Synthesis and characterization of anisotropic cadmium and lead sulfide nanostructures from single source molecular precursors and an insight to their growth mechanisms

by

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ABSTRACT

Synthesis and characterization of anisotropic cadmium and lead sulfide nanostructures from single source molecular precursors and an insight to their growth mechanisms

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This thesis details the synthesis and characterization of anisotropic cadmium and lead sulfide nanostructures from single-source molecular precursors. Six new precursors were synthesized for cadmium and lead sulfide each, by the reaction of the appropriate metal acetate with picolinic (HPic), 2,6-dipicolinic (H₂dipic) or salicylic acid (H₂sal) followed by the addition of thiourea (th) or thiosemicarbazide (ths). The precursors for CdS are [Cd(Hsal)₂(tu)₂] (Cd₁a), [Cd(Hsal)₂(ths)₂]·nH₂O (Cd₁b), [Cd(pic)₂(tu)₂]·0.5H₂O (Cd₂a), [Cd(pic)₂(ths)₂]·2H₂O (Cd₂b), [Cd(dipic)(tu)₂] (Cd₃a) and [Cd(dipic)(ths)₂(H₂O)]·2H₂O (Cd₃b) and the precursors for PbS are [Pb(Hsal)₂(th)₂] (Pb₁a), [Pb(Hsal)₂(ths)₂] (Pb₁b), [Pb(pic)₂(th)₂] (Pb₂a), [Pb(pic)₂(ths)₂] (Pb₂b), [Pb(dipic)(th)(H₂O)]₂·2H₂O (Pb₃a) and [Pb(dipic)(ths)₂]·H₂O (Pb₃b). All of the compounds were characterized spectroscopically and by elemental analysis. Cd₁a, Cd₂a, Cd₂b, Cd₃a, Cd₃b, Pb₂b Pb₃a and Pb₃b formed well-defined crystals and were characterized by single crystal X-ray diffraction.

The precursors were decomposed at or around 170 °C using n-cetyltrimethylammonium bromide (CTAB), sodium dodecylsulphate (SDS), ethylenediamine, oleic acid, oleylamine, trioctylamine or hexadecylamine as surfactants. Systematic variations of surfactants gave small spherical nanoparticles, micro-sized flowers, multipods and nanorods for CdS and nanocubes, truncated nanocubes, hexapods,
octahedrons and dendritic stars for PbS. From XRPD studies it was found that most of the CdS nanostructures were of the stable hexagonal phase. However, in two cases the nanostructures were found to be predominantly of a metastable orthorhombic phase. For PbS system, all the decompositions yielded pure crystalline galena. For CdS system, TEM studies revealed planar defects (such as polysynthetic and multiplet twinning) in the nanocrystals, which gave an explanation for mechanism of growth. For PbS system, in order to elucidate the effect of single source precursors on the mechanism of growth of nanoparticles, the decomposition results were compared with PbS nanostructures synthesized from multiple-source precursors, lead acetate and thiourea or thiosemicarbazide. It was found that in the reactions of multiple source precursors, acidic components in the reaction mixture (oleic acid, acetic acid) led to etching and crystal splitting, which played a crucial role in the formation of anisotropic nanostructures.
In loving memory of my grandfather and my aunt

Sivadas Baul
1926-1998

Smriti lata Kundu
1940-1995
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# TABLE OF CONTENTS

## ACKNOWLEDGEMENTS

1 General Introduction

---

2 Synthesis and molecular structure of single-source molecular precursors to CdS and PbS

### 2.1 Introduction

### 2.2 Experimental

#### 2.2.1 Materials

#### 2.2.2 Instrument and characterization details

#### 2.2.3 Generalized method of synthesis of precursors and synthetic challenges

#### 2.2.4 Synthesis of precursors to CdS

#### 2.2.5 Synthesis of precursors to PbS

### 2.3 Description of molecular structures of precursor compounds

#### 2.3.1 Molecular structures of CdS precursors

#### 2.3.2 Molecular structures of PbS precursors

### 2.4 Conclusion

---

3 Synthesis of various anisotropic CdS nanostructures by decomposition of single-source precursors

### 3.1 Introduction

### 3.2 Experimental procedure

#### 3.2.1 Materials

#### 3.2.2 Instrumentation details

#### 3.2.3 Reaction setup for the synthesis of CdS NPs

### 3.3 Decomposition results

#### 3.3.1 Decomposition of Cd1a, Cd2b and Cd3a in the presence of CTAB

#### 3.3.2 Decomposition of Cd1a in ethylenediamine

#### 3.3.3 Decomposition of Cd1a or Cd2b in oleylamine

#### 3.3.4 Decomposition of Cd1b in oleylamine with added hydrochloric acid and TOPO

#### 3.3.5 Decomposition of Cd1b in oleylamine with the presence of TOP

### 3.4 Results and discussion

### 3.5 Conclusion

---

4 Synthesis of various anisotropic PbS nanostructures by decomposition of single-source precursors and comparison with multiple source precursors

### 4.1 Introduction

### 4.2 Experimental

#### 4.2.1 Materials

#### 4.2.2 Instrumentation and characterization details

### 4.3 Synthesis of the nanomaterials from single source precursors (SSP)

#### 4.3.1 Decomposition of the precursors in the presence of CTAB

#### 4.3.2 Decomposition of the precursors in an aqueous mixture of SDS and CTAB

#### 4.3.3 Decomposition in the presence of oleylamine and dodecanethiol

#### 4.3.4 Decomposition in the presence of ethylenediamine

### 4.4 Synthesis of the nanomaterials from multiple source precursors (MSP)

#### 4.4.1 Decomposition in the presence of oleic acid
4.4.2 Decomposition in presence of oleic acid and trioctylamine ........................................... 61
4.4.3 Decomposition in the presence of CTAB and ethylene glycol ........................................ 62
4.5 Results and discussion ......................................................................................................... 62
4.6 Conclusion .......................................................................................................................... 73

A Additional spectral characterization data for precursors ...................................................... 75

B Supporting information on Chapter 3 .................................................................................... 94

C Supporting information on Chapter 4 .................................................................................... 101

CURRICULUM VITAE .................................................................................................................. 107

REFERENCES ............................................................................................................................... 110
LIST OF FIGURES

Figure 2.1 ESI-MS of precursor Cd1b. ................................................................. 17

Figure 2.2 Experimental peak at 523.42 match the simulated isotopic distribution of Cd(Sal)(ths)$_3$ (molecular wt calculated= 523.99). ................................................................. 18

Figure 2.3 Experimental peak at 432.75 match the simulated isotopic distribution of Cd(HSal)(ths)$_2$ (molecular wt calculated= 432.97). ................................................................. 18

Figure 2.4 Experimental peak at 294.92 match simulated isotopic distribution of Cd(th$_3$)$_2$ (molecular wt calculated= 294.69). ................................................................. 19

Figure 2.5 Experimental peak at 385.83 plotted against the simulated isotopic distributions of Cd(Sal)$_2$ (molecular wt calculated= 385.94) and Cd(th$_3$)$_3$ (molecular wt calculated= 386.96) shows better matching with Cd(Sal)$_2$. ................................................................. 19

Figure 2.6 X-ray crystallographic structure of Cd1a with thermal ellipsoids at the 40% probability level. ........................................................................................................ 21

Figure 2.7 X-ray crystallographic structure of one of the two independent Cd(II) centers in Cd2a with thermal ellipsoids at the 40% probability level ................................................................. 22

Figure 2.8 X-ray crystallographic structure of Cd2b with thermal ellipsoids at the 40% probability level. The crystal lattice water molecules have been omitted ................................................................. 23

Figure 2.9 X-ray crystallographic structure of Cd3a with thermal ellipsoids at the 40% probability level ................................................................. 24

Figure 2.10 X-ray crystallographic structure of Cd3b with thermal ellipsoids at the 40% probability level. The crystal lattice water molecules have been omitted ................................................................. 25

Figure 2.11 Polymer [Pb(dipic)$_n$] formed as white residue during synthesis of precursors Pb3a and Pb3b. Reproduced from the CIF provided in reference 78 ................................................................. 29

Figure 2.12 X-ray crystallographic structure of Pb2b with thermal ellipsoids at 40% probability level ................................................................. 30

Figure 2.13 X-ray crystallographic structure of Pb3a with thermal ellipsoids at 40% probability level ................................................................. 31

Figure 2.14 X-ray crystallographic structure of Pb3b with thermal ellipsoids at 40% probability level ................................................................. 32

Figure 3.1 Reaction set up for the decomposition reactions ................................................................. 39

Figure 3.2 SEM images of the (A) Flowerlike CdS particles from Cd1a. (B) Semi-spherical aggregates of CdS from Cd2b. (C) Round shaped particles from Cd3a. ................................................................. 43
Figure 3.3 Powder XRD of CdS microsized flowers from Cd1a (Figure 3.2A) ........................................ 44

Figure 3.4 TEM image of the rod-like CdS nanostructures generated from the decomposition of Cd1a in ethylenediamine ................................................................. 45

Figure 3.5 Powder XRD data of CdS nanorods. (Figure 3.4) ................................................................. 46

Figure 3.6 (A) Conventional TEM image of spherical CdS nanoparticles synthesized with oleylamine from precursor Cd1a. (B) HR TEM image of one of the particles shown in A reveals polysynthetic twins in the hexagonal phase. (C) Conventional TEM image of spherical CdS nanoparticles synthesized with oleylamine from precursor Cd2b. (D) HR TEM images and FFT of four NPs shown in C confirm all four of them have [001]hex zone axis orientation but are rotated relative to each other along this zone axis. ........................................... 47

Figure 3.7 Powder XRD of spherical CdS nanocrystal (Figure 3.6C) .................................................... 48

Figure 3.8 Polysynthetic (A) and multiplet (B) twinning. (A) represents the hexagonal phase polysynthetically twinned on (032). The zone axis orientation is [100]. (B) is a section of f.c.c. phase (twinned on the symmetry related planes (111) and (11 1) so as to become a triplet. The zone axis orientation is [011]. Taken after reference 114 ......... 49

Figure 3.9 (A) Conventional TEM image of CdS particles synthesized from precursor Cd1b in oleylamine with added HCl (B) Conventional and (C) HR TEM images of semi-rectangular CdS particles synthesized in oleylamine with added TOPO and HCl from precursor Cd1b .................. 50

Figure 3.10 Powder XRD of semi-rectangular CdS nanocrystals (Figure 3.9B) ....................................... 50

Figure 3.11 Conventional and HR TEM images of multi-branched nanoparticles synthesized from precursor Cd1b in oleyl amine in the presence of TOP and HCl. (A) Mixture of rods and bipods generated without using any dodecanethiol in the surfactant. (B) Mixture of rods, bipods, tripods and tetrapods generated in the presence of a small amount of dodecanethiol. (C) HR TEM image one of the bipod structures shown in A, FFT is obtained from the core of the particle. (D) Enlarged image of one of the tetrapod structures from (B). (E) HR TEM image of the tetrapod and FFT obtained from its central part................................................................. 52

Figure 3.12 Powder XRD of multi-branched CdS (mixture of rods and bipods) (Figure 3.11A) ..................... 53

Figure 3.13 Polycrystalline SAED pattern recorded from the multi-branched CdS particles shown in Figure 3.11B, D, E. Rings from the f.c.c. phase have c subscripts and the others are from hexagonal phase, which is the predominant one................................................................. 53

Figure 4.1 PbS nanoparticles synthesized from precursor Pb2b by using CTAB, A (1 hr), B(2 hrs), C&D (5 hrs), E (16hrs), F (16hrs without using CTAB). All scale bars = 1μm ...................... 64

Figure 4.2 (top) different shapes of nanocrystals evolved as a function of growth ratio (R) between {100} and {111} faces, (bottom) growth along {100} faces giving rise to the star-shaped nanocrystals. Taken after reference 126 .................... 66
Figure 4.3 PbS nanoparticles generated with equimolar mixture of CTAB and SDS from precursor Pb2b. ................................................................. 67

Figure 4.4 Nanocubes generated in oleylamine from precursor Pb2a. .......................................................... 68

Figure 4.5 PbS dendrites synthesized from precursor Pb2b and Pb1a in the presence of ethylenediamine (scale bars = 1 µm). ................................................................. 69

Figure 4.6 PbS dendritic stars synthesized from MSP (Pb(OAC)2 and thiourea) in presence of ethyleneglycol and CTAB................................................................. 71

Figure 4.7 (A) TEM, (B) HR TEM and (C) SAED pattern of PbS nanoparticles synthesized from MSP(Pb(OAC)2 and thiourea) using oleic acid as surfactant. ......................................................... 72

Figure 4.8 TEM(A, B, C), HRTEM (D) and SAED (E) of mixture PbS nanocubes and split rods synthesized from (Pb(OAC)2 and thiourea in presence of trioctylamine and oleic acid surfactant mixture................................. 73

Figure A.1 FT-IR spectra of precursor Cd1a (top) and Cd1b (bottom). ................................................................. 75

Figure A.2 FT-IR spectra of precursor Cd2a (top) and Cd2b (bottom). ................................................................. 76

Figure A.3 FT-IR spectra of precursors Cd3a (top) and Cd3b (bottom)................................................................. 77

Figure A.4 FT-IR spectra of Pb1a (top) and Pb1b (bottom). ................................................................. 78

Figure A.5 FT-IR spectra of Pb2a (top) and Pb2b (bottom). ................................................................. 79

Figure A.6 FT-IR spectra of Pb2a (top) and Pb2b (bottom). ................................................................. 80

Figure A.7 13C NMR spectra of precursors Cd1a (top) Cd1b (bottom). ................................................................. 81

Figure A.8 13C NMR spectra of precursors Cd2a (top) Cd2b (bottom). ................................................................. 82

Figure A.9 13C NMR of precursor Cd3a. .................................................................................................................. 83

Figure A.10 13C NMR of Pb1a (top) and Pb2a (bottom). ................................................................. 84

Figure A.11 13C NMR of Pb2b (top) and Pb3a (bottom). ................................................................. 85

Figure A.12 Precursor Cd1a packing structure................................................................. 86

Figure A.13 Precursor Cd2a packing structure................................................................. 87

Figure A.14 Precursor Cd2b packing structure................................................................. 88

Figure A.15 Precursor Cd3a packing structure................................................................. 89

Figure A.16 Precursor Cd3b packing structure................................................................. 90
Figure A.17 Precursor Pb2b packing structure................................................. 91
Figure A.18 Precursor Pb3a packing structure.................................................. 92
Figure A.19 Precursor Pb3b packing structure.................................................. 93

Figure B.1 Absorbance (top left) and Photoluminescence (top right) spectra of CdS NPs. TEM images of the corresponding CdS NPs (bottom)........................................... 95
Figure B.2 TGA of precursor Cd1a in Argon atmosphere..................................... 96
Figure B.3 TGA of precursor Cd1b in Argon atmosphere..................................... 96
Figure B.4 TGA of precursor Cd2a in Argon atmosphere..................................... 97
Figure B.5 TGA of precursor Cd2b in Argon atmosphere..................................... 97
Figure B.6 TGA of precursor Cd3a in Argon atmosphere..................................... 98
Figure B.7 Characteristic TGA of precursor Cd3b in Argon atmosphere.................. 98

Figure B.8 EDS results of the CdS particles prepared hydrothermally from Cd1a Al and Mg peaks are present from the metal support of the samples (Mg-Al alloy)........................................... 99
Figure B.9 EDS results of the CdS particles prepared from Cd2b in ethylenediamine. Al and Mg peaks are present from the metal support of the samples (Mg-Al alloy)......................... 100

Figure C.1 TEM images of PbS Nanocubes generated from precursors Pb1a (A), Pb1b (B), Pb2b (C), Pb3a (D), Pb3b (E) in oleylamine (8mL) and dodecanethiol (1mL) mixture. All scale bars = 100 nm. ................................................................. 101
Figure C.2 TEM image of PbS nanoparticles generated from precursor Pb2b in oleylamine (8 mL) and dodecanethiol (4mL). ................................................................. 101

Figure C.3 SEM images of Dendritic stars generated from precursors Pb2a (A), Pb1a (B), Pb1b (C) in presence of CTAB as surfactant with reaction time of 16 hrs at 170 °C (all scale bars = 1µm)......................................................................... 102
Figure C.4 SEM images of decomposition results from precursors (A) Pb1b, (B) Pb2a and (C) Pb3a. .................................................................................... 102

Figure C.5 Characteristic XRD of the decomposition product from precursor Pb2b showing matching peaks with pure crystalline galena.............................................. 103

Figure C.6 TGA curve of precursor Pb1a under inert atmosphere.......................... 104
Figure C.7 TGA curve of precursor Pb2a under inert atmosphere.......................... 104
LIST OF TABLES

Table 2.1 Selected bond lengths [Å] for CdS precursors................................................................. 25
Table 2.2 Selected bond angles [deg] for CdS precursors............................................................. 26
Table 2.3 Crystallographic data for CdS precursors...................................................................... 27
Table 2.4 Selected bond lengths [Å] of precursors Pb2b, Pb3a and Pb3b........................................ 32
Table 2.5 Selected bond angles [deg] of precursors Pb2b, Pb3a and Pb3b........................................ 33
Table 2.6 X-ray crystallographic structure parameters for PbS precursors..................................... 34
Table 3.1 Summary and comparison of nanoparticle shapes from single source precursors............ 42
Table 4.1 TGA decomposition temperatures................................................................................. 63
Table 4.2 Summary and comparison of nanoparticle shapes from single-source precursor............. 70
Table A.1 IR peak assignments of precursors to CdS................................................................. 77


1 General Introduction

The innate properties of crystalline solids are usually characteristic and independent of size or shape. It is only in the nanometer regime that these variables come into play. The growing interest in inorganic nanocrystals comes from the fact that at the nanometer scale their properties can be tailored by tuning their shapes and sizes. For example, bulk CdSe have characteristic red luminescence, however on the sub 10-nm scale their luminescence can be tuned from red to blue.\(^1\) Similarly, gold nanoparticles, unlike bulk gold, are red, purple or bluish in color and their melting point (for 1.6 nm sized gold nanocrystal) is approximately 350 °C which is significantly lower than that of bulk gold (1064 °C).\(^2\)

These shape- and size-dependent properties arise for two main reasons. First, in nanocrystals the number of surface atoms is a large fraction of the total number of atoms. In any material, surface atoms make a distinct contribution to the free energy. Nanocrystals have the same well-defined facets as present in the extended bulk crystal structure in a much smaller size range. Hence it is possible to alter the thermodynamic properties (such as melting point, etc.) by altering the energetics of nanocrystal surfaces. Second, in nanocrystals the electronic band and the density of energy states are dependent on the size and shape parameters. It has been shown by researchers that the electronic band of a crystal gets quantized and the band gap energy is increased with the gradual decrease of crystal size.\(^3\)-\(^6\) As a result the electron transport property is also influenced by decrease in size. These changes are known as quantum size effects. Similarly the shape or dimensionality of a nanocrystal also plays a crucial role.\(^7\) As the dimensionality (D) decreases from 2D (discs, prisms and plates) to 1D (rods and wires) to 0D (isotropic spheres, cubes and polyhedrons) the density of energy states (\(\rho(E)\)) evolves from
continuous to discrete, following the equation \( \rho(E) \sim E^{D/2-1} \). Shape of nanocrystals also influences the band gap energy. Strong quantum confinement effect is observed when the diameter of CdSe nanocrystal is reduced whereas only a weak quantum confinement is observed as a function of length reduction.\(^8\)

The combination of shape- and size-dependent properties and ease of fabrication make inorganic nanocrystals as promising building blocks for materials with designed functions. The enhanced surface to volume ratio in nanocrystals results in greater catalytic activity. For this reason transition metal oxide (such as, Fe\(_3\)O\(_4\), ZnO, CoO and TiO\(_2\)) and phosphide (such as, Fe\(_2\)P, FeP, Co\(_2\)P and NiP) nanocrystals are studied for their application as support to catalysts and photo-catalysts.\(^9\)-\(^14\) It has also been shown by researchers that in case of Pt nanocrystals, anisotropic shapes also affect the catalytic activity. Shapes with more atoms in corners or edges have higher catalytic activity.\(^15\) Transition metal phosphide nanocrystals are also studied for their ferromagnetic and magnetocaloric properties.\(^16\)-\(^21\) In a ferromagnetic material, strong magnetic properties are seen due to the presence of magnetic domains, in which all of the moments of the individual atoms are aligned with each other, separated by domain walls. As the size of the material is decreased and reaches a critical size, it is no longer energetically favorable for walls to form, and the particles become single domain. This change, with size reduction, leads to larger coercivity values.\(^22\) If the particle is decreased to a small enough size, the particles become thermally unstable, so the material will only possess magnetic properties in the presence of an external magnetic field. This behavior is called superparamagnetism, and NPs possessing this property have found use in the biomedical field for magnetic resonance imaging (MRI) and drug delivery.\(^23\),\(^24\) Optical properties of
nanocrystals have also been manipulated in useful ways. There are three major groups of semiconductor NPs: Group II-VI semiconductors (such as CdS, CdSe, ZnS, ZnSe, PbS, PbSe, etc.), Group III-V semiconductors (such as, InP, InAs, GaP, GaAs, etc.) and Group IV semiconductors (such as Si, Ge, etc.), which are studied for their important optical properties. Optical properties of semiconductor NPs are strongly related to size and shape. This dependence has to do with quantum confinement, which occurs when the size of a semiconductor crystal becomes small enough that it approaches the size of the material’s Bohr exciton radius. The size and composition of the crystal determines the peak emission frequency, so it is possible to tune the size of the bandgap by changing the size of the particle. For these reasons the semiconductor NPs find use in biological diagnostics, optoelectronics, light emitting diodes, etc.25-27

For any successful application, shape and size controlled synthesis of NPs is very crucial. There are various routes to synthesize well-defined nanocrystals in a shape- and size-controlled manner. These methods include vapor-liquid-solid (VLS) methods, chemical vapor deposition (CVD), thermal evaporation and liquid phase colloidal syntheses in aqueous or non-aqueous media.28-35 Among these the liquid phase colloidal synthesis approach has been proven to give better control over shapes and sizes of the nanocrystals. The synthesis takes place in a few steps. When the reaction medium is heated to a sufficiently high temperature, the precursors decompose to give the active atomic or molecular species, also known as monomers. The monomer concentration increases rapidly with increase in temperature and reaches a super-saturation level. The first set of nanocrystals or seeds are nucleated at the next stage. The seeds start growing in size by incorporating more monomers present in the reactant media, which results in a
decrease in monomer concentration. At the last stage the surface of the as-grown nanocrystals is stabilized by the surfactants. It was found that the non-hydrolytic colloidal route provides an easier way of controlling several variables (such as type of surfactants, temperature, monomer concentration etc) and separates the nucleation stage from the growth stage, which results in better monodispersity and crystallinity of the nanocrystals as compared to the ones synthesized in a hydrolytic (i.e. aqueous) route. The ideal precursors for these reactions are usually organometallic compounds, which decompose cleanly at the reaction temperature giving rise to the desired active species. The surfactants commonly used in these synthetic schemes include alkyl phosphine oxides, alkyl phosphonic acids, alkyl phosphines, fatty acids and amines. All of these molecules contain metal coordinating groups as well as solvophilic groups. The metal coordinating groups donate electron to metal atoms and thus prevent aggregation and further growth. In addition, the surfactant molecules bind to the particle surfaces in a manner that dictates the crystallographic axis along which growth will take place and helps in the shape-selective synthesis.

We have been exploring the effect of single-source precursors on the morphology and size of NPs produced. This method can be considered to be the combination of metal-organic chemical vapor deposition (MOCVD) and the liquid phase colloidal route. A single molecule, which contains all the elements required in the final material and has a pre-determined metal-ligand linkage (e.g. metal-carbon for metal carbides, metal-oxygen for metal oxides, metal-sulfur for metal sulfides, etc.) is employed in this technique as a precursor. This molecule is called a single-source molecular precursor. This route of synthesizing nanocrystals has some advantages over the conventional way of using
multiple precursors. First of all, it is a one-step synthesis technique, comparable to MOCVD which requires simpler equipments and methods of fabrication.\textsuperscript{36,37} The presence of only one precursor in the reaction stream eliminates the chances of two or more different reagents reacting at different speeds, minimizes the chances of contamination associated with pre-reaction and allows an intrinsic control over the stoichiometry.\textsuperscript{37-39} In some molecular precursors such as molecular cluster compounds, the phase of the final product can be controlled by the core structure of the precursor molecule.\textsuperscript{40} This was shown in a recent work by O’Brien and co-workers. The authors synthesized Fe\textsubscript{3}S\textsubscript{4} (greigite phase) and Fe\textsubscript{7}S\textsubscript{8} (pyrrhorite phase) NPs from a single-source precursor \([\text{N}^\text{Bu}_4]_2[\text{Fe}_4\text{S}_4(S\text{Ph})_4]\), in which the core has a cubane type structure with Fe and S atoms at alternate corners.\textsuperscript{40} In cases where more than two components are present in the final product, using a single-source precursor can be particularly useful.\textsuperscript{41} This was shown by Veith \textit{et al.} in synthesizing BaTiO\textsubscript{3} and related perovskites. They found that using an equimolar mixture of two different precursors like Ba(OH)\textsubscript{2}·8H\textsubscript{2}O and Ti(O\textsuperscript{3}Pr)\textsubscript{4} in a sol-gel hydroxide route gave a mixture of products and contained impurities of BaCO\textsubscript{3} and Ba\textsubscript{2}TiO\textsubscript{4} even after heating at 1200 °C. However, using \([\text{BaTi(OH)}(O\textsuperscript{3}Pr)_5(HO\textsuperscript{3}Pr)]_2\) as a single-source precursor gave pure crystalline BaTiO\textsubscript{3} at a much lower temperature of 600° C.\textsuperscript{41} Furthermore, the bridging or chelating organic ligands present in these complexes prevent molecular segregation and the loss of volatile organic moieties may impart desirable structural features in the end product such as high surface area, low density, connected channels, or the formation of metastable phases.

In previous work from our group, single-source precursors to MnO, Fe\textsubscript{2}P, Bi\textsubscript{2}S\textsubscript{3} and BiVO\textsubscript{4} NPs have been reported.\textsuperscript{36, 37, 39, 42-44} Some unpublished work has been done
towards synthesizing FeMnP and In$_2$O$_3$ via a single-source precursor route.$^{45,46}$ The work discussed in this thesis focuses on single source precursors to CdS and PbS. There have been several reports on single-source precursors to chalcogenide nanomaterials. Dialkyldithiocarbamates and dialkyldithiophosphates have been used as precursors to chalcogenide nanomaterials by several researchers.$^{47-52}$ Different precursors to CdS and PbS explored by other researchers will be discussed in greater detail in Chapter 2. Despite many advantages, there are some challenges in using single-source precursors that need to be addressed. The precursor may start to decompose when exposed to air or light in cases it is not stable in ambient conditions. In some cases the precursor undergoes structural rearrangement in the process of decomposition and as a result the stoichiometric ratios of metal and ligand in the precursor are not reflected in the end product. In some cases when the precursor is used for CVD, the high molecular weight can lead to lower volatility. Also, incorporating dopants or depositing materials in a non-integral stoichiometry remains a challenge. We have tried to address some of these issues by designing precursors which are stable under ambient conditions and decompose in one step avoiding the possibility of structural rearrangements.

We have also investigated the mechanism of formation of anisotropic CdS and PbS NPs. Traditionally anisotropic shaping in a nanocrystal comes from either of the three following factors. First, seed mediated growth, which is often observed in the vapor-liquid-solid (VLS) or solution-liquid-solid (SLS) processes where nanocrystal seeds facilitate shaping.$^{28,29,53}$ Second, oriented attachment, which results from sharing of high energy faces of adjacent crystals to reduce surface energy and attain thermodynamic stability. This was observed and reported in several different systems
such as PbSe, ZnS, CdTe, etc. Third, selective adhesion of surfactants to specific crystalline facets. This results in stabilization of those facets over others and thus different growth rates are induced to different facets leading to anisotropy. In our study of various nanocrystals [e.g. PbS, CdS, Bi$_2$S$_3$, Fe$_2$P] we have found that crystal defects play an important role in inducing anisotropy to resulting nanocrystals. In PbS we found etching in combination with crystal splitting giving rise to split-end nanorod like structures. In CdS system, our TEM studies show generation of branched nanostructures via polysynthetic and multiplet twinning caused by additives used in the reaction. However, we have also observed some selective adhesion by surfactants and oriented attachment in our study of PbS. The effects of twinning and various other crystal defects in generating anisotropic CdS and PbS nanostructures will be discussed in Chapters 3 and 4 in greater detail.
2 Synthesis and molecular structure of single-source molecular precursors to CdS and PbS

2.1 Introduction

A single-source molecular precursor is essentially an individual molecule that contains all the elements required in the final material and contains a pre-determined metal-ligand linkage (e.g. metal-carbon for metal carbides, metal-oxygen for metal oxides, metal-sulfur for metal sulfides, etc.) A single-source precursor route of synthesizing nanocrystals has some advantages over a multiple precursor technique. First of all, it is a one-step synthesis technique, comparable to MOCVD (metal-organic chemical vapor deposition) which requires simpler equipments and methods of fabrication. Additionally, intimate mixing of materials at the molecular level prevents formation of mixed phases or non-ideal stoichiometry in the end product. The presence of bridging or ligating organic ligands prevents material segregation and imparts certain unusual structural features such as connected channels, low density, high surface area or formation of a metastable phase.

Different researchers have designed and synthesized several precursors to PbS and CdS NPs. Dialkyldithiocarbamate $[\text{M}(\text{S}_2\text{CNRR'}_2)]$ and dialkyldithiophosphate $[\text{M}(\text{S}_2\text{PRR'}_2)]$ (where M = Pb, Cd) complexes of both Pb(II) and Cd(II) are well-studied in this respect. Besides that, Cd(II) complexes of ethylxanthate, thiohydrocarbazide and alkyl substituted tu have been used by O’Brien and colleagues as precursors to CdS. Uses of Cd(II) complexes of $\text{N,N'}$-bis(thiocarbamoyl)hydrazide
have also been reported. Lead dithioimidodiphosphanto [Pb((SP'Pr2)2N)2] complexes have been used to synthesize PbS thin films on glass substrate by chemical vapor deposition. Boudjouk et al. have reported the pyrolysis of lead bisbenzylthiolates to synthesize PbS nanocrystals.

The precursors examined to date are designed for use under non-aqueous conditions, and additional thio-containing molecules are often needed to assist in precursor decomposition. We have explored the synthesis of precursors that can be used in both aqueous and non-aqueous solvent, ideally without the need for additional sulfur containing molecules. To synthesize the precursor complexes, salicylic, picolinic and 2,6-dipicolinic acids were natural choices as they can coordinate as a multidentate ligands that produce stable complexes with both Pb(II) and Cd(II). As a sulfur source, tu and ths were chosen as they are readily available and are inexpensive starting materials.

2.2 Experimental

2.2.1 Materials

Cadmium acetate dihydrate (98%), ths (99%), tu (99%), Hpic (99%), H₂dipic (99%) were obtained from Sigma-Aldrich and salicylic acid was bought from Fischer Scientific. All the chemicals were used without further purification. Ethanol and hexane used for precipitation, washing and dispersion were distilled using standard procedure.

2.2.2 Instrument and characterization details

NMR spectra were recorded on a Bruker Avance-400 MHz NMR spectrometer. Infrared data were recorded on a Nicolet 670 FT-IR spectrometer using attenuated total
reflectance. ESI-MS data were recorded on a MS micrOTOF ESI. Elemental analyses were performed at the Galbraith Laboratories.

**Single crystal X-ray Structural Determination:** X-ray crystallographic data for the precursors are given in Table 2.3 and Table 2.6. The data for \textbf{Cd1a, Cd2a, Cd2b, Cd3a, Cd3b, Pb2b, Pb3a} and \textbf{Pb3b} were collected at 298 K on a Bruker SMART 1000 CCD diffractometer equipped with a Mo-target X-ray tube in a hemisphere with 10 or 15 s exposure times.\textsuperscript{73} The frames were integrated with the Bruker SAINT software package\textsuperscript{74} and corrected for absorption effects using empirical method (SADABS).\textsuperscript{75} The structures were solved using direct methods and refined by full-matrix least-squares on $F^2$ using the Bruker SHELXL software package. The coordinates of cadmium and sulfur atoms were found using direct methods.\textsuperscript{76} The remaining atoms were located in subsequent least squares difference Fourier cycles. Hydrogen atoms were included in idealized positions. Anisotropic displacement parameters were assigned to all non-hydrogen atoms.

\textbf{2.2.3 Generalized method of synthesis of precursors and synthetic challenges}

The precursor complexes are readily prepared by mixing the appropriate hydrated metal (Pb, Cd) acetates with the appropriate carboxylate ligand and either tu or ths in hot water or hot aqueous ethanol. The ability to recrystallize the compounds is affected strongly by their solubilities. The dipicolinato complexes are moderately soluble in water; the picolinates display a higher solubility, while the salicylates are highly soluble. That explains why repeated attempts to obtain crystals of \textbf{Cd1b, Pb1a} and \textbf{Pb1b} were not successful and it is possible that the complexes exist in solution as equilibrium with free ths in the absence of excess ligand as indicated by electrospray mass spectra. In the $^{13}$C
NMR spectra of all of the compounds, the shifts between the free and coordinated ligand were not appreciable to follow, which again indicates the presence of dynamic equilibrium. Lead dipicolinates were found to be less soluble than the cadmium ones, which can be rationalized by formation of neutral coordination polymer [Pb(dipic)]$_n$.\(^{77, 78}\) (shown in Figure 2.11) The coordination polymer [Pb(dipic)]$_n$ is stabilized by hydrogen bonding and aromatic stacking interaction in the crystal structure and comes out of the solution as white crystalline precipitate. The formation of [Pb(dipic)]$_n$ as a side product explains the low yield of the dipicolinato precursors of PbS as compared to CdS. In the case of Pb3b the addition of a slight excess of ths was necessary to produce well-formed crystals. It is believed that extra ths assisted in shifting the equilibrium towards formation of Pb3b.

### 2.2.4 Synthesis of precursors to CdS

*Synthesis of [Cd(Hsal)$_2$(tu)$_2$], Cd1a.* Cd(OAc)$_2$·2H$_2$O (267 mg, 1.00 mmol) and H$_2$Sal (276 mg, 2.00 mmol) were dissolved in a 100-mL beaker in 50-mL water and stirred at reflux until the volume of the solution was reduced to ~ 20 mL. Tu (160 mg, 2.10 mmol) dissolved in 10 mL of water was added slowly, and the clear solution was stirred for 30 min. The solution was left at room temperature for crystallization. Crystals of Cd1a formed after about 24 h, and were washed with hexane and dried in vacuum. Yield, ~250 mg. $^1$H NMR (DMSO-d$_6$): 6.77 (m, ArH), 7.34 (m, ArH), 7.80 (m, ArH), 7.82 (m, ArH), 3.43 (s, br), $^{13}$C NMR (DMSO-d$_6$): 116.51 (ArC), 117.82 (ArC), 119.50 (ArC), 130.22 (ArC), 133.25 (ArC), 161.12 (COH), 173.82 (CO$_2$), 183.70 (CS(NH$_2$)$_2$). Elemental
analysis, % obsd (% calcd) for $C_{16}H_{18}CdO_6N_4S_2$: C, 35.54 (35.66); H, 3.28 (3.36). Decomposes at 174 °C before melting.

*Synthesis of* $[Cd(Hsal)_2(ths)_2] \cdot nH_2O$, **Cd1b**. A similar procedure as described for **Cd1a** was employed, using 184 mg (2.02 mmol) of ths instead of tu. Yield ~270 mg. $^1H$ NMR (DMSO-$d^6$): 6.77 (m, ArH), 7.27 (m, ArH), 7.76 (m, ArH), 8.1 (m, ArH), 4.03 (m, br), $^{13}C$ NMR (DMSO-$d^6$): 116.38 (ArC), 117.55 (ArC), 119.51 (ArC), 130.18 (ArC), 132.58 (ArC), 161.33 (COH), 173.53 (CO$_2$), 181.05 (CSNH$_2$NHNH$_2$).

*Synthesis of* $[Cd(pic)_2(tu)_2] \cdot 0.5H_2O$, **Cd2a**. An aqueous solution (650 mL) of Cd(OAc)$_2$·2H$_2$O (533 mg, 2.00 mmol) and picolinic acid (492 mg, 4.00 mmol) was stirred at 100 °C in a beaker until the volume of the solution was reduced to ~100 mL. An aqueous solution of tu (308 mg, 4.04 mmol) was added and the resulting clear solution was left for crystallization for 24 h to produce colorless crystals. The product was washed with diethyl ether to give ~785 mg (76%) of the compound. Additional product was obtained after concentration of the filtrate. $^1H$ NMR (DMSO-$d^6$): 7.06 (s, broad, H of tu), 7.15 (m, ArH), 7.70 (m, ArH), 8.00 (m, ArH), 8.77 (m, ArH). $^{13}C$ NMR (DMSO-$d^6$): 125.91 (ArC), 126.51 (ArC), 139.18 (ArC), 133.25 (ArC), 146.96 (ArC), 151.92 (CCOOH), 169.74 (CO$_2$) 183.76 (CS(NH$_2$)$_2$). Elemental analysis, % obsd (% calcd) for $C_{28}H_{34}CdO_9N_12S_4$: C, 32.39 (32.44); H, 3.22 (3.28) Melting point: 215 °C.

*Synthesis of* $[Cd(pic)_2(ths)_2] \cdot 2H_2O$, **Cd2b**. Cd(OAc)$_2$·2H$_2$O (266 mg, 1.00 mmol) and picolinic acid (246 mg, 2.00 mmol) were dissolved in 200 mL of water and the resulting solution was stirred at 100 °C in a beaker until the volume of the solution was reduced to ~10 mL. Solid ths (184 mg, 2.02 mmol) was added to the hot solution of cadmium (II)
picolinate and the resulting clear solution was left to cool for two days to yield colorless crystals. Yield ~500 mg, 87%. $^1$H NMR (DMSO-d$_6$): 7.06 (s, broad, H of tu), 7.15 (m, ArH), 7.70 (m, ArH), 8.00 (m, ArH), 8.77 (m, ArH). $^{13}$C NMR (DMSO-d$_6$): 125.95 (ArC), 126.45 (ArC), 139.22 (ArC), 146.74 (ArC), 151.87 (CCOOH), 169.49 (CO$_2$) 181.14 (CSNH$_2$NHNH$_2$). Elemental analysis, % obsd (% calcd) for C$_{14}$H$_{22}$CdO$_6$N$_8$S$_2$: C, 25.01 (29.22); H, 4.18 (3.82). Melting point: 108 °C. The compound is slightly photosensitive which has made it difficult to get better elemental analyses.

**Synthesis of [Cd(dipic)(tu)$_2$]**, Cd3a. Cd(OAc)$_2$·3H$_2$O (532 mg, 2.00 mmol) was dissolved upon heating in 10 mL ethanol/water 1:1 (by volume). A solution of tu (602 mg, 8.00 mmol) in 30 mL 1:1 ethanol/water was added and the mixture was stirred for 30 min, followed by the addition of 2,6-pyridinedicarboxylic acid (415 mg, 2.00 mmol) in 20 mL of warm water. The mixture was allowed to stir, resulting in precipitation of a microcrystalline white compound, which was washed with water and ethanol, then dried in vacuum. Yield ~790 mg, 92 %. $^1$H NMR (DMSO-d$_6$): 8.233 (m, ArH), 7.6 (br, m, H of th), $^{13}$C NMR (DMSO-d$_6$): 165.49(CO$_2$), 149.22 (CCOOH), 141.69 (ArC), 125.33 (ArC), 181.66 (CS(NH$_2$)$_2$). Elemental analysis, % obsd (% calcd) for C$_9$H$_{11}$CdO$_4$N$_5$S$_2$: C, 25.10 (25.13); H, 2.43 (2.55). Melting point: 255 °C.

**Synthesis of [Cd(dipic)(ths)$_2$(H$_2$O)]·2H$_2$O**, Cd3b. This compound was prepared as described for Cd1a, using 729 mg (8.00 mmol) of ths instead of tu. Yield ~925 mg, 90%. $^1$H NMR (DMSO-d$_6$): 8.645 (s, ArH), 8.162 (s, ArH), 7.194 (br, m, H of ths). Elemental analysis, % obsd (% calcd) for C$_9$H$_{13}$CdO$_7$N$_7$S$_2$: C, 21.59 (21.01); H, 3.45 (2.91). Decomposes at 195 °C before melting.
2.2.5 Synthesis of precursors to PbS

*Synthesis of Pb(Hsal)$_2$(tu)$_2$, Pb1a.* Pb(OAc)$_2$·3H$_2$O (379 mg, 1.00 mmol) and H$_2$sal (276 mg, 2.00 mmol) were dissolved in a 100-mL beaker in 50-mL water and stirred at reflux until the volume of the solution was reduced to ~30 mL. Tu (160 mg, 2.10 mmol) dissolved in 10 mL of water was added slowly, and the clear solution was stirred for 30 min. The solution was dried under vacuum to isolate white powders of Pb1a. It was washed with hexane and dried in vacuum. Yield, ~0.300 mg. Melting point ~110 °C. $^1$H NMR (DMSO-d$_6$) 6.84 (m, ArH), 7.34 (m, ArH), 7.76 (m, ArH), 4.38 (s, br), $^{13}$C NMR (DMSO-d$_6$), 116.52 (ArC), 117.89 (ArC), 118.63 (ArC), 130.20 (ArC), 133.45 (ArC), 161.12 (COH), 173.52 (CO$_2$), 183.75 (CS(NH$_2$)$_2$). Elemental analysis, % obsd (%) calcd) for C$_{16}$H$_{18}$N$_4$O$_8$PbS$_2$: C 30.77 (30.32), H 2.60 (2.84) melting point 110 °C.

*Synthesis of Pb(Hsal)$_2$(ths)$_2$·3H$_2$O, Pb1b.* A similar procedure as described for Pb1a was employed, using 184 mg (2.02 mmol) of ths instead of tu. Yield ~320 mg. Melting point ~118 °C. $^1$H NMR (DMSO-d$_6$), 6.77 (m, ArH), 7.27 (m, ArH), 7.76 (m, ArH), 8.1 (m, ArH), 4.03 (m, br), $^{13}$C NMR (DMSO-d$_6$), 116.55 (ArC), 117.90 (ArC), 119.48 (ArC), 130.24 (ArC), 133.34 (ArC), 161.03 (COH), 174.06 (CO$_2$), 181.05 (CSNH$_2$NHNH$_2$). Elemental analysis, % obsd (%) calcd) for C$_{16}$H$_{26}$N$_6$O$_9$PbS$_2$: C 26.76 (24.42), H 3.65 (3.73) melting point 118 °C.

*Synthesis of Pb(pic)$_2$(tu)$_2$·H$_2$O, Pb2a.* An aqueous solution (100 mL) of Pb(OAc)$_2$·3H$_2$O (379 mg, 1.00 mmol) and picolinic acid (246 mg, 2.00 mmol) was stirred at 100 °C in a beaker until the volume of the solution was reduced to ~60 mL. An aqueous solution of tu (154 mg, 2.02 mmol) was added and the resulting clear solution was dried under
vacuum. The product was washed with diethyl ether. $^1$H NMR (DMSO-d$_6$), 7.06 (s, broad, H of tu), 7.15 (m, ArH), 7.70 (m, ArH), 8.00 (m, ArH), 8.77 (m, ArH) $^{13}$C NMR (DMSO-d$_6$), 125.91 (ArC), 126.51 (ArC), 139.18 (ArC), 133.25 (ArC), 146.96 (ArC), 151.92 (CCOOH), 169.74 (CO$_2$) 183.76 (CS(NH$_2$)$_2$).

*Synthesis of Pb(pic)$_2$(ths)$_2$, Pb2b.* Pb(OAc)$_2$:3H$_2$O (379 mg, 1.00 mmol) and picolinic acid (246 mg, 2.00 mmol) were dissolved in 200 mL of water and the resulting solution was stirred at 100 °C in a beaker until the volume of the solution was reduced to ~10 mL. Solid ths (184.00 mg, 2.02 mmol) was added to the hot solution of lead (II) picolinate and the resulting clear solution was left to cool for two days to yield colorless crystals. Yield 470 mg. Melting point ~178 °C. $^1$H NMR (DMSO d$_6$), 7.06 (s, broad, H of tu), 7.15 (m, ArH), 7.70 (m, ArH), 8.00 (m, ArH), 8.77(m, ArH) $^{13}$C NMR (DMSO-d$_6$), 125.95 (ArC), 126.45 (ArC), 139.22(ArC), 146.74 (ArC), 151.87 (CCOOH), 169.49 (CO$_2$) 181.14 (CSNH$_2$NHNH$_2$). Elemental analysis, % obsd (% calcd) for C$_{14}$H$_{18}$N$_8$O$_4$PbS$_2$: C 26.00 (26.51), H 2.97 (2.8) melting point 178 °C.

*Synthesis of [Pb(dipic)(tu)(H$_2$O)]$_2$:2H$_2$O, Pb3a.* Pb(OAc)$_2$:3H$_2$O (279 mg, 1.00 mmol) and was dissolved in 20 mL water, and then 20 mL of an aqueous solution of H$_2$dipic (415 mg, 2.00 mmol) was added. The mixture was allowed to stir resulting in the precipitation of some white Pb(dipic). The solution was filtered and an aqueous solution of tu (154 mg, 2.02 mmol) was added to the filtrate. The resulting solution was stirred overnight and left for crystallization. After 48 hrs, a microcrystalline white precipitate formed, which was washed with water and hexane, then dried in vacuum to yield 256 mg.
of Pb3a. $^1$H NMR (DMSO-$d^6$) 8.233 (m, ArH), 7.6 (br, m, H of th), $^{13}$C 165.49 (CO2), 149.22 (CCOOH), 141.69 (ArC), 125.33 (ArC), 181.66 (CS(NH$_2$)$_2$).

Synthesis of [Pb(dipic)(ths)$_2$]-H$_2$O, Pb3b. A similar method as described for Pb3b was employed using 184 mg (2.02 mmol) of ths instead of tu. Yield 350 mg. Melting point 134 °C. $^1$H NMR (DMSO-$d^6$) 8.645 (s, ArH), 8.162 (s, ArH), 7.194 (br, m, H of ths) $^{13}$C (DMSO-$d^6$), 148.86 (CCOOH), 140.23 (ArC), 127.24 (ArC), 181.02 (CSNH$_2$NHNH$_2$).

2.3 Description of molecular structures of precursor compounds

2.3.1 Molecular structures of CdS precursors

The precursor complexes are readily prepared by mixing cadmium acetate dihydrate with the appropriate carboxylate ligand and either tu or ths in hot water or hot aqueous ethanol. The ability to recrystallize the compounds is affected strongly by their solubilities. The dipicolinato complexes are moderately soluble in water; the picolinates display a higher solubility, while the salicylates are highly soluble.

Repeated attempts to obtain crystals of Cd1b, however, were not successful and it is possible that the product exists as an equilibrium mixture in solution. An ESI-MS of the product designated as Cd1b shows a dominant peak at 523.417 amu corresponding to a formulation of Cd(sal)(ths)$_3$ (see Figure 2.2). In addition to this peak, several other peaks were seen. Those at 432.75 and 294.91 amu match Cd(Hsal)(ths)$_2$ (Figure 2.3) and Cd(ths)$_2$ (Figure 2.4), respectively. Another major peak at 385.83 amu corresponds to Cd(Hsal)$_2$ (Figure 2.5). Furthermore, there are some minor peaks at higher molecular masses that appear to be dimers of the lower molecular weight species. The likely
formulations for molecules from this reaction are Cd(sal)(ths)$_x$ and Cd(Hsal)$_2$(ths)$_x$. All of the ions observed could be attributed to fragments of one or both of these species, but it is not possible to tell from these data if the product derives from a single complex or a mixture. Several equilibria are possible including (1) Cd(sal) + H$_2$sal with Cd(Hsal)$_2$ and (2) either or both of these complexes with free ths. It should be noted that the ESI mass spectral data do confirm, however, that complexes with bound ths are present and that the product is not simply a mixture of either Cd(sal) or Cd(Hsal)$_2$ and isolated ths.

Figure 2.1 ESI-MS of precursor Cd1b.
**Figure 2.2** Experimental peak at 523.42 match the simulated isotopic distribution of Cd(Sal)(ths)₃ (molecular wt calculated= 523.99).

**Figure 2.3** Experimental peak at 432.75 match the simulated isotopic distribution of Cd(HSal)(ths)₂ (molecular wt calculated= 432.97).
Figure 2.4 Experimental peak at 294.92 match simulated isotopic distribution of Cd(thiol$_2$) (molecular wt calculated= 294.69).

Figure 2.5 Experimental peak at 385.83 plotted against the simulated isotopic distributions of Cd(Sal)$_2$ (molecular wt calculated= 385.94) and Cd(thiol)$_3$ (molecular wt calculated= 386.96) shows better matching with Cd(Sal)$_2$. 
The salicylate ligand is known to bind to a single Cd(II) ion via the carboxylate functionality in either a monodentate or bidentate, chelating fashion. In metal complexes salicylic acid can exhibit mono- or di-deprotonation (Hsal− or sal2−), with the latter case involving metal binding to the phenolic oxygen as well as the carboxylate. Only coordination to the carboxylate has been observed for Cd(II) complexes. This is the case for Cd1a, where the bidentate chelating coordination mode is observed. One can view this bonding mode as existing along a continuum in which the metal is symmetrically bound to both carboxylate oxygen atoms to one in which only one oxygen can be considered bound. The binding can thus be somewhat or even highly asymmetric. This is seen in Cd1a where the Cd-O distances are slightly different (2.468(19) Å vs 2.348(2) Å) while those to the other salicylate ligand are quite asymmetric (2.332(19) vs 2.8103(20) Å). A similar coordination mode is observed in the binuclear Cd(II) complex [Cd(H2O)2(sal)2]2, except that for this complex dimerization is achieved by the coordination of one of the chelating carboxylate oxygens to an additional cadmium ion. For that compound, the Cd-O bidentate-chelate distances are 2.3271 (24) Å, 2.4338(23) Å and 2.3116(22) Å while the bridging Cd-O distance is 2.5349(24) Å. The long Cd(1)-O(22) distance of 2.8103(20) Å (which is less than the sum of the listed van der Waals radii: Cd 1.58 Å, O 1.52 Å) indicates a weak, secondary bonding interaction. If one considers all carboxylate oxygens to be bound, then the Cd(II) ion in Cd1a can be thought of as possessing a highly distorted octahedral geometry with cis tu ligands. This is the most commonly found coordination geometry for Cd(II), although with thio-containing ligands a coordination number of 4 as well as 6 has been observed.
Alternatively, one could neglect the secondary Cd-O distance and describe the complex as penta-coordinate, but this is a much rarer occurrence. The Cd(II) ion in Cd(th)$_3$SO$_4$ is penta-coordinate.\textsuperscript{84}

![Figure 2.6](image)

**Figure 2.6** X-ray crystallographic structure of Cd1a with thermal ellipsoids at the 40% probability level.

Compounds Cd2a and Cd2b both possess bidentate, chelating picolinate ligands, with one carboxylate oxygen atom and the pyridyl nitrogen bonded to the Cd(II) ion. Compound Cd2b has crystallographically-imposed two-fold rotational symmetry. The metal ions in Cd2a and Cd2b also show distorted cis-octahedral coordination geometries. Interestingly, the picolinate ligands in Cd2a adopt a trans arrangement of the carboxylate oxygen atom donors, resulting in an O(21)-Cd(1)-O(11) angle of 162.83(5)° while in complex Cd2b the picolinate N donors are trans, giving rise to a N(1)-Cd(1)-N(1A) angle equal to 167.7(1)°. In the coordination polymers [Cd(pic)(NCS)]$_n$, and [Cd$_2$(SO$_4$)(pic)$_2$(H$_2$O)$_3$]$_n$ each picolinate ligand is attached to two Cd(II) ions.\textsuperscript{88} One
metal is bound as found in complexes \textbf{Cd2a} and \textbf{Cd2b}, while the other is chelated by sharing a carboxylate with another additional Cd(II) ion. For \([\text{Cd(pic)(N}_3\text{)}]_n\), the chelating mode as in \textbf{Cd2a} and \textbf{Cd2b} is also observed and each oxygen atom of the carboxylate ligand is attached to another Cd(II) ion; however, they are attached to different metals rather than forming a chelate structure.\textsuperscript{85, 86} The Cd-carboxylate bond distances for \([\text{Cd(pic)(N}_3\text{)}]_n\) vary from 2.247(5)-2.459(5) Å, while those for \([\text{Cd(pic)(NCS)}]_n\) lie in the range is 2.293(3)-2.453(3) Å.\textsuperscript{82} The Cd-O bond distances in \textbf{Cd2a} and \textbf{Cd2b} are well within the same range (2.372(1) Å, 2.323(1) Å). The Cd-N(2.353(2), 2.383(2) Å) bond distances are also comparable to those observed in \([\text{Cd(pic)(NCS)}]_n\) and \([\text{Cd(pic)(N}_3\text{)}]_n\).

\textbf{Figure 2.7} X-ray crystallographic structure of one of the two independent Cd(II) centers in \textbf{Cd2a} with thermal ellipsoids at the 40% probability level.
The only observed ligation mode for Cd with dipicolinate ligand is the tridentate mode in which the pyridyl nitrogen and one oxygen atom from each carboxylate unit are attached to the metal ion. Complex \( \text{Cd3a} \) follows this observation. The penta-coordination is completed by two monodentate S-bound \( \text{tu} \) molecules. In contrast, one \( \text{ths} \) ligand in \( \text{Cd3b} \) is monodentate, while the second molecule acts as a chelating N,S ligand to form a five-membered ring. This bidentate coordination mode has also been observed in several transition metal complexes \([\text{Fe(ths)}_2\text{SO_4}]_n\), \([\text{Cu(ths)}\text{Cl}_2]\), \([\text{Ni(ths)}_2][\text{C}_6\text{H}_4-1,4-(\text{CO}_2)_2]\), \([\text{Ni(ths)}_2(\text{H}_2\text{O})_2][\text{trans-CO}_2\text{CH=CHCO}_2]\), \([\text{Cd(ths)(HS)}_2]\) and \([\text{Zn(ths)}_2(\text{H}_2\text{O})_2][\text{C}_6\text{H}_4-1,4-(\text{CO}_2)_2]\cdot\text{H}_2\text{O}\). Water is also bound to the cadmium ion resulting in a seven-coordinate environment. This higher coordination number is likely responsible for the lengthening of the Cd-S bonds (Table 2.1). In \( \text{Cd3a} \), the Cd-O (2.398(3), 2407(3) Å) and the Cd-N (2.264(3) Å) bonds are close to the range reported in Cd-O (2.2758(14)-
2.3894(14) Å, Cd-N (2.2320(16), 2.2415(16) Å) in (GH)$_2$[Cd(dipic)$_2$] (GH = guanidinium). For Cd3b, the increased coordination number and the water molecule within the coordination sphere causes an increase in the Cd-O and Cd-N bond distances. Tetracoordinate Cd(II) complexes generally exhibit shorter Cd-S bond distances (range: 2.538-2.627 Å) than those found in hexacoordinate complexes (range: 2.638-2.761 Å). By comparison the Cd-S bond-distance in pentacoordinate Cd3a is one of the shortest known (2.518(2) Å), while the values seen for Cd1a, Cd2a, Cd2b and Cd3b lie in the range consistent with other hexacoordinate complexes.

**Figure 2.9** X-ray crystallographic structure of Cd3a with thermal ellipsoids at the 40% probability level.
Figure 2.10 X-ray crystallographic structure of Cd3b with thermal ellipsoids at the 40% probability level. The crystal lattice water molecules have been omitted.

Table 2.1 Selected bond lengths [Å] for CdS precursors.

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Cd1a</th>
<th>Cd2a</th>
<th>Cd2b</th>
<th>Cd3a</th>
<th>Cd3b</th>
</tr>
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Table 2.2 Selected bond angles [deg] for CdS precursors.

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Table 2.3 Crystallographic data for CdS precursors.

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<td>0.619/-0.471</td>
<td>0.714/-0.638</td>
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2.3.2 Molecular structures of PbS precursors

The molecular precursors for PbS were prepared by mixing an aqueous or aqueous ethanolic solution of lead acetate trihydrate with the appropriate aromatic carboxylic acid followed by addition of tu or ths in the next step. It was found that the ability to crystallize the compounds is greatly affected by their solubility and the state of dynamic equilibrium between the free and coordinated ligands in the solvent. Lead dipicolinates were found to be least soluble among the three, which can be rationalized by formation of neutral coordination polymer \([\text{Pb(dipic)}]_n\).\(^7\)\(^8\)\(^9\)\(^4\) The coordination polymer \([\text{Pb(dipic)}]_n\) is stabilized by hydrogen bonding and aromatic \(\pi\)-stacking interactions in the crystal lattice and comes out of the solution as white crystalline precipitate.\(^7\)\(^8\)\(^9\)\(^4\) The formation of \([\text{Pb(dipic)}]_n\) as a side product explains the low yields of the dipicolinate precursors as compared to the other four. In the case of \(\text{Pb3b}\), the addition of a slight excess of ths was necessary to produce well-formed crystals. It is believed that the extra ths assisted in shifting the equilibrium towards formation of \(\text{Pb3b}\). The salicylate complexes were found to be the most soluble followed by the picolinates. In the electrospray mass spectra of the precursor \(\text{Pb1a}\), there was evidence of the existence of several identifiable species. Ions corresponding to the \(\text{Pb(sal)(ths)}_3\), \(\text{Pb(sal)}\), \(\text{Pb(th)s}_2\) were observed; however, only one set of \(^{13}\)C NMR signals for the \(\text{sal}^{2-}\) ligands was observed in solution suggesting a dynamic equilibrium between bound and unbound ths ligands. In the \(^{13}\)C NMR spectra of all of the compounds, the chemical shift difference between the \(^1\)H signals of the free and coordinated ligands was small making analysis difficult. Dynamic equilibrium and the
existence of a mixture of species in solution could explain why all the attempts to crystallize out the salicylate complexes were unsuccessful.

Figure 2.11 Polymer [Pb(dipic)]n formed as white residue during synthesis of precursors Pb3a and Pb3b. Reproduced from the CIF provided in reference 78.

The Pb(II) ion in compound Pb2b adopts a distorted octahedral geometry (Figure 2.12). Each picolinate moiety acts as a bidentate ligand coordinating to the central Pb(II) by both the pyridyl N and the carboxylate O atom, and each ths moiety acts as a monodentate ligand coordinating through the S atom. The Pb-N bond distances of the compound are comparable to those in [Pb(H2tpaa)Cl].\textsuperscript{95} Chelation leads to shorter Pb-N bond distances in Pb2b (2.561(5), 2.620(5)). For comparison, in [Pb(H2tpaa)Cl] the Pb-N distances are 2.645(6) (chelation) and 2.720(6), 2.803(6) (not chelated).
The crystal structure of **Pb3a** consists of dimeric molecules. Each Pb(II) ion is positioned at the center of an octahedron coordinated by three carboxylate oxygen atoms and one pyridyl nitrogen atom from two different dipic$^{2-}$ ions. One sulfur atom from the tu and one oxygen atom from a water molecule are also bound. Of the three carboxylate oxygen atoms, two are bridging to produce the dimeric structure. The Pb-N and Pb-O bond distances in the molecule were compared with other Pb salts of pyridine dicarboxylic acids (H$_2$pdca) reported in the literature.$^{78}$ In the compound **Pb3a** the Pb1-O1 bond distance is 2.461(3) and the Pb1-O2 bond distance is 2.563 (3). The Pb-O bond distances were found to be 2.480(4) in Pb(2,3-pdca), 2.445(10) in Pb(2,4-pdca)-H$_2$O, and 2.445(4) Å in Pb(2,5-Hpdca)$_2$·2H$_2$O which are reasonably similar to the values observed for Pb1-O1. The longer Pb1-O2 is likely a result of bridging nature. The Pb-N bond
distance in Pb3a is 2.491(3) Å, which is again comparable to 2.535(4) in Pb(2,3-pdca), 2.391(9) in Pb(2,4-pdca)-H2O, and 2.448(4) in Pb(2,5-pdcaH)2-2H2O. The Pb-S bonds were compared to those bonds in the compounds [Pb(th)2Cl2] (3.0410(8), 3.0987(8) Å) and [Pb(th)Br2](3.0812(4) Å)96. 97 The Pb-S bond in Pb3a was found to be appreciably shorter at 2.7389(14) Å.

Figure 2.13 X-ray crystallographic structure of Pb3a with thermal ellipsoids at 40% probability level.

In Pb3b (Figure 2.14) the central Pb(II) ion is penta-coordinated with two carboxylate oxygen atoms and one pyridyl nitrogen atom of the dipic2- ligand and two sulfur atoms of the ths ligands. The molecular geometry is distorted trigonal bipyramidal with two S atoms connected axially and the pyridyl N and the carboxylate oxygen atom connected equatorially to the central Pb(II) ion. The Pb-O bond distances are significantly shorter (2.433(8) Å) than those found in Pb(2,4-pdca)-H2O (2.445(10)),
Pb(2,5-pdcaH)$_2$·2H$_2$O (2.445(4)), and Pb(2,3-pdca) (2.480(4)), while the Pb-N bond (2.465(15)) is well within the range (2.391(9)—2.535(4)) exhibited by those compounds.

**Figure 2.14** X-ray crystallographic structure of Pb3b with thermal ellipsoids at 40% probability level.

**Table 2.4** Selected bond lengths [Å] of precursors Pb2b, Pb3a and Pb3b.

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Table 2.5 Selected bond angles [deg] of precursors Pb2b, Pb3a and Pb3b.

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<td>74.96(2)</td>
</tr>
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<td>O(21)-Pb(1)-S(2)</td>
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Table 2.6 X-ray crystallographic structure parameters for PbS precursors.

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<td>crystal system</td>
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<td>space group</td>
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<td>P2/a</td>
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<td>c, (Å)</td>
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<tr>
<td>γ (deg)</td>
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<td>4</td>
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<td>T (K)</td>
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<td>no of data collected</td>
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2.4 Conclusion

Aromatic carboxylate complexes of Cd(II) and Pb(II) form stable adducts with tu or ths. These compounds are easy to synthesize, stable under ambient conditions and possess good solubility in common organic solvents and water. The ability to recrystallize the compounds is affected strongly by their solubilities, fluxional equilibria between free and bound ligands and the formation of metal carboxylate coordination polymer (in case of lead dipicolinate) as a side product. Five of the mixed ligand compounds of Cd(II) and three of Pb(II) formed well-defined crystals and were characterized by X-ray crystallography. It is found that in the picolinato complexes Cd2a, Cd2b, Pb2b the central metal ion are all hexa-coordinate with two pyridyl nitrogen atoms two carboxyl oxygen atoms and two sulfur atoms inside the coordination sphere. Cd3a and Pb3b has a
comparable structure, in both of which the central metal ions are penta-coordinate with two carboxyl oxygen atoms, one pyridyl nitrogen atom and two sulfur atoms. \( \text{Cd3b} \) however shows a hepta-coordinate structure with a chelating ths ligand coordinating through both the sulfur atom and the primary nitrogen atom of \( \text{NHNH}_2 \) group. In addition, two carboxylate oxygen atoms, one pyridyl nitrogen atom and one water molecule are within the coordination sphere making the central \( \text{Cd(II)} \) ion hepta-coordinated. All these compounds have pre-formed metal-sulfur linkage and can be used as single-source molecular precursors for \( \text{CdS} \) or \( \text{PbS NPs} \) in either aqueous or non-aqueous solvents.
3 Synthesis of various anisotropic CdS nanostructures by decomposition of single-source precursors

3.1 Introduction

CdS NPs is one of the most important group II-VI semiconductors, various methods have been developed to control shapes and sizes in this system on the nano-scale over the past few years. These methods include hard templates (such as aluminum oxide membranes), soft templates (such as liquid crystal, micelles, polymers), structure-directing coordinating solvents and vapor liquid solid (VLS) methods etc. We have been exploring the effect of single source molecular precursors on the morphology and size of the NPs synthesized. Various single source precursors have been used by different researchers for this purpose. The various advantages of single-source molecular precursors over the traditional methods of synthesis, and the different types of precursor molecules used to synthesize CdS have been discussed in greater detail in the previous chapter. Cd\{S_{2}CNHR_{2}\}_2 is well-explored in this regard. However in the reports in literature it is often found that presence of additional thio containing molecule is required for the decomposition of single source precursors and also in most of the cases the precursors can be used in either aqueous or organic solvents. We have designed the precursors which can be used in both aqueous and organic media without the help of any other thio containing molecule.

We have also investigated the mechanism of formation of CdS NPs of variable shapes and sizes under the employed reaction conditions. Special attention was given towards understanding the growth mechanism of branched nanostructures. A considerable amount of effort has been directed toward II-VI semiconductors such as
ZnO, ZnSe, CdTe, etc) There are two different hypotheses for the growth of polypodal structures. One proposal postulates that it is an effect of wurtzite-zinc blende polytypism, where the stacking defects in the initial cubic (zinc blende) nucleus initiates the growth of hexagonal (wurtzite) arms from four equivalent facets. An alternate hypothesis is that the initial nucleus has eight wurtzite domains connected to each other by multiple-twinned boundaries. Among these eight domains, four are slow-growing and four are fast-growing, hence the tetrapod shape develops. Some studies on the growth of CdTe, ZnO and ZnSe tetrapods support the latter mechanism. In this chapter we discuss the synthesis of various anisotropic shaped CdS NPs from the single-source precursors and provide data on their mechanism of growth.

3.2 Experimental procedure

3.2.1 Materials

Cetyl trimethylammonium bromide (CTAB; technical grade), tri-n-octylamine (TOA; 98%), hexadecylamine (HDA), 1-dodecanethiol (DDT) (98%), and trioctylphosphine (TOP; technical grade 90%) were obtained from Sigma-Aldrich. Trioctylphosphine oxide (TOPO; 90%) was bought from Strem chemicals. All the chemicals were used without further purification. All the solvents were distilled using standard procedures.

3.2.2 Instrumentation details

TGA studies were performed on a Sieko DT/TGA 200 instrument in alumina pans under an argon-containing atmosphere. Approximately 20 mg of the sample to be studied was placed in an alumina pan in the furnace of a Sieko TGA/DTA instrument. The sample was heated to 400 °C at a rate of 10 °C per minute. Transmission electron microscopy
(TEM) experiments were performed by depositing a drop of suspension diluted in hexane on a carbon coated copper grid. The solvent was evaporated and the sample was analyzed using JEOL 2000FX and JEOL 2010 microscopes that were equipped with energy dispersive spectrometers. Conventional and high-resolution TEM imaging, selected area electron diffraction (SAED) and energy-dispersive spectroscopy (EDS) methods have been used for analysis of the cadmium sulfide NPs. Precautions have been taken to prevent structural changes in the studied material caused by heating effects of the electron beam.

The optical absorption spectra of the samples were measured on a double-beam UV-visible spectrometer; Cary 400 (400 to 900 nm, 1 nm step) using a 4 mm x 10 cm quartz fluorimeter cell (Starna Cells). Photoluminescence emission studies were performed using a Spex Fluorolog 3-211(J-Y Horiba) spectrofluorometer equipped with a photomultiplier tube (PMT) for visible emission detection in a similar cuvette. Typical slit widths were 3x3 nm in excitation and emission using with 2 nm step.

3.2.3 Reaction setup for the synthesis of CdS NPs

Two general decomposition techniques were followed, (1) standard Schlenk technique and (2) solvothermal decomposition using Teflon-lined stainless steel reactor. For the Schlenk reactions, a 100-mL 3-neck flask was fitted with a reflux condenser and the desired amount of the appropriate precursor was added followed by the required volume of surfactant solution. The flask was placed under vacuum and purged with argon three times while stirring rapidly. The reaction mixture was then stirred vigorously while the temperature was elevated to either 120 or 175 °C and maintained at that value for varied amounts of time. In a typical solvothermal decomposition, a measured amount of the
precursor was mixed with the surfactant solution. The mixture was sealed in a 23-mL Teflon-lined stainless steel reactor and then heated at either 120 or 175 °C for 16h. After cooling to room temperature, the yellow to orange precipitate of CdS was collected and washed by centrifugation with water and ethanol.

![Reaction set up](image)

Figure 3.1 Reaction set up for the decomposition reactions.

### 3.3 Decomposition results

#### 3.3.1 Decomposition of Cd1a, Cd2b and Cd3a in the presence of CTAB

200 mg of precursor **Cd1a** or 100 mg of **Cd2b** or 100 mg of **Cd3a** were mixed with 200 mg CTAB and 15 mL of water with stirring for 30 minutes, and the mixture was heated in a Teflon-lined stainless steel Parr bomb for 16 hrs at 175 °C. The autoclave was then cooled to room temperature, and the products were collected and washed repeatedly in water and ethanol and dispersed in hexane.
3.3.2 Decomposition of Cd1a in ethylenediamine

200 mg of precursor Cd1a was stirred with 15 mL of ethylenediamine for 30 minutes and then the mixture was heated in a Teflon-lined stainless steel Parr bomb for 16 hrs at 175 °C. It was then allowed to cool to room temperature. The collected orange-yellow precipitate was washed repeatedly in water and ethanol.

3.3.3 Decomposition of Cd1a or Cd2b in oleylamine

200 mg of the precursor Cd1a or Cd2b were dissolved in 12 mL of oleylamine and the mixture was heated at 120 °C for 16 hrs in Teflon-lined stainless steel Parr bomb. Next the reaction mixture was allowed to cool to room temperature. The solid was collected and washed with ethanol and water.

3.3.4 Decomposition of Cd1b in oleylamine with added hydrochloric acid and TOPO

In one reaction 200 mg of precursor Cd1b was dissolved in 8 mL of oleylamine after which 0.1 mL of dilute HCl was added to the mixture and it was heated to 120 °C in a Teflon-lined stainless steel Parr bomb for 16 hrs. In another separate reaction, 200 mg of precursor Cd1b was dissolved in 8 mL of oleylamine after which 0.1 mL of dilute HCl and 1 gm TOPO were added to the mixture keeping the temperature and the reaction time unchanged. Both the reaction mixtures were allowed to cool to room temperature. The solid was collected and washed with ethanol and water.

3.3.5 Decomposition of Cd1b in oleylamine with the presence of TOP

200 mg of the precursor Cd1b was mixed with 8 mL of oleylamine and 1 g of TOP. The mixture was heated at 120 °C for 16 hrs and allowed to cool to room temperature. The
yellow-orange precipitate was washed with water and ethanol and collected by centrifugation.

3.4 Results and discussion

The decomposition reactions were carried out using both aqueous and organic solvents. A variety of shapes were obtained depending upon the conditions. Table 3.1 gives comparison of the types of structures for our studies as well as those reported for the other single source precursor decompositions. For all of the decomposition reactions the picolinate and salicylate precursors behaved differently as compared to the dipicolinates. It can be assumed that the dipicolinates, being a tridentate ligand was bound to Cd(II) more strongly, and under the applied decomposition condition would hydrolyze at a different rate. It was found that the dipicolinate precursors gave mostly micron-sized particles of irregular shape under aqueous conditions while agglomeration of very small round particles was observed when decomposed using long chain organic amines. Hence more importance was given to salicylate and picolinate precursors which gave more desirable decomposition results. The presence of carboxylic acid and hydroxyl groups in the precursor structures assist their solubility in aqueous solutions, so initial decomposition attempts were carried out under hydrothermal conditions in the presence of CTAB.
Table 3.1 Summary and comparison of nanoparticle shapes from single source precursors.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Conditions</th>
<th>Shape</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(this)$_2$Cl$_2$</td>
<td>TOPO 280 °C</td>
<td>nanorods</td>
<td>50</td>
</tr>
<tr>
<td>Cd(S$_2$C(NHR)$_2$</td>
<td>hexadecylamine 200 °C</td>
<td>Mixture of nanorods, bent nanorods</td>
<td>68</td>
</tr>
<tr>
<td>R = Et, Bu, C$<em>6$H$</em>{13}$, C$<em>{12}$H$</em>{25}$</td>
<td>pyridine, Et$_2$NH</td>
<td>spherical aggregates</td>
<td>65</td>
</tr>
<tr>
<td>Cd(S$_2$CNEt)$_2$</td>
<td>en, H$_2$NNH$_2$H$_2$O 120 °C</td>
<td>nanorods, multiarm nanorods</td>
<td>65</td>
</tr>
<tr>
<td>Cd(n-C$<em>8$H$</em>{17}$O)$_2$PS$_2$$_2$</td>
<td>oleyl amine 160 °C</td>
<td>quantum dots</td>
<td>64</td>
</tr>
<tr>
<td>Cd1a, Cd1b, Cd2a, Cd2b, Cd3a, Cd3b</td>
<td>hydrothermal CTAB</td>
<td>gypsum rose</td>
<td>this work</td>
</tr>
<tr>
<td>Cd1a, Cd1b, Cd2a, Cd2b, Cd3a, Cd3b</td>
<td>en + hexadecylamine</td>
<td>nanorods</td>
<td>this work</td>
</tr>
<tr>
<td>Cd1a, Cd1b, Cd2a, Cd2b, Cd3a, Cd3b</td>
<td>oleylamine</td>
<td>spherical particles</td>
<td>this work</td>
</tr>
<tr>
<td>Cd1a, Cd1b</td>
<td>oleylamine, HCl</td>
<td>ellipsoidal particles, short nanorods</td>
<td>this work</td>
</tr>
<tr>
<td>Cd1a, Cd1b</td>
<td>oleylamine, TOPO, HCl</td>
<td>ellipsoidal particles</td>
<td>this work</td>
</tr>
<tr>
<td>Cd1a, Cd1b</td>
<td>oleylamine, TOP</td>
<td>mixture of nanorods and multipods</td>
<td>this work</td>
</tr>
<tr>
<td>Cd2a, Cd2b, Cd3a, Cd3b</td>
<td>oleylamine, TOP</td>
<td>small nanorods</td>
<td>this work</td>
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</table>
Figure 3.2 shows the results obtained from precursors \textbf{Cd1a}, \textbf{Cd2b} and \textbf{Cd3a}. This procedure yielded flowerlike particles, from several hundred nm to several \textmu m in diameter for \textbf{Cd1a}, while for \textbf{Cd2b} the particles were 2-4 \textmu m in diameter, with the leaflets being about 100-250 nm thick with lengths and widths varying up to micron size. Precursors \textbf{Cd1b} and \textbf{Cd2a} gave similar results with a wider distribution of sizes, whereas \textbf{Cd3a} gave mostly round, micron-sized particles. The XRPD pattern of all the hydrothermal products show sharp peaks corresponding to stable hexagonal CdS (greenockite, JCPDS #01-077-2306). The EDS data confirmed the presence of both Cd and S in the particles in a 1:1 ratio (see supporting information for the characteristic EDS of decomposition product from precursor \textbf{Cd1a}).

\textbf{Figure 3.2} SEM images of the (A) Flowerlike CdS particles from \textbf{Cd1a}. (B) Semi-spherical aggregates of CdS from \textbf{Cd2b}. (C) Round shaped particles from \textbf{Cd3a}. 

<table>
<thead>
<tr>
<th>phase</th>
<th>Space group</th>
<th>Figure of merit</th>
<th>PDF #</th>
</tr>
</thead>
<tbody>
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<td>Pnnn (48)</td>
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<td>00-047-1179</td>
</tr>
<tr>
<td>cubic</td>
<td>F-43m (216)</td>
<td>15.7</td>
<td>04-007-1238</td>
</tr>
</tbody>
</table>

**Figure 3.3** Powder XRD of CdS microsized flowers from Cd1a (Figure 3.2A).

In the thermogravimetric analysis (see supporting information for TGA curves of all of the precursors) of the precursors, a single large decomposition step is observed which roughly corresponds to the weight loss due to the loss of the carboxylate ligand. Previous studies have shown that the organic byproducts of the decomposition may cap the surfaces of growing NPs affecting their shapes and sizes. Other parameters such as temperature, surfactant, concentration of reagent, injection procedure, growth time, presence of structure-directing coordinating solvents also influence the growth of cadmium chalcogenide nanocrystals. The semi-spherical aggregates of CdS formed from the picolinate and salicylate precursors have the same morphology as the formation known as the desert-rose or gypsum rosette. The formation of such crystals was explained by the uneven deposition rates during quick crystallization from supersaturated solutions, resulting in anisotropic shapes.

Decomposition of the precursors was also examined in several different amine solvents: ethylenediamine, hexadecylamine, trioctylamine and oleylamine. Amines are
known to be good solvents for allowing control over the morphology of cadmium chalcogenide NP's.\textsuperscript{112,113} The reaction temperatures used were either 120 or 175 °C, and the reaction time was varied from 2 to 16 hours. The best shaped NPs were obtained when the decompositions were carried out in a mixture of ethylenediamine and hexadecylamine at 175 °C for 2 hours. Rod-like CdS NPs were formed as the final product from all six precursors, when the decomposition reactions were carried out in presence of a mixture of ethylenediamine and hexadecylamine at 175 °C for 2 hours. The representative TEM image shown in Figure 3.4 is obtained from precursor Cd1a decomposed in ethylenediamine. Interestingly, the rod-like CdS nanocrystals were found by XRPD to be predominantly a metastable orthorhombic phase. The hexagonal form was also found to be present in smaller extent. The low decomposition temperature of single source precursors may be responsible for allowing access to the metastable phase. It has been shown in the literature previously that use of diethyldithiocarbamates of nickel and zinc give rise to metastable crystal modification of Ni$_3$S$_4$ and ZnS.\textsuperscript{62,63}

![TEM image of the rod-like CdS nanostructures generated from the decomposition of Cd1a in ethylenediamine.](image)

**Figure 3.4** TEM image of the rod-like CdS nanostructures generated from the decomposition of Cd1a in ethylenediamine.
When using oleylamine as a surfactant, the products obtained by decomposition of the complexes at 120 °C are in the form of spherical particles. The morphology of the decomposition products from precursor Cd\textsubscript{1a} and Cd\textsubscript{2b} are shown in TEM image below Figure 3.6.) Here the XRPD matches with a metastable orthorhombic phase, some of the expected hexagonal phase were also detected. Polycrystalline SAED patterns from these samples confirmed the presence of both phases. The difference between the XRPD and TEM results is that the XRPD analysis shows predominantly the orthorhombic phase while in the TEM study, the hexagonal phase is dominant. This can be explained by the metastability of the orthorhombic phase, which is transformed to the hexagonal phase over a short period of time.

<table>
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<th>Space group</th>
<th>Figure of merit</th>
<th>PDF #</th>
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</thead>
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<tr>
<td>hexagonal</td>
<td>P6\textsubscript{3}mc (186)</td>
<td>7.7</td>
<td>00-006-0314</td>
</tr>
</tbody>
</table>

**Figure 3.5** Powder XRD data of CdS nanorods (Figure 3.4).
Figure 3.6 (A) Conventional TEM image of spherical CdS NPs synthesized with oleylamine from precursor Cd1a. (B) HR TEM image of one of the particles shown in A reveals polysynthetic twins in the hexagonal phase. (C) Conventional TEM image of spherical CdS NPs synthesized with oleylamine from precursor Cd2b. (D) HR TEM images and FFT of four NPs shown in C confirm all four of them have [001]$_{\text{hex}}$ zone axis orientation but are rotated relative to each other along this zone axis.
Table: Properties of CdS phases

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<th>Phase</th>
<th>Space group</th>
<th>Figure of merit</th>
<th>PDF #</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>hexagonal</td>
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<td>13.0</td>
<td>00-0006-0314</td>
</tr>
<tr>
<td>cubic</td>
<td>F-43m (216)</td>
<td>28.8</td>
<td>00-010-0454</td>
</tr>
</tbody>
</table>

Figure 3.7 Powder XRD of spherical CdS nanocrystal (Figure 3.6C).

The HR TEM images of some NPs show the presence of a high density of planar defects (particularly twins) that are likely formed during the NPs’ growth. Twinning generally produces an aggregate symmetry higher than that of each of the individual components since the twinning planes or axes are added symmetry elements. Twin formation could also minimize internal crystal energy. This can be seen in the HR TEM image shown in Figure 3.6B. It reveals polysynthetic twins (see Figure 3.8A). The hexagonal phase particle has a [100] zone axis orientation. Matrix and twin planes are (001) and (00̅1), respectively. The twinning plane is (032). Figure 3.6D shows that there are also some NPs that are almost defect free. For the four NPs observed here FFT confirms that all have the same [001] zone axis orientation (hexagonal phase) but are rotated relative to each other along this zone axis. The distances between them are reasonably uniform and small enough that they could be considered as grain boundaries, taking into account the surfactant layer around them. In our TEM studies of CdS as well as many other materials
[e.g. Bi$_2$S$_3$, PbS, MnO$_x$, Fe$_x$O, Fe$_{1-y}$Mn$_y$O, In$_2$O$_3$, Fe$_2$P] we have never observed NPs totally free of defects (point, linear, planar) even when their size is as small as 2-4 nm. Also we have never observed NP growth via oriented attachment in these materials. $^{36,43-45,59,115}$

Figure 3.8 Polysynthetic (A) and multiplet (B) twinning. (A) represents the hexagonal phase polysynthetically twinned on (032). The zone axis orientation is [100]. (B) is a section of f.c.c. phase (twinned on the symmetry related planes (111) and (111) so as to become a triplet. The zone axis orientation is [011]. Taken after reference 114.

When the salicylate precursors were decomposed using oleylamine in the presence of a very small amount of concentrated HCl, the decomposition products tended to be more ellipsoidal or short rods (Figure 3.9A). When the salicylate precursors Cd1a and Cd1b were decomposed using a mixed surfactant of oleylamine and TOPO in the presence of small amount of HCl, ellipsoidal particles were obtained. Figure 3.9 shows the results from precursor Cd1b. All other precursors gave mostly small, round NPs under the same conditions. The XRPD and polycrystalline SAED patterns of these NPs
match the hexagonal phase. The HR TEM image of a single NP (Figure 3.9) revealed a high density of both linear and planar defects.

**Figure 3.9** (A) Conventional TEM image of CdS particles synthesized from precursor Cd1b in oleylamine with added HCl (B) Conventional and (C) HR TEM images of semi-rectangular CdS particles synthesized in oleylamine with added TOPO and HCl from precursor Cd1b.

<table>
<thead>
<tr>
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<th>Space group</th>
<th>Figure of merit</th>
<th>PDF #</th>
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<td>cubic</td>
<td>F-43m (216)</td>
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</table>

**Figure 3.10** Powder XRD of semi-rectangular CdS nanocrystals (Figure 3.9B).

When the decompositions of the salicylate precursors Cd1a and Cd2b were performed in a mixture of oleylamine and TOP (Figure 3.11A and C), a mixture of nanorods and multipods formed. With all other precursors (Cd2a, Cd2b, Cd3a, Cd3b), very little branching was observed with mostly small rod shaped NPs. It was found that
using precursor **Cd1b** in the presence of a small amount of dodecanethiol (DDT) more tripods and tetrapods were generated, and the branches on the multipods grew as long as 60 nm (Figure 3.11B). Addition of phosphonic acids has been shown to favor twinning and initiate the branching. This is possible in our system since some n-triptylphosphine may decompose to a phosphonic acid under the reaction conditions. The XRPD and polycrystalline SAED patterns of the multi-branched CdS particles given in Figure 3.11 show the presence of both f.c.c. and hexagonal phases; however, it appears that the hexagonal phase is dominant (see supporting information for polycrystalline SAED pattern). The FFT simulated from the particle in Figure 3.11C shows that the core has a \(<011>\) orientation for the f.c.c. phase. Multiplet twinning (Figure 3.8B) on the planes would initiate triplet formation. The generation of stacking faults that initiate the atom sequence for the hexagonal phase are observed in the HR TEM image. Two hexagonal branches continue the NP growth. Other planar defects present in the growing branches are polysynthetic twins similar to those that were observed in the NP shown in Figure 3.11B. The TEM images in Figure 3.11C-E of the tripods and tetrapods can be explained similarly as the formation of the particles with only two branches. Multiplet twinning could result in formation of more than two branches. The FFT obtained from the central part of the tetrapod (Figure 3.11E) shows a hexagon that can be indexed to the \(<111>\) zone axis for the cubic core and \([001]\) zone axis for the fourth hexagonal branch that is aligned with the direction of view.
Figure 3.11 Conventional and HR TEM images of multi-branched NPs synthesized from precursor Cd1b in oleyl amine in the presence of TOP and HCl. (A) Mixture of rods and bipods generated without using any dodecanethiol in the surfactant. (B) Mixture of rods, bipods, tripods and tetrapods generated in the presence of a small amount of dodecanethiol. (C) HR TEM image one of the bipod structures shown in A, FFT is obtained from the core of the particle. (D) Enlarged image of one of the tetrapod structures from (B). (E) HR TEM image of the tetrapod and FFT obtained from its central part.
There are different schools of thought on the generation of multipod-based nanostructures. One theory believes these structures originate from polytypism or co-existence of two crystal phases on different parts of a crystal structure. In polytypic
crystals, two different crystal domains share a common facet; researchers have shown for CdTe and CdSe tetrapods that the core adopts the cubic phase whereas the arms grow in the hexagonal phase. It is further believed that the growth of these branched nanostructures depends on the relatively small energy difference between the two crystalline phases. The other school of thought suggests that the presence of a multiple twin nucleus with four fast- and four slow-growing facets is responsible for the branched nanostructures.

Our HR TEM studies suggest that polysynthetic twinning and multiplets are responsible for the generation of the branched nanostructures. To some extent these two views are simply extremes of the same process. In one case stacking faults lead to clean transition from one phase domain to another (core versus arm) while in the other, planar defects such as various types of twinning lead to growth of NPs.

3.5 Conclusion

Mixed ligand carboxylate tu or ths compounds of Cd(II) can be used as single-source molecular precursors to synthesize CdS NPs in either aqueous or non-aqueous solvents. From the accumulated data, it is clear that nanoparticle shapes are highly sensitive to the solvent/surfactant system employed as well as to the ligands attached to the metal center. In cases where the ligands can bind to one or more of the growing nanoparticle surfaces but not all, asymmetry in the structures results. The systems, however, are still too complex to make detailed predictions about what shape(s) will arise from a given set of ligands, solvents/surfactants and other additives a priori. In our decomposition reactions, the more uniform particle shapes were obtained from salicylate and picolinate precursors. Long chain organic amines were found to be the most effective surfactant giving small
NPs of spherical to ellipsoidal shape. A combination of oleylamine and TOP were found to give branched NPs from salicylate precursors. Aqueous reaction conditions yielded largely micron-sized particles suggesting slower precipitation from aqueous solution than from predominantly organic solvent systems. Additionally, using the mild decomposition conditions, metastable orthorhombic CdS can be accessed, which has not been previously reported from single source precursor methods.

The data obtained in these studies are consistent with the branching in nanocrystals arising from multiplet and polysynthetic twinning. An important aspect of this finding is that an arm in a polypodal structure is not necessarily a single type of phase structure (e.g. f.c.c. or hexagonal) but these arms can also exhibit polysynthetic twinning and maintain a linear geometry as seen in Figure 3.11C. This appears to result when trioctylphosphine is used as an additive in the decomposition reactions.
4 Synthesis of various anisotropic PbS nanostructures by decomposition of single-source precursors and comparison with multiple source precursors

4.1 Introduction

Different morphologies of PbS nanocrystals have been synthesized by various methods. Among those, solvothermal methods of synthesis have attracted considerable interest. Varying the additives in the process to include organic surfactants, polymers, biomacromolecules, coordinating ligands or inorganic ions offer much flexibility in controlling the shape of PbS NPs. Cubes, stars, rods and branched nanowires of PbS have been synthesized using organic surfactants like oleic acid, oleylamine, tri-\(n\)-octylamine, tri-\(n\)-octylphosphine oxide, etc.\(^{116, 117}\) In aqueous solution and in the presence of surfactants like cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB) or sodium dodecylsulphate (SDS), morphology tuning of PbS has been achieved to synthesize nanocubes, hexagons, octahedra and dendritic stars in a controlled manner.\(^{118}\) PbS nanowires as well as nanosheets have been prepared by a polymer-assisted solvothermal method. Rod-like PbS nanocrystals have been obtained using a combination of surfactant and polymer matrix as a template. Another group of researchers have formulated a process to synthesize fluorescent PbS mediated by RNA.\(^{119}\) PbS nanoparticle superlattices have been generated by direct templating in an organic lyotropic liquid crystal and in ionic liquids.\(^{120}\) There have been sonochemical and electrosonochemical approaches to synthesizing PbS NPs, using capping agents like polyvinyl alcohol (PVA) or polyethylene glycol (PEG) and either by direct high intensity ultrasound irradiation or by carrying out the electrolysis under ultrasonic field.\(^{121, 122}\) More recently unconventional shapes like triangles and pyramids have been synthesized
at the air-water interface via reaction between Pb\(^{2+}\) and H\(_2\)S gas in PVK (poly-9-vinylcarbazole) thin films.\(^{123}\)

We have been exploring the effect of single source molecular precursors on morphology and size in nanoparticle synthesis. The various advantages of single-source precursors over other methods of synthesis have been discussed in Chapter 2. Several researchers have reported use of single-source precursors to synthesize PbS NPs. Lead dialkyldithiocarbamates [Pb(S\(_2\)CNRR')\(_2\)] have been explored as single-source precursors in CVD and in solvothermal decompositions in presence of small amount of Bi nanoparticle as catalyst.\(^{51,53}\) However, the temperature required for decomposition of these precursors is reasonably high, varying between 400-450 °C in case of CVD and 250 °C in case of solvothermal decomposition.\(^{51,53}\) In some other cases, where a soft hydrothermal decomposition method is employed to decompose [PbSC(O)(C\(_6\)H\(_5\))\(_2\)] and [Pb(S\(_2\)(P(C\(_6\)H\(_5\))\(_2\)N)] as single-source precursors, assistance of additional thio containing molecule like 1-thioglycerol is required.\(^{124}\) Pyrolysis of bis-benzylthiolate compounds of lead [Pb(SCH\(_2\)C\(_6\)H\(_5\))\(_2\)] has been done by researchers at a comparatively low temperature of 150 °C and without any extra source of sulfur, however it resulted in mostly micro-dimensional particles of irregular shape and size.\(^{71}\) We have tried to address these issues in the design of precursors. The precursors synthesized by us undergo clean solvothermal decomposition at 170 °C without the assistance of any other thio-containing compounds. In some of the decompositions dodecanethiol was used in conjunction with the surfactant oleylamine. However, the precursors were found to decompose even without the presence of dodecanethiol.
We have also investigated the mechanism of formation of PbS NPs of various shapes and sizes. In our study of PbS nanostructures we observe some selective adhesion by surfactants and oriented attachment in our system. However, we have also found that etching in combination with crystal splitting plays an important role in inducing anisotropic shapes to resulting nanocrystals. In this chapter, we discuss the decomposition of six lead(II) carboxylate-tu ths precursors to crystalline PbS NPs, compare the decomposition results with multiple source precursors and provide data on the mechanism of growth of NPs.

4.2 Experimental

4.2.1 Materials

Lead acetate trihydrate (98%), ths (99%), tu (99%), CTAB (cetyltrimethylammonium bromide, technical grade), SDS (dodecylsulphonic acid, sodium salt) tri-n-octylamine (TOA; 98%), hexadecylamine and 1-dodecanethiol (98%) were obtained from Sigma-Aldrich. Ethylenediamine was bought from Fischer Scientific. All the chemicals were used without further purification. Ethanol and hexane used for precipitation, washing and dispersion of the NPs were distilled prior to use employing standard procedures.72

4.2.2 Instrumentation and characterization details

Powder X-ray diffraction (XRD) data were obtained with a Rigaku D/Max-2100PC diffractometer operating with unfiltered Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. The contribution from Kα2 radiation was removed using the Rachinger algorithm. Goniometer alignment was verified by daily analysis of a Rigaku-supplied SiO2 reference standard. The processing of the powder diffraction results and phase identification was
accomplished using the program JADE. TGA studies were performed on a Sieko DT/TGA 200 instrument in an alumina pan under an argon-containing atmosphere. Approximately 20 mg of the sample to be studied was placed in a alumina pan in the furnace of a Sieko TGA/DTA instrument. The sample was heated to 400 °C at a rate of 10 °C per minute. Transmission electron microscope (TEM) experiments were performed by depositing a drop of suspension diluted in hexane on a carbon coated copper grid. The solvent was evaporated and the sample was analyzed using a JEOL 2000FX and JEOL 2010 microscopes that were equipped with energy dispersive spectrometers (EDS). Conventional and high resolution TEM imaging, selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) methods have been used for the analysis of PbS NPs. Precautions have been taken to prevent structural changes in the studied material caused by heating effects of the electron beam. Scanning electron microscope (SEM) experiments were performed by depositing a drop of diluted hexane suspension of sample on an aluminum stub. The solvent was evaporated and the stub was coated by a thin layer of gold in a CRC-150 sputter coater. The sample was then analyzed by an environmental scanning electron microscope, FEI quanta 400 fitted with a field emission gun.

4.3 Synthesis of the nanomaterials from single source precursors (SSP)

4.3.1 Decomposition of the precursors in the presence of CTAB

In a typical procedure for the synthesis of PbS NPs by hydrothermal method 0.100 g of the Pb2b was put in a stainless autoclave, to which 20 mL of distilled water and 0.05 g of CTAB was added. The autoclave was sealed and maintained at 170 °C for 2hrs. The
reaction was quenched by putting the autoclave in liquid N\textsubscript{2} for 15 minutes. The black precipitate was collected by addition of ethanol and centrifugation. It was washed repeatedly with ethanol and re-dispersed in hexane. The same procedure as before was repeated changing the time intervals to 5hrs, 8 hrs and 16hrs for three different reactions.

4.3.2 Decomposition of the precursors in an aqueous mixture of SDS and CTAB

Approximately 0.100 g of the Pb2b was placed in a stainless autoclave. To this was added 20 mL of distilled water, 0.025 g of CTAB and 0.025 g SDS. The autoclave was sealed and maintained at 160 °C for 16 hrs. The reaction was quenched by putting the autoclave in liquid N\textsubscript{2} for 15 minutes. The black precipitate was collected by addition of ethanol and centrifugation. It was washed repeatedly with ethanol and re-dispersed in hexane.

4.3.3 Decomposition in the presence of oleylamine and dodecanethiol

The appropriate precursor (0.100 g) was mixed with 8 mL of oleylamine by stirring for 30 minutes. To this mixture was added 1 mL of dodecanethiol and the resulting solution was stirred for 10 minutes. The mixture was heated in a Teflon-lined stainless steel powerbomb for 16 hrs at 170 °C. It was then allowed to cool in room temperature. The black precipitate was collected by addition of ethanol and centrifugation. It was washed repeatedly with ethanol and re-dispersed in hexane.

4.3.4 Decomposition in the presence of ethylenediamine

The appropriate precursor (0.100 g) was mixed with 8 mL of oleylamine by stirring for 30 minutes. The mixture was heated in Teflon-lined stainless steel powerbomb for 2 hrs at 120 °C. It was then allowed to cool in room temperature. The black precipitate was
collected by addition of ethanol and centrifugation. It was washed repeatedly with ethanol and re-dispersed in hexane.

### 4.4 Synthesis of the nanomaterials from multiple source precursors (MSP)

#### 4.4.1 Decomposition in the presence of oleic acid

Commercially available oleic acid was dried by heating 5mL with 1mL of acetic anhydride at 70 °C for 30 minutes followed by drying under vacuum at 120 °C for 30 minutes. Next, 1mmol (0.379 g) of Pb(OAc)$_2$.3H$_2$O was added to the resulting dry oleic acid and stirred at 50 °C for 30 minutes to convert into Pb(oleate)$_2$. The resulting solution was then dried under vacuum for 30 minutes at 120 °C to remove the acetic acid produced in the course of reaction. To this mixture dry tu (0.076 g) was added directly under the flow of argon and the reaction mixture was heated. Solution changed color to black at 120 °C. An aliquot was collected 10 minutes after it changed color. The black precipitate was collected upon addition of ethanol and centrifugation. It was washed repeatedly with ethanol and re-dispersed in hexane.

#### 4.4.2 Decomposition in presence of oleic acid and trioctylamine

Commercially available oleic acid was dried by heating 5mL with 1mL of acetic anhydride at 70 °C for 30 minutes followed by drying under vacuum at 120 °C for 30 minutes. Next, 1mmol (0.379 g) of Pb(OAc)$_2$.3H$_2$O was added to the resulting dry oleic acid and stirred at 50 °C for 30 minutes to convert into Pb(oleate)$_2$. The resulting solution was then dried under vacuum for 30 minutes at 120 °C to remove the acetic acid produced in the course of reaction. To this mixture, 1mmol (0.076g) tu in 6 mL trioctylamine was added under a flow of argon and the resulting mixture was heated at
170 °C. An aliquot was collected from the reaction 10 minutes after the solution changes color to black. The solid was collected upon addition of ethanol and centrifugation. It was washed with ethanol repeatedly and re-dispersed in hexane.

4.4.3 Decomposition in the presence of CTAB and ethylene glycol

1mmol (0.379 g) of Pb(OAc)$_2$.3H$_2$O and 1mmol (0.076gm) of tu was added to 10 mL of ethylene glycol in a three-neck flask with a reflux condenser. This was stirred for about 10 minutes. Next, 0.200 g of CTAB was added to this mixture and the mixture was heated rapidly to 200 °C when the color was changed to black indicating formation of lead sulfide. An aliquot was collected 10 minutes after it changed color. The solid was collected upon addition of ethanol and centrifugation. It was washed repeatedly with ethanol and re-dispersed in hexane.

4.5 Results and discussion

The bulk decompositions of the precursors were followed by thermogravimetric analysis (TGA). All of the precursors undergo a single decomposition step around 170 °C, giving rise to pure crystalline galena PbS as the end product. The decomposition temperature of the precursors is listed in Table 4.1. On the basis of the TGA results it is reasonable to conclude that during the single large decomposition step the organic parts of the single-source precursor are removed leaving behind the residue of PbS.
Table 4.1 TGA decomposition temperatures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb1a</td>
<td>168</td>
</tr>
<tr>
<td>Pb1b</td>
<td>167</td>
</tr>
<tr>
<td>Pb2a</td>
<td>174</td>
</tr>
<tr>
<td>Pb2b</td>
<td>183</td>
</tr>
<tr>
<td>Pb3a</td>
<td>176</td>
</tr>
<tr>
<td>Pb3b</td>
<td>178</td>
</tr>
</tbody>
</table>

Based on the TGA results, the decomposition reactions were conducted at 170 °C temperature using a variety of surfactants. The morphologies and structures of the solution decomposition products were examined by SEM and TEM. As shown by several previous reports in the literature, the shapes and sizes of decomposition products are dependent on surfactants, concentration and ratio of reagents and precursors, hydrophobicity, temperature and time of growth. It is well established that the preferential adsorption of various surfactants on different crystal faces promotes the growth along one face while inhibiting the growth along others, thus generating anisotropic nanostructures. The growth mechanism of dendritic and star-shaped PbS NPs has been investigated and reported by several other groups. To monitor the growth of NPs with time, the reaction was quenched at intervals of 1, 2, 5, 8 and 16 hrs. The reactions were carried out in a stainless-steel lined Teflon vessel maintained at 170 °C in the hydrothermal oven. In Figure 4.1, SEM images are shown for (A) 1 hr, (B) 2 hrs, (C) and (D) 5hrs, (E) 16 hrs. It is also compared with a reaction where no surfactant has been used (Figure 4.1F).
Facets appear to form in a way as to increase the proportion of low index planes on the initially-formed nanoparticle seed crystals. For cuboctahedral NPs such as PbS, the resulting shape of the nanostructure is determined by the growth ratio (R) of \{100\} and
{111} faces. The surface energies associated with different crystallographic planes are usually different and a general sequence can be elucidated as $\gamma_{\{111\}} < \gamma_{\{100\}} < \gamma_{\{110\}}$.\textsuperscript{126} As shown in Figure 4.2, when $R$ is 1.73, an octahedron is formed that is bounded by {111} faces, whereas when $R$ is 0.58 a cube bound by {100} faces results. However for the particles with $0.58 < R < 1.73$ both {100} and {111} faces are present. In Figure 4.3A, the truncated octahedra obtained with CTAB after 2 hrs of reaction time have six square {100} faces and eight hexagonal {111} faces, similar to $R = 1.15$ as shown in the schematic. The polar $-\text{NMe}_3^+$ head group of CTAB stabilizes charged {111} faces that contain only Pb or only S. As a result, sharing of non-polar and energetically higher {100} faces takes place, which is shown in the intermediate pictures B and C with 5 hrs of reaction time, where NPs are aligned along their {100} faces. Thus with 16 hrs of reaction time dendritic stars are formed. Oriented attachment with sharing of {100} facets would give rise to the highest dipole moments along the $<100>$ axis. This particular growth pattern has been observed and discussed in several other materials such as PbSe, CdTe or ZnO by other researchers.\textsuperscript{55, 127, 128}
When the decomposition reactions were carried out using an equimolar mixture of CTAB and SDS, several different sub-microstructures were found to co-exist in the product. The dominant structures were octahedral nanostructures with six arms oriented in the <100> directions and nanocubes with slightly truncated or rounded edges (Figure 4.3). SDS is a polar surfactant which is adsorbed preferentially on the polar {111} faces like CTAB. However it can be safely assumed that in case of SDS the interaction between Pb$^{2+}$ and the SO$_3^-$ group creates a stronger bond when compared to R-S$^-$ and -NMe$_3$ interactions in CTAB. Hence the presence of SDS in the reaction mixture effectively lowers the energy of {111} to a greater extent. Researchers have reported similar observations using SDS as an anionic surfactant in combination with CTAB. As a result, the growth along {100} is further promoted forming slightly truncated cubes (R~0.7) and the star-shaped particles are formed with six arms along the <100> directions as shown in Figure 4.3B. These stars undergo further growth along the same direction to give rise to the hexapods as shown in Figure 4.3A. It has been shown that in a mixture of cationic and anionic surfactant, higher excess of either is required to form a mixed micelle or a vesicle. With

Figure 4.2 (top) different shapes of nanocrystals evolved as a function of growth ratio (R) between {100} and {111} faces, (bottom) growth along {100} faces giving rise to the star-shaped nanocrystals. Taken after reference 126.
nearly equimolar ratios ionic pairs are formed between oppositely charged headgroups. Therefore the equimolar mixture can be considered as a double-tailed surfactant that forms bilayers in solution. Due to very close packing of oppositely charged headgroups, the effective hydrophobic volume also increases and results in the formation of a planar lamellar structure as opposed to a vesicle or mixed micelle. The possible formation of planar lamellar structure explains the observed co-existence of several submicron structures as shown in Figure 4.3A.

Figure 4.3 PbS NPs generated with equimolar mixture of CTAB and SDS from precursor Pb2b.

When the decomposition reactions were carried out in presence of oleylamine and dodecanethiol, nanocubes were obtained (Figure 4.4). Previous reports on the mechanism of growth of PbSe nanocrystals discuss the effect of oleylamine. The driving force in the formation of the cubes lies in the higher growth rate along the <111> direction as compared to the <100> faces. Oleylamine is relatively non-polar and non-selective, binding to both {100} and {111} faces. Since the intrinsic surface energy of the {111} faces is more than that of {100} growth takes place along {111} giving rise to a cubic nanocrystal from a tetradecahedral seed. It has been shown by Cheon et al. that the
presence of dodecanethiol molecules in the reaction mixture has a different effect. Dodecanethiol tends to bind to the \{111\} faces via a $\mu_3^-$ bonding mode, thus lowering the energy of the \{111\} faces as compared to \{100\}. An increase in the amount of dodecanethiol tends to produce truncated cubes and ultimately truncated octahedra. We found a similar observation for increasing amounts of dodecanethiol (Appendix C).

![Figure 4.4 Nanocubes generated in oleylamine from precursor Pb2a.](image)

When the decomposition reactions were carried out in presence of ethylenediamine, a mixture of dendritic structures along with some interlinked quasi-cube shaped nanocrystals were obtained (Figure 4.5). Ethylenediamine like oleylamine is a non-selective capping agent. When the precursor decomposes at elevated temperature and PbS seeds form, the growth of the seeds is largely governed by kinetic parameters. Faster growth along the \{111\} faces give rise to cubes. These cubes partially share their \{100\} faces to decrease surface energy and grow along the eight $<111>$ directions leading to the growth of dendritic structures. Even though in some images the dendrites appear to have four or six horns different three dimensional projections of the dendritic stars from different directions show that the dendrites have eight horns.
Figure 4.5 PbS dendrites synthesized from precursor Pb2b and Pb1a in the presence of ethylenediamine (scale bars = 1 μm).

Table 4.2 gives a summary of the types of structures obtained from our single source precursors decompositions and compares those results obtained from other precursor molecules reported in the literature. It is clear from the results that the compatibility with both aqueous and organic solvents helps to synthesize different shapes and sizes of nanostructures without the help of any other thio-containing molecule.
Table 4.2 Summary and comparison of nanoparticle shapes from single-source precursor.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Reaction conditions</th>
<th>Shapes obtained</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb[(S$_2$CNRR')$_2$] R= C$<em>5$H$</em>{11}$, C$<em>6$H$</em>{10}$, C$_2$H$_5$, CH$_3$, C$_2$H$_5$ R'= C$<em>5$H$</em>{11}$, C$<em>6$H$</em>{10}$, CH(CH$_3$)$_2$, C$_4$H$_9$</td>
<td>CVD 400-450 °C</td>
<td>granular, platelets, cubic crystallite</td>
<td>51</td>
</tr>
<tr>
<td>Pb[(S$_2$CNEt)$_2$)$_2$</td>
<td>TOPO + Bi nanoparticle as catalyst 250 °C</td>
<td>nanowire</td>
<td>53</td>
</tr>
<tr>
<td>2,2'-bipyridyl(Pb(SC(O)(C$_6$H$_5$)$_2$)$_2$)[, [Pb(S$_2$P(C$_6$H$_5$)$_2$)$_2$N]]</td>
<td>1-thioglycerol, NaOH ~2atm, 121 °C</td>
<td>cubes, truncated cubes, rods</td>
<td>124</td>
</tr>
<tr>
<td>Pb(SCH$_2$C$_6$H$_5$)$_2$</td>
<td>Pyrolysis 150 °C</td>
<td>irregular size</td>
<td>71</td>
</tr>
<tr>
<td>Pb(S$_2$P(OR)$_2$)$_2$</td>
<td>oleylamine, n-decane, oleic acid 160 °C</td>
<td>nanocubes</td>
<td>66</td>
</tr>
<tr>
<td>Pb(SCOC$_6$H$_5$)$_2$</td>
<td>Ethylenediamine Room temperature</td>
<td>dendrites</td>
<td>52</td>
</tr>
<tr>
<td>Pb(SCOC$_6$H$_5$)$_2$</td>
<td>Oleylamine Room temperature</td>
<td>spherical particle</td>
<td>52</td>
</tr>
<tr>
<td>Pb$_2$a, Pb$_2$b, Pb$_3$a, Pb$_3$b</td>
<td>Hydrothermal, CTAB, 2h 170 °C</td>
<td>truncated octahedron</td>
<td>This work</td>
</tr>
<tr>
<td>Pb$_2$a, Pb$_2$b, Pb$_3$a, Pb$_3$b</td>
<td>Hydrothermal CTAB, 16h 170 °C</td>
<td>dendritic stars</td>
<td>This work</td>
</tr>
<tr>
<td>Pb$_2$a, Pb$_2$b, Pb$_3$a, Pb$_3$b</td>
<td>Hydrothermal, CTAB + SDS 160 °C, 16h</td>
<td>mixture of octahedrons, truncated nanocubes</td>
<td>This work</td>
</tr>
<tr>
<td>Pb$_1$a, Pb$_1$b, Pb$_2$a, Pb$_2$b, Pb$_3$a, Pb$_3$b</td>
<td>Solvothermal Oleylamine + dodecanethiol 170 °C, 16h</td>
<td>nanocubes</td>
<td>This work</td>
</tr>
<tr>
<td>Pb$_1$a, Pb$_1$b, Pb$_2$a, Pb$_2$b, Pb$_3$a, Pb$_3$b</td>
<td>Solvothermal Ethylenediamine 120 °C, 2h</td>
<td>dendritic stars</td>
<td>This work</td>
</tr>
</tbody>
</table>
Synthesis of similar anisotropically-shaped nanostructures starting with multiple sources precursors required slight modification of reaction conditions. Dendritic stars were formed by using CTAB in ethylene glycol as surfactant (Figure 4.6). The morphological evolution of dendritic star shaped NPs was found to be faster when compared to the SSPs, which can be rationalized by the slower hydrolysis rates of the later.

Figure 4.6 PbS dendritic stars synthesized from MSP (Pb(OAC)₂ and tu) in presence of ethyleneglycol and CTAB.

Oleic acid assisted decompositions resulted in a mixture of cubes, truncated cubes and rods (Figure 4.7). Recent work by our group as well as by other researchers have shown the effect of air, oxygen, water vapor or acidity of reaction media in the anisotropic growth of NPs. Oleic acid is a strongly coordinating surfactant, which increases the nucleation rate and hence the growth rate of the system. Sungawa reported that crystal splitting is often observed in systems where the growth rate is high.¹³¹ Defects are produced as a result of high growth rate in the direction of growth, and the fiber branches as the growth continues. This crystal splitting growth mechanism was observed by us in
Fe$_2$P system.$^{36}$ The same phenomenon has also been noted by other researchers in Bi$_2$S$_3$ and Sb$_2$S$_3$ systems.$^{132-136}$

![Figure 4.7](image)

**Figure 4.7** (A)TEM, (B)HR TEM and (C)SAED pattern of PbS NPs synthesized from MSP(Pb(OAC)$_2$ and tu) using oleic acid as surfactant.

Increasing amount of amine present in surfactant resulted in nanocubes. Nanocubes were obtained with traces of split-end rods (Figure 4.8) in presence of a mixture of trioctylamine and oleic acid (5:1 volume ratio). Reactions with oleylamine did not give interesting results.
Figure 4.8 TEM(A, B, C), HRTEM (D) and SAED (E) of mixture PbS nanocubes and split rods synthesized from (Pb(OAC)$_2$ and tu in presence of trioctylamine and oleic acid surfactant mixture.

4.6 Conclusion

Mixed ligand aromatic carboxylate tu or ths complexes of Pb(II). can be used as molecular precursors for PbS semiconducting NPs in either aqueous or non-aqueous solvents. The mechanism of growth of NPs depend on various factors such as type of surfactant, time of growth, temperature etc. Growth ratio between {100} and {111} faces of the nanocrystal was altered by using various surfactants and it was found to affect the resulting shapes and sizes. The growth reactions were monitored with time and some oriented attachment was observed involving {100} faces of truncated nanocubes to form dendritic stars over time. As a general rule, particles synthesized in the aqueous conditions were bigger in size than those synthesized in long chain organic amines such
as oleylamine or hexadecylamine. The precursors were found to give clean decompositions without the aid of any sulfur containing molecule. Difference in the aromatic groups in precursor structure did not seem to affect the nanoparticle shape and sizes greatly. The results obtained by decomposition of single-source precursors were compared with those from multiple sources. It was found that in presence of acidic components such as acetic acid or oleic acid crystal splitting takes place along the direction of growth of crystal which results in formation of anisotropic nanocrystals.
A Additional spectral characterization data for precursors

FT-IR of the precursors to CdS

Figure A.1 FT-IR spectra of precursor Cd1a (top) and Cd1b (bottom).
Figure A.2 FT-IR spectra of precursor Cd2a (top) and Cd2b (bottom).
**Figure A.3** FT-IR spectra of precursors Cd3a (top) and Cd3b (bottom).

**Table A.1** IR peak assignments of precursors to CdS.

<table>
<thead>
<tr>
<th>Cd1a</th>
<th>Cd1b</th>
<th>Cd2a</th>
<th>Cd2b</th>
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Figure A.4 FT-IR spectra of Pb1a (top) and Pb1b (bottom).
Figure A.5 FT-IR spectra of Pb2a (top) and Pb2b (bottom).
Figure A.6 FT-IR spectra of Pb2a (top) and Pb2b (bottom).
$^{13}$C NMR of precursors to CdS

Figure A.7 $^{13}$C NMR spectra of precursors Cd1a (top) Cd1b (bottom).
Figure A.8 $^{13}$C NMR spectra of precursors Cd2a (top) Cd2b (bottom).
Figure A.9 $^{13}$C NMR of precursor Cd3a.
FT-IR of the precursors to PbS

Figure A.10 $^{13}$C NMR of Pb1a (top) and Pb2a (bottom).
Figure A.11 $^{13}\text{C}$ NMR of Pb2b (top) and Pb3a (bottom).
Figure A.12 Precursor Cd1a packing structure.
Figure A.13 Precursor Cd2a packing structure.
Figure A.14 Precursor Cd2b packing structure.
Figure A.15 Precursor Cd3a packing structure.
Figure A.16 Precursor Cd3b packing structure.
Figure A.17 Precursor Pb2b packing structure.
Figure A.18 Precursor Pb3a packing structure.
Figure A.19 Precursor Pb3b packing structure.
B Supporting information on Chapter 3

Optical studies

The optical absorbance spectra was measured for the nanoparticle samples shown in Figure B.1 over the range 300-600 nm. An excitonic peak is observed around 476 nm, which assigned to the 1s electron-heavy hole pair transition. Another peak at lower wavelength (not shown in the diagram) probably arises from a combination of two transitions, a first excited state transition and a 1s transition from spin-orbit split-off valence band. The absence of a sharp peak in UV-Vis spectra indicates a broad size distribution of the crystals. The photoluminescence peaks differ in intensities, however the peak position and band-shape remains the same for all the samples, indicating involvement of same initial and final states in the photo excitation and a fast relaxation from the excited level.
Figure B.1 Absorbance (top left) and Photoluminescence (top right) spectra of CdS NPs. TEM images of the corresponding CdS NPs (bottom).
Figure B.2 TGA of precursor Cd1a in Argon atmosphere.

Figure B.3 TGA of precursor Cd1b in Argon atmosphere.
Figure B.4 TGA of precursor Cd2a in Argon atmosphere.

Figure B.5 TGA of precursor Cd2b in Argon atmosphere.
Figure B.6 TGA of precursor Cd3a in Argon atmosphere.

Figure B.7 Characteristic TGA of precursor Cd3b in Argon atmosphere.
Figure B.8 EDS results of the CdS particles prepared hydrothermally from Cd1a Al and Mg peaks are present from the metal support of the samples (Mg-Al alloy).
Figure B.9 EDS results of the CdS particles prepared from Cd2b in ethylenediamine. Al and Mg peaks are present from the metal support of the samples (Mg-Al alloy).
C Supporting information on Chapter 4

Figure C.1 TEM images of PbS Nanocubes generated from precursors Pb1a (A), Pb1b (B), Pb2b (C), Pb3a (D), Pb3b (E) in oleylamine (8mL) and dodecanethiol (1mL) mixture. All scale bars = 100 nm.

Figure C.2 TEM image of PbS NPs generated from precursor Pb2b in oleylamine (8 mL) and dodecanethiol (4mL).
Figure C.3 SEM images of Dendritic stars generated from precursors Pb2a (A), Pb1a (B), Pb1b (C) in presence of CTAB as surfactant with reaction time of 16 hrs at 170 °C (all scale bars = 1μm).

Figure C.4 SEM images of decomposition results from precursors (A) Pb1b, (B) Pb2a and (C) Pb3a.
Figure C.5 Characteristic XRD of the decomposition product from precursor Pb2b showing matching peaks with pure crystalline galena.
Figure C.6 TGA curve of precursor Pb1a under inert atmosphere.

Figure C.7 TGA curve of precursor Pb2a under inert atmosphere.
Figure C.8 TGA curve of precursor Pb2b under inert atmosphere.

Figure C.9 TGA curve of precursor Pb3a under inert atmosphere.
Figure C.10 TGA curve of precursor Pb3b under inert atmosphere.
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**Education**

PhD in Chemistry, (Fall 2005 - anticipated Fall 2009)
Rice University, Houston, United States

Indian Institute of Technology, Madras, India

Bachelor of Science (B.Sc.) with Chemistry honors, (2000 - 2003)
Presidency College, Kolkata, India

**Research Experience**

Graduate Research Assistant - Rice University (Fall 2005 - present)

- Synthesized and characterized Organometallic precursors of sulfide nanostructures
- Carried out controlled decompositions of precursors using standard schlenk technique, under inert atmosphere to synthesize semiconducting sulfide NPs
- Characterized structural and optical properties of nanoparticles
- Functionalized nanoparticles to synthesize semiconductor-gold nanocomposite

Undergraduate Research Assistant - IIT Madras (2004 - 2005)

- Spectroscopically followed the dynamics of metal driven self assembly of Pd(II) and nitrogen based ligands

**Awards and Recognitions**

- Robert A. Welch Foundation Pre-doctoral Fellowship (2008)
- Dean’s Travel Award, Rice University (2008)
- Center of Biological and Environmental Nanotechnology Travel Award (2008)
- Ranked 70 in all India based graduate aptitude test with a percentile score of 97.99 (2005)
Skills

Instrumentation skills

- High Resolution and Conventional Transmission Electron Microscopy (HR TEM and TEM) and Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS)
- Single Crystal X-ray Diffraction, X-ray powder Diffraction (XRD)
- Fourier-transform Infrared spectroscopy (FT-IR), Fourier-transform Nuclear Magnetic Resonance Spectroscopy (FT-NMR), Mass spectra, UV-Visible Spectroscopy (UV-Vis), Raman Spectroscopy, Circular Dichroism Spectropolarimeter (CD-Spectropolar)
- Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC)
- Inductively Coupled Plasma (ICP)

Computer Skills

- Experienced in use of Microsoft Excel, Origin, Photoshop, Image pro
- Experienced in use of Jade XRD software

Language Skills

- Fluent in English

Teaching Experience

- General Chemistry Laboratory - Rice University (2005 - 2007)
- General Chemistry Discussion leader - Rice University (2007 - 2008)
Description: Tutored supervised and trained undergraduate students in general chemistry laboratory and theory. Proctored and graded exams.

Academic Services and Organization

- American Chemical Society membership (2006 - present)

Publications


Oral presentations


Poster presentations

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