The use of metal complexes to deposit metal chalcogenide thin films and

nanoparticles

A Thesis presented by

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STATEMENT OF SOURCES

DECLARATION

I hereby declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from the published or unpublished work of others has been acknowledged in the text and a list of references is given.

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ABSTRACT

This thesis consists of four chapters. The first chapter describes the properties, methods of deposition and applications of semiconductors. The second chapter focuses on the deposition of metal chalcogenides thin films from single molecular precursors of the type $[M{N(EPR_2)_2}_2]$, were M = Pt, Pd, Ni; E = S or Se and $R = {}^iPr$ or Ph. Ligands of the type $R_2P(E)NP(E)R_2$, where $R = {}^iPr$ or Ph were prepared to synthesize these precursors. Single X-ray structures of $[Pt{N({}^iPr_2PSe)_2}_2]$ and $[Pd{N(SPh_2)_2}_2]$ are reported and discussed. The X-ray structure of the platinum complex shows a square-planar conformation whereas the six membered $PtSe_2P_2N$ ring adopts a distorted "boat" conformation.

The third chapter describes the deposition of metal sulphide thin films from $[M(S_2COR)_2]$, were M = Pt, Pd, Ni, Cd, Co, Cu and R = Et or ⁱPr. Single X-ray structures of $[M(S_2COR)_2, M = Pt, Pd, and Ni, R = Et$ are reported and discussed. The NiS thin films are polycrystalline and their θ values are in good agreement with the literature values. The phases do not seem to be affected by temperature whereas the morphology of the films changes with temperature. The morphology of the films has been found to be greatly influenced by varying the temperature. All the ligands and precursors were characterised by elemental analysis and by using spectroscopic techniques such as infrared (IR), mass spectrometry (MS), proton and carbon nuclear magnetic resonance (¹H and ¹³C NMR). Thin films of PtSe₂, Pt, PdSe₂, Pd₄Se, Pd₁₇Se₁₅, PdS, and PdS₂ were deposited by aerosol assisted chemical vapour deposition (AACVD) and low pressure deposition (LP-MOCVD) using metal-organic vapour metal complexes of iminobis(dialkylphosphinato)dichalcogenide ligands. Thin films of NiS, CdS, Pt, PdS, $Pd_{16}S_7$, and Co_9S_8 were deposited by AACVD using the respective metal xanthate complexes. The films were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX).

The fourth chapter focuses on the preparation of nanoparticles and nanorods from cadmium complexes. The synthesis of CdS nanoparticles and nanorods are described in detail. The synthetic route used for the synthesis of the CdS nanoparticles is the thermolysis of metal complexes, [Cd(S₂CNMe₂)₂] and [Cd{-SC(=S)OCH(CH₃)₂}₄], in tri-octylphosphine oxide (TOPO) and hexadecylamine (HDA). The optical properties of the nanoparticles were studied by using ultraviolet (UV)-visible and photoluminescence (PL) spectroscopy. There were blue shifts in the band gaps for all CdS samples; however, photoluminescence was very poor. The hexagonal phase of CdS was observed for all CdS samples using XRD measurements. The transmission electron microscopy (TEM) images show that the TOPO capped CdS nanoparticles have a spherical shape whereas the HDA capped particles are rod shaped. Nanoparticles of CdS were characterised by UV-vis, PL, XRD and TEM.

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List of abbreviations and symbols chemicals

MeOH	Methanol
THF	Tetrahydrofuran
R	Alkyl group
ⁱ pr	Isopropyl group
Et	Ethyl group
Me	Methyl group
^t Bu	Tert-butyl group
E	Chalcogenide element (S or Se)
ТОР	Tri-n-octylphosphine
ТОРО	Tri-n-octylphosphine oxide
NaOMe	Sodium methoxide
М	Transition metal

Ligands and precursors prepared in this project

NH(SeP ⁱ Pr ₂) ₂	Iminobis(diisopropylseleniumphosphine)
NH(SP ⁱ Pr ₂) ₂	Iminobis(diisopropylthiophosphine)
NH(SePPh ₂) ₂	Iminobis(diphenylseleniumphosphinato)
NH(SPPh ₂) ₂	Iminobis(diphenylthiophosphinato)
$[Pt\{N(SeP^{i}Pr_{2})_{2}\}_{2}]$	[Bis{bis(imidodiisopropylselenophosphinato)}platinum(II)]
$[Pt{N(SPiPr_2)_2}_2]$	[Bis {bis(imidodiisopropylthiophosphinato)}platinum(II)]
$[Pd{N(SeP^{i}Pr_{2})_{2}}_{2}]$	[Bis {bis(imidodiisopropylselenophosphinato)} palladiun(II)]
$[Pd{N(SPiPr_2)_2}_2]$	[Bis{bis(imidodiisopropylthiophosphinato)} palladium(II)]
$[Pd{N(SePPh_2)_2}_2]$	[Bis{bis(imidodiphenylselenophosphinato)}palladium(II)]
$[Pd{N(SPPh_2)_2}_2]$	[Bis {bis(imidodiphenylthiophosphinato)}palladium(II)]
$[Pt{N(SPPh_2)_2}_2]$	[Bis{bis(imidodiphenylthiophosphinato)}platinium(II)]
$[Ni \{N(SeP^{i}Pr_{2})_{2}\}_{2}]$	[Bis{bis(imidodiisopropylselenophosphinato)}nickel(II)]
$[Ni \{N(SP^{i}Pr_{2})_{2}\}_{2}]$	[Bis{bis(imidodiisopropylthiophosphinato)}nickel(II)]
$[Ni \{N(SPPh_2)_2\}_2]$	[Bis{bis(imidodiphenylthiophosphinato)}nickel(II)]
$[Ni \{N(SePPh_2)_2\}_2]$	[Bis{bis(imidodiphenylselenophosphinato)nickel(II)]
[Ni(S ₂ COEt) ₂]	[Bis(ethylxanthato)nickel(II)]
[Ni(S ₂ CO ⁱ Pr) ₂]	[Bis(isopropylxanthato)nickel(II)]
[Pd(S ₂ COEt) ₂]	[Bis(ethylxanthato)palladium(II)]
$[Pd(S_2CO^{i}Pr)_2]$	[Bis(isopropylxanthato)palladium(II)]
[Pt(S ₂ CO Et) ₂]	[Bis(ethylxanthato)platinum(II)]
[Pt(S ₂ CO ⁱ Pr) ₂]	[Bis(isopropylxanthato)platinum(II)]
[Cd(S ₂ CO Et) ₂]	[Bis(ethylxanthato)cadmium(II)]

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$[Cd(S_2CO^{i}Pr)_2]$	[Bis(isopropylxanthato)cadmium(II)]
[Co(S ₂ COEt) ₂]	[Bis(ethylxanthato)cobalt(III)]
[Co(S ₂ CO ⁱ Pr) ₂]	[Bis(isopropylxanthato)cobalt(III)]
[Cu(S ₂ OEt) ₂]	[Bis(ethylxanthato)copper(II)]
$[Cd(S_2CNMe_2)_2]$	[Tetramethyldithiocarbamates cadmium(II)]
[Cd{-SC(= S)OCH(CH ₃) ₂ } ₄]	[Bis(isopropylxanthatodisulfide)cadmium(II)]

Techniques and Methods

NMR	Nuclear magnetic resonance
MS	Mass Spectrometer
FT-IR	Fourier Transform Infrared
UV-Vis	Ultraviolet visible spectroscopy
PL	Photoluminescence
TGA	Thermogravimetric analysis
CVD	Chemical vapour deposition
AACVD	Aerosol assisted chemical vapour deposition
LP-MOCVD	Low pressure metal organic chemical vapour deposition
MBE	Molecular beam epitaxy
ALD	Atomic layer deposition
XRD	X-ray diffraction
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
EDAX	Energy dispersive X-ray analysis

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MO	Molecular orbitals

LCAO Linear combination of atomic orbital

Symbols and Constants

a.u.	Arbitrary units
α	Absorption coefficient
Ε	Energy
Μ	Mobility
Т	Temperature
Λ	Wavelength
K	Wave vector
K _{sp}	Solubility product
Σ	Conductivity
$\mathbf{E_{f}}$	Fermi energy
В	Magnetic field
λ _{exc}	Excitation wavelength (Luminescence)
8	Dielectric coefficient
min	Minutes
h	Hour
t	Time
R	Radius
D -	Diameter

,

E	Elementary charge
a _B	Bohr radius
Hz	Hertz
Á	Angstrom
С	Celcius
Eg	Band gap energy
K	Kelvin
НОМО	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
Λ	Wavelength
S	Singlet
d	Doublet
m	Multiplet
eV	Electron volt
MHz	Megahertz
ORTEP	Oak ridge thermal ellipsoid plot
Ppm	Parts per million
Sccm	Standard cubic centimeters per minute

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DEDICATION

THIS WORK IS DEDICATED TO MY WIFE, PARENTS AND TO THE MEMORY OF MY LATE SISTER, KHATHUTSHELO MUSETHA AND LATE FRIEND, JIM CHAPMAN.

Chapter 1

General introduction to semiconductor thin films

1

1.1 Background

Semiconductor materials are distinguished by having their specific electrical conductivity between that of conductors and insulators. Materials act as semiconductors due to the nature of the chemical bonding within the material and the resulting configuration of the electrons associated with this bonding character. Both silicon and germanium have electronic structures with four valence electrons available for bonding, silicon having the configuration [Ne]3s²3p². Although there are many techniques available for preparing semi-conducting thin films, it is generally difficult to maintain the stoichiometry of the materials.¹⁻⁴

1.2 Band theory

In general, for most semiconductor and insulators, conductivity (σ) increases rapidly with temperature, whereas for metals, there is a gradual decrease in conductivity with increasing temperature. The electronic properties of solid materials can be described by band theory. In the present study, only a brief outline of the important conclusions of the band theory will be given. In simplified terms, the basis for band theory originates from the behaviour of the atomic orbital in infinite structures, where there is overlap between the atomic orbitals to lead into the formation of continuous bands.



Figure 1.1 Band gap dependence on interatomic spacing

The electronic properties of a solid depend on the nature of these bands, their width, the number of electrons they can hold and the number of electrons in the entire system (hence "quantum dots" of semiconductors have different band structure from the bulk material). The width of the bands depends on the degree of overlap of the respective orbital. Weakly interacting orbitals lead to narrow bands whereas strongly interacting orbitals lead to wide bands. The electrons in a wide band are considered to be dispersed over the entire lattice, whereas electrons in a narrow band are more associated with the nuclei. The differences between metals, semiconductors and insulators depend largely on their respective band structures and the magnitude of any energy gap between full and empty bands.

The qualitative diagrams employed in band theory are derived differently by chemists and physicists/material scientists. The chemist's approach is to take the orbital of each atom, apply a linear combination of atomic orbital (LCAO) approximation and extend to the level of an infinite 3-dimensional structure. By contrast, the physicists use a

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free-electron model that ignores the orbital of each atom and instead builds up the electronic bands using only the wave functions of the electrons. The chemists approach to band theory, therefore, is to extend molecular orbital (MO) theory to infinite three-dimensional structures. In diatomic molecules, an atomic orbital from one atom overlaps with an atomic orbital from the second atom to produce two molecular orbitals, which are delocalized over both atoms. One of the MOs represents a bonding orbital of lower energy than the atomic orbital; the other MO forms an antibonding orbital of higher energy than the atomic orbital. For increasingly large molecular clusters the number of MOs increases, consequently the average energy gap between adjacent orbitals is reduced. Hence the energy gap between electronic levels in the bonding and antibonding orbitals diminishes until a continuum of energy levels is obtained. In contrast, the free electron model used by physicists postulates that band gaps are derived from the interaction of free electrons with the changes in periodic potential through the crystal lattice. Qualitatively the two models produce very similar band diagrams in 2- or 3-dimensions, differences are apparent, however, in 1-D.

The energy corresponding to the highest filled electronic state at 0 K is called the Fermi energy, E_f . Figure 1.1a represents the electron band structure found for many transition metals, where the outermost band is only partially filled with electrons, whereby the electrons can move freely. Each transition metal atom has one 4s electron, hence in the solid, comprised of N atoms, the 4s band can accommodate 2N electrons so the band is half filled, facilitating electron conduction. The electron band structure of metals such as magnesium, where there is an overlap of empty and filled bands, is shown in Figure 1.1b. However, when a solid is formed there is overlap of the 3s and 3p bands. The band structure for insulators and semiconductors are similar

in the sense that one band is completely filled (valence band) and the others are empty (conduction band). The difference between the two structures lies in the magnitude of the band gap E_g . For insulators the band gap is relatively wide (generally > 4 eV), whereas for semiconductors it is smaller (< 4 eV). The Fermi level for the latter band structures lies within the "forbidden gap" between the valence and the conduction edges. In the presence of an electric field, only electrons with energies greater than the Fermi energy are acted upon and participate in the conduction process. These electrons are called free electrons. For semiconductors and insulators, electron states in the valence band can only become available if electrons are promoted across the energy band gap into the conduction band. This can only be achieved if the electrons are supplied with a minimum energy equal to the band gap energy and are usually accomplished with an external non-electrical source such as light or heat.

Figure 1.2 shows the excitation process and the implications of Fermi function for the electrical conductivity of a semiconductor. At higher temperatures, a larger fraction of the electron can bridge this gap and participate in the electrical conduction. Increasing the temperature leads to an increase in the number of carriers and a corresponding increase in conductivity.

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Figure 1.2 Fermi-Dirac distributions as a function of temperature

At low temperatures, the valence band is completely full, making the material an insulator. For every electron excited into the conduction band, a vacant electron state, known as a positive hole, is left in the valence band. The number of electrons excited thermally depends on both the band gap and the temperature. At a given temperature, the larger the band gap, the lower the probability that an electron may be promoted to the conduction band. Increasing the temperature results in greater thermal energy for electron excitation and therefore enhances the conductivity. ¹⁻⁶

1.3 Theory of semiconductors

Since the introduction of the transistor in the 1950s and the development of the integrated silicon chip in the 1970s, semiconductor based devices have been increasingly impinging on our everyday lives⁶. The trend is likely to continue, with increasing demand for new, technologically advanced consumer products such as

mobile cell phones and laptop computers. Although silicon-based technology is by far the most advanced amongst semiconductor technology, there is increasing interest in use of compound semiconductors (e.g. GaAs, ZnO etc.) that possess electrical and optical properties that are absent in silicon. One of the main reasons that semiconductors are useful in electronic devices is that their electronic properties can be greatly altered in a controllable way by adding small amount of impurities.

The conductivities are particularly sensitive to the variations in temperature, impurities and light. Generally the conductivity of semiconductors is given by equation 1.1,

 $\alpha = ne\mu$

eq. 1.1

where n is the carrier concentration (the concentration of carriers per cm³), e is the charge on the carriers and μ is their mobility (the ratio of the drift velocity and the electric field).

The temperature-dependence of the bandgap energy can be determined with the following expression for E_g as a function of the temperature T:

$$E_{g}(T) = E_{g}(0) - \alpha T^{2}/T + \beta$$
 eq. 1.2

where $E_g(0)$, α , and β are the fitting parameters.

This conductivity is due to the generation of charge carriers which are thermally excited. In contrast, the conductivity of a metal decreases at higher temperatures due to electron-phonon collisions. Dopants are introduced in order to enhance the conducting potential of a semiconductor. The quantity of the dopant is not the only factor that can limit the electrical properties of the semiconductor, the type of impurity is also particularly important. Another limiting factor is due to defects found in the crystal lattice. These impurities can either be unintentional due to lack of control during the growth of the semiconductor or they can be added deliberately to provide mobile current carriers in the semiconductor. Semiconductors can be divided into two types, intrinsic and extrinsic. Semiconductors that rely on temperature to conduct charge or emit light are called intrinsic semiconductors. However, the presence of impurities in the material will generate extra carriers at a much higher concentration than those that are generated thermally in the intrinsic semiconductor. These 'doped' semiconductors are called extrinsic semiconductors. They contain impurities (or foreign atoms) incorporated into the crystal structure of the semiconductor. High impurities concentration has detrimental effects on the electrical quality of the material. In many devices the intrinsic conductivity is undesirable, and larger band gap materials give better performance. The band gaps of some compound are given in Table 1.1.
Table 1.1 Properties of some semiconductors

Materials	Groups	Band Gaps/eV
GaAs		1.43
GaN		3.37
GaSb	III-V	0.72
InP		1.34
CdS		2.42
ZnS		3.68
ZnO	II-VI	3.35
CdTe		1.56
PbS		0.41
РbТе	IV-VI	0.31

1.4 Deposition of Semiconductor Thin Films

There are a number of methods by which semi conducting material can be deposited on substrates. These methods can be divided into two groups; i.e. chemical and physical techniques.

1.4.1 Thin Film Deposition Techniques

There are many vapour phase deposition/growth techniques available. Most important of these are chemical vapour deposition (CVD), vapour phase epitaxy (VPE) and physical vapour deposition (PVD) techniques. The techniques are based in the formation of vapour of the material to be deposited, so that the vapour is condensed on the substrate surface as a thin film. Usually the process must be performed in vacuum or in controlled atmosphere, to avoid interaction between vapour and air.

Chemical vapour deposition or CVD is a generic name for a group of processes that involve depositing a solid material from a gaseous phase and is similar in some respects to physical vapour deposition (PVD). A range of other techniques are available for the deposition of semiconductor thin films, namely evaporation, sputtering, metal-organic chemical vapour deposition (MOCVD), aerosol-assisted chemical vapour deposition (AACVD), atomic layer deposition (ALD) and molecular beam epitaxy (MBE). Each technique has intrinsic strengths and weaknesses, as well as specific advantages for specific applications.

Volatility of compounds is a prerequisite for deposition in the conventional CVD. It is a function of intermolecular forces (van der Waals interaction, pi-stacking or hydrogen bonds) which are affected by molecular weight, geometry and, for solids, lattice structure. Several CVD techniques have been employed for the growth of a variety of materials in this work, including low pressure metal-organic chemical vapour deposition (LP-MOCVD) and AACVD.

1.4.2 Physical Vapour Deposition or Vacuum Deposition Techniques

PVD can be divided into two processes, evaporation and sputtering.

1.4.2.1 Physical Vapour Deposition (PVD) by Evaporation

During evaporation the material being deposited is heated under ultra high vacuum to vaporise the species which condense on the substrate surface. The base pressure in the reaction chamber is generally lower than 10⁻⁷ Torr, where the mean free path of the evaporated species is enough to allow it to condense on the substrate surface without collisions with residual gas molecules. However, deposition of alloy films using an evaporation technique is somewhat difficult because of differences in vapour pressures of the various elements, e.g. the growth of alloys containing both As and P. PVD differs in that the precursors are solid, with the material to be deposited being vaporised from a solid target and deposited onto the substrate.

1.4.2.2 Physical Vapour Deposition (PVD) by Sputtering

Sputtering is the deposition of particles vaporised from surface, which is called the "sputtering target", by the physical sputtering process. Physical sputtering is a nonthermal vaporization process. Surface atoms are physically ejected by momentum transfer from an energetic bombarding particle which is usually a gaseous ion accelerated from plasma. Sputtering deposition can be performed in high vacuum or low pressure where the sputtered particles do not suffer gas phase collisions in the space between the target and the substrate.

There are several advantages of using sputtering deposition. Unlike vacuum evaporation, alloy films can be produced by sputtering deposition due to the target providing a stable, long-lived vaporisation source. The second advantage is that in some configurations, reactive deposition can be easily accomplished using reactive gaseous species that are activated in plasma.¹⁶⁻¹⁷

1.4.3 Chemical Vapour Deposition (CVD)

The family of CVD techniques is the most flexible method to create nanostructures today. With many forms of CVD existing, it can be used efficiently toward many applications. The CVD technique has been used for many years in the semiconductor industry to thin film deposition (epitaxy) on substrates. In a traditional sense, CVD is used to create layers of semiconductors, insulators, or conductors in a sort of 'sand wich' of layers. CVD has been proved to be a useful method for the deposition of thin films for many applications. The CVD techniques are a vapour deposition technique based on homogeneous or heterogeneous chemical reactions. Depending on conditions such as vapour pressure and temperature, both types of reaction or only one of them, takes place during deposition process. These processes employ various gaseous, liquid and solid chemical as sources of elements (precursors) of which the film is to be formed. A large variety of single crystalline, polycrystalline and amorphous thin films of metals have been formed. Dielectrics and semiconductors of III-V and II-VI groups were prepared by the CVD technique.¹⁸⁻¹⁹ The factors affecting uniformity of surface morphology are from a variety of sources, depending on whether the vacuum or fluid are enough to support mass transport (e.g. if mass transport is not enough, it can result in a non uniform surface morphology over the substrate surface area). The third step is the actual deposition of the film on the substrate surface where adsorption occurs. Deposition behaviour is determined by the source and transport factors and by conditions at the deposition surface. There are three principal factors which determine the deposition behaviour on the surface, the substrate surface condition, the reactivity of the arriving material, and the energy input.¹⁸⁻²⁰

The Process Steps for Thin film Deposition

Precursor gases (often diluted in carrier gases) are delivered into the reaction chamber at approximately ambient temperatures. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase, which are deposited onto the substrate. The substrate temperature is critical and can influence what reactions take place.

A CVD apparatus consists of several basic components:

- Gas delivery system For the supply of precursors to the reactor chamber.
- Reactor chamber Chamber within which deposition takes place.

• Substrate loading mechanism – A system for introducing and removing substrates, mandrels e.t.c.

• Energy source – Provides the energy/heat that is required to get the precursors to react/decompose.

• Vacuum system – A system for removal of all other gaseous species other than those required for the reaction/deposition.

• Exhaust system – System for removal of volatile by-products from the reaction chamber.

• Exhaust treatment systems – In some instances, exhaust gases may not be suitable for release into the atmosphere and may require treatment or conversion to safe/harmless compounds.

• Process control equipment – Gauges, controls etc to monitor process parameters such as pressure, temperature and time.

Energy Sources

There are several suitable sources of heat for CVD processes. These include:

- Resistive heating e.g. tube furnaces

- Radiant heating e.g. halogen lamps
- Radio frequency heating e.g. induction heating

- Lasers: or lasers as a source of photo energy.

Other energy sources may include UV-Visible light.

The condition of the substrate surface includes roughness, level of contamination, degree of chemical bonding with the formed materials, and crystallographic parameters, in the case of epitaxy. The second factor is the reactivity which refers to the probability of arriving molecules reacting with the surface and becoming incorporated into the film. Finally the third factor is the energy input to the surface. Growth temperature (substrate temperature) is the basic source of energy input. A schematic representation of a CVD process is illustrated in Figure 1.3





Figure 1.3 Schematic diagram of the CVD process

A volatile precursor is transported to the substrate in the reactor by a carrier gas (1). At the substrate, the precursor sorbs (2) and reacts (3) to liberate the by products that subsequently desorbs (6) and transported out of the reactor (7). The target atoms then diffuse (4) to form nuclei of the materials (e.g. PtSe₂), where subsequent growth occurs (5).

1.4.3.1 Metal-organic Chemical Vapour Deposition (MOCVD)

One form of CVD, known as MOCVD, offers various advantages over the traditional process. The use of organometallic compounds means that lower temperatures can be used for the deposition process which saves time, energy and costs. MOCVD is a technique for growing solid films on a substrate by gas-phase and surface reactions; it is a relatively new process, pioneered in 1981 by Manasevit.²¹

MOCVD reactors are generally operated at intermediate pressures (e.g. 1-200 mbar) so that chemical reactions occur both in the gas phase and on, or close to, the substrate. MOCVD offers the potential for large area growth, and has the advantages of good composition control, high film uniformity, and good doping control and most importantly, it gives excellent conformational step coverage on non-planar device geometries. An essential requirement for a successful MOCVD process is the availability of precursors with the appropriate properties and decomposition characteristics. For an instance, the precursor must have an adequate temperature window between precursor evaporation and decomposition, and for many electronic applications.

MOCVD relies on the volatility of the precursor material, such that it would sublime into the vapour phase (without first decomposing) and then react over a heated substrate, decomposing to deposit a solid species, for example (equation 1.3), a metal sulphide thin film. The process proceeds under non-equilibrium conditions by generating chemically active species which induce the growth of the solid network. At the centre of this deposition process is the parent, or carrier gas containing the element(s) required as the film constituent(s).

 $Me_3In + H_2S \rightarrow In_xS_y + by$ -products eq. 1.3

The goal of modern MOCVD is to provide films with the following characteristics:

- Good thickness uniformity
- Controlled composition and stoichiometry
- High purity and density

- Good adhesion to substrate
- A high degree of structural perfection
- Good mechanical, optical and electrical properties

To achieve these goals, reactor design is important. In conventional MOCVD (atmospheric pressure), a carrier gas is bubbled through the liquid and /or solid precursors, and assuming that the compound exhibits its equilibrium vapour pressure, the precursors are carried into the reactor. The chemical reactions that occur in the gas phase determine the composition and structure of the solid film.

The MOCVD process offers a very flexible approach to the decomposition of metal oxide thin films, and has the advantage of rapid deposition for covering large areas of the substrate. In addition, stoichiometry, morphology, and even crystal structure and orientation can be tailored by controlling the deposition parameters. Also, since unlike other techniques, MOCVD does not require line of sight with the vapour source, it has excellent conformal step coverage at device dimensions over 2μ , which is particularly important in micro-electronic applications.

The principal disadvantages of conventional MOCVD are the nonavailability of suitable precursors with sufficient volatility and stability, as well as adequate purity and the need to obtain high vapour pressures of sometimes-hazardous precursors. It is also difficult to completely rule out the unwanted vapour phase reactions between the metal precursors and gases above the substrate, which presumably generate undesirably large mixed metal intermediates and oxide complexes. In conventional MOCVD the precursors are typically highly volatile materials such as metal alkyls, or

hydrides such as arsine or hydrogen selenide. These compounds have several disadvantages, the alkyls are highly pyrophoric, and the majority of the hydrides are gases of considerable toxicity. Therefore, there have been considerable efforts directed towards the development of alternate precursors for conventional MOCVD e.g. by forming adducts of the parent alkyls.

A number of modified MOCVD techniques have been used to overcome the problems associated with conventional MOCVD. However, MOCVD offers significant advantages over physical vapour deposition (PVD) method, in many aspects, simple apparatus, mild process conditions, control over composition (excellent composition control), high deposition rates (deposition capability), and possible large scale processing, film uniformity.²²⁻³⁶

LP-MOCVD is an attractive technique. In general, most reactions involving hazardous toxic vapour phase precursors are undertaken at reduced pressure from safety perspective. Additionally, the enhancement of kinetic steps often occurs at reduced pressure in the chemical deposition system.

General introduction to semiconductor thin films



Figure 1.4 Apparatus for Low pressure Metal Organic Chemical Vapour Deposition (LP-MOCVD)

This approach depends on the sublimation of the precursors with or without a carrier gas. If the vapour pressure of the precursor is high enough to rely on the carrier gas, for example, WF_6 has a vapour pressure of 1000 Torr at 25 °C, and thus the precursor can be used without carrier gas and feed rate limitations usually do not occur. A number of II/VI and III/VI semiconductor materials have been deposited using this technique.³⁷⁻⁶²

1.4.3.2 Aerosol-Assisted Chemical Vapour Deposition (AACVD)

In AACVD an aerosol is injected directly into a vapourising chamber where the precursor and solution evaporate. In contrast, LP-MOCVD and/or convectional CVD rely on the delivery of the precursor at its equilibrium vapour pressure at the source

temperature. In general, aerosol delivery systems are suitable techniques where the precursor is thermally sensitive and slowly decompose if heated for extended periods of time needed to elevate the vapour pressure. It is also a useful method for multicomponent systems as several precursors can be dissolved in the same solution and the relative delivery rates of precursors are defined by composition. The AACVD process is illustrated in Figure 1.5.



Figure 1.5 Schematic representation of the AACVD process

A single source precursor is dissolved in an organic solvent (1) and is converted into droplets by a piezoelectric modulator (2). The aerosol of precursor and solvent is the transported by a carrier gas into a hot zone where it evaporates. The vapour of the precursor is then transported to the substrate where it evaporates. The vapour of the precursor is then transported to the substrate where it adsorbs and reacts to form a film and by-products (3) and (4). AACVD is an example of a family of assisted CVD techniques, liquid injection CVD and spray pyrolysis.⁶³⁻⁸¹

1.4.4 Atomic layer deposition (ALD)

ALD is a modification of MOCVD, in which gaseous precursors are successively introduced to the substrate surface in a repeated cycle. Between the cycles, the volatile reaction products are flushed from the reactor by purging with an inert gas or by evacuation. ALD process has a self-limiting mechanism in which the growth surface becomes saturated with precursor or reactant molecules, so that film growth automatically stops (or `self-limits`) at one or sometimes two monolayer. Under these conditions the film growth rate becomes independent of the precursor pulse length. ALD relies on the surface exchange reactions between chemisorbed metal-containing precursor fragments and adsorbed nucleophilic reactant molecules. The surface-controlled growth in ALD leads to highly uniform coverage (or conformality) of planar substrates, as well as non-planar surface containing trenches or vias, and high surface area (high aspect ratio geometries) substrates such as silica and alumina powders. The precursor must have favourable stereochemistry for rapid reaction with adsorbed nucleophilic reactants, leading to a facile and clean elimination of its ligands. ⁸²⁻⁸⁴

1.4.5 Molecular beam epitaxy (MBE)

Molecular beam epitaxy (MBE) was developed in the early 1970s as a means of growing high-purity epitaxial layers of compound semiconductors. Since that time it has evolved into a popular technique for growing III-V compound semiconductors as well as several other materials. MBE can produce high-quality layers with very abrupt interfaces and good control of thickness, doping, and composition. Because of the high degree of control possible with MBE, it is a valuable tool in the development of

General introduction to semiconductor thin films

sophisticated electronic and optoelectronic devices. In MBE, the constituent elements of a semiconductor in the form of 'molecular beams' are deposited onto a heated crystalline substrate to form thin epitaxial layers. The 'molecular beams' are typically from thermally evaporated elemental sources, but other sources include metal-organic group III precursors metallorganic molecular beam epitaxy (MOMBE), gaseous group V hydride or organic precursors (gas-source MBE), or some combination (chemical beam epitaxy or CBE). ⁸⁵⁻⁹⁰ To obtain highpurity layers, it is critical that the material sources be extremely pure and that the entire process be done in an ultra-high vacuum environment. Another important feature is that growth rates are typically on the order of a few Å/s and the beams can be shuttered in a fraction of a second, allowing for nearly atomically abrupt transitions from one material to another.91-93

MBE is a method of laying down layers of materials with atomic thicknesses on to substrates. This is done by creating a 'molecular beam' of a material which impinges on to the substrate. The resulting 'super lattices' have a number of technologically important uses including quantum well lasers for semi conducting systems, and giant magneto-resistance for metallic systems.⁶²

1.5 Precursors for Semiconductor Thin Films

In the preparation of thin film semiconductor materials, a principal concern is the choice of precursor to deliver the necessary constituent atoms to the substrate. The precursor used for thin film deposition can be a solid, liquid, vapour or gas. In the transport step, the most important factor is uniformity over the substrate area.

The composition and microstructure of solid state materials determines their properties. The development of new, tuneable materials for technological demands requires flexible routes.

Basic requirements for compounds destined for materials science applications are purity, high yield synthetic routes, easy handling, facile storage and non-toxicity. Appropriate precursors should provide solubility or volatility which will determine the type of transformation, solution or in the vapour phase. Clean and low temperature decomposition pathways are desired for most applications. A stoichiometric matching of materials is then required if homogeneity is a goal. Materials are deposited from the gaseous state during CVD. Thus precursors for CVD processes must be volatile, but at the same time stable enough to make possible to be delivered to the reactor.

The deposition of electronic materials is an important and diverse area of contemporary research. Generally precursor compounds will only provide a single element to the deposited material, with others being volatilised during the CVD process. However, sometimes precursors may provide more than one. Such materials simplify the delivery system, as they reduce the number of reactants required to produce a given compound.

The 'precursor issues' are important for commercial and environmental reasons and include:

• The nature of the precursor: The most commonly used precursors were metal alkyls and/or main group hydrides, but such metal alkyls are often pyrophoric

and the hydrides are highly toxic. Such precursors therefore require special equipment to guard against safety and environmental hazards.

- The tendency for homogeneous reaction in the MOCVD apparatus: this so called pre-reaction causes snowing of the film that principally affects the morphology of the growing layer.
- The need, in many cases, for large imbalance in the mole ratios of the precursor materials. This is due to differences in volatility, thermal reactivity of the precursors, and selective desorption from the growing layer. Furthermore, the large excess of precursor exacerbates problems with waste.

Recently, it has been pointed out that the inorganic chemistry of the precursor (criteria for precursor materials) is important in the control of:

- Impurities, especially dopants in the final material, which may originate from the precursor.
- The phase of the final materials as determined by the decomposition temperature of the precursor.

• Contamination of the material with the products of homogeneous reaction within the reactor (homogeneous pre-reaction) of the precursors, e.g. 'snow' falling onto the substrate limiting morphology, this problem may in particular be limited by using single molecule precursor.

• Vapour pressure. Suitable precursors are needed for deposition of materials under low pressure conditions, LP-MOCVD. Many single molecule precursors have rather low pressures and may need an MOMBE or LP- MOCVD approach.

For a compound to be considered as a suitable MOCVD⁶³ precursor, certain properties should be adhered to.⁶³ These include:

• The precursor should be relatively easy to synthesise, and prepared with a good degree of reproducibility.

• Highly volatile at moderate sublimation temperatures (low decomposition temperature).

• A sufficiently large temperature window between evaporation and decomposition.

• Clean decomposition without the incorporation of residual impurities (able to decompose cleanly to yield volatile and non-toxic by products).

- Compatibility with other precursors in the system.
- Easily synthesized in high yield, purity, cost and have long shelf life.

Various modifications have been made to conventional MOCVD methodologies in attempts to overcome such challenges. The use of precursor that has both the metal and the chalcogen in a single molecule can overcome some of the above problems. The conventional CVD process requires volatile precursors, which evaporate and provide steady, reproducible transport rates in the reactor. Another requirement is for a clean thermal decomposition pathway that leads to the deposition of good quality films at high rates and low temperatures.²⁰

Many MOCVD reactions involving hazardous toxic vapour phase precursors are undertaken at low pressure partly for reasons of safety; kinetic steps may also be enhanced at low pressure; solid precursors can be sublimed with or without a carrier gas. The vapour pressure of the precursor may be high enough not to require a carrier

gas, for example, WF_6 (VP 1000 Torr at 25 °C) can be used without a carrier gas to grow thin films; feed rate limitations usually do not occur.

Typical Precursor Materials: CVD precursor materials fall into a number of categories such as:

- Halides TiCl₄, TaCl₅, WF₆.
- Hydrides SiH₄, GeH₄, AlH₃(NMe₃)₂, NH₃.
- Metal organic Compounds.
- Metal alkyls AlMe₃, Ti(CH₂tBu)₄.
- Metal alkoxides Ti(OⁱPr)₄.
- Metal dialylamides Ti(NMe₂)₄.
- Metal β -diketonates Cu(*acac*)₂.

Table 1.2: Some typical precursors for MOCVD

Туре	Examples	Typical properties
Metal alkyls	Me ₂ Zn, Me ₃ Ga	Pyrophoric liquid or low
		MP solid
Metal hydrides	MH_3L (M = Ga or Al)	Useful in specialised
		applications
Hydrides	H ₂ S, PH ₃ , NH ₃	Permanent gases, highly
		toxic
Alternative group V or VI	BuSH, As(NR ₂) ₃	Reduced toxicity, lower
· .		temperatures and no pre-
		reaction
Coordination Complex	$[M(acac)_n (M = Cu \text{ or } Co)]$	Oxide deposition
Single source	$[M(S_2CNR)_3]$ (R = alkyls)	Metal sulphide and
		photovoltaic applications.

1.6 Applications of semiconductor thin films

1.6.1. Microelectronics

There is a continual drive for miniaturisation of electronic systems in the microelectronic industry, in addition to ensuring long-term reliability and low production costs. Applications in the field of electronics and microelectronics for which thin films play a significant role include the film capacitors, diodes (p-n junctions), transistors and photoconductors. The most common II-VI materials used as photoconductors are CdS, CdSe. Lead chalcogenide thin films have long been used for thin film infrared detectors.⁶⁵ Copper indium diselenide is used in thin film form for photovoltaic solar energy conversion. Using this as the absorber layer and utilizing CdS along with ZnO as the window layer and hetero-junction patner, the solar conversion efficiency of the structure has attained more than 16 %.^{13, 66}

1.6.2. Optoelectronics

When the thermal equilibrium of a semiconductor is disturbed by the generation of electron and holes, recombination processes exist to restore the system to equilibrium. For direct band gap semiconductor, recombination can occur relatively with potentially high efficiency and forms the basis for a wide variety of photonic device applications. There are four basic groups that comprise photonic devices. Light emitting diodes (LEDs) and diode lasers (light amplification by stimulated emission of radiation) convert electrical energy to optical energy, whereas photo detectors and solar cells convert optical energy into an electrical output. Emission-based devices such as LEDs and injection lasers typically employ III-V compound semiconductors like GaAs as active elements.⁶⁷⁻⁶⁸

1.6.3 Other applications

CVD has applications across a wide range of industries such as coatings. Coatings for a variety of applications such as wear resistance, corrosion resistance, high temperature protection, erosion protection and combinations thereof. Thin films of magnetic materials have found extensive use in coating for commercial materials such as data storage in computers.⁶⁹

Preforms can be infiltrated using CVD techniques to produce ceramic matrix composites such as carbon-carbon, carbon-silicon carbide and silicon carbide-silicon carbide composites. This process is sometimes called chemical vapour infiltration (CVI).

There has been an improvement in optical data storage capabilities on computer memory and compact disks. Organic polymer materials are deposited as a storage medium. CVD can be used to produce components that are difficult or uneconomical to produce using conventional fabrication techniques. Dense parts produced via CVD are generally thin-walled and may be deposited onto a mandrel. Thin films properties and applications are summarised in Table 1.3.

Table 1.3 Thin films applications

Thin film property	Typical applications		
Optical	Reflective/antireflective coatings, interference filters,		
	decoration (colour, lustre), memory discs, wave guides.		
Electrical	Insulation, conduction, semiconductor devices, piezoelectric		
	drivers		
Magnetic	Memory disc		
Chemical	Barriers to diffusion or alloying, protection again oxidation		
	or corrosion, gas/liquid sensors		
Mechanical	Hardness, adhesion, micromechanics		
Thermal	Barrier layers, heat sinks		

Chapter 2

Deposition of Platinum, Palladium and

Nickel Chalcogenide Thin Films

2.1 General Introduction

The deposition of metal sulfide thin films has attracted considerable attention due to their use in many applications as discussed in chapter one. The platinum group metal chalcogenides are very useful in the electronics industry and they also have wide applications as catalysts in various industrial processes.⁷⁰⁻⁷⁴ Nakamoto ⁷⁵ and Kuriacose ⁷⁶ have reported the synthesis of thiocarbamato complexes of platinum and palladium from the reaction of an aqueous solution of ammonium dithiocarbamate with platinum or palladium salts. These complexes have been used as precursors for the preparation of the metal sulphide thin films. Revaprasadu, *et al.*⁷⁷ deposited PtS and PdS thin films from bis(n-hexyl(methyl)dithiocarbamato)platinum(II) and bis(n-hexyl(methyl)dithiocarbamato)palladium(II), respectively.

There have been many reports on the synthesis and coordination chemistry of dichalcogenoimidodiphosphinate ligands of the type $R_2P(E)NHP(E)R_2$, were E = O, S, Se, and the R = Et, ⁱPr, or ⁿBu.⁷⁸⁻⁹³ The coordination chemistry of these ligands are interesting as a consequence of the steric control that this ligand system may impart compared to, for example, acetylacetone (*acac*). They are readily prepared and offer an opportunity to vary both the donor atom and R group more easily than in the case of acetylacetone. Mixed donor imidodiphosphates can be easily prepared and show interesting structural differences using this ligand. Contrary to the complexes formed with *acac*, the ones with imidodiphosphinates show a variety of conformations of the six membered ring MEPNPE', where M = metal, and E, E'= chalcogenide.

Metal complexes of imidodiphosphinato ligands are of particular interest due to the flexibility of the E-P-N-P-E back bone and their large E...E "bite", allowing the formation of chelate rings and resulting in a symmetrical coordination pattern through the donor atoms. Transition metal complexes incorporating Woollins ligands {(iminobis(phosphinechalcogenide)} have demonstrated improved thermal and chemical stability over organic-based ligands such as β -diketone complexes, which are susceptible to oxidation, polymerisation and hydration. These metal complexes are excellent as single source precursors for chemical vapour deposition. The possibility of the selective coordination of metallic centres with imidodiphosphinate ligands through the manipulation of the R groups and the donor atoms E and E' play important roles in the deposition process. Dithiophosphinato complexes have found applications as solvent extraction reagents for metals, insecticides and pesticides, flotation agents for mineral ores, and additives to lubricant oils and can be used as a precursor for use in MOCVD. Metal complexes of the type $[M{N(EPR_2)_2}_2]$, where M = Ni, Pt, Pd, Sb, Zn, Hg, In, Ga, Pb, Cd, Co; R = Et, ⁱPr, Ph, ⁿBu; and E = S, Se or O have been prepared. 94-105

2.2 Experimental

2.2.1 Reagents

The following chemicals were used during this study without further purification: potassium tetrachloroplatinate(II) (95 %, Aldrich), potassium tetrachloropalladate (II) (95 %, Aldrich), nickel(II) chloride hexahydrate (Aldrich), chlorodiisopropyl alcohol (96%,Aldrich),chlorodiphenylphosphine(96%,Aldrich),1,1,1,3,3,3-hexamethyldisilazane (99,9 %, Aldrich), selenium powder (99.5+ %, Aldrich), sulfur

powder (Aldrich), petroleum ether (BDH), methanol (99 %, BDH), ethanol (BDH), tetrahydrofuran (99 %, BDH), sodium methoxide (95 %, Aldrich), carbon disulfide (Aldrich).

2.2.2 Synthesis of ligands

2.2.2.1 Synthesis of NH(SePⁱPr₂)₂

The synthetic method is based on a literature procedure for preparing related compounds.⁷⁹ The reaction was performed under nitrogen using standard Schlenk line techniques. A solution of ⁱPr₂PCl (4.87 g, 5.0 mL, 32 mmol) in toluene (100 mL) was added drop wise to a solution of NH(SiMe₃)₂ (2.58 g, 3.4 mL, 16 mmol) in hot (50-60 °C) toluene (50 mL) over 30 min. Heating and stirring was continued for 3 h after which time the reaction was cooled to room temperature and the selenium powder was added (2.53 g, 31 mmol). The reaction was then refluxed for a further 6 h and cooled to 0 °C. The resulting white precipitate was filtered off. Excess selenium was removed by dissolving the product in CH₂Cl₂ and filtering through celite, followed by the removal of solvent *in vacuo*. The crude product was recrystallized from CH₂Cl₂ and hexane (2:3 ratio) to give 4.25 g, 10.47 mmol, and 65 % yield of pure compound. Mp: 170 °C. Anal. Calcd for C₁₂H₂₉NP₂Se₂: C, 35.38; H, 7.13; N, 3.44. Found: C, 35.49; H, 7.45; N, 3.42. FT-IR (KBr disc): v(N-H) 3211(s); δ (N-H) 1385(m); v (PNP) 878(s); v(PSe) 489 cm⁻¹. ¹H NMR (CDCl₃): 1.3 ppm (24 H, CH₃); 2.3 (4 H, CH); 7.1 (1H, NH). MS: m/z = 408 corresponds to [M + H]⁺.

2.2.2.2 Synthesis of NH(SPⁱPr₂)₂

A solution of NH(PⁱPr₂)₂ was prepared as described under section **2.2.2.1** Heating and stirring were continued for 3 h after which time the reaction was cooled to room temperature and sulfur powder added (1.0 g, 31 mmol). The reaction was then refluxed for further 6 h and cooled to 0 °C. The resulting white precipitate was filtered off and washed with CS₂ (2 x 10 mL) and light petroleum ether (2 x 10 mL). The crude product was recrystallised from CH₂Cl₂/hexane in 3:2 ratio. Yield: 0.17 g, 34 %. Mp: 165 °C. Anal. Calcd for C₁₂H₂₉NP₂S₂: C, 46.01; H, 9.27; N, 4.47; S, 20.45. Found: C, 45.79; H, 9.65; N, 4.54; S, 19.82. FT-IR (KBr disc): v(N-H) 3243(s); δ (N-H) 1386(m); v(PNP) 879(s); v(PSe) 476 cm⁻¹. ¹H NMR (CDCl₃): 1.2 ppm (24 H, CH₃); 2.4 (4 H, CH); 7.2 (1H, NH). MS: m/z = 314 corresponding to [NH(SPⁱPr₂)₂]⁺ with the expected isotopic distribution patterns.

2.2.2.3 Synthesis of NH(SePPh₂)₂

The compound NH(PPh₂)₂ (7.70 g, 20 mmol) and grey selenium (3.16 g, 40 mmol) were heated to reflux in sodium-dried toluene (150 mL) under nitrogen for 4 h. After cooling the solution the white precipitate was filtered off, washed with toluene (3 x 15 mL) and diethyl ether (3 x 15 mL) and dried *in vacuo*. Yield: 9.1 g, 84 %. Mp: 210 °C. Anal. Calcd for C₂₄H₂₁NP₂Se₂: C, 53.06; H, 3.90; N, 2.60. Found: C, 52.53; H, 3.80; N, 2.49. FT-IR (KBr disc): v(PNP) 922(s); v(PSe) 593(m), 545(m) cm⁻¹. MS: m/z = 544 corresponds to [NH(SePPh₂)₂]⁺.

2.2.2.4 Synthesis of NH(SPPh₂)₂

A solution of $(Ph_2)_2PCl$, (4.87 g, 5.1 mL, 27 mmol) in toluene (100 mL) was added drop wise to a solution of NH(SiMe₃)₂, (2.58 g, 3.4 mL, 13.5 mmol) in hot (50-60 °C) toluene (50 mL) over 30 min. Heating and stirring were continued for 3 h after which time the reaction mixture was cooled to room temperature and the selenium powder was added (2.53 g, 31 mmol). The reaction was then refluxed for further 6 h and cooled to 0 °C. A white precipitate was obtained which was then filtered off, washed with toluene (3 x 15 mL) and diethyl ether (3 x 15 mL) and dried *in vacuo*. Yield: 5.2 g, 86 %. Mp: 218-220 °C. Anal. Calcd for $C_{24}H_{21}NP_2S_2$: C, 64.13; H, 4.71; N, 3.12. Found: C, 62.89; H, 4.87; N, 3.48. FT-IR (KBr disc): v(PNP) 919(vs); v(PS) 649(s), 626(w) cm⁻¹. MS: m/z = 448 corresponds to [NH(SPPh_2)_2]⁺.

2.2.3 Synthesis of precursors

2.2.3.1 Synthesis of [Pt{N(SePⁱPr₂)₂}₂]

An aqueous solution of K₂PtCl₄ (0.10 g, 0.25 mmol, 10 mL) was added to a yellow solution of NH(SePⁱPr₂)₂ (0.2 g, 0.49 mmol) and CH₃ONa (0.027 g, 0.49 mmol) in methanol (30 mL). A yellow precipitate began to form after five minutes. The mixture was stirred for a further 30 min and the product, a yellow solid, was collected by filtration. The crude product was recrystallized from dichloromethane to give 0.09 g, (40 % yield) of the product. Mp: 138 °C. Anal. Calcd for C₂₄H₅₆N₂P₄PtSe₄: C, 28.61; H, 5.60; N, 2.78; P, 12.30. Found: C, 31.24; H, 6.38; N, 2.98; P, 12.33. FT-IR (KBr disc): v(PNP) 1181(s); v(PSe) 476(m); (NPSe) 412 cm⁻¹. ¹H NMR (CDCl₃): 1.2 ppm (48 H, CH₃); 7.2 ppm (1H, NH). MS: m/z = 1008 corresponding to $[Pt\{N(^{i}Pr_2PSe)_2\}_2]^+$

2.2.3.2 Synthesis of [Pt{N(SPⁱPr₂)₂}₂]

CH₃ONa (0.01 g, 0.16 mmol) and NH(SPⁱPr₂)₂ (0.05 g, 0.16 mmol) in methanol (30 mL) was added to an aqueous solution of K_2 PtCl₄ (0.03 g, 0.08 mmol, 10 mL). The solution was refluxed for 2 h giving a yellow solution. The solvent was removed in *vacuo* and the yellow solid crude product was recrystallised from acetone.

Yield: 0.032 g, 49 %. Mp: 169 °C. Anal. Calcd for $C_{24}H_{56}N_2P_4PtS_4$: C, 36.16; H, 6.88; N, 3.42. Found: C, 37.60; H, 7.15; N, 3.39. FT-IR (KBr disc): v (PNP) 1222(s); v (PS) 628(m); v (NPS) 413 cm⁻¹. ¹H NMR (CDCl₃): 1.2 ppm (48 H, CH₃); 2.3 ppm (8H, CH); 7.2 ppm (1H, NH). MS: m/z = 819 corresponding to [Pt{N(SPⁱPr₂)₂}₂].

2.2.3.3 Synthesis of [Pd{N(SePⁱPr₂)₂}₂]

An aqueous solution of K₂PdCl₄ (0.08 g, 0.25 mmol, 10 mL) was added to a yellow solution of NH(SePⁱPr₂)₂ (0.2 g, 0.49 mmol) and CH₃ONa (0.0266 g, 0.492 mmol) in methanol (30 mL). The resulting blood red solution was stirred and then the solvent was removed *in vacuo* to give red solid product. The product was extracted from dichloromethane yielding 0.12 g, 0.13 mmol, 58 % of pure compound. Mp: 186 °C. Anal.Calcd for C₂₄H₅₆N₂P₄PdSe₄: C, 31.37; H, 6.14; N, 3.05; P, 13.48. Found: C, 31.50; H, 6.34; N, 2.98; P, 13.55. FT-IR (KBr disc): v (PNP) 1182(s); v (PSe) 476(m); v (NPSe) 412 cm⁻¹. ¹H NMR (CDCl₃): 1.3 ppm (48 H, CH₃); 2.6 ppm(8H, CH); 7.2 ppm (1H, NH). MS: m/z = 918 corresponds to [Pd{N(ⁱPr₂PSe)₂}₂].

2.2.3.4 Synthesis of [Pd{N(SPⁱPr₂)₂}₂]

Deprotonation of NH(SPⁱPr₂)₂ (0.05 g, 0.16 mmol) with CH₃ONa (0.00865 g, 0.16 mmol) in methanol (30 mL) to give Na[N(ⁱPr₂PS)₂] was followed by addition of an aqueous solution of K₂PtCl₄ (0.03 g, 0.08 mmol, 10 mL). The solution turned from yellow to red/orange immediately. The mixture was stirred for further 30 min and the solvent was removed *in vacuo* and the solid product was recrystallised from acetone. Yield: 0.035 g, 59 %. Mp: 164 °C. Anal. Calcd for C₂₄H₅₆N₂P₄PdS₄: C, 39.42; H, 7.72; N, 3.83. Found: C, 39.71; H, 7.74; N, 3.73. FT-IR (KBr disc): v(PNP) 1200(s); v(PS) 543(m); (NPS) 420 cm⁻¹. ¹H NMR (CDCl₃): 1.3 ppm (48 H, CH₃); 2.3 ppm (8H, CH); 7.2 ppm (1H, NH). MS: m/z = 731 corresponds to [Pd{N(SPⁱPr₂)₂}₂].

2.2.3.5 Synthesis of [Pd{N(SePPh₂)₂}₂]

An aqueous solution of K₂PdCl₄ (0.03 g, 0.092 mmol, 10 mL) was added to a yellow solution of NH(SePPh₂)₂ (0.1 g, 0.18 mmol) and CH₃ONa (0.01 g, 0.16 mmol) in acetone (10 mL). The solution turned red immediately and then turned orange. The reaction mixture was stirred 1 h at room temperature and the solvent was removed *in vacuo*. The solid crude product was recrystallised from CH₂Cl₂ and dried under vacuum. The red filtrate was allowed to evaporate to give a pure red product. Yield: 0.09 g, 83 %. Mp: 270 °C. Anal. Calcd for C₄₈H₄₀N₂P₄PdSe₄: C, 48.40; H, 3.39; N, 2.35. Found: C, 48.60; H, 3.15; N, 2.29. FT-IR (KBr disc): v (PNP) 1153(m), 804; v(PSe) 537(vs) cm⁻¹. MS: m/z = 544 correspond to [NH(SePPh₂)₂]⁺ and 1192 corresponds to [Pd{N(SePPh₂)₂}]⁺.

2.2.3.6 Synthesis of [Pt{N(SePPh₂)₂}₂]

An aqueous solution of K₂PtCl₄ (0.04 g, 0.09 mmol, 10 mL) was added to a yellowish solution of NH(SePPh₂)₂ (0.1 g, 0.18 mmol) and CH₃ONa (0.01 g, 0.18 mmol) in acetone (10 mL) under nitrogen to give an intense yellow solution. A yellow precipitate begins to be formed. The mixture was stirred for 1 h. The precipitate was filtered off and then recrystallised from acetone. Yield: 0.1 g; 87 %. Mp: 210 °C. Anal. Calcd for C₄₈H₄₀N₂P₄PtSe₄: C, 45.05; H, 3.15; N, 2.19. Found: C, 46.86; H, 2.77; N, 2.12. FT-IR (KBr disc): v (PNP) 1174(s), 803(s); v (PSe) 545 (vs) cm⁻¹. MS: m/z = 544 corresponds to [NH(SePPh₂)₂]⁺ and 1280 corresponds to [Pt{N(SePPh₂)₂}₂]⁺.

2.2.3.7 Synthesis of [Pd{N(SPPh₂)₂}₂]

An aqueous solution of K₂PdCl₄ (0.036 g, 0.111 mmol, 10 mL) was added to a solution of NH(SPPh₂)₂ (0.1 g, 0.22 mmol) and CH₃ONa (0.012 g, 0.22 mmol) in acetone (10 mL). The solution turns orange immediately and the reaction mixture was stirred for 1 h. The solvent was removed *in vacuo* and the solid crude product was recrystallised from CH₂Cl₂. The orange filtrate was evaporated by vacuum line to give a pure product. Yield: 0.1g, 90 %. Mp: 310 °C. Anal. Calcd for C₄₈H₄₀N₂P₄PdS₄: C, 57.45; H, 4.02; N, 2.79. Found: C, 57.80; H, 3.66; N, 2.67. FT-IR (KBr disc): v (PNP) 1157(m), 805(s); v (PS) 536(m) cm⁻¹. MS: m/z = Molecular ions peaks [Pd{N(SPPh₂)₂}]⁺ at 1002 and [N(SPPh₂)₂]⁺ at 448 revealed the expected, characteristic, isotopic distribution patterns.

2.2.3.8 Synthesis of [Pt{N(SPPh₂)₂}₂]

An aqueous solution of K₂PtCl₄ (0.038 g, 0.09 mmol, 10 mL) was added to a solution of NH(SPPh₂)₂ (0.1 g, 0.18 mmol) and CH₃ONa (0.01 g, 0.18 mmol) in acetone (10 mL). The solution was stirred for 14 h under nitrogen to give an intense yellow solution. The product was filtered, washed with distilled water (10 mL) and methanol (10 mL). Yield: 0.08 g, 67 %. Mp: 205 °C. Anal. Calcd for C₄₈H₄₀N₂P₄PtS₄: C, 52.79; H, 3.69; N, 2.57. Found: C, 56.05; H, 3.77; N, 2.68. FT-IR (KBr disc): v (PNP) 1109 (m); v (PS) 562(m) cm⁻¹. MS: m/z = Molecular ions peaks [Pt{N(SPPh₂)₂}₂]²⁺ at 1091 and [N(SPPh₂)₂]⁺ at 448 revealed the expected, characteristic, isotopic distribution patterns.

2.2.3.9 Synthesis of [Ni{N(SePⁱPr₂)₂}₂]

An aqueous solution of NiCl₂.6H₂O (0.0292 g, 0.122 mmol, 10 mL) was added to a yellow solution of NH(SePⁱPr₂)₂ (0.1 g, 0.245 mmol) and CH₃ONa (0.0133 g, 0.245 mmol) in methanol (20 mL). A brown precipitate began to form after five minutes. The mixture was stirred at room temperature for a further 30 min and the product, a brown solid, was collected by filtration. The crude product was washed three times with methanol (3 x 10 mL). Yield: 0.091 g, 83 %. Mp: 138 °C. Anal. Calcd for $C_{24}H_{56}N_2P_4PNiSe_4$: C, 33.09; H, 6.48; N, 3.22. Found: C, 29.06; H, 5.68; N, 2.79. FT-IR (KBr disc): v (PNP) 1178(s); v (PSe) 480(m); (NPSe) 416 cm⁻¹. MS: m/z = 871 corresponds to [Ni {N(SePⁱPr₂)₂}] and 407 corresponds to NH(SePⁱPr₂)₂.

2.2.3.10 Synthesis of [Ni{N(SPⁱPr₂)₂}₂]

An aqueous solution of NiCl₂.6H₂O (0.1 g, 0.319 mmol, 10 mL) was added to a yellow solution of NH(SPⁱPr₂)₂ (0.0379 g, 0.159 mmol) and CH₃ONa (0.018 g, 0.319 mmol) in methanol (20 mL). A green precipitate began to form after five minutes. The mixture was stirred at room temperature for a further 30 min and the product, a green solid, was collected by vacuum filtration. The crude product was washed three times with methanol (3 x 10 mL). Yield: 0.183 g, 84 %. MP = 125 °C. Anal. Calcd for C₂₄H₅₆N₂P₄NiS₄: C, 42.17; H, 8.26; N, 4.60. Found: C, 42.03; H, 8.29; N, 4.03. FT-IR (KBr disc): v (PNP) 1208(s); v (PSe) 646(m); (NPS) 425 cm⁻¹. MS: m/z = 683 corresponds to [Ni {N(SPⁱPr₂)₂}₂].

2.2.3.11 Synthesis of [Ni{N(SPPh₂)₂}₂]

A methanolic solution of NiCl₂.6H₂O (0.265 g, 0.111 mmol, 10 mL) was added to a solution of NH(SPPh₂)₂ (0.1 g, 0.222 mmol) and CH₃ONa (0.0120 g, 0.111 mmol) in methanol (10 mL). The solution was stirred at room temperature overnight. The product was filtered, washed three times with methanol (3 x 10 mL). Yield: 0.071 g, 67 %. Anal. Calcd for C₄₈H₄₀N₂P₄NiS₄: C, 60.32; H, 4.22; N, 2.93. Found: C, 60.44; H, 4.27; N, 2.88. FT-IR (KBr disc): v (PNP) 1152 (s); v (PS) 808(m); 540(m) cm⁻¹. MS: m/z = 449 corresponds to [N(SPPh₂)₂]⁺ ligands.

2.2.3.12 Synthesis of [Ni{N(SePPh₂)₂}₂]

A methanolic solution of NiCl₂.6H₂O (0.0876 g, 0.368 mmol, 10 mL) was added to a solution of NH(SePPh₂)₂ (0.4 g, 0.736 mmol) and CH₃ONa (0.0397 g, 0.73 mmol) in acetone (10 mL). The solution was stirred at room temperature for 14 h under

nitrogen. The product was filtered, washed with distilled water (10 mL) followed by three times with methanol (3 x 10 mL). Yield: 0.351 g, 83 %. Anal. Calcd. for $C_{48}H_{40}N_2P_4NiSe_4$: C, 50.43; H, 3.53; N, 2.45. Found: C, 50.47; H, 3.55; N, 2.42. FT-IR (KBr disc): v(PNP) 1190 (s); v(PS) 806(m); 527(vs) cm⁻¹.

2.3 Thin film deposition by CVD

2.3.1 Deposition techniques

A standard method was adopted for the cleaning of the substrates prior to the CVD process in order to achieve reproducible results. The following procedure was used to clean conventional microscopic slides:

- Substrate (glass) were immersed in 50 % nitric acid overnight.
- This was followed by rinsing the substrates in deionised water.
- The substrates were then placed in the micro-oven for drying at 150 °C for 1 h.

Growth of thin films by AACVD: The precursor was dissolved in toluene with the average amount utilised being 0.2 g in 30 mL of toluene. The solution was placed in a two necked 100 mL flask with a gas inlet that allowed nitrogen to pass into the solution (to aid transport of aerosol). The tube held a number of glass substrate that were distributed along the length of these and they were heated in a carbolite furnace to the temperature prior to deposition. An aerosol was then generated by the piezoelectric modulator of an ultrasonic humidifier and nitrogen gas passed through the aerosol mist, directing the aerosol to the CVD reactor. A Platon flow gauge was used to control the flow rate of 200 sccm, enabling controlled delivery of aerosol droplets into the deposition chamber. The aerosol was then allowed to flow over the substrate for a specified time.

Preparation of thin films by LP-MOCVD: Film deposition experiments were conducted in a cold-wall and low pressure MOCVD reactor, equipped with a graphite susceptor heated by a 1 kW tungsten-halogen lamp and with a water-cooled reflector. For each run, the reactor was loaded with a *ca.* 200 mg of the precursor and then evacuated (0.05 Torr) with a rotary evaporator, *via* a liquid nitrogen trap. A Carbolite tube furnace was used to transport the precursor (0.2 g) under vacuum. The substrate was placed on the suspector, the temperature of the suspector varied between 200-600 °C and the running time varied between 1 h and 2 h. To start a deposition run the loaded reactor was glass.

2.3.2 Instrumentation and physical measurements

2.3.2.1 Elemental analysis

Elemental analysis was conducted at the Microanalytical laboratories at the University of Manchester, UK.

2.3.2.2 Thermogravimetric analysis (TGA)

TGA measurements were carried on a Seiko SSC/S200 model under nitrogen atmosphere (flow rate 20 mL/min), from 25 to 500 °C, with a heating rate of 10 °C/min.

2.3.2.3 Infrared spectra

Infrared spectra were recorded using a Perkin Elmer Paragon 1000 FT-IR (4000-400 cm^{-1} , resolution $\pm 4 \text{ cm}^{-1}$). Samples were prepared as KBr pellets.

2.3.2.4 NMR spectroscopy

NMR studies (¹H and ¹³C) were carried out using a Bruker AC300 FTNMR spectrometer, using CDCl₃ or DMSO as solvents.

2.3.2.5 Mass Spectroscopy

Mass spectra were recorded on a Kratos concept 1S instrument.

2.3.2.6 X-ray diffraction (XRD)

X-ray diffraction studies were performed using secondary graphite monochromated Cu Ka radiation (40 kV) on either a Philips X'Pert Materials Diffractometer (APD) or Bruker AXS D8 diffractometer. Measurements were taken using a glancing angle incidence detector at an angle of 3 °, for 20 values over 10-95 ° in steps of 0.04° with a count time of 2 s. The scans were done over 2 θ values of 5-90° and a step size of 0.01° or 0.02°.

2.3.2.7 Scanning electron microscopy (SEM)

Films were carbon coated using Edward's E306A coating system before SEM analysis. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) for films deposited in the earlier part of this study were carried out on a Phillips 525 SEM instrument with an EDAX 9100 EDS unit. Prior to characterisation, samples were either carbon coated (using an Edwards coating system E 306A) to allow EDAX analysis or otherwise gold coated (Edwards sputter coater S150B).

2.4 Results and discussions

The ¹H NMR spectra, mass spectra, and microanalysis were satisfactory for all compounds. The synthesis of ligands NH(EPR₂)₂, (where E = S, Se, and the $R = {}^{i}Pr$, Ph₂) were carried out according to previously reported methods. The synthesis of the precursors involves the deprotonation of the N-H moiety, using sodium methoxide to form anionic species which subsequently reacted with the metal salt to form the complexes. The compounds prepared were found to be ideal for use as single source precursors; they are air stable and readily obtained in good synthetic yields.

2.4.1 Infrared

The solid-state (KBr pellets) IR spectra of the complexes were also examined and the bands for the v(P-S) or v(P-Se) and v(P-N-P) stretching vibrations were assigned. The v(NH) band is observed around 3000 cm⁻¹ for all compounds. Characteristic v(PNP) bands were also observed at 800-930 cm⁻¹. Characteristic bands were observed, indicating the change in bond order that occured upon removal of the amine proton, in particular the marked increase in the frequency of the v(PNP) vibration to 1100-1200 as the negative charge is delocalised over the ligand. As observed in related systems there is an increase in the frequency of v(PNP) vibration in the complexes compared with the free ligand.
Table 2.1	Infrared spe	ctra (cm ⁻¹) of	f the ligands

	[NH(EP ⁱ Pi	[NH(EP ⁱ Pr ₂) ₂]		[NH(EPPh ₂) ₂]	
	$\overline{\mathbf{E}} = \overline{\mathbf{S}}$	$\overline{E} = Se$	$\overline{\mathbf{E}} = \mathbf{S}$	$\overline{E} = Se$	
v(N-H)	3243 (s)	3211(s)	3051(s)	3468 (s)	
δ(N-H)	1386 (m)	1385(m)	1323 (s)	1436 (s)	
v(PNP)	879 (s)	878(s)	919 (vs)	922 (s)	
υ(P-E)	476 (s)	489 (m)	649 (s)	593(m)	

Table 2.2 Infrared spectra (cm^{-1}) for the precursors

Compound formula	v(PNP)	v(PE)	υ(NPE)
1. $[Pt{N(SeP'Pr_2)_2}_2]$	1181(s)	476(m)	412
2. [Pt{N(SP ⁱ Pr ₂) ₂ } ₂]	1222(s)	628(m)	413
3. $[Pd{N(SeP^{i}Pr_{2})_{2}}_{2}]$	1182(s)	476(m)	412
4. $[Pd{N(SP^{i}Pr_{2})_{2}}_{2}]$	1200(s)	543(m)	420
5. $[Pt{N(SePPh_2)_2}_2]$	1174(s)	803(s)	545(vs)
6. [Pt{N(SPPh ₂) ₂ } ₂]	1109(m)	562(m)	540
7. [Pd{N(SePPh ₂) ₂ } ₂]	1153(m)	804(m)	537(vs)
8. [Pd{N(SPPh ₂) ₂ } ₂]	1157(m)	805(s)	536(m)
9. [Ni{N(SeP ⁱ Pr ₂) ₂ } ₂]	1178(s)	480(m)	416(m)
10. [Ni{N(SP ⁱ Pr ₂) ₂ } ₂]	1208(s)	646(m)	425(m)
11. [Ni{N(SePPh ₂) ₂ } ₂]	1190(s)	806(m)	527(vs)
12. [Ni{N(SPPh ₂) ₂ } ₂]	1152(s)	808(m)	540(m)



There is closeness in results for the v(P-S) vibration in all complexes. Furthermore, it has been observed⁷⁹, in related systems, that there is a marked increase in the frequency of the v(PNP) vibration of the compound compared to the free ligand. The deprotonation of the ligand on complexation leads to the loss of the (N-H) band in the IR spectra.

2.4.2 Single crystal X-ray structure analysis of [Pt{N(SeⁱPr₂)₂}₂]

Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into dichloro-methane solutions of the precursor. Data were collected at 100(2) K using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) by the Bruker APEX diffractometer. Details of data collection and structure refinements are presented in Table 2.3.

All X-ray measurements were made at room temperature using suitable crystals for data collection. All calculations were carried out using SHELXTL package. All non-hydrogen atoms were refined with isotropic atomic displacement parameters. Hydrogen atoms were placed in calculated positions, assigned anisotropic thermal parameters and allowed to ride on their parent carbon atoms. The structure is isomorphous with the selenium analogue. Accurate lattice parameters were determined from least squares refinement of well centered reflection in the range 2.03 $\leq \Theta \leq 28.27$. During dot collection three standard reflections were periodically observed and show no significant intensity variations. The range of h, k, and l are $-6\leq h \leq 13$, $-19 \leq k \leq 19$; $-15 \leq l \leq 13$. Total numbers of measured and observed independent reflection are 10821 and 4077 (R_{int} = 0.0410). The final R and R_w values are given in the Table 2.3. The ORTEP representation of the complex is illustrated in Figure 2.1.

The selected intra and intermolecular bond lengths and angles for the complex are summarised in Table 2.4. The crystal system is monoclinic with the space group of P2(1)/C.

The X-ray crystal structure has been previously reported but the method used here is different from the literature. The PtSe₂P₂N ring of the previously reported⁷⁹ structure adopts a pseudo-chair confirmation whereas the recent structure reveals square-planar structure where the six membered PtSe₂P₂N ring adopts a distorted "boat" conformation. The crystal structure cores are similar to those reported in the literature.⁷⁹ The platinum complex structure reveals that the complex consists of square-planar metal centre with two chelating ligands. When compared with the free ligand, the P-S bond is lengthened and the P-N bonds are shortened, consistent with some electron delocalisation around the rings. This suggests that some π delocalisation occurs upon deprotonation and chelate formation. The six membered rings PtSe₂P₂N of the recent structure adopt a linear pseudo chair conformation. The conformational differences of the PtSe₂P₂N rings do not appear to have dramatic effects on the bond lengths, although there are a number of noticeable angular changes. Thus, whilst Se(1)-Pt-Se(2) is 90°, the equivalent angle is enlarged to 101° in the reported literature. The Se atoms are arranged in a linear tetrahedron with the Se-Pt-Se angles varying from 180 and 90°. The P(1)-N(1)-P(2) angle is also significantly reduced than the reported literature,⁷⁹ from 138 to 127°. The packing diagram shows a sandwich structure, which further confirms 1(metal):2 (ligand) ratios (Figure 2.2).

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Figure 2.1 Single X-ray structure of $[Pt{N(Se^{i}Pr_{2})_{2}}_{2}]$



Figure 2.2 Packing diagram of [Pt{N(SeⁱPr₂)₂}₂]

<u></u>	1
Empirical formula	$C_{24}H_{56}N_2P_4PtSe_4$
Formula weight	1007.52
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal System, space group	Monoclinic, P2(1)/C
Unit cell dimensions	$a = 10.2460(11) A \alpha = 90^{\circ}$
	$b = 8.765(3) \text{ A} \beta = 101.34(6)^{\circ}$
	$c = 11.8990(12) A \gamma = 90^{\circ}$
Volume	1737.7(3) A ³
Z, Calculated density	2, 1.926 mg/m^3
Absorption coefficient	8.428 mm^{-1}
F(000)	976
Crystal size	0.20 x 0.15 x 0.05 mm
Theta range for data collection	2.03 to 28.27 deg
Limiting indices	-6 < = h < = 13, -19 < = k < = 19, -15 < = 1 < 1 < = 13
Reflections collected/unique	10821/4077 [R(int) = 0.0410]
Completeness to theta = 26.41	94.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6780 and 0.2835
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4077/18/168
Goodness-of-fit on F ²	1.047
Final R indices [I > 2 sigma (I)	R1 = 0.0640, wR2 = 0.1819
R indices (all data)	R1 = 0.0729, wR2 = 0.1870
Largest diff. peak and hole	3.535 and -5.751 e.A ⁻³

Table 2.3 Crystal data and structural refinement details for [Pt{N(SeⁱPr₂)₂}₂]

	<u>.</u>	2	
 Pt(1) - Se(1)	2.5231(10)	Se(1) - Pt(1) - Se(1)	180.0
Pt(1) - Se(2)	2.5323(10)	Se(1) - Pt(1) - Se(2)	90.06(3)
P(1) - Se(1)	2.187(2)	P(1) - Se(1) - Pt(1)	94.62(7)
P(2) - Se(2)	2.195(2)	P(2) - Se(2) - Pt(1)	100.04(7)
N(1) – P(1)	1.592(8)	N(1) - P(1) - Se(1)	116.7(3)
N(1) – P(2)	1.592(8)	N(1) - P(2) - Se(2)	119.2(3)
		P(2) - N(1) - P(1)	138.0(5)

Table 2.4 Selected bond length (Å) and angles (deg) for [Pt{N(SeⁱPr₂)₂]₂]

2.4.3 Single crystal X-ray structure analysis of [Pd{N(SPh₂)₂}₂]

Crystals suitable for X-ray diffraction studies were obtained by dissolving the complex in hot dimethylsulfoxide (DMSO). Crystal were formed immediately on cooling and filtered to separate them from DMSO. Data were collected at 293(2) K using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) on Bruker APEX diffractometer. Details of data collection and structure refinements are shown in Table 2.5.

This structure was solved by direct methods using SHELXL-93 [31] and refined by full-matrix least-squares on F^2 . X-ray crystallography studies revealed that the complex is tetrahedrally coordinated by two ligands through sulfur atoms of the ligand, as shown in Figure 2.3. The compound consists of discrete, monomeric molecules in which the ligands are found to be bidentate, conferring distorted tetrahedral coordination geometry around the palladium centres. Selected inter atomic distances and angles are summarised in Table 2.6.

Non-hydrogen atoms were refined isotropically and hydrogens were included in fixed positions. However, the P—S bonds in the complex are significantly longer than those of the free ligand, while the P—N bonds are significantly shorter. This suggests that some p-delocalisation occurs upon deprotonation and chelate formation. Despite this, the conformation of the PdS_2P_2N rings in the compound (Figure 2.3) adopts a puckered, pseudo boat geometry, with sulfur and phosphorus atoms at the apices. The resulting PdS_2P_2N chromophores are found to be puckered. The bond lengths and angles are in good agreement with the previously reported literature even though the methods for preparation are different.⁹⁶ The packing diagram of $[Pd\{N(SPh_2)_2\}_2]$ is shown in Figure 2.4.



Figure 2.3 Single X-ray structure of $[Pd{N(SPh_2)_2}_2]$



Figure 2.4 Packing diagram of $[Pd{N(SPh_2)_2}_2]$

Table 2.5 Crystal data and structural refinement details for $[Pd{N(SPh_2)_2}_2]$

	2
Empirical formula	$C_{48}H_{40}N_2P_4PdS_4$
Formula weight	1003.34
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal System, space group	Monoclinic, C2/C
Unit cell dimensions	$a = 25.031(10) A \alpha = 90^{\circ}$
	$b = 8.765(3) A \beta = 114.36(6)^{\circ}$
	$c = 22.325(8) A \gamma = 90^{\circ}$
Volume	4462(3) A ³
Z, Calculated density	4, 1.494 mg/m^3
Absorption coefficient	0.784 mm^{-1}
F(000)	2048 *
Crystal size	0.40 x 0.15 x 0.15 mm
Theta range for data collection	1.79 to 26.41 deg
Limiting indices	-31 < = h < = 31, -10 < = k < =10, -27 < =1 < 1 < = 27
Reflections collected/unique	16060/4556 [R(int) = 0.0287]
Completeness to theta $= 26.41$	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8915 and 0.7445
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4556/726/392
Goodness-of-fit on F ²	1.021
Final R indices [I > 2 sigma (I)	R1 = 0.0324, wR2 = 0.0771
R indices (all data)	R1 = 0.0417, $wR2 = 0.0820$
Largest diff. peak and hole	$0.637 \text{ and } -0.490 \text{ e.A}^{-3}$

		1	
Pd(1) - S(1)	2.3417(8)	S(1) - Pd(1) - S(1)	180.0
Pd(1) - S(2)	2.3278(9)	S(2) - Pd(1) -S(1)	80.93(3)
S(1) - P(1)	2.0241(11)	P(1) - S(1) - Pd(1)	98.46(4)
S(2) – P(2)	2.0265(12)	P(2) - S(2) - Pd(1)	108.26(16)
P(1) – N(1)	1.601(2)	N(1) - P(1) - S(1)	115.96(9)
P(2) – N(1)	1.596(2)	N(1) - P(2) - S(2)	117.72(8)
		P(2) - N(1) - P(1)	121.48(14)

Table 2.6 Selected bond length (Å) and angles (deg) for [Pd{N(SPh₂)₂}₂]

2.4.4 The TGA analysis of [Pt{N(SePⁱPr₂)₂}₂]

The thermogravimetric analysis (TGA) curve shown in Figure 2.5 reveals that the complex decomposed between *ca.* 213-348 °C with a weight loss of 87 %(Table 2.12). This is a one-step decomposition which makes the precursor suitable for both LP-MOCVD and AACVD deposition of thin films.



Figure 2.5 TGA curve of [Pt{N(SePⁱPr₂)₂}₂]

2.4.5 Growth of PtSe₂ thin films from [Pt{N(SePⁱPr₂)₂}₂]

Deposition experiments were carried out at various deposition temperatures between 400-475 °C, but the films were grown between 400 to 450 °C. The precursors were held in a tube furnace heated at temperatures in the range 400-475 °C. The precursor temperature was kept constant at 225 °C and the substrate temperatures were varied between 400-475 °C.

Good quality crystalline films were grown on the glass substrate at these temperatures region. The films obtained were brownish in colour, adherent to the glass substrate surface but could be removed by scratching the surface using a scalpel. No growth of thin films was observed below 400 °C and above 450 °C.



Figure 2.6 XRD pattern of PtSe₂ films deposited from $[Pt{N(SeP^{i}Pr)_{2}}_{2}]$ at (a) 400, (b) 425, and (c) 450 °C with $T_{prec} = 225$ °C

Energy dispersive X-ray (EDAX) confirms the presence of platinum and selenide in ca. 1:2 ratios. X-ray diffraction patterns of the PtSe₂ (JCPDS 18-0970) thin films deposited on glass indicate that the films are highly crystalline.

At higher deposition temperatures, the degree of crystallinity of the as deposited films improved as indicated by the intensity of the XRD peaks, i.e. greater resolution (Figure 2.6).

The XRD patterns obtained from the films revealed only single phase (hexagonal) were deposited with a preferred orientation along the (001) plane (Figure 2.6).

The precursor was also used for the growth of platinum selenide thin film by AACVD to investigate any phase changes of $PtSe_2$ films. However, films were noncrystalline materials, which were confirmed by the XRD.

Table 2.7: XRD data of PtSe₂ thin films

	PtSe ₂ - JCPDS (18-0970) ¹⁷⁴		
hkl	d(lit)/Å (% I)	d(exp)/Å (% I)	
001	5.08 (40)	5.13 (95)	
101	2.72 (100)	1.42 (33)	
102	1.99 (50)	1.07 (3)	
200	1.61 (5)	1.84 (3)	
003	1.69 (5)	0.94 (3)	

The morphology of the films was investigated by SEM in Figure 2.7. The particle sizes were found to be *ca*. 2 μ m at 450 °C. A densely packed morphology for PtSe₂ grown at T_{growth} = 400 °C (Figure 2.7a) with a less dense morphology was observed at

higher temperatures, $T_{growth} = 450$ °C (Figure 2.7c). The particles grown at both temperatures have a ribbon-like shape, with uniform coverage.



Figure 2.7 SEM images of $PtSe_2$ films grown at 400 °C, (a) top view, (b) Cross view and 450 °C (c) top view (d) Cross view

2.4.6 The TGA analysis of [Pd{N(ⁱPr₂PSe)₂}₂]

The TGA curve shows that the complexes decomposed between ca. 320-373 °C (Figure 2.8) with a weight loss of 90 %, leaving 10 % residue which corresponds to the theoretical calculated Pd(12 %, Table 2.12).



Figure 2.8 TGA curve of $[Pd{N(SeP^{i}Pr_{2})_{2}}_{2}]$

2.4.7 Growth of palladium selenide thin films from [Pd{N(ⁱPr₂PSe)₂}₂]

The precursor is highly volatile which makes it suitable for LP-MOCVD and AACVD techniques. LP-MOCVD of palladium sulfide thin films were deposited at various growth temperatures between 400-475 °C at a fixed precursor temperature of 345 °C. XRD shows that the films grown from $[Pd\{N(Pr_2PSe)_2\}_2]$ were found to be different phases of palladium selenide films depending on the growth temperatures, orthorhombic PdSe₂ (JCPDS 11-0453)¹⁷⁴ at 425 °C, cubic Pd₁₇Se₁₅ (JCPDS 29-1437) ¹⁷⁴ at 450 °C, and tetragonal Pd₄Se (JCPDS 11-0498)¹⁷⁴ at 475 °C. XRD peaks are

indicated in Figure 2.9-2.11. Table 2.8 summarises palladium sulphide with their different phases.

P	dSe ₂ - JCPDS (11-	0453)
hkl	d(lit)/Å (% I)	d(exp)/Å (% I)
111	3.61 (40)	4.83 (87)
102	3.19 (80)	4.01 (30)
200	2.87 (60)	3.61 (33)
021	2.74 (60)	3.42 (31)
131	1.79 (80)	2.26 (22)

Table 2.8: XRD data of palladium chalcogenide thin films

Pd₄Se-JCPDS (11-0498)

hkl	d(lit)/Å (% I)	d(exp)/Á (% I)
430	2.12 (11)	2.05 (7)
511	2.04 (81)	1.90 (50)
441	1.85 (2)	1.20 (2)

Pd₁₇Se₁₅- JCPDS (29-1437)

hkl	d(lit)/Å (% I)	d(exp)/Å (% I)
310	3.35 (50)	3.35 (57)
311	3.19 (100)	3.20 (83)
410	2.57 (70)	2.57 (56)
330	2.50 (35)	2.49 (40)
511	2.04 (81)	2.04 (54)
600	1.77 (35)	2.07 (26)



Figure 2.9 XRD patterns of Pd₄Se at 475 °C



Figure 2.10 XRD patterns of PdSe₂ at 425 °C



Figure 2.11 XRD patterns of Pd₁₇Se₁₅ at 450 °C

Analysis of the film by SEM shows poor morphologies at 450 °C (Figure 2.12a, b). The films deposited were black in color and adhered well to the glass substrates. A defined platelet-like morphology was formed at $T_{substrate} = 475$ °C (Figure 2.12c). No images were obtained on films obtained at 425 °C.



Figure 2.12 SEM images of $PdSe_2$ films grown at 450 °C, (a) top view, (b) Cross view and at 475 °C, (c) top view

2.4.8 The TGA analysis of [Pt{N(SPⁱPr₂)₂}₂]

The TGA curve shows that the complex decomposed between *ca*. 263 °C – 369 °C (Figure 2.13) with a weight loss of 93 %, leaving 7 % residue which corresponds to the theoretical calculated $PtS_2(8 \%, Table 2.12)$.



Figure 2.13 TGA curve of $[Pt{N(SP^{i}Pr_{2})_{2}}_{2}]$

2.4.9 Growth of PtS₂ thin films from [Pt{N(SPⁱPr₂)₂}₂]

Thin films were deposited between 300-500 °C for both the AACVD and LP-MOCVD. A polycrystalline platinum film was obtained at 450 °C by LP-MOCVD.

The EDAX confirms the presence of platinum and sulphur in 1:1 ratio. The fact that only platinum film is deposited rather than PtS_2 has to do with the relatively weak coordination of platinum to sulphur in the precursor molecule. The XRD pattern shows a cubic platinum film (JCPDS 04-0802) at 450 °C (Figure 2.14).



Figure 2.14 XRD pattern of Pt film deposited from [Pt{N(SPiPr)₂}₂]

Both the LP-MOCVD and AACVD give only the platinum films with the best film obtained at substrate temperature of 450 °C and precursor temperature of 325 °C by LP-MOCVD. The XRD patterns show no evidence of the presence of elemental sulphur. As the growth temperature increases, the platinum film becomes less crystalline as indicated by the intensity of the peaks.

Table 2.9 XRD data of platinum thin films

hkl d(lit)/Å (% I) d(exp)/Å (% I) 110 2.45 (16) 1.20 (87) 200 1.96 (53) 1.96 (36) 220 1.39 (31) 1.38 (18) 311 1.18 (33) 1.18 (20)	Pt-JCPDS (04-0807) 174		
1102.45 (16)1.20 (87)2001.96 (53)1.96 (36)2201.39 (31)1.38 (18)3111.18 (33)1.18 (20)	hkl	d(lit)/Å (% I)	d(exp)/Å (% I)
200 1.96 (53) 1.96 (36) 220 1.39 (31) 1.38 (18) 311 1.18 (33) 1.18 (20)	110	2.45 (16)	1.20 (87)
220 1.39 (31) 1.38 (18) 311 1.18 (33) 1.18 (20)	200	1.96 (53)	1.96 (36)
311 1.18 (33) 1.18 (20)	220	1.39 (31)	1.38 (18)
	311	1.18 (33)	1.18 (20)

The SEM images show spherical grains arranged in a reasonably uniform array on the substrate surface with particle size of ca. 2-3 μ m in diameter (Figure 2.15). There appears to be a reasonable degree of depth to the coating as indicated by the SEM image. The films have a poor morphology probably as a result of evaporation of platinum and sulphur from the surface of the film.





Figure 2.15 SEM micrographs of Pt thin film from $[Pt\{N(SP^{i}Pr)_{2}\}_{2}]$ at 450 °C, (a) top view, (b) Cross view

2.4.10 The TGA analysis of [Pd{N(SPⁱPr₂)₂}₂]

The TGA curve shows that the precursor was highly volatile decomposed at 280-376 °C(Table 2.12).

2.4.11 Growth Pd₁₆S₇ thin films from [Pd{N(SPⁱPr₂)₂}₂]

LP-MOCVD was used to deposit thin films of palladium sulphide between 300-500 °C. Energy dispersive X-ray (EDAX) analyses of the films shows that the film is rich in phosphorus, consisting of 36 % phosphorus, 2 % sulphur and 62 % palladium. A trace of phosphorus is incorporated during the decomposition of the precursor. The XRD pattern shows that the film deposited is cubic PdS₂ (JCPDS 11-0497), which is crystalline at a growth temperature of 500 °C (Figure 2.16).

Table 2.10: XRD data of PdS₂ thin films

PdS ₂ -JCPDS (11-0497) ¹⁷⁴				
hkl	d(lit)/Å (% I)	d(exp)/Å (% I)		
021 210	2.90 (30) 3.65 (60)	3.24 (92) 3.07 (85)		
211	2.20(100)	2.92 (67)		
113	1.98 (60)	2.67 (46)		
023	1.82 (60)	2.33 (68)		

AACVD was also attempted between 300-500 °C. The same phase of PdS_2 was obtained at 425 °C and 450 °C but with a poor crystallinity.



Figure 2.16 XRD pattern of PdS₂ film deposited from $[Pd{N(SPiPr)_2}_2]$

As the growth temperature increases to 475 °C and 500 °C the sulphur peak disappeared and the XRD shows only palladium peaks. This approach enables a comparison to be made of the different techniques to deposit the same materials from the same precursors.





Figure 2.17 SEM micrographs of PdS₂ thin film from $[Pd\{N(SP^{i}Pr)_{2}\}_{2}]$ at 500 °C (a) top view, (b) Cross view.

The SEM images (Figure 2.17) of PdS_2 thin film grown at 500 °C shows that the film has featureless nanocrystalline morphology on the glass substrate and is densely packed. Oriented platelets $1.5 \ \mu m$ in diameter, which are fairly densely packed. The cross view SEM image shows that the platelets are densely packed and of uniform length.

2.4.12 The TGA analysis of [Pd{N(SePPh₂)₂}₂]

The TGA curve shows that the complex decomposes between *ca*. 274-393 °C having a weight loss 76 %, leaving 24 % residue which corresponds to the theoretically calculated PdSe(22 %, Table 2.12).

2.4.13 Growth Pd₁₇Se₁₅ thin films from [Pd{N(SePPh₂)₂}]

Attempts to grow thin films by LP-MOCVD proved unsuccessful. This might be due to its low volatility and higher residue observed on TGA analyses that might have resulted in a decomposed product in the precursor chamber. AACVD was also attempted to give $Pd_{17}Se_{15}$ (JCPDS 29-1437) thin films. They were deposited at various growth temperatures between 400-475 °C maintaining the precursor temperature at 290 °C.



Figure 2.18 XRD pattern of Pd₁₇Se₁₅ from [Pd{N(SePPh₂)₂}]

The XRD patterns indicated the film to have poor crystallinity (Figure 2.18). The XRD pattern showed a broad hump at $2\theta = 22^{\circ}$, indicating the amorphous nature of the film. The broad peak also indicates the poorly formed crystals.

2.4.14 The TGA analysis of [Pd{N(SPPh₂)₂}₂]

TGA curve shows that the complex decomposed at between *ca*. 298 - 386 °C having a weight loss of approximately 75 % (Table 2.12). Residue from the decomposition of this complex is PdS₂ (total % = 75 + 17 = 92 %), which is close to 100 %.

2.4.15 Growth PdS thin films from [Pd{N(SPPh₂)₂}₂]

LP-MOCVD of $[Pd\{N(SPPh_2)_2\}_2]$ was carried out and proved unsuccessful. This might also be due to the low volatility of the precursor as indicated by TGA.



Figure 2.19 XRD pattern of PdS film deposited from [Pd{N(SPPh₂)₂}]

AACVD was also attempted showing only low deposition on the glass substrates. The

precursor is slightly soluble in toluene and THF that makes it difficult to deposit thin films. Pyrolysis of the precursor was also carried out at 600 °C. The XRD shows a crystalline orthorhombic phase of PdS (Figure 2.19). The hump at

the low angle is due to diffraction from the glass substrate.

Table 2.11: XRD data of PdS thin films

PdS-JCPDS (25-1234) ¹⁷⁴				
hkl	d(lit)/Å (% I)	d(exp)/Å (% I)		
201 112	2.89 (74) 2.67 (48)	2.88 (87) 2.66 (73)		
212	2.17 (11)	2.24 (48)		
312	1.73 (30)	1.74 (32)		

Energy dispersive X-ray (EDAX) analyses of the thin film show that it was rich in phosphorus, consisting of 30 % phosphorus, 7 % sulphur, 51 % oxygen and 11 % palladium. Phosphorus is incorporated during the decomposition of the precursor.

2.4.16 The TGA analysis of [Pt{N(SePPh₂)₂}₂]

The TGA curve shows that the complex decomposed between *ca*. 254–484 °C with a weight loss 53 %(Table 2.12).

2.4.17 Growth of PtSe₂ thin films from [Pt{N(SePPh₂)₂}₂]

LP-MOCVD was done between 300- 475 °C. No films were obtained at this temperature range. This is due to low volatility of the precursor leaving a large amount of residue. AACVD was done between 300-550 °C.

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Four peaks were detected: a strong reflection at (100), (101) and two minor planes at (102) and (003) which corresponds to hexagonal $PtSe_2$ structure in Figure 2.20.



Figure 2.20 XRD pattern of PtSe₂ from [Pt{N(SePPh₂)₂}₂]

Analyses of the as-deposited films show that only one phase of $PtSe_2$ (JCPDS 18-0970)¹⁷⁴ thin films at 475 °C was deposited.

Less crystalline films were obtained at temperatures below and above 475 °C. There was a distinct increase in grain size (actual size) as the temperature of deposition was increased (Fig. 2.21a and 2.21c). A dense but uneven morphology was observed in both films. The average grain size is $0.5 \mu m$.



Figure 2.21 SEM micrographs of PtSe₂ thin film from [Pt{N(SePPh₂)₂}₂] at 450 °C (a) top view, (b) Cross view and at 475 °C (c) top view, and (d) cross view

Viewing the images sequentially, we could observe that as the temperature increased the size of the grains increased.

2.4.18 The TGA analysis of [Pt{N(SPPh₂)₂}₂]

The TGA curve shows that the complexes decomposed between *ca.* 317–467 °C with a weight loss of approximately 72 %, leaving 28 % residue which corresponds to the theoretical calculated Pt(24 %, Table 2.12).

2.4.19 Growth PtS thin films from [Pt{N(SPPh₂)₂}₂]

LP-MOCVD proved unsuccessful due to the low volatility of the precursor. AACVD was also carried out at various temperatures. The XRD showed poor crystallinity of the Pt (JCPDS 04-802) thin films (Figure 2.22). AACVD was done but the precursor was partially soluble in toluene and THF.



Figure 2.22 XRD pattern of Pt thin film deposited from [Pt{N(SPPh₂)₂}]

No peaks corresponded to PtS; this indicates that the as-deposited films are either amorphous or contain a small amount of crystalline phase. The XRD pattern matches well with the literature data for the cubic phase of platinum.⁹⁷

Energy dispersive X-ray (EDAX) analyses of the powder shows that it was rich in phosphorus, consisting of 34 % phosphorus, 21 % sulphur, 35 % oxygen and 8 % platinum. EDAX indicated the presence of sulphur which contradicted the XRD patterns.

2.4.20 The TGA analysis of [Ni{N(SePⁱPr₂)₂}₂]

The TGA curve shows the initial decomposition at *ca.* 195 °C. The second major decomposition occurs between *ca.* 300-328 °C having a weight loss of 77 %, leaving 23 % residue which correspond to the theoretical calculated NiSe₂(26 %, Table 2.12). The TGA curve indicates that this precursor is supposed to be good for deposition of thin films.

2.4.21 Growth of NiSe₂ thin films from [Ni{N(SePⁱPr₂)₂}₂]

Growth of the thin films by both LP-MOCVD and AACVD were attempted. No deposition was obtained between 300-500 °C using LP-MOCVD. AACVD was done between 300-500 °C. Little deposition was obtained at 450 °C. No images were observed on SEM.

2.4.22 The TGA analysis of [Ni{N(SPⁱPr₂)₂}₂]

The TGA indicate initial decomposition at ca. 187 °C(Table 2.12).

2.4.23 Growth of NiS₂ thin films from [Ni{N(SPⁱPr₂)₂}₂]

Again no deposition was obtained between 300-500 °C using LP-MOCVD and AACVD.

2.4.24 The TGA analysis of [Ni{N(SPPh₂)₂}₂]

The TGA curve shows that the precursor decomposed between *ca*. 347-389 °C with a weight loss of 64 %(Table 2.12).

2.4.25 Growth of NiS₂ thin films by [Ni{N(SPPh₂)₂}₂]

No deposition was obtained between 300-500 °C using LP-MOCVD and AACVD.

2.4.26 The TGA analysis of [Ni{N(SePPh₂)₂}₂]

The TGA curve show that the precursor decomposed between *ca.* 308-401 °C with a weight loss of 64 %(Table 2.12).

2.4.27 Growth of NiSe₂ thin films from [Ni{N(SePPh₂)₂}₂]

No deposition was obtained between 300-500 °C in both LP-MOCVD and AACVD.

This is due to the low volatility of the precursor.

Table 2.12 The TGA data of $[M{N(EPR_2)_2}_2]$, E = S or Se, R = Ph or ⁱPr

Compound	% loss(0-500 °C)	Experimental %	Theoretical %
		residue	residue(nature of
			residue)
$[Pt\{N(SeP^{i}Pr_{2})_{2}\}_{2}]$	87	13	Pt(19 %)
$[Pt\{N(SP^{i}Pr_{2})_{2}\}_{2}]$	93	7	PtS ₂ (8 %)
$[Pd\{N(SeP'Pr_2)_2\}_2]$	90	10	Pd(12 %)
$[Pd{N(SP^{i}Pr_{2})_{2}}_{2}]$	99	1	Pd(15%)
$[Pd{N(SePPh_2)_2}_2]$	76	24	PdSe ₂ (22 %)
$[Pd\{N(SPPh_2)_2\}_2]$	75	25	PdS ₂ (17 %)
$[Pt\{N(SePPh_2)_2\}_2]$	53	47	PtSe ₂ (28 %)
$[Pt\{N(SPPh_2)_2\}_2]$	72	28	PtS ₂ (24 %)
$[Ni\{N(SeP^{i}Pr_{2})_{2}\}_{2}]$	77	23	NiSe ₂ (26 %)
$[Ni\{N(SP^{i}Pr_{2})_{2}\}_{2}]$	101	-	NiS(13 %)
$[Ni{N(SPPh_2)_2}_2]$	64	36	NiS ₂ (13 %)
$[Ni{N(SePPh_2)_2}_2]$	64	36	NiSe ₂ (19%)

2.5 Conclusions

Compounds of the type $[M\{N(EPR_2)_2\}_2]$, M = Pt(II), Pd(II); $R = {}^{i}Pr$, Ph_2 and E = S, Se were used as single source precursors for the deposition of metal chalcogenide thin films *via* a low-pressure metal-organic chemical vapour deposition (LP-MOCVD) and aerosol assisted chemical vapour deposition (AACVD). The X-ray structures of $[Pt\{N(SeP^{i}Pr_2)_2\}_2]$ and $[Pd\{N(SPPh_2)_2\}_2]$ were obtained. The structures are square-
planar geometry with the six membered PtSe₂P₂N rings adopting a distorted "boat" conformation. The structure is not similar to the one reported by Cupertino et al.⁷⁹. All the complexes were characterised by elemental analysis, IR, MS, ¹H and ¹³C NMR. Thin films of PtSe₂, Pt, PdSe₂, Pd₁₇Se₁₅, and PdS₂ were deposited by AACVD and LPMOCVD techniques. The morphology, crystallinity and stoichiometry were investigated by XRD, SEM, and EDAX. Polycrystalline PtSe2 (hexagonal) films were grown between 400 - 450 °C from $[Pt{N(SeP^{i}Pr_{2})_{2}}]$ and crystallinity increases with temperature as indicated by the intensity of the peaks $\{(001(a), (b), (c)\}$. A strong XRD peak was observed at 18.20° (001) in all the samples followed by two minor peaks at 32.5° (101) and 55.30° (200). The ribbon-like densely packed morphology with average particle size of ca. 2 µm at 400 °C and less dense morphology at 450 °C was obtained. Pt (cubic) instead of PtS2 film was obtained due to weak coordination of Pt to S in the precursor molecule. Spherical grains with average particle size of ca. 2-3 µm in diameter. Different phases of palladium selenide were obtained depending on temperature. Platelet-like morphology was obtained. The R group (isopropyl or phenyl) plays an important role in the decomposition, crystallinity and stoichiometry of the materials.

The type of the ligand plays an important role to control the stoichiometry of the asdeposited films and in some cases may provide routes for the growth of specific phases. Much scope remains for the development of these precursors for lower deposition temperatures and well defined phases. No depositions were observed using nickel complex even though they show one stage decomposition by TGA. Using LP-MOCVD, the reason might be that the settings of vapour pressure were not done properly.

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Chapter 3

Deposition of metal sulphide thin films from xanthate precursors

3.1 Introduction

Xanthates (o-ethyldithiocarbonates) were first discovered by Zeise¹⁰⁶ in 1822. They have been used by industry as floatation agents for the thiophilic minerals of the transition metals such as copper, zinc, cobalt, nickel and gold, separation and quantitative determination of a larger number of cations and trifluoroethylxanthate has been used as a reagent for the analytical determination of gold.¹⁰⁶⁻¹⁰⁷

Xanthate and dithiocarbamates ligands have been studied recently due to their structural similarities.

RO

R₂N-C

Dithiocarbamate

Xanthate

R = alkyl or aryl

Xanthates are usually prepared by mixing an alcohol with potassium hydroxide and carbon disulfide (equation 3.1).

 $KOR + CS_2 \rightarrow ROCS_2K$ eq. 3.1

Xanthate ligands can act as monodentate, bidentate or bridging to two or even three metal centers with sulphur, which lead to a variety of complexes.

The transition metal xanthates have been extensively studied for their broad applications in industry. Metal xanthates have been prepared previously to determine their composition and structure. The metal is located at a center of inversion, is coordinated by two equivalent xanthate groups, each group behaving as a bidentate ligand through the two sulphur atoms.



Metal alkyl xanthate, R = alkyl or aryl; M = Cd, Zn, Pd, Pt, AS, Sb and Bi.¹⁰⁸⁻¹¹⁵

Metal-xanthate complexes have low solubility products and high stability constants, and therefore xanthates exhibit high efficacy for the removal of metal ions.

Cheon, *et al.*¹¹⁶ have reported deposition of NiS and PdS thin films from both a thermal and photochemical CVD route using single-source precursors of the type $M(S_2COCHMe_2)_2$, M = Ni and Pd. O'Brien, *et al.*¹¹⁷ have recently reported the deposition of binary nickel sulfide films from nickel complexes of various alkyl dithiocarbamate derivatives nickel using a low-pressure metal-organic chemical vapour deposition technique. The morphology of the films was shown to be predominantly in the shape of wires. NiS nanowhiskers have also been reported by reacting a nickel substrate and sulfur in ethylenediamine.¹¹⁸ The authors report a change of morphology and composition with variation in reaction conditions.

Nickel sulfide has been studied because of its potential as a transformation toughening agent for materials used in semiconductor applications. Their uses as catalysts and coatings for photogalvanic cells have also been reported. The existence of various compositions of nickel sulfide including $Ni_{3+x}S_2$, Ni_3S_2 , Ni_4S_{3+x} , Ni_6S_5 , Ni_7S_6 , Ni_9S_8 , NiS, Ni_3S_4 and NiS_2 makes such studies both interesting and challenging.^{116, 118}

Cadmium chalcogenide thin films are useful materials in solid-state solar cells, photoconductors, field effect transitors, sensors, and transducers. The morphology and microstructure of polycrystalline CdS films are major concern in the fabrication process of CdTe solar cells. Afzaal, *et al*¹¹⁹⁻¹²⁰ reported the deposition of CdS and CdSe by LP_MOCVD using [Cd{N(EPⁱPr₂)₂}₂], (E = S, Se) as single source precursors.

Yellow, transparent, and well-adherent to the glass surface CdS thin films were grown at growth temperature of 425 °C and 450 °C. At 475 °C, slightly dark yellow-brown films were obtained. Analysis of the as-deposited films show that hexagonal phase of CdS (JCPDS-06-0314) is prepared, regardless of difference in growth temperature. XRD pattern show a preferred orientation along the (002) plane independent of growth temperature. At higher temperature (475 °C) the film were found to be amorphous. SEM indicate that the morphology of the film at 450 °C consist of randomly oriented domains of compacted thin acicular crystallites and the film thickness to be 1.75 μ m thick. EDAX analysis, the films was found to be slightly cadmium rich (52 %) and also, 2 % of phosphorus was detected.

Sebastian, *et al.*¹²¹ deposited both intrinsic CdS and n-CdS, which exhibited hexagonal Greenockite structure, with a preferred orientation along (002) for n-CdS.

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Meyer, et al.¹²² deposit both undoped and In-doped films of CdS. The SEM of CdS shows a columnar microstructure, low porosity and good adherence to the substrate. Barreca, et al.¹²³ prepared ZnS and CdS thin films using $M(O^{-i}Pr Xan)_2$ [M = Zn, Cd; $O^{-i}PrXan = S_2COCH(CH_3)_2$ as single source precursors. All the CdS reported exhibit a hexagonal phase by XRD. SEM shows a smooth and regular surface morphology.

3.2 Experimental

3.2.1 Materials and methods

All chemicals used were of analytical grade quality and were used without further purification. Deionized water was used for all experimental work. Ethylxanthic acid, potassium salt, o-isopropylxanthic acid, potassium salt, methanol, potassium tetrachloroplatinate(II), potassium tetrachloropalladate(II), cadmium(II)chloride; and cobalt hexahydrate, cobalt(II)chloride (98 %, Fluka Chemika), copper(II)nitrate hydrate (95 %, BDH), cadmium chloride anhydrous, cadmium chloride (99 %, Aldrich).

3.2.2 Preparation of metal xanthate precursors

Metal alkylxanthate compounds, $[M(S_2COR)_2]$, M = Ni, Pt, Pd, Cd, Co and Cu; R = Et or ⁱPr were prepared by stoichiometric reaction of potassium alkylxanthate and metal salts following the literature procedure.¹⁰⁸All reactions were carried out at room temperature.

3.2.2.1 Synthesis of $[Ni(S_2COR)_2]$, R = Et or ⁱPr.

A methanolic solution of NiCl₂·6H₂O (0.371 g, 1.56 mmol, 10 mL) was added to $C_2H_5OCS_2K$ (0.5 g, 3.12 mmol) in methanol (10 mL). Brown solution was obtained which turns blue after 15 min. The metal xanthate forms rapidly and precipitates. The reaction mixture was stirred for 1 h. The mixture was filtered and washed three times with water (3 x 10 mL) followed by methanol (3 x 10 mL). The resulting metal dixanthate was dried at room temperature in air. Yield: 0.75 g, 80 %. MP = 142 °C. [Ni(C₂H₅OCS₂)₂] : Microanalysis: Anal. Calcd. for C₆H₁₀O₂NiS₄: C, 23.93; H, 3.35; S, 42.60. Found: C, 23.80; H, 3.27; S, 42.75. ¹H NMR (CDCl₃) ordered as δ (ppm), multiplicity, relative ratio, assignment; 4.65 (q, 2H, S₂COCH₂CH₃); 1.45 (t, 3H, S₂COCH₂CH₃). ¹³C NMR (CDCl₃) ordered as δ (ppm), 68.75 (S₂COCH₂CH₃). MS: m/z = 301 correspond to [M + H]⁺.

Similar procedure was used to prepare [Ni(C₃H₇OCS₂)₂]. Except that 0.0682 g(0.287 mmol, 10 mL) of NiCl₂·6H₂O and 0.1 g (0.574 mmol) in methanol (10 mL) of C₃H₇OCS₂K were used. Yield: 0.74 g, 74 %. MP = 120 °C. [Ni(C₃H₇OCS₂)₂] : Microanalysis: Anal. Calcd for C₈H₁₄O₂NiS₄: C, 29.19; H, 4.29; S, 38.97. Found: C, 29.32; H, 4.19; S, 38.75. ¹H NMR (CDCl₃) ordered as δ (ppm), multiplicity, relative ratio, assignment, 1.5 ppm [d, 6H, S₂COCH(CH₃)₂]; 1.48 [q, 1H, S₂COCH(CH₃)₂]. MS: m/z = 329 corresponds to [M + H]⁺.

3.2.2.2 Synthesis of $[Pd(S_2COR)_2]$, R = Et or ⁱPr

An aqueous solution of K_2PdCl_4 (0.102 g, 0.312 mmol, 10 mL) was added to $C_2H_5OCS_2K$ (0.1 g, 0.624 mmol) in methanol (10 mL). The mixture turns yellow immediately. The reaction mixture was stirred for 1 h. The mixture was filtered and

washed three times with water (3 x 10 mL) and then with methanol (3 x 10 mL). The resulting metal dixanthate was dried at room temperature in air. Yield: 0.085 g, 78 %. MP = 153 °C. [Pd(C₂H₅OCS₂)₂] : Microanalsis: Anal. Calcd for C₆H₁₀O₂PdS₄: C, 25.50; H, 3.74; S, 34.03. Found: C, 25.55; H, 3.66; S, 34.70. ¹H NMR (CDCl₃) ordered as δ (ppm), multiplicity, relative ratio, assignment; 4.68 (q, 2H, S₂COCH₂CH₃); 1.60 (t, 3H, S₂COCH₂CH₃). ¹³C NMR (CDCl₃) ordered as δ (ppm), 68.75 (S₂COCH₂CH₃), 14.01 (S₂COCH₂CH₃).

[Pd(C₃H₇OCS₂)₂] was prepared by similar procedure using 0.0936 g (0.287 mmol, 10 mL) of K₂PdCl₄ and 0.1 g (0.574 mmol) of C₃H₇OCS₂K in methanol solution (10 mL). A yellow precipitate was formed immediately. Yield: 0.075 g, 69 %. MP = 144 °C. [Pd(C₃H₇OCS₂)₂] : Microanalysis: Anal. Calcd for C₈H₁₄O₂PdS₄: C, 25.50; H, 3.73; S, 34.03. Found: C, 25.55; H, 3.66; S, 34.70. ¹H NMR (CDCl₃) ordered as δ (ppm), multiplicity, relative ratio, assignment, 1.5 ppm [d, 6H, S₂COCH(CH₃)₂]; 1.48 [q, 1H, S₂COCH(CH₃)₂]. MS: m/z = 329 correspond to [M + H]⁺.

3.2.2.3 Synthesis of $[Pt(S_2COR)_2]$, R = Et or ⁱPr.

An aqueous solution of K₂PtCl₄ (0.13 g, 0.312 mmol, 10 mL) was added to $C_2H_5OCS_2K$ (0.1 g, 0.624 mmol) in methanol (10 mL). The reaction mixture was stirred for 1 h. A yellow precipitate was formed. The mixture was vacuum filtered and washed three times with a water (3 x 10 mL) and then with methanol (3 x 10 mL). The yellow product was dried at room temperature in air. Yield: 0.46 g, 65 %. MP = 130 °C. [Pt(C₂H₅OCS₂)₂] : Microanalysis: Anal. Calcd. for C₆H₁₀O₂PtS₄: C, 16.47; H, 2.30; S, 29.32. Found: C, 16.47; H, 2.03; S, 29.08.

Similar procedure was used to prepare [Pt(C₃H₇OCS₂)₂] using 0.12 g (0.287 mmol, 10 mL) of K₂PtCl₄ and 0.1 g (0.574 mmol) of C₃H₇OCS₂K in methanol (10 mL). The resulting platinum dixanthate complex was dried at room temperature in air. Yield: 0.088 g, 66 %. MP = 140 °C. [Pt(C₃H₇OCS₂)₂] : Microanalysis: Anal. Calcd. for C₈H₁₄O₂PtS₄: C, 20.64; H, 3.03; S, 27.55. Found: C, 20.65; H, 2.93; S, 27.92.

3.2.2.4 Synthesis of $[Cd(S_2COR)_2]$, R = Et or ⁱPr.

An aqueous solution of CdCl₂ (0.0571 g, 0.312 mmol, 10 mL) was added to $C_2H_5OCS_2K$ (0.1 g, 0.624 mmol) in methanol (10 mL). A white precipitate was formed immediately. The reaction mixture was stirred for 1 h. The mixture was vacuum filtered and washed three times with water (3 x 10 mL) and then with methanol (3 x 10 mL). The white product was dried at room temperature in air. Yield: 0.095 g, 86 %. MP = 165 °C. [Cd($C_2H_5OCS_2$)₂] : Microanalysis: Anal. Calcd for $C_6H_{10}O_2CdS_4$: C, 20.31; H, 2.84; S, 36.15 Found: C, 20.25; H, 2.55; S, 35.72. ¹H NMR (CDCl₃) ordered as δ (ppm), multiplicity, relative ratio, assignment; 4.41 (q, 2H, S₂COCH₂CH₃); 1.39 (t, 3H, S₂COCH₂CH₃). MS: m/z = 353 correspond to [M + H]⁺.

A similar procedure was used to prepare $[Cd(C_3H_7OCS_2)_2]$ using 0.053 g (0.287 mmol, 10 mL) of CdCl₂ and 0.1 g (0.574 mmol) of C₃H₇OCS₂K in methanol (10 mL). Yield: 0.098 g, 89 %. MP = 173 °C. $[Cd(C_3H_7OCS_2)_2]$: Microanalysis: Anal. Calcd for C₈H₁₄O₂CdS₄: C, 25.10; H, 3.69; S, 33.50 Found: C, 25.32; H, 3.56; S, 33.91.

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3.2.2.5 Synthesis of $[Co(S_2COR)_2]$, R = Et or ⁱPr.

An aqueous solution of CoCl₂.6H₂O (0.07 g, 0.312 mmol, 10 mL) was added to $C_2H_5OCS_2K$ (0.1 g, 0.624 mmol) in methanol (10 mL). A black precipitate started to form immediately. The reaction mixture was stirred for 1 h. The mixture was vacuum filtered and washed three times with a water (3 x 10 mL) and then with methanol (3 x 10 mL). The resulting cobalt dixanthate complex was dried at room temperature in air. Yield: 0.075 g, 80 %. M.P. = 123 °C. [Co(C₂H₅OCS₂)₂]: Microanalysis: Anal. Calcd for C₆H₁₀O₂CoS₄: C, 23.91; H, 3.34; S, 42.56. Found: C, 22.03; H, 3.33; S, 41.09.

A similar procedure was used to prepare $[Co(C_3H_7OCS_2)_2]$ using 0.0682 g (0.287 mmol, 10 mL) of $CoCl_2 \cdot 6H_2O$ and 0.1 g (0.574 mmol) of $C_3H_7OCS_2K$ in deionised water (10 mL). Yield: 0.084 g, 89 %. M.P. = 162 °C. $[Co(C_3H_7OCS_2)_2]$: Microanalysis: Anal. Calcd for $C_8H_{14}O_2CoS_4$: C, 20.64; H, 3.03; S, 27.55 Found: C, 20.65; H, 2.93; S, 27.92.

3.2.2.6 Synthesis of [Cu(C₂H₅OCS₂)₂]

An aqueous solution of Cu(NO₃)₂ (0.075 g, 0.312 mmol, 10 mL) was added to $C_2H_5OCS_2K$ (0.1 g, 0.624 mmol) in methanol (10 mL). The precipitate formed immediately. The reaction mixture was stirred for 1 h. The mixture was filtered and washed three times with water (3 x 10 mL) and then with methanol (3 x 10 mL). The resulting copper dixanthate complex was dried at room temperature in air. Yield: 0.085 g, 86 %. M.P. = 122 °C. [Cu(C₂H₅OCS₂)₂] : Microanalysis: Anal. Calcd for C₆H₁₀O₂CuS₄: C, 23.55; H, 3.29; S, 41.92. Found: C, 22.55; H, 3.14; S, 41.16.

Table 3.1 Microanalysis of metal xanthate precursors

Precursors	Found (calculated)			
	%C	%Н	%S	
1. Ni(S ₂ COC ₂ H ₅) ₂	23.80 (23.93)	3.27 (3.35)	42.75 (42.60)	
$2. Pd(S_2COC_2H_5)_2$	20.63 (20.66)	2.88 (2.89)	36.81 (36.77)	
3. Pt(S ₂ COC ₂ H ₅) ₂	16.47 (16.47)	2.03 (2.30)	29.08 (29.32)	
4. Co(S ₂ COC ₂ H ₅) ₂	22.03 (23.91)	3.33 (3.34)	41.09 (42.56)	
5. Cd(S ₂ COC ₂ H ₅) ₂	20.25 (20.31)	2.55 (2.84)	35.72 (36.15)	
6. Cu(S ₂ COC ₂ H ₅) ₂	22.55 (23.55)	3.14 (3.29)	41.16 (41.92)	
7. Ni(S ₂ COCHMe ₂) ₂	29.32 (29.19)	4.19 (4.29)	38.75 (38.97)	
8.Pd(S ₂ COCHMe ₂) ₂	25.55 (25.50)	3.66 (3.74)	34.70 (34.03)	
9. Pt(S ₂ COCHMe ₂) ₂	20.65 (20.64)	2.93 (3.03)	27.92 (27.55)	
10. Co(S ₂ COCHMe ₂) ₂	27.46 (29.17)	4.21 (4.28)	37.07 (38.94)	
11.Cd(S ₂ COCHMe ₂) ₂	25.32 (25.10)	3.56 (3.69)	33.91 (33.50)	

3.3 Results and discussions

3.3.1 Single X-ray structure of [Ni(S₂COEt₂)₂]







Figure 3.2 Packing diagram of [Ni(S₂COEt₂)₂]

Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of hexane/dichloromethane mixture. Data were collected at 100(2) K using graphitemonochromated Mo Ka radiation ($\lambda = 0.71073$ Å) by Bruker APEX diffractometer. Data was collected using a Bruker-based diffractometer equipped with a LT-2 low temperature apparatus operating at 100 K.

Details of data collection and structure refinements are shown in Table 3.2.

The crystal structure of nickel xanthate has been determined by three dimensional Xray diffraction techniques and refined by a full matrix least squares method on F^2 . Crystals are orthorhombic, space group pbca, Z = 4 with cell dimensions a =7.4077(7), b = 7.0961(7), and c = 20.7565(19). Intensity data for a platelike crystal 0.70 x 0.50 x 0.20 mm were obtained. X-ray crystallography studies revealed each complex to have nickel at a center of inversion coordinated by two equivalent xanthate groups behaving as a bidentate ligand through four sulphur atoms, as shown in Figure 3.1. The packing diagram showing intermolecular Ni....S interactions is shown in Figure 3.2. The complex is similar to the one reported in the literature.¹¹¹

Table 3.2 Crystal data and structural refinement details for [Ni(S2COEt2)2]

	1
Empirical formula	C ₆ H ₁₀ NiO ₂ S ₄
Formula weight	301.09
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal System, space group	Orthorhombic, pbca
Unit cell dimensions	$a = 7.4077(7) A \alpha = 90^{\circ}$
	$b = 7.0961(7) \text{ A} \beta = 90^{\circ}$
	$c = 20.7565(19) A \gamma = 90^{\circ}$
Volume	1091.08(18) A ³
Z, Calculated density	4, 1.833 mg/m ³
Absorption coefficient	2.507 mm ⁻¹
F(000)	616
Crystal size	0.70 x 0.50 x 0.20 mm
Theta range for data collection	1.96 to 26.38 deg
Limiting indices	-9 < = h < = 7, -7 < = k < = 8, -25 < =1 < = 25
Reflections collected/unique	5655/1111 [R(int) = 0.0230]
Completeness to theta $= 26.41$	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6340 and 0.2728
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	1111/0/62
Goodness-of-fit on F ²	1.097
Final R indices [I > 2 sigma (I)	R1 = 0.0225, $wR2 = 0.0600$
R indices (all data)	R1 = 0.0240, wR2 = 0.0611
Largest diff. peak and hole	$0.617 \text{ and } -0.495 \text{ e.A}^{-3}$

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		1	
Ni(1) – S(1)	2.2197(5)	S(1) - Ni(1) - S(1)	180.0(2)
Ni(1) – S(2)	2.2175(5)	S(2) – Ni(1) – S(1)	79.416(15)
S(1) – C(1)	1.7019(17)	C(1) - S(1) - Ni(1)	83.48(6)
S(2) - C(1)	1.6914(17)	C(1) - S(2) - Ni(1)	83.79(6)
O(1) – C(1)	1.308(2)	C(1) - O(1) - C(2)	117.37(13)
O(1) – C(2)	1.468(2)	O(1) - C(2) - C(3)	106.57(14)
C(2) - C(3)	1.501(2)		

Table 3.3 Selected bond length (Å) and angles (deg) for [Ni(S₂COEt₂)₂]

3.3.2 Single crystal X-ray structure of [Pd(S₂COEt₂)₂]

The single crystal was obtained by slow diffusion of n-hexane into a dichloromethane solution of the complex at room temperature. Interatomic distances and angles are listed in Table 3.4.

The palladium X-ray structure was previously reported.¹¹⁰ The structure reveals that it is square planar. X-ray analysis of the present structure reveals that $[Pd(S_2COEt_2)_2]$, lies on an inversion center and adopts a square planar geometry defined by the four sulphur atoms of the two dithiocarbonate (xanthate) ligands. The ORTEP diagram shows the atom numbering (Figure 3.3) and the packing diagram shows intermolecular Pd...S interactions (dashed lines, Figure 3.4). Details of data collection and structure refinements are shown in Table 3.4.



Figure 3.3 ORTEP diagram showing atomic numbering of [Pd(S₂COEt₂)₂]



Figure 3.4 Packing diagram of [Pd(S₂COEt₂)₂]

Table 3.4 Crystal data and structural refinement details for [Pd(S2COEt2)2]

	2
Empirical formula	$C_6H_{10}PdO_2S_4$
Formula weight	348.78
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal System, space group	Orthorhombic, pbca
Unit cell dimensions	$a = 7.465(3) A \alpha = 90^{\circ}$
	$b = 7.166(3) A \beta = 90^{\circ}$
·	$c = 20.678(8) A \gamma = 90^{\circ}$
Volume	1106.2(8) A ³
Z, Calculated density	4, 2.094 mg/m ³
Absorption coefficient	2.397 mm^{-1}
F(000)	688
Crystal size	0.30 x 0.20 x 0.20 mm
Theta range for data collection	1.97 to 26.69 deg
Limiting indices	-9 < = h < = 8, -9 < = k < = 9, -26 < = 1 < = 26
Reflections collected/unique	7653/1162 [R (int) = 0.0438]
Completeness to theta $= 26.41$	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6457 and 0.5333
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	1162/0/62
Goodness-of-fit on F ²	1.241
Final R indices [I > 2 sigma (I)	R1 = 0.0443, wR2 = 0.0984
R indices (all data)	R1 = 0.0494, $wR2 = 0.1006$
Largest diff. peak and hole	1.183 and -1.047 e.A^{-3}

2				
Pd(1) - S(1)	2.3280(16)	S(1) - Pd(1) - S(1)	180.0(2)	
Pd(1) – S(2)	2.3192(16)	S(2) - Pd(1) - S(1)	75.43(5)	
S(1) - C(1)	1.692(6)	C(1) - S(1) - Pd(1)	84.6(2)	
S(2) - C(1)	1.681(6)	C(1) - S(2) - Pd(1)	85.1(2)	
O(1) – C(1)	1.302(7)	C(1) - O(1) - C(2)	118.1(4)	
O(1) – C(2)	1.459(6)	O(1) - C(2) - C(3)	106.9(5)	
C(2) - C(3)	1.493(9)			

Table 3.5 Selected bond length (Å) and angles (deg) for [Pd(S₂COEt₂)₂]

3.3.3 Single X-ray structure of [Pt(S₂COEt₂)₂]

The single crystals were obtained using the same procedure as described in 3.3.2. Selected bond lengths and angles for this complex are given in Table 3.6.

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Hydrogen atoms were placed in calculated positions, assigned anisotropic thermal parameters and allowed to ride on their parent carbon atoms. The range of h, k, and l are -9 < = h < = 5, -8 < = k < = 9, -24 < =1 < = 25. Total numbers of measured and observed independent reflection are 5878 and 1163 [R (int) = 0.0320]. The final R and R_w values are given in the Table 3.6.



Figure 3.5 ORTEP diagram showing atomic numbering of [Pt(S₂COEt₂)₂]



Figure 3.6 Packing diagram of [Pt(S₂COEt₂)₂]

Table 3.6 Crystal data and structural refinement details for [Pt(S2COEt2)2]

	3
Empirical formula	$C_6H_{10}PtO_2S_4$
Formula weight	437.47
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal System, space group	Orthorhombic, pbca
Unit cell dimensions	$a = 7.6472(9) A \alpha = 90^{\circ}$
	$b = 7.2460(8) A \beta = 90^{\circ}$
	$c = 20.523(2) A \gamma = 90^{\circ}$
Volume	1137.2(2) A ³
Z, Calculated density	4, 2.555 mg/m ³
Absorption coefficient	13.038 mm^{-1}
F(000)	816
Crystal size	0.20 x 0.20 x 0.20 mm
Theta range for data collection	1.98 to 26.40 deg
Limiting indices	-9 < = h < = 5, -8 < = k < = 9, -24 < = 1 < = 25
Reflections collected/unique	5878/1163 [R (int) = 0.0320]
Completeness to theta = 26.41	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.1802 and 0.1802
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	1163/ 0/ 62
Goodness-of-fit on F ²	1.057
Final R indices [I > 2 sigma (I)	R1 = 0.0207, wR2 = 0.0420
R indices (all data)	R1 = 0.0289, wR2 = 0.0444
Largest diff. peak and hole	0.669 and -0.573 e.A ⁻³

The complex reveal that it is a monomeric square planar which is similar to the reported structure stoichiometrically and geometrical.¹¹¹ The S atoms are arranged in a distorted tetrahedron with the S—Pt—S angles varying from 180 and 75 $^{\circ}$.

		3	
Pt(1) – S(1)	2.3316(10)	S(1) - Pt(1) - S(1)	179.999(1)
Pt(1) - S(2)	2.3242(10)	S(2) - Pt(1) - S(1)	104.95(3)
S(1) - C(1)	1.705(4)	C(1) - S(1) - Pt(1)	85.64(13)
S(2) – C(1)	1.693(4)	C(1) - S(2) - Pt(1)	86.15(14)
O(1) - C(1)	1.313(5)	C(1) - O(1) - C(2)	117.3(3)
O(1) - C(2)	1.469(5)	O(1) - C(2) - C(3)	107.0(3)
C(2) - C(3)	1.495(6)		

Table 3.7 Selected bond length (Å) and angles (deg) for [Pt(S₂COEt₂)₂]

3.4 Deposition of metal chalcogenides thin films from $[M(S_2COR)_2]$, M = Pt, Pd, Ni, Cd and Co; R = Et or ⁱPr

3.4.1 The TGA analysis of [Ni(S₂COR₂)₂], R = Et or ⁱPr

Thermogravimetric analyses of $[Ni(S_2COR)_2]$ was carried out at atmospheric pressure with N₂ as the carrier gas. The heating rate was 10 °C/min. The TGA curve shown in Figure 3.7, reveals that the precursor decomposed between *ca*. 155-200 °C with a weight loss of 67 %, leaving 33 % residue which corresponds to theoretical calculated NiS(30%).

Only one stage decomposition was observed on both complexes.



Figure 3.7 TGA curve of [Ni(C₂H₅OCS₂)₂]

The TGA curve of $[Ni(C_3H_7OCS_2)_2]$ in Figure 3.8, showed a massive weight loss between *ca*. 167-202 °C corresponding to 72 % weight loss (Figure 3.8), leaving 28 % residue which correspond to theoretical calculated NiS.



Figure 3.8 TGA curve of [Ni(C₃H₇OCS₂)₂]

3.4.2 Deposition of NiS thin films from $[Ni(S_2COR_2)_2]$, R = Et or ⁱPr

TGA analyses showed that the precursors are highly volatile, making them suitable for AACVD and LP-MOCVD studies.

Thin films of NiS were deposited from $[Ni(S_2COR)_2]$, R = Et or ⁱPr at 200 °C, 250 °C, and 300 °C by AACVD. Good quality crystalline films were grown on the substrate at these temperature regions. The films obtained were grey in colour, adherent to the glass substrate. The crystallinity of the prepared NiS samples was investigated by XRD as shown in Figure 3.9-3.14. X-ray diffraction data for NiS reveal that the films prepared by the present methods are polycrystalline in nature and their observed d values are in good agreement with literature value (JCPDS: 12-0041) data file, shown in Table 3.1.



Figure 3.9 XRD pattern of NiS from [Ni(C₂H₅OCS₂)₂] at 200 °C

The observed values suggest that the formed materials is NiS with rhombohedral crystal structure. It is interesting to find out that all the samples can be indexed as

rhombohedral phase NiS with characteristic (110), (101), (300), (021), and (330) planes(Figure 3.9).

The indices are assigned according to those in JCPDS (12-0041). The (300) orientation is dominant but also the other main peaks indicate that the as-grown materials are NiS.



Figure 3.10 XRD pattern of NiS from [Ni(C₂H₅OCS₂)₂] at 250 °C

Growth of NiS from $[Ni(C_3H_7OCS_2)_2]$ at 200 °C(Figure 3.12) differs from those grown from ethylxanthate at a similar temperature. This is due to the instrument noise. This can be seen by NiS deposited at 250 °C(Figure 3.13) which is similar to the NiS deposited from ethyl xanthate precursor at the same temperature.



Figure 3.11 XRD pattern of NiS from [Ni(C₂H₅OCS₂)₂] at 300 °C



Figure 3.12 XRD pattern of NiS from [Ni(C₃H₇OCS₂)₂] at 200 °C



Figure 3.13 XRD pattern of NiS from [Ni(C₃H₇OCS₂)₂] at 250 °C



Figure 3.14 XRD pattern of NiS from [Ni(C₃H₇OCS₂)₂] at 300 °C

NiS- JCPDS (12-0041) ¹⁷⁵					
hkl	d(lit)/Á (% I)	d(exp)/Å (% I)	hkl	d(lit)/Á (% I)	d(exp)/Á (% I)
110	8.81 (60)	4.80 (43)	401	1.74 (40)	1.82 (17)
101	2.95 (40)	2.94 (26)	321	1.63 (18)	1.63 (10)
300	2.78 (100)	2.78 (88)	330	1.60 (35)	1.59 (22)
021	2.51 (65)	2.51 (30)	012	1.55 (25)	1.55 (11)
220	2.41 (12)	2.39 (14)	600	1.39 (8)	1.39 (6)
211	2.23 (55)	2.23 (23)	520	1.33 (4)	1.33 (4)
131	1.86 (95)	1.86 (37)	312	1.30 (10)	1.30 (5)
410	1.82 (45)	1.81 (22)	042	1.26 (8)	1.25 (7)
			440	1.20(6)	1.19 (5)

Table 3.8 X-ray data of NiS (rhombohedral) thin films from $[Ni(S_2COR)_2]$, R = Et or ⁱPr

Only one phase of NiS has been observed regardless of growth temperature which indicates the thermal stability of the precursors.

The surface morphology of the NiS deposited was studied by SEM. The SEM studies show that the morphology of the films changed with temperature. At 200 °C NiS films with rod-like dimensions were observed (Figure 3.15). These structures were approximately 500 nm in length and 250 nm in breadth, with uniform coverage on the substrate. At 200 °C and 250 °C (Figure 3.16) the films observed could be described as granular nodular in shape similar to those grown at 250 °C from $[Ni(C_2H_5OCS_2)_2]$. At 250 °C the films have a twinned cube shape with interpenetrating structures. This

Deposition of Metal sulphide thin films from xanthate precursors

shape is very uniform across the substrate with particles sized from 400-500 nm. There is a further change of morphology at 300 °C (Figure 3.17), where granular close-to spherical particles are observed. The coverage is non-uniform with clustered growth predominant on the substrate.



Figure 3.15 SEM micrographs of NiS from [Ni(C2H5OCS2)2] at 200 °C

There is a distinct increase in grain size as the temperature of deposition is increased from 200 to 300 °C (Figure 3.15-3.17). However the films grown at 300 °C are similar to those grown from the ethyl analogue at this temperature. Clustered growth of spherical particles is predominant on the substrate.



Figure 3.16 SEM micrographs of NiS from [Ni(C₂H₅OCS₂)₂] at 250 °C



Figure 3.17 SEM micrographs of NiS from [Ni(C₂H₅OCS₂)₂] at 300 °C

The NiS grown at 200 °C differs from that grown from the ethylxanthate at the same temperature. The particles of the films grown at 200 °C and 250 °C from $[Ni(C_3H_7OCS_2)_2]$ are irregular shaped similar to those grown at 250 °C from $[Ni(C_2H_5OCS_2)_2]$. The films grown at 300 °C (Figure 3.18a) are also similar to those grown from the ethyl derivative. The spherical particles form clusters on the substrate.



Figure 3.18 SEM micrographs of NiS from $[Ni(C_3H_7OCS_2)_2]$ at (a) 200 °C, (b) 250 °C, and (c) 300 °C

EDAX clearly confirms the presence of nickel and sulphur as 1:1 ratio, in all samples. Cheon, *et al.*¹¹⁶ has grown NiS thin films by thermal and photolytic processes. The films grown by the thermal process were found to have relatively rough surface and are highly orientated polycrystalline materials, and while those grown by the photolytic process were smooth and were either non oriented polycrystalline or non diffraction materials. SEM showed that the films consisted of granules. O'Brien, *et al.*⁵⁶ obtained two different kinds of nickel sulphide (NiS_{1.03} and NiS) phases using Ni(SCNRR')₂, RR' = Et₂, MeE_t, MeⁿBu and MeⁿHex. Different shapes (wire, tangled wires and platelets) were obtained depending on the growth conditions.

3.4.3 The TGA analysis of $[Cd(S_2COR)_2]$, R = Et or ⁱPr

The TGA analysis of $[Cd(C_2H_5OCS_2)_2]$ reveals that the precursor decomposed between *ca.* 160-169 °C with a weight loss of approximately 58 %, leaving 42 % residue which corresponds to the theoretical calculated CdS(40 %).

TGA analysis of $[Cd(C_3H_{57}OCS_2)_2]$ shows that the precursor decomposed between 165-335 °C with a weight loss of 62 %, leaving 38 % which correspond to the theoretical calculated CdS(38 %).

3.4.4 Deposition of CdS thin films from [Cd(S₂COR)₂], R = Et or ⁱPr

Clearly from the TGA analysis both complexes are expected to be suitable for deposition of thin films by AACVD and LP-MOCVD.

Deposition experiments were carried out by AACVD between 200-300 °C. The planes obtained confirm that the formed material is CdS (Figure 3.19-3.24) with

hexagonal crystal structure. The indices are assigned according to the literature JCPDS (41-1049) as indicated in Table 3.9. The (101) orientation is dominant but also the other main peaks indicate that the as-grown materials are CdS. At 300 °C the CdS films are more crystalline as compared to those obtained at 200 and 350 °C.



Figure 3.19 XRD pattern of CdS from [Cd(C₂H₅OCS₂)₂] at 200 °C



Figure 3.20 XRD pattern of CdS from [Cd(C₂H₅OCS₂)₂] at 250 °C



Figure 3.21 XRD pattern of CdS from $[Cd(C_2H_5OCS_2)_2]$ at 300 °C



Figure 3.22 XRD pattern of CdS from [Cd(C₃H₇OCS₂)₂] at 200 °C



Figure 3.23 XRD pattern of CdS from [Cd(C₃H₇OCS₂)₂] at 250 °C

The XRD pattern of CdS films from $[Cd(C_3H_7OCS_2)_2]$ at 200 °C (Figure 3.22) and 250 °C (Figure 3.23) are similar to the XRD of CdS from $[Cd(C_2H_5OCS_2)_2]$ at

300 °C (Figure 3.24). The XRD pattern of CdS films from $[Cd(C_2H_5OCS_2)_2]$ at 250 °C(Figure 3.23) is similar to the one at 300 °C (Figure 3.24) from $[Cd(C_3H_7OCS_2)_2]$. Both materials show that they are less crystalline as compared to others.



Figure 3.24 XRD pattern of CdS from [Cd(C₃H₇OCS₂)₂] at 300 °C

Table 3.9 X-ray data of CdS (hexagonal) thin films from $[Cd(S_2CORO)_2]$, R = Et or ⁱPr

CdS- JCPDS (41-1049) ¹⁷⁴						
hkl	d(lit)/Ấ (% I)	d(exp)/Å (% I)	hkl	d(lit)/Å (% I)	d(exp)/Ấ (% I)	
100	3.58 (75)	3.50 (67)	110	2.07 (55)	2.07 (39)	
002	3.37 (60)	3.36 (67)	103	1.89 (40)	1.90 (30)	
101	3.16 (100)	3.17 (85)	201	1.79 (18)	1.74 (26)	
102	2.45 (25)	2.40 (10)				
All the CdS films deposited at different temperatures were indexed as the hexagonal phase CdS with the characteric (100), (002), (101), (102), (110) and (200) planes visible in the XRD patterns.

The morphology of the CdS thin films were investigated by SEM.



Figure 3.25 SEM micrographs of CdS from [Cd(C₂H₅OCS₂)₂] at 200 °C

Poor coverage of the substrates is observed for deposition at 200 °C (Figure 3.25), and 250 °C (Figure 3.26) with individual spherical shape particles (Shallow circular domes randomly present on the surface).



Figure 3.26 SEM micrographs of CdS from [Cd(C₂H₅OCS₂)₂] at 250 °C

CdS films deposited from $[Cd(C_2H_5OCS_2)_2]$ at 300 °C (Figure 3.27) showed that the morphology of the films has improved. Full coverage of the substrate is observed for

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films at 300 °C. SEM images reveal that the films consist of densely packed grains. At higher growth temperature, an increase in particle size was observed. The morphology is similar to the one reported by Hasoon, *et al.*¹²⁴



Figure 3.27 SEM micrographs of CdS from [Cd(C₂H₅OCS₂)₂] at 300 °C

In conclusion, the increase in temperature resulted in markedly different surface morphology, as much finer grains than those observed in Figure 3.25 and 3.26. This shows homogenous nucleation of CdS particles.

SEM of the CdS thin films deposited from $[Cd(C_3H_7OCS_2)_2]$ at 200 °C (Figure 3.28a) is similar to CdS images at 200 (Figure 3.25) and 250 °C (Figure 3.26) from $[Cd(C_2H_5OCS_2)_2]$. At 300 °C (Figure 3.28a and 3.28b) uniform materials are observed. This further confirms that temperature plays an important role on the morphology of the films. The morphology of the films is similar to the one previously reported by Hasoon, *et al.*¹²⁴

Afzaal, *et al.*¹²⁰ deposited CdS thin films from $[Cd{N(SP^iPr_2)_2}_2]$. XRD pattern has indicated that only hexagonal CdS films were deposited with the preferred orientation along the (002) plane. SEM studies indicated that the morphology of film consists of randomly orientated domains of compacted thin acicular crystallites with ca. 1.75 µm in thickness. The results seem to indicate that ultrasonication suppresses the growth of CdS grains. There was nucleation of CdS throughout the substrate surface. The film was of denser and more uniform structures.

An EDAX profile of the films confirms the presence of cadmium and sulphur as 1.1 ratios. Similarities in the EDAX profiles between 200-300 °C suggest that the stoichiometry of the films is not affected greatly by the growth temperature.



Figure 3.28 SEM micrographs of CdS from $[Cd(C_3H_7OCS_2)_2]$ at (a) 200 °C, (b) 250 °C, and (c) 300 °C

3.4.5 The TGA analysis $[Pd(S_2COCHR_2)_2]$, R = Et or ⁱPr

The TGA analysis shows that the first decomposition step is associated with the rapid loss in weight of 44 % from $[Pd(C_2H_5OCS_2)_2]$. This is followed by a much lower decomposition step, in which there is evidence of a two step breakdown. About 58 % weight loss of the precursor is observed, leaving 42 % residue which correspond to the theoretical calculated PdS(40 %).

The TGA curve of $[Pd(C_3H_7OCS_2)_2]$ in is similar to that of ethyl palladium complex with the first decomposition step having a weight loss of 46 %. About 66 % of the precursor decomposes, leaving 37 % residue which corresponds to the theoretical calculated PdS(37 %).

3.4.6 Deposition of PdS from $[Pd(S_2COCHR_2)_2]$, R = Et or ⁱPr

Deposition of palladium sulphide thin films was carried out by AACVD between 200-300 °C. XRD shows that the $Pd_{16}S_7$ phase was deposited in this temperature region (Figure 3.29-3.31) with cubic crystal structure. The indices are assigned according to those in JCPDS 11-001. The XRD patterns of the films grown at various growth temperatures show a preferred orientation as the (222) plane regardless of the growth temperatures.



Figure 3.29 XRD pattern of Pd₁₆S₇ from [Pd(C₂H₅OCS₂)₂] at 200 °C



Figure 3.30 XRD pattern of $Pd_{16}S_7$ from $[Pd(C_2H_5OCS_2)_2]$ at 250 °C



Figure 3.31 XRD pattern of Pd₁₆S₇ from [Pd(C₂H₅OCS₂)₂] at 300 °C

Table 3.10 X-ray data	1 of Pd ₁₆ S7 (Cubic)	thin films	from	$[Pd(S_2COR)_2]$, $R = Et$
or ⁱ Pr					

$Pd_{16}S_{7}$ - JCPDS (11-0001) ¹⁷⁵					
hkl	d(lit)/Å (% I)	d(exp)/Å (% I)	hkl	d(lit)/Å (% I)	d(exp)/Å (% I)
211	3.64 (80)	3.64 (39)	422	1.82 (60)	1.82 (52)
222	2.58 (60)	2.63 (62)	510	1.74 (60)	1.73 (37)
310	2.82 (30)	2.88 (73)	521	1.62 (30)	1.63 (18)
400	2.23 (60)	2.23 (25)	440	1.57 (60)	1.60 (41)
330	2.09 (80)	2.09 (39)	530	1.53 (60)	1.55 (22)
332	1.90 (30)	1.86 (84)			

The shape of the palladium sulphide films was investigated by SEM. No images were observed at 200 °C, this is due to the amorphous nature of the palladium chalcogenide

films. The SEM of $Pd_{16}S_7$ thin films deposited at 250 °C (Figure 3.32) are dense but uneven on the substrate.



Figure 3.32 SEM micrographs of Pd₁₆S₇ from [Pd(C₂H₅OCS₂)₂] at 250 °C



Figure 3.33 SEM micrographs of Pd₁₆S₇ from [Pd(C₂H₅OCS₂)₂] at 300 °C

At 300 °C (Figure 3.33) the film is dominated by submicron grains. Gross discontinuities in the PdS films and high density of pinholes were observed.

Cheon, *et al.*¹¹⁴ prepared PdS films from $[Pd(S_2COCHMe_2)]$ and the diffraction of the films showed nonoriented polycrystalline tetragonal PdS. SEM images showed that the films were smooth with shallow circular domes randomly present on the flat surface.

3.4.7 The TGA analysis of $[Pt(S_2COR)_2]$, R = Et or ⁱPr

The TGA analysis shows that in the initial decomposition there was massive weight loss of 30 %. This is followed by a small weight loss, giving 41 % mass of the precursor decomposed, leaving about 59% residue which correspond to the theoretical calculated $PtS_2(59 \%)$. The TGA of $[Pt(C_3H_7OCS_2)_2]$ in is similar to ethyl palladium complex.

3.4.8 Deposition of Pt thin films from $[Pt(S_2COR)_2]$, R = Et or ⁱPr

Platinum thin films were deposited by AACVD between 200-300 °C. Yellow platinum films were observed. XRD patterns show that the films at 200 °C (Figure 3.34) and 250 °C (Figure 3.35) are not crystalline. Broadened peaks suggest some amorphous nature in the films; the pattern corresponds to that of Pt film.



Figure 3.34 XRD pattern of Pt from [Pt(C₂H₅OCS₂)₂] at 200 °C



Figure 3.35 XRD pattern of Pt from [Pt(C2H5OCS2)2] at 250 °C



Figure 3.36 XRD pattern of Pt from [Pt(C₂H₅OCS₂)₂] at 300 °C

The XRD of the platinum at 300 °C (Figure 3.36) from $[Pt(C_2H_5OCS_2)_2]$ reveals that the films are crystalline. From the observed values, the deposited material is indexed

3.4.10 Deposition of Co_9S_8 thin films from $[Co(S_2COR)_2]$, R = Et or ⁱPr

From the TGA analysis, both precursors are expected to be suitable for AACVD and LP-MOCVD.

Deposition of cobalt sulphide thin films was achieved by AACVD between 200-300 °C. Thin films were found to be reflective and silvery. The films were homogeneous and cover the glass substrate uniformly. The XRD patterns are shown in Figure 3.37-39 which corresponds to Co_9S_8 phase. The films had a predominant (222), (400), (600) with relatively weak intensities when compared with other diffraction peaks.



Figure 3.37 XRD pattern of Co₉S₈ films from [Co(C₂H₅OCS₂)₂] at 200 °C

At higher temperature, the degree of crystallinity of the as-deposited films improved as indicated by XRD (Figure 3.39).



Figure 3.38 XRD pattern of Co₉S₈ films from [Co(C₂H₅OCS₂)₂] at 250 °C



Figure 3.39 XRD pattern of Co_9S_8 from $[Co(C_2H_5OCS_2)_2]$ at 300 °C

All the films gave very narrow, strong peaks in the XRD patterns. The diffraction patterns observed are summarised in Table 3.12.

Table 3.12 X-ray data of Co_9S_8 (Cubic) thin films from $[Co(S_2COR)_2]$, where R = Et or ⁱPr

Co ₉ S ₈ -JCPDS (03-0631) ¹⁷⁵			
hkl	d(lit)/Á (% I)	d(exp)/Å (% I)	
311	4.10 (67)	4.29 (91)	
400	3.17 (40)	3.77 (55)	
531	2.55 (40)	2.48 (61)	
511	2.11 (60)	2.83 (23)	

The morphology of the films was investigated by SEM. At lower temperature the films are small with shallow circular domes randomly present on the flat surface.

At higher temperatures the films are smooth and featureless. The coverage is nonuniform with clustered growth predominant on the substrate. The spherical particles form clusters on the substrate.



Figure 3.40 SEM micrographs of Co₉S₈ from [Co(C₂H₅OCS₂)₂] at 200 °C

There is, however a change of morphology at 250 and 300 °C. The coverage is nonuniform with clustered growth predominant on the substrate. EDAX analysis of the as deposited films shows the presence of cobalt and sulphur



Figure 3.41 SEM micrographs of Co_9S_8 from $[Co(C_2H_5OCS_2)_2]$ at 250 °C



Figure 3.42 SEM micrographs of Co_9S_8 from $[Co(C_2H_5OCS_2)_2]$ at 300 °C

3.4.11 The TGA analysis of [Cu(C₂H₅OCS₂)₂]

TGA analysis shows that the precursor decomposed between 77-209 °C with a weight loss of 68 %, leaving 32 % which correspond to the theoretical calculated CuS(32 %).

3.4.12 Deposition of CuS thin films from [Cu(C₂H₅OCS₂)₂]

Depositions of thin films were attempted by AACVD between 200-300 °C. Very low solubility of $[Cu(C_2H_5OCS_2)_2]$ precursor in tetrahydrofuran or toluene leads to little or no deposition on the glass substrate. No images were obtained due to poor coverage of the materials on the glass substrate. A summary of the colour of the films deposited at different temperature is given in Table 3.13.

Compound	% loss(0-500 °C)	Experimental %	Theoretical %
		residue	residue(nature of
			residue)
[Ni(C ₂ H ₅ OCS ₂) ₂]	67	33	NiS(30 %)
[Ni(C ₃ H ₇ OCS ₂) ₂]	72	28	NiS(28 %)
$[Cd(C_2H_5OCS_2)_2]$	58	42	CdS(40 %)
[Cd(C ₃ H ₇ OCS ₂) ₂]	62	38	CdS(38 %)
$[Pd(C_2H_5OCS_2)_2]$	58	42	PdS(40 %)
$[Pd(C_3H_7OCS_2)_2]$	66	34	PdS(37 %)
[Pt(C ₂ H ₅ OCS ₂) ₂]	41	59	PtS ₂ (59 %)
$[Pt(C_3H_7OCS_2)_2]$	57	43	PtS ₂ (56 %)
$[Co(C_2H_5OCS_2)_2]$	63	37	CoS ₂ (41 %)
[Co(C ₃ H ₇ OCS ₂) ₂]	69	31	CoS(28 %)
$[Cu(C_2H_5OCS_2)_2]$	68	32	CuS(32 %)

Table 3.13 The TGA data of $[M(S_2COR)_2]$, R = Et or ⁱPr

Table 3.14 Metal sulfide thin film properties

Precursors	Deposition by AACVD			
	T = 200 °C	T = 250 °C	T = 300 °C	
1. Ni(S ₂ COC ₂ H ₅) ₂	Grey	Grey	Grey	
$2. Pd(S_2COC_2H_5)_2$	Black	Black	Black	
3. Pt(S ₂ COC ₂ H ₅) ₂	Shiny black	Shiny black	Shiny black	
4. Co(S ₂ COC ₂ H ₅) ₂	Shiny black	Shiny black	Shiny Black	
5. Cd(S ₂ COC ₂ H ₅) ₂	Yellow	Yellow	Yellow	
6. Cu(S ₂ COC ₂ H ₅) ₂	Insoluble	-	-	
7. Ni(S ₂ COCHMe ₂) ₂	Grey	Grey	Grey	
8.Pd(S ₂ COCHMe ₂) ₂	Black	Black	Black	
9. Pt(S ₂ COCHMe ₂) ₂	Yellow	Yellow	Yellow	
10. Co(S ₂ COCHMe ₂) ₂	Shiny black	Shiny black	Shiny black	
11.Cd(S ₂ COCHMe ₂) ₂	Yellow	Yellow	Yellow	

3.5 Conclusions

Thin films of metal sulphide were grown from the single-source precursors of the type $[M(S_2COCHR_2)_2]$, M = Ni, Pd, Pt, Cd and Co, and R = ethyl or isopropyl at low temperature under AACVD conditions. In all the samples, the $[M(S_2COR)_2, M = Pt, Pd, and Ni, R = Et X$ -ray structures adopt a square planar geometry. All the metal complexes were characterised by elemental analysis, IR, MS, ¹H NMR and ¹³ C. Thin films of NiS, CdS, Pt, PdS, Pd₁₆S₇, and Co₉S₈ were deposited by (AACVD) using the

respective metal xanthate complexes. The structural characteristics of the films were investigated by XRD, SEM, and EDAX. XRD studies show that the NiS is highly orientated rhombohedral phase. All the samples were indexed as rhombohedral NiS with characteristic XRD peaks for (110), (101), (300), (021), and (220) planes. All samples show a strong peak at 32.20 ° which is assigned to rhombohedral phase (300) diffraction. The NiS thin films are polycrystalline and their features are in good agreement with those reported in literature. The phases do not seem to be affected by temperature whereas the morphology of the films changes with temperature. In contrast the morphology of the films has been found to be greatly influenced by varying the temperature.

The morphology of the films show granular, rod-like and twinned cube shape depending on the temperature of deposition. All the samples of CdS films deposited at different temperature were indexed as the hexagonal phase. Shallow circular domes and grains were obtained by SEM. Broad peaks for Pt films were obtained and the films were indexed as cubic phase. This shows that Pt films are amorphous in nature. Poorly resolved XRD pattern of Co_9S_8 was obtained by XRD. Shallow circular domes were obtained by SEM.

 $[M(S_2COCHR_2)_2]$, M = Ni, Pd, Pt, Cd and Co, and R = ethyl or isopropyl proved to be suitable precursors, with low volatility and stability as well as adequate purity, for the film deposition. This has been demonstrated by one phase deposition.

Chapter 4

Synthesis of CdS Nanoparticles and

Nanorods

4.1. General Introduction

There has already been much progress in the synthesis, assembly and fabrication of nanomaterials, and, equally importantly, in the potential applications of these materials in a wide variety of technologies. Preparation, characterization and exploitation of nanosized materials remain the major challenges in the next decade. Nanotechnology has shown potential application in the chemical, energy, electronics and space industries.¹²⁵⁻¹²⁶

Reducing the size of solid materials to nanometric scales leads to a change in their properties. As the size of the solid becomes smaller the band gap gradually becomes larger due to quantum effects. The particle shape, size, and size distribution play important roles in determining its electrical, optical, magnetic and chemical properties.¹²⁷⁻¹²⁸ The control of the size, distribution, and shape of nanocrystals has been a primary focus of research recently.

In this chapter the synthesis of CdS nanoparticles and nanorods from $[Cd(S_2CNMe_2)_2]$ and $[Cd\{-SC(=S)OCH(CH_3)_2\}_4]$ precursors will be described. The synthetic route used is the 'one-pot' thermolysis of single-molecule precursors in a high boiling point co-ordinating solvent. The optical properties of the particles were studied using absorption and photoluminescence spectroscopy. The particles were characterized using X-ray diffraction and electron microscopy techniques.

4.2 Optical properties of nanoparticles

Quantum size effects have been observed experimentally for many nanocrystalline semiconductors.¹²⁹⁻¹³² The optical absorption spectrum of a nanocrystalline

semiconductor provides an accessible and simple method for the evaluation of quantum size effects. The absorption of a photon, leading to excitation of an electron from the valence band to the conduction band of the semiconductor along with a hole in the conduction band, is associated with the band gap energy, E_g . The absorption of photons with energy similar to that of the band gap, $hv \ge E_g$, leads to an optical transition producing an electron in the conduction band of the semiconductor along with a hole in the valence band. In the absorption process, a photon of discrete energy excites an electron from the valence to the conduction band. This absorption spectrum can be used to determine the energy gap of a semiconductor material.

For crystalline materials the electronic transitions occurring on the absorption of light are subject to certain selection rules. Besides $hv \ge E_g$, there is the additional requirement that the wave vector must be conserved.

The absorption (A) of light by a semiconductor material with thickness, I, can be described by an expression analogous to the Beer's law (eq. 4.1),

$$A = \alpha I \qquad eq. 4.1$$

where α represents the absorption coefficient of the solid and a function of the radiation frequencies.

For crystalline materials the electronic transitions occurring on absorption of light are subject to selection rules as in the molecules. The requirement, besides $hv \ge E_g$, is that the wave-vector, k, should be conserved:

$$K_e + K_{photon} = K'_e$$
 eq. 4.2

where K_e and K'_e are the electron wave vectors. K_{photon} is small when compared with the wave vectors of the electron before (K_e) and after excitation (K'_e), which leads to the conservation rule:

$$K_e = K'_e$$
 eq. 4.3

Therefore for excitation across the narrowest part of the energy gap to occur, the minimum of the conduction band must have the same vector as the maximum of the valence band. Materials with this type of electronic transition are known as direct band gap semiconductors, e.g. GaAs.



Figure 4.1 Excitation across the band gap by photon absorption: (a) direct process; (b) indirect process.¹³¹

For other semiconductors the lowest energy electronic transition between the valence band and conduction band is formally forbidden. In these indirect band gap semiconductors, e.g. Si, the transitions require the additional interaction of a photon in order that the conservation rule is maintained.

Semiconductors in which there is conservation of the wave vector for optical transitions are referred to as direct band gap semiconductors (Figure 4.1). An important parameter that determines the efficiency of the process, by which a semiconductor absorbs light photons and generates electron-hole pairs, is known as the absorption coefficient, α . The band structure of the semiconductor determines the characteristics of α , which, for direct band gap, is given by:

$$\alpha hv = \alpha_0 (hv - E_g)^n$$
 eq. 4.4

where α_0 is a constant, E_g is the energy band gap and hv is the photon energy.

Equation 4.4 gives useful expression relating the absorption coefficient and the photon energy of a direct transition near the threshold. The probability of an electronic transition occurring is greater for direct electron transitions than indirect transitions. For a direct band gap semiconductor, such as ZnO or GaAs, the minimum value of energy E (k) in the conduction band and maximum value of E (k) in the valence band coincide at the same value of k. As a result electronic transitions are most likely to occur for this configuration. Hence absorption coefficients for direct band gap semiconductors are large, e.g., 99 % of light photons with energies near the band gap of CdTe (~1.45 eV) are absorbed by a 1 µm thick layer. By comparison similar behavior by crystalline silicon (an indirect band gap semiconductor) requires

20 μ m thicknesses. In an indirect band gap semiconductor like silicon, an electron cannot be directly excited to the conduction band with energy E_g and additional energy is required in the form of lattice vibrational energy (phonons). The electron then undergoes a change in momentum and we obtain an indirect transition with energy

$$hv = E_g + E_{phonon}$$
 eq. 4.5

The optical absorption spectrum of a nanocrystalline semiconductor provides an accessible and straightforward method for the evaluation of quantum size effects. The absorption of a photon, leading to excitation of an electron from the valence band to the conduction band, is associated with the band gap energy (Eg). The absorption of photons with energy similar to that of the band gap, $hv \ge E_g$, leads to an optical transition producing an electron in the conduction band of the semiconductor along with a hole in the valence band. Absorption of photons with energy much greater than E_g leads to excitations above the conduction band edge; the electrons can lose the excess energy by radiation-less processes.¹³¹⁻¹³³

4.3 Photoluminescence

The luminescence spectra of these materials show a typical red shift in the emission in respect to the corresponding absorption spectrum. Semiconductor nanoparticles often exhibit narrow close-to-band-edge luminescence with lower energy emissions attributed to trapping states (surface-trapped carriers) and defects.¹³⁴ As the particles size decreases the surface/volume ratio increases thereby increasing the number of surface traps. These surface states or defects, normally associated with semiconductor

nanoparticles, are passivated by tri-n-octylphosphine oxide (TOPO). It is well known that the photoluminescence properties of the nanoparticles are strongly dependent on its surface states, surface passivation and size distribution. Smaller nanoparticles are expected to have an increased emission due to the increase oscillator strength. All luminescence spectra have a substantial Stoke's shifts, previously attributed to the systematic metal vacancies being effective trapping sites.¹³⁵⁻¹³⁸ Narrow band (15-20 nm), size-tuneable luminescence, with efficiencies at least of order 10 %, observed at room temperature.

4.4 Synthesis of semiconductor nanoparticles using single-molecule precursors

Several synthetic methods for the preparation of semiconductor nanoparticles have been reported.^{133, 139-147} An ideal synthetic route should produce nanoparticles that are pure, crystalline, reasonably monodispersed and have a surface, which is indecently derivatized. Particles satisfying such criteria may be useful in the fabrication of semi conducting devices. The use of single source molecular precursors has proved to be an efficient route for producing pure high quality, crystalline semiconductor nanocrystallites that are stabilized from the surrounding chemical environment by a capping agent. The fabrication of nanoparticles from single molecule precursors is a one-step process, typically carried out at temperatures in the range 200-300 °C. Trindade and O'Brien, *et al.*¹³¹ pioneered this route that has been used to synthesize nanoparticles such as [M = Zn, Cd; E = S, Se].

There is a wide range of advantages for using this method:

• One involatile precursor is involved, purification of which is easier than that of two or more volatile precursors, and hence there is less chance of the incorporation of impurities into the nanoparticles.

- The route avoids the need for volatile, sometimes toxic and/or pyrophoric precursors.
- Some II-VI and III-V nanoparticles are air sensitive. All precursor synthesis is carried out under anaerobic conditions, with the resulting precursors being air and moisture stable.
- Low temperature deposition routes are possible.
- Although there are theoretical models predicting the optical properties of semiconductor nanoparticles, the properties of nanoparticles obtained by new synthetic routes are sometimes hard to anticipate and may lead to particles with unique and unanticipated, but useful properties.



Figure 4.2 Single-source approach for preparing semiconductor nanocrystallites in TOPO.

The synthesis involves the rapid injection of precursor into a hot coordinating solvent (e.g. TOPO) to produce a homogeneous nucleation followed by growth to give surface derivatised nanocrystallites (Figure 4.2).

The use of dithio-/diseleno-carbamato complexes of cadmium/zinc containing asymmetric alkyl groups has proved to be the precursors that give nanoparticles of the highest quality.^{140, 142, 148} These precursors are non-air sensitive, stable for a period of months, and easy to prepare and pyrolyse cleanly to give the highest yield. The bis (dialkyldiseleno-carbamato)cadmium(II)/zinc(II) compounds with unsymmetrical R groups like the methyl-hexyl compound, [Cd(Se₂(NMeHex)₂], produced CdSe nanoparticles of good quality. These observations suggest that the presence of the alkyl groups determine the mechanistic pathway by which the precursor decomposes. Studies on similar compounds, which produce particulate material on thermolysis, have also shown this to be the case.¹⁴⁹ A slight change to the alkyl group drastically alters the deposition mechanistic pathway. Moreover, the mechanism by which a certain precursor decomposes is of fundamental importance to the quality of the resulting nanoparticles. TOPO-capped CdS and CdSe have been synthesized at 250 °C using [Cd(S₂CNMeHex)₂] and [Cd(Se₂CNMeHex)₂] as the precursors. The nanoparticles prepared show a blue shift in the optical spectra in relation to bulk materials. The optical spectra of CdSe shows well-defined excitonic features and the corresponding photoluminescence spectrum was Stoke's shifted in relation to the band edge.

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There have been many other types of precursors, all having the metal sulfur bond, that have been used for the synthesis of CdS nanoparticles. The closeness in structure of xanthates in relation to dithiocarbamates makes them ideal precursors for CdS nanoparticles. Cadmium ethylxanthate was thermolysed in TOPO at 160 °C to give monodispersed, spherical TOPO-capped CdS nanoparticles with an average particle size of 4.2 nm.¹¹² The thermolysis of the identical xanthate precursor in hexadecylamine (HDA) at various temperatures gave rod-shaped CdS nanoparticles.¹⁵⁰ Spherical and non-spherical MS particles (M = Cd, Zn, Pb, Hg, Ni, Cu, Mn) have also been synthesized using metal alkylxanthates in HDA.¹⁵⁰ The authors described the use of reaction time, temperature and/or concentration to achieve size and spectroscopic tunability of the particles. A cadmium(II) complex of dithiobiurea, [Cd(SCNHNH₂)₂Cl₂] has also been used to synthesize CdS nanoparticles with a narrow size distribution.¹³⁰ A comparative study of CdS nanoparticles, synthesized under similar conditions in TOPO using bis(methylhexyldithiocarbamato)-cadmium(II), cadmium ethylxanthate and a cadmium complex of dithiobiurea, revealed very little differences in the optical and structural properties of the nanoparticles. The narrow PL spectra are characteristic of emission from particles of CdS in the 3-5 nm size regime.¹⁵¹⁻¹⁵² The absorption spectra show excitonic features typical of particles in the nanosize regime. The powder X-ray patterns confirms the wurtzite phase in all samples of CdS.

Metal complexes of alkylthioureas have also proven to be very good precursors for nanoparticle synthesis. A series of cadmium(II) complexes with N-alkyl/aryl and N,N'-dialkyl/aryl thioureas (RNHCSNHR'; where $R = R' = CH_3$, CH_2CH_3 , C_6H_5

al.¹⁵³⁻¹⁵⁴. and/or R'=H) were synthesized by Moloto, et The $[CdCl_2(CS(NH_2)NHCH_3)_2]$, $[CdCl_2(CS(NH_2)NHCH_2CH_3)_2]$ and $[CdCl_2(CS(NH_2)_2]$ complexes were thermolysed in TOPO at 200 °C to give CdS with crystallite sizes of 4.8 nm, 4.3 nm and 32.2 nm from the respective complexes.¹⁵⁴ There was evidence of agglomeration in all samples from the TEM measurements. Mono- and di-substituted alkylthiourea complexes of lead and copper have been used to prepare PbS and Cu_xS_y nanoparticles.¹⁵⁴ The X-ray diffraction pattern of the PbS confirms a cubic rock-salt phase, with the particles having a predominantly truncated octahedral shape. The copper alkylthiourea complex was added directly into the hot TOPO to give a mixture of nanoparticles suspended in solution and bulk material, which settle at the bottom of the reaction flask. The XRD pattern of the nanoparticles gave a mixture of sulfides of two major stoichiometries, Cu₁₈S (digenite) and Cu₃₁S₁₆ (djurleite). The TEM images showed well defined, triangular and hexagonal shaped particles.

4.5 Shape Control of Nanoparticles

One of the recent trends in nanomaterials research is the control of particle shape. The shape of semiconductor nanocrystals does have significant effect on their electronic, magnetic, catalytic and electrical properties.¹⁵⁵⁻¹⁵⁸ Metal chalcogenides such as CdSe, CdS and PbS remain materials of considerable interest in shape control due to their wide variation in one dimensional morphology with changes in reaction conditions.

For a given solution in the synthesis of nanocrystals one could obtain a variety of shapes, e.g. dots, rods, spindles and tetrapods. As the size of the nanoparticles

decreases to their Bohr radius, all the electronic properties begin to change. In this size regime the properties become dependent not only on size but also on their shape. For example if an electron-hole pair (exciton) is formed in a sphere with zero degrees of freedom, the system is known as a "quantum dot". In this system the exciton is confined in all three dimensions (x, y, z). If the particle is elongated, for example along the c-axis, the exciton formed will still be confined in the x and y direction (a and b) but can be transported along the z, exhibiting the rod-like structure. This suggests that it is confined in two directions but can move along the z-axis and equally extended in x and y (e.g. nanodisks), the exciton's motion is confined in one direction but has room to move along x and y. These are referred to as 2-D structures.

Colvin, *et al.*¹⁵⁹ reported the observance of tetrapod and rod-like morphologies of CdSe and CdTe. The influence of temperature, monomer concentration, reaction time and capping group on the particle morphology was also studied by Li *et al*¹⁵⁰. It was found that the thermolysis of cadmium ethylxanthate in hot hexadecylamine (HDA) gave rod or spherical shape particles depending on the reaction conditions. Moderate temperatures (< 200 °C), high monomer concentration and long reaction times (3 h) gave long multi-armed nanorods. An increase in temperature (260 °C) induced the formation of short single-armed rods. Recently the thermolysis of an *N*-alkyldithiocarbamato complex of cadmium in HDA gave 1-D CdS nanostructures (single-rods, bent rods or multi-rods) at moderate to high temperatures ¹⁶⁰. The shape of the nanocrystals varied from longer rods to shorter rods with increased

width by simply increasing the quantity of precursor in the bulk solution from 0.05 g/8 mL HDA to 1g/8 mL HDA at 250 °C.

4.6 General Applications of nanoparticles

Research on nanomaterials has found promising technological applications in many different areas such as microelectronic devices, photo catalysis, eletrocatalysis, biomedicine, and chemical processes.¹⁶¹

4.6.1 Medical and pharmaceutical

Nanomedicine could improve the health and well being of the entire population. Medical technologies provide early detection and diagnosis of diseases or illnesses and enable targeted delivery of pharmaceuticals, nutraceuticals, gene therapy, and sensors; bioengineered tissues to replace damaged or diseased tissues.¹⁶²

4.6.2 Drug delivery systems

Shrinking machines down to the size where they can be inserted into the human body in order to detect and repair diseased cells is a popular example for the benefits of nanotechnology. Machine systems will be able to sense and rearrange patterns of molecules in the human body, providing the tools needed to bring about a state of health, regardless of a disease's cause.

Current medical applications of nanotechnology are far more likely to involve improved delivery methods, such as pulmonary or epidermal methods to avoid having to pass through the stomach, encapsulation for both delivery and delayed release, and eventually the integration of detection with delivery, in order for drugs to be delivered exactly where they are needed, thus minimizing side effects on healthy tissue and cells. As far as navigation goes, delivery will be by exactly the same method that the human body uses, going with the flow and `dropping anchor' when the drug encounters its target. ¹⁶³

4.6.3 Health monitoring

Several nano-devices are being developed to keep track of daily changes in patient's physiological variables such as the levels of glucose, of carbon dioxide, and of cholesterol, without the need for drawing blood in a hospital setting. This way, patients suffering from diabetes would know at any given time the concentration of sugar in their blood; similarly, patients with heart diseases would be able to monitor their cholesterol levels constantly.¹⁶⁴

Detecting cancerous tumors when they are only a few cells in size. Nanoparticles are targeted to cancer cells for use in the molecular imaging of a malignant lesion. Large numbers of nanoparticles are safely injected into the body and preferentially bind to the cancer cell, defining the anatomical contour of the lesion and making it visible. These nanoparticles give us the ability to see cells and molecules that we otherwise cannot detect through conventional imaging. The ability to pick up what happens in the cell to monitor therapeutic intervention and to see when a cancer cell is mortally wounded or is actually activated is critical to the successful diagnosis and treatment of the disease.

4.6.4 Disease diagnosis and screening

Nanoparticles can be used to pinpoint harmful bacteria in body scans. A new nanoparticle test for dangerous bacteria such as Escherichia coli was found to be more sensitive in such a way that it could detect a single bacterial cell within minutes. An injection of magnetic nanoparticles into bloodstream could reveal precisely where harmful viruses are lurking. The particles are coated with antibodies to a particular virus, so they will form clumps that should be visible on conventional body scans if

that virus is present.¹⁶⁵

4.6.5 Food processing and storage

Waiting a day or two (Test and Hold) for results in food industry can be costly and inconvenient. This can be obviously expensive for industry having large quantity of stock. The nanoparticles are added to a solution of the test sample, such as ground beef. If the bacterium sought is present the nanoparticles will quickly attach to it. The sample is then separated by weight in a centrifuge. The target bacteria, being heavier than the nanoparticles, will separate away from them. But those dye molecules already attached will fluoresce in this heavier sample, identifying the bacteria. ¹⁶⁶

4.6.6 Energy storage, production and conversion

Semiconductor nanoparticles have shown great promise in the photonics applications, such as solar cells and light emitting devices, because the wavelength response of the device can be tuned by simply varying the size of the quantum dot.¹⁶⁷ Nanoparticles are used in solar energy conversion. Today's solar panels are made with silicon. The
silicon usually has impurities, which limits its efficiency. Purifying a chemical is too expensive. For that reason, smaller is better.

4.6.7 Construction

Nanomaterials make asphalt and concrete more resistant to water; materials to block ultraviolet and infrared radiation; materials for cheaper and durable housing, surfaces, coatings, glues, concrete, and heat and light exclusion; and self-cleaning for windows, mirrors and toilets.¹⁶⁸

4.6.8 Electronic, Optical and Magnetic applications

Nanomaterials exhibit a great potential applicability in electronic systems. The wide band gap II/VI semiconductors are of current interest for optoelectronic applications such as blue lasers, light emitting diodes, and optical devices based on nonlinear properties. Group II and VI quantum dots will be used in future photonic applications such as solar cells and light emitting diodes, because the wavelength responses of the devices can be tuned by simply varying the size of the quantum dots. Cadmium chalcogenides are also useful material in solid-state photoconductors, field effect transistors, sensors, and transducer. The properties of the nanoparticles change as the size changes and of those properties is the part of the light spectrum it absorbs. ZnSe and ZnS materials are used in blue/blue-green lasers. Zinc sulphide has been used widely in the fields of displays, sensors and lasers.¹⁴⁸ Cadmium selenide fluorescing particles are used in biological labels alongside, or even replacing, fluorescing molecular probes.^{149, 169}

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4.6.9 Data storage

Group 15 chalcogenides are used in a range of applications e.g. semiconductors, optical data storage media, electro-active materials, thermoelectric coolers and photodiode arrays. Miniaturised data storage systems with the necessary long-term stability and capacity comparable to the stock of national libraries, PCs with the power of today's computer centres, minidisks, which contain e.g. all classical music records, minichips, which contain e.g. all classical music reaction chains, and light weight plastic windows with hard transparent protective layers or bearings without lubricant for the automobile industry.¹⁷⁰

4.6.10 Catalysis

These materials have possible future applications as photo catalysts in photoreactions. Nanocrystalline TiO₂ finds widespread applications in photo catalysis, solar energy conversions, ductile ceramics, sensors and mesoporous membranes.¹⁷¹

4.6.11 Agriculture

Nanotechnological materials are in development for the slow release and efficient dosage of fertilizers for plants and of nutrients and medicines for livestock. Other agricultural developments include nano-sensors to monitor the health of crops and farm animals and magnetic nano-particles to remove soil contaminants.¹⁶⁴

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4.7 Experimental

4.7.1 Materials

All chemicals used were of analytical grade quality and were used without further purification. Deionized water was used for all experimental work. Tetramethyl thiuram disulfide (97 %, Aldrich), 2,5 dimercapto-1,3,4, thiadiazole (98 %, Aldrich), isopropyl xanthic disulfide (95 %, Aldrich), methanol; toluene; hexadecylamine (HDA, 90 %, Aldrich); tri-*n*-octylphosphine oxide (TOPO, 90 % Aldrich), tri-*n*-octyl phosphine (TOP, 99 %, Aldrich); potassium tetrachloroplatinate(II); potassium tetrachloropalladate(II); cadmium chloride; and cobalt hexahydrate; cobalt(II) chloride (98 %, Fluka Chemika); copper(II) nitrate hydrate (95 %, BDH); cadmium chloride anhydrous; cadmium chloride (99 %, Aldrich).

4.7.2 Synthesis of Precursors

4.7.2.1 Synthesis of [Cd(S₂CNMe₂)₂]

[Cd(S₂CNMe₂)₂] was prepared by refluxing {(CH₃)₂NCS₂}₂ (1 g, 4.16 mmol) and CdCl₂.H₂O (0.837 g, 4.16 mmol) in deionised water for 3 h. The resulting precipitate was vacuum filtered. The product was washed several times with water followed by methanol and dried at room temperature. The resulting product is slightly soluble in various solvent. The product can be obtained in high purity without further purification. Yield: 0.105 g, 72 %. MP = 367 °C. C₆H₁₂N₂S₄Cd: Mol. Mass, 353.44; Anal. Calcd: C, 20.45; H, 3.41; N, 7.90. Found: C, 20.35; H, 3.54; N, 7.88. FT-IR (KBr disc): v (C-N) 1219(s); δ (C-S) 941(m). MS: m/z = 352 correspond to [M + H]⁺.

4.7.2.2 Synthesis of [Cd{-SC(=S)OCH(CH₃)₂}₄]

[Cd{-SC(=S)OCH(CH₃)₂}₄] was synthesized by dissolving [-SC(=S)OCH(CH₃)₂]₂ (1 g, 3.6 mmol) and Cd(CH₃COO)₂ (0.74 g, 3.7 mmol) in ethanol and refluxing the mixture for 24 h. The precipitate was washed (3 x 10 mL) with methanol. The resulting precipitate was vacuum filtered and dried at room temperature. Yield: 1.68 g, 72 %. MP = 70 °C. $C_{16}H_{28}O_4S_8Cd$: Mol. Mass, 652; Anal. Calcd: C, 29.40; H, 4.29; S, 39.26. Found: C, 29.66; H, 4.68; S, 36.78.

4.7.3 Preparation of nanoparticles

4.7.3.1 Synthesis of CdS Nanoparticles from [Cd(S₂CNMe₂)₂] in Tri-noctylphosphine oxide (TOPO)

[Cd(S₂CNMe₂)₂] (0.5 g, 1.42 mmol) was dispersed in TOP (10 mL) and then injected into hot TOPO (30 g, 78 mmol) at 250 °C. A decrease in temperature of 20-30 °C was observed. The reaction was allowed to continue for 45 min. The solution was allowed to stabilize at 250 °C. A sample was syringed after 5, 10, 20, 30 and 45 min for UV analysis. After completion of the reaction, methanol was added to the cooled mixture (70 °C), to flocculate the nanoparticles. The solid was separated by centrifugation, washed three times with methanol. The resulting yellow solid precipitate, TOPO capped CdS nanoparticles, were dispersed in toluene. The solution was centrifuged and the resulting precipitate was dissolved in toluene.

4.7.3.2 Synthesis of CdS nanoparticles from [Cd(S₂CNMe₂)₂] in hexadecylamine (HDA)

HDA (6.25 g, 25 mmol) was loaded into a reaction flask and then heated to 240 °C under a nitrogen flow. $[Cd(S_2CNMe_2)_2]$ (0.5 g, 1.42 mmol) was dispersed in 5 mL

TOP and the solution was rapidly injected into a hot solution of HDA (240 °C). After mixing the solution turns yellow rapidly. Heating was continued to recover the temperature and the reaction was maintained for a 30 min. The solution was cooled gradually under ambient condition to a *ca*. 70 °C and an excess of methanol was added. The flocculant precipitate formed was centrifuged and the upper-layer was decanted, then the isolated solid was dispersed in toluene. The above centrifugation and isolation procedure was then repeated three times for the purification of the prepared CdS nanocrystals.

4.7.3.3 Synthesis of CdS nanoparticles from $[Cd{-SC(=S)OCH(CH_3)_2}_4]$ in HDA $[Cd{-SC(=S)OCH(CH_3)_2}_4]$ (0.5 g, 0.77 mmol) was dissolved in TOP (10 mL) and injected into hot HDA (30 g, 78 mmol) at 200 °C. The reaction was allowed to continue for 45 min. A decrease in temperature of 20-30 °C was observed. The solution was allowed to stabilize at 200 °C. After completion of the reaction, methanol was added to the cooled mixture (70 °C), to flocculate the nanoparticles. The solid was separated by centrifugation, washed three times with methanol. The resulting yellow solid precipitate, HDA capped CdS nanoparticles were dispersed in toluene. The solution was centrifuged and the resulting precipitate was dissolved in toluene.

4.8 Results and discussion

4.8.1 Synthesis of CdS nanoparticles from [Cd(S2CNMe2)2] in TOPO

The TGA curve shows that the complex decomposed between 302-370 °C (Figure 4.3) with a weight loss of 68 %.



Figure 4.3 TGA curve of [Cd(S₂CNMe₂)₂]

4.8.1.1 Optical and structural properties

The onset of absorption in the UV spectrum of semiconductor nanoparticles is attributed to the band gap absorption. The band gap of particles in the nanometer size regime is blue shifted (shift to shorter wavelengths) relative to the bulk materials counterpart because of quantum confinement. The particle growth was monitored by measuring the optical absorption spectrum of samples withdrawn at various time intervals from the reaction vessel. The spectra of all CdS samples isolated at various time intervals give features of an ideal sample having particles of narrow size and uniform size distribution



Figure 4.4 Optical absorption spectra of CdS nanoparticles

The band gaps of all the samples (5-45 min) show blue shift in relation to bulk CdS (515 nm, Figure 4.4). The absorption edges for the samples are as follows: 5 min (468 nm, 2.60 eV); 10 min. (473 nm, 2.57 eV); 20 min (486 nm, 2.51 eV); 30 min (495 nm, 2.46 eV) and 45 min (500 nm, 2.44 eV). The shift in the band edge to the red is observed with increase in time from 5 min to 45 min, an indication of the increase in particle size. An excitonic peak is seen at *ca*. 460 nm typical of CdS. The increase in particle size with time is consistent with an Ostwald ripening process.¹⁷²

The photoluminescence spectra of all samples (5-45 min) were very poor. The emission peaks were broad in the 500-700 nm regions. The emission is probably due to recombination from surface defects (predominantly sulfur vacancies).

4.8.1.1 Structural Characteristics

X-ray diffraction spectroscopy is used to study the crystallinity of the nanoparticles. Typically the XRD pattern has broad peaks, an indication of the nanometric size of the particles. The XRD pattern shows that the CdS nanoparticles are crystalline with a predominantly hexagonal phase (Figure 4.5).



Figure 4.5 XRD pattern of TOPO capped CdS nanoparticles from [Cd(S₂CNMe₂)₂]

The CdS (110), (103), and (112) planes of wurtzite CdS are clearly distinguishable shown in Figure 4.5.

Table 4.1 X-Ray data of CdS (hexagonal) nanoparticles from [Cd(S₂CNMe₂)₂]

CdS- JCPDS (06-0314) ¹⁷⁶					
hkl	d(lit)/Á (% I)	d(exp)/Á (% I)	hkl	d(lit)/Ấ (% I)	d(exp)/Ấ (% I)
100	3.58 (75)	3.56 (65)	110	2.07 (55)	2.06 (48)
002	3.37 (60)	3.36 (86)	103	1.89 (40)	1.89 (35)
101	3.16 (100)	3.16 (83)	112	1.76 (45)	1.75 (41)
102	2.45 (25)	2.42 (20)			·

The morphology of the as prepared CdS sample was investigated by transmission electron microscopy (TEM). The TEM image (Figure 4.6) shows monodisperse, close to spherical TOPO-capped CdS particles. There is evidence of some agglomeration of the particles in the TOPO matrix. The particle size is in ca. 3-5 nm size range. The determination of the size distribution is difficult as a result of the aggregation.



Figure 4.6 TEM images of CdS nanoparticles capped by TOPO

4.8.2 Synthesis of CdS nanoparticles from [Cd(S₂CNMe₂)₂] in HDA

A similar procedure for the preparation from the precursor was used as described in

4.3.1. TOPO was replaced by HDA as a solvent.

4.8.2.1 Optical and structural properties

The shape of the band edge of the HDA capped CdS sample is similar to that of the TOPO capped sample. The band edge is observed at 480 nm, a blue shift of 35 nm in relation to the bulk material (Figure 4.7). The blue shift is indicative of size quantization.



Figure 4.7 Optical absorption spectra of HDA capped CdS nanoparticles

The photoluminescence spectrum of CdS is red shifted in relation to the corresponding absorption spectra, exhibiting an emission maximum at 520 nm ($\lambda_{exc.}$ = 480 nm) in Figure 4.8. This stokes shifted band edge luminescence has been attributed to emission from a "dark exciton".¹³⁶⁻¹³⁸ The broad emission is due to the broad size

distribution of the particles. There is some evidence of emission trap from trap states in the 480-530 nm region.



Figure 4.8 PL spectra of HDA capped CdS nanoparticles

4.8.2.2 Structural Characteristics

The XRD pattern of the particles can be indexed to hexagonal CdS with strong (110), (103), and (112) reflections in Figure 4.9. The peaks are sharper than those observed for spherical CdS nanoparticles in TOPO in Figure 4.5.



Figure 4.9 XRD pattern of CdS from [Cd(S2CNMe2)2] in HDA

The TEM micrographs (Figure 4.10) of the HDA capped CdS shows particles that are in the shape of rods. This is in contrast to the TOPO capped particles which are spherical. The particles have an average length 40 nm and breadth of 16 nm. The particles are close to monodisperse with an aspect ratio of ± 3 . There are many two and three arm rod shaped structures with some tetrapods also observed. The sharper XRD peaks are also evidence of larger (or rod shaped) particles. The observance of rod shaped particles in HDA was also reported by Li, *el al.*¹⁵⁰, used cadmium xanthate as a precursor.





Figure 4.10 TEM of HDA capped CdS nanorods from [Cd(S₂CNMe₂)₂]

HDA absorbs selectively with its amine on the surface of the CdS favoring the formation of anisotropic or elongated morphology and appreciable mobility as compared with TOPO.¹⁵⁰ TOPO is known to bind very strongly to the surface of the crystal preventing elongated growth, therefore there are no reports of rod shaped particles in TOPO. The tetrapod structures are formed when the wurtzite rods (or arms) form out of the (111) faces of the original zinc blende nucleus.

4.8.3 Preparation of CdS nanoparticles from [Cd{-SC(=S)OCH(CH₃)₂}₄] in HDA

The TGA for the $[Cd{-SC(=S)OCH(CH_3)_2}_4]$ complex shows a multistep decomposition (Figure 4.11).



Figure 4.11 TGA curve of [Cd{-SC(= S)OCH(CH₃)₂}₄]

4.8.3.1 Optical and structural properties

The absorption spectrum exhibits an excitonic shoulder at *ca.* 330 nm with the band edge observed at 510 nm giving a weak emission peak (Figure 4.12).



Figure 4.12 Optical absorption spectra of CdS nanoparticles from

 $[Cd{-SC(=S)OCH(CH_3)_2}_4]$

4.8.3.2 Structural Characteristics

The XRD pattern shows the presence of the characteristic (002), (110), and (112) planes indexed to the hexagonal phase of CdS (Figure 4.13). The narrow peaks at (100), (002) and (101) show that these nanocrystals are elongated towards the c-axis. The sharpness and strength of the diffraction peaks suggests that the particles are crystalline.



Figure 4.13 XRD pattern of CdS nanoparticles from [Cd{-SC(= S)OCH(CH₃)₂}₄]

The TEM images show particles that are rod shaped. The rods are slightly shorter than those obtained using the $[Cd(S_2CNMe_2)_2]$ precursor in Figure 4.9. The average length is 18 nm and average breadth is 10 nm (Figure 4.14). There appears to be spherical particles on the TEM grid, however this shape is probably due to particles lying 'upside down' on the grid. The rods are similar to the one reported by Christian *et al*.¹⁷³ The rod-like morphology were predominant with rod diameters of 7 nm, and aspect ratios of ±3.





Figure 4.14 TEM images of HDA capped CdS nanorods from [Cd{-SC(= S)OCH(CH₃)₂}₄]

4.9 Conclusions

 $[Cd(S_2CNMe_2)_2]$ and $[Cd\{-SC(= S)OCH(CH_3)_2\}_4]$ were used as single molecule precursors for the preparation of nanoparticles and nanorods in HDA and TOPO. It was difficult to recrystallize the cadmium complexes due to their low solubility. The optical absorption spectra show blue shift in the band gap of the CdS nanoparticles. The photoluminescence obtained shows very poor results. The hexagonal phase of CdS was observed for all the CdS samples using powder X-ray diffraction. The TEM images reveal that the TOPO capped CdS nanopaticles have a spherical shape whereas the HDA capped particles were rod shaped.

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