to estimate the crystallite size due to agglomeration of the particles [59]. EDS spectrum of HDA-capped CdS nanoparticles reveal that the prepared samples are mainly composed of Cd and S, confirming the presence of CdS nanoparticles in hexagonal phase [59]. Other traces of elements like C, O, Al and P are observed were observed in both ZnS and CdS. The carbon observed in both samples is attributed to the carbon from the capping agent hexadecylamine (HDA) or the carbon grid of the sample holder, Al is from aluminium-carbon grid used during coating, O may be due to oxidation of S atom to O atom while the P is due to the trioctyl phosphine (TOP).

The SEM images reveal that the surface of HgS sample is fairly smooth indicating almost uniform particles. Both the particles tend to aggregate to secondary particles indicating that the alkyl groups play a very important role in controlling the morphology of the as-prepared nanoparticles [60]. Figure 9 (c) shows typical EDS patterns of the HgS particles. As expected, the observed major peaks are due to the presence of mercury and sulfur indicating the presence of HgS particles in the sample.

CONCLUSION

Zn(II), Cd(II) and Hg(II) complexes of diakylphenyl dithiocarbamates were synthesized and characterize by elemental analyses and spectroscopic techniques. The single crystal X-ray structures of the Zn complex revealed that the Zn atoms are bonded to four sulfur atoms and crystallized as a dimeric molecule with a distorted tetrahedral geometry around each Zn atom.

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The single crystal X-ray structure of the Hg complex shows two mercury compounds in the monomeric unit and toluene molecules within the crystal lattice. The metal complexes were used as single source precursors to synthesized HDA capped ZnS, CdS and HgS nanoparticles with sizes ranging from 7-22 nm. The XRD patterns indicates that ZnS nanoparticles existed in the cubic phase with average crystallite size of 9 nm, the CdS nanoparticles contained small crystallites in the hexagonal phase with size ranges from 7-14 nm while the HgS nanoparticles existed in hexagonal phase with crystallite sizes of 8-22 nm. The optical absorption and emission spectra of the as-synthesized particles showed quantum confinement with absorption that is blue shifted.

Supplementary Materials

CCDC 907752 and 907753 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 1: Crystal data and structure refinement for Complexes 1 and 2 (polymorphs I and

II)

| | 1 | 2 | 3 (56) |
|--|--|---|---|
| Empirical formula | C ₉₃ H ₉₆ N ₈ S ₁₆ Hg ₄ | C ₃₆ H ₄₀ N ₄ S ₈ Zn ₂ | C ₃₆ H ₄₀ N ₄ S ₈ Zn ₂ |
| Formula weight | 2641.26 | 915.94 | 915.94 |
| Temperature (K) | 173(2) | 173(2) | 173(2) |
| Wavelength | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic | Triclinic |
| Space group | <i>P</i> -1 | $P2_{1}/c$ | <i>P</i> -1 |
| Unit cell dimensions | | | |
| <i>a</i> (Å) | 10.9135(2) 10.2405(6) | | 8.7163(3) |
| b (Å) | 15.3173(3) 17.8168(10) | | 10.5618(3) |
| <i>c</i> (Å) | 15.6160(3) | 14.6214(8) | 12.0172(3) |
| α (°) | 101.0320(10) | | 66.341(2) |
| $\beta(^{\circ})$ | 101.4750(10) | 132.510(3) | 79.577(2) |
| γ (°) | 99.1740(10) | | 83.156(2) |
| Volume (Å ³) | 2457.50(8) | 1956.53(19) | 995.26(5) |
| Ζ | 1 | 2 | 1 |
| D_{calc} (Mg m ⁻³) | 1.785 | 1.547 | 1.528 |
| Absorption coefficient (mm ⁻¹) | 6.616 | 1.677 | 1.657 |
| $F(0\ 0\ 0)$ | 1286 | 944 | 472 |
| Crystal size (mm) | 0.31 x 0.20 x 0.15 | 0.28 x 0.28 x 0.28 | 0.20 x 0.18 x 0.16 |
| θ range (°) | 1.95 to 28.00 | 2.21 to 28.00 | 3.10 to 28.28 |
| Limiting indices | -14<=h<=14, | -13<=h<=13, | -11<=h<=11, |
| | -20<=k<=20, | -23<=k<=23, | -14<=k<=14, |
| | -20<=l<=20 | -19<=l<=18 | -16<=l<=16 |
| Reflections collected | 51370 | 29865 | 31692 |
| Independent reflections | 11661 | 4679 | 4931 |
| | [R(int) = 0.0283] | [R(int) = 0.0462] | [R(int) = 0.0341] |
| Completeness to $\theta = 28.45^{\circ}$ (%) | 98.3 | 98.5 | 99.8 |
| Max. and min. transmission | 0.4369 and 0.2335 | 0.6509 and 0.6509 | 0.7022 and 0.3245 |
| Data / restraints / parameters | 11661 / 0 / 564 | 4679 / 2 / 228 | 4471 / 28 / 235 |
| Goodness-of-fit on F^2 | 1.075 | 1.134 | 1.111 |
| Final <i>R</i> indices $[I > 2 \Box(I)]$ | $R_1 = 0.0187,$ | $R_1 = 0.0511,$ | $R_1 = 0.0127,$ |
| | $wR_2 = 0.0451$ | $wR_2 = 0.1308$ | $wR_2 = 0.0322$ |
| R indices (all data) | R1 = 0.0232, | R1 = 0.0627, | R1 = 0.0135, |
| | wR2 = 0.0482 | wR2 = 0.1367 | wR2 = 0.0326 |

| Largest | diff. | peak | & | hole | 1.165 and -1.120 | 2.171 and -0.621 | 0.462 and -0.621 |
|---------------------|-------|------|---|------|------------------|------------------|------------------|
| (e.Å ³) | | | | | | | |

Absorption correction - Semi-empirical from equivalents; Refinement method - Full-matrix

least-squares on F^2 .

| | Molecule 1 | Molecule 2 | | Molecule 1 | Molecule 2 |
|-------------|------------|------------|--------|-------------|-------------|
| Bond | | | | | |
| distances | | | | | |
| Hg—S | 2.3834(6) | 2.3848(6) | Hg—S | 2.8139(6) | 2.7880(6) |
| Hg—S | 2.3985(6) | 2.4091(6) | Hg—S | 2.8850(6) | 2.9348(6) |
| C—S | 1.708(2) | 1.710(2) | C—S | 1.693(2) | 1.689(2) |
| C—S | 1.748(2) | 1.746(2) | C—S | 1.758(2) | 1.755(2) |
| Bond angles | | | | | |
| S—Zn—S | 68.437(17) | 67.492(17) | S—Zn—S | 114.191(18) | 114.297(18) |
| S—Zn—S | 69.348(18) | 69.652(18) | S—Zn—S | 124.056(19) | 124.879(19) |
| S—Zn—S | 93.550(17) | 95.875(17) | S—Zn—S | 166. 58(2) | 165.47(2) |
| S—C—S | 119.42(13) | 119.47(14) | S—C—S | 120.53(13) | 120.17(13) |

Table 2: Bond distances and angles (Å / °) for the two Hg complexes in compound 1

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| | 2 | 3 (56) | | 2 | 3 (56) |
|-------------|------------|-----------|--------|------------|-----------|
| Bond | | | | | |
| distances | | | | | |
| Zn—S | 2.3200(10) | 2.3501(7) | Zn—S | 2.3333(11) | 2.4007(5) |
| Zn—S | 2.4647(11) | 2.3659(6) | Zn—S | 2.3927(11) | 2.4431(6) |
| Zn—S | 2.8539(11) | 2.7513(6) | | | |
| C—S | 1.716(4) | | C—S | 1.718(4) | |
| C—S | 1.737(4) | | C—S | 1.738(4) | |
| Bond angles | | | | | |
| S—Zn—S | 69.41(3) | | S—Zn—S | 106.34(4) | |
| S—Zn—S | 76.02(4) | | S—Zn—S | 108.39(4) | |
| S—Zn—S | 89.03(3) | | S—Zn—S | 114.74(4) | |
| S—Zn—S | 94.99(4) | | S—Zn—S | 137.12(4) | |
| S—Zn—S | 104.98(4) | | S—Zn—S | 164.33(4) | |
| S—C—S | | | S—C—S | | |

Table 3: Bond distances and angles (Å / °) for Zn complex and the polymorph

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| Nanoparticles | h | С | λ_c | E_{g}^{*} | eV |
|---------------|----------|----------|-------------|-------------|------|
| ZnS3 | 6.63E-34 | 3.00E+08 | 3.35E-07 | 5.934E-19 | 3.71 |
| CdS3 | 6.63E-34 | 3.00E+08 | 3.29E-07 | 6.042E-19 | 3.78 |
| HgS3 | 6.63E-34 | 3.00E+08 | 3.16E-07 | 6.291E-19 | 3.93 |

Table 4: Energy band gaps of ZnS, CdS and HgS nanoparticles

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Figure 1: Superimposed thermogravimetric analysis profiles of the metal complexes.

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Figure 2: Molecular structure of the mercury complex (1)



Figure 3: Packing diagram of the mercury complex

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Figure 4: Molecular structure of the zinc complex (2)

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Figure 5: Packing diagram of the zinc complex

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Figure 6: The root mean square deviation overlay picture of the two Hg(II) molecules in the asymmetric unit of Complex **Hg**.



Figure 7: Absorption and emission spectra of the ZnS, CdS and HgS nanoparticles

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Figure 8: XRD diffraction patterns of HDA-capped ZnS, CdS and HgS nanoparticles

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Figure 9: TEM, SEM and EDX of HDA-capped metal sulfides nanoparticles