Novel Precursors for Chalcogenide Materials

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<td>APCI</td>
<td>Atmospheric Pressure Chemical Ionisation</td>
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<td>BE</td>
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<td>sccm</td>
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<tr>
<td>SQUID</td>
<td>Superconducting Quantum Interference Device</td>
</tr>
<tr>
<td>'BuOK</td>
<td>tertiary potassium butoxide</td>
</tr>
<tr>
<td>TEM</td>
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<tr>
<td>THF</td>
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<td>TMEDA</td>
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<td>XPS</td>
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<td>XRD</td>
<td>X-ray Diffraction</td>
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<tr>
<td>ZFC</td>
<td>Zero Field Cooled</td>
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Abstract

Metal chalcogenides (sulfides, selenides and tellurides) are materials of current interest due to their properties such as optoelectronic, magnetooptic, thermoelectric and piezoelectric displays. These semiconducting materials have potential applications in solar cell devices, infrared detectors and ambient thermoelectric generators. Previously, these materials have been deposited by multiple-source precursor route with several problems associated with this technique.

This work describes the synthesis of metal complexes (Zn, Cd, Fe, Ni, Pd, Pt) using the imidodichalcogenodiphosphinate ligand. Their thermal decomposition together with structural and spectroscopy analysis was carried out. The complexes were used as single source precursors for the deposition of cadmium selenide, cadmium phosphide, cadmium sulfide, zinc selenide, iron selenide and the tellurides of nickel, palladium, platinum and iron as thin films and powders. These were deposited by AACVD and pyrolysis. The deposited thin films and powders were characterised by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX), X-ray photoelectron spectroscopy (XPS) and superconducting quantum interference device (SQUID).

The cadmium complexes \([\text{Cd}\{\text{Pr}_2\text{P(Se)NP(Se)}\text{Pr}_2\}\text{]_2}\) and \([\text{Cd}\{\text{Pr}_2\text{P(S)NP(Se)}\text{Pr}_2\}\text{]_2}\) deposited the mixture of hexagonal CdSe and monoclinic \(\text{Cd}_2\text{P}_3\) films at the flow rate of 160 sccm at 475 and 500 °C. At the flow rate of 240 sccm, only hexagonal CdSe was deposited from \([\text{Cd}\{\text{Pr}_2\text{P(Se)NP(Se)}\text{Pr}_2\}\text{]_2}\) at all temperatures. Hexagonal CdS and the mixture of orthorhombic \(\text{Cd}_6\text{P}_7\)/cubic \(\text{Cd}_7\text{P}_{10}\) were deposited from \([\text{Cd}\{\text{Pr}_2\text{P(S)NP(S)}\text{Pr}_2\}\text{]_2}\). The zinc complexes \([\text{Zn}\{\text{Pr}_2\text{P(Se)NP(Se)}\text{Pr}_2\}\text{]_2}\) and \([\text{Zn}\{\text{Pr}_2\text{P(S)NP(Se)}\text{Pr}_2\}\text{]_2}\) both deposited cubic ZnSe at all temperatures with the flow rates of 160 and 240 sccm.

The iron complexes \([\text{Fe}\{\text{SePPh}_2\text{N}\}\text{]_2}\) and \([\text{Fe}\{\text{SePPh}_2\text{NPPh}_2\text{S}\}\text{N}\}\text{]_2]\) deposited orthorhombic FeSe\(_2\) mixed with monoclinic Fe\(_3\)Se\(_4\) by pyrolysis at 500 and 550 °C. An unresolved pattern was observed from the complex \([\text{Fe}\{\text{SePPh}_2\text{NPPh}_2\text{S}\}\text{N}\}\text{]_2]\) at 550 °C. XPS analysis of the deposited FeSe\(_2\) showed the surface oxidation of the material, while the magnetic measurements on the sample using SQUID confirmed its ferromagnetic properties.

The telluride complexes of nickel, palladium, platinum and iron deposited the metal telluride respectively as: hexagonal NiTe, hexagonal PdTe, hexagonal PtTe\(_2\) (mixed with rhombohedral PtTe) and hexagonal FeTe\(_2\). Conductivity studies on NiTe and PdTe revealed them to be insulators, while the magnetic measurements on FeTe\(_2\) indicated its antiferromagnetic behaviour.
Declaration

I hereby declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of the University of Manchester or any other University or institute of learning.

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Temidayo Timothy Oyetunde
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To Dad, Mum, Siblings, Relatives and all well wishers
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Chapter 1 Introduction

1.1. Classification of Solids

Solids can be classified based on the extent of their ability to conduct electrical current as: conductors, semiconductors or insulators. Before there can be current flow in solids, electrons must be able to move to new energy states. This means that empty states must be available to electrons. The empty states are allowed energy states that are not already occupied by electrons. As an example, if there are relatively few electrons in an empty band, there are other available unoccupied states into which the electrons can move.\(^1\)

The electronic properties of solid materials can be explained by band theory. This originates from the behaviour of atomic orbitals in infinite structures, having sufficient overlap between orbitals resulting in the formation of effectively continuous bands.\(^2\) The electrical properties of solid materials are a consequence of their band structure. This is their width, the number of electrons they hold, and the number of electrons in the whole system. Metals, semiconductors and insulators differ solely on their respective band structures and the size of the energy gap between full and empty bands. The expansion of quantum mechanical theory which

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\(^1\) For a detailed explanation of how empty states allow for current flow, see Chapter 1.1. Classification of Solids.

\(^2\) For a comprehensive review of band theory, consult the latest edition of the textbook "Introduction to Solid State Physics."
governs the interaction of atomic orbitals on neighbouring atoms results in energy bands. When identical atoms are separated by a large distance i.e. in isolation, they have identical energy levels available to the electrons associated with them. These energy levels are called degenerate. As the separation decreases, the energy level splits since no two electrons can possess identical quantum numbers (based on Pauli’s exclusion principle). When a number, \( N \), of atoms having degenerate energy levels are in close proximity (for instance in a crystal lattice), the \( N \)-fold degenerate energy levels are split into \( N \) discrete energy levels, half with higher energy and half at lower energy than the component atomic orbitals. Hence as the number of atoms and the resultant energy levels increases, the energy gap between levels is proportionately smaller. In systems having many atoms, the energy levels are closer to one another and form a continuum of energy levels called electronic band.

For solids at 0 K, four different types of band structures can be identified. The band gap \((E_g)\) is the energy difference between the lowest conduction band (conduction band edge) and the highest point of the valence band (valence band edge). The energy corresponding to the highest filled state at 0 K is called the Fermi energy, \((E_f)\). In an insulating material, all the electrons are in the valence band with no electrons in the conduction band. Hence, the band gap is of high magnitude to allow promotion of electrons into the conduction band [Fig 1.1(a)]. For semiconductors, the Fermi level is within the same bandgap as for insulators, but the bandgap is smaller than that of an insulator [Fig 1.1(c)]. Consequently, electrons are able to acquire sufficient energy to migrate into the conduction band through a variety of mechanisms which includes ambient thermal energy. The exact position is then determined by the conductivity type and the level of doping in the semiconductor. Insulators have wide bandgaps probably 3 eV or more, while that of semiconductors ranges from 2.5 eV to 0.1 eV. Quite often, this lies within the energy
range consisting of the IR-VIS-UV region of the electromagnetic spectrum. In the
electron band structure for conductors (metals) [Fig. 1.1(b)] e.g. copper, their
outermost band is partially filled with electrons which are able to move freely.
Electron conduction is possible because of the availability of the single $s$
valence
electron of the 4s band, being half-filled. Another variety of this conductivity is
found in metals such as magnesium, in which there is an overlap of an empty band
and a filled band. An isolated magnesium atom has two 3s electrons, but when a
solid is formed, there is an overlap between the full 3s and the empty 3p band$^{1-4}$.

1.2. **Semiconductors**

Semiconductors are solid-state materials containing a relatively smaller
number of current carriers which are intermediate between conductors and insulators.
The fundamental differences in these materials can be explained in terms of their
conduction mechanisms$^5$. At absolute zero, semiconductors behave as insulators
because of the insufficient thermal energy for electrons promotion to the conduction
band. However in metals, the bands overlap which form a continuum and leads to
high electron mobility, hence high conductivity. At elevated temperatures, the
conductivity of metals decreases because of the scattering of carrier electrons due to
electron-photon collisions. On the contrary for semiconductors, there is the
promotion of electrons to the conduction band which results in an increased
electronic conductivity since the charge carriers are thermally generated.
<table>
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<th>Compound</th>
<th>Band-Gap&lt;sup&gt;a&lt;/sup&gt; (eV)</th>
<th>Type&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Structure</th>
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<td>1.11</td>
<td>i</td>
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<td>d</td>
<td>Zinc blende</td>
<td>6.101</td>
<td></td>
</tr>
<tr>
<td><strong>IV-VI</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbS</td>
<td>0.37</td>
<td>d</td>
<td>NaCl</td>
<td>5.936</td>
<td>Infrared sensors</td>
</tr>
<tr>
<td>PbSe</td>
<td>0.26</td>
<td>d</td>
<td>NaCl</td>
<td>6.124</td>
<td>Infrared sensors</td>
</tr>
<tr>
<td>PbTe</td>
<td>0.29</td>
<td>d</td>
<td>NaCl</td>
<td>6.460</td>
<td>Infrared sensors</td>
</tr>
</tbody>
</table>

Table 1.1. Properties of some compound semiconductors. <sup>a</sup> At 300 K. <sup>b</sup> d, direct; i, indirect.
The majority of important semiconducting materials are isoelectronic with elemental silicon, since silicon (Si) and germanium (Ge) are examples of elemental semiconductors [Table 1.1]. Compound semiconductors are solids consisting of two or more elements which displays semiconducting properties and can be classified as follows: (i) 2-elements, binary system (ii) 3-elements, ternary system (iii) 4-elements, quaternary system. The most important semiconductor materials include the III-V (13-15) materials e.g. GaAs, InP and II-VI (12-16) materials e.g. CdS, ZnSe.

<table>
<thead>
<tr>
<th>Group 12</th>
<th>Group 13</th>
<th>Group 14</th>
<th>Group 15</th>
<th>Group 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>C</td>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
</tr>
<tr>
<td>Cd</td>
<td>In</td>
<td>Sb</td>
<td>Te</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.2. Elements involved in semiconducting properties**

Often, the compound semiconductor materials are formed by combining elements displaced on either side of silicon by one place (e.g. III = Ga or In and V = N or As for a III-V material) or two places (e.g. II = Zn or Cd and VI = S, Se or Te for a II-VI material) in the periodic table. There are other materials which are of specialist importance e.g. ternary materials such as CuInE₂ (E = S and Se) which are applicable in solar cell technologies as are III-VI materials like InₓSᵧ. The properties of these materials are complicated due to the possibility of forming a wide range of similar phases. An important feature of compound semiconductors is their wider band range than that of elemental silicon. Hence, they cover a wider range of the electromagnetic spectrum especially, the visible region.
1.2.1 Intrinsic Semiconductors

Intrinsic semiconductors are chemically pure materials having electrical conductivity because of crystal defects or thermal excitation. These include some chemically pure elements such as Si, Ge, Se, Te and chemical compounds like GaAs, InSb, InAs etc. For example, silicon crystals are formed by covalent bonding of atoms in a diamond structure. In a silicon atom, the covalent bonds are formed by sharing electrons between the central atom and the nearest four neighbours around it. Since the central silicon atom has four electrons in the outer shell, it requires extra four electrons from its neighbours to complete the bond formation. Hence, the shared electrons complement the original four which results in eight electrons in the outermost shell of silicon.\(^1\)

![Fig. 1.2. Electrons and holes in an intrinsic semiconductor.](image)

At absolute zero, an intrinsic semiconductor e.g. a dielectric, has zero conductivity because the valence band is fully filled i.e. no available free states and the conduction band lies above the valence band at a distance \(E_g\) which is empty. At elevated temperatures, thermal excitation of the electrons of the valence band occurs and a fraction of the valence electrons jump to the conduction band. Thus, electrons appear in the conduction band and free levels available for valence electrons in the...
valence band. The electron migration creates a hole, which has a positive charge carrier in its vacant site. Valence electrons from the neighbouring atoms jump to the vacant site and transfer the hole to the position where the electron came (Fig. 1.2.). Under the influence of an applied electric field, electrons in the valence band are now able to make a transition to free levels and produce electric current. The applied external field causes the electrons in the conduction band and valence band to move in an ordered manner (Fig. 1.3.).

\[ E \]

![Diagram](image)

**Fig. 1.3.** The movement of electrons in the conduction band and of holes in the valence band of a semiconductor under the influence of an applied electric field \( E \).

Hence, the electron-hole pair formation results in electrical conductivity in the crystal. Therefore, the current carried by the holes coincide both in magnitude and direction with that produced by the electrons in their respective bands. Examples of intrinsic semiconductors include elemental semiconductors e.g. Si, Ge and compound semiconductors of two or more elements e.g. CdS, GaAs, CuInS\(_2\).
1.2.2 Extrinsic Semiconductors

Extrinsic semiconductors are doped semiconductors. These are semiconductors in which impurities (dopants) have been added through the process of doping. Intrinsic semiconductors do contain impurity atoms which make their own energy levels called impurity levels. These can be found in both the allowed and forbidden bands of a semiconductor at various distances from the top of the valence band and the bottom of the conduction band. At times, impurities are added intentionally to a semiconductor to produce desired properties. Through doping, two types of extrinsic semiconductors can be identified and this is based on the type of carrier whose density is increased: (i) \textit{n}-type, this occurs when the electron density is increased (ii) \textit{p}-type, this is when the hole density is increased.

For an \textit{n}-type semiconductor, e.g. the addition of pentavalent phosphorus to silicon, only four electrons from the outer shell of phosphorus enter into the bonding of the crystal and the fifth electron orbits around the nucleus (Fig. 1.4(a)). This electron is loosely bound to the nucleus and requires only a small amount of energy to move the conduction band. Since the impurity atom donates an electron to the crystal lattice, it is called a donor. Hence, in the crystal lattice, a large number of electrons are found which makes the electron concentration higher than that of the holes. Therefore, these semiconductors are called \textit{n}-type semiconductors because the charge carriers are negative donors. These donors create a new energy level which is just below the conduction band (Fig.1.5. (b)).

When a boron atom is introduced into a silicon crystal, all the three valence electrons of boron will be involved in forming covalent bond with four electrons from silicon (Fig. 1.4(b)). One of the bonds will have a missing electron, which is a hole. This is then displaced further from the boron atom by a nearby electron and the
boron atom becomes negatively charged. Hence, the hole gets attracted by the B\(^-\) ion. Therefore, a hole or an empty energy state is created in the valence band structure of silicon. Hence, the boron atom acts as an electron acceptor and referred to as an acceptor. This follows that a large number of holes are found in the crystal lattice which increases their concentration than that of the electrons. These semiconductors are known as \( p \)-type semiconductors due to the acceptor-type dopants which are positive.

Fig. 1.4. Crystal lattice structure of (a) \( n \)-type and (b) \( p \)-type semiconductors\(^8\).

Fig. 1.5. Energy band diagrams for (a) \( p \)-type (b) \( n \)-type semiconductors\(^8\).
The positive dopants in a $p$-type semiconductor create an acceptor level, which is just above the valence band (Fig. 1.5(a)).

Alternatively, extrinsic conduction can also be determined by other factors such as crystal lattice defects i.e. vacant sites in the lattice, the presence of an atom in incorrect lattice site and higher or lower valency atoms residing on a lattice site.

1.2.3. Direct and Indirect band gap semiconductors

Semiconductors can also be classified based on electron transfer mechanism from the valence band to the conduction band. The kinetic energy of electrons is described by the following equation:

$$E = \frac{k^2}{2m_n}$$ (1.1)

where $m_n$ is the effective mass of the electron and $k$ is the crystal momentum. In some semiconductors e.g. GaAs and CdS, the conduction band minimum lies directly above the valence band maximum which affords the electron promotion from the valence to the conduction band with no change in the crystal momentum. These semiconductors are called direct band gap semiconductors. In these semiconductors, conservation of the wave vector for optical transitions occurs, which results in transitions having large absorption coefficients (Fig. 1.6). Moreover, the recombination energy is released in form of photons in a spontaneous process. Direct band gap semiconductors are used in the fabrication of optoelectronic devices and lasers.

However in indirect band gap semiconductors, the lowest electronic transition between the valence and conduction bands is formally forbidden. The reason for this is that the conduction band minimum and valence band maximum are situated at different values of $k$, which prohibits a direct transition of electrons (Fig. 1.6).
the energy equal to the band gap $E_g$ is insufficient for electron promotion, extra energy is therefore needed in the form of lattice vibrations to make the indirect transition possible. Consequently, indirect band gap semiconductors have small absorption coefficients. Examples of these include elemental semiconductors like silicon and germanium.

![Electronic transitions in (a) direct and (b) indirect band gap semiconductors.](image)

1.2.4. **Semiconductor devices: p-n junctions**

The manipulation of the resistivity of semiconductor materials through intentional doping with carefully selected impurities plays an important factor in the manufacture of semiconductor devices e.g. diodes and transistors\(^1\). A p-n junction is the metallurgical boundary between the n- and p- regions of a semiconductor crystal, in which p-type and n-type semiconductors form a contact structure (Fig.1.7). In simple terms, a p-n junction is formed through the appropriate doping of a material to produce the p-type and n-type conduction layers. In a p-n junction, only the positions of the Fermi levels with respect to the conduction and valence bands differ. Hence, the p-n junction is the basic building block of a variety of devices.
including the integrated circuits. This junction can be fabricated using some basic methods discussed below:\(^1\):

(a) Fusion Method: This involves the incorporation of a seed into a crystal through melting in oxygen or an inert atmosphere. An example of this is the fusion of \(n\)-type germanium and indium which produces a single crystal precipitate having a \(p-n\) junction feature.

(b) Diffusion Method: This is the movement and spreading of an acceptor impurity into an \(n\)-type semiconductor or a donor impurity into a \(p\)-type semiconductor either from a gaseous, liquid or solid phase. This process is accelerated through heating. An example is the heating and exposure of silicon to a gaseous atmosphere containing an \(n\)-type dopant such as antimony (Sb).

(c) Epitaxial Growth Technique: This is the replica growth of a single layer of substrate e.g. \(p\)-type silicon on an \(n\)-type silicon wafer. The epitaxial layer is formed through the additional growth of the semiconducting material on the substrate.

![Diagrammatic representation of a \(p-n\) junction.](image)

When the \(n\)- and \(p\)-type semiconductors of different Fermi levels come in contact, the system reaches equilibrium with the Fermi level being constant throughout the materials. This is because the majority carriers diffuse across the junction to equalise the free electron and hole-density in the crystal. Hence, the
electronic bands adjust to this condition, thereby producing a distortion of the energy bands at the \( p-n \) junction called band bending. This results in an electric field across the junction known as in-built field. The equilibrium produces a depletion region (or space-charge region) with no mobile carriers; hence a potential barrier needs to be present before electronic conduction can occur.

The application of an external battery across a \( p-n \) junction causes current to flow, which is primarily determined by the polarity of the applied voltage and its consequences on the space-charge region. For example, when the positive terminal of a battery is connected to the \( n \)-type material and the negative terminal to the \( p \)-type material (Fig.1.8), the free electrons in the \( n \)-type are attracted to the positive terminal of the battery and away from the junction. Also, holes in the \( p \)-type material migrate to the negative terminal of the battery and away from the junction. Consequently, the depletion region becomes wider which causes an increase in the potential gradient until it reaches that of the external battery. This type of \( p-n \) junction is called reverse-biased junction.

![Fig.1.8. Schematic diagram of a reverse-biased junction.](image)

However, when the positive terminal of an external battery is connected to the \( p \)-type material and the negative terminal to the \( n \)-type material, the \( p \)-type electrons...
at the positive terminal break their electron-pair bonds and enter the battery to make new holes. Simultaneously, the negative terminal electrons of the battery enter the \( n \)-type material and diffuse toward the junction. Hence, the depletion zone becomes narrower with the decrease of the energy barrier to an insignificant value. Then, extra electrons of the \( n \)-type material penetrate the depletion zone, flow across the junction and move towards the positive terminal of the battery through the \( p \)-type material holes. As long as the external voltage is being supplied, the electron flow continues. Under this condition, the junction is referred to as forward-biased (Fig.1.9).

![Diagram of a forward-biased junction](image)

**Fig.1.9.** Schematic representation of a forward-biased junction.

### 1.3. Semiconductor Thin Films\(^{14}\)

A thin film is a low-dimensional material created by condensing, one-by-one, atomic/molecular/ionic species of matter, which is typically less than several microns. Thin films are produced from the deposition of individual atoms on a substrate. In the course of time, thin films have been widely applied in electronic devices, optical coatings, instrument hard coatings and decorative parts. Because of the need to develop new materials e.g. nanomaterials and artificial super lattices, the development of thin film technology continues on a daily basis.
Film deposition on a substrate can be done by thermal evaporation, chemical decomposition, and/or evaporation of source materials through irradiation of energetic photons. The following are characteristic features of thin-film growth:

1. A random nucleation process proceeded by nucleation and growth.
2. Some deposition factors e.g. growth temperature, growth rate and substrate chemistry determines the nucleation and growth stage.
3. Significant modification of the nucleation stage by external factors e.g. electron or ion bombardment.
4. The film stress, film microstructure and associated defects are determined by the deposition conditions at the nucleation stage.
5. The crystal phase and film orientation are governed by the deposition conditions.

All the basic film properties such as composition, thickness, microstructure etc are controlled by the deposition conditions. Moreover, thin films display peculiar properties which are not seen in bulk materials:

a. Unique material properties obtained from the atomic growth process.

b. Size effects including the quantum size effects, characterised by the thickness, crystalline orientation and multilayer aspects.

The properties of thin films are governed by the deposition technique involved. Several deposition methods are available to grow semiconductor thin films. These include physical vapour deposition (evaporation & sputtering), metal-organic chemical vapour deposition (MOCVD), aerosol-assisted chemical vapour deposition (AACCVD) and low-pressure metal organic chemical vapour deposition (LP-MOCVD).
1.3.1. Physical Vapour Deposition (PVD)\textsuperscript{15}

Physical vapour deposition (PVD) can be divided into two main methods: evaporation and sputtering. Both methods involve a layer formation on a substrate in three steps: (i) a condensed phase material being converted into the gaseous or vapour phase (ii) gaseous phase transportation to the substrate surface and (iii) nucleation and growth of a new layer.

In evaporation, the deposited material is directly heated by a laser beam through a stream of high-energy electrons to create a molten region at the surface which vaporises the material. Deposition of the evaporated material on the substrate occurs and this is maintained at a lower temperature than that of the vapour. Conventional evaporation processes involve heating the deposited material under high vacuum conditions of $10^{-5}$ to $10^{-8}$ Torr. Due to the differences in the vapour pressures of various elements, deposition of alloys using this technique can be complicated. Therefore, it might be difficult to maintain the stoichiometry of the target and deposited films, since the target will be richer in less volatile species.

The sputtering method involves the surface deposition of vapourised particles through a physical sputtering process. This is a non-thermal vaporisation process through which surface atoms are ejected physically by momentum transfer from an energetic bombarding particle. Mostly, this is a gaseous ion accelerated from a plasma. The sputtered ions are then transported to the substrate surface, where their condensation results in film deposition. Deposition by sputtering can either be at high or low vacuum pressure, having no gas phase collisions of the sputtered particles in the space between the target and substrate. Sputtering deposition can be effectively monitored and widely applicable to an array of materials e.g. metals, alloys and semiconductors\textsuperscript{16}. Advantages of the sputtering method include alloy
deposition from a stable, long-lived vaporisation source and the ease of reactive deposition through the activation of reactive gaseous species in a plasma.

1.3.2 Vapour-Phase Epitaxy (VPE)

The vapour-phase epitaxial growth using metal halides as transport agents is collectively known as vapour phase epitaxy (VPE). When compared with other deposition techniques, the most striking factor of VPE is the *in situ* generation of the reactive precursors. Vapour phase epitaxy is the technique containing both the substrate and the film in crystalline form, with a continuous crystalline morphology moving between the surface and film. For instance, the deposition of GaAs through VPE involves flowing the mixture of AsCl$_3$/H$_2$ over liquid Ga in the precursor zone. This forms GaCl which is mixed with a flow of AsCl$_3$/H$_2$ in the downstream. Thereafter, both the reaction and material growth occur either in the depletion zone or on silicon$^{17}$.

1.3.3. Atomic Layer Deposition (ALD)/Atomic Layer Epitaxy (ALE)

ALD involves the alternate introduction of gaseous precursors into the reaction chamber where they reach a saturated adsorption level on the substrate surface. In contrast to thermal CVD, which involves pyrolysis of precursor molecules, ALD proceeds through sequential surface exchange reactions (e.g. hydrolysis) between the metal precursor (e.g. [HfCl$_4$] / H$_2$O). ALD is carried out at low pressure (e.g. 2 mbar) and to avoid gas-phase reactions the precursor pulses are separated by an inert gas purge. Under optimum conditions, film growth proceeds through self-limiting surface reactions of a saturated adsorbant in which one ALD cycle produces one monolayer of material$^{22(a)}$. ALE is a specialist variant of the much more widely used technique of ALD. Compounds of ALE involve the sequential deposition of single monolayers of one or more semiconductor materials at a time$^{18}$. Mainly, ALE is
conducted under high vacuum conditions because of the necessity to maintain a controlled atmosphere, though not exclusively\textsuperscript{19}. Atomic layer epitaxy has been widely applied to prepare III/V materials through the sequential introduction of the source gases containing the Group 13 and 15 precursors in the reaction chamber. The Group 13 molecule chemisorbs to the active sites on the substrate fully, which is the self-limiting adsorption proceeded by the site-selective Group 15 molecule reaction with Group 15 centres. This results in the self-limiting desorption\textsuperscript{20,21}. Under ideal conditions and appropriate temperatures, a greater control of stoichiometry is achieved which the sequential film deposition of one atomic layer per time. A major prominent advantage of ALE is in the growth of very uniform thin film and has been used to prepare different materials e.g. ceramics, oxides and superconductors\textsuperscript{22(b)}.

1.3.4. Molecular Beam Epitaxy (MBE)

MBE is an epitaxial process which uses an evaporation method to generate fluxes of precursor materials, a molecular beam of the desired dopants and the precursor’s reactions at the substrate surface to deposit thin films\textsuperscript{23}. The precursors are either heated or introduced into the reaction chamber and the film growth in the MBE process requires an ultra-high vacuum condition with low pressure e.g. $10^{-10}$ Torr. With the MBE process, high purity thin films and complex layered structures (nanostructures) can be deposited with a precise control of incorporated dopants. With low growth rates of 1 monolayer of material per second, films of highest quality can be obtained which is an important factor in microelectronic production. Technically, a variety of terms can be applied in MBE, based on the precursor used. For instance, when organometallic precursors are used, this is called organometallics MBE (OMMBE).
1.4. Chemical Vapour Deposition (CVD)

Chemical vapour deposition (CVD) is a process for depositing films of materials on the surface of a substrate from the vapour phase through the decomposition of chemicals\textsuperscript{24}. The vapour phase contains the metal-containing species and is transported into a reactor containing the substrate, where the species adsorbs and reacts to deposit a film of a particular material\textsuperscript{23}. Although photo- and plasma-assisted methods are also used, most often, the process is powered by heat during which the deposition is controlled by a chemical reaction. Basically, the process (Fig.1.10) involves the transportation (1) of a volatile precursor onto a substrate in a reactor, where adsorption (2) occurs followed by a surface reaction (3) to liberate the supporting ligands. Subsequently, these are desorbed (6) and transported out of the reactor (7). For a metal CVD, the metal atoms diffuse (4) to form a stable nucleus, where subsequent growth occurs (5). Also, under certain conditions gas phase reactions may occur. Specific metal-containing precursor, surface, temperature and other deposition conditions (e.g. presence of a reactive gas) may be important to the details of the surface reactions\textsuperscript{25}. Once a continuous film is formed, growth occurs on the deposited film and the quality of the grown layers is determined by the mechanism of the deposition process, which is of crucial importance\textsuperscript{26}. When compared with other techniques e.g. physical vapour deposition, chemical vapour deposition has some advantages. These include the complex topography coating of a surface with a layer of uniform thickness (conformal coverage), low deposition temperatures and selective deposition (coating) on a particular surface (growth surface) and not the other surface (non-growth surface). For thermally sensitive substrates, the deposition temperature might be a source of concern\textsuperscript{25}. 
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Fig. 1.10. Schematic diagram of the CVD process\textsuperscript{27}. Gas phase reactions can occur between steps (1) and (2).

1.4.1. Variations of CVD

The various CVD techniques are differentiated by the initiation of their mass transport. For instance, the conventional CVD uses thermal energy to activate the chemical reactions in which volatile precursors are delivered from the bubblers or gases from cylinders at low (reduced) pressure in the reactor for safety reasons. Also, kinetic steps are aided under LPCVD conditions\textsuperscript{26}. Although it is possible for CVD to be done at atmospheric pressure (APCVD), hence low pressure CVD (LPCVD) has some advantages. At lower pressure, the less volatile precursors can be easily controlled and the system contained with ease. Also, the deposition of particulate materials on the substrate which are detrimental to morphology through a homogeneous gas-phase reaction can be avoided\textsuperscript{24}. There are other types of this process which include plasma-enhanced CVD (PECVD) and photo-assisted CVD (PACVD), which use plasma and light to activate the chemical reactions.
The metal-organic CVD (MOCVD) has its precursor defined already by using organometallics as the precursors and it is widely applied to deposit semiconducting and electronic materials. However, there are certain restrictions on this method by the precursors which are important for commercial and environmental reasons. These include: (i) The nature of the precursor which are mostly metal alkyls and/or main group hydrides, which are highly toxic and often pyrophoric. (ii) The possibility of a homogeneous reaction which can cause ‘snowing’ of the film, thereby affecting morphology of the growing layer. (iii) Large imbalance in the mole ratios of precursor due to volatility differences, thermal reactivity of the precursors, coupled with selective desorption from the growing layer.

Aerosol-assisted CVD (AACVD) can be used for precursors which are less volatile but can be dissolved in organic solvents, thereby preventing the problem of unfavourable precursor sublimation characteristics. In this process, transportation of the precursors to the substrate occurs through a liquid/gas aerosol, which is generated electronically. Basically, this is a four-stage process (Fig.1.11) which involves the dissolution of the precursor in an organic solvent (1) and converted into droplets by a piezoelectric modulator (2). The solvent and aerosol of the precursor is then transported to a hot zone for evaporation by a carrier gas. The vapour of the precursor is transported to the substrate for adsorption and further reaction to form a film (3) and by-products (4). Aerosol delivery systems are quite suitable for precursors with low volatility and thermally unstable ones which may decompose if heated for prolonged times. Also, this technique is useful for multi-component
systems since the transportation rates of the precursors depend on their concentrations in the precursor solution.

**Fig.1.11.** Schematic diagram of the AACVD process\(^{36}\).

Some of the advantages of AACVD include: (i) Simplification of the vapour precursor generation and delivery method when compared with the conventional ones. (ii) Using single source precursors thereby providing molecular mixing of chemical precursors to synthesise multi-component materials. (iii) The deposited phases are formed rapidly at low temperatures due to small diffusion distances. (iv) Since the process can be performed in an open atmosphere, it is a relatively low cost process to deposit oxide without any sophisticated reactor.

**Fig.1.12.** Schematic representation of the AACVD set up.
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A recent development in CVD techniques is the supercritical fluid CVD (SCFCVD), which uses super critical fluids (SCF’s) to transport precursors\(^\text{29}\). When compared with other techniques, SCFCVD seems to have an advantage over others due to the special properties of supercritical fluids. These include high diffusivity, low viscosity and high solvating power. Consequently, thermally unstable or non-volatile precursors can be used and it is also possible to coat objects with complicated shapes. See Appendix 1 for an outline of liquid injection CVD.

1.4.2. Applications of CVD

By controlling the various processes involved in CVD, highly uniform coatings with structural control over a broad range of scale levels from atomic to reactor scale can be obtained\(^\text{30}\). CVD methods are widely applied in various coatings to improve the mechanical or thermal properties of a material e.g. optical coatings, protective coatings and decorative coatings. However, the most important use of this technique is in depositing functional materials used in various electronic applications. These can be categorised as follows: (i) Semiconductors capable of being deposited as both \(n\)-type and \(p\)-type. (ii) Conductors, mostly metals. (iii) Superconductors, especially high temperature materials based on perovskite-type oxides. (iv) Dielectric materials to produce capacitors. (v) Electroluminescent or luminescent materials important in display. (vi) Insulators\(^\text{31,25,32}\).

1.4.3. Side Effects of CVD

As mentioned before, CVD has a wide range of applications due to its versatility, hence making it advantageous in some ways. These include the ability to control the deposited phase and its morphology through the nature of the precursor, due to the growth under non-equilibrium conditions. Also, there is the potential for both conformal and large-area growth, with the possibility of getting reproducibly
high purity levels in the grown materials\textsuperscript{24}. However in some cases in CVD, some unexpected abnormal structures do appear which are not suitable for application. These include protrusions\textsuperscript{33-35}, fibers\textsuperscript{36,37} and voids\textsuperscript{38-40}. Quite often, these growth morphologies are created or eliminated by trial-and-error adjustments of operating conditions. Hence, through a theoretical understanding of the formation mechanism of such abnormal features, it is better to optimize reactor designs than to rely only on trial-and-error methods\textsuperscript{30}.

1.5. CVD Precursors

Thin films grown from CVD have many properties such as: degree of crystallinity, crystallographic orientation, composition and impurity (or dopant) concentration, which are all particularly important. These properties can be influenced by the precursor chemistry whose principal effects lie in the mechanism of decomposition of the compound\textsuperscript{27}. The morphology and probably the structure of the deposited film may be influenced by the nature of the molecular species present at the interface. This effect is largely attributed to the shape of the precursor. However, growing conformal films by CVD requires significant mobility of the surface species to deposit dense films. For a compound to be used as a successful precursor, it must have certain criteria which are: (i) the precursor must be of high purity to exclude the incorporation of extrinsic impurities acquired during precursor synthesis, especially if they can act as dopants. (ii) The precursor should decompose cleanly on the substrate surface without incorporating unwanted intrinsic impurities from the ligands. (iii) Moderate vapour pressure and quantitative volatility when heated is required of the precursor. (iv) Stability in the gas phase at the volatilization temperature (v) Its clean decomposition at the temperature of the substrate (this may be a little higher than that needed to volatilize the precursor)\textsuperscript{5}. (vi) Through a sensible choice of compound, toxicity should be minimised.
The precursors used for CVD are of two types:

(a) Multiple-source precursors.
(b) Single-source precursors.

Furthermore, based on the constituents of a precursor, CVD precursors can be divided to three types: (i) inorganic precursors - these do not contain carbon; (ii) metal-organic – these have organic ligands but do not have metal-carbon bonds; and (iii) organometallics – these have both organic ligands and metal-carbon bonds. In the CVD of any material, it is of vital importance to consider the metal-containing molecule which can be used as the precursor. For the CVD of a specific metal, the factors guiding the choice of the precursor might be complex and depend on the application being considered.25

1.5.1. Multiple-source Precursors

The conventional CVD processes use different element sources (precursor molecules) to form elements making up the material to be deposited. The precursor molecules are introduced into the reactor in their vapour form, hence, they can be described as multiple-molecule precursor vapour delivery. These precursors are highly volatile compounds e.g. metal alkyls (Me₂Cd, Me₃In, Et₂Zn, Et₃Al, iPr₃Ga) and hydrides (H₂S, H₂Se, NH₃, PH₃, AsH₃, SiH₄). However, these are highly toxic and pyrophoric, together with being moisture sensitive. Environmental and safety conditions are therefore of vital importance for the industrial processes of these compounds. Multiple-source precursors undergo a homogeneous reaction in the gas phase known as pre-reactions because of the coordinative unsaturation of their molecules. This results in snowing which affects both the morphology and stoichiometry of the deposited film. Adduct precursors can be used to avoid the homogeneous preReaction inside the reactor. Though they (adduct precursors) are
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non-pyrophoric and safer to handle, they dissociate in the vapour phase because of their weaker bonds.\(^1\)

1.5.2. Single-source Precursors

In attempts to reduce toxic hazards, eliminate homogeneous pre-reactions, lower deposition temperatures, and use cheaper precursors, considerable efforts have been directed towards the development of alternative precursors for use in MOCVD. To avoid intrinsically less reactive compounds, another alternative is to use single-molecule (or “single-source”) precursors. These are compounds in which all the elements (metal and chalcogen) in the film to be deposited are contained in a single molecule.\(^2\),\(^3\) Obviously, using one molecule instead of several results in simplified installations in terms of flow and temperature controls and reduces leak incidence. Also, environmental and safety conditions (which are important for industrial processes) are taken care of when compared with multiple-source routes. Potentially, single-source precursors show some or all of the following benefits over the conventional MOCVD precursors: (i) Air and moisture stability. (ii) Less toxicity. (iii) Possibility of low-temperature growth. (iv) Controlling impurity incorporation into film through ligand design. (v) Elimination of chemical incompatibility between precursors, hence limiting pre-reaction. (vi) The ease of purifying one non-volatile compound than two or more volatile precursors. (vii) Differences in thermal behaviour between precursors are no longer a problem. (viii) Intrinsic control of film stoichiometry. However, despite the numerous potential advantages of single-source precursors, they are not without drawbacks. The main disadvantage is their lack of volatility due to high molecular weight, which can be problematic in conventional atmospheric pressure CVD. By using a low-pressure environment or a solution of the precursor in an aerosol-assisted CVD or liquid injection CVD, this problem can be dealt with. Other problems associated with single-source precursors are: (i) the
difficulty in depositing materials with defined non-integral stoichiometries or when dopants are required due to the presence of two or more elements in a specific ratio in the compound, (ii) carbon contamination (see Appendix 2).

1.6. Single-source Precursors for Chalcogenide Films

There have been extensive studies on the single-source molecule approach for the metal chalcogenides, because of their application as electronic materials. Most importantly are the 12-16 (II-VI) and 13-16 (III-VI) compounds, which form a series of direct-gap semiconductors with widely spread bandgap energies, based on the composition. Many chalcogen-containing ligands have been developed for the synthesis of precursors having direct metal-chalcogen bonds. These include thiolates, selenolates, xanthates, thiobiurets, dithiobiurets, monothiocarbamates, dithiocarbamates, diselenocarbamates, dithiocarbamates, dichalcogenoimidodiphosphinates etc. Most metal chalcogenides can be applied in optoelectronic or photovoltaic devices, e.g. cadmium chalcogenides and ternary semiconductors like CuInS$_2$ are photovoltaics. Many transition metal chalcogenides can be used as lubricants coatings, electrode materials, or catalysts because of their layered structures.

1.6.1. Metal Alkyl as Precursors to II-VI Materials

Metal alkyls can be prepared easily by the reaction of the main group halides ($X = \text{Cl, Br, I}$) with the appropriate alkyl Grignard reagent ($\text{RMgI}$) or the alkyl lithium salt ($\text{RLi}$) e.g. the cadmium alkyls (Eqn.1.2)\textsuperscript{45}

$$\begin{align*}
\text{CdX}_2 + 2\text{RMgX} \quad \text{ether} \quad \text{CdR}_2 + 2\text{MgX}_2 \\
\text{CdX}_2 + 2\text{RLi} \quad \text{ether} \quad \text{CdR}_2 + 2\text{LiX}
\end{align*}$$

(1.2)
Because any remnant of impurities left in the precursor will be carried over into the semiconductor layers, removal of these impurities is very important. For example, Me₂Cd can be purified to electronic grade by thermal decomposition of its adducts with low-volatility bidentate amines, followed by distillation of the volatile Me₂Cd. Traditionally, ZnSe and ZnS MOCVD had been achieved using Me₂Zn / H₂Se or Me₂Zn / H₂S. However, homogeneous gas-phase pre-reactions due to facile elimination of alkyl groups on Me²Zn by acidic hydrogen on H₂Se or H₂S can lead to premature deposition of ZnSe or ZnS. Also, the toxicity of H₂Se, H₂S means that specialist reactor design is required to remove residual H₂Se, H₂S. One solution to the pre-reaction problem is to use alkyl selenides or sulfides which do not contain an acidic hydrogen e.g. thiophene, C₄H₄S, selenophene, C₄H₄Se and Et₂Se. The problems associated with this approach include: (i) the thermal stability of R₂Se because the growth temperature is too high for II-VI devices and (ii) the toxicity of Se sources. Another solution to pre-reaction problem is to use Me₂Zn adducts, in particular Me₂Zn(NEt₃). Pre-reaction with H₂Se and/or H₂S is eliminated, and low temperature growth of ZnSe/ZnS is allowed. The serious problem of toxicity of H₂Se, H₂S remains. The elimination of pre-reaction is not due to simple adduct blocking because Me₂Zn(NEt₃) is dissociated in gas-phase, even at room temperature. The isolation and crystal structure of [MeZnSBu¹](pyridine) adduct suggests that N donors suppress pre-reaction with H₂Se or H₂S by formation of adducts such as [MeZnSH](N-donor). Although pre-reactions can be eliminated using R₂Se/R₂S, or Me₂Zn-amine adducts, the serious problem of the toxicity of the Group VI precursor remains. This is the major driving force for the use of directly bonded II-VI single-source precursors.
**1.6.2. Chalcogenolate Complexes**

Generally, the Group 12 metal chalcogenolates are non-volatile and polymeric compounds, e.g. cadmium or zinc form complexes with ligands like thiolates to give involatile polymeric structures\(^2\). By reducing the molecularity of these complexes through adduct formation, Steigerwald *et al* have prepared various precursors from 1,2-bis(diethylphosphino)ethane (depe) and M(ER)\(_2\) (M = Zn, Cd, Hg; E = S, Se, Te). The thermal decomposition of [Cd\(_2\)(SeC\(_6\)H\(_5\))\(_4\)(depe)]\(_n\) gave subnanometers clusters of CdSe. Through the insertion of sulfur into the Zn-C bond of dimethylzinc, Hampden-Smith *et al* prepared [Zn(Set)Et\(_{10}\)] which gave cubic ZnS from pyrolysis\(^4\). Based on 2,4,6-tri-\(\text{tert}\)-butylphenylchalcogenolate, various precursors were prepared by Bochmann *et al*\(^5\) with the general preparation method of an example shown below in equations 1.3, 1.4 and 1.5:

\[
\begin{align*}
\text{HgX}_2 + 2 \text{LiE} & \rightarrow [\text{Hg(E= S, Se, Te)}]_2 + 2\text{LiX} & (1.3) \\
\text{M[N(SiMe\(_3\))]_2} + 2 \text{HE} & \rightarrow [\text{M(E= S, Se)}]_2 + 2\text{HN(SiMe\(_3\))]_2} & (1.4) \\
\text{M[N(SiMe\(_3\))]_2} + 2 \text{LiE} & \rightarrow [\text{M(E= S, Te)}]_2 + 2\text{LiN(SiMe\(_3\))]_2} & (1.5)
\end{align*}
\]
The dimeric compounds formed have been used in LP-MOCVD to deposit II-VI materials\textsuperscript{57,58}; e.g. deposition of polycrystalline CdS from [Cd(SC\textsubscript{6}H\textsubscript{5}Bu\textsubscript{3}-2,4,6)]\textsubscript{2} at 450°C. However, the mercury analogues decompose easily to elemental Hg and diaryl dichalcogenides, which suggests that they are more suitable for photo-assisted CVD rather than thermal MOCVD. In a related work by Arnold and co-workers, silicon-based ligands M[E\textsubscript{Si}Si(SiMe)\textsubscript{3}]\textsubscript{2} (M = Zn, Cd, Hg; E = S, Se, Te), have been used to deposit a range of chalcogenides\textsuperscript{59,60}. The most prominent of these is the telluride thin film deposition by LP-MOCVD\textsuperscript{61}. The tellurium-containing ligand, HTeSi(SiMe\textsubscript{3})\textsubscript{3}, (HSitel) is a potential source for metal tellurolates\textsuperscript{62,63} and metal complexes of Sitel are generally prepared by equation 1.6 below:

\[
M[N(SiMe\textsubscript{3})\textsubscript{2}] + 2HTeSi(SiMe\textsubscript{3})\textsubscript{3} \rightarrow [M\{TeSi(SiMe\textsubscript{3})\textsubscript{3}\}\textsubscript{2}] + 2HN(SiMe\textsubscript{3})\textsubscript{2} \quad (1.6)
\]

The decomposition in the MOCVD occurs via an elimination pathway as shown in equation 1.7:

\[
[M\{TeSi(SiMe\textsubscript{3})\textsubscript{3}\}\textsubscript{2}] (g) \rightarrow (MTe)\textsubscript{n} + Te\{Si(SiMe\textsubscript{3})\textsubscript{3}\}; (M = Zn, Cd, Hg) \quad (1.7)
\]

ZnTe had been deposited onto quartz, silicon, InAs and GaSb substrates, while the cadmium precursor gave hexagonal material with a better stoichiometry\textsuperscript{64}.

1.6.3. Chalcogeno-urea Complexes

From the spray pyrolysis of aqueous mixtures of cadmium chloride and thiourea, [SC(NH\textsubscript{2})\textsubscript{2}], CdS had been deposited from a single-source precursor. This was formed by the direct reaction of the parent compounds in the sprayed solution during which certain intermediate complexes were claimed. Factors responsible for this included the pH, CdCl\textsubscript{2}/SC(NH\textsubscript{2})\textsubscript{2} molar ratio and the use of anhydrous or hydrated cadmium chloride\textsuperscript{65,66}. A tetrahedrally coordinated cadmium complex, Cd[SC(NH\textsubscript{2})\textsubscript{2}]\textsubscript{2}Cl\textsubscript{2}, was confirmed by Niinisto et al, having complex thermal
characteristics when exposed to air and under spray pyrolysis. Deposition of CdS from this precursor was inconclusive due to the possibility of having significant traces of chlorine and other impurities. Similarly, Liu and Wang prepared thin films of CdSe using the same approach of spray pyrolysis through an aqueous solution of cadmium chloride and N,N-dimethylselenourea.

1.6.4. Dialkyl dichalcogenocarbamate Complexes

The metal complexes of dialkyldithio/diselenocarbamato ligands, having the general formula \([\text{M(E}_2\text{CNR}_2)_2]\) (symmetrical) or \([\text{M(E}_2\text{CNRR'}_2]\) (unsymmetrical) \((\text{R, R'} = \text{alkyl; E = S, Se; M = Zn, Cd})\) have been used as precursors to deposit II-VI thin films. Under an inert atmosphere, the solid-state pyrolysis of dithiocarbamate complexes gives the corresponding metal sulfide. However, the phase of the metal sulfide deposited and stoichiometry depends on the pyrolysis conditions and organic ligands in the precursor. Dialkyl dichalcogenocarbamate complexes are stable crystalline solids with some volatility, and some of their single-crystal structure determinations indicated dimeric units. These include \([\text{Zn(S}_2\text{CNMeR}_2)_2]\) \((\text{R} = \text{Et, nPr, iPr, or nBu})\), \([\text{Cd(S}_2\text{CNET}_2)_2]\) (Fig.1.13), \([\text{Zn(Se}_2\text{CNET}_2)_2]\), \([\text{Cd(Se}_2\text{CNET}_2)_2]\) and \([\text{Zn(S}_2\text{CNET}_2)_2]\) \((\text{R} = \text{Et, nPr, iPr, or nBu})\).

Fig.1.13. Structure of \([\text{Cd(S}_2\text{CNET}_2)_2]\).
The pioneer work on these precursors was done by Saunders et al by using diethylidithiocarbamates \([M(S_2CNEt_2)_2]\) \((M = \text{Zn, Cd})\) to deposit ZnS, CdS and \(\text{Zn}_x\text{Cd}_{1-x}\text{S}\) by LP-MOCVD\(^{77}\). Good quality CdS or \(\text{Zn}_x\text{Cd}_{1-x}\text{S}\) were deposited using LP-MOCVD by Frigo et al\(^{78}\) using an equimolar mixture of \([\text{Cd}(S_2CNEt_2)_2]\) and \([\text{Zn}(S_2CNEt_2)_2]\) but the ZnS films were of low quality. However, under the same conditions, attempts to deposit CdSe and ZnSe on glass substrates using metal diethyldiselenocarbamates resulted in the deposition of elemental selenium\(^{75}\). When \([\text{Zn}(S_2CNEt_2)_2]\) was used in a cold-wall reactor by Nomura et al\(^{79}\), cubic ZnS was deposited epitaxially on Si(111). The introduction of a carrier gas (\(N_2\)) improved the crystallinity and morphology of the deposited material having (111)-oriented \(\beta\)-ZnS. Fainer et al\(^{80}\) used either He or \(H_2\) as the carrier gas in both LP-MOCVD and plasma-enhanced MOCVD (PE-MOCVD) to grow different phases of CdS from \([\text{Cd}(S_2CNEt_2)_2]\) on various substrates: \(\text{SiO}_2\), \(\text{Al}_2\text{O}_3\) (sapphire), (111)-Si and (111)-InP. Pike and co-workers\(^{81}\) prepared thin films of ZnS through ultrasonic spray pyrolysis of a toluene solution of \([\text{Zn}(S_2CNEt_2)_2]\) and proposed the decomposition mechanism for the products. The gas chromatography mass spectrometer (GC-MS) analysis indicated clean elimination of ZnS from the precursor as shown by the equations below:

\[
\begin{align*}
\text{[Zn(S}_2\text{CNEt}_2\text{)_2]} & \rightarrow \text{ZnS} + \text{EtNCS} + \text{Et}_2\text{NCS}_2\text{Et} & (1.8) \\
\text{Et}_2\text{NCS}_2\text{Et} & \rightarrow \text{Et}_2\text{NH} + \text{CS}_2 + \text{C}_2\text{H}_4 & (1.9)
\end{align*}
\]

Although diethyldiselenocarbamates have been shown to be poor sources to deposit ZnSe or CdSe, the mixed-alkyl diethyldiselenocarbamates complexes \([\text{MeM(Se}_2\text{CNEt}_2\text{)]}\) \((M = \text{Zn, Cd})\) had been used to deposit ZnSe and CdSe thin films\(^{82}\). Moreover, air-stable unsymmetrical precursors of \([\text{M}(S_2\text{CNRR'})_2]\) \((M = \text{Cd or Zn}; \text{RR'} = \text{alkyl groups})\) deposited sulfides or selenides in MOCVD\(^{83-85}\). In terms of volatilization, experiments conducted on unsymmetrically substituted
[Zn(S$_2$CNMe$_2$)]$_2$, [Zn(S$_2$CNMe$_8$Pr)]$_2$, and [Zn(S$_2$CNMe$_8$Bu)]$_2$ revealed their easy volatility well above their melting points$^{76}$. For instance, ZnS film was deposited from [Zn(S$_2$CNMe$_8$Bu)]$_2$ by LP-MOCVD. Based on the deposition studies done with [Cd(S$_2$CNEt$_2$)$_2$] and [Cd(S$_2$CNMe$_8$Bu)$_2$], polycrystalline CdS films were obtained, and the methyl butyl derivative was found to be more volatile$^{86}$. In terms of the unsymmetrical derivatives for the growth of chalcogenides, bis(n-hexyl(methyl)dithio/selenocarbamato) cadmium/zinc has been shown to be the best$^{87}$. In a recent development, optoelectronic quality hexagonal CdS films were deposited in supercritical fluid experiments using [Cd(S$_2$CNHexyl)$_2$]. The deposited CdS was in a stoichiometric amount and had a higher magnitude of photoluminescence efficiency when compared with those produced without thiol$^{88}$. Due to the limitation encountered by the volatility of these precursors, (which determines the deposition results), there have been several attempts to produce more volatile dithiocarbamates. In a comproportionation reaction, dithiocarbamate complexes were obtained from trimethylpropylenediamine as a weakly bonded polymeric structure (Fig.1.14.). This is more volatile than the simpler dithiocarbamates and has been used to deposit CdS on glass or GaAs substrates at 350°C$^{89,90}$.

![Fig.1.14. Structure of [MeCd(MeN(CH$_2$)$_3$NMe$_2$)]$_n$.](image)
1.6.5. Heteroleptic Dialkyldichalcogenocarbamate Complexes

To increase the volatility of dichalcogenocarbamato complexes, the dialkyldichalcogenocarbamato ligand can be associated with an alkyl ligand, thereby forming heteroleptic complexes with the general formula \([M(R)(Q_{2\text{CNR}_2})]\). \((\text{Me})\text{Zn(diethylzinc carbamate)}^{91}\) and \((\text{Me})\text{Zn(diethylselenium carbamate)}^{82}\) have been shown to be dimers with \([Q\text{Zn(µ-Q)}]_2\) core solid structures. Using an insertion reaction, these compounds were first prepared by Noltes\(^92\):

\[
2\text{MeZn}(\text{NET}_2) + 2\text{CS}_2 \rightarrow [\text{MeZn(S}_2\text{CNET}_2)_2]\quad (1.10)
\]

However, a more convenient route to these compounds is via a comproportionation reaction:

\[
\text{Me}_2\text{Zn} + \text{Zn(S}_2\text{CNET}_2)_2 \rightarrow [\text{MeZn(S}_2\text{CNET}_2)_2]\quad (1.11)
\]

Complexes having the general formula \(M(R)(S_{2\text{CNR}_2})\) \((R \text{ or } R’ = \text{Me or Et, } M = \text{Zn; } R = \text{Me, } R’ = \text{Et, } M = \text{Cd})\) have been shown to sublime under mild conditions.

Thin films of ZnS, ZnSe, CdSe, and Zn\(_{0.5}\)Cd\(_{0.5}\)Se were deposited on glass substrates by LP-MOCVD from \([(R)\text{Zn(S}_2\text{CNET}_2)]_2\) \((R = \text{Me}^{91}, \text{Me}_3\text{C, and Me}_3\text{CCH}_2^{91})\), \([(R)\text{Zn(Se}_2\text{CNET}_2)]_2\) \((R = \text{Me, Et}^{82}, [(\text{Me})\text{Cd(Se}_2\text{CNET}_2)]_2\) and \([(\text{Me})\text{Zn}_{0.5}\text{Cd}_{0.5}(\text{SeCNET}_2)]_2^{82}\) in a hot-wall reactor. From the comparative study of \([(\text{Me})\text{Zn(S}_2\text{CNET}_2)]_2, [(\text{Me})\text{Cd(Se}_2\text{CNET}_2)]_2, \text{and } [(\text{Me}_3\text{CCH}_2)\text{Cd(S}_2\text{CNET}_2)]_2, \text{thin films of the respective metal chalcogenides have been deposited on both glass and (100)-GaAs substrates in a cold-wall reactor}^{82}\). CdS films deposited at 425°C from \([(\text{Me})\text{Cd(S}_2\text{CNET}_2)]_2\) were of better quality than that of \([(\text{Me}_3\text{CCH}_2)\text{Cd(S}_2\text{CNET}_2)]_2, \text{though both precursors gave improved quality films at 400°C. A series of heteroleptic bis(dialkyldithiocarbamate) complexes with the general formula }LM(R_2NCS_2)_2 \text{ (M = Zn, Cd, Mn, Mn:Zn or Zn:Cd and L = 1, 10-phenanthroline, 2,2'-}
bipyridine, or 4,4'-bipyridine) have been used as precursors to deposit thin films of ZnS, CdS, (Zn, Cd)S, or (Zn, Mn)S by MOCVD\textsuperscript{94,95}.

### 1.6.6. Dithiocarbonate (Xanthate) Complexes

Zink et al reported the comparative thermal and photolytic MOCVD to grow ZnS film from zinc xanthate (bis(O-isopropylthiocarbonate)zinc(II)) under low pressure on glass and silicon wafer substrates. Polycrystalline, highly (0002)-oriented, hexagonal \( \beta \)-ZnS films were produced having trace amounts of C and O contamination\textsuperscript{96}. From \([\text{M(S}_2\text{COC}_3\text{H}_7)_2]\) (\( \text{M} = \text{Zn, Cd} \)), nanocrystalline ZnS and CdS thin films were deposited onto Si/SiO\(_2\) substrates between 200 and 450\(^{\circ}\)C by CVD\textsuperscript{97}. Also, the properties of \([\text{M(S}_2\text{COCHR})_2]\) (\( \text{M} = \text{Cd}; \text{R} = \text{Et or } ^1\text{Pr} \)) were investigated as a potential single-source precursor for the deposition of CdS thin films\textsuperscript{98}.

### 1.6.7. Monothiocarboxylate Complexes

Aerosol-assisted CVD (AACVD) deposition studies done by Hampden-Smith and co-workers resulted in the deposition of CdS, ZnS, and Cd\(_x\)Zn\(_{1-x}\)S, using the precursors with the general formula \( \text{M(SOCR)}_2(\text{tmeda}) \) (tmeda = N,N,N,N-tetramethylethylenediamine), (\( \text{M} = \text{Zn, Cd} \)) (\( \text{R} = \text{Me or } ^1\text{Bu} \))\textsuperscript{99}. X-ray crystal structure determinations of \([\text{Zn(SOCCH}_3)_2(\text{tmeda})]\) and \([\text{Cd(SOCCH}_3)_2(\text{tmeda})]\) revealed that they are isostructural monomeric complexes in the solid state. In each case the metal atom has a distorted tetrahedral coordination, with two nitrogen and two sulfur donor atoms. From the toluene solutions of these complexes at low temperatures, highly oriented crystalline films of ZnS and CdS were deposited. When the solutions of the precursors were mixed in Cd/Zn ratios of 6:4, 5:5, 4:6 and 2.5:7.5, Cd\(_x\)Zn\(_{1-x}\)S films were grown at 175\(^{\circ}\)C. Using the more thermally stable thiopivalate analogues \([\text{M(SOCC(\text{Me})_3)}_2(\text{tmeda})]\) (\( \text{M} = \text{Zn, Cd} \)), films of Cd\(_x\)Zn\(_{1-x}\)S
with the stoichiometry of the solution as Cd/Zn = 1 could be grown under feed rate and evaporation rate-limited reactions\textsuperscript{99}.

1.6.8. Chalcogenophosphinate Complexes

Dialkyldiselenophosphinate ligands were first developed by Kudchadker \textit{et al}\textsuperscript{100}. The reaction of “Woollins reagent” [N(Ph\textsubscript{2}PSe\textsubscript{2})\textsubscript{2}] with RONa in ROH involving the cleavage of the four membered ring P\textsubscript{2}Se\textsubscript{2} resulted in diselenophosphinate ligands\textsuperscript{101}. The sulfur derivatives of the dichalcogenophosphinate complexes have been studied extensively, while the seleno analogue is limited because of the difficult synthetic process. Using thiophosphinate complexes, Takahashi \textit{et al}\textsuperscript{102}, deposited CdS from dimethyl thiophosphinate [Cd(S\textsubscript{2}PMe\textsubscript{2})\textsubscript{2}]. With this precursor, a highly compensated semi-insulating material can be obtained due to phosphorus incorporation acting as a p-type dopant. Furthermore, Evans and Williams\textsuperscript{103} indicated that highly orientated cadmium sulfide films could be grown from the diethylthiophosphinate precursor [Cd(Et\textsubscript{2}PS\textsubscript{2})\textsubscript{2}] without phosphorus incorporation. With a homemade cold-wall low-pressure reactor, thin films of CdS and ZnS have been deposited from [Cd(S\textsubscript{2}PBu\textsubscript{2})\textsubscript{2}] and [Zn(S\textsubscript{2}PBu\textsubscript{2})\textsubscript{2}] respectively\textsuperscript{104}. In a recent development, O’Brien \textit{et al}\textsuperscript{105,106} have reported the synthesis of various metal complexes of bis(dialkylselenophosphinyl)selenide [(R\textsubscript{2}PSe\textsubscript{2})Se] (R = Ph, \textsuperscript{1}Pr) with the general formula [M(R\textsubscript{2}PSe\textsubscript{2})\textsubscript{n}] (M = Zn, Cd, Pb, In, Ga, Cu, Bi, Ni; R = Ph, \textsuperscript{1}Pr) and [Mo\textsubscript{2}O\textsubscript{2}Se\textsubscript{2}(Se\textsubscript{2}P\textsubscript{i}Pr\textsubscript{2})\textsubscript{2}]. These have been used to grow metal selenide thin films by CVD. From the reaction of NEt\textsubscript{3} with Ph\textsubscript{2}PCl or \textsuperscript{1}Pr\textsubscript{2}PCl and HSiCl\textsubscript{3} in cold toluene, the ligands [(R\textsubscript{2}PSe\textsubscript{2})Se] (R = Ph, \textsuperscript{1}Pr) were synthesised (equation 1.12 and 1.13).

\begin{equation} \text{R}_2\text{PCl} + \text{HSiCl}_3 + \text{NEt}_3 \xrightarrow{\text{toluene}} \text{R}_2\text{PSiCl}_3 + (\text{HNEt}_3)\text{Cl} \quad (1.12) \end{equation}

\begin{equation} \text{R}_2\text{PSiCl}_3 + 3\text{Se} \xrightarrow{\text{toluene}} (\text{R}_2\text{PSe}_2)_2\text{Se} + \text{Si}_2\text{Cl}_6 \quad (1.13) \end{equation}
The complexes are obtained as precipitates through reaction of respective metal salts in methanolic solutions.

1.6.9. Thiosemicarbazide Complexes

These complexes are prepared by the reaction of thiosemicarbazide with metal salts in hot water. Because of their air and moisture stability, they are suitable as single-source precursors for metal sulfide thin films or nanoparticles. The preparation of tri-n-octylphosphine oxide (TOPO) capped CdS nanorods without a shape-directing agent was reported by O’Brien et al.\textsuperscript{107} Also, the thermolysis of lead thiosemicarbazide in TOPO at 240°C deposited hexagonal PbS nanoparticles\textsuperscript{108}, while CdSe was grown from a seleno-semicarbazide complex of cadmium\textsuperscript{109}.

1.6.10. Dimorpholinodithioacetylacetonate Complexes\textsuperscript{110}

The dimorpholinodithioacetylacetonate ligand was prepared from the reaction of morpholine with sulfur and allyl propyl ether for several hours at 110°C. This was then reacted with cadmium nitrate to give the corresponding complex. From the AACVD studies, thin films consisting of CdS nanorods were obtained.

1.6.11. Thiobiuret and Dithiobiuret Complexes

Thiobiurets, dithiobiurets and their related compounds have attracted considerable attention due to their possible applications in plastics and resins\textsuperscript{111} and for their physiological and therapeutic properties\textsuperscript{112}. Recently, thio-/dithiobiuret complexes have been synthesised for the deposition of materials e.g. Co, Ni, Fe, Zn, Cd, In, and Cu\textsuperscript{113}. The thiobiuret ligand is produced from the reaction of \(N,N’\)-dialkylcarbamyl chloride, sodium thiocyanate and dialkylamine to give 1,1,5,5-tetraalkyl-2-thiobiuret, which is followed by the addition of methanolic solution of metal acetate to give the complex. Dithiobiuret complexes which start with \(N,N’\)-dialkylthiocarbamyl chloride also follows the same preparation method (Scheme 1).
All these complexes have been used as single-source precursors for the deposition of metal chalcogenide thin films by AACVD\textsuperscript{113}.

\begin{align*}
\begin{array}{c}
\text{Cl} & \text{N} & \text{R} & \text{E} & \text{R} \\
\text{NaSCN} & \text{CH}_2\text{CN} & \text{HNR}_2 \\
\end{array}
\begin{array}{c}
\text{R} & \text{N} & \text{NH} & \text{N} & \text{R} \\
\text{M(OAc)}_2 & \text{CH}_2\text{OH} \\
\end{array}
\end{align*}

\begin{itemize}
\item $R = \text{Me, Et or } \text{iPr}$
\item $E = \text{O or S}$
\item $n = 2 \text{ or } 3$
\item $M = \text{Fe, Co, Ni, Cu, Zn, Cd, In}$
\end{itemize}

\textbf{Scheme 1.1.} Synthesis of thiobiurets or dithiobiurets ligand and their metal complexes.

\subsection*{1.6.12 Dichalcogenoimidodiphosphinate Complexes}

Dichalcogenoimidodiphosphinate anions [\text{EPR}_2\text{NPR}_2\text{E}^{-}] are acyclic ligands containing two chalcogens bridged by a PNP fragment, with each phosphorus atom carrying two aryl or alkyl substituents. The deprotonation of the NH group in the neutral precursors EPR\textsubscript{2}N(H)PR\textsubscript{2}E results in the anionic ligands and were first synthesised by Schmidpeter et al in 1960s\textsuperscript{114} (Figure 1.15).

\begin{align*}
\begin{array}{c}
\text{N} & \text{H} & \text{P} & \text{R} & \text{E} \\
\text{R} & \text{N} & \text{P} & \text{R} & \text{E} \\
\end{array}
\end{align*}

\textbf{Fig.1.15.} Structure of the dichalcogenoimidodiphosphinate anion.

Woollins \textit{et al}\textsuperscript{115} developed the selenium analogue of the compound, in which the coordination chemistry of the phenyl derivative was performed with main group and transition metals. It was later discovered that the more volatile isopropyl ligands were excellent precursors for binary metal selenides\textsuperscript{116,117}. The oxidation of the phosphorus (III) system with sulfur or selenium in boiling toluene gives the respective sulfur or selenide analogues as shown by equations 1.14 to 1.16 below:

\[ M(OAc)_2 + \text{CH}_2\text{OH} \rightarrow \text{M} \text{[complex]} + \text{HAc} \]
\[
\text{NH(SiMe}_3\text{)}_2 + \text{^iPr}_2\text{PCl} \xrightarrow{50-70^\circ\text{C}} \text{stirring (3h)} \quad \text{NH(P}^\text{iPr}_2\text{)}_2 + 2\text{ClSiMe}_3 \quad (1.14)
\]

\[
\text{NH(P}^\text{iPr}_2\text{)}_2 \xrightarrow{\text{E} = \text{S, Se}} \text{reflux} \quad \text{NH(EP}^\text{iPr}_2\text{)}_2 \quad (1.15)
\]

\[
2\text{NH(EP}^\text{iPr}_2\text{)}_2 \xrightarrow{\text{NaOMe} + \text{MX}_2} \xrightarrow{\text{MeOH}} \text{M[((EP}^\text{iPr}_2\text{)}_2\text{N}]_2 + 2\text{NaCl} \quad (1.16)
\]

Zinc and cadmium complexes [M[(EP}^\text{iPr}_2\text{)}_2\text{N}]_2 (M = Zn, Cd; E = S, Se) and [M[(SePPh}_2\text{)}_2\text{N}]_2 (M = Zn, Cd) have been synthesised and used as precursors for zinc/cadmium selenide thin films by LP-MOCVD\textsuperscript{116,118}. The complex [MeCd[(SeP}^\text{iPr}_2\text{)}_2\text{N}]_2 was prepared through the comproportionation of Me\textsubscript{2}Cd and [Cd[(SeP}^\text{iPr}_2\text{)}_2\text{N}]_2 in anhydrous toluene. A single crystal structure indicated dimeric units with the diselenoimidodiphosphinate binding to one cadmium atom and bridges with the next, which is four coordinated and bound to three selenium atoms and one carbon atom\textsuperscript{119}. However, the tellurium analogue of [Cd[(SeP}^\text{iPr}_2\text{)}_2\text{N}]_2 could not be prepared by the direct reaction of NH(P}^\text{iPr}_2\text{)}_2 with tellurium. An alternative approach developed by Chivers and co-workers involved the metallation of PR\textsubscript{2}N(H)PR\textsubscript{2} with NaH before reaction with tellurium, which generates Na[N(TeP}^\text{iPr}_2\text{)}_2] (R = Ph, ^iPr\textsuperscript{120}). The metathetical reactions of this reagent with metal halides then give the homoleptic complexes of the type M[(TeP}^\text{iPr}_2\text{)}_2\text{N}]_2 (M = Cd, Hg) as shown in equations 1.17 and 1.18:

\[
\text{Na[(P}^\text{iPr}_2\text{)}_2\text{N]} + 2\text{Te} \xrightarrow{\text{Hot Toluene}} (\text{tmeda})\text{Na[N(TeP}^\text{iPr}_2\text{)}_2] \quad (1.17)
\]

\[
\text{MX}_2 + 2(\text{tmeda})\text{Na[N(TeP}^\text{iPr}_2\text{)}_2]} \xrightarrow{\text{Hot Toluene}} \text{M[((TeP}^\text{iPr}_2\text{)}_2\text{N}]_2 -2\text{NaX, -tmeda} \quad (1.18)
\]

\[(M = \text{Cd, Hg}; X = \text{Cl, I}; \text{tmeda = tetramethylethylenediamine})\]

Pure CdTe films were obtained from the AACVD of [Cd[(TeP}^\text{iPr}_2\text{)}_2\text{N}]_2], while the mercury analogue deposited only hexagonal tellurium\textsuperscript{121}. 

---

*Chapter 1: Introduction*
1.7. Transition Metal Chalcogenide Complexes

The chalcogenides of titanium and molybdenum have applications as lubricant coatings, electrode materials or catalysts. Using the corresponding thiolates \([M(S^tBu)_4]\) (M = Ti, Mo) as the precursor, thin films of TiS\(_2\) and MoS\(_2\) have been deposited by LP-MOCVD. The deposited films were amorphous with low levels of oxygen and carbon contaminants\(^{122}\). Thin films of TiS\(_2\) and TiSe\(_2\) have been deposited by Winter et al, using the adducts of titanium tetrachloride with cycloalkanethiol and alkylselenium compounds. TiS\(_2\) films were grown on glass and silicon substrates in a hot-wall reactor from the mixture of the adduct with cyclohexanethiol, with the films exclusively (001)-oriented at 400°C and above. Also, under similar conditions, deposition of TiSe\(_2\) films occurred which had preferred (001)-orientation at 500°C\(^{123}\). Thin films consisting of S/Ti atomic ratios within 0.5-1.5 were obtained from the LP-MOCVD studies on \((\eta^5-C_5H_5)_2Ti(S^tBu)_2\) and \((\eta^5-C_5H_5)_2Ti(SEt)_2\), based on the deposition temperature and the precursor\(^{124}\).

Nomura et al\(^{125}\) have grown copper-deficient sulfides Cu\(_{1.96}\)S films on passivated or non-passivated (111)-Si substrate by LP-MOCVD from copper(II) bis(diethylidithiocarbamate) \([Cu(S_2CNEt)_2]_2\). Copper-deficient sulfides are applicable as semiconductor materials in optoelectronics and photovoltaics. Also, the same precursor had been used to grow Cu\(_2\)S films under RPECVD experiments\(^{95}\). Furthermore, deposition of high-purity Cu\(_2\)S and Cu\(_2\)Se have been reported by O’Brien et al from the precursor Cu[Q\(_2\)CN(Me)Hex]\(_2\) (Q = S or Se)\(^{84}\) respectively. From the symmetrical and unsymmetrical dialkyldithiocarbamate complexes of iron [Fe(S\(_2CNRR’\))\(_3\)], (R = Me, \(^8\)Bu; R’ = \(^3\)Pr, \(^8\)Bu) thin films of FeS\(_2\) were deposited by AACVD\(^{126}\). Also, cubic manganese sulfide films were deposited from [Mn(S\(_2CN(Me)\(^8\)Hex)\(_3\)] by AACVD\(^{127}\). Cobalt selenide thin films have been deposited from [Co\{((SeP^tPr\(_2\))\(_2\)N\}_2], [Co(SeP^tPr\(_2\))\(_2\)] and [Co(Se\(_2CNEt\)_2)] by
The precursor \([\text{Co}(\text{SePPr}_2)_2]\) gave a mixture of cobalt selenide and cobalt phosphide in individual films, while \([\text{Co}\{\text{SePPr}_2\text{N}_2}\}\) gave cobalt selenide or cobalt phosphide based on the deposition temperature\(^{129}\). Recently, O’Brien and co-workers reported the deposition of nickel sulfides, selenides or phosphides from the precursor \([\text{Ni}\{\text{Pr}_2\text{P(E)NP(E)Pr}_2\}_2}\) \((E = S, E’ = \text{Se}; E = E’ = S; E = E’ = \text{Se})\) by both AACVD and LPCVD. The deposited material was based on the deposition temperature and the CVD technique\(^{130}\).

### 1.8. Aims and Scope of the present study

The aim of this investigation is to synthesise new chalcogenide precursors containing single or mixed donor atoms (e.g. S alone or S and Se), which are suitable for CVD studies. Comparative studies of cadmium and zinc dichalcogenoimidodiphosphinato complexes were done to see whether the results would be different when compared with those of LPCVD, and also whether \(\text{CdS}_x\text{Se}_{1-x}\) or \(\text{ZnS}_x\text{Se}_{1-x}\) could be deposited. Also, tellurium complexes of Ni, Pd, Pt and Fe were synthesised followed by conductivity studies. Furthermore, new complexes of Fe were synthesised using “Woollins ligand” to deposit iron selenide, as there are no reports on these materials by any deposition method.
1.9. References


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CHAPTER 2:
CADMIUM AND ZINC PRECURSORS
Chapter 2 Cadmium and Zinc Precursors

2.1. Introduction

The intermediate energy band gap of II-VI semiconducting materials has led to an interest in this area, and their potential for application in a range of devices. They have found application in devices such as blue/green laser diodes due to the direct nature of their band gaps. Most importantly, the cadmium chalcogenides are useful materials in solid-state solar cells, photoconductors, field effect transistors, sensors and transducers. Due to its photosensitive nature, cadmium selenide is largely used to produce optoelectronic devices such as photo electrochemical (PEC) cells, photoconductors, thin film transistors and gamma ray detectors. It has a direct band gap of 1.74 eV and has mainly n-type conductivity both in thin film and bulk.

Thin films of cadmium selenide have been prepared by various techniques which include air annealing, spray pyrolysis, electrodeposition, chemical bath deposition, dip technique, hot wall deposition technique and MOCVD.

Cadmium phosphide is an n-type semiconductor with a band gap of ~ 1.2 eV which can be used in optoelectronics, quantum electronics and shows promise for thermo photovoltaic (TPV) devices. There are only a few reports on the deposition of cadmium phosphide films which include gas phase deposition, electron beam evaporation, and MOCVD.

Another important Group II-VI semiconducting material is cadmium sulfide, which has a wide band gap of 2.42 eV. Due to its low resistance and high transmission, it can be used as an effective window layer in solar cell structure. Cadmium sulfide also finds applications as optical filters, multilayer light emitting diodes (LED), photodetectors and gas sensors. Previously, cadmium sulfide
films have been prepared by flash evaporation\textsuperscript{23}, sputtering\textsuperscript{27}, laser deposition\textsuperscript{28}, vacuum evaporation\textsuperscript{29}, chemical vapour transport\textsuperscript{30}, spray pyrolysis\textsuperscript{31}, chemical bath deposition\textsuperscript{32,33}, sol-gel spin coating (nanocrystalline thin films)\textsuperscript{34} and MOCVD\textsuperscript{14}. Recently, a high-quality near-stoichiometric cadmium sulfide films were deposited by supercritical-fluid CVD using hexyl dithiocarbamate\textsuperscript{35}.

Another important Group II-VI semiconducting material is zinc selenide, which is \textit{n}-type with a direct band gap of 2.7eV\textsuperscript{36}. It has been widely studied due to its potential for use in semiconductor devices and as a window material in solar cells\textsuperscript{37}. It has a wide range of applications from blue LEDs to infra-red optics\textsuperscript{38}. Zinc selenide thin films have been deposited by various methods which include vapour phase epitaxy\textsuperscript{39}, molecular beam epitaxy\textsuperscript{40}, sputtering\textsuperscript{41}, chemical bath deposition\textsuperscript{42} and chemical vapour deposition (CVD)\textsuperscript{43}.

Using single-source precursors (SSPs), O’Brien \textit{et al} reported the deposition of ZnSe and CdSe thin films from complexes obtained from diselenoimidodiphosphinate ligands $[M\{(SePPh\textsubscript{2})\textsubscript{2}N\}]_2$, ($M = \text{Zn(II), Cd(II)}$)\textsuperscript{44}. Replacement of the phenyl group with isopropyl increased the volatility of these precursors which deposited metal sulfide or selenide thin films from $[M\{(EPPr\textsubscript{2})\textsubscript{2}N\}]_2$, ($M = \text{Zn(II), Cd(II)}$ and $E = \text{S or Se}$) by LP-MOCVD\textsuperscript{45}.

However, there are no reports to date on the deposition of phosphide/selenide and sulfide/phosphide from the same precursor. This chapter reports the deposition of these materials by AACVD from the complex $[\text{Cd}\{(EPPr\textsubscript{2})\textsubscript{2}N\}]_2$, ($E = \text{S,S; Se,Se; S,Se}$) and the single crystal X-ray structure of 3. The complexes of zinc $[\text{Zn}\{(EPPr\textsubscript{2})\textsubscript{2}N\}]_2$ ($E = \text{Se,Se; E = S,Se}$) (4) and (6) deposited cubic zinc selenide, while all attempts to grow thin films of zinc sulfide from the precursor
Chapter 2: Cadmium and Zinc Precursors

[Zn{__Pr2__N}] (5) under similar conditions were unsuccessful. A mechanism for the formation of different types of films is proposed based upon analysis by pyrolysis GC-MS method.

2.2. Synthesis of Precursors

2.2.1. Ligands Synthesis

2.2.1.1 Preparation of imido(tetraisopropyldiselenodiphosphinate) [Pr2P(Se)NHP(Se)Pr2]46

A solution of chlorodiisopropylphosphine (25 g, 164 mmol) in toluene (50 ml) was added dropwise to a solution of 1, 1, 1, 3, 3, 3-hexamethyldisilazane (13.2 g, 82 mmol) in hot toluene (50 ml) over 30 minutes. Heating at 90 °C and stirring was continued for 3 hours after which reaction was cooled to room temperature and selenium powder (12.53 g, 16 mmol) was added. The mixture was further refluxed for 6 hours which turned orange, cooled to 0 °C and left overnight. This was concentrated under vacuum and washed with diethyl ether and cold toluene which gave a white crystalline powder. Yield: 9.5 g (30 %). Elemental analysis: Calculated for C12H29NP2Se2: C, 35.37; H, 7.18; N, 3.44; P, 15.22%. Found: C, 35.36; H, 7.15; N, 3.38; P, 15.34 %. 195P{__1H} NMR, (δ, CDCl3, 400 MHz): δ = 1.34 (m, 24H, 8xCH(CH3)2); 2.70 (m, 4H, 4xCH(CH3)2); 3.10 (s, 1H, -NH). 31P{__1H} NMR: 90.05 ppm. 1JP,Se = 751 Hz.

2.2.1.2 Preparation of imido(tetraisopropylthiodiphosphinate) [Pr2P(S)NHP(S)Pr2]47

A solution of chlorodiisopropylphosphine (25 g, 26 ml, 164 mmol) in toluene (50 ml) was added dropwise to a solution of 1, 1, 1, 3, 3, 3-hexamethyldisilazane (13.2 g, 17 ml, 82 mmol) in hot toluene (50 ml) over 30 minutes. Heating and stirring were continued for 3 hours at 90 °C after which the reaction was cooled to
room temperature and sulfur powder (5.3 g, 164 mmol) was added. The reaction mixture was then refluxed for a further 6 hours and cooled to 0 °C overnight. The resulting white precipitate was concentrated under vacuum and filtered off. This was later washed with CS$_2$ (2 x 50 ml) and light petroleum ether (2 x 50 ml) which gave white crystalline needle-like powder. Yield: 9.5 g (37 %). Elemental analysis: Calculated for C$_{12}$H$_{29}$NP$_2$S$_2$: C, 45.99; H, 9.33; N, 4.47; S, 20.42; P, 19.78%. Found: C, 45.94; H, 9.85; N, 4.42; S, 19.46; P, 19.67 %. $^1$HNMR, ($\delta$, CDCl$_3$, 400MHz): $\delta$ = 1.30 (m, 24H, 8xCH(CH$_3$)$_2$); 2.50 (m, 4H, 4xCH(CH$_3$)$_2$); 2.80 (s, 1H, -NH). $^{31}$P{$^1$H}NMR: 90.62 ppm.

2.2.1.3 Preparation of imido(tetraisopropylthioselenodiphosphinate) 
$[^1]$Pr$_2$P(S)NHP(Se)$[^1]$Pr$_2$]$^{46}$

A solution of chlorodiisopropylphosphine (19.37 g, 127 mmol) in toluene (40 ml) was added dropwise to a solution of 1, 1, 1, 3, 3, 3-hexamethyldisilizane (10.33 g, 64 mmol) in hot toluene (40 ml) over 30 minutes and heated at 90 °C for 3 hours. This was then cooled to room temperature and selenium powder (5.05 g, 64 mmol) added and the solution stirred overnight. Sulfur powder (2.05 g, 64 mmol) was added and stirred for further 6 hours. An ash/off-white product was obtained and filtered off, which gave a white powder. This was dissolved in hot dichloromethane (DCM) and filtered to remove excess reactant, followed by solvent removal on the rotavap. A white crystalline powder obtained and dried under vacuo. Yield: 12.9 g (56 %). Elemental analysis: Calculated for C$_{12}$H$_{29}$NP$_2$SSe: C, 39.99; H, 8.12; N, 3.89; P, 17.20; S, 8.88 %. Found: C, 39.90; H, 8.21; N, 3.93; P, 16.02; S, 8.79 %. $^1$HNMR, ($\delta$, CDCl$_3$, 400 MHz): $\delta$ = 1.34 (m, 24H, 8xCH(CH$_3$)$_2$); 2.50 (m, 2H, Se=P-CH(CH$_3$)$_2$); 2.75 (m, 2H, S=P-CH(CH$_3$)$_2$); 3.20 (s, 1H, -NH). $^{31}$P{$^1$H}NMR: 93.04, 89.15 ppm. $^1$J$_{P,Se}$ = 504 Hz.
2.2.2 Cadmium Complexes

2.2.2.1 Synthesis of \(\text{Cd}[\text{Pr}_2\text{P(Se)}\text{NP(Se)}\text{Pr}_2]\)\(^{46}\) (1)

Imidodiselenodiphosphinate ligand (4.55 g, 11.18 mmol) was dissolved in dry MeOH, stirred for 30 minutes and NaOMe (0.60 g, 11.18 mmol) added. A brown colouration observed followed by gentle heating which became progressively darker and transparent. \(\text{CdCl}_2\) (1.28 g, 5.59 mmol) was added which gave a cloudy white suspension immediately. The reaction was continued for 3 hours which gave a cloudy white suspension, which was filtered and the off-white residue dissolved in hot dichloromethane. The resulting solution was filtered to remove excess reactant followed by solvent removal under vacuum. A pink powder obtained. Yield: 4.0 g (77 %). Elemental analysis calculated for \(\text{C}_{24}\text{H}_{56}\text{N}_2\text{P}_4\text{Se}_4\text{Cd}\): C, 31.15; H, 6.10; N, 3.03; P, 13.40; Cd, 12.16 %. Found: C, 31.09; H, 6.30; N, 2.95; P, 13.10; Cd, 12.07 %. \(^{31}\text{P}\{^{1}\text{H}\}\) NMR (CDCl\(_3\)): 56.4 ppm. \(^1J_{\text{P-Se}} = 385\) Hz.

2.2.2.2 Synthesis of \(\text{Cd}[\text{Pr}_2\text{P(S)}\text{NP(S)}\text{Pr}_2]\)\(^{47}\) (2)

Imidodithiodiphosphinate ligand (4.20 g, 13.41 mmol) was dissolved in dry MeOH, stirred for 30 minutes and NaOMe (0.72 g, 13.41 mmol) added. After 30 minutes, \(\text{CdCl}_2\) (1.53 g, 6.71 mmol) was added and the reaction turned to a cloudy white suspension. Reaction mixture was continued for 3 hours which gave a cloudy white suspension, filtered and dissolved in hot dichloromethane. The resulting solution was filtered to remove excess reactant followed by solvent removal under vacuum. A white powder was obtained. Yield: 3.1 g (63 %). Elemental analysis calculated for \(\text{C}_{24}\text{H}_{56}\text{CdN}_2\text{P}_4\text{S}_4\): C, 39.10; H, 7.66; N, 3.80; S, 17.36; P, 16.82; Cd, 15.26 %. Found: C, 39.15; H, 7.60; N, 3.73; S, 16.97; P, 16.56; Cd, 15.26%. \(^{31}\text{P}\{^{1}\text{H}\}\) NMR (CDCl\(_3\)): 62.49 ppm.
2.2.2.3 Synthesis of Cd[\text{\textit{t}}\text{Pr}_2\text{P(Se)NP(Se)\textit{t}}\text{Pr}_2\text{]}_2^{46} (3)

Imidothioselenodiphosphinate ligand (5.9 g, 16 mmol) was dissolved in dry methanol, stirred for 30 minutes and sodium methoxide NaOMe (0.86 g, 16 mmol) added. After 20 minutes, cadmium chloride (1.87 g, 8 mmol) was added and gave a cloudy white suspension. The reaction was continued for 4 hours which gave a white suspension, filtered and dissolved in hot dichloromethane. The resulting solution was filtered to remove excess reactant followed by solvent removal under vacuo, which gave a white powder. Yield: 2.4 g (61%). Microanalysis calculated for C_{24}H_{56}N_{2}P_{4}S_{2}SeCd: C, 34.67; H, 6.79; N, 3.37; S, 7.70; P, 14.92; Cd, 13.53 %. Found: C, 34.59; H, 6.83; N, 3.29; S, 7.29; P, 14.35; Cd, 12.81 %. \( ^1\text{H} \text{NMR, (δ, CDCl}_3, 400 \text{ MHz)}, \delta = 1.28 (\text{m}); 2.00 (\text{s}). \)

\[ ^{31}\text{P} \{ ^1\text{H} \} \text{NMR: 56.41, 63.91 ppm.} \]

\[ ^{1}J_{P\text{-Se}} = 154 \text{ Hz.} \]

2.2.3 Zinc Complexes

2.2.3.1 Synthesis of Zn[\text{\textit{t}}\text{Pr}_2\text{P(Se)NP(Se)\textit{t}}\text{Pr}_2\text{]}^{46} (4)

Imidodiselenidodiphosphinate ligand (4.75 g, 11.67 mmol) was dissolved in dry MeOH, stirred for 30 minutes and NaOMe (0.63 g, 11.67 mmol) was added. An orange/yellow colouration observed followed by gentle heating which gave a clear transparent dark-brown solution. ZnCl\(_2\) (0.80 g, 5.83 mmol) was added which gave a cloudy white suspension immediately. The reaction was continued for 3 hours and a cloudy white suspension was obtained, filtered and dissolved in hot dichloromethane. The resulting solution was filtered to remove excess reactant followed by solvent removal under vacuum. A white powder was obtained. Yield: 3.0 g (59 %). Elemental analysis calculated for C_{24}H_{56}N_{2}P_{4}Se_{2}Zn: C, 32.82; H, 6.43; N, 3.19; P, 14.12; Zn, 7.45 %. Found: C, 32.72; H, 6.46; N, 3.10; P, 13.74; Zn, 7.14 %. \( ^{31}\text{P\{}^{1}\text{H}\} \text{NMR (CDCl}_3): 58.86 \text{ ppm.} \)

\[ ^{1}J_{P\text{-Se}} = 519 \text{ Hz.} \]
2.2.3.2 Synthesis of Zn\textit{Pr}2P(S)NP(S)\textit{Pr}2\textsuperscript{47} \hspace{1em} (5)

Imidodithiodiphosphinate ligand (4.25 g, 13.57 mmol) was dissolved in dry MeOH, stirred for 30 minutes and NaOMe (0.73 g, 13.57 mmol) added. After 30 minutes, ZnCl\textsubscript{2} (0.93 g, 6.79 mmol) was added and a cloudy white suspension observed. The reaction was continued for 3 hours which gave a cloudy white suspension which was filtered and dissolved in hot dichloromethane. The resulting solution was filtered to remove excess reactant followed by solvent removal under vacuum. A white powder obtained. Yield: 2.9 g (61 %). Elemental Analysis calculated for C\textsubscript{24}H\textsubscript{56}N\textsubscript{2}P\textsubscript{4}S\textsubscript{4}Zn: C, 41.76; H, 8.18; N, 4.06; S, 18.54; P, 17.97; Zn, 9.48 %. Found: C, 41.55; H, 7.95; N, 3.97; S, 18.11; P, 17.45; Zn, 9.17 %. \textsuperscript{31}P \{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}): 63.76 ppm.

2.2.3.3 Synthesis of Zn\textit{Pr}2P(Se)NP(S)\textit{Pr}2\textsuperscript{46} \hspace{1em} (6)

Imidothioselenodiphosphinate ligand (5.9 g, 16 mmol) was dissolved in dry methanol, stirred for 30 minutes and sodium methoxide NaOMe (0.86 g, 16 mmol) added. After 20 minutes, zinc chloride ZnCl\textsubscript{2} (1.11 g, 8 mmol) was added and gave a cloudy white suspension. The reaction mixture continued for 4 hours which gave a cloudy white suspension, filtered reactant followed by solvent removal under vacuum, which gave a white powder. Yield: 2.4 g (62 %). Microanalysis calculated for C\textsubscript{24}H\textsubscript{56}N\textsubscript{2}P\textsubscript{4}S\textsubscript{2}Se\textsubscript{2}Zn: C, 36.75; H, 7.20; N, 3.57; P, 15.81; S, 8.16; Zn, 8.35. Found: C, 36.68; H, 7.26; N, 3.50; P, 15.98; S, 7.88; Zn, 8.34. \textsuperscript{1}NMR, (\delta, CDCl\textsubscript{3}, 400 MHz), \delta = 1.28 (m); 2.00 (s). \textsuperscript{31}P \{\textsuperscript{1}H\} NMR: 58.98, 63.49 ppm. \textsuperscript{1}J\textsubscript{P,Se} = 508 Hz.
2.3. Results and Discussion

Cadmium and zinc complexes of dichalcogenimidodiphosphinate ligand were synthesised from chlorodiisopropylphosphine and hexamethyldisilazane, which produced the ligand \([\text{NH}(\text{EP}_2\text{Pr}_2)_2]\). This contains an acidic NH proton which can be easily deprotonated to form anionic chelate complexes:

A scheme showing the synthesis of the ligand and complex is shown below:

\[
\begin{align*}
\text{\textsuperscript{1}Pr}_2\text{PCl} + \text{NH(SiMe}_3)_2 & \xrightarrow{\text{Toluene}} \text{NH(PR}_2)_2 \quad \text{E = S, Se} \\
\text{E = S,S & Se,Se} & \quad \xrightarrow{\text{NaOMe}} [\text{NH(EPR}_2)_2] \quad \xrightarrow{\text{MX}_2, M = \text{Zn, Cd}} [\text{M\{('Pr}_2\text{PE}_2)_2\} \quad]
\end{align*}
\]

**Scheme. 2.1** Schematic representation of synthesis of ligands and complexes.

The reaction of the ligand \([\text{NH(EPR}_2)_2]\) with the appropriate metal salts formed the neutral complexes with the general formula ML₂.

**Fig.2.1.** Diagrammatic representation of the neutral complex ML₂.

The dithio- and thioseleno complexes gave good yields (61 - 63%), while the lowest yield was obtained from the zinc diseleno complex. However, the cadmium diseleno
complex gave the highest yield of 77%. All the complexes were both air and moisture stable except for the diselenide ones, which changed colour gradually. Also, they were all soluble in organic solvents which made them suitable for AACVD.

2.3.1. X-ray single crystal structure of \[\text{[Cd}^{1} \text{Pr}_{2} \text{P(Se)NP(S)}^{1} \text{Pr}_{2} \text{]}_{2} (3)\]

X-ray crystallographic studies show that the complex is tetrahedrally coordinated through both the sulfur and selenium atoms of the ligand (Fig. 2.2). The crystal lattice shows the presence of monomeric independent units separated by Van der Waals distances. The donor atoms consist of two sulfur and selenium together with the cadmium atom being four-coordinate. The Cd-Se bond lengths range from Cd(1)-Se(1) 2.5984(10) to Cd(1)-Se(2s) 2.6164(7) Å. These are shorter than those in (1), which are from 2.625(2) to 2.636(2) Å\(^{46}\). Although the Se(1)-Cd-Se(2) bond angles are generally lower when compared with (1), the Se(1)-Cd(1)-Se(1s) bond angle in (3) gave a higher value of 111.81(3)°. The Cd-S bond lengths in (3) are longer than those reported for (2)\(^{47}\), which are from 2.6006(18) to 2.6024(19) Å. The S-Cd-S bond angle has a value of 109.65(9) °. Selected bond angles and bond lengths are given in table 2.1. Structural refinement parameters are given in table 2.2.
Fig. 2.2. X-ray single crystal structure of $[\text{Cd}^\text{iPr}_2\text{P(Se)NP(S)}^\text{iPr}_2]^2$ (3) showing disorder.

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(1)-Se(1)</td>
<td>2.5996(8)</td>
</tr>
<tr>
<td>Cd(1)-Se(2)</td>
<td>2.5984(10)</td>
</tr>
<tr>
<td>Cd(1)-S(1)</td>
<td>2.6006(18)</td>
</tr>
<tr>
<td>Cd(1)-S(2)</td>
<td>2.6024(19)</td>
</tr>
<tr>
<td>Se(1)-P(2)</td>
<td>2.1177(10)</td>
</tr>
<tr>
<td>Se(2)-P(4)</td>
<td>2.1052(11)</td>
</tr>
<tr>
<td>S(1)-P(1)</td>
<td>2.171(2)</td>
</tr>
<tr>
<td>S(2)-P(3)</td>
<td>2.174(2)</td>
</tr>
<tr>
<td>N(1)-P(1)</td>
<td>1.587(2)</td>
</tr>
<tr>
<td>N(1)-P(2)</td>
<td>1.593(2)</td>
</tr>
</tbody>
</table>

Table 2.1. Selected bond lengths and angles for $[\text{Cd}^\text{iPr}_2\text{P(Se)NP(S)}^\text{iPr}_2]^2$ (3).
Table 2.2. Crystal data for [Cd\{Pr2P(Se)NP(S)\Pr2\}]_2 (3).

<table>
<thead>
<tr>
<th>Compound</th>
<th>[Cd{Pr2P(Se)NP(S)\Pr2}]_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
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</tr>
<tr>
<td>Formula Weight</td>
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<td>Temperature (K)</td>
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<tr>
<td>Crystal Size (mm^3)</td>
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<tr>
<td>Wavelength (Å)</td>
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</tr>
<tr>
<td>Crystal System</td>
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<td>Space Group</td>
<td>P\bar{1}</td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.3089(5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>12.8812(6)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>16.2889(8)</td>
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<tr>
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<td>79.1010(10)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>77.9720(10)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>69.9810(10)</td>
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<tr>
<td>Volume (Å^3)</td>
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<tr>
<td>Z</td>
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<tr>
<td>Density_{calcd} (mg m^{-3})</td>
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<td>Unique Reflections</td>
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<tr>
<td>Max. Min. Transm.</td>
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<td>Data/Rest/Parameters</td>
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<tr>
<td>Final R ([I&gt;2\sigma(I)])</td>
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</tr>
<tr>
<td>R Indices (all data)</td>
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</tr>
<tr>
<td>Diff. Peak and Hole (e.Å^{-3})</td>
<td>0.885 and -0.835</td>
</tr>
</tbody>
</table>
2.3.2. X-ray single crystal structure of Zn[^Pr_2P(Se)NP(S)^Pr_2]_2 (6)

The complex crystallized in the triclinic space group $P\bar{1}$. The zinc atom is tetrahedrally coordinated to the donor atoms, the sulfur and selenium atoms of the imidodiphosphinate ligand (Fig.2.3). The crystal lattice revealed independent monomeric units separated by Van der Waals distances. Selected bond lengths and bond angles are given in table 2.3 and crystallographic data are listed in table 2.4.

The sulfur and selenium atoms are disordered as observed for Pt[^Pr_2P(Se)NP(S)^Pr_2]_2 and [Cd[^Pr_2P(Se)NP(S)^Pr_2]_2] complexes and refined with equal occupancies for both atoms. Hence, there is no doubt about the conformation of the ZnSSeP$_2$N ring. The Zn-Se (2.483(3) Å) bond length is slightly longer than the Zn-S (2.332(11) Å) bond length. However, this is closer to the value observed for (5) (2.345(1) Å). Also, the S(1)-P(1)-N(1) bond angle is larger (~116°) when compared to the value reported in (5). As observed before, the P-N-P bond angle is considerably enlarged which can be due to the presence of the $^3$Pr group.

![Fig.2.3. X-ray single crystal structure of Zn[^Pr_2P(Se)NP(S)^Pr_2]_2 (6).](image-url)
Table 2.3. Selected bond angles and bond lengths for Zn[Pr₂P(Se)NP(S)₃Pr₂]₂ (6)

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<tr>
<th>Bond Length (Å)</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
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<td>Zn(1)-Se(2)</td>
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<td>Zn(1)-S(1)</td>
<td>2.332(11)</td>
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<td>Zn(1)-S(3)</td>
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<td>S(1)-P(1)</td>
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<td>S(3)-P(3)</td>
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<td>Se(4)-P(4)</td>
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<td>P(2)-N(1)</td>
<td>1.590(2)</td>
</tr>
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<td>S(1)-Zn(1)-S(3)</td>
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<td>Se(4)-Zn(1)-Se(2)</td>
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<td>S(1)-Zn(1)-Se(2)</td>
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<td>S(1)-Zn(1)-Se(2)</td>
<td>109.0(4)</td>
</tr>
<tr>
<td>P(1)-S(1)-Zn(1)</td>
<td>107.6(5)</td>
</tr>
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<td>P(2)-Se(2)-Zn(1)</td>
<td>100.93(11)</td>
</tr>
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<td>N(1)-P(1)-S(1)</td>
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<td>N(2)-P(4)-Se(4)</td>
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<td>P(4)-N(2)-P(3)</td>
<td>139.21(14)</td>
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Table 2.4. Crystal data and structural refinement for Zn\([\text{Pr}_2\text{P(Se)NP(S)}\text{Pr}_2]_2\) (6).

<table>
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<tr>
<th><strong>Compound</strong></th>
<th><strong>Zn([\text{Pr}_2\text{P(Se)NP(S)}\text{Pr}_2]_2)</strong></th>
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</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
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<td>Temperature (K)</td>
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<td>Crystal Size (mm(^3))</td>
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<td>Wavelength (Å)</td>
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<td>Crystal System</td>
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<td>(c) (Å)</td>
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<td>(\gamma) (°)</td>
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<td>Unique Reflections</td>
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</tr>
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<td>Max. Min. Transm.</td>
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<td>Data/Rest/Parameters</td>
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<td>R Indices (all data)</td>
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</tr>
<tr>
<td>Diff. Peak and Hole (e.Å(^{-3}))</td>
<td>0.565 and -0.339</td>
</tr>
</tbody>
</table>
2.4. Thermogravimetry Analysis (TGA)

Thermogravimetry analysis (TGA) of the complexes gave an understanding of their decomposition process and volatility. TGA of the complexes (1) to (6) indicated a single step decomposition ranging from 257 to 395 °C (Fig. 2.4 & 2.5). Complex (1) had a rapid weight loss between 293 and 390 °C with a final residue of 2 %. This is lower than the calculated residue value of 21 % for the combined Cd and Se, and 15 % Cd and P content of the precursor. The observed residue value 2 % for (2) is lower than the calculated residue value of 19 % for both Cd and S, and Cd and P content of the precursor. Similarly, the observed residue value 1 % for (3) is lower than the 23 and 17 % calculated for the combined Cd and Se, and Cd and P content of (3).

The zinc precursors also exhibited similar features with a single step decomposition and rapid weight loss. Complex (4) decomposed between 277° to 395 °C with a final residue of 1 %. This is lower than the calculated value of 16 % for ZnSe. Similarly, the decomposition residue of 1 % for (5) is lower than the calculated value of 14 % for ZnS. The same feature is displayed by (6) having a solid
decomposition residue of 1%, which is also lower than the calculated value of 18% for ZnSe. These data are consistent with (1) - (6) being volatile.

Fig. 2.5. Thermogravimetry analysis (TGA Section 5.5) of complexes Zn[Pr$_2$P(Se)NP(Se)$^i$Pr$_2$] (4), Zn[Pr$_2$P(S)NP(S)$^i$Pr$_2$] (5) and Zn[Pr$_2$P(Se)NP(S)$^i$Pr$_2$]$_2$ (6).

2.5. AACVD studies of Cd[Pr$_2$P(Se)NP(Se)$^i$Pr$_2$] (1)

Deposition was carried out at substrate temperatures from 450 to 525 °C, with argon flow rates of 160 and 240 sccm onto glass substrates. No deposition was seen below 450 °C. The deposited films were black and well adherent to the surface. XRD studies of the deposited films revealed that hexagonal CdSe film (ICDD 01-077-2307) was exclusively deposited at all temperatures, with the preferred orientation mostly along the (100) plane (Fig. 2.6). The film deposited at 525 °C 160 sccm showed the preferred orientation to be along the (002) plane. Cadmium selenide films grown from [MeCd{(SeP$^i$Pr$_2$)$_2$N}]$_2$ [Cd{(SeP$^i$Pr$_2$)$_2$N}]$_2$ by LPCVD also gave hexagonal cadmium selenide although with different preferred orientations. However, at 475° and 500 °C (160 sccm), a mixture of both hexagonal cadmium selenide and monoclinic cadmium phosphide (Cd$_2$P$_3$) films (ICDD 00-022-0125) were deposited. Traces of Cd$_2$P$_3$ were observed
at 2θ values of 12.88, 27.08 and 29.06° respectively. Though the peak at 12.88 was not seen at 475°C, but was more pronounced in the film at 500 °C (Fig. 2.7).

Fig. 2.6. XRD of hexagonal CdSe at (a) 525 °C and (b) 500 °C (240 sccm).

Fig. 2.7. XRD of hexagonal CdSe and monoclinic Cd$_2$P$_3$ at (a) 500 °C and (b) 475 °C at the flow rate of 160 sccm. Marked peaks are those for Cd$_2$P$_3$. 

2 Theta (deg.)
The SEM studies showed that the morphologies of the as-deposited CdSe films depended on the growth temperature, due to the gradual changes observed for the films. For example, the film grown at 525 °C revealed a morphology containing opened two-fold rectangular crystallites which are randomly displaced (Fig. 2.8a). However, at 500 °C, the morphology consists of randomly fused orientated platelets containing rice-like grains or particles (Fig. 2.8b). The surface morphology can be likened with previous CdSe films grown from \([\text{MeCd}((\text{SePPr}_2)_2\text{N})_2]^{48}\), \([\text{Cd}((\text{SePPr}_2)_2\text{N})_2]^{45}\) and \([\text{Cd}((\text{SePPh}_2)_2\text{N})_2]^{44}\). For the films having a mixture of both CdSe and Cd$_2$P$_3$, the scanning electron microscopy indicated the morphology to be randomly orientated flakes at 500 °C, while the film at 475 °C had the morphology of well aggregated and fused triangular crystallites (Fig. 2.9).

![SEM images of hexagonal cadmium selenide deposited from (1) on glass at (a) 525 °C (b) 500 °C (c) 475 °C and (d) 450 °C at the flow rate of 240 sccm.](image)

**Fig. 2.8.** SEM images of hexagonal cadmium selenide deposited from (1) on glass at (a) 525 °C (b) 500 °C (c) 475 °C and (d) 450 °C at the flow rate of 240 sccm.
EDX studies of the hexagonal CdSe films showed a cadmium-rich film having a cadmium-selenium ratio of ~1:1 together with 10% phosphorus. For the films having both CdSe and Cd$_3$P$_3$, the EDX indicated a phosphorus-rich film having a higher phosphorus content of 26 and 29%. The ratio of cadmium to phosphorus was seen to be greater than 1:1 while that of cadmium to selenium is ~1:1.

2.6. AACVD studies of Cd[Pr$_2$P(S)NP(S)Pr$_2$] (2)

Deposition was carried out at substrate temperatures of 500 and 525 °C under the argon flow rate of 160 and 240 sccm onto glass substrates. No deposition was observed below 500 °C and the films were transparent and well adherent to the glass surface. Brown films were deposited at 500 °C, while reddish-brown films were seen at 525 °C. At 525 °C (240 sccm) (Fig. 2.10) and 500 °C (160 sccm) (Fig. 2.11), hexagonal CdS (ICDD 01-077-2306 and 01-075-1545 respectively) was deposited as indicated by the powder XRD pattern. The as-deposited films at 500 °C had some phosphorus contamination. However, at 525 °C (160 sccm), cubic Cd$_6$P$_7$ (ICDD 00-022-0126) and orthorhombic Cd$_7$P$_{10}$ (ICDD 00-054-0206) was observed (Fig. 2.12). At 500 °C (240 sccm), both the hexagonal CdS and orthorhombic Cd$_7$P$_{10}$ were deposited (Fig. 2.13).
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Fig. 2.10. XRD pattern of hexagonal CdS deposited at 525 °C (240 sccm).

Fig. 2.11. XRD pattern of hexagonal CdS deposited at 500 °C (160 sccm).

Fig. 2.12. XRD pattern of orthorhombic Cd$_7$P$_{10}$ deposited at 525 °C (160 sccm). Marked peaks indicate cubic Cd$_6$P$_7$. 
Fig. 2.13. XRD pattern of hexagonal CdS deposited at 500 °C (240 sccm). Marked peaks indicate orthorhombic Cd$_7$P$_{10}$.

SEM studies of the hexagonal CdS film indicated the effect of temperature and flow rate on morphology. The as-deposited CdS film at 525 °C (240 sccm) revealed the images to be ribbon crystallites (Fig. 2.14(a)), while that of 500 °C (160 sccm) consisted of clustered needle-like structures (Fig. 2.14(b)). The cadmium phosphide films had randomly oriented crystallites (Fig. 2.15) while the CdS/Cd$_7$P$_{10}$ film contained dense ribbon-like primary crystallites (Fig. 2.16).

Fig. 2.14. SEM images of hexagonal CdS film deposited at (a) 525 °C at the flow rate of 240 sccm and (b) 500 °C at the flow rate of 160 sccm.
From the EDX analysis, the ratio of phosphorus to cadmium was greater than 1:1 for the cadmium phosphide films deposited at 525 °C. The hexagonal cadmium sulfide films at 500 °C showed cadmium-rich films along with phosphorus contamination. The CdS/Cd$_7$P$_{10}$ films contained 42 % cadmium, 39 % phosphorus and 20 % sulfur.
2.7. AACVD studies of [Cd\textsuperscript{Ⅳ}Pr\textsubscript{2}P(Se)NP(S)\textsuperscript{Ⅳ}Pr\textsubscript{2}]\textsubscript{2} (3)

Deposition was carried out at substrate temperatures of 475 to 525 °C, with argon flow rates of 160 and 240 sccm onto glass substrates. The deposited films were black and adhere very well to the surface. XRD studies of the deposited films indicated that hexagonal cadmium selenide (ICDD 01-077-2307) was exclusively deposited at all temperatures, having the preferred orientation mostly along the (100) plane. The deposited film at 525 °C (240 sccm) had the preferred orientation along the (002) plane (Fig. 2.17). The as-deposited film at 500 °C (240 sccm) also revealed traces of cubic cadmium sulfide (ICDD 04-003-5332) in addition to the hexagonal CdSe (Fig. 2.18).

![XRD of hexagonal CdSe deposited at 525 °C](image)

**Fig. 2.17.** XRD of hexagonal CdSe deposited at 525 °C (a) at the flow rate of 240 sccm and (b) at the flow rate of 160 sccm.
Fig. 2.18. XRD pattern of hexagonal CdSe and cubic CdS deposited at 500 °C at the flow rate of 240 sccm. Marked peaks are those of CdS.

Traces of CdS were observed at 2θ values of 29.16°, 48.5° and 60.5° respectively. However, the as-deposited films at 500 and 475 °C at the flow rate of 160 sccm gave a mixture of both hexagonal CdSe and monoclinic Cd$_2$P$_3$. As already mentioned in the AACVD studies of (1), traces of Cd$_2$P$_3$ were observed at 2θ values of 27.08° and 29.06°. The intensity of the cadmium phosphide peaks increased in the film deposited at 500 °C (Fig. 2.19).
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**Fig. 2.19.** XRD patterns of hexagonal CdSe and monoclinic Cd$_2$P$_3$ deposited at (a) 500 °C and (b) 475 °C at the flow rate of 160 sccm. Marked peaks are those of Cd$_2$P$_3$.

The morphology of the hexagonal cadmium selenide films at 525 °C at the flow rate of 240 sccm consisted of randomly dispersed triangular crystallites (Fig. 2.20(a)), while rod-like structures were seen at the lower flow rate (Fig. 2.20(b)). At 475 °C (240 sccm), the morphology consisted of clustered grains (Fig. 2.20(c)). The as-deposited film at 500 °C (240 sccm) containing CdSe/CdS consisted of dense flake-like structures (Fig. 2.21). The CdSe/Cd$_2$P$_3$ film at 475 °C contained randomly dispersed triangular structures, while that of 500 °C was polygonal crystallites (Fig. 2.22).
Fig. 2.20. SEM images of hexagonal CdSe deposited at 525 °C (a) flow rate of 240 sccm (b) flow rate of 160 sccm and (c) 475 °C at flow rate of 240 sccm.

Fig. 2.21. SEM image of CdSe/CdS deposited at 500 °C at the flow rate of 240 sccm.
EDX analysis of the cadmium selenide films showed the stoichiometry of cadmium to selenium as 1:1 with phosphorus contamination. The analysis of the as-deposited film at 500 °C (240 sccm) confirmed the presence of sulfur together with the 1:1 ratio of cadmium and selenium. The films having the mixture of CdSe and Cd$_3$P$_3$ (475 and 500 °C) indicated phosphorus-rich films together with 1:1 ratio of cadmium to selenium. A summary of the AACVD studies on cadmium complexes (1), (2) and (3) is presented in table 2.5.
Table 2.5. Summary of the AACVD studies on cadmium complexes (1) to (3).

<table>
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<th>Precursor</th>
<th>Deposition T/Flow Rate (°C/sccm)</th>
<th>Material Deposited</th>
<th>Phase</th>
</tr>
</thead>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>525/240</td>
<td>CdSe</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
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<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>500/240</td>
<td>CdSe</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>500/160</td>
<td>CdSe/Cd₂P₃</td>
<td>Hexagonal/Monoclinic</td>
</tr>
<tr>
<td></td>
<td>475/240</td>
<td>CdSe</td>
<td>Hexagonal</td>
</tr>
<tr>
<td></td>
<td>475/160</td>
<td>CdSe/Cd₂P₃</td>
<td>Hexagonal/Monoclinic</td>
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<tr>
<td></td>
<td>450/240</td>
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<td>Hexagonal</td>
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<tr>
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<td>450/160</td>
<td>CdSe</td>
<td>Hexagonal</td>
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<td>Hexagonal/Monoclinic</td>
</tr>
</tbody>
</table>
2.8. AACVD studies of Zn[Pr$_2$P(Se)NP(Se)Pr$_2$] (4)

Deposition was carried out substrate temperatures of 500 and 525 °C at argon flow rates of 160 and 240 sccm onto glass substrates. All the deposited films were yellow, transparent and well adherent to the glass surface at both the deposition temperatures and flow rates. The X-Ray powder diffraction (XRPD) pattern of the as-deposited films showed the exclusive deposition of cubic ZnSe (ICDD 00-037-1463) (Fig. 2.23 & 2.24).

![XRD pattern of cubic zinc selenide deposited at flow rates of 240 sccm (a) 525 °C and (b) 500 °C.](image)

**Fig. 2.23.** XRD pattern of cubic zinc selenide deposited at flow rates of 240 sccm (a) 525 °C and (b) 500 °C.

Also, the as-deposited films had improved crystallinity as shown by the increased intensity of the XRD pattern at 525 °C for both flow rates. However, there is a peak/shoulder in the pattern which corresponds mostly to the (100) plane of the hexagonal phase, but none of the other reflections of this was detected. The identity of this reflection is not clear as it is unlikely that the phase is textured given that the cubic phase appears to be randomly orientated.
Fig. 2.24. XRD pattern of cubic zinc selenide deposited at flow rate of 160 sccm (a) 525 °C and (b) 500 °C.

SEM analysis of the films at the flow rate of 240 sccm revealed a dense fibrous network structure at 525 °C, while porous particles containing thin fibres was the morphology for the deposited film at 500 °C (Fig. 2.25).

Fig. 2.25. SEM images of cubic zinc selenide deposited at the flow rate of 240 sccm (a) 525 °C and (b) 500 °C.
However, at the lower flow rate, a marked change in the morphology of the films was noticed. The as-deposited film at 525 °C consisted of random particles, while porous particles were the morphology of the deposited film at 500 °C (Fig. 2.26).

![SEM images of cubic zinc selenide deposited at the flow rate of 160 sccm (a) 525 °C and (b) 500 °C. Poor coverage of the morphology is seen.](image)

EDX analysis confirmed the presence of zinc and selenium in near stoichiometric ratio for all the films alongside with phosphorus contamination. The deposited films at 525 °C (240 and 160 sccm) contain higher amounts of zinc and selenium when compared with that obtained at 500 °C.

### 2.9. AACVD studies of Zn[P(Se)NP(S)P]2 (6)

Deposition was carried out at substrate temperatures of 500° and 525 °C, with argon flow rates of 160 and 240 sccm onto glass substrates. The optimum temperature appeared to be within this range as there was no deposition below 500 °C. The deposited films were yellow at the flow rate of 240 sccm, while brown films were seen for the films at 160 sccm. All the films were well adherent to the glass surface. X-ray powder diffraction pattern (XRPD) of the as-deposited film indicated that cubic zinc selenide (ICDD 00-037-1463) was deposited at both 500 and 525 °C (Fig. 2.27). The crystallinity of the as-deposited films was improved at 525 °C, as shown by the intensity of the XRD pattern.
Fig. 2.27. XRD pattern of cubic zinc selenide deposited at the flow rate of 240 sccm (a) 525 °C and (b) 500 °C.

As it was already discussed in the AACVD studies of (4), a minor peak arising from the hexagonal phase was also noticed in the XRD pattern. Previously, there were reports about the growth of hexagonal ZnSe from [Zn{(SePPh₂)₂N₂}]⁴⁴ and [Zn{(SePPr₂)₂N₂}]⁴⁵ by LP-MOCVD. However, cubic ZnSe was deposited from [Zn(Se₂CNMe₆Hex)₂]⁴⁹ and [Zn(t-Bu₂PSeNR)₂] (R = iPr, c-C₆H₁₁)⁵⁰ both having the preferred (111) orientation. SEM studies of the as-deposited films at the flow rate of 240 sccm revealed an interwoven fibrous network at 525 °C (Fig. 2.29(a)), while a less pronounced network of fibres was observed for the film at 500 °C (Fig. 2.29(b)). At 160 sccm, the deposited film at 525 °C had a morphology of woven fibres though seems to be slightly disordered when compared with the film at 240 sccm (Fig. 2.30(a)). Tiny droplet/globular morphology were observed for the deposited film at 500 °C at the flow rate of 160 sccm (Fig. 2.30(b)).
Fig. 2.28. XRD pattern of cubic ZnSe deposited at the flow rate of 160 sccm (a) 525 °C and (b) 500 °C.

Fig. 2.29. SEM images of cubic zinc selenide deposited at the flow rate of 240 sccm (a) 525 °C and (b) 500 °C.
Fig. 2.30. SEM images of cubic zinc selenide deposited at the flow rate of 160 sccm (a) 525 °C and (b) 500 °C.

EDX analysis of the cubic ZnSe films indicated that the films were rich in zinc, though with phosphorus contamination. A near stoichiometric ratio of 1:1 for Zn and Se was observed for all the films. A summary of the AACVD studies on zinc complexes (4) and (6) is presented in table 2.6.

Table 2.6. Summary of the AACVD studies on zinc complexes (4) and (6).

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Deposition T/Flow Rate (°C/sccm)</th>
<th>Material Deposited</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn{(i)Pr2P(Se)NP(Se)2Pr2}2] (4)</td>
<td>525/240</td>
<td>ZnSe</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>525/160</td>
<td>ZnSe</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>500/240</td>
<td>ZnSe</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>500/160</td>
<td>ZnSe</td>
<td>Cubic</td>
</tr>
<tr>
<td>[Zn{(i)Pr2P(S)NP(S)2Pr2}2] (5)</td>
<td>525/240</td>
<td>N/G</td>
<td>N/G</td>
</tr>
<tr>
<td></td>
<td>525/160</td>
<td>N/G</td>
<td>N/G</td>
</tr>
<tr>
<td></td>
<td>500/240</td>
<td>N/G</td>
<td>N/G</td>
</tr>
<tr>
<td></td>
<td>500/160</td>
<td>N/G</td>
<td>N/G</td>
</tr>
<tr>
<td>[Zn{(i)Pr2P(Se)NP(S)2Pr2}2] (6)</td>
<td>525/240</td>
<td>ZnSe</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>525/160</td>
<td>ZnSe</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>500/240</td>
<td>ZnSe</td>
<td>Cubic</td>
</tr>
<tr>
<td></td>
<td>500/160</td>
<td>ZnSe</td>
<td>Cubic</td>
</tr>
</tbody>
</table>

N/G means no growth
2.10. XPS studies

The atomic coverage and atomic oxidation states of the deposited films were determined using XPS. For the films grown from both Cd((SePPr$_2$)$_2$N)$_2$ (1) and [Cd(Pr$_2$P(S)NP(Se)Pr$_2$)$_2$] (3) precursors at the various deposition temperature and flow rates, the Cd 3d spectra indicated symmetrical narrow peaks corresponding to 3d$_{5/2}$ and 3d$_{3/2}$ spin orbit split states (Fig. 2.31). The XPS spectra revealed Cd 3d$_{5/2}$ peak at 405.3 eV and 405.6 eV for the CdSSe and CdSe$_2$ precursors respectively. This corresponds to cadmium selenides and also matches very well with reported literature values$^{51,52}$. The Cd 3d$_{3/2}$ peak is seen at 412 eV, which matches the BE value for Cd 3d$_{3/2}$ selenides$^{51}$. Since the films used to measure XPS had been previously exposed to air during XRD, hence, significant oxidation of the surfaces might have occurred.

Fig. 2.31. XPS of Cd 3d peaks of cadmium selenide deposited from (a) [Cd(Pr$_2$P(S)NP(Se)Pr$_2$)$_2$] (3) and (b) Cd((SePPr$_2$)$_2$N)$_2$ (1).
Moreover, these precursors indicated a high level of oxygen (32 – 40%). On the other hand, the Se 3d spectra revealed two different types of selenium at 53.9 eV and 54.3 eV respectively (Fig. 2.32). The binding energy values for the Se 3d doublets can only be assigned to a metallic selenide. Furthermore, the films deposited from the precursors above also indicated cadmium phosphide, which is present as phosphate from the XPS BE positions. The P 2p peaks appeared at around 134 eV which corresponds to a metaphosphate (Fig. 2.33).

![Fig. 2.32. XPS of Se 3d peaks of cadmium selenide deposited from (a) [Cd\{'Pr\text{\textsubscript{2}}P(S)NP(Se)'Pr\text{\textsubscript{2}}\}_{2}] (3) and (b) Cd[(Se\text{\textsubscript{2}}P\text{\textsubscript{2}})_{2}N]_{2} (1).](image)
Chapter 2: Cadmium and Zinc Precursors

The peak at 138.7 eV is due to Se auger. The occurrence of the phosphides as phosphates might be due to the stability of the phosphides in air. Probably, they are more reactive (less stable) than the selenides and any surface phosphides which may be formed initially proceeded to form phosphate species as observed. The acute surface sensitivity of XPS is finding the surface species and not locating the bulk properties as the XPS probing depth is limited to 60 angstroms.

Fig. 2.33. XPS of P 2p peaks of cadmium phosphide deposited from (a) [Cd(Pr₂P(S)NP(Se)Pr₂)]₂ (3) and (b) Cd[(SePr₂)₂N]₂ (1).

From the Cd[(SPPr₂)₂N]₂ (2) precursor, both cadmium phosphide and cadmium sulfide were deposited. The XPS of cadmium phosphide showed two different environments for cadmium: Cd 3d₅/₂ (405.4 and 407 eV) and Cd 3d₃/₂ (411.9 and 413.8 eV). The low energy peaks of Cd 3d are indicative of CdO species.
(but some studies of CdSe show similar BEs), in which the high energy peaks have unusually high binding energies for cadmium\textsuperscript{53} (Fig. 2.34) and may show a charge shifted peak. The P 2p\textsubscript{3/2} spectrum at 134.9 eV is indicative of a phosphate species like a phosphorus bonded to oxygen suggestive of P\textsubscript{2}O\textsubscript{5} bonds\textsuperscript{54} (Fig. 2.35).

![Fig. 2.34. XPS of Cd 3d peaks for the cadmium phosphide film.](image)

Moreover, the cadmium sulfide deposited revealed two cadmium environments exhibiting the same chemistry with spin orbit split features: Cd 3d\textsubscript{5/2} and Cd 3d\textsubscript{3/2} at 405.1 and 411.9 eV respectively\textsuperscript{53} (Fig. 2.36). The S 2p spectra exhibited two peaks arising from a spin-orbit splitting of 1.17 eV between the S 2p\textsubscript{3/2} (161.4 eV) and S 2p\textsubscript{1/2} (162.57 eV) states (Fig. 2.37). The binding energies of the cadmium and sulfur peaks were indicative of cadmium sulfide chemistry\textsuperscript{53}. Moreover, the oxidized species of sulfur (165.8 eV) and phosphorus (133.7 eV) were also detected in the same film.
Fig. 2.35. XPS of P 2p peaks at 134.9 eV.

Fig. 2.36. XPS of Cd 3d peaks of cadmium sulfide.
Furthermore, the surface atomic coverage and chemical shifts in the deposited films from the zinc precursors \( \text{Zn}[^1\text{Pr}_2\text{P}(|\text{Se})\text{NP}(|\text{Se})^1\text{Pr}_2] \) (4) and \( \text{Zn}[^1\text{Pr}_2\text{P}(|\text{Se})\text{NP}(|\text{S})^1\text{Pr}_2]_2 \) (6) were determined using XPS. For the films grown from the two precursors at both deposition temperatures and flow rates, the Zn 2p spectra consists of symmetrical narrow peaks corresponding to 2p\(_{3/2}\) and 2p\(_{1/2}\) spin split orbitals. The XPS spectra showed a Zn 2p\(_{3/2}\) peak at 1022.5 eV (Fig. 2.38). This corresponds to either ZnO or ZnSe \(^{55,56}\). The presence of oxide is inevitable because of handling of the sample in an open atmosphere. Also, water vapour and other gases in the atmosphere might be the source of oxygen contamination.
Fig. 2.38. XPS of Zn 2p peaks of zinc selenide deposited from (a) Zn[\text{Pr}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Pr}_2]_2 (6) and (b) Zn[\text{Pr}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Pr}_2] (4).

The obtained values for the binding energies of Zn 2p$_{3/2}$ and Se 3d seemed to be in agreement with previously reported values of 1021.6 eV & 54.2 eV$^{55}$ and 1020.6 eV & 53.3 eV$^{56}$ for bulk crystalline zinc selenide. The Se 3d peak revealed a doublet having a dominant component at 54.1 eV and a smaller one centered at about 55.1 eV respectively (Fig. 2.39). However, no Se peak was seen for the ZnSe$_2$ (4) precursor (Fig. 2.39(b)).
Fig. 2.39. XPS of Se 3d peaks of zinc selenide deposited from (a) Zn[Pr$_2$P(Se)NP(S)Pr$_2$]$_2$ (6) and (b) Zn[Pr$_2$P(Se)NP(Se)Pr$_2$] (4).

The Se 3d spectra exhibited a doublet indicative of ZnSe and free Se at 54.1eV and 55.1eV respectively. This occurs when atoms of an element are present in different oxidation states, thereby resulting in core-level peaks having different binding energies. Consequently, increase in the oxidation state of an atom results in corresponding increase in the binding energy. Hence, the Se 3d peaks at 54.1eV and 55.1eV can be assigned to be zinc selenide and free selenium respectively. Oxidised Se is not seen to be present because a higher BE Se 3d peak should be seen in this case. The absence of Se 3d peak for the ZnSe$_2$ (4) precursor indicates that no Se is present in the top 60 Å on this surface (the maximum escape depth for
photoelectrons at XPS in this range). This does not rule out the presence of selenide bulk species.

### 2.11. Mechanistic studies on Cd[(SP\(_2\)Pr\(_2\))\(_2\)N] (2) by Py-GC-MS

In order to understand the formation of cadmium phosphide and cadmium sulfide films by AACVD, the decomposition behaviour of the precursor Cd[Pr\(_2\)P(S)NP(S)Pr\(_2\)] (2) was investigated by pyrolysis GC-MS (Dr. Bart Van Dongen) in order to elucidate plausible decomposition pathways. Furthermore, complementary DFT calculations were done by Dr. Mark Vincent. The free energies of the dissociative and rearrangement reactions of the species which might have resulted in the deposition products were computed. The proposed scheme (Scheme 2.2) gives a plausible decomposition mechanism based upon the analysis of the Py-GC-MS results; the main intermediates and products are shown.

![Py-GC-MS study](image)

**Fig. 2.40.** Py-GC-MS study for the decomposition of Cd[Pr\(_2\)P(S)NP(S)Pr\(_2\)] (2).
Each intermediate species is postulated from a corresponding fragment in the Py-GC-MS experiment and is shown with the corresponding \( m/z \) value. The key steps are as follows:

1) The initial loss of an isopropyl group.
2) Elimination of the close-shell molecule \( ^3\text{Pr}_3\text{P}_2\text{S}_2\text{N} \).
3) The loss of two further isopropyl groups from the same atom.
4) Removal of the closed-shell ion \( ^4\text{Pr}_2\text{PS}^+ \), which gave a major peak in the MS spectrum, to leave the neutral species Cd(SPN).

**Scheme 2.2.** Plausible decomposition mechanism for the deposition of cadmium sulfide and cadmium phosphide from \( \text{Cd}[^3\text{Pr}_2\text{P(S)}\text{NP(S)}^3\text{Pr}_2] \) under Py-GC-MS conditions.
The free energies associated with each of these proposed steps by DFT calculations were computed employing a locally implemented version of the M06\textsuperscript{57} functional in the Gaussian03 suite of programmes\textsuperscript{58}, together with a SDD pseudopotential and based on cadmium and a 6-31G\textsuperscript{**} basis on all other atoms. For simplicity, the isopropyl groups were modelled as methyl groups. The free energies of each of the optimized structures were determined using the harmonic oscillator and rigid rotor approximations, at a temperature of 800 K. It was discovered that each of the four steps shown were endergonic by 20, 109, 221 and 332 kJ mol\textsuperscript{-1} respectively. The low values for the first two steps could be attributed to the formation and subsequent loss of the stable molecule Pr\textsubscript{3}P\textsubscript{2}S\textsubscript{2}N. Investigations revealed that for the corresponding neutral species that were postulated to be involved in the CVD process the values were 178, 82, 197 and 223 kJ mol\textsuperscript{-1} respectively. Reaction energies of this magnitude suggested that the proposed mechanism was unreasonable.

Also, there was an investigation in which first and final steps in the proposed mechanism were modified. For the first step, the removal of one of the entire ligand was considered rather than a single isopropyl group and found to be more energetically costly, but by only 34 kJ mol\textsuperscript{-1}. An alternative to the final step is

\[
\text{Cd(Pr}_2\text{P(S)NPS)} \rightarrow \text{Cd(PrP(S)NPS)} + \text{Pr}
\]

followed by

\[
\text{Cd(PrP(S)NPS)} \rightarrow \text{Cd(SPN)} + \text{PrPS}
\]
These two steps were computed to be endergonic by 71 and 215 kJ mol\(^{-1}\) respectively, suggesting that such a two-step mechanism might be somewhat more favourable than a single step 4 mechanism, which is endergonic by 223 kJ mol\(^{-1}\).

It might be possible to speculate the deposition of both CdS and CdP species from the formation of Cd(SPN) in step 4. The formation of (PN)CdS from Cd(SPN) is energetically uphill, but by only 5 kJ mol\(^{-1}\), so that Cd(SPN) may isomerize to (PN)CdS, with the latter losing the stable species PN upon deposition of CdS. In order to form the Cd\(_x\)P\(_y\) species observed, having a P/Cd ratio greater than unity, some of the remaining cadmium in the atmosphere might have catalyzed the reaction converting the gaseous PN into P\(_2\) and N\(_2\). Thus, the reaction can be predicted as:

\[
\text{Cd} + 2\text{PN} \rightarrow \text{Cd}(\text{P}_2)(\text{N}_2)
\]

this is exergonic by 144 kJ mol\(^{-1}\) and suggested that the Cd-P species were formed via decomposition of this complex. The conversion of CdP to Cd\(_x\)P\(_y\) phases is also possible. However, earlier studies with the nickel complex suggested that this is not the dominant route\(^{59}\).
2.12. Conclusion

This chapter presented a comprehensive study for the growth of cadmium selenide/cadmium phosphide and cadmium sulfide/cadmium phosphide thin films from single-source precursors by AACVD. At 475 °C with the flow rate of 160 sccm, the precursors $[\text{Cd}^{i\text{Pr}_2\text{P}(\text{Se})\text{NP(Se)}^{i\text{Pr}_2}}]_2$ and $[\text{Cd}^{i\text{Pr}_2\text{P}(\text{S})\text{NP(Se)}^{i\text{Pr}_2}}]_2$ deposited the mixture of CdSe and Cd$_2$P$_3$ films. When the flow rate was changed to 240 sccm, only cadmium selenide was deposited at 525 °C, 500 °C, 475 °C and 450 °C from $[\text{Cd}^{i\text{Pr}_2\text{P}(\text{Se})\text{NP(Se)}^{i\text{Pr}_2}}]_2$. At 500 °C with the flow rate of 240 sccm, $[\text{Cd}^{i\text{Pr}_2\text{P}(\text{S})\text{NP(Se)}^{i\text{Pr}_2}}]_2$ gave the mixture of CdSe/CdS.

Similarly at the flow rate of 160 sccm, the precursor $[\text{Cd}^{i\text{Pr}_2\text{P}(\text{S})\text{NP(Se)}^{i\text{Pr}_2}}]_2$ deposited cadmium sulfide and mixture of cadmium phosphide at 500 °C and 525 °C respectively. When the flow rate was changed to 240 sccm, cadmium sulfide was deposited at 525 °C, while the mixture of cadmium sulfide and cadmium phosphide was observed at 500 °C.

At all temperatures and flow rates $[\text{Zn}^{i\text{Pr}_2\text{P}(\text{Se})\text{NP(Se)}^{i\text{Pr}_2}}]_2$ and $[\text{Zn}^{i\text{Pr}_2\text{P}(\text{S})\text{NP(Se)}^{i\text{Pr}_2}}]_2$ deposited cubic ZnSe unlike the LPCVD which gave the hexagonal form. However, all attempts to deposit ZnS from $[\text{Zn}^{i\text{Pr}_2\text{P}(\text{S})\text{NP(Se)}^{i\text{Pr}_2}}]_2$ at various deposition temperatures and flow rates were unsuccessful as there was no deposition seen, possibly owing to the volatility of the compound as shown by the TGA, whereas LPCVD gave a ZnS film.

The pyrolysis GC-MS analysis of $[\text{Cd}^{i\text{Pr}_2\text{P}(\text{S})\text{NP(Se)}^{i\text{Pr}_2}}]_2$ modelled by DFT calculations indicated the probable mechanism for the formation of cadmium sulfide and cadmium phosphide thin films.
2.13. References

Chapter 2: Cadmium and Zinc Precursors


CHAPTER 3:
IRON
IMIDOPHOSPHINATO
COMPOUNDS
3.1 Introduction

There has been considerable attention given to iron chalcogenides because of their interesting magnetic properties, including their likely applications in magnetic semiconductors and spintronics\(^1,2\). The recent discovery of the superconductivity of \(\beta\)-FeSe, iron selenides, and tellurides with their solid solutions has received a renewed attention\(^3\). Apart from being a superconductor, FeSe-layer materials can be used as test objects to study the physics of pnictides\(^4\). Iron diselenide (FeSe\(_2\)) is a p-type semiconductor material having a band gap of 1.0 eV and can be used as an electrode material in tandem photovoltaic devices\(^5\). Iron selenide has two main stoichiometric phases: FeSe and FeSe\(_2\), with both phases containing Fe\(^{2+}\) ions\(^6\). Various iron selenide films have been reported by electrodeposition\(^7\), spray pyrolysis\(^8\), or hydrothermal techniques\(^9\). A low-temperature solution chemistry method was used to synthesise the PbO-type \(\beta\)-FeSe, which gave predominantly two-dimensional single-crystal nanosheets\(^10\).

An organometallic polymer approach based on 1, 2, 3-triselena ferrocenophane gave FeSe\(_2\) nanorods by phase-selection\(^11\). The gas phase thermolysis of [Fe\(\{^{\prime}\text{Bu}_2\text{P(Se)NR}\}_2\)] (R = \(^{\prime}\text{Pr}, \text{cyclohexyl}) deposited thin films of hexagonal FeSe in a horizontal reactor at substrate temperature of 400-420°C\(^12\). Also, from the cluster compound [(\(\mu^2\)-H)\(_2\)Fe\(_3\)(\(\mu^3\)-Se)(CO)\(_9\)], iron selenide thin films have been deposited at 400-500°C on titanium substrates in a hot-wall low-pressure reactor\(^13\).

To the best of our knowledge, there are no reports of iron complexes containing dichalcogenoimidodiphosphinato ligands and their usage as a molecular precursor for the preparation of iron selenide materials as thin films or nanoparticles. Herein, we report the synthesis and characterisation of iron (II)
dichalcogenoimidodiphosphinate complexes \([\text{Fe}\{\text{Ph}_2\text{P}(\text{E}1)\text{NP}(\text{E}2)\text{Ph}_2\}\}_2]\) (E1 = E2 = Se; E1 = S, E2 = Se) and the single crystal X-ray structure of (I). Furthermore, pyrolysis of the as- synthesised compounds has been performed to yield iron selenide as powders. The resulting materials have been analysed by XRD, SEM/EDAX, TGA studies and magnetic measurements.

3.2. Synthesis of Precursors

3.2.1 Ligands Synthesis

3.2.1.1. Preparation of imido(tetradiphenyldiselenodiphosphinate) \([\text{Ph}_2\text{P}(\text{Se})\text{NHP}(\text{Se})\text{Ph}_2]\)^14

A solution of chlorodiphenylphosphine (23.88 g, 20 ml, 108.23 mmol) in toluene (25 ml) was added dropwise to a solution of 1,1,1,3,3,3-hexamethydisilazane (8.73 g, 11.42 ml, 54.12 mmol) in toluene over 30 minutes. Heating and stirring continued for 3 hours at 90 °C after which the reaction was cooled to room temperature. Selenium powder (8.55 g, 108.23 mmol) was added and the reaction further refluxed for 6 hours. Solution was cooled overnight and decanted to remove the solvent. A grey/off-white residue obtained and washed several times with toluene, DCM and diethyl ether. The product was recrystallized from DCM and solvent removed under vacuum to give a white powder. Yield: 12 g (40%).

Elemental analysis: Calculated for C\text{24}H\text{21}NP\text{2}Se\text{2}: C, 53.04; H, 3.90; N, 2.58; P, 11.41. Found: C, 53.43; H, 3.70; N, 2.50; P, 11.55. \(^{31}\)P-\({}^1\)H NMR: 52.63 ppm; \(^1J_{P-Se} = 787\) Hz. ES +ve MS: \(m/z\) 544 corresponds to NH(Ph\text{2}PSe)\text{2}.  

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3.2.1.2. Preparation of imido(tetradiphenylthioselenodiphosphinate)
[Ph₂P(S)HNPs(Se)Ph₂]₁⁵

This was prepared using the procedure reported for the isopropyl analogue₁⁵ in which selenium powder (4.27 g, 54.12 mmol) was added to the reaction mixture and stirred overnight. This was followed by sulfur powder (1.73 g, 54.12 mmol) which was also stirred for 7 hours. The off-white product was recrystallized from dichloromethane to give a whitish-yellow powder. Yield: 14.1 g (52%). Elemental Analysis: Calculated for C₂₄H₂₁NP₂SSe: C, 58.06; H, 4.27; N, 2.82. Found: C, 57.60; H, 4.28; N, 2.93. ³¹P-{¹H} NMR: 52.76, 52.72 ppm; ¹Jₚ-Sₑ = 496 Hz. ES +ve MS: m/z 496 corresponds to [Ph₂P(S)HNPs(Se)Ph₂].

3.2.2. Iron Complexes

3.2.2.1. Synthesis of [Fe{(SePPh₂)₂N}₂] (1)

Iminotetraphenyldiselenodiphosphinate ligand (5.0 g, 9.45 mmol) and tert-potassium butoxide (⁷BuOK 1.06 g, 9.45 mmol) was dissolved in methanol (50 ml) to deprotonate the ligand in-situ. The mixture was stirred under nitrogen at room temperature for 40 minutes followed by the dropwise addition of anhydrous FeCl₃ as a powder solution (0.51 g, 3.15 mmol). After stirring for 5 hours, the resulting deep-brown solution was filtered and recrystallized in hot dichloromethane yielding a yellow powder. Yield: 1.95 g (54%). M. Pt: 236 °C. Elemental analysis for C₇₂H₆₀N₃P₆Se₆Fe Calcd: C, 51.3; H, 3.6; N, 2.5; P, 11.1; Fe, 3.3. Found: C, 50.8; H, 3.2; N, 2.4; P, 11.02; Fe, 3.1. ¹H NMR (d₈-Toluene): 7.3 - 6.9 (m, 48H, ArH), 8.4 - 7.8 (m, 12H, ArH); ³¹P {¹H} NMR: 33.9, 29.4 ppm. ES +ve MS: m/z 1148 corresponds to [Fe{(SePPh₂)₂N}₂].
3.2.2.2. Synthesis of \([\text{Fe}\{(\text{SePPh}_2\text{NPPh}_2\text{S})_2\text{N}\}_2]\) (2)

The same procedure for (1) was used to prepare (2) which gave a brownish-green sample. Yield: 1.13 g (22%). M. Pt: 217 °C. Elemental analysis for \(\text{C}_{72}\text{H}_{60}\text{N}_3\text{P}_6\text{S}_3\text{Se}_3\text{Fe}\). Calcd: C, 56.1; H, 3.9; N, 2.7; P, 12.1; S, 6.2; Fe, 3.6. Found: C, 55.7; H, 4.1; N, 2.4; P, 11.5; S, 6.9; Fe, 3.2. \(^1\)H NMR (\(\text{d}_8\)-Toluene): 7.2 - 6.8 (m, 48H, ArH), 8.3 - 7.6 (m, 12H, ArH); \(^{31}\)P \(\{^1\text{H}\}\) NMR: 47.38, 30.41 ppm. ES +ve MS: \(m/\text{z}\) 1048 corresponds to \([\text{Fe}\{(\text{SePPh}_2\text{NPPh}_2\text{S})_2\text{N}\}_2]\).

3.3. Results and Discussion

The reaction of anhydrous iron (III) chloride with the appropriate dichalcogenoimidodiphosphinate ligand in methanol produced complexes (1) and (2) in good yields. The reaction scheme follows the one described in Scheme 2.1 in chapter 2. Complex (1) was obtained as iron (II) compound, indicating a reduction of \(\text{Fe}^{3+}\) by the ligand during the course of the reaction. While in solution, the anionic ligand \(\text{RSe}^-\) looses electrons thereby becoming the neutral type \(\text{RSeSeR}\), while \(\text{Fe}^{3+}\) gains the electron to become \(\text{Fe}^{2+}\). The neutral ligand \(\text{RSe}\) reacts with the \(\text{Fe}^{3+}\) to produce the final \(\text{Fe}^{2+}\) complex, with the loss of one mole of the ligand. Hence, instead of the expected octahedral geometry of \(\text{Fe}^{3+}\), the structure indicated a tetrahedral, having two units of the ligand. The crystal structure is discussed in further details in section 3.3.1 below. The reaction can be summarised by the following equations 3.1 to 3.4: (\(\text{RSe}^- = [(\text{Ph}_2\text{PSe})_2\text{N}]^-\))

\[
\begin{align*}
2 \text{RSe}^- & \rightarrow \text{RSeSeR} + 2\text{e}^- \quad (3.1) \\
\text{Fe}^{3+} + \text{e}^- & \rightarrow \text{Fe}^{2+} \quad (3.2) \\
2\text{RSe}^- + 2\text{Fe}^{3+} & \rightarrow 2\text{Fe}^{2+} + \text{RSeSeR} \quad (3.3) \\
6\text{RSe}^- + 2\text{Fe}^{3+} & \rightarrow 2[\text{Fe}^{2+}(\text{RSe})_2] + \text{RSeSeR} \quad (3.4)
\end{align*}
\]
Iron (II) occurs in a wide range of coordination geometries and spin-states. Iron (II) at the high spin state has 4 unpaired electrons with the $d^6$ configuration consisting of $t_{2g}^4 e_g^2$ in octahedral geometry, and with a coordination number of four which makes it possible to have a tetrahedral geometry. However at the octahedral low spin states, iron (II) is diamagnetic consisting of $t_{2g}^6$, with no unpaired electron and a coordination number of six and being able to have an octahedral geometry.

For both iron (II) and iron (III) in terms of spin states, there are two choices for the spin state based on how the splitting energy ($\Delta$) compares with the electron-pairing energy ($\Pi$). Highest value of spin (‘high spin’) states occur when more electron-pairing energy is needed to put two electrons into the same lower orbital, than it takes the splitting energy to raise one electron into an upper orbital. This results in the complex having the highest possible number of electrons. In tetrahedral complexes, the ligands are diagonally across the cube faces from each other. The $t_2$ orbitals point closer to the ligands and are therefore more unfavourable places for electrons to occupy than are the $e_g$.

High spin iron (II), iron (III) and low spin iron (III) species are often characterized by their magnetic properties.$^{21}$

It would have been more interesting to perform the complexation experiment using iron (II) salt to determine the product, the crystal structure and the material which can be deposited by deposition studies. However, there was not sufficient time to investigate this proposition.
3.3.1. X-ray single crystal structure of [Fe{Ph₂P(Se)NP(Se)Ph₂}]₂ (1)

The single-crystal X-ray structure of complex (1) (Fig. 3.1) shows iron in a tetrahedral environment with a Se₄ donor set. The structure consists of a complex having a distorted tetrahedral FeSe₄ core (105-116°), in which the central iron is tetrahedrally coordinated to four selenium atoms.

![Fig. 3.1. X-ray single crystal structure of [Fe{Ph₂P(Se)NP(Se)Ph₂}]₂ (1).](image)

The crystal lattice shows the presence of monomeric independent units separated by Van der Waals distances. To the best of our knowledge, there are no reports yet on any iron complex containing the imidodichalcogenodiphosphinate ligand. The Fe-Se bond lengths are somewhat longer when compared with the Fe-S values in [Fe{(Me₄P₂S₂)N}₂]¹⁷, [Fe₂(µ-OMe)₂(SON(CNEt₂)₂)₂]¹⁸, and [Fe(S₂CNRR)₃] (R = Et, Me; R’ = iPr, Et)¹⁹. Selected bond angles and bond lengths are given in table 3.1. Structural refinement parameters and crystal data are given in table 3.2.
Table 3.1. Selected bond lengths and angles for [Fe\{Ph₂P(Se)NP(Se)Ph₂\}_2] (1).

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Bond Length (Å)</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (1) – Se (1)</td>
<td>2.4921(13)</td>
<td>Fe (1) – Se (3)</td>
</tr>
<tr>
<td>Fe (2) – Se (2)</td>
<td>2.4599(13)</td>
<td>Fe (1) – Se (4)</td>
</tr>
<tr>
<td>P (1) – Se (1)</td>
<td>2.181(2)</td>
<td>P (2) – Se (2)</td>
</tr>
<tr>
<td>P (3) – Se (3)</td>
<td>2.174(2)</td>
<td>P (4) – Se (4)</td>
</tr>
<tr>
<td>P (1) – N (1)</td>
<td>1.590(6)</td>
<td>P (2) – N (1)</td>
</tr>
<tr>
<td>P (3) – N (2)</td>
<td>1.588(6)</td>
<td>P (4) – N (2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angle (°)</th>
<th>Bond Angle (°)</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se (2) – Fe (1) – Se (4)</td>
<td>105.19(5)</td>
<td>Se (2) – Fe (1) – Se (3)</td>
</tr>
<tr>
<td>Se (2) – Fe (1) – Se (1)</td>
<td>116.34(5)</td>
<td>Se (4) – Fe (1) – Se (3)</td>
</tr>
<tr>
<td>Se (4) – Fe (1) – Se (1)</td>
<td>106.91(5)</td>
<td>Se (1) – Fe (1) – Se (3)</td>
</tr>
<tr>
<td>P (1) – N (1) – P (2)</td>
<td>135.5(4)</td>
<td>P (3) – N (2) – P (4)</td>
</tr>
<tr>
<td>N (1) – P (1) – Se (1)</td>
<td>119.5(2)</td>
<td>N (1) – P (2) – Se (2)</td>
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<tr>
<td>N (2) – P (3) – Se (3)</td>
<td>117.6(2)</td>
<td>N (2) – P (4) – Se (4)</td>
</tr>
<tr>
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<td>93.91(6)</td>
<td>P (2) – Se (2) – Fe (1)</td>
</tr>
<tr>
<td>P (3) – Se (3) – Fe (1)</td>
<td>92.25(6)</td>
<td>P (4) – Se (4) – Fe (1)</td>
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</table>
Table 3.2. Crystal data and refinement parameters for [Fe{(SePPh$_2$)$_2$N}]$_2$ (1).

<table>
<thead>
<tr>
<th><strong>Compound</strong></th>
<th>[Fe{(SePPh$_2$)$_2$N}]$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C$<em>{48}$H$</em>{40}$FeN$_2$P$_4$Se$_4$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1140.39</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100(2)</td>
</tr>
<tr>
<td>Crystal Size (mm$^3$)</td>
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<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
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<td>Crystal System</td>
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<tr>
<td>Space Group</td>
<td>Pī</td>
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<tr>
<td>a (Å)</td>
<td>13.639(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.6984(19)</td>
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<tr>
<td>c (Å)</td>
<td>14.156(2)</td>
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<td>α (°)</td>
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<tr>
<td>γ (°)</td>
<td>70.397(3)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>2283.1(6)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density$_{calcd}$ (mg m$^{-3}$)</td>
<td>1.659</td>
</tr>
<tr>
<td>Absp. Coeff. (mm$^{-1}$)</td>
<td>3.695</td>
</tr>
<tr>
<td>F(000)</td>
<td>1128</td>
</tr>
<tr>
<td>θ Range (°)</td>
<td>1.57 to 25.11</td>
</tr>
<tr>
<td>Ref. Coll.</td>
<td>11996</td>
</tr>
<tr>
<td>Unique Ref.</td>
<td>7910 [R(int) = 0.0404]</td>
</tr>
<tr>
<td>Max. Min. Transm.</td>
<td>0.5559 and 0.396755</td>
</tr>
<tr>
<td>Data/Rest/Parameters</td>
<td>7910/6/532</td>
</tr>
<tr>
<td>Goodness-of-Fit on F$^2$</td>
<td>1.143</td>
</tr>
<tr>
<td>Final R [I&gt;2σ(I)]</td>
<td>R1 = 0.0591, wR2 = 0.1492</td>
</tr>
<tr>
<td>R Indices (all data)</td>
<td>R1 = 0.0786, wR2 = 0.1587</td>
</tr>
<tr>
<td>Diff. Peak and Hole (e.Å$^{-3}$)</td>
<td>0.997 and -0.708</td>
</tr>
</tbody>
</table>
3.4. Thermogravimetry Analysis (TGA)

Prior to the deposition studies on the precursors, their thermal properties were determined by TGA which revealed their suitability for the experiment. The volatility of the precursors indicated their single-step decomposition with a rapid weight loss. Complex (1) decomposed between 263 and 412 °C at 60%, while that of complex (2) occurred between 303 and 438 °C at 72% (Fig. 3.2).

![Graph showing Thermogravimetry Analysis](image)

**Fig. 3.2.** Thermogravimetry analysis (TGA Section 5.5) of [Fe{(SePPh₂)₂N}]₂ (1) and [Fe{(SePPh₂NPPh₂S)₂N}]₂ (2).

The solid decomposition residue of 40% observed for (1) is quite close to the calculated value of 33% for FeSe₂. Similarly, complex (2) having a final weight residue of 28% is in agreement with the calculated value of 28% for FeSe₂.
3.5. Pyrolysis of $[\text{Fe}((\text{SePPh}_{2})_{2}\text{N})_{2}]$ (1)

Pyrolysis of complex (1) at both 500 and 550 °C deposited black powders which were pulverized and analyzed by XRD. The powder XRD (PXRD) pattern of the pyrolysed samples at both 500 and 550 °C indicated the orthorhombic ferroselite FeSe$_2$ (ICDD no. 04-003-1738) mixed with monoclinic Fe$_3$Se$_4$ (ICDD no. 03-065-2315) (Fig. 3.3 & 3.4). The traces of Fe$_3$Se$_4$ were observed at $2\theta$ values of 29.09, 31.77 and 42.82° respectively. At both temperatures, the prominent peaks were the (111), (120) and (211), while the Fe$_3$Se$_4$ peaks were more intense at 550 °C. Also at 500 °C, the tallest peak corresponds to the (120) but at 550 °C, it was the (111) peak. The intensity of the (211) peak was the same at both temperatures.

![XRD pattern of orthorhombic FeSe$_2$ deposited at 500 °C. Marked peaks correspond to monoclinic Fe$_3$Se$_4$.](image)

SEM studies of the deposited material at 500 °C revealed the morphology to be randomly dispersed polygonal crystallites (Fig. 3.5(a)). At the higher deposition temperature (550 °C), similar morphology was also observed only that the particles were of bigger sizes (Fig. 3.5(b)).
Fig. 3.4. XRD pattern of orthorhombic FeSe$_2$ deposited at 550 °C. Marked peaks correspond to monoclinic Fe$_3$Se$_4$.

Fig. 3.5. SEM images of orthorhombic iron selenide deposited at (a) 500 °C and (b) 550 °C.

Energy dispersive analysis of X-rays (EDAX) shows that the samples consisted of iron: selenium ratios of 1:1.9 at 500 °C and 35:65 at 550 °C, both containing approximately 5% phosphorus. The 1:2 ratio of Fe: Se is closer in the deposited material at 500 °C.
3.6. Pyrolysis of [Fe{(SePPh\(_2\)NPPh\(_2\)S)}\(_2\)N]\(_2\) (2)

As with the previous complex, this precursor was pyrolysed at both 500 and 550 °C and black powder deposits obtained, pulverized and analyzed by XRD. The pattern indicated by the powder X-ray diffraction pattern (PXRD) revealed the deposition of orthorhombic ferroselite FeSe\(_2\) (ICDD no. 04-003-1738) mixed with monoclinic Fe\(_3\)Se\(_4\) (ICDD no 03-065-2315) at 500 °C (Fig. 3.6). Traces of Fe\(_3\)Se\(_4\) were seen at 2\(\theta\) values of 29.09 and 31.77°. However, at the higher deposition temperature (550 °C), a different pattern was obtained which could not be matched to any material (Fig. 3.7). The reason for this remained unclear.

![Fig. 3.6. XRD pattern of orthorhombic FeSe\(_2\) deposited at 500 °C. Marked peaks correspond to Fe\(_3\)Se\(_4\).](image)

The morphology of the deposited material at 500 °C revealed an irregular polygonal crystallites as indicated by the scanning electron microscopy (SEM). However, despite the fact that the obtained XRD pattern at 550 °C could not be matched to any material, a similar morphology was also observed for the structure of the material at this temperature (Fig. 3.8 (a&b)).
Fig. 3.7. XRD pattern obtained from pyrolysis of complex (2) at 550 °C.

Fig. 3.8. SEM images of orthorhombic FeSe$_2$ deposited at (a) 500 °C (b) unmatched pattern at 550 °C.

The iron to selenium ratio for the material deposited at 500 °C is quite close to 1:2 with the remaining 10% as sulfur as revealed by the EDAX. Although the material obtained at 550 °C has a higher content of iron, the iron to selenium ratio is also quite close to 1:2 with 12% sulfur content.
3.7. XPS Studies

The surface atomic coverage and surface chemistry of the powders obtained from pyrolysis was determined using XPS. For compound 1, the Fe 2p peak indicated iron oxide with no sign of metallic iron or iron selenide which should appear ca. 707 eV (Fig. 3.9). The 2p3/2 and 2p1/2 peak at 713 and 728 eV respectively suggested that the samples were easily oxidized on exposure to air.

![XPS of Fe 2p peaks indicating iron bounded to oxygen on the surface.](image)

This showed that the surface of the deposited powders was contaminated with oxygen. Hence, iron at the surface and near surface region of the powder seemed to be attached to oxygen. Similarly, the selenium 3p peak located at 161.7 eV also revealed a selenium atom bounded to oxygen, more typically of selenium oxide (Fig. 3.10). Furthermore, previous reports on FeSe2 nanorods\textsuperscript{11} and thin films\textsuperscript{16} also observed similar surface oxidation of the material.
Fig. 3.10. XPS spectra of Se 3p peak deposited from (1) indicating an oxygen-attached selenium.

For compound (2), the XPS spectra also revealed similar observations both for the Fe 2p and Se 3p peaks. The binding energy of Fe 2p\textsubscript{3/2} peak at 713 eV corresponds to iron oxide as seen in 1 (Fig. 3.11), while the Se 2p\textsubscript{3/2} at 159.5 eV is more consistent with a selenide oxide species (Fig. 3.12). The S and Se peaks were identified by the overlapping S and Se 2p features near 160 eV as the Se 2s was covered by the S 2s peak.
Fig. 3.11. XPS spectra of Fe 2p of FeSe$_2$ deposited from [Fe{((SePPh$_2$NPPh$_2$S)$_2$N}] (2), indicating iron bonded to oxygen.

Fig. 3.12. XPS spectra of Se 2p peak indicating an oxygen-bonded selenium.
3.8. Magnetic studies on iron selenide powders

The magnetic properties of the deposited powders were investigated by using the superconducting quantum interference device (SQUID) magnetometer with a magnetic field of 100 Oe between 5 and 300 K. Generally, iron selenides are ferromagnetic with a Curie temperature higher than 300 K\(^{20}\). From the deposited iron selenide powders from (1) and (2), temperature-dependent magnetization of materials with field/zero-field (FC/ZFC) cooling process was observed for the powders. The divergence of the field cooling (FC) and zero field cooling (ZFC) with decreasing temperature indicated the formation of an ordered magnetic state (hence their ferromagnetism), probably due to their high Curie temperature (Fig 3.13 and 3.14). For the iron selenide powders deposited from (2), a transition temperature around 280 K was observed. Furthermore, the field dependence of the magnetization curve of the powders from (1) and (2) exhibited hysteresis at 5 K, 30 K and 300 K.

![Figure 3.13](image)  
*Fig. 3.13. Temperature dependence of magnetization curves for FeSe\(_2\) from (1) with an applied field of 100 Oe under FC and ZFC conditions.*
Fig. 3.14. Temperature dependence of magnetization curves for FeSe$_2$ from (2) with an applied field of 100 Oe under FC and ZFC conditions.

The iron selenide obtained from (2) seemed to be more ferromagnetic as compared to that from (1) due to the greater divergence observed in the magnetization curves. As typical of ferromagnetic materials, the hysteresis loops obtained from the deposited iron selenide from both (1) and (2) exhibited a linear decrease in the room temperature magnetization with the increase in the magnetic field (Fig 3.15 and 3.16). This might be due to the reduced thermal fluctuation of magnetic dipoles. From the magnetic measurements on complex (1), the plot of $\chi T$ against temperature indicated a decrease, probably due to the zero field splitting of Fe$^{2+}$ (Fig. 3.17). Also, the plot of magnetization against field revealed that the sample was not saturated because of the anisotropy of Fe$^{2+}$ (Fig. 3.18).
Fig. 3.15. Temperature-dependent hysteresis loops obtained from deposited FeSe$_2$ sample from (1) at (a) 5 K (b) 30 K and (c) 300 K.
Fig. 3.16. Temperature-dependent hysteresis loops obtained from deposited FeSe$_2$ sample from (2) at (a) 5 K (b) 30 K and (c) 300 K.
Fig. 3.17. Plot of $\chi T$ against temperature for $[\text{Fe} \{\text{SePPh}_2\text{N}\}_2]$ (1).

Fig. 3.18. Plot of magnetization against field for $[\text{Fe} \{\text{SePPh}_2\text{N}\}_2]$ (1).
3.9. Conclusion

Iron complexes of imidodiselenodiphosphinato $[\text{Fe}\{(\text{SePPh}_2\text{N})_2\}]$ (1), and imidothioselenodiphosphinato $[\text{Fe}\{(\text{SePPh}_2\text{NPPh}_2\text{S})_2\text{N}\}]$ (2) have been synthesized. The X-ray single crystal structure of complex (1) revealed a distorted tetrahedral containing FeSe$_4$ unit. Thermogravimetry analysis showed the single step decomposition of the complexes with 40% and 28% final residue weight respectively. Pyrolysis of complexes (1) and (2) deposited orthorhombic iron selenide (FeSe$_2$). SEM images of the deposited FeSe$_2$ indicated polygonal crystallites with increased sizes. XPS measurements showed the surface oxidation of the materials in which iron and selenium were bounded to oxygen. Magnetic measurements revealed the ferromagnetic behaviour of the FeSe$_2$ powders.
3.10 References

8. Same as reference 6.
Chapter 3: Iron Imidophosphinato compounds


CHAPTER 4:
TELLURIDE PRECURSORS
4.1. Introduction

Dichalcogenido-imidodiphosphinates, \([\text{N(PR}_2\text{E)}_2]^-(A)\) (R = alkyl, aryl; E = S, Se) are chelating ligands that readily form cyclic complexes with main group metals, transition metals, lanthanides and actinides\(^1\). Recently, a useful synthesis of the tellurium analogue \([\text{N(PPh}_2\text{Te)}_2]^-(B)\) was developed by Chivers \textit{et al.}\(^2\) using the anion \([\text{N(PPh}_2]^-(\text{B})\) generated prior to the reaction with elemental tellurium. Hence, sodium salts of the ditellurido ligands \([\text{N(PR}_2\text{Te)}_2]^-(\text{B})\) were obtained in good yields (R = \(^i\text{Pr}, \text{Ph}, \text{tBu})\(^25,6\). Metal complexes of the ditellurido ligands \([\text{N(PR}_2\text{Te)}_2]^-(\text{B})\) have shown novel structures and new reaction chemistry in which the tellurium donor sites exhibits greater flexibility than sulfur or selenium having a tellurium-centered ligand bridging two metal centres. Metal tellurides have potential applications as low band gap semiconductor materials in solar cells, thermoelectric devices and telecommunications\(^3,4\). Metal complexes of the isopropyl derivative anion \([\text{N(PPr}_2\text{Te)}_2]^-(\text{C})\) have been used as single-source precursors for pure metal telluride thin films or novel nanomaterials e.g. CdTe, PbTe, In\(_2\)Te\(_3\)\(^7,9\).

Scheme 1 below shows the synthesis of the tellurium analogue of the dichalcogenoimidodiphosphinate ligand.
Chapter 4: Telluride Precursors

Scheme 4.1. Synthesis of dichalcogenoimidodiphosphinate ligand.

Nickel telluride is an important intermetallic compound of the 3d transition metal chalcogenides series, for which various properties have been previously studied\textsuperscript{10-13}. The nickel-telluride system consists of two ordered compounds: NiTe and NiTe\textsubscript{2}, with a range of continuous solid solutions between them\textsuperscript{14}. Oftedal\textsuperscript{15} reported that NiTe has a hexagonal structure of the NiAs-(B8)-type, while Tengnér\textsuperscript{16} reported NiTe\textsubscript{2} to have the hexagonal Cd(OH)\textsubscript{2}-(C6)-type structure. In a crystal of nickel telluride, the Ni\textsuperscript{2+} ions occupy a simple hexagonal lattice while the Te\textsuperscript{2-} ions occupy a close-packed hexagonal lattice, both lattices penetrating each other\textsuperscript{10}. There are not many reports on the deposition of nickel telluride thin films, only a few such as deposition by flash evaporation\textsuperscript{17} and by AACVD\textsuperscript{18}.

To date, there seems not to be any report yet on the deposition of palladium telluride either as thin film or nanoparticles. The early synthesis of palladium ditelluride was reported by Thomassen\textsuperscript{19} and Wöhler \textit{et al}\textsuperscript{20} by preparing it as the only compound from the reaction of the constituent elements. Also, Groeneveld\textsuperscript{21} prepared the compound by fusing the elements in the correct atomic proportions. Palladium monotelluride was also prepared by Thomassen by dry fusion of the elements in evacuated tubes\textsuperscript{19}. About nine binary phases of the palladium-tellurium system are known which include: Pd\textsubscript{17}Te\textsubscript{4}, Pd\textsubscript{3}Te, Pd\textsubscript{20}Te\textsubscript{7}, Pd\textsubscript{8}Te\textsubscript{3}, Pd\textsubscript{7}Te\textsubscript{3}, Pd\textsubscript{9}Te\textsubscript{4}, Pd\textsubscript{3}Te\textsubscript{2}, PdTe and PdTe\textsubscript{2}\textsuperscript{22}. However, the most important of these seems to be PdTe.
Chapter 4: Telluride Precursors

and PdTe$_2$ because of their similar structural type with NiAs and CdI$_2$ respectively$^{21,22}$. 

Both nickel telluride and palladium telluride have applications in the fabrication of new electronic materials$^{23}$. 

Similarly, there are no reports yet on the deposition of platinum telluride, either as thin films or nanoparticles. Early synthesis involved both wet and dry procedures as the main synthetic route$^{21}$. The wet method involved the reaction of hydrogen telluride on a solution of platinum metal salt, while the dry route was based on the direct fusion of the weighed constituents. In the platinum-tellurium system, the most important phases are the PtTe and PtTe$_2$$.^{24}$ According to Groeneveld$^{21}$, PtTe$_2$ has CdI$_2$ structural type while PtTe consists of an orthorhombic structure$^{24}$. 

FeTe$_2$ is an example of crystalline transition metal ditellurides in the 3d series known to exhibit 3D magnetic ordering and semiconductivity$^{25}$. FeTe$_2$ is a marcasite containing the narrow 3d band (about 1 eV) known to exhibit good magnetic properties$^{25}$, semiconductivity$^{26}$, as well as high electrical conductivity$^{27}$, and high thermoelectric powder values$^{27}$. Traditionally, FeTe$_2$ had been prepared by direct contact of the element in sealed tubes$^{28}$, while new synthetic routes involved OMVPE and MOCVD$^{29,30}$. Through solution-based solvothermal reduction, FeTe$_2$ nanoparticles were obtained$^{25,28}$. From the precursor \([\text{Fe\{Bu$_2$P(E)NR\}}_2]\) by gas-phase deposition, thin films of FeTe$_2$ were obtained by Song and Bochmann$^{31}$. 

In this work, telluride complexes of nickel, palladium, platinum and iron have been prepared from the phenyl substituted anion \([\text{N(PPh$_2$Te)}_2]^-\) (B) to serve as single-source precursor for metal tellurides. Samples were pyrolysed under vacuum in a quartz glass reactor using a tube furnace and then cooled under nitrogen to room
temperature. The black deposits were further analysed by XRD. Prior to this, the thermal properties of the precursors were determined by TGA which showed all the precursors to be suitable for the experiment.

4.2. Synthesis of Precursors

4.2.1. Synthesis of Ligand

(a) Synthesis of $[\text{NaN}(\text{PPh}_2)_2]_2$: Toluene (75 ml) was added to a mixture of solid $[\text{HN}(\text{PPh}_2)_2]$ (13.3 g, 34.45 mmol) and NaH (0.836 g, 34.84 mmol). The amine TMEDA (10.4 ml, 69.09 mmol) was added to the suspension, which was heated to 100 °C for 6 hours. The resulting suspension was allowed to settle, and the yellow mother liquor decanted. The crude solid was suspended in hexane, washed with hexane (3 x 20 ml) and dried under vacuum to give a creamy white powder. Yield: 9.0 g, 65%.

(b) Synthesis of $(\text{TMEDA})\text{Na}[(\text{TePPh}_2)_2\text{N}]_8$: Toluene (20 ml) was added to solid NaN(PPh$_2$)$_2$ (4.13 g, 10.14 ml) and tellurium powder (2.64 g, 20.67 mmol). The reagent TMEDA (1.52 ml, 10.14 mmol) was added to the suspension and heated at 80 °C for 3 hours. The resulting mixture was filtered at room temperature through a sintered glass to give a clear deep red solution. This was decanted and the residue washed with hexane (3 x 15 ml), followed by drying under vacuum to give a yellow polycrystalline powder. Yield: 2.0 g, 24%.

4.2.2. Synthesis of Complexes

4.2.2.1 Synthesis of $[\text{Ni}(\text{Ph}_2\text{P(Te)NP(}\text{Te})\text{Ph}_2)_2]^{32}$ (1): A solution of $(\text{TMEDA})\text{Na}[(\text{TePPh}_2)_2\text{N}]$ (0.8 g, 0.992 mmol) in THF (20 ml) was added via cannula to a solution of Ni(OAc)$_2$ (0.1223 g, 0.496 mmol) in THF (15 ml) at room temperature. A colour change from green to brown observed and the solution stirred
for 2 hours, followed by solvent removal under vacuo. Fresh THF (20 ml) was added and the solution filtered. Hexane (25 ml) was added and left overnight after which solvent was removed to give brown powder. Yield: 0.4 g, 65%. Elemental analysis calculated for C_{48}H_{40}NiN_{2}P_{4}Te_{4}: C, 43.07; H, 3.01; N, 2.09; P, 9.26%. Found: C, 45.25; H, 4.11; N, 2.64; P, 11.89%. \textsuperscript{1}H NMR, (\textsuperscript{1}H, CDCl\textsubscript{3}, 400 MHz), \( \delta = 7-8 \) ppm (m, ArH); \textsuperscript{31}P \{\textsuperscript{1}H\} NMR: 88.51 ppm.

4.2.2.2 Synthesis of [Pd(Ph\textsubscript{2}P(Te)NP(Te)Ph\textsubscript{2})\textsubscript{2}]\textsuperscript{33} (2): A solution of (TMEDA)Na[(TePPh\textsubscript{2})\textsubscript{2}N] (0.8 g, 0.992 mmol) in THF (25 ml) was added via cannula to a solution of Pd(OAc)\textsubscript{2} (0.111 g, 0.496 mmol) in THF (20 ml) at room temperature. The resulting dark orange solution was stirred for 2 hours, followed by solvent removal under reduced pressure. Fresh THF (25 ml) was added and the solution filtered. The clear filtrate was left overnight which gave an orange deposit from which solvent was removed to give dark orange powder. Yield: 0.5 g, 74%. Elemental analysis calculated for C_{48}H_{40}PdN_{2}P_{4}Te_{4}: C, 41.59; H, 2.91; N, 2.02; P, 8.95%. Found: C, 43.77; H, 3.08; N, 2.54; P, 10.34%. \textsuperscript{1}H NMR, (\textsuperscript{1}H, CDCl\textsubscript{3}, 400 MHz), \( \delta = 7-8 \) ppm (m, ArH); \textsuperscript{31}P \{\textsuperscript{1}H\} NMR: 65.18 ppm.

4.2.2.3 Synthesis of [Fe(Ph\textsubscript{2}P(Te)NP(Te)Ph\textsubscript{2})\textsubscript{3}] (3): A solution of (TMEDA)Na[(TePPh\textsubscript{2})\textsubscript{2}N] (1.5 g, 1.859 mmol) in THF (25 ml) was added via cannula to a that of anh. FeCl\textsubscript{3} (0.1 g, 0.619 mmol) in THF (15 ml) at room temperature. The resulting brown solution was stirred for 2 hours, followed by solvent removal under reduced pressure. Fresh THF (25 ml) was added, filtered and concentrated under vacuo. Hexane (25 ml) was added and refrigerated overnight followed by solvent removal under vacuum. A brown powder obtained. Yield: 0.9 g, 74%. Elemental analysis calculated for C_{72}H_{60}FeN_{3}P_{6}Te_{6}: C, 43.77; H, 3.06; N, 2.13; P, 9.42%. Found: C, 45.80; H, 4.10; N, 2.84; P, 10.27%.
4.2.2.4 Synthesis of \([\text{Pt(Ph}_2\text{P(Te)NP(Te)Ph}_2\text{)]^{33}}\) (4): A solution of (TMEDA)\(\text{Na}[(\text{TePPh}_2\text{)}_2\text{N}]\) (0.8 g, 0.992 mmol) in THF (25 ml) was added via cannula to a solution of \(\text{PtCl}_2\) (0.132 g, 0.496 mmol) in THF (15 ml) at room temperature. Solution turned brown immediately and was stirred for 2 hours, followed by solvent removal under reduced pressure. Fresh THF (25 ml) was added and the solution filtered. The clear yellow filtrate was concentrated under vacuum and hexane (30 ml) was added. This was refrigerated after which solvent was removed to give yellow powder. Yield: 0.3 g, 42%. Elemental analysis calculated for \(\text{C}_{48}\text{H}_{40}\text{PtN}_2\text{P}_4\text{Te}_4\): C, 39.09; H, 2.74; N, 1.90; P, 8.41%. Found: C, 40.93; H, 3.45; N, 2.54; P, 9.85%. \(^1\text{H} \text{NMR, (}\delta, \text{CDCl}_3, 400 \text{MHz}), \delta = 7-8 \text{ ppm} \text{ (m, ArH); } ^{31}\text{P \{}^1\text{H}\} \text{NMR: 25.43 ppm.}

4.3. Results and Discussion

The bis(phosphine)amine \([\text{HN(PPh}_2\text{)}_2\text{]}\) was prepared from the commercially available reagents (Me\(_3\text{Si})_2\text{NH and PPh}_2\text{Cl. In the literature, this amine was reported as an in situ reagent whose isolation has limited characterization}^{34}. This was sodiated by NaH and yielded the sodium amide \([\text{NaN(PPh}_2\text{)}_2\text{]}\), previously reported without detailed characterization\(^6\). Oxidation of the amide with elemental tellurium in the presence of \(\text{N,N,N'},\text{N'}\)-tetramethylethylene diamine (TMEDA) produced the ditellurido ligand (TMEDA)\(\text{Na}[(\text{TePPh}_2\text{)}_2\text{N}]\) (Scheme 4.1). The complexes were prepared by the addition of the corresponding metal salt to a solution of the ditellurido ligand in THF at room temperature (Scheme 4.2). All the complexes were unstable in air.
Scheme 4.2. Synthesis of ditellurido complexes.

4.4. Thermogravimetry Analysis (TGA)

The thermogravimetry analysis on the complexes (1) - (4) to determine their thermal properties indicated their suitability for deposition studies. All the complexes were suitable for deposition studies having a single-step decomposition with a rapid weight loss (Fig. 4.1). However, complex (3) was an exception to this having two decomposition steps.

![Thermogravimetry Analysis (TGA)](image)

Fig. 4.1. Thermogravimetry analysis (TGA Section 5.5) of complexes (a) [Ni(Ph₂P(Te)NP(Te)Ph₂)₂] (1); (b) [Pd(Ph₂P(Te)NP(Te)Ph₂)₂] (2); (c) [Fe(Ph₂P(Te)NP(Te)Ph₂)₃] (3) and (d) [Pt(Ph₂P(Te)NP(Te)Ph₂)₂] (4).
Complex (1) decomposed between 280 and 370 °C with a final residue of about 20%, which is higher than the calculated value of 14% for NiTe from the precursor. The rapid weight loss in complex (2) occurred between 270 and 363 °C, with a residue amount of 20% which is closer to 17% calculated value for PdTe in the precursor. Although the decomposition occurred in complex (3) in two steps, however, the observed residue value of 25% is quite close to the calculated value of 22% for a residue value containing FeTe₂ and elemental tellurium. The decomposition in complex (4) was between 274 and 348 °C with 18% final residue which also is almost in agreement with the calculated value of 22% for PtTe.

4.5. Pyrolysis of [Ni(Ph₂P(Te)NP(Te)Ph₂)]₂ (1)

Complex (1) was pyrolysed at 500 °C under constant flow of nitrogen which gave black deposit and later pulverized prior to XRD analysis. XRD of the pyrolysed sample confirmed the deposition of hexagonal nickel telluride NiTe (ICDD 00-038-1393), having the preferred orientation along the (101) plane (Fig. 4.2).

![Fig. 4.2. XRD pattern of hexagonal nickel telluride deposited from (1) at 500 °C.](image-url)
SEM studies to determine the morphology of the material revealed them to be tiny fused crystallites as seen at higher magnification (Fig. 4.3.)

**Fig. 4.3.** SEM images of hexagonal nickel telluride deposited at 500 °C (a) 5 µm (b) 2 µm and (c) 1 µm.

EDX analysis on the hexagonal crystallites showed a high nickel content i.e. NiTe ratio of 3:1 with phosphorus contamination (7%). In a previous study, hexagonal nickel telluride Ni_{0.51}Te was also deposited from [Ni\{(SeP^2Pr_2)(TeP^2Pr_2)N\}_2]^{35}.

### 4.6. Pyrolysis of [Pd(Ph_2P(Te)NP(Te)Ph_2)] (2)

The pyrolysis of complex (2) at 500 °C also deposited black residue which was pulverized and analyzed by XRD. The X-Ray Diffraction pattern of the pyrolysed sample indicated the deposition of hexagonal palladium telluride PdTe (ICDD 00-029-0971) (Fig. 4.4).
Fig. 4.4. XRD pattern of hexagonal palladium telluride deposited from (2) at 500 °C.

SEM studies of the deposited material indicated their morphology to be tiny crystallites mixed with globules (Fig. 4.5.). EDX analysis on the sample revealed a high tellurium content with the PdTe ratio as 1:1.5 also with phosphorus contamination (5%).

Fig. 4.5. SEM images of hexagonal palladium telluride deposited from (2) at (a) 5 µm (b) 2 µm and (c) 1 µm.
4.7. Pyrolysis of \([\text{Fe(Ph}_2\text{P(Te)NP(Te)Ph}_2]_3\) (3)

At 500 °C, complex (3) was pyrolysed and black deposits were obtained, pulverized and analysed by XRD. The X-Ray Diffraction pattern of the pyrolysed sample indicated the deposition of hexagonal iron telluride \(\text{FeTe}_2\) (ICDD 04-003-2015) and hexagonal tellurium (ICDD 01-079-0736) (Fig. 4.6). The presence of tellurium was revealed by its characteristic diffraction peaks from the primary reflections of \(2\theta\) at 23.02° corresponding to the \((100)\) plane and additional reflections of \(2\theta\) at 27.56, 38.28, 43.35, 45.94 and 62.85° for the \((011), (012), (111), (003),\) and \((113)\) respectively. Others were 67.87 and 81.97° for the \((023)\) and \((024)\) planes respectively.

![XRD pattern of hexagonal FeTe₂ and hexagonal tellurium deposited from (3) at 500 °C. Asterisks indicate hexagonal tellurium.](image)

The morphology of the deposited material consists of tiny bits of crisp flakes as revealed by the SEM (Fig. 4.7). EDX analysis showed the iron to tellurium ratio as \(\sim 1:2\) together with phosphorus (10%). The deposition of a metal telluride and tellurium might be expected since this had been previously reported \(^9,18\). It might be explained that the high ratio of \(\text{Te:M}\) in the precursor could be responsible for the deposition of elemental tellurium \(^1\).
Chapter 4: Telluride Precursors

4.8. Pyrolysis of [Pt(Ph$_2$P(Te)NP(Te)Ph)$_2$] (4)

The pyrolysis of complex (4) at 500 °C also deposited black residue which was analysed by XRD. The X-Ray Diffraction pattern revealed a mixture of both the rhombohedral platinum telluride PtTe (ICDD 01-088-2262) and hexagonal platinum tellurium PtTe$_2$ (ICDD 04-003-1897) (Fig. 4.8). Traces of PtTe were observed at 2θ values of 26.32, 31.60, 41.10, 44.84, 55.11 and 56.66°. These correspond to the (101), (104), (107), (018), (0012) and (024) planes respectively. SEM analysis of the deposited powder showed the morphology to be uniformly arranged flat flakes (Fig. 4.9).

Fig. 4.7. SEM images of hexagonal FeTe$_2$ and tellurium deposited from (3) at 500 °C (a) 5 µm (b) 2 µm and (c) 1 µm.
**Fig. 4.8.** XRD pattern of hexagonal PtTe$_2$ and rhombohedral PtTe deposited from (4) at 500 °C. Marked peaks are for PtTe.

**Fig. 4.9.** SEM images of hexagonal PtTe$_2$ and rhombohedral PtTe deposited from (4) at 500 °C (a) 5 µm (b) 2 µm and (c) 1 µm.
4.9. XPS analysis of FeTe$_2$

The surface atomic coverage and surface chemistry of the powder obtained from (3) were determined by XPS. The Fe 2p peak appeared at 714 and 728 eV for the 2p$_{3/2}$ and 2p$_{1/2}$ respectively (Fig. 4.10). This indicates iron oxide/hydroxide suggesting the probable surface oxidation of the sample prior to XPS analysis. Iron telluride should have binding energy at 707 eV for the 2p$_{3/2}$ peak$^{36}$. Furthermore, the tellurium 3d scan showed weak peak at ca. 576 eV which only matches tellurium oxide species (Fig. 4.11). Typically, tellurium 3d has binding energies at 572-573 eV$^{37}$.

Fig. 4.10. XPS of Fe 2p peak of FeTe$_2$ deposited from [Fe(Ph$_2$P(Te)NP(Te)Ph$_2$)$_3$] (3)
4.10. Conductivity studies on NiTe and PdTe

To test their conductivities, a film for each of the sample was prepared by vacuum filtering their dispersion on a PVDF membrane. After filtration the film was dried at 60° under vacuum for 24 hours. Four silver electrodes were then painted onto the surface on the film and four silver wires were attached to the electrodes. The wires were then connected to a Keithley 2400 source meter. The I-V curve showed no current flowing when 0-2 V was applied. This indicated that the samples had high resistance.
Fig. 4.12. 4-point probe conductivity measurements of exfoliated samples of NiTe and PdTe.

Prior to the conductivity measurements, the presence of the constituent elements was determined by EDX (Fig. 4.13 for PdTe).

Fig. 4.13. EDX analysis for the sonicated sample of PdTe.

Also, the TEM images of the prepared flakes for the samples revealed their 2D structure (Fig. 4.14 and 4.15).
Fig. 4.14. TEM images of palladium telluride films.

Fig. 4.15. TEM images of nickel telluride films.
4.11. Magnetic measurements on iron telluride powders

Iron tellurides are antiferromagnetic whose magnetic properties depend on the function of temperature between 2.5 K and 300 K\textsuperscript{25, 38, 39}. From the magnetic measurement, it should be possible to evaluate phase relationships which exist in iron telluride systems. DC magnetization plots of FeTe\textsubscript{2} powders deposited from complex (3) are shown in Fig. 4.16. Magnetization versus temperature for ZFC and FC experiments at 100 Oe magnetic fields are given in Fig. 4.16. It showed the superimposition of the ZFC and FC curves on each other and increased with decreasing temperature. Hence, this might have indicated the antiferromagnetic behaviour of the sample.

![Fig. 4.16. Zero field-cooled (ZFC) and field-cooled (FC) curves of hexagonal iron telluride deposited from [Fe(Ph\textsubscript{2}P(Tr(Te)NP(Te)Ph\textsubscript{2}))\textsubscript{3}] (3) at 100 Oe.](image)
In the amorphous state, FeTe\textsubscript{2} displays strong antiferromagnetic coupling between localized moments though without a long-range magnetic ordering and transits to a spin-glass state at 6 K\textsuperscript{25,40}. However the crystalline state shows 3D antiferromagnetic ordering at ~ 83 K\textsuperscript{41}. From Fig. 4.16 shown above, we might as well assume that the antiferromagnetic transition temperature, \( T_N \) occurred at around 75 K. Previously, the magnetic properties of various iron and tellurium having integral stoichiometric ratios have been studied. An example is FeTe as an antiferromagnetic material with transition temperature of 70 K\textsuperscript{42}, while FeTe\textsubscript{2} transits as an antiferromagnetic material at 100 K\textsuperscript{25}.

4.12. Conclusion

Ditellurido-imidodiphosphinato complexes [M\{TePPh\textsubscript{2}N\}\textsubscript{2}] (M = Ni, Pd, Pt) and [Fe\{TePPh\textsubscript{2}N\}\textsubscript{3}] have been synthesised through the sodiation of the anion \[\text{N(PPh}_2\text{)}\textsubscript{2}\] prior to the reaction with elemental tellurium. The thermal properties of the complexes showed their suitability for deposition studies from their single-step decomposition pattern to the respective metal tellurides. SEM images of the powders revealed their morphologies to be polygonal crystallites. Conductivity studies on NiTe and PdTe indicated these materials to be insulating due to their high resistance. Magnetic measurements on the orthorhombic FeTe\textsubscript{2} showed its antiferromagnetic behaviour with the transition temperature at 75 K. XPS measurements on FeTe\textsubscript{2} revealed the surface oxidation of the material.
References


CHAPTER 5:
GENERAL EXPERIMENTAL
5.1. Chemicals

Zinc (II) chloride, cadmium (II) chloride, sodium methoxide, sodium hydride, anhydrous iron (III) chloride, chlorodiisopropylphosphine, chlorodiphenylphosphine, 1,1,1,3,3,3-hexamethyldisilazane, tert-potassium butoxide, nickel (II) acetate, palladium (II) acetate, platinum (II) chloride, selenium powder, tellurium powder and deuterated chloroform were used as purchased from Sigma Aldrich. Diethyl ether, petroleum ether, toluene, methanol, carbon disulfide, dichloromethane, hexane, tetrahydrofuran, and tetramethylethenediamine were purchased from Fisher Chemicals.

5.2. Handling of air-sensitive compounds

All synthetic procedures were done under an inert atmosphere using a double manifold Schlenk-line, attached to an Edwards E2M8 vacuum pump, and a dry nitrogen cylinder. All flasks were evacuated, and then purged with nitrogen at least three times prior to use, with external heat applied where deemed necessary. Solid air-sensitive compounds were handled in a glove box under an inert atmosphere of dry nitrogen. Liquid air-sensitive chemicals were transferred to Schlenk type flasks either by cannula or using syringes. Dry solvents were used throughout the syntheses, either distilled over standard drying agents (Na/benzophenone, CaH$_2$ etc.) or purchased and stored in flasks over molecular sieves. Deuterated solvents for NMR measurements were frozen at liquid nitrogen temperature, degassed under vacuum and then flushed with nitrogen. After repeating this procedure three times, the deuterated solvents were stored under nitrogen over molecular sieves.
5.3. Characterization methods

NMR spectra were recorded using a Bruker Avance (III) 400 MHz FT-NMR spectrometer, using CDCl₃ or d₈-toluene as solvent. ¹H NMR spectra were referenced to the solvent signal and the chemical shifts were reported relative to Me₄Si. ³¹P NMR spectra were referenced externally to an 85% solution of H₃PO₄ and the chemical shifts were reported relative to H₃PO₄. ⁷⁷Se NMR spectra were reported relative to the external standard (PhSe)₂. Mass spectra were recorded on a Micromass Platform II instrument by electrospray (ES) and atmospheric pressure chemical ionisation (APCI). Mass spectrometer was performed by the Mass spectrometry unit of the School of Chemistry.

5.4. Elemental analysis

CHNS analysis was done using Thermo Flash 2000 & Carlo Erba EA 1108 elemental analyzers. A weighed sample in a tin container was decomposed in the analyzer by flash combustion. The sample burns and combustion gases (carbon dioxide, water vapour, nitrogen and sulfur dioxide) released which were separated and analysed using a gas chromatography column (GC) to determine the amount of each element present in the original sample. Metal analyses were performed on Fisons Horizon ICP-OES. The weighed sample was decomposed by acid digestion, and then made up with water to form an aqueous solution. This was introduced into the ICP spectrometer and the emission wavelengths of the interested elements measured. By measuring the intensity of the emission wavelengths, the concentration of elements in the solution were then determined. Elemental analyses were performed by the microanalysis section of the School of Chemistry.
5.5. Thermogravimetry analysis

Thermal analyses were performed using Seiko SSC5200/S220TG/DTA model with a heating rate of 10 °C min\(^{-1}\) under nitrogen. A weighed sample was placed on the balance in the heating furnace and any weight change measured using a controlled heating programme. Melting points were recorded on a Gallenkamp melting point apparatus. TGA was performed by the school of chemistry microanalysis team of the School of Chemistry.

5.6. Cleaning of glass substrates

The substrate used in this work was glass and was cleaned prior to CVD experiments to remove impurities and residues. The procedures involved were as follows:

- Degreased the glass slides in trichloroethylene and placed in acetone to remove organic residues.
- Rinsed the substrates in deionised water.
- Placed the rinsed substrates in 50% nitric acid for 30 minutes and further ultrasonication for 10 minutes in deionised water.
- Rinsed finally in deionised water and air-dried.

5.7. Film deposition by AACVD

In a typical deposition experiment, 200 mg of the precursor was dissolved in 20 ml of toluene in a two-necked 100 ml round-bottom flask with a gas inlet which allowed the carrier gas (argon) to pass into the solution to aid the transport of the aerosol. The flask was connected to the reactor tube by a piece of reinforced tubing. For the deposition, the flow rate of the carrier gas was 160 or 240 sccm and was controlled by a Platon flow gauge. Seven glass substrates (ca. 1 x 3 cm) were placed
inside the reactor tube, which was placed in a Carbolite furnace. The precursor solution in the round-bottom flask was kept in a water bath above the piezoelectric modulator of a PIFCO ultrasonic humidifier (Model No. 1077). The generated aerosol droplets of the precursor were transferred into the hot wall deposition zone of the reactor by the carrier gas. Both the solvent and the precursor were evaporated and the precursor vapour reached the heated substrate surface where thermally induced reactions and film deposition occurred.

5.8. Pyrolysis

The pyrolysis experiments were done in a quartz reactor using a Carbolite heating furnace. The sample was heated at 500 or 550 °C under vacuum for 90 minutes and subsequently cooled to room temperature for 1 hour. 500 mg of the sample was used for each experiment.

5.9. X-ray diffraction (XRD)

X-ray diffraction studies were performed on a Bruker AXS D8 diffractometer using monochromated Cu-Kα radiation. The samples were mounted flat and scanned from 10 to 85° in a step size of 0.05 with a count rate of 9 seconds. The diffraction patterns were then compared to the documented patterns in the ICDD index.

5.10. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX)

All samples were coated with carbon to avoid charging of the sample by the electron beam, using Edward’s coating system E306A before scanning electron microscopy (SEM) was carried out. SEM was performed using a Philips XL30 FEG SEM. Energy dispersive X-ray (EDX) analyses were done using DX4 instrument.
5.11. XPS measurements

The XPS spectra were recorded using a Kratos Axis Ultra spectrometer employing a monochromated Al Kα X-ray source and an analyser pass energy of 80 eV (wide scans) or 20 eV (narrow scans) resulting in a total energy resolution of ca. 1.2 and 0.6 eV, respectively. Uniform charge neutralisation of the photoemitting surface was achieved by exposing the surface to low energy electrons in a magnetic immersion lens system (Kratos Ltd.). The system base pressure was 5 x 10^{-10} mBar. Spectra were analysed by first subtracting a Shirley background and then obtaining accurate peak positions by fitting peaks using a mixed Gaussian/Lorenzian (30/70) line shape. During fitting, spin orbit split components were constrained to have identical line width, elemental spin orbit energy separations and theoretical spin orbital area ratios.

Quantitative analysis was achieved using theoretical Scofield elemental sensitivities and recorded spectrometer transmission functions. All photoelectron binding energies (BE) were referenced to C1s adventitious contamination peaks set at 285 eV BE. The analyser was calibrated using elemental references; Au 4f7/2 (83.98 eV BE), Ag3d5/2 368.26 eV BE) and Cu2p3/2 (932.67 eV BE). XPS measurements were performed by Dr. Paul Wincott.

5.12. Pyrolysis GC-MS

Small quantities of precursors were dissolved in dichloromethane, 5 ml was inserted in pyrolysis tubes dried at 80 °C and analysed by normal flash pyrolysis gas chromatography mass spectrometry (Py-GC-MS). Samples were pyrolysed using a CDS 5200 series pyroprobe pyrolysis unit by heating at 300 °C for 10 seconds. The fragments obtained were analysed using a Agilent 7890A linked to an Agilent 5975 MSD single quadrupole MS operated in electron ionisation (EI) mode (scanning
between 50 and 800 atomic mass unit at 2.7 scans s\(^{-1}\); ionisation energy 40 eV). The chromatography conditions were as follows: HP5 fused column (J+W Scientific); bonded phase 5% diphenyldimethylpolyolsiloxane, length 30 m, inner diameter 0.32 mm; film thickness 0.25 mm. The temperature employed for analysis was: initial temperature 40 °C for 2 minutes, followed by heating at 8 °C min\(^{-1}\) to 300 °C. The pyrolysis transfer line and injector temperatures were set at 350 °C, the heated interface at 280 °C, the EI source at 230 °C and the MS quadrupole at 150 °C. The carrier gas (helium) pressure was kept at 14 psi with flow rate of 1 cm\(^3\) min\(^{-1}\) and the samples were introduced in split mode (split ratio 50:1). Pyrolysis GC-MS experiments were done by Dr. Bart Van Dongen.

5.13. Magnetic measurements

Magnetic measurements were performed in the temperature range 2-300 K, with a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. All samples were restrained in eicosane to avoid orientation effects in high magnetic fields. Data were recorded for the diamagnetic contribution of the sample holder and eicosane, which was measured in advance. Zero-field cooled (ZFC) and field-cooled (FC) curves were collected under an applied magnetic field of 100 Oe. Isothermal magnetisation curves were recorded between -4 and 4 T magnetic fields at temperatures of 300 K and 5 K. Magnetic measurements were performed by Dr. Floriana Tuna.

5.14. Single crystal X-ray structure determination

Single-crystal X-ray diffraction for the compounds were collected using graphite-monochromated Mo K\(\alpha\) radiation (\(\lambda = 0.71073\ \text{Å}\)) on a Bruker APEX diffractometer. The structure was solved by direct methods and refined by full-matrix least squares\(^1\) on F\(^2\). All non-hydrogen atoms were refined anisotropically. Hydrogen
atoms were included in calculated positions, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All calculations were carried out using the SHELXTL package\textsuperscript{2}. Single crystal X-ray diffraction data collection and structure determination were performed by Dr. James Raftery or Dr. Madeleine Helliwell.

5.15 Conductivity Test

This was done by using a tip sonicator called Ultra Sonic Tip GEX600, 700W, at 30\% amplitude. TEM samples were prepared by pipetting a few drops of the sample onto a holey carbon grid and allowed to dry in air. Bright field imaging and EDX were performed on a Jeol 2100. The dispersion was vacuum filtered through a Buchner funnel onto a PVDF membrane (pore size of 0.02 \(\mu\)m). Four electrodes were painted onto the film and these were connected to a Keithley 2400 source meter via silver wire. This gives an I-V curve from which the resistance as the inverse of the slope, R, could be determined. Conductivity tests were performed by Arlene O’Neill in Prof. Jonathan Coleman’s research group at Trinity College, Dublin in Ireland.

5.16 References


CHAPTER 6:
CONCLUSION AND
FUTURE WORK
6.1 Conclusion

Chalcogenide materials i.e. materials containing a chalcogen and metal/metals (sulfides, selenides or tellurides) have found applications in photovoltaic technology which uses cheap and readily available elements. Previously, MOCVD method has been widely applied to produce thin films of metal chalcogenides. In order to eliminate the problems associated with MOCVD, single-source precursors with appropriate physico-chemical properties have been developed as alternative routes to deliver chalcogenide materials. In this study, a novel series of metal complexes (Zn, Cd, Fe, Ni, Pd, and Pt) were synthesized using the dichalcogenidodiphosphinato ligands\(^*\). The characterization techniques used for the complexes include MS, NMR, elemental analysis and X-ray single crystal structure. The thermal properties of the complexes were determined by TGA which revealed their suitability for deposition studies. The complexes were used as single-source precursors for the deposition of sulfide, selenide and telluride materials.

The second chapter presented a comprehensive study on the growth of cadmium selenide and cadmium selenide/cadmium phosphide from the precursors $[\text{Cd}^{\{\text{iPr}_2\text{P(Se)NP(Se)Pr}_2\}^2}]$ and $[\text{Cd}^{\{\text{iPr}_2\text{P(S)NP(Se)Pr}_2\}^2}]$ by AACVD based on the deposition temperature and flow rate of the carrier gas. Similarly, the precursor $[\text{Cd}^{\{\text{iPr}_2\text{P(S)NP(S)Pr}_2\}^2}]$ also deposited cadmium sulfide, cadmium phosphide and cadmium sulfide/cadmium phosphide depending on the temperature and flow rate. However, the zinc precursors $[\text{Zn}^{\{\text{iPr}_2\text{P(Se)NP(Se)Pr}_2\}^2}]$ and $[\text{Zn}^{\{\text{iPr}_2\text{P(S)NP(Se)Pr}_2\}^2}]$ deposited only zinc selenide at all deposition temperature and flow rates. All attempts to deposit zinc sulfide from the precursor $[\text{Zn}^{\{\text{iPr}_2\text{P(S)NP(S)Pr}_2\}^2}]$ were unsuccessful as there was no deposition observed. The pyrolysis GC-MS analysis of the precursor $[\text{Cd}^{\{\text{iPr}_2\text{P(S)NP(S)Pr}_2\}^2}]$ indicated
the formation of a neutral species [CdSPN], from which cadmium sulfide and cadmium phosphide were deposited. This was modelled by DFT calculations.

The third chapter described the synthesis of iron complexes [Fe\{(SePPh\_2)\_2N\}_2] and [Fe\{(SePPh\_2NPPh\_2S)\_2N\}_2] from the imidodiphosphinate ligand. The X-ray single crystal structure determination of [Fe\{(SePPh\_2)\_2N\}_2] showed iron in a distorted tetrahedral environment with a Se\_4 donor set. Pyrolysis of the complexes at 500 and 550 °C deposited orthorhombic FeSe\_2, though no distinguishable pattern was seen for the complex [Fe\{(SePPh\_2NPPh\_2S)\_2N\}_2] at 550 °C. The morphology of the deposited powders was characterized by scanning electron microscopy (SEM) and indicated polygonal crystallites at both temperatures. The surface atomic coverage and surface chemistry of the deposited powders indicated the surface oxidation of FeSe\_2 in which both elements were bonded to oxygen. Magnetic measurements on FeSe\_2 powder confirmed its ferromagnetic behaviour.

In the fourth chapter, the synthesis of ditellurido-imidophosphinato complexes of nickel, palladium, platinum and iron was reported. This was achieved through the sodiation of the anion [N(PPh\_2)\_2]\^- prior to the reaction with elemental tellurium. Pyrolysis of the synthesized complexes at 500 °C deposited the respective metal tellurides. The structures of the materials were found to be polygonal crystallites as indicated by SEM analysis. Conductivity studies on NiTe and PdTe showed no current flow when films of these were connected to a meter source via silver wire. Magnetic measurements on the orthorhombic FeTe\_2 revealed its antiferromagnetic properties, having a transition temperature at 75 K. XPS measurements on FeTe\_2 showed both iron and tellurium attached to oxygen, hence the surface oxidation of the material.
Thus, the imidodichalcogenidodiphosphinate ligands \([\text{EPR}_2\text{N}]^-\) (\(\text{E} = \text{S, S; Se, Se; S, Se; Te, Te; R} = \text{Ph, }^3\text{Pr}\)) have been successfully used to prepare complexes of Zn, Cd, Ni, Pd, Pt and Fe. These have been used as single-source precursors to deposit functional materials by AACVD and pyrolysis.

### 6.2 Future work

The future work on this project will involve the synthesis of PCP ligand [\(\text{HC}(<\text{PR}_2\text{E})_2\text{N}\)] (\(\text{E} = \text{Se, Te; R} = \text{Ph; E} = \text{Se, R} = ^3\text{Pr}\)) to prepare zinc and cadmium complexes, followed by their AACVD or pyrolysis studies. Also, it will be of interest to prepare the mixed chalcogen of this ligand (\(\text{E} = \text{S, Se; S, Te; Se, Te}\)) to synthesize zinc and cadmium complexes and their deposition studies. Furthermore, the isopropyl analogue of the iron complexes [\(\text{Fe}\{\text{(EPR}_2\text{N})_2\}\] (\(\text{E} = \text{Se, Se; S, Te}\)) will be prepared to determine the effect of the increase in volatility of the alkyl group in the complex. This can later be extended to the tellurium analogue and probably the mixed chalcogen as well. The future work on the tellurium complexes will involve the synthesis of the isopropyl analogue of [\(\text{M}\{\text{(PPh}_2\text{Te})_2\text{N}\}_2\] (\(\text{M} = \text{Pd, Pt}\)) and that of [\(\text{Fe}\{\text{P}^3\text{Pr}_2\text{Te})_2\text{N}\}_3\]. This is to determine the effect of the change in the alkyl group on the likely-deposited material.

* The following complexes have not been reported previously:

1. \(\text{Cd}[^3\text{Pr}_2\text{P(Se)NP(S)}^3\text{Pr}_2]_2\)
2. \(\text{Zn}[^3\text{Pr}_2\text{P(Se)NP(S)}^3\text{Pr}_2]_2\)
3. [\(\text{Fe}\{\text{(SePPh}_2\text{N})_2\text{N}\}_2\]
4. [\(\text{Fe}\{\text{(SePPh}_2\text{NPh}_2\text{S})_2\text{N}\}_2\]
5. [\(\text{Ni}\{\text{Ph}_2\text{P(Te)NP(Te)Ph}_2\}_2\]
6. [\(\text{Pd}\{\text{Ph}_2\text{P(Te)NP(Te)Ph}_2\}_2\]
7. [\(\text{Fe}\{\text{Ph}_2\text{P(Te)NP(Te)Ph}_2\}_3\]
8. [\(\text{Pt}\{\text{Ph}_2\text{P(Te)NP(Te)Ph}_2\}_2\]

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APPENDICES
Liquid Injection Chemical Vapour Deposition (LICVD)\textsuperscript{1}.

Liquid injection CVD has been widely used for the deposition of metal oxide thin films. As in AACVD, the precursor is dissolved in an inert solvent (usually a hydrocarbon such as nonane). The precursor is held at room temperature and when required it is delivered at a precisely controlled rate into a heated evaporator and transported by carrier gas to the heated substrate to deposit the thin film. LICVD shares the advantages of AACVD (given on page 44) – allows the use of low volatility precursors, allows the use of thermally unstable precursors, can use precursor cocktails. A disadvantage of this is one hot zone which is due to lack of flexibility and the need to match precursor volatilities.

Carbon Contamination for Single-Source Precursors

A major disadvantage of single-source precursors is carbon contamination. Conventional multisource CVD of III-V and II-VI materials usually involve a metal alkyl (e.g. Me₂Zn, Me₃Ga) and a hydride co-reagent which contains “active, acidic hydrogen”. The hydrogen removes the alkyl radical as a stable hydrocarbon CH₄ and films are generally pure – with low levels of carbon. Thus in single-source precursors, active hydrogen is not present, which might be a bigger risk of carbon contamination. Hence, careful precursor design is required to ensure low carbon levels which might involve intramolecular transfer of hydrogen.