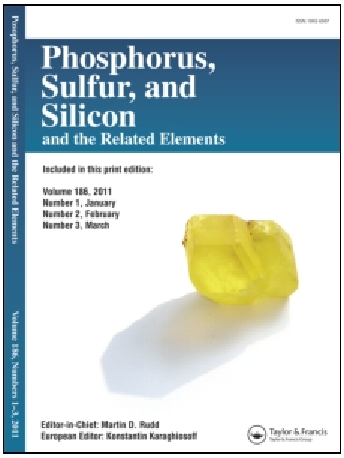

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Chemistry of Aminopropylchalcogenolate Complexes of Zinc, Cadmium, Mercury and Their Nanoparticles

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Chemistry of Aminopropylchalcogenolate Complexes of Zinc, Cadmium, Mercury and Their Nanoparticles

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The chemistry of aminopropylchalcogenolate complexes of zinc, cadmium, mercury and their nanoparticles are described. A variety of Zinc (II), Cadmium (II), and mercury (II) complexes containing 3-aminopropylchalcogenolate ligand has been prepared by in situ reduction of bis(3-aminopropyl)dichalcogenide to 3-aminopropylsodiumchalcogenolate followed by reaction with metal halides. Nanoparticles have been prepared by solvo-thermal decomposition of these complexes in quinolene solvent at 200°C. The complexes have been characterized by elemental analyses and IR. The prepared nanoparticles have been characterized by XRD, UV-Vis, PL, SEM, and TEM. The TEM images show that the nanoparticles are in the range of 10–20 nm.

Keywords 3-Aminopropyldichacogenide; ligand; metalchalcogenolate complexes; nanoparticles; solvo-thermal

INTRODUCTION

The chemistry of metal chalcogenolates continues to be an attractive area of research. There are several obvious reasons for the sustained interest in metal chalcogenolates. The emerging application as single source precursors for low decomposition temperature synthesis of metal chalcogenides has further accelerated work on these complexes. Group II - chalcogenides (M_xE_y; M=Zn, Cd, Hg; E=Se, Te) find several applications in catalysis and material science. The single source

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precursor is one of the best route to synthesize monodisperse semiconductor nanoparticles of group II–VI.[1] Semiconductor nanocrystals are expected to potentially contribute to an easier and cheaper photovoltaic conversion of solar energy. The group II metal chalcogenolates have an attractive potential to serve as precursors for the preparation of metal chalcogenides.[2,3]

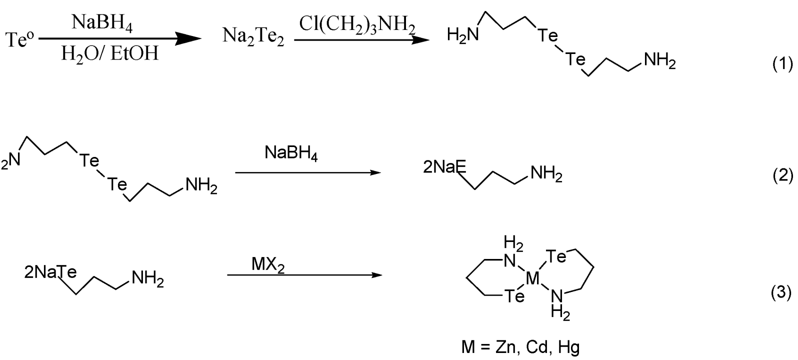
In general, monomeric group II metal chalcogenolates are difficult to obtain due to the formation of polymeric or oligomeric complexes through bridging of chalcogenolate ligands.[4] To suppress polymerization, sterically demanding chalcogenolate ligands,[5] strongly coordinating auxiliary ligands (e.g., tertiary phosphines)[6] or internally functionalized ligands[7] have been employed. Aminopropylchalcogenolates, $H_2N(CH_2)_3E^-$, represent a family of internally functionalized ligands which contain both hard as well as soft donor atoms.

In view of the above potential applications, we have synthesized aminopropylchalcogenolate complexes of zinc, cadmium, and mercury, which act as single source molecular precursors for group II–VI semiconductor materials. These single source molecular precursors further have been utilized to synthesize the nanoparticles and characterized by modern instrumental techniques.

RESULTS AND DISCUSSION

Synthesis of Ligand Bis(3-aminopropyl)ditelluride

Bis(3-aminopropyl)dichalcogenide ligand was synthesized by the route depicted in Scheme 1. Elemental tellurium was reduced by sodium borohydride to form disodiumditelluride, which reacted with 3-chloropropylamine to form (3-aminopropyl)ditelluride in good yield. The ligand has been purified and fully characterized.[8,9]



SCHEME 1 Synthesis of bis(3-aminopropyl)ditelluride and its metal complexes.

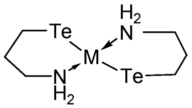
The IR spectra of bis(3- aminopropyl)dichalcogenide shows band at 3355 cm^{-1} due to v(NH_2) and v(C—H) band appears at 2900 cm^{-1}, a band at 1570 cm^{-1} attributed to v(N—H) bending and band at 1200 cm^{-1} due to v(C—N).[10]

^1H NMR spectra show the multiplate at $\delta 1.8$ ppm due to mid CH_2 protons and two triplet peaks at δ 2.5 ppm and δ 2.6 ppm are assigned to Te—CH_2 and N—CH_2 protons, respectively.

^{13}C NMR spectra show peaks at δ 1.3, 35.8 and 43.9 ppm are assigned to Te-CH_2, mid CH_2 and N-CH_2 carbons, respectively.

Synthesis of Zinc (II), Cadmium (II) and Mercury (II) Complexes

A variety of Zinc (II), Cadmium (II) and mercury (II) containing 3-aminopropylchalcogenolate has been prepared employing the route depicted in Scheme 1. The reaction of bis(3-aminopropyl)-dichalcogenide with sodium borohydride generated 3-aminopropylsodiumchalcogenolate in situ which reacts with metal halides, i.e., $ZnBr_2$, $CdCl_2$ and $HgCl_2$ give 3-aminopropylmetalchalcogenolate complexes. Due to poor solubility, these complexes have not been fully characterized. In IR spectra vN-H appeared at 3422–3450 cm^{-1}, which shifted downfield (~25 cm^{-1}) as compared to free ligand. This indicates that the nitrogen coordinates to metal atom. The elemental analyses gave the composition of complexes as $C_6H_{16}MN_2Te_2$. Based on IR and elemental analyses, the tentative structure of complexes is as shown in Figure 1.



M = Zn, Cd, Hg

FIGURE 1 Proposed structure of 3-aminopropylmetalchalcogenolate complexes.

Preparation of Semiconductor Nanoparticles from 3-aminopropylmetalchalcogenolate Complexes

Nanoparticles were prepared by solvo-thermal route[11] by injecting of 3-aminopropylmetalchalcogenolate complexes in quinoline to a vigorously stirred quinoline maintained at 200°C under argon atmosphere. After complete injection of the precursor solution, the temperature dropped by 20°C, and the color of the solution changed from pale yellow

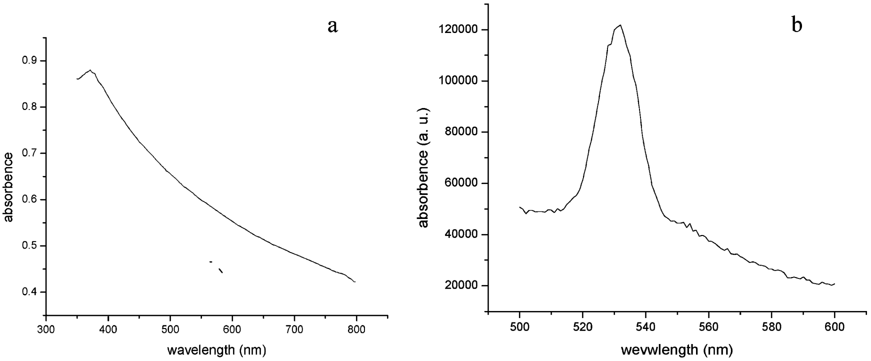


FIGURE 2 (a) UV-Vis; and (b) PL spectra of cadmium telluride nanoparticle.

to dark brown. The reaction mixture was stirred for 1 h, and the solution was allowed to cool to room temperature. The anhydrous methanol was added, which resulted in the formation of flocculate of colloidal particles. The gray powder obtained by centrifugation of colloidal solution was washed with methanol, vacuum dried and stored under argon. The gray powder did not dissolve in organic solvents indicating the particles are uncapped with quinoline.[12] The lattice structures and size of the prepared nanoparticles are calculated by X-ray powder diffraction (XRD) and the morphology has been studied by SEM and TEM.

UV-Vis spectra (Figure 2a) of cadmium telluride show the band at 376 nm. The broadening of the absorption is mainly due to the size distribution of the CdTe nanoparticles. It is observed from UV-Vis spectra that the wide edge is located at 628 nm (1.97 eV) which clearly represents a blue shift to the band gap of bulk CdTe (1.50 eV). As we know the band gap of the semiconductors increases as their corresponding size decreases and subsequently the blue shift of the absorption edge of the CdTe nanoparticles result from the known quantum size effect. Room temperature PL spectra of the CdTe nanoparticles are shown in Figure 2b. Under the excitation wavelength of 450 nm, a higher emission peak is observed at 530nm and the PL excitation wavelength was recorded at 435 nm. The blue shift in the PL spectra from the bulk may also be related to the quantum effects of the CdTe nanoparticles.

The SEM and TEM images of the cadmium telluride nanoparticles are shown in Figure 3. The SEM image shows that the particles assume sphere like agglomerated structures with the average particle size 50–100 nm, which also supported by the TEM image of CdTe nanoparticles showing the agglomeration. This is because of the fact that the particles are not capped. We could able to see the individual particles after the 30 min sonication in chloroform. These are in the range of 10–15 nm.

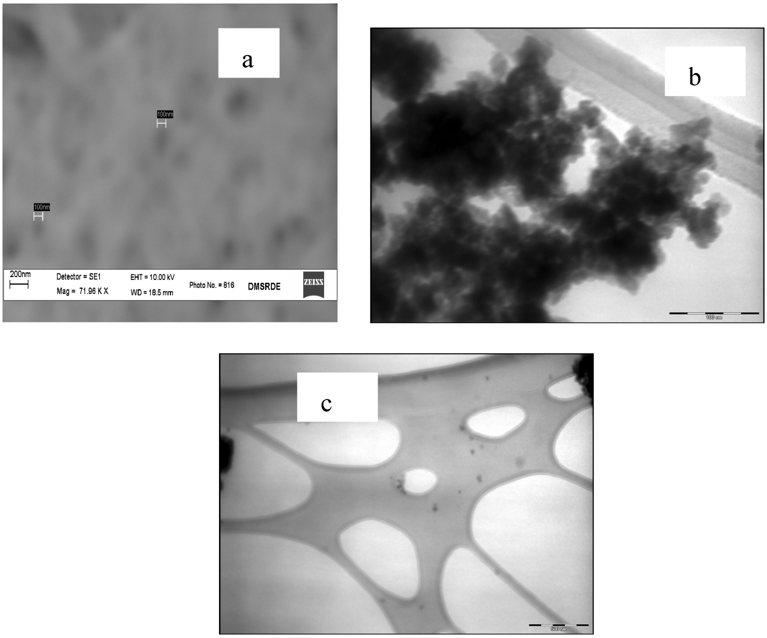


FIGURE 3 (a) SEM image; and (b & c) TEM images of CdTe nanocrystals.

The formation of CdTe nanoparticles was also supported by the EDAX analysis (Figure 4). X-ray diffraction analysis (XRD) is used to examine the crystal structure of the products. The XRD pattern of the cadmium telluride nanostructure is shown in Figure 5. It is cleared that the CdTe nanoparticles are having pure cubic crystal structure with lattice parameters close to reported data (JCPDS # 75-2086) ($a = 6.41$ A°) and is preferentially oriented in the c axis direction. The lattice parameter is calculated to be $a = 6.45$ A° ± 0.003, which is in agreement with that of cadmium telluride reported in the JCPDS diffraction file.[13] From the width of XRD peaks, the average diameter of the nanoparticles is estimated to be 10-15 nm from the Scherrer equation.[14] UV-Vis spectra of ZnTe nanoparticles show the bands at 363, 400, 482, and 539 nm (Figure 6a) respectively. The broadening of the absorption is mainly due to the size distribution of the ZnTe particles. It is observed from the UV-Vis spectra that the wide edge is located at 650 nm (1.90 eV), which clearly represents a blue shift to the band gap of bulk ZnTe.

Room temperature PL spectra of the ZnTe nanoparticles are shown in Figure 6b. Under the excitation wavelength of 450 nm, a higher emission peak is observed at 612 nm and the PL excitation wavelength

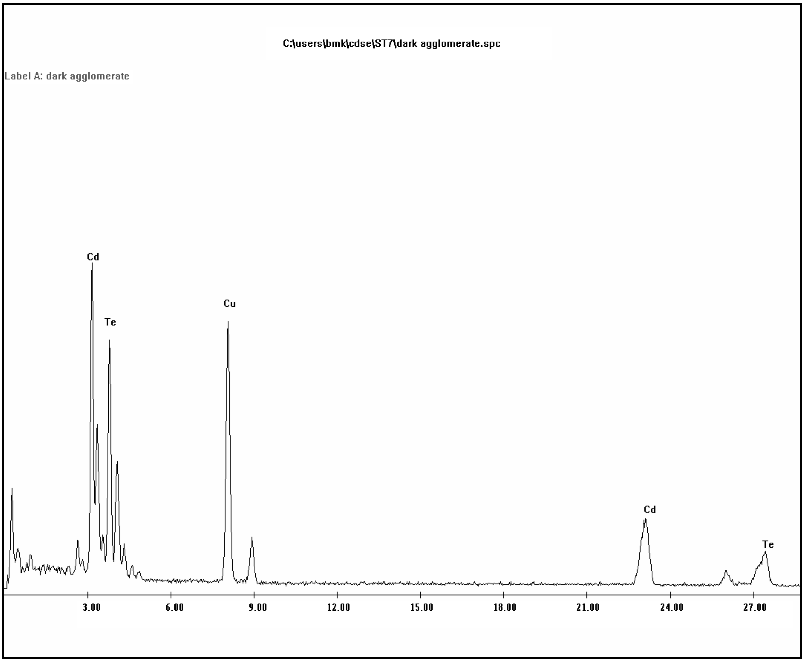


FIGURE 4 EDAX spectra of CdTe nanocrystals.

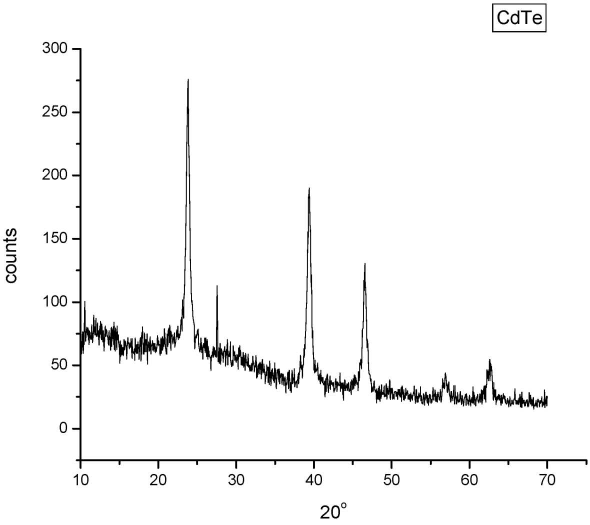


FIGURE 5 XRD pattern of CdTe Nanoparticles.

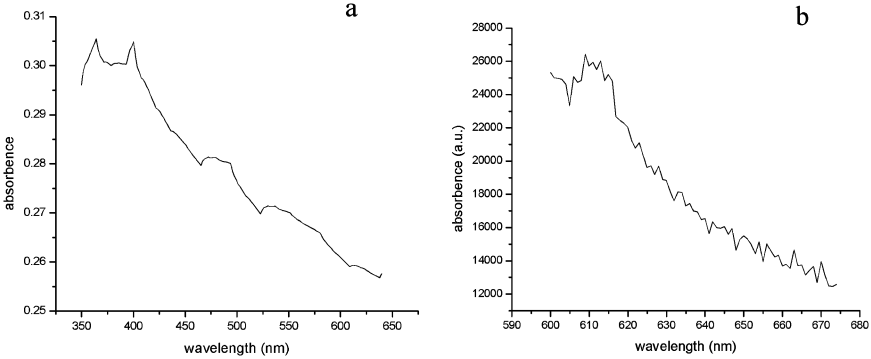


FIGURE 6 (a) UV-Vis; and (b) PL spectra of zinc telluride nanoparticle.

was recorded at 532 nm. The blue shift in the PL spectra from the bulk may also be related to the quantum effects of the ZnTe nanoparticles.

The TEM image of Zinc telluride nanoparticles are shown in Figure 7. The TEM image clearly reveals that ZnTe nanoparticles are agglomerated; it is obvious because these particles are not capped. The formation of ZnTe nanoparticles was also supported by the EDAX analysis.

UV-Vis spectra of mercury telluride nanoparticles dispersed in a chloroform solution showed a broad tailing into the infrared end. The spectra do not exhibit a prolonged edge or strong blue shift unlike the thiol capped HgTe reported by Rogach.[15] The broad nature of the spectra make difficult to assign a band edge, and hence no estimation of band gap was made.[16] Room temperature PL spectra of the HgTe nanoparticles are shown in Figure 8 under the excitation wavelength of 360 nm and a higher emission peak is observed at 450 nm.

The XRD pattern of the mercury telluride nanostructure is shown in Figure 9. It is cleared from the figure that HgTe is pure hexagonal

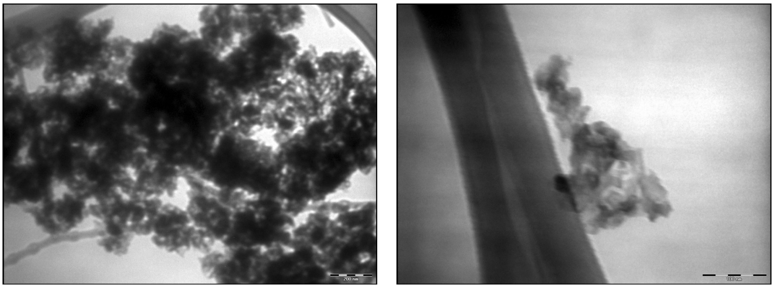


FIGURE 7 TEM image of ZnTe nanocrystals.

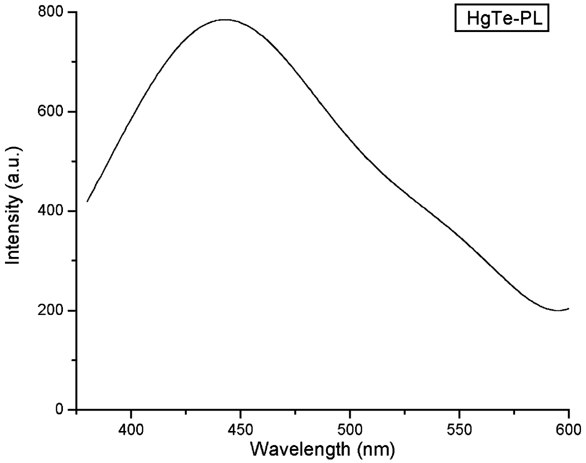


FIGURE 8 PL spectra of HgTe nanocrystals.

crystal structure with lattice parameters close to reported data (JCPDS # 80-0087) ($a = 4.383$ A°) . The lattice parameter $a = 4.40$ A° ± 0.003, which is in agreement with that of mercury telluride reported in the JCPDS diffraction file.[17]

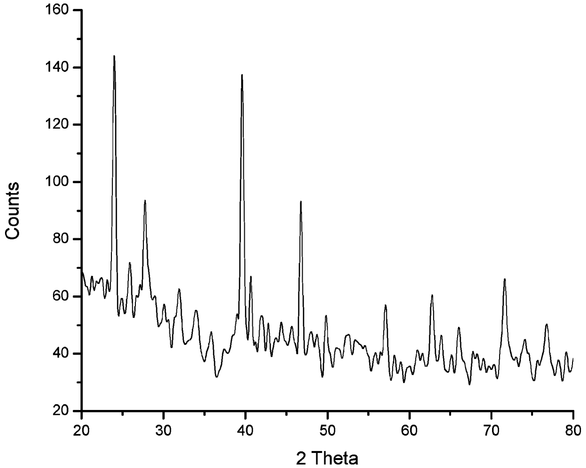


FIGURE 9 XRD pattern of HgTe nanoparticles.

EXPERIMENTAL

Melting point and boiling points are uncorrected. All the reactions were performed under inert atmosphere using standard vacuum line techniques. Solvents were carefully purified by standard procedure,[12] and they were freshly distilled and degassed prior to use. The chemicals Cadmium Chloride, Zinc Chloride, Mercury Chloride, 3-Chloropropylamine, and Tellurium powder were from E-Merck, Germany, and they were used as received.

The FT-IR spectra were recorded on Nicolate Magna IR 750 spectrometer using KBR pellets. ^{1}H and ^{13}C spectra were obtained at 400 MHz on a Bruker 400 MHz Spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal standard for ^{1}H and ^{13}C, respectively.

X-ray diffraction (XRD) pattern were measured by using a Philip PW 1700 series automated powder diffractometer using Cu-Ka radiation at 40 kV/40 mA with a secondary graphite-crystal monochromator. SEM images were recorded on CARL ZIESS EVO 50 low vacuum scanning electron microscopy at 10 kV. The samples were gold coated prior to examination under microscope and the TEM images were recorded on JEOL JEM CX II transmission electron microscope at an operating voltage of 80 kV. At first, a colloidal suspension of prepared nanoparticles was formed in methanol. A fine 400 mesh copper grid coated with colloidal film was taken and this was coated again with a layer of carbon using a vacuum evaporator to enhance the conductivity. Two drops of the colloidal suspension was taken on the grid and was air dried completely before microscope viewing.

Synthesis of Bis(Aminopropyl)ditelluride

An alkaline solution of $NaBH_4$ (0.295 g, 7.8 mmol) in 10 mL of degassed distilled water was slowly added to magnetically stirred slurry of tellurium powder (1.0 g, 7.8 mmol) in 40 mL water at room temperature during 30 min. The reaction mixture was refluxed until the tellurium metal dissolved. The solution turned dark red indicating the formation of Na_2Te_2. To this solution, 3-aminopropylchloride (1.02 g, 7.8 mmol) was added dropwise with constant stirring at 0°C. The reaction mixture was refluxed for 3 h. The organic layer was extracted with chloroform and washed with degassed water. The organic extract was dried over sodium sulfate. Solvent was evaporated on rotary evaporator. The product was washed with hexane and dried under vacuum. A dark brown viscous liquid of bis(aminopropyl)ditelluride obtained. Color : dark brown, viscous liquid, Yield 1.10 g, 55%, b.p. = 153°C; IR (NaCl palate, cm^{-1}): 3355 ν (N—H), 1570 δ (N—H), 1197 ν(C—N); ^{1}H NMR (δ ppm, $CDCl_{3,}$): 1.8 (m, mid CH_2), 2.5 (t, Te—CH_2), 2.6 (t, N—CH_2); ^{13}C NMR (δ ppm, $CDCl_{3,}$): 1.3 (Te—$\underline{C}H_2$), 35.8(mid $\underline{C}H_2$), 43.9 (N—$\underline{C}H_2$).

Synthesis of Zinc (II), Cadmium (II) and Mercury (II) Complexes with Bis (Aminopropyl) ditelluride—General Procedure

To an ethanolic solution of Bis(aminopropyl)ditelluride (1.0 g, 2.6 mmol) in 30 mL of degassed ethanol, a solution of sodium borohydride (0.253 g, 6.68 mmol) in 10 mL ethanol was added slowly at 0°C for 30 min. The reaction mixture was stirred under inert atmosphere until the dark brown colors disappear. To this, metal halides (2.6 mmol) in 10 mL ethanol, were added dropwise with constant stirring at 0°C. The reaction mixture was refluxed for 6 h. The precipitate was filtered and washed with degassed ethanol/water and dried under vacuum. The obtained product is not soluble in polar and non-polar solvents.

Bis(aminopropyl)Zinctellurolate

Color, light yellow; yield, 0.80 g, 58.8%; m.p., 270°C (dec.) anal. Found: C, 15.90; H, 3.90; N, 6.21%; Calc. For $C_6H_{16}ZnN_2Te_2$: C, 16.50; H, 3.69; N, 6.41%; IR (KBr, cm^{-1}): 3422 ν (NH_2), 2950 ν (C—H), 1250 ν (C—N).

Bis(aminopropyl)Cadmiumtellurolate

Color, yellow; yield, 0.800 g, 53%; m.p. 250°C (dec.), anal. Found: C, 15.32; H, 3.8; N, 5.31%; Calc. For $C_6H_{16}CdN_2Te_2$: C, 14.89; H, 3.33; N, 5.79%; IR (KBr, cm^{-1}): 3449 ν(NH_2), 2940 ν(C—H), 1250 ν (C—N).

Bis(aminopropyl)Mercurytellurolate

Color yellowish green, solid; yield, 0.700 g, 35%; m.p., 190°C (dec.) anal. Found: C, 13.10; H, 3.25; N, 4.61%; Calc. For $C_6H_{16}HgN_2Te_2$:C, 12.60; H, 2.82; N, 4.90%; IR (KBr, cm^{-1}): 3450 ν(NH_2), 2930 ν (C—H), 1240 ν (C—N).

Preparation of Semiconductor Nanoparticles from 3-Aminopropyl Metal Chalcogenolate Complexes

In a typical procedure for the preparation of nanoparticles (NPs)[11], a solution of 3-aminopropyl metal chalcogenolate complexes (1 mmol) dispersed in quinoline (10 mL) was injected dropwise into a vigorously stirred quinoline (20 mL) maintained at 200°C under argon atmosphere. After complete injection of the precursor solution the temperature dropped by 20°C and the color of the solution changed from pale yellow to dark brown. After stirring for 1 h, heating was removed and the solution was allowed to cool to room temperature. The addition of anhydrous methanol resulted in the formation of flocculate of colloidal particles. The brown powder obtained by centrifugation of colloidal solution was washed with methanol, vacuum dried, and preserved under argon. The brown powder did not dissolve in organic solvents indicating the particles are uncapped with quinoline. [12]

REFERENCES

[1] (a) M. A. Malik, P. O'Brien, and N. Revaprasadu, *Phosphorus, Sulfur, and Silicon*, **180**, 689 (2005); (b) C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.*, **115,** 8706 (1993).

[2] P. J. Bonasia and J. Arnold; *J. Organomet. Chem.*, **449,** 147 (1993).

[3] S. Dey, V. K. Jain, J. Singh, V. Trehan, K. K. Bhasin, and B. Varghese, *Eur. J. Inorg. Chem.*, 744 (2003).

[4] (a) H. J. Gysling , *The chemistry of Organic Selenium and Tellurium Compounds,* (Wiley, New York, 1986), Vol. 1, p. 679; (b) I. G. Dance, *Polyhedron,* **5,** 1037 (1986), and references therein; (c) A. P. Arnold, A. J. Canty, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans*. 607 (1982); (d) A. P. Arnold and A. J. Canty, *Inorg. Chim. Acta*, **55,** 171 (1981).

[5] J. Arnold, *Prog. Inorg. Chem.*, **43,** 353 (1995).

[6] A. Singhal, V. K. Jain, B. Varghese, and E. R. T. Tiekink, *Inorg. Chim. Acta*, **285,** 190 (1999).

[7] J. R. Dilworth and B. Wheatley, *Coord. Chem. Rev*., **199,** 89 (2000).

[8] S. K. Tripathi, PhD Thesis, Jiwaji University Gwalior, India, 2001.

[9] (a) S. K. Tripathi, B. L. Khandelwal, and S. K. Gupta, *Phosphorus, Sulfur, and Silicon*, **177,** 2285 (2002); (b) S. K. Tripathi, S. B. Mishra, M. Nasim, and B. L. Khandelwal, *Phosphorus, Sulfur, and Silicon*, **180,** 1019 (2005); (c) S. K. Tripathi, S. B. Mishra, M. Nasim, and B. L. Khandelwal, *The Chemistry and Application of Alkaxy, Aryldoxy and Allied Derivatives of Elements*, edited by R. Bohra, A. Singh, and R. C. Mehrotra, RBSA Publisher, S. M. S. Highway, Jaipur, 291–296 (2002); (d) J. D. Singh, M. D. Milton, B. L. Khandelwal, S. Karthikeyan, and T. P. Singh, *Phosphorus, Sulfur, and Silicon*, **136,** 299 (1998).

[10] A. Khanna, A. Bala, and B.L. Khandelwal, *J. Orgmet. Chem*., **494,** 119 (1995).

[11] D. Selvakumar, Santosh K. Tripathi, R. Singh, and M. Nasim, *Chem. Lett*. **37,** 34 (2008).

[12] M. A. Olshavvsky, A. N. Goldstein and A. P. Alvisatos, *J. Am. Chem. Soc.*, **112,** 9438 (1990).

[13] JCPDS file No.JSPS # 75-2086.

[14] H.P. Kling and L. E. Alexander, *X-ray Diffraction Procedure* (John Wiley and Sons, New York, 1959).

[15] A. Rogach, S. Kershaw, M. Burt, M. Harrison, A. Kornowski, A. Eychmuller and H. Weller, *Adv. Mater*., **11,** 552 (1999).

[16] M. Green, G. Wakefield and P. J. Dobson, *J. Mater. Chem*., **13,** 1076 (2003).

[17] JCPDS file No. JSPS # 80-0087.