

**SYNTHESIS AND CHARACTERIZATION OF SUBSTITUTED
DITHIOCARBAMATES LIGANDS AND COMPLEXES AS SOURCE OF
METAL (Pb, Ni & Co) SULPHIDE NANOPARTICLES**



A Dissertation

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DECLARATION

I declare that this work contains no material which has been accepted for the awards of any other degree in any university. To the best of my knowledge, this work contains no material previously published except where the reference has been made in text.

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DEDICATION

This dissertation is dedicated to my younger brother (Ramotho-motho) and my cousin (Fulufhelo) who were always supported me from day one of my Masters registration. Without their love and support, none of this would have been possible.

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CONFERENCES ATTENDED

Conference	Title of the presentation	Year	Type of presentation
SACI convention in Durban, South Africa	Nickel Sulfide Nanoparticles: Synthesis, the effect of substituted dithiocarbamates complexes and temperature	2015	Poster
NYRS in Johannesburg, South Africa	A tempted synthesis of nickel sulfide nanoparticles from benzimidazole based ligand (by varying temperature and concentration)	2015	Oral
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LIST OF PUBLICATIONS

1. C. S. Thangwane, T. Xaba and M. J. Moloto, The formation of the mixed morphology of nickel sulfide nanoparticles derived from substituted benzimidazole dithiocarbamate nickel (II) complexes, Chalcogenide Letters, Vol. 14, No. 9, 2017, 407 - 417
2. C. S. Thangwane, T. Xaba and M. J. Moloto, Influence of Temperature and Capping Molecules on the Synthesis of Cubic Structured Lead Sulfide Nanoparticles from Substituted Benzimidazole Dithiocarbamate Complex, Asian Journal of Chemistry; Vol. 29, No. 12 (2017), 2711 - 2716

ABSTRACT

Lead, nickel and cobalt dithiocarbamates complexes were synthesized using methanol and water as solvents. All complexes were refluxed at 60 °C, cooled at room temperature, washed with methanol to remove the impurities and dried under the fume hood. A combination of Fourier transformer infrared (FTIR), elemental analysis (EA) and thermogravimetric analysis (TGA) were used to characterize these complexes. There was shifting of bands from low to high frequencies of the dithiocarbamates complexes compared to benzimidazole derivatives. The absence of the N-H band and the presence of new C=S bands confirmed that the complexes can be used in the preparation of metal sulphide nanoparticles. Elemental analysis showed that there was a percentage mismatch for the complexes I, III, IV and V. Complexes II and VI calculated percentages were within the limits with the found percentages except for sulphur which was low. The TGA curves decomposed to form a mixture of metal and metal sulphides for complex I, II, III and IV except for complex VI which gave metal sulphide only. All benzimidazole complexes decomposed at higher temperatures and were considered as stable complexes.

Lead sulphide (PbS) is an important group IV-VI metal chalcogenide semiconductor. It has a direct narrow band gap of 0.41 eV at 300K and a large excitonic Bohr radius of 18 nm. Lead sulphide absorption band can be tuned to anywhere between near IR to UV (0.4µm) covering the entire visible spectrum, while achieving the quantum confinement region. The synthesis of lead sulphide nanoparticles was conducted by varying the effect of the reaction conditions such as the type of capping agents and temperature. Lead dithiocarbamate complex derived from benzimidazole, $[\text{Pb}(\text{S}_2\text{N}_2\text{C}_8\text{H}_5)_2]$ was thermolysed in hexadecylamine (HDA) and trioctylphosphine oxide (TOPO) at different reaction temperatures (140, 160 and 180 °C) to produce HDA and TOPO capped PbS nanoparticles. The nanoparticles were characterized using X-ray diffraction (XRD) for structural analysis, transmission electron microscopy (TEM) for shape and size, Ultraviolet visible (UV/Vis) and Photoluminescence (PL) spectroscopy for optical properties. An increase in temperature gave a decrease in the sizes of the nanoparticles when using the HDA capped lead benzimidazole dithiocarbamate complex. The observed morphology was cubes. TOPO capped lead benzimidazole dithiocarbamate complex gave no specific trend when temperature was varied. A cross-like layer with quasi spherical particles on top was observed at 160 °C. At 180 °C, the cross-like layer decomposed into rods- like materials with

quasi spherical particles on top for TOPO capped PbS nanoparticles. For lead 2-methylbenzimidazole $[\text{Pb}(\text{S}_2\text{N}_2\text{C}_9\text{H}_7)_2]$ dithiocarbamate complex, TOPO capped PbS produced agglomerated cubic morphology at low temperature but as the temperature was increased agglomerated cylindrical shapes were observed. HDA capped PbS produced polydispersed nanocubes which were increasing in size when the temperature was increased. Nanoparticles displayed a blue shift in band edges with good photoluminescence behaviour which was red shifted from their respective band edges all temperatures and capping agents. XRD confirmed the crystal structure of cubic phase (galena) of PbS at all temperatures except for HDA capped PbS nanoparticles at 140 °C from lead benzimidazole dithiocarbamate complex which confirmed the crystal structure of face-centred cubic phase of PbS nanoparticles.

Nickel sulphide has much more complicated phase diagram than cobalt sulfides and iron sulfides. Their chemical composition has many crystalline phases such as α -NiS, β -NiS, NiS₂, Ni₃S₂, Ni₃S₄, Ni₇S₆ and Ni₉S₈. Ni₃S₂ phase has shown potential as a low-cost counter electrode material in dye sensitised solar cells, while the α -NiS phase has been applied as a cathode Material in lithium-ion batteries. The synthesis of nickel sulphide nanoparticles was done by varying the effect of the reaction conditions such concentration and temperature. Nickel benzimidazole dithiocarbamate $[\text{Ni}(\text{S}_2\text{N}_2\text{C}_8\text{H}_5)_2]$ and nickel 2-methylbenzimidazole $[\text{Ni}(\text{S}_2\text{N}_2\text{C}_9\text{H}_7)_2]$ dithiocarbamates complexes were thermolysed in hexadecylamine (HDA) at different reaction temperatures (140, 160 and 180 °C) and precursor concentrations (0.30, 0.35 and 0.40 g) to produce HDA capped NiS nanoparticles. It was observed that increasing both temperature and precursor concentration increased the size of the nanoparticles. Anisotropic particles were observed for both complexes when varying precursor concentration and temperature. Nickel benzimidazole dithiocarbamate complex produced stable shapes (spheres and cubes) of nickel sulphide nanoparticles. Nickel 2-methylbenzimidazole dithiocarbamate complex produced a mixture of spheres, cubes, triangles and rods nickel sulphide nanoparticles at all concentrations. But when varying temperature, it only produced that mixture at 160 °C. The optical measurements supported the presence of smaller particles at all temperatures and concentrations. XRD showed the presence of C₇OS₈ and pure nickel as impurities. However, the crystal structure of cubic Ni₃S₄ was observed at low temperatures and an introduction of monoclinic Ni_xS₆ at high temperature (180 °C) when varying temperature for both complexes. When varying concentration using nickel benzimidazole dithiocarbamate complex, XRD showed the presence of NiSO₄.6H₂O impurities at high temperatures. At 160 °C a mixture of

hexagonal NiS and cubic Ni₃S₄ was observed. At low temperatures only nickel as a metal was found as an impurity and the crystal structure of cubic Ni₃S₄ was observed. When nickel 2-methylbenzimidazole complex was used, C₇OS₈ and pure nickel were found as impurities but the crystal structure of cubic Ni₃S₄ was observed.

Cobalt sulphide (CoS) belongs to the family of group II-IV compounds with considerable potential for application in electronic devices. They have a complex phase diagram and their chemical composition have many phases such as Co₄S₃, Co₉S₈, CoS, Co_{1-x}S, Co₃S₄, Co₂S₃ and CoS₂. The synthesis of cobalt sulphide nanoparticles was conducted by varying the effect of temperature on size and shape of the nanoparticles. Nickel benzimidazole dithiocarbamate, [Ni(S₂N₂C₈H₅)₂] and nickel 2-methylbenzimidazole [Ni(S₂N₂C₉H₇)₂] complexes were thermolysed in hexadecylamine (HDA) at different reaction temperatures (140, 160 and 180 °C) to produce HDA capped CoS nanoparticles. Cobalt benzimidazole dithiocarbamate complex produced close to spherical shapes nanoparticles at all temperatures. The images showed that as temperature was increased, the size of the particles decreased. All the main reflection peaks were indexed to face-centred cubic Co₃S₄ and there were some impurities of C₇OS₈ at all temperatures. The optical measurements supported the presence of smaller particles at all temperatures. Cobalt 2-methylbenzimidazole dithiocarbamate complex produced big and undefined morphology. The optical properties were also featureless and XRD only showed impurities of C₇OS₈. The impurity is thought to be generated from a side reaction between benzimidazole and carbon disulphide to give this persistent organic moiety.

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SYMBOLS AND CONSTANTS

a.u	arbitrary units
°C	degree celsius
cm	centimeter
ml	millilitre
E	energy
E _g	band gap
eV	electron volts
nm	nanometer
QDs	quantum dots
CPS	counts per second
h	hour

LIST OF ABBREVIATIONS

FT-IR	Fourier transformer infrared
UV/vis	Ultraviolet visible
EA	Elemental analysis
PL	photoluminescence
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
XRD	X-ray diffraction
DTC	dithiocarbamates
HDA	hexadecylamine
TOP	tri-octylphosphine
TOPO	tri-n-octylphosphine oxide

DISSERTATION OUTLINE

Chapter 1

This chapter focuses on the introduction of the nanoparticles and dithiocarbamate complexes. It also focuses on their applications, literature reports on the methods of synthesis on dithiocarbamates and nanoparticles. Aim, objectives, problem statement and purpose of study are also described.

Chapter 2

This chapter deals with the experimental and analytical procedures used in the preparation of ligands, complexes and nanoparticles. The characterization techniques are reviewed.

Chapter 3

This chapter focuses on the findings of the complexes; results obtained from different techniques such as FTIR spectroscopy, elemental analysis and TGA are interpreted, discussed and concluded.

Chapter 4

This chapter focuses on the findings of HDA and TOPO capped PbS nanoparticles from different complexes. Results obtained from different techniques are interpreted and discussed. The synthetic parameters such as temperature and type of capping agents are studied for their influence on the size, structure, composition and arrangement of lead sulphide nanoparticles.

Chapter 5

This chapter focuses on the findings of HDA capped NiS nanoparticles from different complexes. The reaction conditions such as temperature and precursor concentration are studied for their influence on size and shape of the nanoparticles. Results obtained from different techniques are interpreted and discussed.

Chapter 6

This chapter focuses on the findings of HDA capped CoS nanoparticles from different complexes. Temperature is studied for its influence on size and shape of the nanoparticles. Results obtained from different techniques are interpreted and discussed.

Chapter 7

General conclusions based on the interpretation of data are drawn. Recommendations for the future work are also put forward in this chapter.

Chapter 1

Background and literature review

1.1 Nanoparticles

Nanotechnology and nanoscience deal with matter at the scale of 1 billionth of a meter (i.e., 10^{-9} m = 1 nm), and these also deals with the manipulation of matter at the atomic and molecular scale. In simple terms, it can be defined as engineering at a very small scale. It is an exciting area of scientific development which promises more for less. It offers the ability to both improve the existing technologies and create smaller, cheaper, lighter and faster devices that can do more and cleverer things, use less raw materials and consume less energy. It can be applied to many research and development areas such as medicine, manufacturing, computing, textiles and cosmetics. Nanoparticles are the most vital components in the fabrication of a nanostructures, and are far smaller than the world of everyday objects that are described by Newton's laws of motion, but bigger than an atom or a simple molecule that are governed by quantum mechanics. One of the major challenges that concerns nanoparticles synthesis and potential applications containing nanoparticles is the controlled design of such systems. They must be synthesized to possess desired surface properties, composition, geometry, and the structure and must be arranged properly for specific applications containing them to work.

Nanocrystals are crystals with at least one dimension between 1 and 100 nm which have a finite number of atoms (~100 to ~10,000 atoms) (Fahlman, 2007). In 1857, It was recognised that dyes consist of tiny amounts of metals (Faraday, 1857). A century later, semiconductor nanocrystals were discovered (Brus, 1984). The colloidal particles display a remarkable tendency to remain single-crystalline and later they were named as nanocrystals. Nanocrystals have high surface area and a large fraction of the atoms are on its surface. A small nanocrystal of 1 nm diameter will have as much as 30% of its atoms on the surface, while a larger nanocrystal of 10 nm will have approximately 15% of its atoms on the surface (Rao et al., 2002). Nanocrystals are characterized by a single-domain crystalline lattice. Interest in nanocrystals has been growing gradually due to their unique properties as a bridge between

atoms and bulk solids as well as their potential applications (Halperin W. P., 1986). In principle, the electron confinement by a nanocrystal provides the most powerful means to manipulate the electronic, optical, and magnetic properties of a solid material. This is an explanation why nanocrystals have been the primary source for discovering and studying quantum size effects, with examples of quantized excitation (Murray et al., 2000), Coulomb blockade (Maheshwari et al., 2008), metal-insulator transition (Markovich et al., 1999), and super-paramagnetism (Jeong et al., 2007). It has been discovered that size and shape of nanocrystals are key elements for the determination of their unique chemical and physical properties. Bulk materials have their own characteristics and innate properties such as colour band-gap energy and phase transition temperature. Semiconductors with reduced dimension display unique electronic, optical, magnetic and photochemical properties that significantly differ from their bulk materials (Sangeetha et al., 2014). This is due to their high surface area to volume ratios and quantum confinement (Roco, 1999). It has been reported that crystal morphology plays an important role due to the size and shapes of the crystal and it is one of the desired goals in material science to understand exact control of the morphology of semiconductor materials (Quadri et al., 1996). Quantum confinement region can be achieved by tuning the optical properties of the semiconducting materials (Shinji et al., 1998). Quantum confinement is observed when size of the nanoparticles is below Bohr radius. To reduce the size of the particles below Bohr radius, the surface of the particles needs to be passivated at the time of formation (Soo et al., 1994). And to achieve the quantum confinement regime, introduction of capping agents plays an important role in the synthesis of nanoparticles. Capping agents such as amines (Huixiang et al., 2005) and thiols (Aparna et al., 2008) are very good capping molecules that produce semiconductor nanoparticles below the Bohr radius.

1.2 Preparative methods for the synthesis of nanoparticles

Different methods for the synthesis of nanoparticles have been reported, which generally follow two routes; precipitation from solution, often at room temperature and often involving the reduction of a metal salt and the decomposition of molecular precursors at high temperature in either the solid, liquid (solution) or vapour phase. The chemical methods for the production of nanoparticles are discussed as follows;

1.2.1 Colloidal route

The first routes to be reported to the small particles involved the controlled precipitation of dilute colloidal solutions and the cessation of growth immediately after nucleation. Particles were typically monomeric in the early years thereafter nucleation and growth were properly inspected. Furthermore small crystals which are less stable dissolve, and then recrystallize on larger and more stable crystals and the process is called Ostwald ripening. The colloidal stability can be upgraded by using solvents with a low dielectric constant. For this route to be effective nanoparticles must have low solubility. It can be achieved by the correct choice of solvent, temperature, passivating agent and pH. Highly monodispersed particles are obtained if nucleation and growth processes are distinctly separate. The particles prepared by this route are not adequately stable at higher temperatures before annealing without agglomeration (Rossetti et al., 1985). Brus have made important contributions to this field, especially in the studies of CdS. An aqueous solution of ammonium sulphide and cadmium sulphate were used to prepare CdS nanoparticles (Rossetti et al., 1984), reported by Brus and co-workers. The synthesised stable CdS nanoparticles were achieved by using acetonitrile as the solvent in the presence of a styrene or maleic anhydride copolymer (Rossetti et al., 1984). CdS and ZnS nanoparticles have also been synthesized from aqueous and methanolic solution with organic capping agent (Rossetti et al., 1984). Hines reported the synthesis of PbS nanocrystalline quantum dots using this route. Photoluminescence spectra exhibited strong emission peaks near-infrared (Hines and Scholes, 2003). Jun reported shape control of semiconductor and metal oxide nanocrystals using nonhydrolytic colloidal routes, the observed morphology observed were polyhedrons, rods, wires, plates, prisms, branched rods, stars, inorganic dendrites and dumbbells (Jun et al., 2006). Spherical CuS nanoparticles have been synthesized via a simple colloidal synthesis route, using copper acetate monohydrate and thiourea as copper and sulphur sources. XRD patterns displayed the hexagonal phase of CuS (Dutta and Dolui, 2008). Romano-Trujillo reported lead selenide nanoparticles using this route. Extran ($\text{Na}_5\text{P}_3\text{O}_{10}$, NaOH and H_2O) was used as surfactant and the size of PbSe nanoparticles was varied by changing the molar concentration of Pb: Se. The observed particles size was found to be between 14 and 20 nm as calculated from the XRD patterns and it was in good agreement with sizes from SEM and TEM (Romano-Trujillo et al., 2012). Monodispersed cubic ZnS and hexagonal CdS nanoparticles were synthesized via the colloidal-route and N-butyl aniline was used as a surfactant. The average diameters obtained were 4 nm and 6 nm respectively (Onwudiwe and Strydom, 2013). Orthorhombic AgGaS₂ nanocrystals were synthesized using

this route. These orthorhombic AgS nanocrystals displayed great potential in visible-light-driven photocatalysis (Fan et al., 2014).

1.2.2 Synthesis in confined matrices

Different matrices such as molecular sieves (Johnson and La Mer, 1947, Wang and Herron, 1987), gels (Petit et al., 1994, Towey et al., 1990), glasses (Gao et al., 1994), micelles/microemulsions (Abe et al., 1995, Watzke and Fendler, 1997) and zeolites (Green and O'Brien, 1998) have been used for the preparation of semiconductor nanoparticles to restrict growth with diameters ranging from 13 to 125 Å. In determining the properties of the particles and the properties of the system, which include internal/external surface properties of zeolites and the liability, the matrix may also play a role. The growth of particles in the internal cavities of zeolites limits the particle size of the material to less than 20 nm. Reports show 13 Å of the smallest particles to be molecular in nature and they exhibit discrete absorption bands in their optical spectra. Two theoretical methods were proposed, which take into account the effect of non-parabolicity, to explain the observed size-dependent optical shifts for PbS nanocrystals. It was reported that the effective mass approximation fails for PbS nanocrystals. Phenyl capped cadmium and zinc chalcogenides nanoparticles produced 13 micelle solutions where silyl chalcogenide was reacted with a microemulsion containing the metal ion to form nanoparticles. The crystal surface composition was interesting due to its ability to react further with other silyl groups owing to excess Cd^{2+} sites effectively growing larger and developing a different surface capping (Steigerwald et al., 1988). CdS has been synthesized in two different zeolites by ion exchange from the sodium cationic form to the cadmium cationic form, followed by exposure to H_2S gas. Different particles sizes were found depending on the amount of cadmium ions used (Green and O'Brien, 1998). Nanoclusters size could be controlled by either using the potassium or sodium resin, which changed pore diameters. Lee studied the optimization of Ge nanoparticles confined in a carbon matrix for lithium battery anode material. Different sizes of Ge nanoparticles confined in a carbon matrix were obtained from XRD and TEM which showed that Ge nanoparticles' size increased from 8 to 100 nm as the annealing temperature of the as-prepared samples increased from 400 to 800 °C (Lee et al., 2007). Spherical copper sulphide nanoparticles embedded in PVA matrix was reported (Nath and Kalita, 2012). The thin films were deposited on glass substrates at room temperature using same volumes and moles of copper acetate and thiourea in an alkali medium. UV-visible absorption and PL

measurements showed an enhancement of band gap. MoS₂ nanocrystals confined in a DNA Matrix were reported (Goswami et al., 2013), the average size of highly crystalline nanocrystals was ~5 nm. UV–vis studies along with band gap calculations confirmed the quantum confinement of the nanocrystals (Goswami et al., 2013). Deng and co-workers reported a strategy to stabilize single-atom coordinative unsaturated iron sites by embedding highly dispersed FeN₄ centres in the graphene matrix at room temperature. FeN₄ centre was highly dispersed and well stabilized by the graphene matrix, which then enhanced the activity and stability for the oxidation of benzene to phenol (Deng et al., 2015).

1.2.3 Metal-organic routes

(Murray et al., 1993) first reported a popular method for preparing high quality, crystalline monodispersed nanoparticles. Volatile metal alkyl (dimethylcadmium) and a chalcogen source TOPSe (trioctylphosphine selenide) were mixed in tri-n-octylphosphine (TOP) and injected into hot TOPO (tri-n-octylphosphine oxide), a polar coordinating Lewis base solvent at high temperatures (120-300 °C). Thermolysis of precursors in high boiling point coordinating solvent such as TOPO was reported to be an effective method not only for II-VI, but also for III-V nanomaterials, which are difficult to prepare because of their increased covalent nature, highly toxic reagents used and fast oxidation (Murray et al., 1993, Revaprasadu et al., 1999a). During the preparation CdSe nanoparticles, nucleation was achieved by the introduction of concentrated reagents resulting in immediate supersaturation and the formation of the nuclei followed by slow growth and annealing, consistent with Ostwald ripening. Afterward the solvent was added to a cooled solution, thereby increasing the barriers to flocculation. Nanoparticles were then separated from decomposition by-products in the centrifuge, and they were dissolved in a solvent (e.g. toluene) followed by centrifugation to dispose the by-products resulting in an optically clear solution of TOPO-capped nanoparticles. The coordinating solvent plays a significant role in stabilizing the nanocrystalline colloidal dispersions and passivating the nanoparticles surface. The advantage of this method over other methods is not only the production of monodispersed particles but the gram scales of materials can be produced. The group III-V nanomaterials were also prepared using a similar approach as above by thermolysis of single molecular source precursors at 167 °C in 4-ethylpyridine acting both as a solvent and a capping agent. Nanoparticles of high quality were produced showing distinct quantum size effects in their optical properties (Revaprasadu et al., 1999a). Similar approach

was used (Murray et al., 1993) to synthesise TOPO capped InP nanoparticles which was reacted with P (SiMe₃)₃ in hot TOPO with subsequent annealing of the particles in the presence of a surfactant such as dodecylamine (Guzelian et al., 1996). The use of hazardous compounds such as dimethylcadmium, Cd(CH₃)₂ in this method is one of limitations especially at high temperatures. To overcome this problem, the use of single molecule precursors, a single compound containing all the elements is required for the formation of nanocrystal, such as alkyldiseleno- or alkyledithiocarbamate complexes (Trinidad and O'Brien, 1997, Trinidad and O'Brien, 1996). Nanometric particles of InP are readily prepared by the decomposition of the complex In(PBu₂)₃ at 167 °C in 4-ethylpyridine; the resulting materials show marked quantum confinement effects, and was investigated using optical absorption and photoluminescence spectroscopies and transmission electron microscopy. Mourdikoudis reported anisotropic growth of a highly symmetrical crystal structure using this route. Reaction conditions such as precursors, solvents, temperature, reducing agents, reaction time, and types and ratios of surfactants, such as alkyl amines, carboxylic acids, and phosphine oxides yielded anisotropic particles of Fcc Ni nanoparticles (Mourdikoudis et al., 2013).

1.2.4 Single-source precursor method

The single source or 'one-pot' method involves the thermolysis of the precursor in a high boiling point coordinating solvent such as tri-n-octylphosphine oxide (TOPO) or hexadecylamine (HDA). In this method the metal-chalcogenide bond is present at the complex stage and it has proven to be a very efficient route to high-quality nanoparticles. This method has an advantage over the other methods of preparation because it avoids the use of volatile, pyrophoric and toxic decomposition by-products. In this method the resulting precursors are air and moisture stable. The use of this method reduces the chances of incorporating impurities into the nanoparticles, and low deposition rates are possible. Revaprasadu reported the use of this method in preparing InS and InSe nanoparticles using metal thio- and seleno- precursors (Revaprasadu et al., 1999b). Nair reported the synthesis of CdS nanocrystals using [Cd (NH₂NHNH₂)₂Cl₂] as a single-source precursor and anisotropic shaped particles were found. The observed rods displayed a very slight blue shift in relation to bulk CdS (Nair et al., 2002). The synthesis of CdS nanoparticles from the complex of cadmium with dithiothiurea was also reported (Nair et al., 2003). Cai reported the synthesis of hexadecylamine (HDA)-capped CdS nanoparticles prepared by the single-source precursor method. Parameters such as reaction

temperature, monomer concentration and reaction time affected the size and shape of the nanoparticles (Cai et al., 2008). Mthethwa reported the synthesis of HDA capped CdS nanoparticles prepared from CdS heterocyclic cadmium dithiocarbamates as single source precursors and it was found precursor concentrations have an effect in the production of quantum dots as the presence of anisotropic particles were observed at lower concentration (Mthethwa et al., 2009). Ramasamy and co-workers reported Co₄S₃ phase in a monodispersed form using single-molecule precursor-based approach. Parameters such as reaction temperature precursor concentration affected the size and shape of the nanoparticles yielding different phases of cobalt sulphide (Ramasamy et al., 2010). Nyamen also used the similar approach by synthesizing TOPO and HDA capped ZnS from Zn (II) heterocyclic piperidine and tetrahydroquinoline dithiocarbamates as precursors. Both complexes gave close to spherical and elongated particles of ZnS when passivated by HDA at different reaction temperatures and the thermolysis in TOPO produced spherical particles only (Nyamen et al., 2014). Roffey reported phase control during the synthesis of nickel sulphide nanoparticles from decomposition of the iso-butyl derivative dithiocarbamate precursors. It was found that there was temperature-dependence of the phase of the nickel sulphide formed. At low temperatures (150 °C), pure α-NiS was formed. Upon raising the temperature, increasing amounts of β-NiS were produced and at 280 °C pure form was formed (Roffey et al., 2016). High quality close to spherical SnS nanoparticles using single molecular precursor route were reported. HRTEM and XRD analysis revealed the orthorhombic crystal phase. It was also reported that the oriented attachment mechanism could have been the reason for the anisotropic SnS nanoparticle growth formed (Pullabhotla and Mabila, 2016).

1.3 Metal sulphides used: their applications and literature review

Since nanoparticles are not stable, their properties (electrical, optical, chemical, mechanical, magnetic, etc.) can be selectively controlled by engineering the size, morphology, and composition of the particles. These new substances will have improved properties from their parent material. Nanoparticles can make metals stronger and harder, gives ceramics enhanced formability and ductility, enables normally insulating materials to conduct heat or electricity, and make protective coatings transparent. Hence industries can re-engineer many products and design novel product or processes to function at unprecedented levels. Nanoparticles are being used in many fields such as in manufacturing, medicine material and the environment.

1.3.1 Lead sulphide nanoparticles

Lead sulphide with the chemical formula PbS, is an inorganic compound. It is also known as galena, which is the principal ore and important compound of lead. It is one of the earliest materials to be used as a semiconductor as it tends to crystallize in sodium chloride. When heated to decomposition lead sulphide becomes toxic and forms lead and sulphur oxides. The crystal structure most commonly used for PbS is the face-centered cubic galena structure. PbS is an important group IV-VI metal chalcogenide semiconductor. It has direct narrow band gap of 0.41 eV at 300K and a large excitonic Bohr radius of 18 nm (Mousa, 2011b). Lead sulphide absorption band can be tuned to anywhere between near IR to UV (0.4 μ m) covering the entire visible spectrum, while achieving the quantum confinement region (Wang et al., 1987). It can be used in different fields, such as fabrication of solar cells, IR detectors, light emitting diodes, optical communications and tunable IR lasers (Karami et al., 2013). Due to the above properties and its applications being carried out, it has attracted considerable attention in recent years. Different methods such as solvothermal, electrodeposition, chemical methods, microwave irradiation, etc. have been used to synthesise PbS nanoparticles. Moloto and co-workers reported TOPO capped PbS and Cu_xS_y nanoparticles from alkylthiourea lead and copper complexes using a single source precursor method which showed quantum confinement effects with a blue shift in their absorption spectra (Moloto et al., 2005). Yang reported PbS nanobelts (width 50-120 nm and length over 3 μ m) which were self-assembled in a simple reverse micelle solvent system containing the surfactant of polyoxyethylene dodecyl ether (C₁₂E₉) (Yang et al., 2006). A wet chemical route was used by Navaneethan in the synthesis of N-Methylaniline (N-MA) capped lead sulphide (PbS) nanoparticles, the observed morphology was spherical nanoparticles with the particle size around 5 nm (Navaneethan et al., 2009). Mousa reported different sizes of aggregated quantum dots of PbS synthesized using lead oxide as lead source and bis(tri methylsilyl) sulphide as sulphur source (Mousa, 2011a). Wattoo and co-workers reported the preparation of lead sulphide nanoparticles from N, N-dialkyl amine dithiocarbamate using a single source precursor and dual sources methods. The composites were fabricated by stabilizing chemically synthesized semiconductor PbS nanocrystals into lauryl methacrylate and ethyleneglycol dimethacrylate matrix in the presence of tri-n-octylphosphine. It was found that incorporation of the PbS nanoparticles showed the stability and functionality into the tailored polymer matrix and TEM revealed that nanoparticles are

almost cubical in morphology (Wattoo et al., 2012). Nabiyouni and co-workers synthesized PbS nanoparticles at room temperature via a simple chemical reaction where thiophenol was used as the capping agent and sodium sulfide was used as a sulfur source. It was found that electronic absorption spectra as well as particle sizes depend on the used capping agents (Nabiyouni et al., 2012). Borhade did a comparative study on PbS and Co doped PbS nanoparticles and their catalytic activities using hydrothermal methods. XRD revealed cubic structure of PbS nanoparticles with particle size of 31 nm (Borhade and Uphade, 2012). PbS nanowires were prepared by chemical precipitation method. In this method, sodium sulfide and lead acetate concentration, type and concentration of synthesis additive, pH, bath temperature, and ultrasonic wave radiation were effective parameters that can change the morphology and the particle sizes (Karami et al., 2013). Sangeetha reported the synthesis of PbS in aqueous medium at room temperature and it was found that the as-prepared PbS semiconductor nanoparticle was monodisperse and have a very narrow size distributions and narrow band gap than other semiconductor chalcogenide (Sangeetha et al., 2014). The result showed that the obtained nanoparticle is cubic in nature with average grain size of 11 nm (Sangeetha et al., 2014). Sakthivel also studied lead sulphide nanoparticles using hydrothermal methods. The structural and microscopic investigations of the sample showed formation of clustered cubic PbS nanoparticles with cubic crystal structure (Sakthivel et al., 2014).

1.3.2 Nickel sulphide nanoparticles

Transition metal sulfides exhibit interesting electronic, optical, thermoelectric and photoelectric properties (Friemelt et al., 1993, Oviedo-Roa R. et al., 2006, Srivastava and Avasthi, 1992). Nickel sulphide is an important member in the family of transition metal sulfides. These nanoparticles are desirable materials to produce due to many applications they find in alternative energy. Nickel sulphide has much more complicated phase diagram than cobalt sulfides and iron sulfides. Their chemical composition have many crystalline phases such as α -NiS, β -NiS, NiS₂, Ni₃S₂, Ni₃S₄, Ni₇S₆ and Ni₉S₈ (Kullerud and A., 1962). Ni₃S₂ phase has shown potential as a low cost counter electrode material in dye sensitised solar cells (Mulumudi et al., 2011), while the α -NiS phase has been applied as a cathode Material in lithium-ion batteries (Han et al., 2003). It is a p-type semiconductor with a narrow band gap of 0.4 eV. Numerous methods have been used to synthesize NiS nanoparticles. A sonochemical method (Wang et al., 2002) and a micro-emulsion system (Khiew et al., 2004) were used to

synthesize NiS nanoparticles. Zhang and Ghezelbash reported the synthesis urchin-like NiS using solvothermal method (Ghezelbash and Korgel, 2005, Zhang et al., 2005). Hu reported the synthesis of NiS hollow nanospheres via γ -irradiation method (Hu et al., 2003). Ghezelbash reported the solventless thermolysis of a nickel alkylthiolate molecular precursor which produced nanorods and triangular nanoprisms of NiS (Ghezelbash et al., 2004). Ni₃S₄ nanocrystal was synthesised by the thermal decomposition of NiCl₂ and elemental sulphur in oleylamine (Ghezelbash and Korgel, 2005). A template-promoted growth was reported by Morris and co-workers (Barry et al., 2010) for NiS nanoparticles, where NiS nanoparticles were grown on an anodic alumina templates by decomposing nickel xanthate complex in supercritical CO₂ at 450 °C. Furthermore hollow spheres of NiS were synthesized using silica nanospheres as templates (Zhu et al., 2011). In addition another method deploying Na₂SO₄ or Na₂S was used to sulfurize Ni(OH)₂ in a Teflon-lined autoclave at 180 °C for the synthesis of NiS hollow spheres (Wang et al., 2011). Tatsumisago and co-workers (Aso et al., 2011) reported a thermal decomposition method for different stoichiometries of NiS nanocrystals. Thermal decomposition of single-source precursors such as alkyl xanthates (Pradhan et al., 2003) and their pyridine adducts (Alam et al., 2008), mercaptobenzothiazole (Geng et al., 2007), (tetramethylethylenediamine) Ni(SCOC₆H₅) (Tian et al., 2009), 1,1,5,5-tetra-isopropyl-2-thiobiuret (Abdelhady et al., 2012) and polysulfide [Ni(N-methylimidazole)₆]S₈ (Beal et al., 2010) in a hot coordinating solvent formed a mixture of rods and spheres of NiS, ellipsoidal NiS nanoparticles, alpha or beta NiS nanocrystals, and NiS₂ or Ni_{1-x}S nanocrystals, respectively. Wilton-Ely and co-workers (Wilton-Ely et al., 2008) prepared multimetallic assemblies using piperazine-based dithiocarbamate building block and Ni(dppe)Cl₂. These systems have been used to functionalise gold nanoparticles (Knight et al., 2009). Banerjee reported a simple chemical route of preparing pure and copper doped NiS Nanoparticles, the nanoparticles were found to be nanocrystalline with rhombohedral phase and the crystallite size of NiS nanoparticles was found to be 43.09 nm (Banerjee et al., 2013). Chauhan reported the preparation of [Ni(S₂CN (CH₂)₄CHOH) (dppe)]⁺X⁻ as a single-source precursor for the nickel sulfides nanoparticles (Chauhan et al., 2014). Roffey reported the solvothermal decomposition of a nickel dithiocarbamate in primary amine, it was found that there is temperature-dependence of phase of the nickel sulphide formed: At low temperatures (150 °C), pure α -NiS was formed but Upon raising the temperature, increasing amounts of β -NiS were produced and at 280 °C this was formed in pure form (Roffey et al., 2016). To the best of our

knowledge and findings, $[\text{Ni}(\text{S}_2\text{N}_2\text{C}_8\text{H}_5)_2]$ and $[\text{Ni}(\text{S}_2\text{N}_2\text{C}_9\text{H}_7)_2]$ species have never been explored as possible single-source precursor for the nickel sulfides nanoparticles.

1.3.3 Cobalt sulphide nanoparticles

Semiconductor nanocrystals are promising candidates for future electronic and photonic devices. They have unique physical and chemical properties (Zhou et al., 2005). CoS is a semiconductor has a band gap energy equal to 0.90 eV. Cobalt sulphide (CoS) belongs to the family of group II-IV compounds with considerable potential for application in electronic devices (Ramasamy et al., 2010). They have a complex phase diagram and their chemical composition have many phases such as Co_4S_3 , Co_9S_8 , CoS, Co_{1-x}S , Co_3S_4 , Co_2S_3 and CoS_2 (Rao and Pisharody, 1976). They can be used as ultra-high density magnetic recording (Whitney et al., 1993), in solar energy as absorbers (Smith et al., 1980), anodes for Li-ion batteries (Yue et al., 2007), , and catalysts for hydrodesulphurization and dehydrodearomatization (Feng et al., 2008). Cobalt sulphide is also used in selective coatings and solar cells, temperature sensors, optical filters, optical wave guides and IR detectors (Cruz-Vazquez et al., 2000, Deshmukh and Mane, 2011, Donald Okli and Cecilia okoli, 2012, Ezema and Osuji, 2007, Nnabuchi and Chinedu, 2010, Sifuentes et al., 2000, Yu et al., 2002). The properties of cobalt sulphide strongly depend on the particle size, shape, distribution and surface. It is notable that various synthetic routes affected the properties, morphologies and stoichiometric compositions (Khaorapapong and Ogawa, 2011). Literature has shown a lot of reports on the synthesis of cobalt sulfides micro- and nanocrystals with various morphologies, such as Co_9S_8 and CoS_2 nanoparticles (Qian et al., 1999), CoS nanowires (Bao et al., 2008a, Ge and Li, 2003), thin film (Srouji et al., 2005), sea urchinlike Co_9S_8 (Liu, 2005) and Co_3S_4 octahedron (Bao et al., 2008c). Yin and co-workers reported the colloidal synthesis of hollow cobalt sulphide nanocrystals based on the Kirkendall effect (Yin et al., 2006). Chen reported Co_3S_4 nanotubes also based on the Kirkendall effect (Chen et al., 2007). Ramasamy and co-workers reported Co_4S_3 phase in a nanodispersed form using single-molecule precursor-based approach. Parameters such as reaction temperature precursor concentration affected the size and shape of the nanoparticles yielding different phases of cobalt sulphide (Ramasamy et al., 2010). Hierarchical structured Co_{1-x}S microrods have been first fabricated in a high yield by one pot-surfactant-assisted hydrothermal method (Liu et al., 2012). The synthesis of amorphous

CoS nanorods has been made by simple chemical precipitation method (Ariponnammal and Srinivasan, 2013).

1.4 Reaction conditions

During the synthesis of nanoparticles, reaction conditions such as temperature, precursor concentration, capping agents were varied.

1.4.1 Effect of temperature

Temperature is one of the major factors that contribute significantly on size and shape of the nanoparticles. The final morphology of nanoparticles is governed by the preferred growth regime of the reaction which can proceed in either a thermodynamic or a kinetic growth regime (Peng et al., 2000a, Peng and Peng, 2002). Thermodynamically, all nanocrystals will grow toward a shape that has the lowest energy at equilibrium and low monomer concentration, yielding stable, isotropic-shaped nanocrystals (e.g., dots, cubes). In contrast, non-equilibrium kinetic conditions are facilitated by low reaction temperatures and high monomer concentration yielding selective anisotropic structures (e.g., rods, tetrapod's) (Hu et al., 2001, Peng, 2003, Peng et al., 2000b). Sibokoza and co-workers reported the effect of temperature on synthesis of cobalt sulphide nanoparticles using cobalt diethyldithiocarbamate complex. The temperature was varied at 80, 145 and 210 °C. The observed morphology of cobalt sulphide nanoparticles was spherical in shape. It was observed that low temperature produced agglomerated particles. At high temperatures, mono-dispersed particles were observed (Sibokoza et al., 2017).

1.4.2 Effect of additive type

Capping agents have chemical group with an affinity for either cation or the anion. The complexing properties of the coordinating molecules play a significant role under the growth conditions of the semiconductor nanocrystals. The nanocrystal grows inside a shell of capping agents. The final particle size is determined by the growth kinetics. If bonding with the surface atoms of the quantum dot is too weak there will be uncontrolled growth of the semiconductor beyond the quantum size regime but if the bonding is too strong the particle growth will be controlled. To produce quantum dots of the desired size, the growth conditions have to be selected such that the binding of the capping agents is neither too strong nor too weak. Capping

agents are used as improving agents in nanomaterials synthesis to control the mechanism and kinetics of the reaction. They can affect the morphology and particle sizes of the final product (Phuruangrat et al., 2008). The size distribution of the nanoparticles can be controlled by adding capping agents (Lelong et al., 2008). Different surfactants have been employed in the synthesis of nanoparticles. Among the synthesis parameters, the additive type had more effects on morphology of the synthesized PbS samples. In this study, the effects of HDA and TOPO were investigated on the morphology and particle sizes of PbS nanoparticles by varying temperature, and the amounts of the other parameters of synthesis were kept constant

1.4.3 Effect of concentration

The concentration of the precursor plays an important role on both size and shape of the nanoparticles. The concentration of the precursor has a profound effect on the size with high concentration favouring large size (Cheng et al., 2010). The growth process of nanoparticles is directed by the balance between kinetic and thermodynamic control. The concentration of the precursor affects the shape of the nanoparticle. The effect of the concentration on shape is quite complex, but it have been proposed that chemical potential of nanoparticle are related to the formation of nanoparticles with different size and morphology (Sakthivel et al., 2014). The chemical potential of the reaction is mainly determined by monomer concentration at fixed temperature.

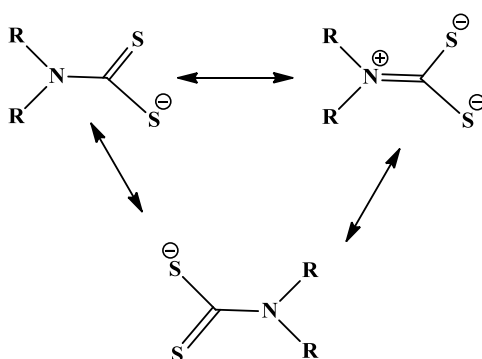
1.4.4 Ostwald ripening

Particle ripening occurs after particle growth. This can either focus or defocus the particle size distribution as there is an exchange of monomer from particle to particle in solution. It is thermodynamically more favourable for small particles to lose monomer and for large particles to gain, growing at the former's expense during Ostwald ripening. This process is driven by the favourable reduction of the percentage of surface particles with hanging bonds, therefore increasing the monomer coordination and reducing particle surface energy. This process leads to the larger particles growing faster than the smaller particles which are decreasing further in diameter, overall defocussing the particle size. Eventually this leads to the total dissolution of the smaller particles, thereby reducing the total number of particles in the system. The process

can be prevented by the use of capping agents, lowering the reaction temperature or by adding more monomer (Kwon and Hyeon, 2011).

1.5 Dithiocarbamates

Carbon disulphide has been proven to be a versatile ligand (Baird and Wilkinson, 1967) with a great tendency to react with various amines resulting in the formation of an important class of compounds known as dithiocarbamates. Dithiocarbamates have attracted more academic interest due to their synthetic flexibility and dual nature of acting as monodentate, bidentate chelating or bridging ligands (Sharma et al., 2012) coordinating through both sulphur atoms and both tetra and hexa-coordinated complexes of many transition metal ions have been isolated (El-Masry et al., 2000, Pawar et al., 2011). These compounds are known to bind strongly to many metal ions through sulphur atoms. They are being applied in chemical processes, such as vulcanization, antimicrobial activity (Pawar et al., 2011) pharmaceutical industry (El-Masry et al., 2000) medicine etc. They have interesting electrochemical and optical properties owing to their redox behaviour and strong coordination ability (Lou et al., 2006). Dithiocarbamates (DTC) ligands readily form chelates with all transition metal ions through its two donor sulphur atoms. Sulphur atoms of dithiocarbamate ligands possess δ -donor and π -back-donation characteristics of the same order of magnitude. These ligands are special because there is an additional π -electron flow from nitrogen to sulphur *via* a planar delocalised π -orbital system, as shown below (Scheme 1).



Scheme 1: Resonance structures of dithiocarbamate ligand.

This effect results in strong electron donation and hereafter a high electron density on the metal leading to its next higher oxidation state (Pandeya et al., 1986).

1.6 Transition metal dithiocarbamates complexes

Dithiocarbamates (DTC) form complexes with all transition metals. Their ability to form complexes with all metals is related to the presence of sulphur atoms and delocalization of a positive charge from a metal to the periphery of the complex. Transition metal dithiocarbamate complexes were first reported in 1900 and since then DTC complexes have been extensively studied. Bhatt and co-workers studied the reactions of mono and bis(cyclopentadienyl) hafnium(IV) chloride with potassium salts of dithiocarbamic acids in 1:1 and 1:2 molar ratios in refluxing tetrahydrofuran. The complexes were monomeric, non-electrolyte in nature and have showed the bidentate behaviour of ligands (Bhatt et al., 2001). Das synthesized (dithiocarbamato) -Ph-benzyl-2-(arylazo) imidazolepalladium (ii) perchlorates and studied their redox reactions. Electrochemical studies revealed azo group reduction (Das and Sinha, 1998).

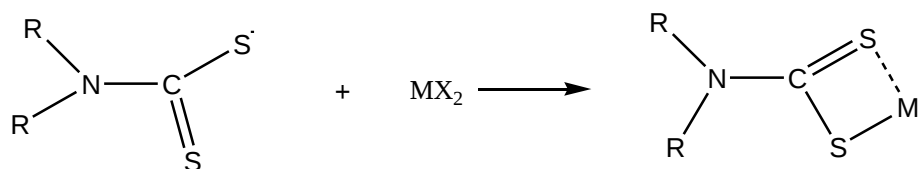
1.7 Synthetic methods

Transition metal dithiocarbamates can be synthesised using different methods. The most used method is the direct addition of the dithiocarbamates salt to the metal salt.

1.7.1 Direct ligand addition

This method has few limitations; several researchers have used this method to prepare a large number of complexes (Karlin, 2005). Most of the transition metal complexes have been prepared using this method. From literature, a number of Pd and Pt DTC complexes have been prepared using this method (Manav et al., 2004, Manav et al., 2006). Different ratios have been used in the slow addition of a solution of the metal salt to a solution of DTC ligand. The desired complex precipitate while stirring the mixture for few hours at room temperature (Jian et al., 2002) or under reflux (Mohamed et al., 2009). Purification of the products is always achieved by recrystallization. This method is not suitable for complexes that are not air stable. Prakasam and co-workers reported the synthesis, NMR spectral and single crystal X-ray structural studies on Ni(II) dithiocarbamates with NiS₂PN, NiS₂PC, NiS₂P₂ chromophores using direct ligand addition method (Prakasam et al., 2007). Tarique extensively studied the first series transition metals with different nitrogen and sulphur containing ligands using this method (Tarique, 2011, Tarique, 2012, Tarique, 2015, Tarique and Aslam, 2008c, Tarique and Aslam, 2008b, Tarique

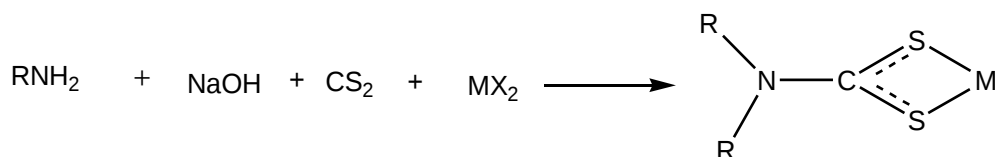
and Aslam, 2008a, Tarique and Aslam, 2009, Tarique and Aslam, 2010). Zedan successfully studied binuclear Complexes of Co(II), Ni(II), Cu(II) and Zn(II) With Mixed Ligand triethylenetetraamine dithiocarbamate & glycine using this method (Zedan, 2010). Onwudiwe reported the synthesis, characterization and thermal studies of Zn(II), Cd(II) and Hg(II) Complexes of N-Methyl-N-Phenyldithiocarbamate (Onwudiwe and Ajibade, 2011). Synthesis, characterization and biological evaluation of novel dithiocarbamate metal complexes was reported using this method (Jayaraju et al., 2012). Venugopal also used this method in the synthesis of novel hetero cyclic dithiocarbamate metal complexes and study of their biological activity (Venugopal et al., 2015). Onwudiwe and co-workers also carried out the syntheses, characterization, and antimicrobial properties of nickel (II) dithiocarbamate complexes containing NiS₄ and NiS₂P moieties (Onwudiwe et al., 2016).



Scheme 2: Preparation of metal complexes by direct ligand addition.

1.7.2 One-pot synthesis of dithiocarbamates metal complexes.

In this method, the ligand and the complex are reacted in a single step. Sodium hydroxide, the amine and carbon disulphide are dissolved in the suitable solvents and are allowed to react for a certain time followed by the addition of aqueous solution of the metal salt (Arul et al., 2007). The intermediate step in this reaction is carried out at room temperature or at lower temperatures. The mixture is vigorously stirred and the metal complex precipitates while stirring at room temperature or upon refluxing for several hours (Siddiqi et al., 2006b).

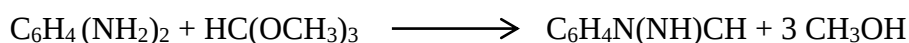


Equation 1: One-pot synthesis of DTC metal complexes

Desired complexes can still be produced by reacting a ketone, metal salt and amine. The addition of hydrazine hydrate to the above reactants has been shown by Nami and co-workers to results in metal complexes (Nami and Siddiqi, 2004). A convenient and efficient method has been developed by Chaturvedi and co-workers which involves coupling of amines with alcohols via a Mitsunobi Zwitterion (Chaturvedi and Ray, 2006). High yielding DTC has been developed from the reaction of amines, acetylacetone and carbon disulphide using this method(Siddiqi et al., 2006b). Azizi and co-workers also used this method in synthesis of dithiocarbamates accelerated in water (Azizi et al., 2006b). He also studied catalyst-free one-pot synthesis of dithiocarbamates under solvent-free conditions(Azizi et al., 2006a). Sha reported one-pot synthesis of S-alkyl dithiocarbamates via the reaction of N-tosylhydrazones, carbon disulfide and amines(Shaa and Wei, 2013).

1.7.2.1 Benzimidazole: Structure, properties and uses

Benzimidazole is a heterocyclic aromatic organic compound consisting of the fusion of benzene and imidazole. It is a white solid with a chemical formula of $C_7H_6N_2$ that dissolves in methanol. N-ribosyl-dimethylbenzimidazole is the most noticeable benzimidazole compound in nature, which serves as an axial ligand for cobalt in vitamin B12 (Barker et al., 1960). It has fungicidal properties. It binds to the fungal microtubules, the spindle microtubules and it blocks nuclear division and stops hyphal growth. The nitrogen, hydrogen and carbon atoms are usually used as ligands for transition metal complexes. It can be prepared by deprotonating an N, N'-disubstituted benzimidazolium salt at the 2-position with a base (Huynh et al., 2005). Benzimidazole is commercially available. Nevertheless its synthesis involves condensation of o-phenylenediamine with formic acid (Wagner and Millett, 1943).

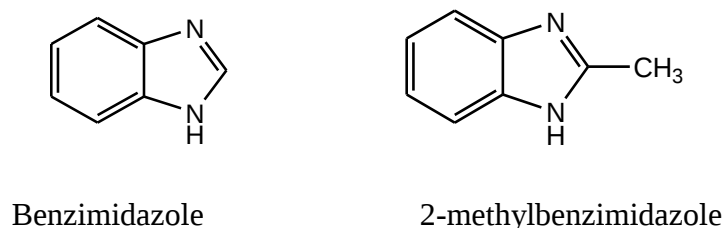


Equation 2: Preparation of benzimidazole

By changing the carboxylic acid used, this method is generally able to yield 2-substituted benzimidazole (Wagner and Millett, 1943). It is an extension of the well-elaborated imidazole system. Imidazole is fused into many important biological molecules like benzimidazole. Imidazole is a 5-membered ring organic compound also known as 1, 3-diazole with the formula

(CH)₂N(NH)CH. It has two equivalent tautomeric nitrogen atoms because the proton can be located on either of the two nitrogen atoms. It is a highly polar compound which is proved by a calculated dipole of 3.61D. It is classified as aromatic due to the presence of a sextet of π -electrons, consisting of a pair of electrons from the protonated nitrogen atom and one from each of the remaining four atoms of the ring. Imidazole is amphoteric meaning it can function as both an acid and as a base. An alkyl group attached to imidazole ring was used to check how it will affect the coordination of the complexes and the shape and size of the nanoparticles.

Due to the increasing interest in the study of sulphur and nitrogen containing ligands, this communication describes the preparation and characterization of complexes of Ni, Co and Pb transition metals with benzimidazole and 2-methylbenzimidazolidithiocarbamate (Scheme 2) with the aim to observe the coordination behaviour of the dithiocarbamate moiety using one-pot synthesis method.



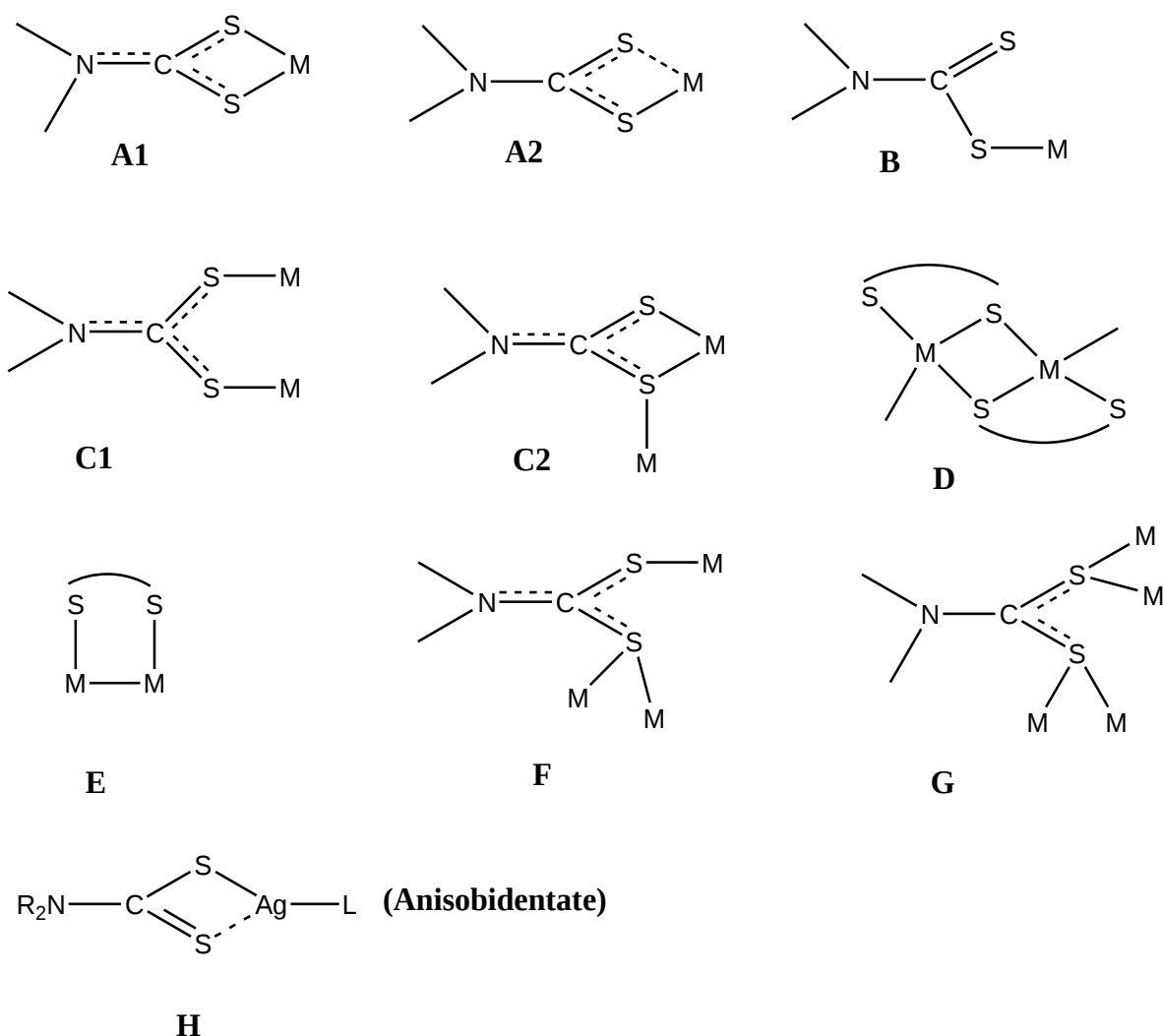
Scheme 3: Amine structures

1.7.3 Other methods

Transition metal dithiocarbamates can also be prepared by oxidative-addition of thiurams disulphides to metal centres. DTC moiety can be incorporated in this method by reductive scission of the S-S bond of the thiuram disulphide (Victoriano, 2000a). Victoriano reported the scission of S-C bond of monosulphides to DTCs or dithiocarbamate-thiocarboxamido complexes (Victoriano, 2000b). Addition of carbon disulphide to metal amides normally yields metal DTCs. Transition metals that can form stable amide complexes such as Ti, Zr and Hf (Karlin, 2005) are favoured by this method. Horgarth reviewed the method where the S-C bond of organic isothiocynsnste has been inserted to metal-bound thiolates (Karlin, 2005). Transition metal DTC complexes have been formed through the reaction of primary or secondary amines with metal bound xanthates (Karlin, 2005).

1.8 Binding modes

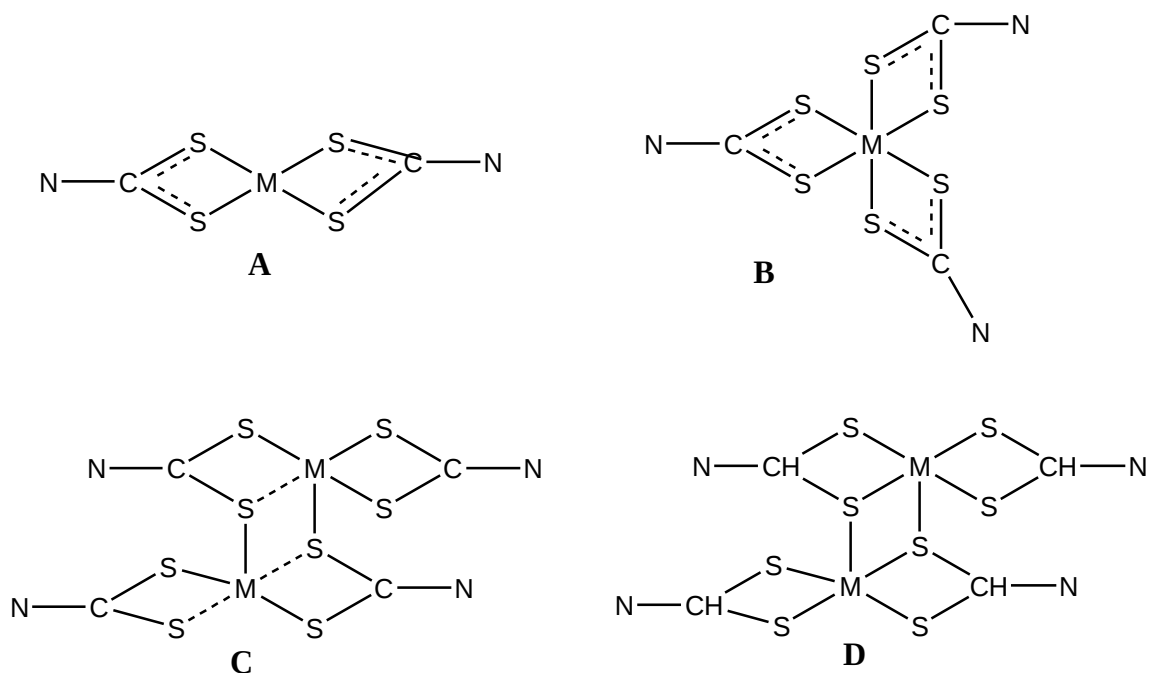
The ligation forms of DTC are presented in Scheme 3. One ligand can accommodate one to four metal atoms in different ways (Cotton et al., 1996). The DTC moiety can form complexes where both S atoms are coordinated to the same metal atom forming a four coordinate ring chelate. The most common form of bonding is the simple chelating bidentate binding mode Scheme 3(A) and is normal for all transition metals in all accessible oxidation states (Cotton et al., 1996, Karlin, 2005). The bidentate coordination can be symmetrical Scheme 3(A1) and unsymmetrical Scheme 3(A2). The unsymmetrical bidentate coordination is known as the anisobidentate (Karlin, 2005). The DTC ligand can also act as a monodentate ligand Scheme 3(B) (Cotton et al., 1996, Yilmaz et al., 2003). This binding mode is formed when there is no room for bidentate coordination (Karlin, 2005). In a solution they can be an interconversion between the bidentate and the monodentate. After the interconversion the monodentate is highly asymmetric and is referred as the anisobidentate mode Scheme 3(H) (Karlin, 2005). It is difficult to differentiate between the anisobidentate and the monodentate binding modes. Furthermore DTCs can accommodate more than one metal atom acting as a bridging ligand. A number of ways have been reported where the dithiocarbamates ligand can bridge two metal centres Scheme 3(C-E) (Karlin, 2005, Nami and Siddiqi, 2004). The sulphur atoms can bind to different metals or to each metal centre Scheme 3(C2) and η^1 - η^1 -manner Scheme 3(C1). One sulphur atom can bridge two metal centres such that the three M-S interactions are equivalent Scheme 3(D). Moreover both sulphur atoms can bridge two metal centres in different ways Scheme 3(E, F) (Karlin, 2005). Three (F) to four (G) metals can also be accommodated by the ligand even though both binding modes are rare and limited to the late transition metals.



Scheme 4: Dithiocarbamates coordination modes

1.9 Structural features of dithiocarbamates

DTC complexes can assume four structural geometries (Scheme 4) when no other coordinating ligands are present; namely the square planar coordination geometry (A), octahedral coordination geometry (B), four coordinate dimer (C) and the five coordinate dimer (D). The most common structural arrangements are the square planar and octahedral geometries. Bis (dithiocarbamate) complexes such as Ni(II) and Pt(II) exhibit the square planar structures (Manav et al., 2004). The dimeric structures (C, D) are prevalent in the Cu and Zn complexes. Complexes of general structure $M(DTC)_2X_2$; where $X = Cl, Br$ and I form octahedral geometry (Plyusnin et al., 1997).



Scheme 5: Structural arrangements of dithiocarbamates complexes

1.10 Problem statement

A lot of emphasis has been put on the production of nanoparticles of the highest quality, controlling the size distribution and shape of semiconductor has been very challenging to chemists, engineers and nanotechnologists. One of the difficulties in the preparation of nanoparticles is to develop suitable methods for achieving specific morphologies by controlling the growth of the nanoparticles. In this research a single-source molecular precursor route will be used since it avoids problems encountered by employing the organometallic route, the metal chalcogenide bond is already in place in this route and also avoids the use of volatile, sometimes toxic precursors.

It was also established the type of the ligands also affects the morphology of the nanoparticles so this work interest also lies in studying the behaviour and binding of the substituted benzimidazole molecules to metal atoms such as Pb, Co and Ni. The binding of substituted dithiocarbamates ligand through the S atom of the CS group suggests that these compounds could be used as precursors in the preparation of the nanoparticles. Dithiocarbamates complexes are interesting hybrid complexes, with both hard nitrogen and soft sulphur donor atoms and are able to coordinate to a wide range of metal centres.

1.11 Purpose of the study

Generally metal chalcogenide nanoparticles are prepared by using a conventional route in which metal salt and sources of chalcogens such as thiourea, thioacetamide, sodium sulphide, thiosulfate, and others are dissolved in solution and stirred with factors such as concentration, time and temperature being controlled. This route provides particles with generally larger sizes closer to 20 nm whereas the alternative single-source precursor route produces particles with smaller sizes but with the general problem of polydispersity in size and shape. An effort was made by general synthesis and design of the ligand based on benzimidazole. It was reacted with metal to make precursor complexes to generate desirably particles which are generally smaller in size and shape.

1.12 Aim and objectives of the study

(a) The aim of the study was to synthesize metal sulphide (PbS, NiS, CoS) nanoparticles by using dithiocarbamates as complexes.

(b) Objectives

- To prepare and characterize metal complexes using FTIR spectroscopy, elemental analysis (EL), Thermogravimetric analysis (TGA).
- To study the effect of concentration of precursors (0.3, 0.35 and 0.4 g) on the size and shape of nanoparticles.
- To synthesize and characterize the metal sulphide (CoS, NiS and PbS) nanoparticles from dithiocarbamate metal complexes using TEM, XRD, PL, UV-vis spectroscopy.
- To study the effect of temperature (140, 160 and 180 °C) on size and shape of the nanoparticles.
- To study the effect of the capping agents (HDA and TOPO) on the size and shape of the nanoparticles.

Chapter 2

Research methodology

Experimental section

2.1. Materials

Lead acetate trihydrate (99.5 %), cobalt chloride hexahydrate (98 %), trioctylphosphine (97 %), hexadecylamine (90 %), Benzimidazole (98 %), 2-methylbenzimidazole (98 %), carbon disulphide (99 %), sodium hydroxide (99.86 %), were purchased from Sigma Aldrich and used without any purification. Solvents such as methanol (99.5 %) of analytical grade were also purchased from Sigma Aldrich. Distilled water was used as a solvent as well.

2.2 Experimental procedures

(a) Preparation of lead benzimidazole dithiocarbamate complex (I)

The ligands and complexes were synthesized according to a method previously reported by (Siddiqi et al., 2006a) and was modified as follows.

Sodium hydroxide (0.78 g, 0.02 mol) was dissolved in 40 ml of distilled water and added to benzimidazole (2.36 g, 0.02 mol); the mixture was cooled under stirring in an ice bath for an hour. Carbon disulphide (1.52 ml, 0.02 mol) was added dropwise to the suspended mixture and it was stirred for overnight at 25 °C. Lead (II) acetate (3.79 g, 0.01mol) was dissolved in 40 ml of distilled water and it was added drop-wise to the corresponding solution of the dithiocarbamate ligand. The mixture was refluxed for 4 hours at 60 °C in a water bath. The reaction mixture was left for three days to complete under the fume hood. The precipitate formed was filtered, washed with excess distilled water and dried with excess methanol. The black colour was observed for benzimidazole-dithiocarbamates complex. Percentage yield: 60.36 %. CHNS analysis: Calculated: C, 32.37; H, 1.7; N, 9.44; S, 21.6. Found: C, 35.77; H, 2.38; N, 8.80; S, 2.25%.

(b) Preparation of lead 2-methylbenzimidazole dithiocarbamate complex (II)

The complex was synthesised following the same method as with 2.2(a), with the exception that 2-methylbenzimidazole (2.64 g, 0.02 mol) was used. Percentage yield: 45.36 %.CHNS analysis: Calculated: C, 34.77; H, 2.27; N, 9.01; S, 20.63. Found: C, 35.36; H, 2.57; N, 8.34; S, 8.91%.

(c) Preparation of nickel benzimidazole dithiocarbamate complex (III)

Sodium hydroxide (0.78 g, 0.02 mol) was dissolved in 40 ml of distilled water and added to benzimidazole (2.36 g, 0.02 mol); the mixture was cooled under stirring in an ice bath for an hour. Carbon disulphide (1.52 ml, 0.02mol) was added dropwise to the suspended mixture and it was stirred for overnight at 25 °C. Nickel (II) chloride (2.37 g, 0.01 mol) was dissolved in 40 ml of distilled water and it was added drop-wise to the corresponding solution of the dithiocarbamate ligand. The mixture was refluxed for 4 hours at 60 °C in a water bath. The reaction mixture was left for three days to complete under the fume hood. The precipitate formed was filtered, washed with excess distilled water and dried with excess methanol. The green-black colour was observed for benzimidazole dithiocarbamates complex. Percentage yield: 52.63 %.CHNS analysis: Calculated: C, 43.16; H, 2.26; N, 12.58; S, 28.81. Found: C, 46.45; H, 3.46; N, 11.88; S, 7.17%.

(d) Preparation of nickel 2-methylbenzimidazole dithiocarbamate complex (IV)

The complex was synthesised following the same method as with 2.2(c), with the exception that 2-methylbenzimidazole (2.64 g, 0.02 mol) was used. The green- black colour was observed for 2-methylbenzimidazole dithiocarbamates complex. Percentage yield: 35.88 %.CHNS analysis: Calculated: C, 45.68; H, 2.98; N, 11.84; S, 27.1. Found: C, 22.34; H, 2.49; N, 2.25; S, 9.06%

(e) Preparation of cobalt benzimidazole dithiocarbamate complex (V)

Sodium hydroxide (0.78 g, 0.02 mol) was dissolved in 40 ml of distilled water and added to benzimidazole (2.36 g, 0.02 mol), the mixture was cooled under stirring in an ice bath. Carbon disulphide (1.52 ml, 0.02mol) was added drop-wise to the suspended mixture and it was stirred for overnight at 25 °C. Nickel (II) chloride (2.37 g, 0.01 mol) was dissolved in 40 ml of distilled

water and it was added dropwise to the corresponding solution of the dithiocarbamate ligand. The mixture was refluxed for 4 hours at 60 °C in a water bath. The reaction mixture was left for three days to complete under the fumehood. The precipitate formed was filtered, washed with excess distilled water and dried with excess methanol. The black colour was observed for benzimidazole dithiocarbamates complex. Percentage yield: 42.28 %.CHNS analysis: Calculated: C, 43.14; H, 2.26; N, 12.58; S, 28.79. Found: C, 19.56; H, 2.62; N, 4.33; S, 1.99%.

(f) Preparation of cobalt benzimidazole dithiocarbamate complex (VI)

The complex was synthesised following the same method as with 2.2(e), with the exception that 2-methylbenzimidazole (2.64 g, 0.02 mol) was used. The blue-black colour was observed for 2-methylbenzimidazole dithiocarbamates complex. Percentage yield: 47.31 %.CHNS analysis: Calculated: C, 45.66; H, 2.98; N, 11.83; S, 27.09. Found: C, 46.71; H, 3.12; N, 10.88; S, 11.94%.

2.3 Synthesis of nanoparticles

(a) Synthesis of lead sulphide nanoparticles using complex I and II

Lead (II) sulphide nanoparticles were synthesized at different reaction temperatures and different capping agents. The complex (0.3 g) was dissolved in 5 ml of tri-octylphosphine (TOP). The solution was injected into 6.0 g of hot hexadecylamine (HDA) and (TOPO) in a three-necked flask at different temperatures (140 °C, 160 °C and °C 180 °C). The reaction was allowed to stabilize at the desired temperature for an hour. After an hour the reaction was allowed to cool to 70 °C then excess methanol was added flocculate the particles. The black precipitate or nanoparticles formed was separated by centrifugation and washed three times with methanol.

(b) Synthesis of nickel sulphide nanoparticles using complex III and IV

Nickel nanoparticles were synthesized at different reaction temperatures and different precursor concentrations. The complex (0.3, 0.35 and 0.4 g) was dissolved in 5 ml of tri-octylphosphine (TOP). The solution was injected into 6 g of hot hexadecylamine (HDA) in a three-necked flask at different temperatures (140 °C, 160 °C and °C 180 °C). The reaction was allowed to stabilize at the desired temperature for an hour. After an hour the reaction was

allowed to cool to 70 °C then excess methanol was added flocculate the particles. The black precipitate or nanoparticles formed was separated by centrifugation and washed three times with methanol.

(c) Synthesis of cobalt sulphide nanoparticles using complex V and VI

Cobalt sulphide nanoparticles were synthesized at different reaction temperatures and different capping agents. The complex (0.3 g) was dissolved in 5 ml of tri-octylphosphine (TOP). The solution was injected into 6 g of hot hexadecylamine (HDA) in a three-necked flask at different temperatures (140 °C, 160 °C and °C 180 °C). The reaction was allowed to stabilize at the desired temperature for an hour. After an hour the reaction was allowed to cool to 70 °C then excess methanol was added flocculate the particles. The dark purple precipitate or nanoparticles formed was separated by centrifugation and washed three times with methanol.

2.4 Instrumentation

(a) FT-IR spectroscopy

FTIR spectroscopy was used to study the functional groups in order to determine the molecular structure. Infrared spectra were recorded on FT-IR Perkin Elmer 400 spectrometer. Spectra were collected over the range from 650 to 4000 cm^{-1} .

(b) Microanalysis

Elemental analysis was used to check the percentage composition of C-H-N-S. The C, H, N, S elemental analysis was carried out with Leco-CHNS 932 analyzer. Roughly 2.0 mg of sample was introduced into Ag capsule and was placed in a furnace, which was maintained at 800 °C. The products of combustion in the CHNS analysis (CO_2 , H_2O and SO_x gases) were carried through the system by the He carrier. Adjustments for blank, calibration and weights were applied to the final integrated signal and the results were displayed as weight percentage of carbon, hydrogen, nitrogen and sulfur.

(c) Thermogravimetric analysis

Thermogravimetric analysis (TGA) records weight loss as a function of temperature. Thermogravimetric analysis was carried out using Perkin Elmer Pyris 6 manager TGA under

an inert atmosphere of dry nitrogen, and at a heating rate of $20\text{ }^{\circ}\text{C}.\text{min}^{-1}$. The sample preparation for thermogravimetric analysis was done by weighing 13 mg of the complexes. These complexes were decomposed at temperature range of 30 to $800\text{ }^{\circ}\text{C}$.

(d) Optical characterization

UV/Vis and PL spectroscopy were used to determine the optical properties. Absorption spectra of the particles were measured using a Perkin Elmer Lambda 20 UV-VIS Spectrophotometer. The samples were placed in quartz cuvettes (1-cm path length) with toluene as the solvent. Emission spectra of the particles were recorded on a Perkin Elmer LS 45 PL spectrometer with a xenon lamp at room temperature. The samples were placed in glass cuvettes (1 cm) with toluene as solvent.

(e) Transmission Electron microscopy

TEM was used to determine the morphology of the particles. Analyses were done on a LEO JEM 912 electron microscope with an acceleration voltage of 120 KV and a tungsten wire filament. The samples were prepared by placing a drop of dilute solution of sample in toluene on to a copper grid. The sample was allowed to dry completely at room temperature.

(f) X-ray diffraction analysis

XRD was used to reveal the crystalline nature of the nanoparticles. X-ray diffraction (XRD) patterns on powdered samples were carried out in the 2θ on a D8 diffractometer. Samples were placed in silicon zero background sample holder. Measurements were taken using a glancing angle of incidence detector at an angle of 2° using CuK α 1 source, for 2θ values over $20^{\circ} - 90^{\circ}$ in steps of 0.05° with a scan speed of $0.01^{\circ}2\theta.\text{s}^{-1}$.

RESULTS AND DISCUSSION

Chapter 3

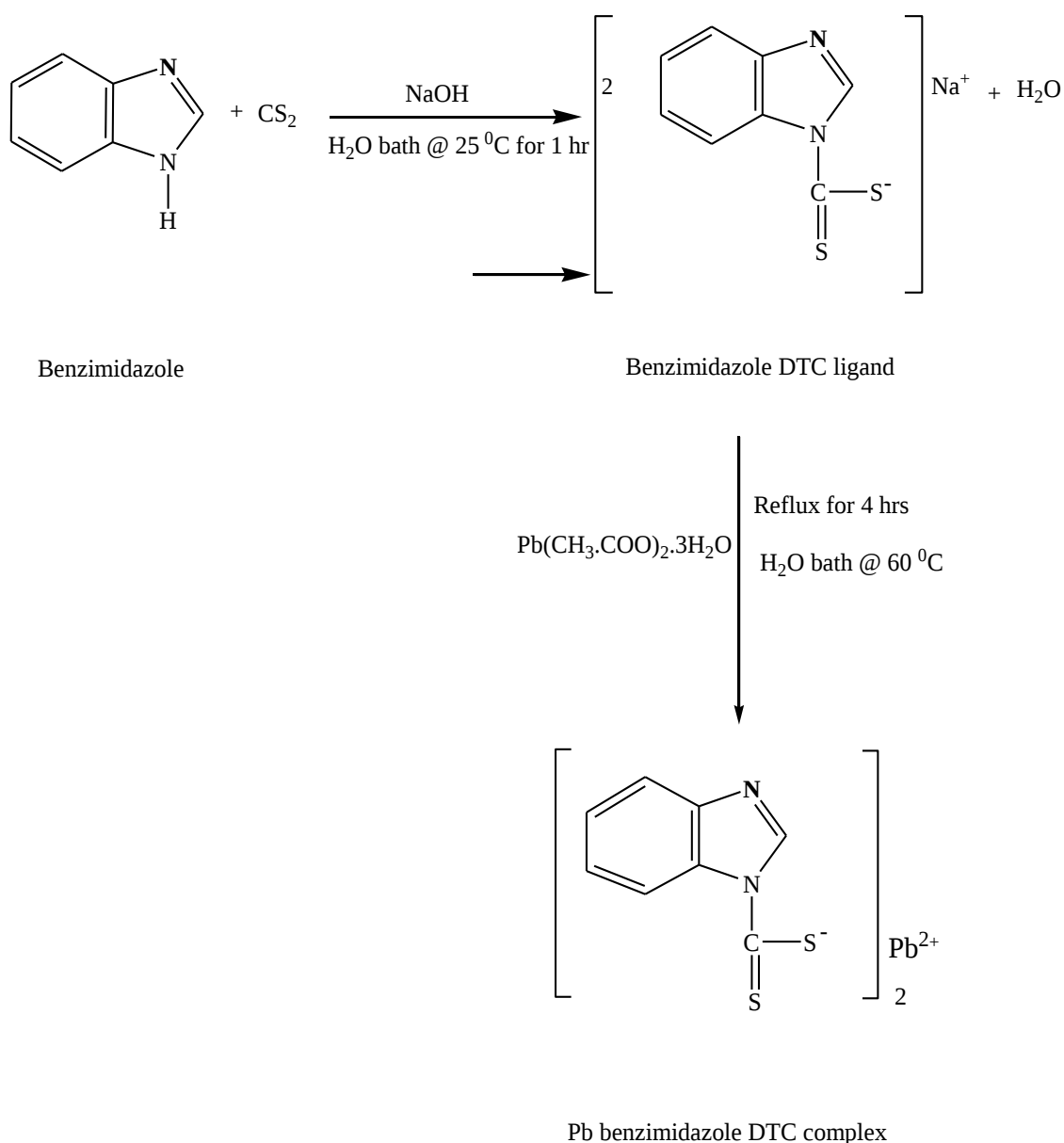
Characterization of benzimidazoledithiocarbamate and 2-methyldithiocarbamate complexes of lead, nickel and cobalt

3.1 Background of the specific ligands prepared and their complexes

The ligands and the complexes were prepared separately before one-pot synthesis method was used. Benzimidazole was reacted with carbon disulphide and sodium hydroxide to form the ligand. Then it was washed, dried, dissolved in methanol and then added to the metal chlorides to form the complexes. Different reaction temperatures were used in the preparation of the ligand which was 0, 25, 30, 60 and 70 °C. Sodium hydroxide or potassium hydroxide was reacted with carbon disulfide and benzimidazole in a 1:1 mole ratio under different reaction times ranging from 1 to 3 days. The prepared ligand was recrystallized with dichloromethane-methanol binary solvent (50:50 – v: v) and kept in an ice-cold environment (0 °C). FTIR spectroscopy and elemental analysis of the ligands prepared at higher temperatures (30, 60 and 70 °C) showed characteristic peaks of benzimidazole (NH vibration band), which made the reaction unsuccessful. The ligands prepared at low temperatures from 0 and 25 °C shown expected IR bands immediately after recrystallization before drying and the complex was prepared in the ratio of 2:1 at lower temperatures. FTIR spectra of the complexes showed that most of the functional groups have shifted to higher frequencies but sulfur atom was absent. Elemental analysis also gave evidence of no sulfur found in the resulting products and in some scenarios percentages were found to either higher or lower than the expected. Therefore it was observed that the ligand forms in the preparation but after washing and drying it reverts back to benzimidazole. The ligands were not stable to moisture and heat. The products were kept under vacuum and at low temperature (0 °C). Even under these conditions of preventing higher temperatures and atmosphere free of oxygen the product reverts back to benzimidazole or 2-methylbenzimidazole. The approach of using the starting materials based on benzimidazole

and its alkyl derivative was changed to a one pot synthesis of the ligand in situ formation followed by the introducing the metal salt.

From elemental analysis, sulfur was present but in lower percentages in all complexes. The possible reason could be due to the volatility of carbon disulphide, which means a lot of it evaporated before it was added or in the addition process leading to unreliable values. The two complexes, I and III showed values that appear dimeric as confirmed by both elemental analysis and FTIR spectroscopy. The FTIR spectra exhibited the doublet C=S band at 1058 and 1040 cm^{-1} region. For complex II and VI, the calculated percentages were within the limits and conform to the molecular structure formulated for the products. Complex IV and V showed that the leaving groups such as the chlorides and hydroxides are still present in the complexes as impurities as evident from elemental Analysis calculations. These complexes showed that oxygen was also present as an impurity and this was also confirmed by FTIR spectroscopy which showed C=O as an impurity from the preparation of benzimidazole. From the found percentages, these complexes also showed that there were some of the unreacted metals (lead, nickel and cobalt) and this was confirmed by TGA and XRD. The TGA curves showed a mixture of metal and metal sulphides after decomposing in all metals from complex I, II, III and IV except for cobalt from Complex VI which decomposed to form only metal sulphide and this was confirmed by final residue calculations. XRD displayed the presence of nickel and lead peaks when different conditions were varied. XRD for cobalt and nickel nanoparticles depicted some impurities of C_7OS_8 . This indicates that carbon dioxide reacted with benzimidazole to give side reactions of sulphur rich organic molecules as impurities picked up by XRD and this made it difficult to correlate the elemental analysis data obtained with those calculated. These complexes were not stable to moisture and heat. The complexes were amorphous powder, soluble in tri-octylphosphine (TOP) only.



Scheme 6: Targeted complex reaction equation of lead benzimidazole dithiocarbamate

3.2 Spectroscopic and thermogravimetric analysis

FTIR spectroscopy was used to determine the functional groups and formation of any new bonds in the complexes prepared. Fig. 2 and 3 shows FTIR spectra of benzimidazole and 2-methylbenzimidazole derived metal complexes I-VI. Dithiocarbamates ligands are capable of forming bonds with the metal through sulphur atom. They are known to display absorption bands in the 800 - 1550 cm^{-1} region. The significant IR bands are shown in Table 1 These complexes exhibited bands at 1200 - 1080, 1080 - 1040, 1474 - 1412 and 3260-3382 cm^{-1} which were due to the contribution of $\nu(\text{C-N})$, $\nu(\text{C=S})$ weak bands, $\nu(\text{C=N})$ strong bands and $\nu(\text{OH})$

vibration respectively. These complexes act as mono- or bi-dentate. When they act as a bi-dentate, the $\nu(\text{C}=\text{S})$ bands are displayed as singlet. But, for a monodentate behaviour $\nu(\text{C}=\text{S})$ bands are displayed as a doublet. The absence of $\nu(\text{N}-\text{H})$ absorption bands at 3116 and 1624 cm^{-1} and the presence of $\nu(\text{C}-\text{N})$, $\nu(\text{C}=\text{S})$ in the complexes confirmed that there was a reaction between the ligands and the metals. The presence of $\nu(\text{OH})$ absorption bands in some of the complexes indicates the presence of water molecules present in the compounds which is confirmed later by TGA. It was observed that all the significant bands were present but they were some impurities of $\text{C}=\text{O}$ at the frequency of 1710 cm^{-1} for complex I and V which is also an impurity from benzimidazole. The impurity as evident from FTIR of unreacted benzimidazole conforms to the percentage of elemental analysis of the same complexes that shows these impurities. This is such that the percentages of complex I changed drifting away from the calculated ones with the increase in C and increase in H.

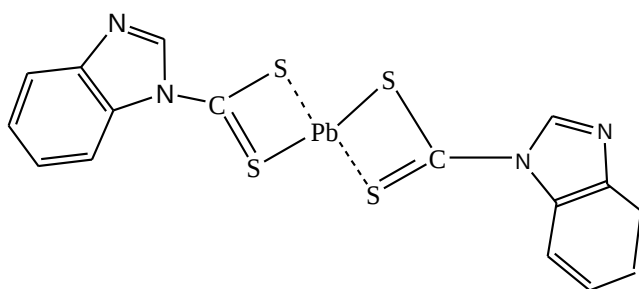


Figure 1: Expected complex of lead benzimidazole dithiocarbamate complex

Table 1: FTIR spectral data for complexes I to VI

Assignment/s	Frequencies (cm^{-1})					
	I	II	III	IV	V	VI
C=N Stretching	1443	1451	1450	1452	1458	1455
C=S Stretching	1058	1080	1040	1080	1043	1078
C-N (aliphatic), Stretching	1100	1152	1100	1174	1088	1175
O-H, Stretching	3382	-	3310	-	-	3260
NCSS bending mode	-	-	1505	-	-	-

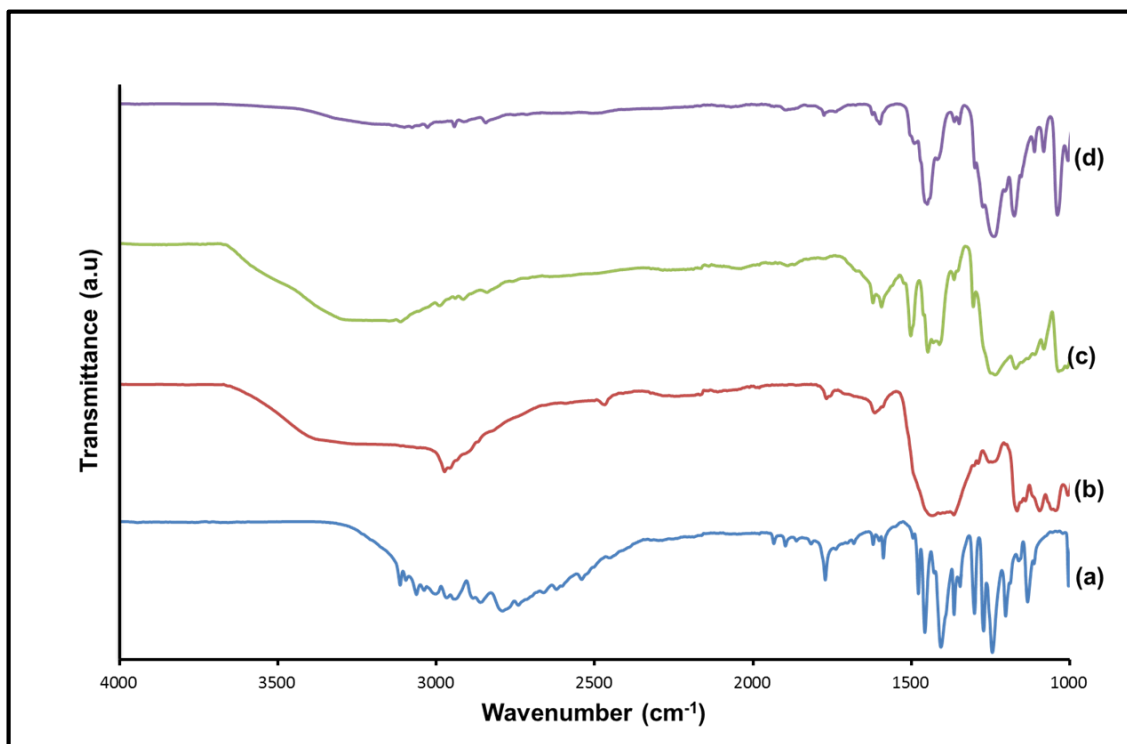


Figure 2: IR spectra for (a) benzimidazole and its complexes I(b), III(c), and V(d)

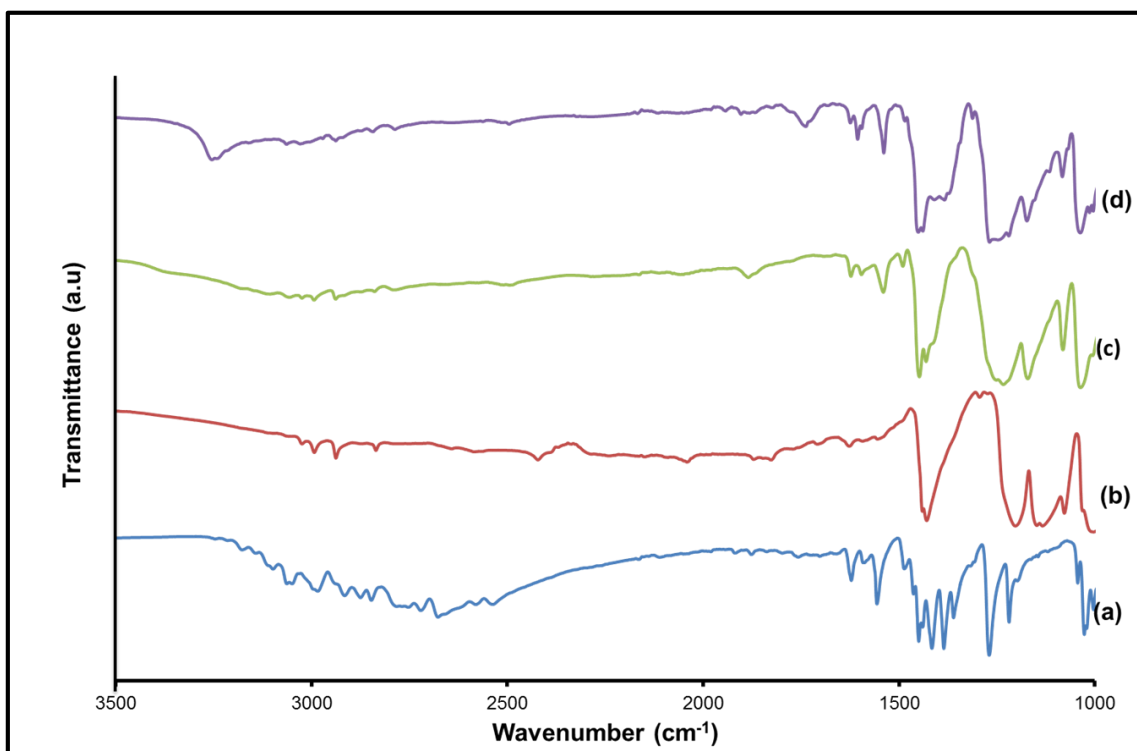


Figure 3: IR spectra for (a) 2-methylbenzimidazole and its complexes II(b), IV(c), and VI(d)

Thermal decomposition of the complexes often leads to the confirmation of the significant bonding between the metal centre and sulphide from the dithiocarbamate ligand formation. Figure 4(a-f) shows TGA spectra of complex I-VI respectively. Complex I (Fig. 4(a)) displayed that up to 112 °C, there was 3% loss in weight and it was due to removal of water molecules. From 112 °C to 265 °C the decomposition was due to benzimidazole dithiocarbamate ligands. These spectrum shows that there was a mixture of PbS₂ and Pb nanoparticles within 255 °C-800 °C region and this was confirmed by XRD which showed the mixture of Pb and PbS nanoparticles at low temperature. The PbS₂ nanoparticles decomposed above 800 °C and displayed a large loss of weight. Complex II (Fig. 4(b)) displayed three decomposition steps. The first decomposition step was due to methyl groups and evaporation of benzene groups from 90-137 °C by 17%. The second decomposition step was due to imidazole molecules from 137-217 °C by 7%. These spectrum shows that PbS₂ nanoparticles were stable within 235-800 °C region. The PbS₂ nanoparticles decomposed above 800 °C. Complex III indicated two-step decomposition of nickel dithiocarbamate complex. The decomposition trend of nickel dithiocarbamate complex III displayed the first decomposition temperature from 30-135 °C which was due to evaporation of methanol and water; the second decomposition step was due to the loss of benzimidazole molecules from 135-456 °C (Fig. 4(c)). The third decomposition step was due to the sulphides present in the complex from 541-757 °C.

The observed final residue was 39.00 %, which is comparable with theoretical of 40.77 % nickel sulphide (Ni₃S₄). The observed final residue had a mixture of nickel sulphide and nickel as a metal and this was confirmed by XRD which showed the presence of nickel as a metal. Complex IV (Fig. 4(d)) indicated two-step decomposition of nickel dithiocarbamate complex. The decomposition rate was faster compared to the one of complex III (Fig. 4(c)), because of weak Van der Waal's forces between the substituted methyl group and benzimidazole. The decomposition trend of nickel dithiocarbamate complex displayed the first decomposition temperature from 66-135 °C which was due to the methyl group present in the complex, methanol and water molecules present in the complex; the second decomposition step was due to the loss of benzimidazole molecules and sodium chloride (impurity) from 137 °C to 374 °C and this was confirmed by elemental analysis which showed less abundant percentages because of impurities found in the complex. The final residue showed a mixture of nickel sulphide and nickel as a metal and this was also confirmed by XRD which showed the presence of the metal. The observed final residue was 33.00 %, which is comparable with theoretical of 36.14 %

nickel sulphide (Ni_3S_2). Figure 4(e)) shows the TGA curve which indicates the three-step decomposition of cobalt dithiocarbamate complex V. The decomposition trend of cobalt dithiocarbamate complex displayed the first decomposition temperature from 90-175 °C which is due to evaporation of water and some part of the complex; the second decomposition step was due to the loss of benzimidazole and sodium chlorides in solution from 259-576 °C; and the last decomposition step was due to loss of sulphides from 636 °C-825 °C. The observed final residue was 39.00 %, which is comparable with theoretical of 43.10 % cobalt sulphide (Co_3S_2). Complex VI (Fig. 4(f)) Indicated two-step decomposition of cobalt dithiocarbamate complex. The decomposition trend of cobalt dithiocarbamate complex displayed the first decomposition temperature from 87 °C-168 °C which is due to evaporation of water and methyl groups present in the complex; the second decomposition step was due to the loss of benzimidazole dithiocarbamate ligand from 270 °C to 423 °C; the observed final residue was 28.00 %, which is comparable with theoretical of 22.05 % cobalt sulphide (CoS_2). It was observed that benzimidazole dithiocarbamate complexes were the stable ones in all the three metals since they decompose at high temperatures.

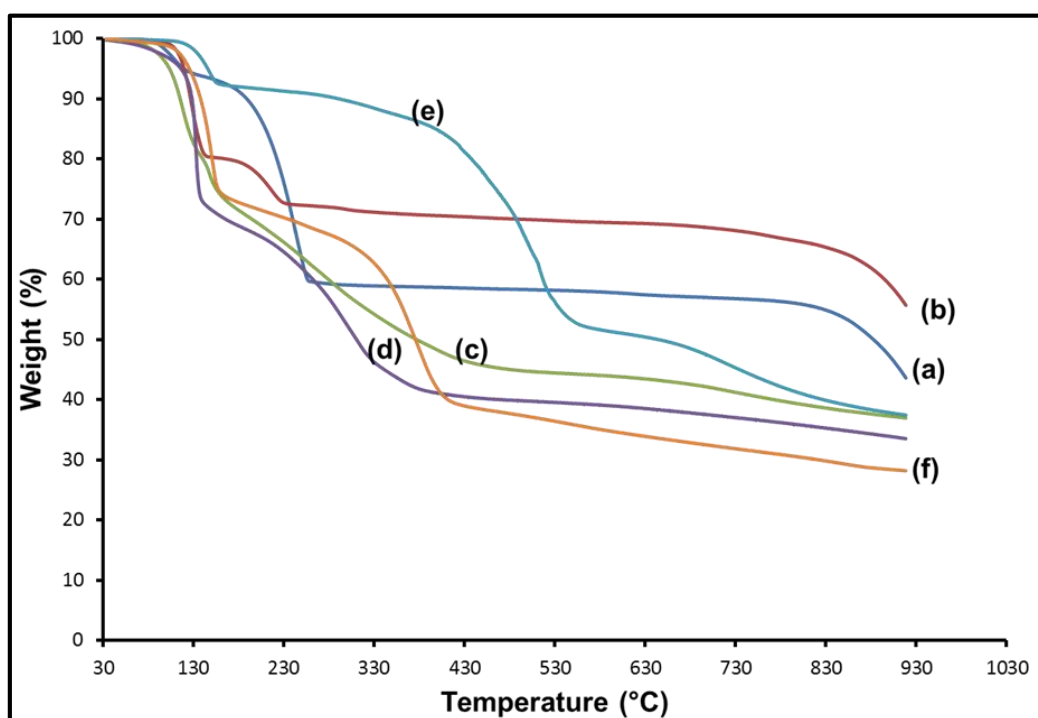


Figure 4: TGA curves for complexes I(a), II(b), III(c), IV(d), V(e) and VI(f).

3.3 Conclusions

Benzimidazole and 2-methylbenzimidazole complexes of lead, nickel and cobalt were synthesized for their use as precursors in the preparation of lead, nickel and cobalt sulphide nanoparticles. Techniques such as microanalysis, FTIR spectroscopy and TGA were used to characterize the complexes. There was a percentage mismatch from elemental analysis for the complexes I, III, IV and V. Complexes II and VI calculated percentages were within the limits with the found percentages except for sulphur. The found percentages on complex I and III showed that the formed complexes were dimers and this was confirmed by FTIR spectroscopy which exhibited the doublet C=S band. Complex IV and V showed that the leaving groups such as the sodium chlorides and hydroxides were still present in the complexes as impurities. FTIR spectroscopy confirmed the presence of $\nu(\text{C}=\text{S})$ singlet peak in all four complexes which indicates completely symmetrical bonding of the dithiocarbamate ligand to metal in a bidentate mode except for complex I and III which displayed a doublet peak which indicates monodentate coordination mode (dimeric molecules). The TGA curves decomposed to form a mixture of metal and metal sulphides for complex I, II, III and IV except for Complex VI. All benzimidazole complexes decomposed at higher temperatures and were considered as the most stable complexes.

Chapter 4

Characterization of lead sulphide nanoparticles using benzimidazole dithiocarbamate and 2-methyldithiocarbamate complexes

4.1 HDA/TOPO capped PbS nanoparticles

This chapter focuses on the synthetic parameters studied for their influence on the size, structure, composition and arrangement of lead sulphide nanoparticles. The synthetic procedure followed was thermal decomposition of benzimidazole dithiocarbamate and 2-methyldithiocarbamate complexes of lead in an inert environment in the presence of trioctylphosphine (solvent), capping agents-tri-octylphosphine oxide (TOPO) and hexadecylamine (HDA). The reaction condition such as reaction temperature and type of capping agents were varied in order to determine their influence on the properties of nanoparticles. Temperature was varied from 140, 160 to 180 °C using lead benzimidazole dithiocarbamate complex I while keeping other parameters constant. HDA is an organic amine with terminal NH₂ group whereas TOPO contains the P=O used for interfacial bonding to the nanoparticles. The synthetic conditions (Table 2) for both capping agents were kept the same in order to establish the influence of temperature as well as the capping molecule used.

Table 1: Variation of temperature in the preparation of TOPO/HDA-PbS nanoparticles using complex I and II for 60 min

Surfactant (HDA/TOPO) mass (g)	Complex I / II mass (g)	Temperature (°C)
6.0	0.3	140
6.0	0.3	160
6.0	0.3	180

4.1.1 (a) HDA-PbS Nanoparticles prepared using complex I(Temperature variation)

Table 2 shows reaction conditions for the preparation of HDA capped PbS nanoparticles by varying reaction temperatures using complex I, while keeping all the other parameters the same. UV visible spectroscopy has been widely used to characterize the semiconductor nanoparticles. As the particle size decrease, absorption wavelength will be shifted to shorter wavelength, since the band gap increases for the nano sized particles. This is the quantum confinement effect of the semiconductor nanoparticles. The absorption co-efficient of the bulk PbS is 3020 nm. UV/Vis spectra of HDA capped PbS nanoparticles prepared at different reaction temperatures from complex I are shown in Fig. 5(a-c). These spectra showed featureless features and this were confirmed by PL which showed the emission maxima at the same wavelength. There was no observable trend. The absorption band observed at 650 nm was for surface-modified particles, especially by the organic groups; it is related to the inhomogeneity of the radii and the phonon broadening and is attributed to the lower energy side of the transitions $1S_e-1S_h$. Moloto reported similar scenario but the difference is this absorption is narrow. This indicates that the capping group has an influence on the optical properties of PbS nanoparticles (Moloto et al., 2005).

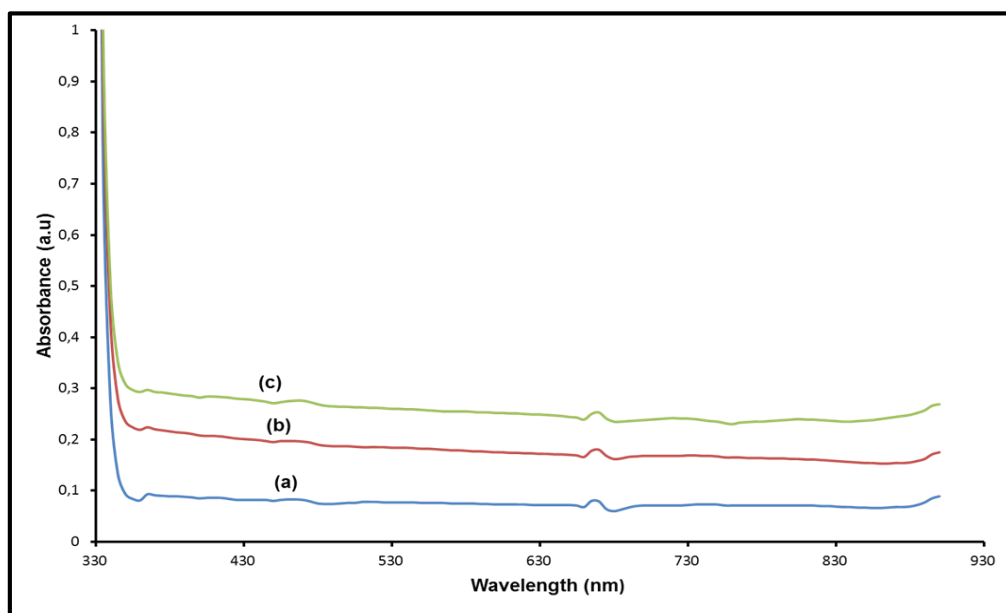


Figure 5: UV-VIS spectra of PbS nanoparticles prepared with 0.3 g of complex I with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Figure 6 shows the photoluminescence spectra of HDA capped PbS nanoparticles. The emission wavelength maxima were observed at 436 nm (Table 3). The emission peak for the sample prepared at high temperature (Fig. 6(c)) has a narrow shape, which indicates the monodispersity and good passivation of the particles. However, for the nanoparticle prepared at low temperatures, the emission peaks were broad which indicate polydispersity of particles and this could be due to temperature fluctuations.

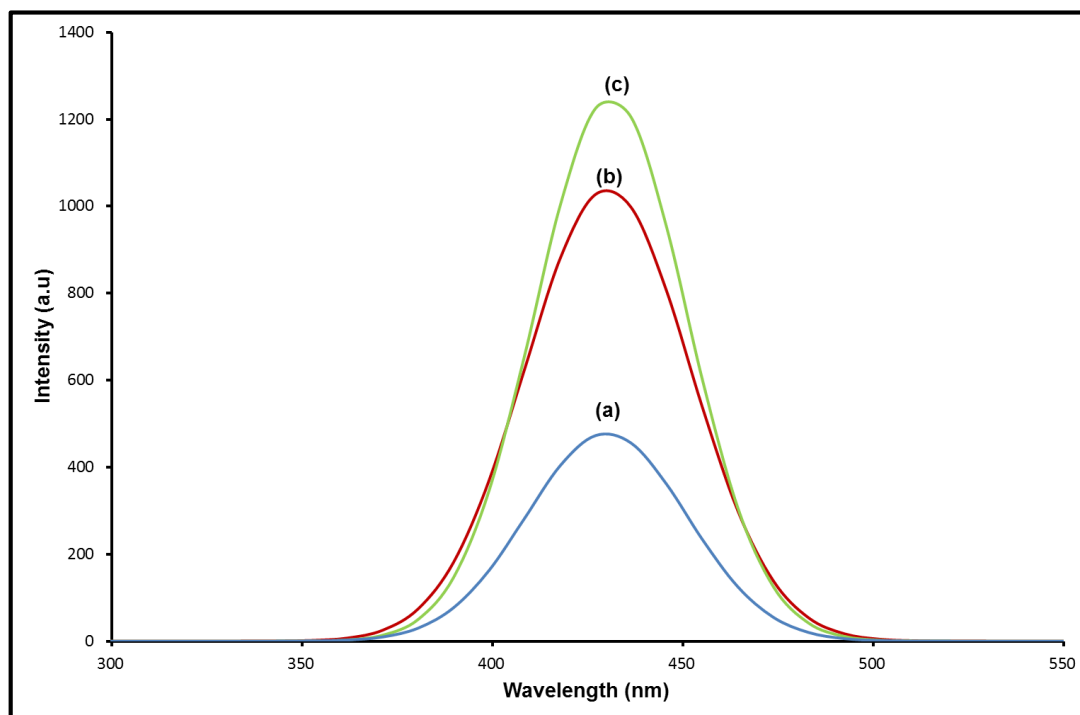


Figure 6: PL spectra of PbS nanoparticles prepared with 0.3 g of complex I with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Table 2: Absorption band edges and emission maxima of PbS nanoparticles prepared with 6 g HDA at 140 °C, 160 °C and 180 °C.

Reaction temperature (°C)	Absorption band edge (nm)	Emission maximum (nm)
140	-	436
160	-	436
180	-	436

The TEM images of PbS nanoparticles prepared at different reaction temperatures are shown in Fig. 7(a-c). The TEM of these nanoparticles show a decrease in particle size as the reaction temperature was increased and this can be due to an effect of decomposition rate, i.e. at high temperature, decomposition is likely to occur quickly with many nucleation sites existing simultaneously, while at lower temperature decomposition is slower, so with less nucleation sites each particle is then able to grow larger. This was confirmed by XRD which depicted wide peak width at higher temperatures meaning smaller particles. The observed morphology of the nanoparticles was found to be cubes which are consistent with the findings of (Ding et al., 2003, Wattoo et al., 2012). This reaction is favoured by thermodynamic growth regime as it is well known that at thermodynamic reaction all nanocrystals grow toward a shape that has the lowest energy at equilibrium. At lower temperatures Fig. 7(a-b), polydispersity of particles was observed and this can be due to the initial stage of particle's formation and they need more time to fully form and a higher temperature. Better dispersed nanoparticles were observed at higher temperature (Fig. 7(c)). The average particle sizes for the temperatures 140, 160 and 180 °C, were found to be 32.82 ± 5.06 , 16.56 ± 1.84 and 14.70 ± 0.60 , respectively. The average sizes at higher temperatures were smaller than the excitonic Bohr radius (18 nm) of bulk PbS. Fig. 7(c) was found to be the best temperature since it produced monodispersed PbS nanoparticles and this was confirmed by narrow emission peak in Fig. 7(a). This could be due to a HDA providing a large capping density at higher temperatures.

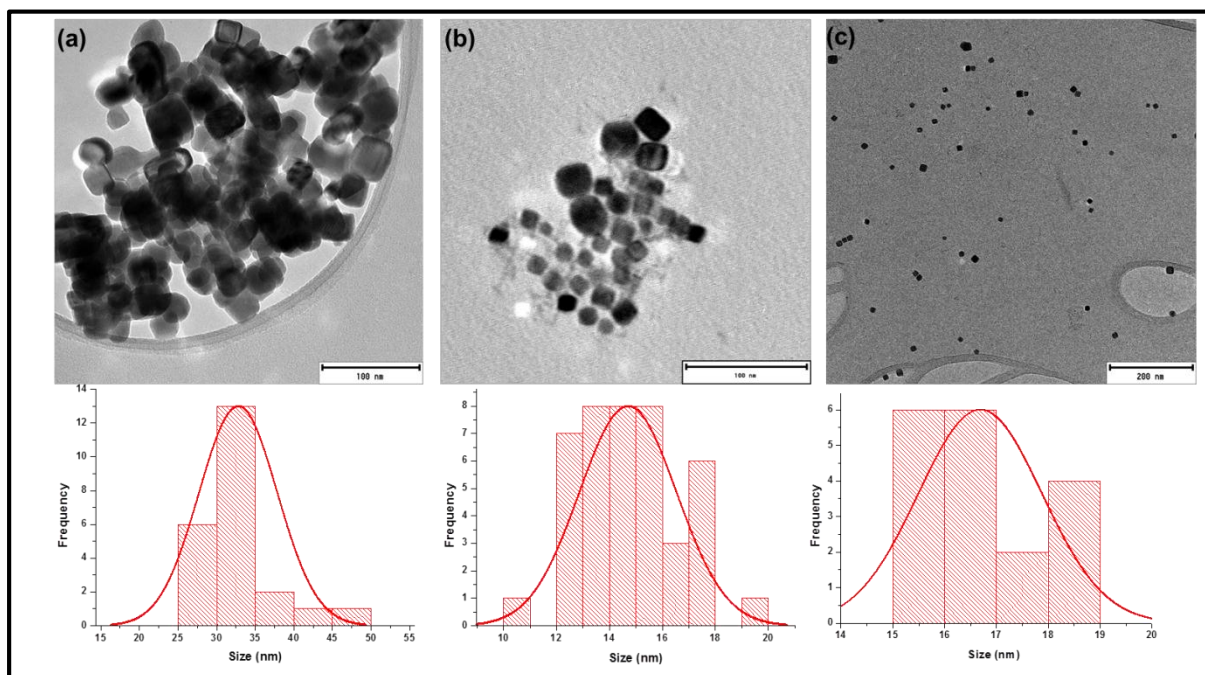


Figure 7: TEM images and their histograms of PbS nanoparticles prepared with 0.3 g of complex I with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Figures 8(a-c) shows XRD pattern of HDA capped PbS nanoparticles. The strong and sharp peaks suggest that the as-obtained products were well crystalline. All the diffraction can be indexed to face-centered cubic phase of PbS and it was in good agreement with the standard value (JCPSS file no. 5-592). But at low temperature, Fig. 8(a) there were some impurities of lead observed shown by a star sign and this indicates that the reaction was incomplete at that temperature. The presence of the mixture Pb and PbS was also confirmed by TGA.

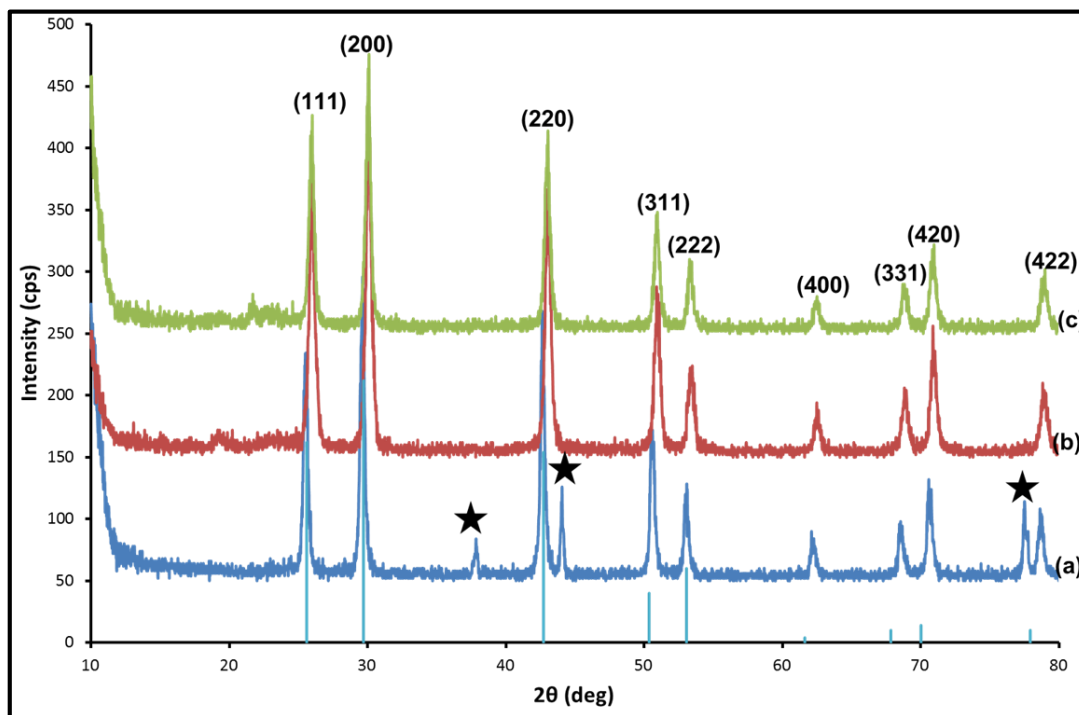


Figure 8: Powder X-ray diffractogram of PbS nanoparticles synthesized from 0.3 g complex 1 in 6 g HDA from (a) 140 °C, b) 160 °C and (c) 180 °C.

(b) TOPO-PbS Nanoparticles prepared using complex I (Temperature variation)

The preparation of the TOPO-capped PbS nanoparticles was done under similar conditions with complex I as for HDA. The conditions are outlined in Table 2. The optical and morphological features were explored for the synthesized nanoparticles using UV/vis and PL spectroscopy, TEM and XRD techniques.

The absorption spectra of TOPO capped PbS nanoparticles prepared at different reaction temperatures of complex I are given in Fig. 9(a-c). Lead sulphide nanoparticles show a blue shift in relation to bulk PbS. The nanoparticles band edges do not follow any trend and this might be due to change in shapes as the temperature was increased and this was confirmed by TEM. However the absorption band edge for the particles synthesised at 160 °C (Fig. 9(b)) was distinctly sharper and pronounced than the band edges (Fig. 9(a) and (c)). The absorption bands edges observed are shown in Table 4.

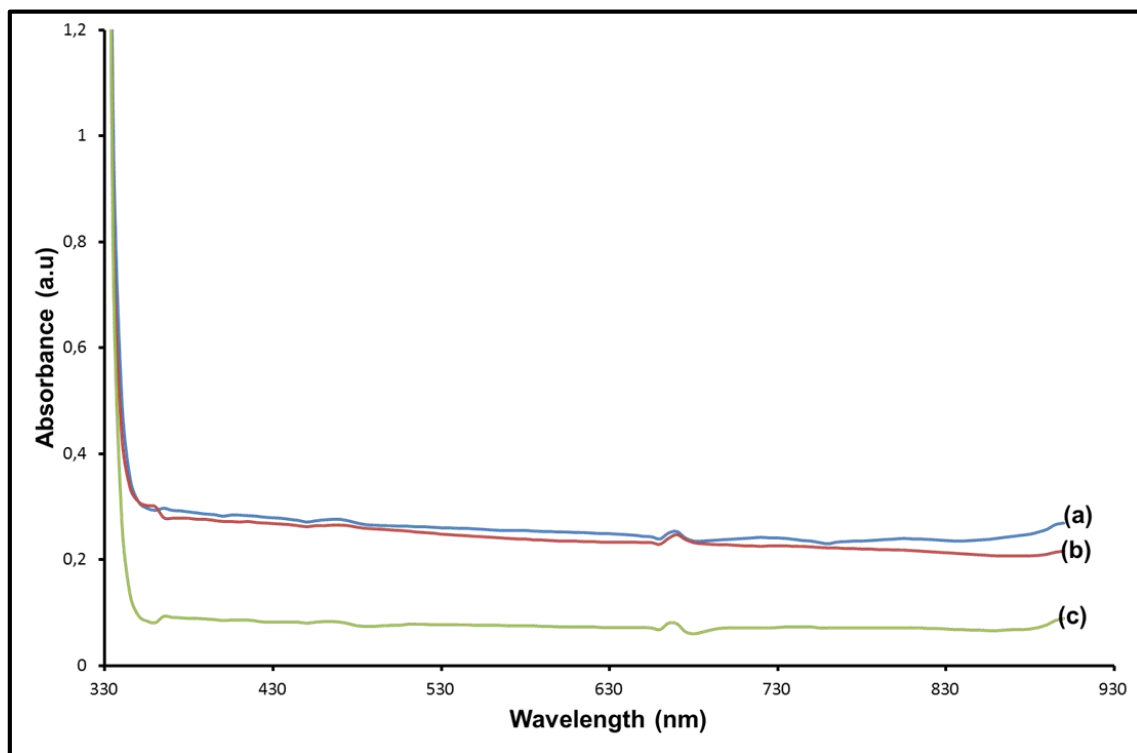


Figure 9: UV-VIS spectra of PbS nanoparticles prepared with 0.3 g of complex I with 6 g of TOPO at (a) 140 °C, (b) 160 °C and 180 °C.

Figure 10 shows the emission spectra of TOPO capped PbS nanoparticles at different temperatures. The emission peaks show red shift in relation to the absorption band edges in Fig. 9. The emission peaks for the sample prepared at low temperature have a narrow shape, which indicates narrow size distribution of the particles. However, for the nanoparticles prepared at high temperatures, broad peaks indicate polydispersity of the particles and this was confirmed by TEM which shows anisotropic particles. The emission spectrum at 140 °C (Fig 10 (a)) was blue shifted from other emission spectra which indicate the smaller particle sizes or narrow size distribution and this was confirmed by XRD which showed wide diffraction peaks widths. The emission maxima are shown in Table 4.

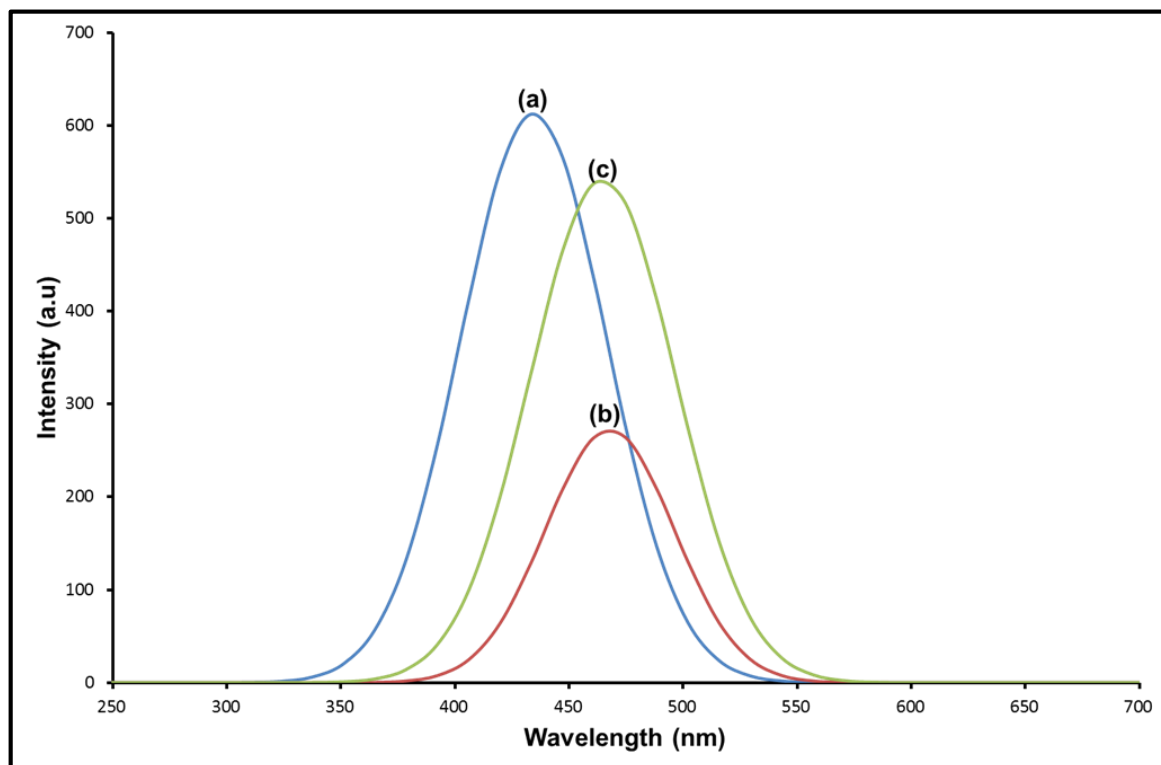


Figure 10: PL spectra of PbS nanoparticles prepared with 0.3 g of complex I with 6 g of TOPO at (a) 140 °C, (b) 160 °C and 180 °C.

Table 3: Absorption band edges and emission maxima of TOPO-capped PbS nanoparticles prepared using 6 g TOPO for 1 hour at 140 °C, 160 °C and 180 °C.

Reaction temperature (°C)	Absorption band edge (nm)	Emission maximum (nm)
140	355	433
160	365	474
180	360	474

Figures 11(a-c) shows TEM images of the TOPO capped PbS nanoparticles. At low temperature Fig. 11(a) TEM clearly shows that the particles are aggregated. As the temperature was increased to 160 °C a cross-like layer was observed with quasi spherical particles on top. Further increasing the temperature to 180 °C, the cross-like layer decomposed into rods-like materials with quasi spherical particles on top. The average diameter of quasi spherical particles was found to be 5.263 ± 0.67 nm (Fig. 11(b)) shown by the distribution curve. The average diameter of quasi spherical particles at 180 °C was 2.56 ± 1.085 nm Fig. 11(c) shown

by the distribution curve. There is no specific trend observed and this is due to the change in shape of cross like layer to rod-like materials or anisotropic particles observed.

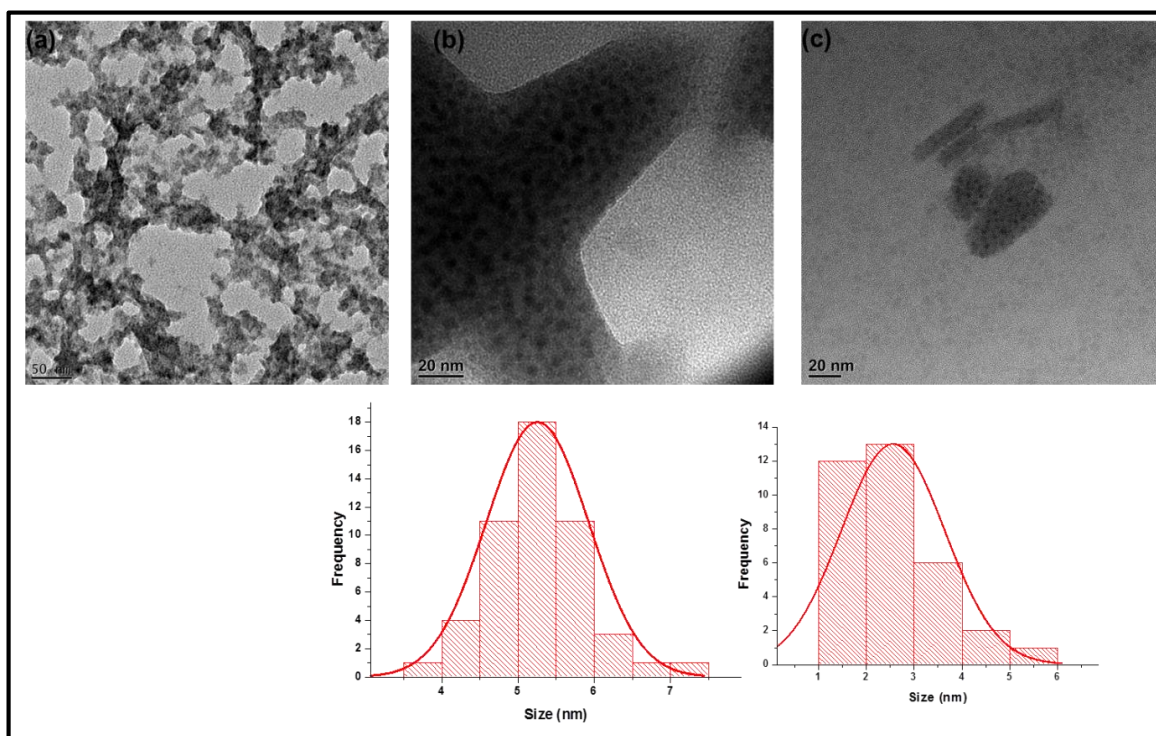


Figure 11: TEM images and their histograms of PbS nanoparticles prepared with 0.3 g of complex I with 6 g of TOPO at (a) 140 °C, (b) 160 °C and 180 °C.

Samples were analysed by XRD for further study, Fig. 12(a-c) shows the XRD patterns of these samples at different temperatures. There were eight peaks in the XRD pattern as seen in this Figure, related to each sample that are characteristic of PbS compound. The sharp peaks of the XRD pattern indicate that the synthesized PbS nanoparticles are well crystalline. All the diffraction can be indexed to the cubic phase of PbS and it was in good agreement with the standard value (JCPDS file no.03-065-2935). No peaks due to impurities were found. It was noticed that at low temperature, the widths of diffraction peaks are wider than those observed at high temperatures suggesting that the particles at low temperature are small. In addition, there was no significant change in the position of the peaks therefore it shows that temperature only arrests the nanoparticle growth and does not introduce any phase change.

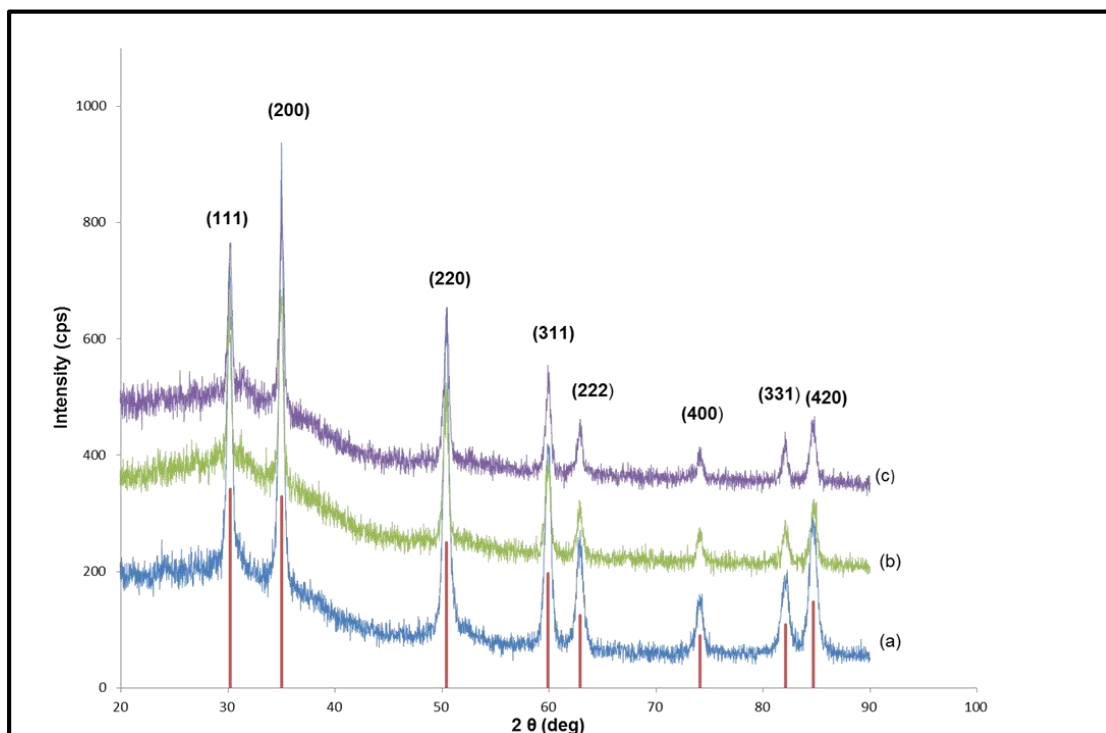


Figure 12: Powder X-ray diffractogram of PbS nanoparticles synthesized from 0.3 g complex I in 6 g TOPO from (a) 140 °C, (b) 160 °C and (c) 180 °C.

(c) HDA-PbS Nanoparticles prepared using complex II (Temperature variation)

The preparation of the HDA-capped PbS nanoparticles was conducted under similar conditions with complex I but in this case complex II was used. The conditions are outlined in Table 2. The optical and morphological features were explored for the synthesized nanoparticles using UV vis, PL and FTIR spectroscopy, TEM and XRD techniques. Figure 13(a-c) shows the absorption spectra of HDA capped PbS nanoparticles prepared at different temperatures (Table 2) from complex II which were blue shifted relative to the bulk PbS material (E.g. = 3020 nm), suggesting the formation of nanometer sized material. These spectra show that as the temperature increases the size of the nanoparticles also increases. The absorption around 650 is discussed in Fig. 5. At low temperature the absorption spectrum is sharper with the band edge observed at 336. This could be due to smaller sizes of PbS observed and this was confirmed by TEM. When the temperature was increased to 160 °C the band edge was well defined and this indicates that the particles are well distributed or resolved and this was also confirmed by PL which shows narrow emission peak and TEM which shows good distribution of particles. As the temperature was increased to 180 °C a broad band edge was observed and

this indicates polydispersity of the particles and this was confirmed by PL which shows a broad emission peak.

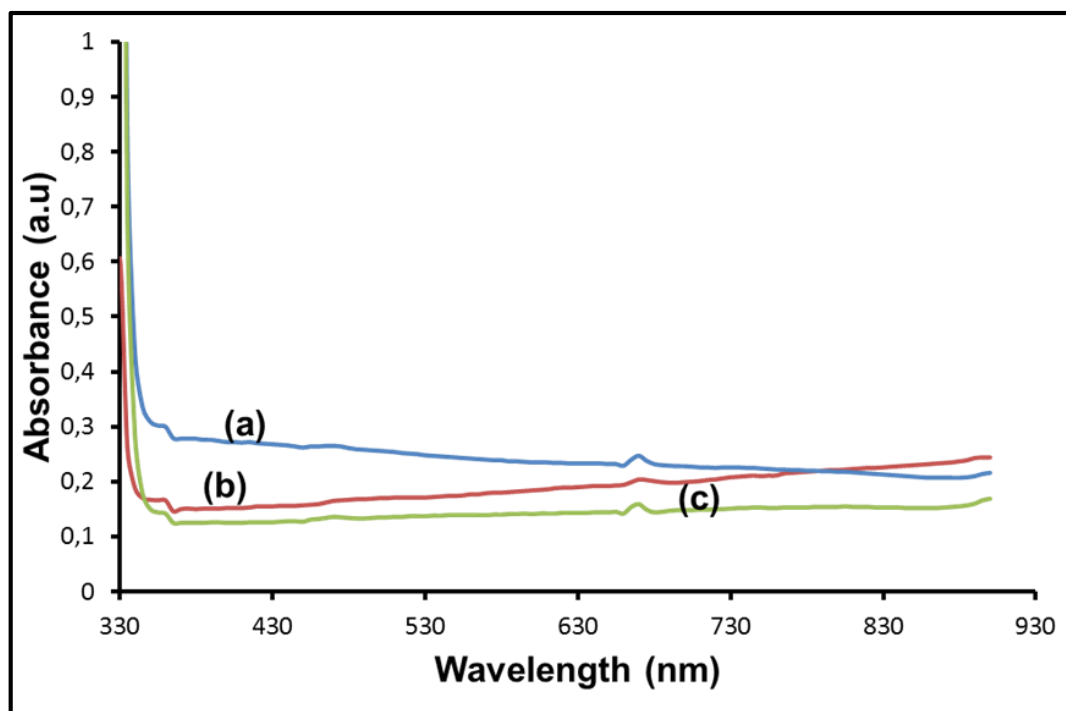


Figure 13: UV-VIS spectra of PbS nanoparticles prepared with 0.3 g of complex II with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

The emission spectra of the samples prepared at different temperatures are given in Fig. 14 (a-c). The emission maxima of the samples were slightly red shifted from their respective band edges of the absorption spectra. The emission peaks for the sample prepared at 160 °C have a narrow shape, which indicates good passivation of the particles. However, the nanoparticles prepared at high temperature (180 °C) show the broad emission peak which indicates that the particles are polydispersed or agglomerated. The emission maximum shift to lower wavelength as the temperature was decreased. The emission peaks maxima are shown in Table 5. The difference between the absorption and emission peak wavelength at low temperatures is very small. This indicates the emission associated with the transition of electrons from trap state to conduction band (Navaneethan et al., 2009).

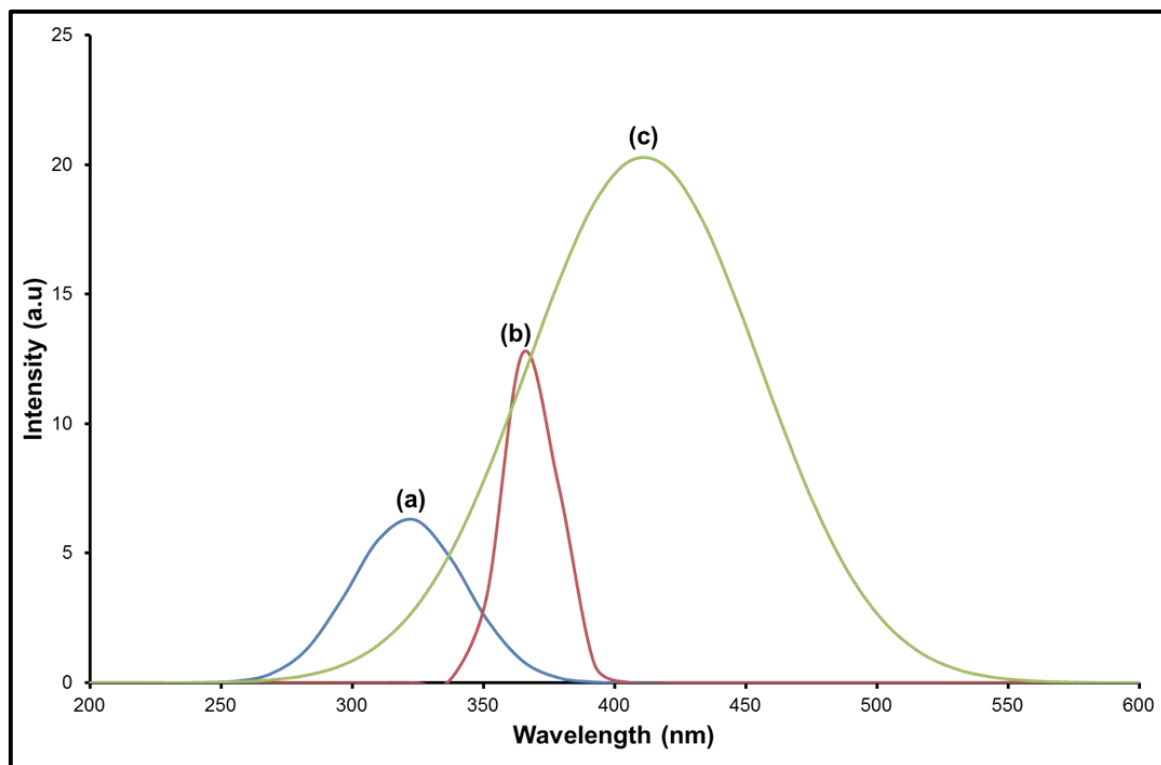


Figure 14: PL spectra of PbS nanoparticles prepared with 0.3 g of complex II with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Table 4: Absorption band edges and emission maxima of PbS nanoparticles prepared with 6 g HDA at 140 °C, 160 °C and 180 °C.

Reaction temperature (°C)	Absorption band edge (nm)	Emission maximum (nm)
140	335	336
160	345	364
180	346	405

The TEM images of HDA capped PbS nanoparticles synthesized at different temperatures are shown in Figure 15(a-c). The observed morphology of HDA capped PbS nanoparticles was found to be cubes. It was observed that when the temperature increases the size of the nanoparticles also increases and this can be due to Ostwald ripening. The estimated average particle sizes were found to be 16.89 ± 8.02 nm, 22.089 ± 7.53 nm and 27.91 ± 6.949 nm for

nanocrystals prepared at 140 °C, 160 °C and 180 °C respectively. These results were consistent with those obtained from XRD. There is no significant change in shape when the temperature was varied and this is due to thermodynamic growth regime. Nevertheless the particles were found to be polydispersed as shown by the distribution curves.

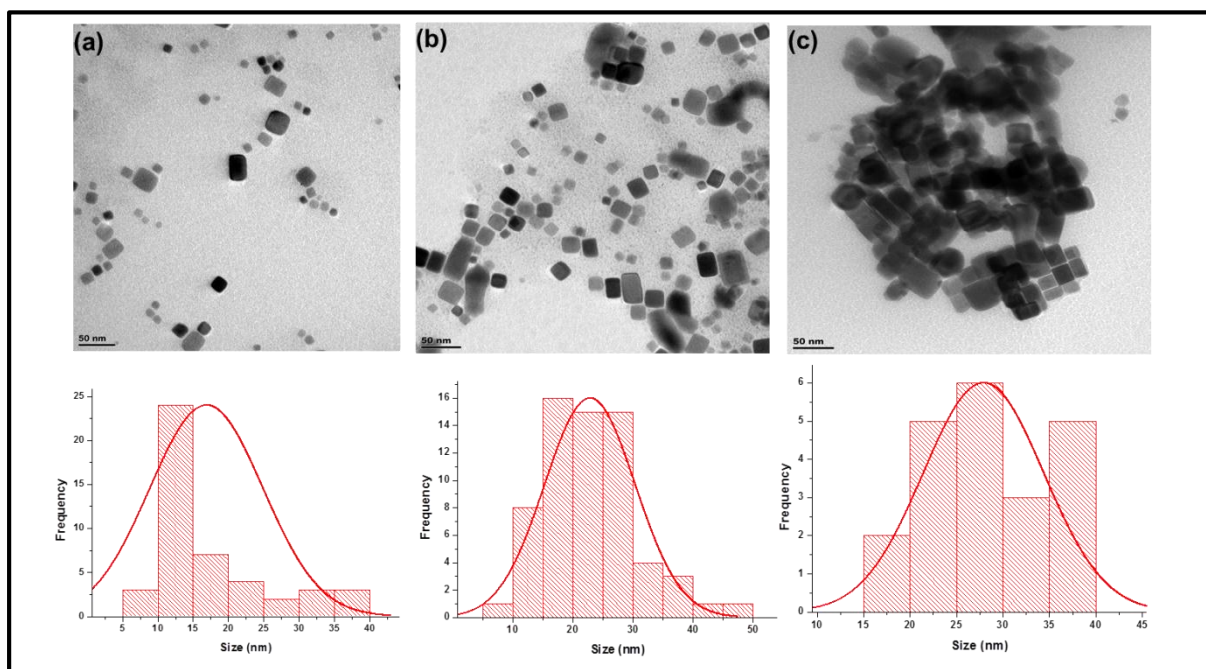


Figure 15: TEM images and their histograms of PbS nanoparticles prepared with 0.3 g of complex II with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Fig. 16 shows the XRD patterns of HDA capped PbS nanoparticles at different temperatures. The presence of the (111), (200) and (311), (222), (400), (331) and (420) planes in the diffraction patterns is the characteristic of the cubic phase (galena) of PbS and it was in good agreement with the standard value (JCPDS file no.03-065-2935). No peaks due to impurities were found. There is no significant change in the position of the peaks which means temperature only arrests the nanoparticle growth and does not introduce any phase change. The peak width showed that as the temperature was increased the size of the particles increased.

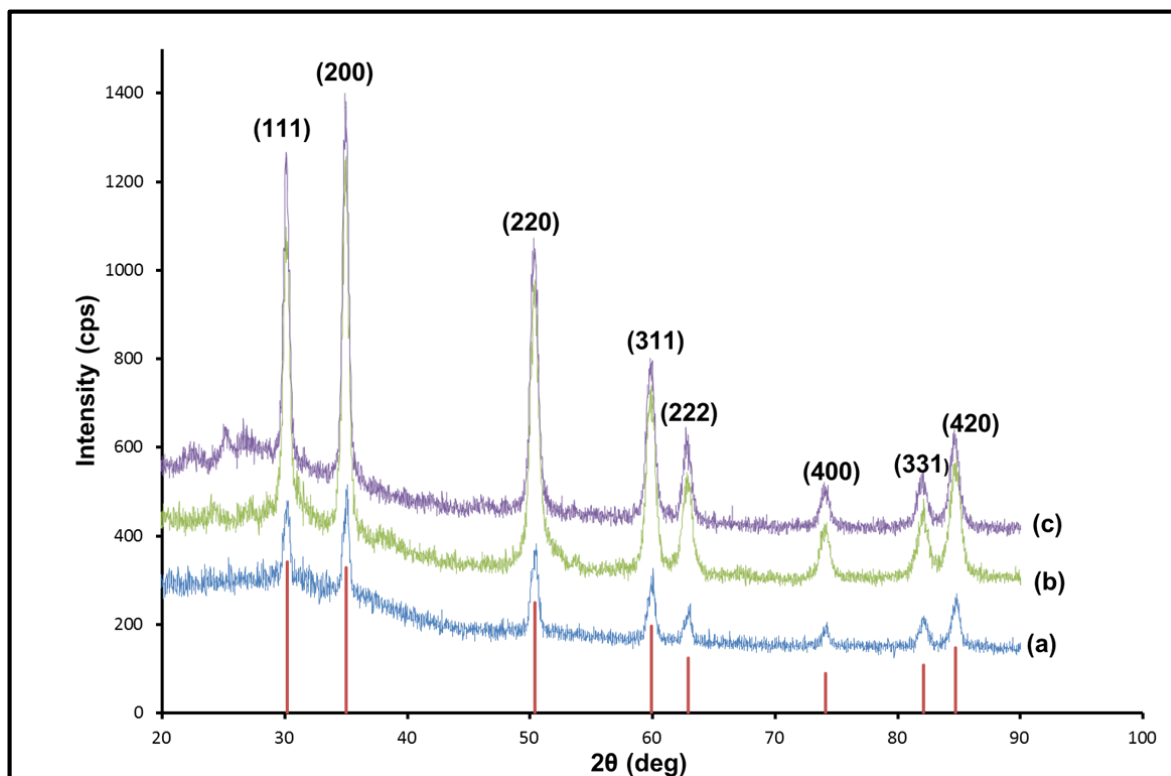


Figure 16: Powder X-ray diffractogram of PbS nanoparticles synthesized from 0.3 g complex II in 6 g HDA from a) 140 °C, b) 160 °C and c) 180 °C.

(d) TOPO-capped PbS Nanoparticles prepared using complex II (Temperature variation)

The preparation of the TOPO-capped PbS nanoparticles was conducted under similar conditions with complex I but in this case complex II was used. The conditions are outlined in Table 2. The optical and morphological features were explored for the synthesized nanoparticles using UV/vis and PL spectroscopy, TEM and XRD techniques. Absorption spectra of TOPO capped PbS nanoparticles prepared at different temperature are shown in Fig. 17. The absorption band edges show no specific trend. The absorption band edges show a blue shift in relative to the bulk PbS of 3020 nm and this conforms the quantum size effect of PbS. The broadening of the band edges at higher temperatures is an indication of a broader size distribution or the presence of larger elongated particles as confirmed by TEM which showed the presence of cylindrical shapes. The absorption band edges are shown in Table 6.

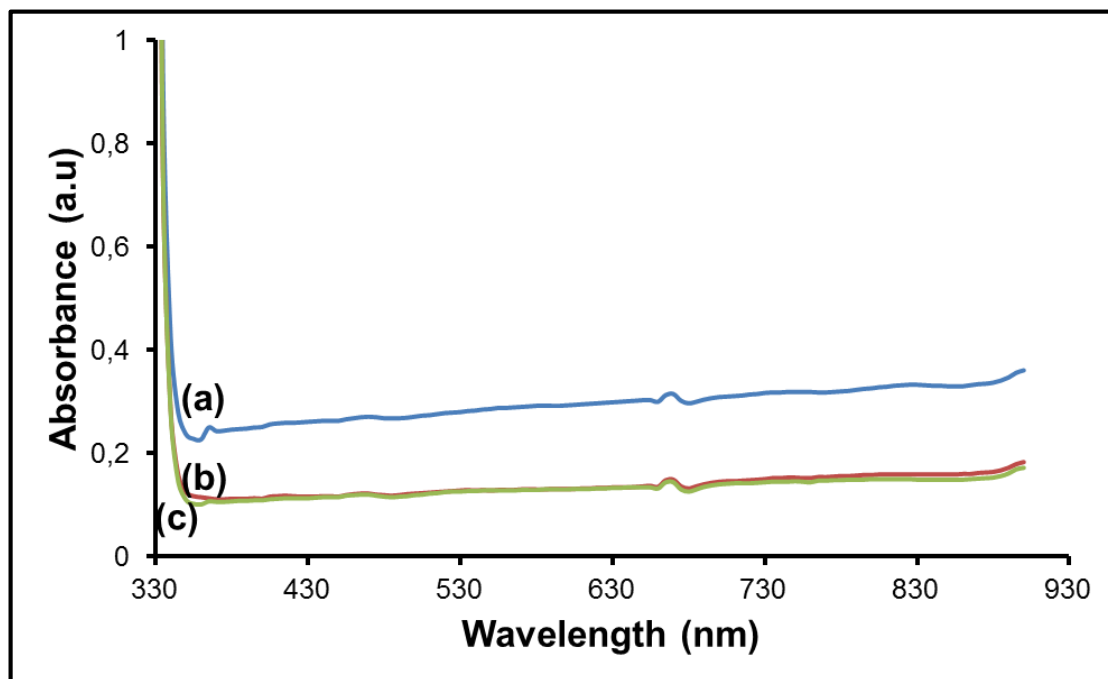


Figure 17: UV-VIS spectra of PbS nanoparticles prepared with 0.3 g of complex II with 6 g of TOPO at (a) 140 °C, (b) 160 °C and 180 °C.

Figure 18 shows emission spectra of TOPO capped PbS nanoparticles prepared at different temperatures from complex II. The corresponding photoluminescence spectra shows broad emission peaks with the maxima at 436 nm, 417 nm and 427 nm from low temperature to high temperature and this is an indication of large size distribution or bigger particles. The emission spectra show red shift in relative to the absorption spectra. Spectrum at 160 °C shows a blue shift from emission spectrum at 140 °C, this can be due to change of shape and this was confirmed by TEM.

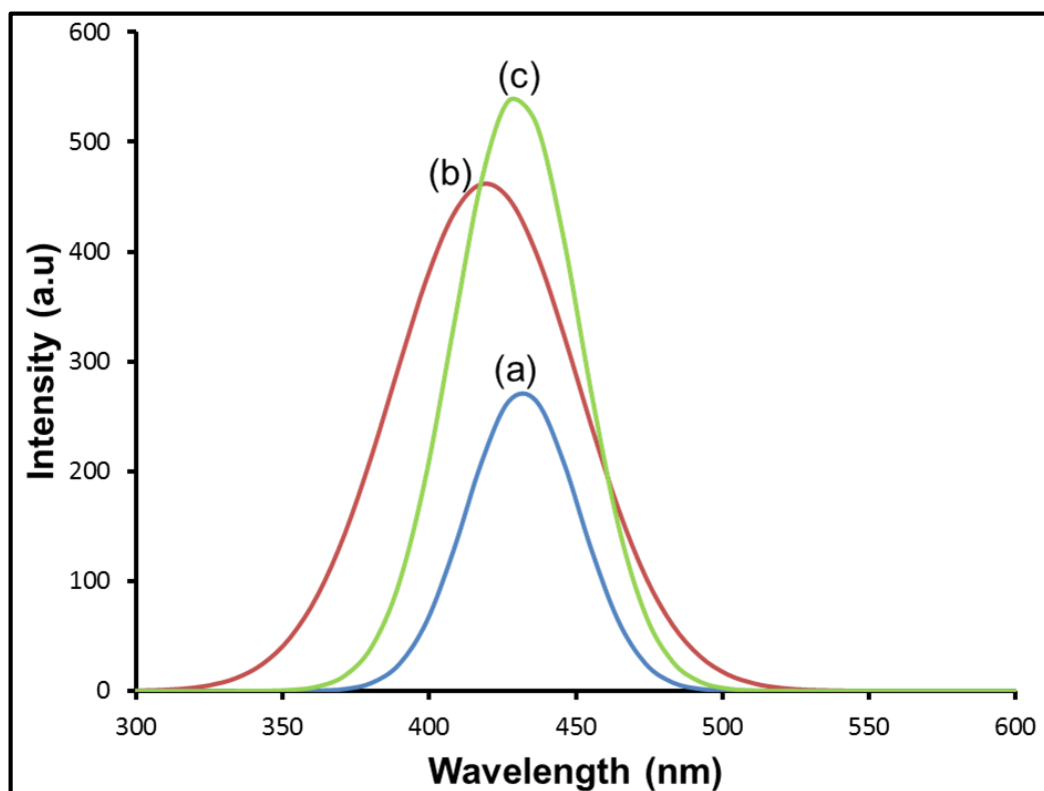


Figure 18: PL spectra of PbS nanoparticles prepared with 0.3 g of complex II with 6 g of TOPO at (a) 140 °C, (b) 160 °C and 180 °C.

Table 5: Absorption band edges and emission maxima of PbS nanoparticles prepared with 6 g TOPO at 140 °C, 160 °C and 180 °C.

Reaction temperature (°C)	Absorption band edge (nm)	Emission maximum (nm)
140	375	436
160	363	417
180	365	427

Figure 19 shows TOPO capped PbS nanoparticles synthesized at different temperatures. All TOPO capped images shows agglomerated particles as the temperature was varied and it can be due to the large steric hindrance of TOPO creating a small capping density for the particles. The observed morphology was found to be cubes at low temperature but as the temperature was increased cylindrical shapes were observed. For further study, the samples were analysed by XRD.

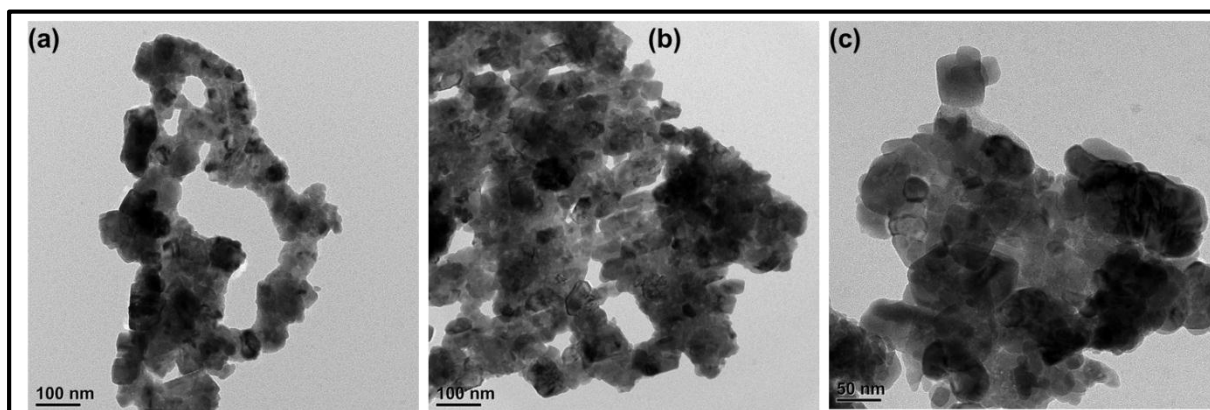


Figure 19: TEM images and their histograms of PbS nanoparticles prepared with 0.3 g of complex II with 6 g of TOPO at (a) 140 °C, (b) 160 °C and 180 °C.

Figure 20 shows the XRD patterns of TOPO capped PbS samples at different temperatures. As seen in this figure, there are eight peaks in the XRD pattern related to each sample that are characteristic of PbS compound. The presence of the (111), (200) and (311), (222), (400), (331) and (420) planes in the diffraction patterns is the characteristic of the cubic phase (galena) of PbS and it is in good agreement with the standard value (JCPDS file no.03-065-2935). No peaks due to impurities were found. To determine the particle sizes of TOPO capped nanoparticles, Debye-Scherrer equation was employed and is given by Eq. 5:

$$D = 0.9\lambda / B \cos \Theta \quad (5)$$

Where, D (nm), λ (nm), θ (degrees), and B (nm) are the average particle size, the X-ray wavelength, the diffraction angle and the maximum peak width in half-height, respectively. The average size of the particles at 140, 160 and 180 °C were found to be 19.88, 15.38 and 16.50 nm determined from the XRD technique based on the Debye-Scherrer equation. The obtained data show no specific trend and this can be due to change of shapes from cubes Fig. 20(a) to cylindrical shape (Fig. 20(b) and (c) and this was also confirmed by PL.

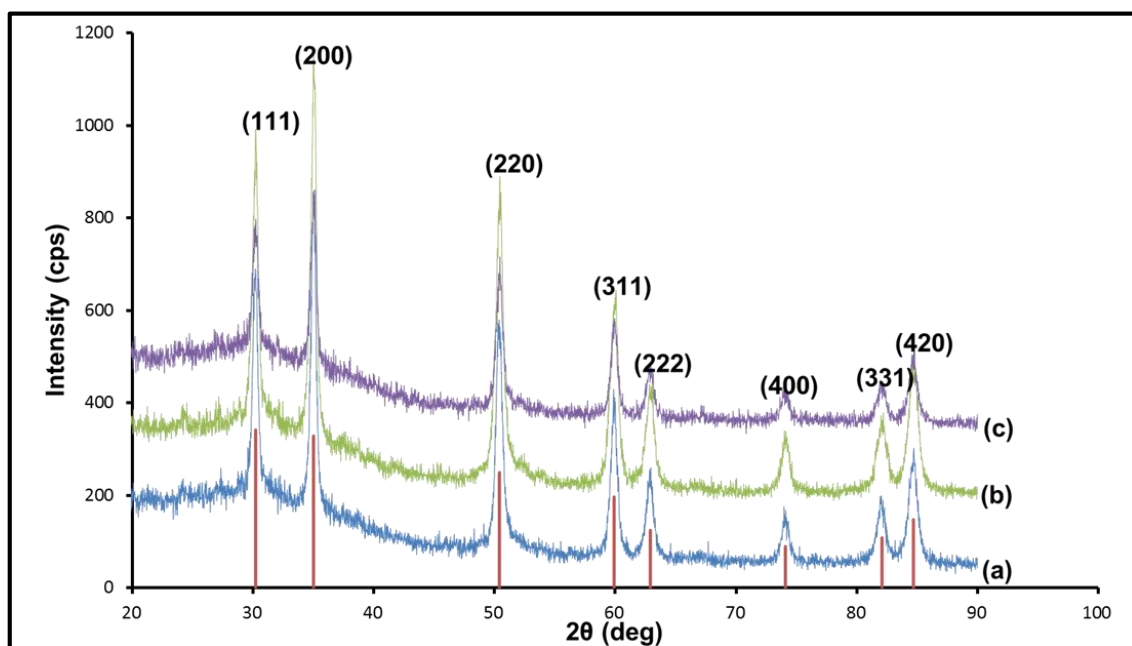


Figure 20: Powder X-ray diffractogram of PbS nanoparticles synthesized from 0.3 g complex II in 6 g TOPO from a) 140 °C, b) 160 °C and C) 180 °C.

4.2 Conclusions

Lead (II) sulphide nanoparticles were synthesized from lead complexes of benzimidazole dithiocarbamate (I) and 2-methylbenzimidazole dithiocarbamate (II). The effect of temperature and type of capping agent were studied. The optical measurements support the presence of smaller particles for both capping agents. HDA gave better resolved particles than TOPO at all temperatures and it was considered as the best capping agent. It also exhibited cubic morphology at all temperatures for both complex I and II. TOPO displayed anisotropic shapes at all temperatures. From HDA-PbS nanoparticles using complex I, UV/vis depicted featureless spectra and this was confirmed by PL which depicted PL maxima at the same wavelength. TEM showed that as the temperature was increased the size of the particles decreased and this was confirmed by XRD which followed the same trend. Nanoparticles at 180 °C were monodispersed and this was supported by PL which showed narrow emission peak and XRD which depicted wide peak width, therefore it was considered as the best temperature. The optical properties for TOPO capped PbS nanoparticles using complex I and II showed no specific trend and this was confirmed by TEM and XRD which gave no specific trend. TEM showed undefined morphology at low temperature but showed a cross-like particle with squasi spheres on top at 160 °C and a mixture of rods-like material with squasi spheres. It also showed

well dispersed particles at 160 °C and this was supported by UV/Vis which showed pronounced band edge and this was considered as the best temperature. Optical properties for HDA capped PbS nanoparticles using complex II showed that as the temperature was increased the size of the particles increased and this was confirmed by TEM and XRD which followed the same trend. TEM showed better dispersity of particles at low temperatures and it was supported by optical measurements which showed pronounced absorption band edges and narrow emission peaks. TOPO capped PbS nanoparticles from complex II displayed agglomerated particles and gave no specific trend on optical properties, TEM and XRD. The cubic morphology was observed at low temperature but as the temperature was increased cylindrical shapes were observed. XRD patterns for all temperatures were well crystalline and matched cubic phase of PbS (Galena) except for HDA capped PbS from complex I at low temperature which matched face centred cubic phase. There was no significant change in the position of the peaks which means temperature only arrests the nanoparticle growth and does not introduce any phase change for both complexes except complex 1 at low temperature which introduced a new phase.

Chapter 5

Characterization of HDA-capped nickel sulphide nanoparticles using benzimidazole dithiocarbamate and 2-methyldithiocarbamate complexes

5.1 HDA capped nickel sulphide nanoparticles

This chapter focuses on the modification of synthetic parameters in order to influence the size, structure, composition and arrangement of nickel sulphide nanoparticles. The synthetic procedure followed was thermal decomposition of benzimidazole dithiocarbamate and 2-methyldithiocarbamate complexes of nickel in an inert environment in the presence of trioctylphosphine (solvent) and hexadecylamine (capping agent). The reaction condition such as precursor concentration and temperature of the reaction were varied in order to determine their influence. Temperature was varied from 140, 160 to 180 °C using 0.3 g of complex III and IV while keeping other parameters constant. The best temperature was chosen (160 °C) and the amount of precursor concentration was varied from 0.3, 0.35 to 0.4 g while keeping other parameters constant.

5.1.1 (a) HDA-nickel sulphide Nanoparticles prepared using complex III (Temperature variation)

Table 6 shows reaction conditions for the preparations of Ni_3S_4 nanoparticles at different temperatures using complex III, while keeping all the other parameters the same.

Table 6: Variation of temperature in the preparation of HDA- Ni_3S_4 nanoparticles using complex III.

Surfactant (HDA) mass (g)	Complex III mass (g)	Temperature (°C)
6	0.3	140
6	0.3	160
6	0.3	180

UV-Vis spectral analysis has been widely used to characterize semiconductor nanoparticles. As the particle size decreases, the absorption edge shifts to shorter wavelength, due to the band gap increase of the smaller particles (Deyu et al., 2003). The absorption bands are blue shifted from the bulk nickel sulphide and this indicates quantum size effect. Absorption spectra for the nickel sulphide nanoparticles synthesized at different temperatures from complex III are shown in Fig. 21(a-c). All the spectra show one major absorption peak. The absorption bands were observed at a) 365 nm, b) 370 nm and c) 380 nm respectively (Table 8). These spectra indicate that as the temperature increases the size of the particles also increases and this is confirmed by PL and TEM images. This trend is expected, as it is well known that high temperature generate a large number of nuclei, which in turn leads to the formation of large particles by Ostwald ripening.

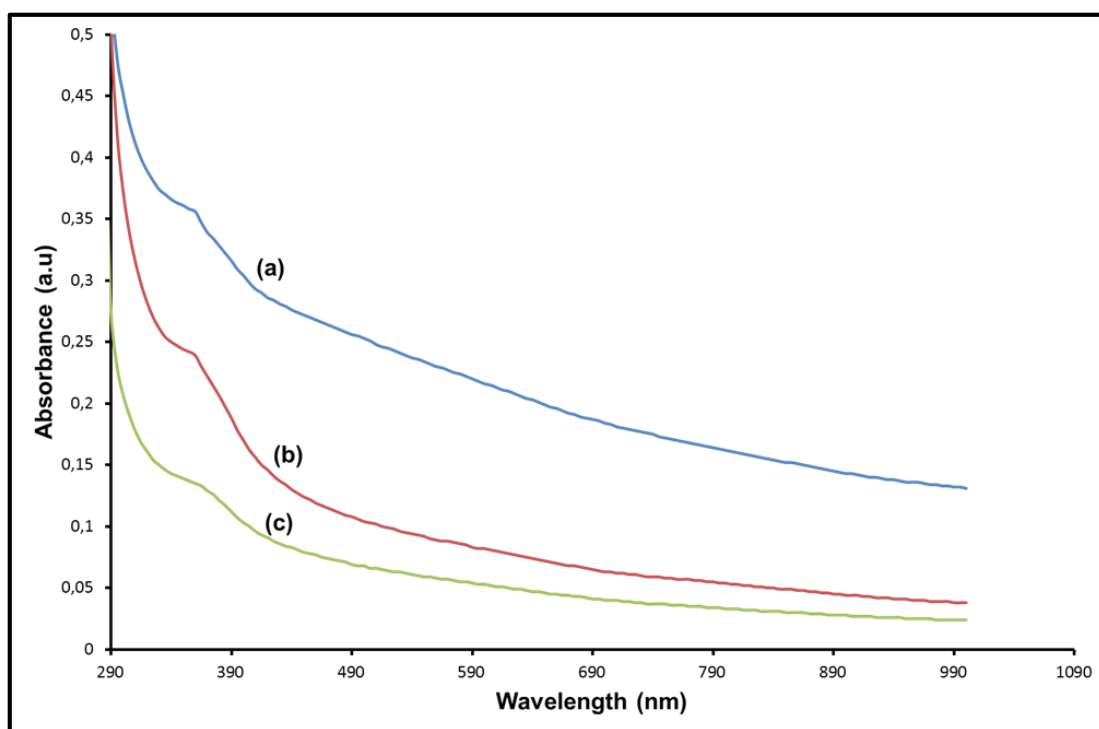


Figure 21: UV-VIS spectra of Ni_3S_4 nanoparticles prepared with 0.3 g of complex III with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

The emission spectra for the nickel sulphide nanoparticles synthesized at different temperatures from complex III is shown in Fig. 22(a-c). The entire spectra show one major emission peak. The emission peaks are red shifted in relation to the absorption peaks. The corresponding photoluminescence spectra were observed with the strong emission peaks centred at 698 nm

when excited at 520 nm. The sharp emission peaks observed are an indication of narrow size distribution and this was confirmed by distribution curves. As the temperature was increased the emission peaks also broadens and this shows that the particles sizes are getting bigger.

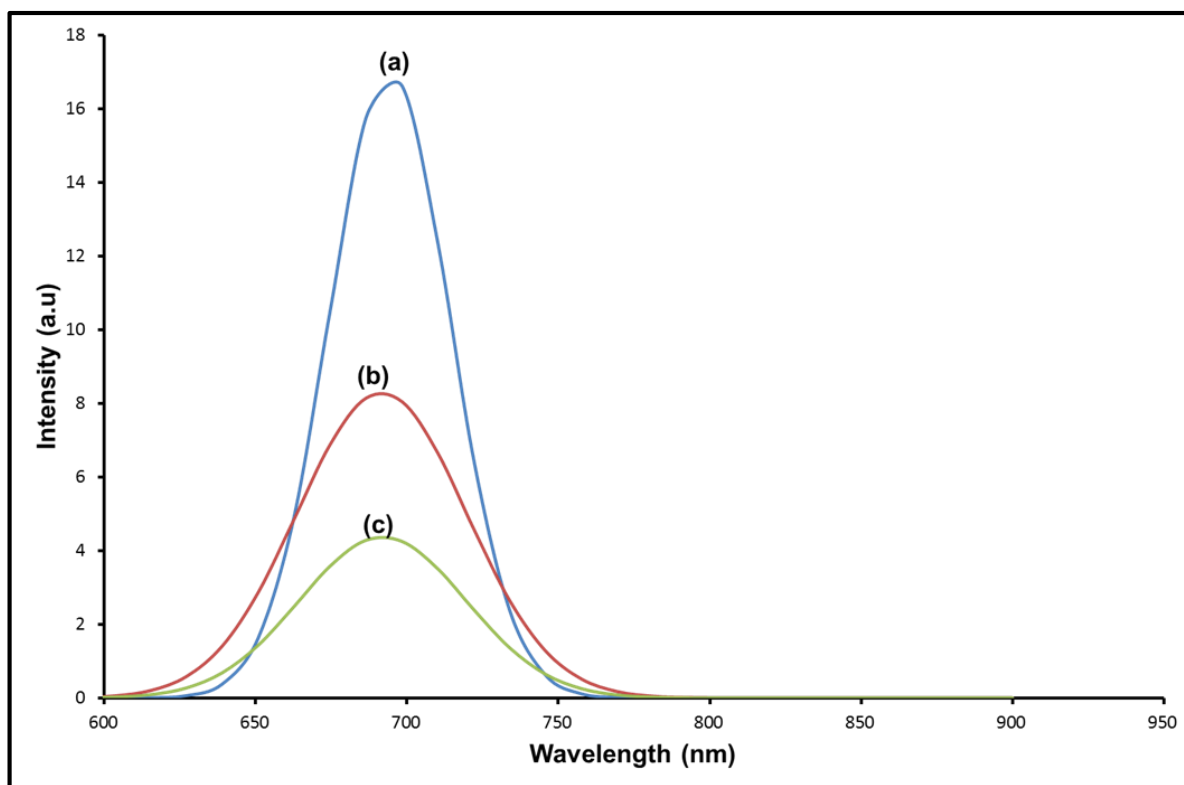


Figure 22: PL spectra of Ni₃S₄ nanoparticles prepared with 0.3 g of complex III with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Table 7: *absorption bands and emission maxima of Ni₃S₄ nanoparticles prepared with 6 g of HDA at 140 °C, (b) 160 °C and 180 °C.*

Reaction temperature (°C)	Absorption bands (nm)	Time (Minutes)
140	365	60
160	370	60
180	380	60

The TEM images of particles prepared from complex III at different temperatures are shown in Fig. 23(a-c). When the temperature was increased to 180 °C, the particle size was also increasing this can be due to Ostwald ripening effect. At all temperatures, a mixture of spheres and cubes were observed with the average diameter of 2.926 ± 0.719 nm, 5.813 ± 1.312 nm and 7.891 ± 3.581 nm respectively. At low temperature the particles are not clearly resolved

and this could be due to incomplete reaction. It was observed that particles were well dispersed and well resolved at 160 °C fig. 23(b). This reaction is favoured by thermodynamic growth regime as it is well known that at thermodynamic reaction all nanocrystals grow toward a shape that has the lowest energy at equilibrium. These results are in good agreement with absorption spectra results shown in Fig. 22.

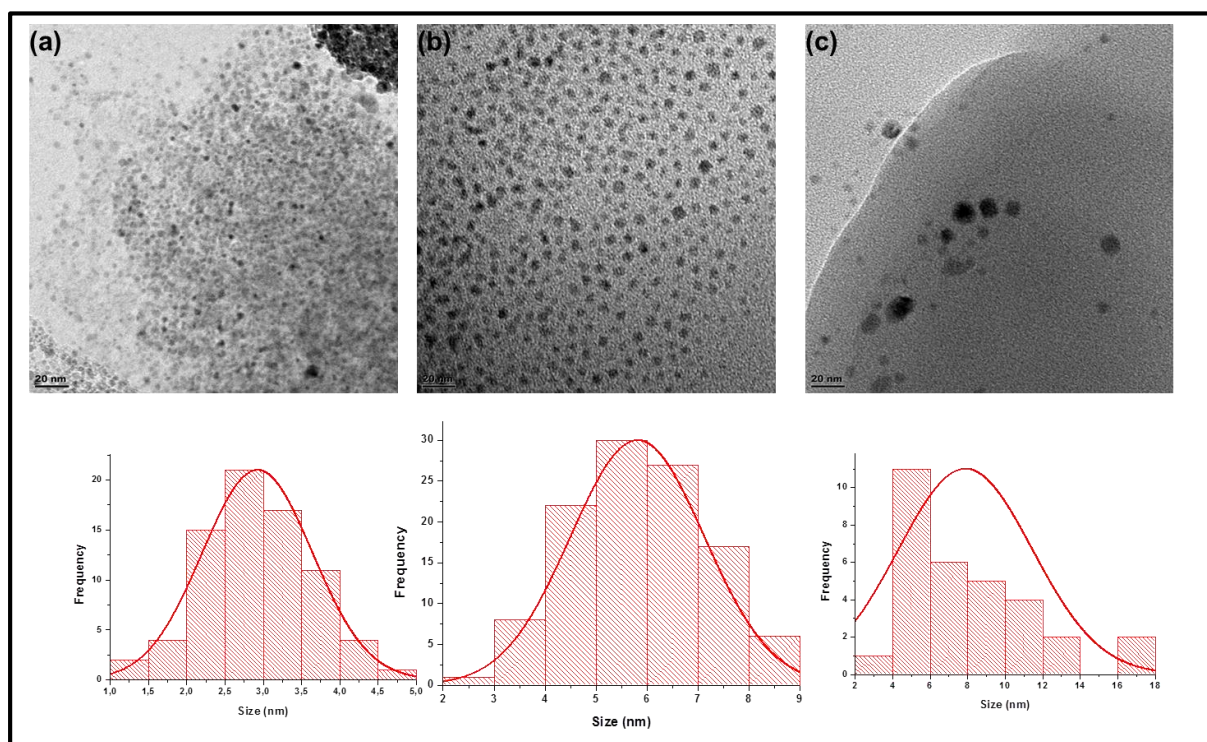


Figure 23: TEM images and their histograms of Ni_3S_4 nanoparticles prepared with 0.3 g of complex III with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Fig. 24 shows XRD pattern of particles synthesized at different temperatures from complex III. Low (140 °C) and high (180 °C) temperatures show some impurities of C_7OS_8 (peaks marked by a sphere) and pure nickel and this was confirmed by TGA which showed a mixture of nickel and nickel sulphide at the final residue and also some impurities of oxygen. However middle temperature (160 °C) only shows Ni as an impurity. The presence of these impurities can be due to incomplete reaction time or that the particles were not washed enough. Four major peaks were observed and they were indexed to cubic Ni_3S_4 with 2θ values at 26 °, 37 °, 64 ° & 77 °. These diffraction peaks matches well with the standard XRD pattern (JCPDS No. 00-043-1469). At high temperature an introduction of monoclinic Ni_xS_6 phase was observed (marked

by a square) and this indicates that temperature does not only arrests the nanoparticle growth it also introduced phase change.

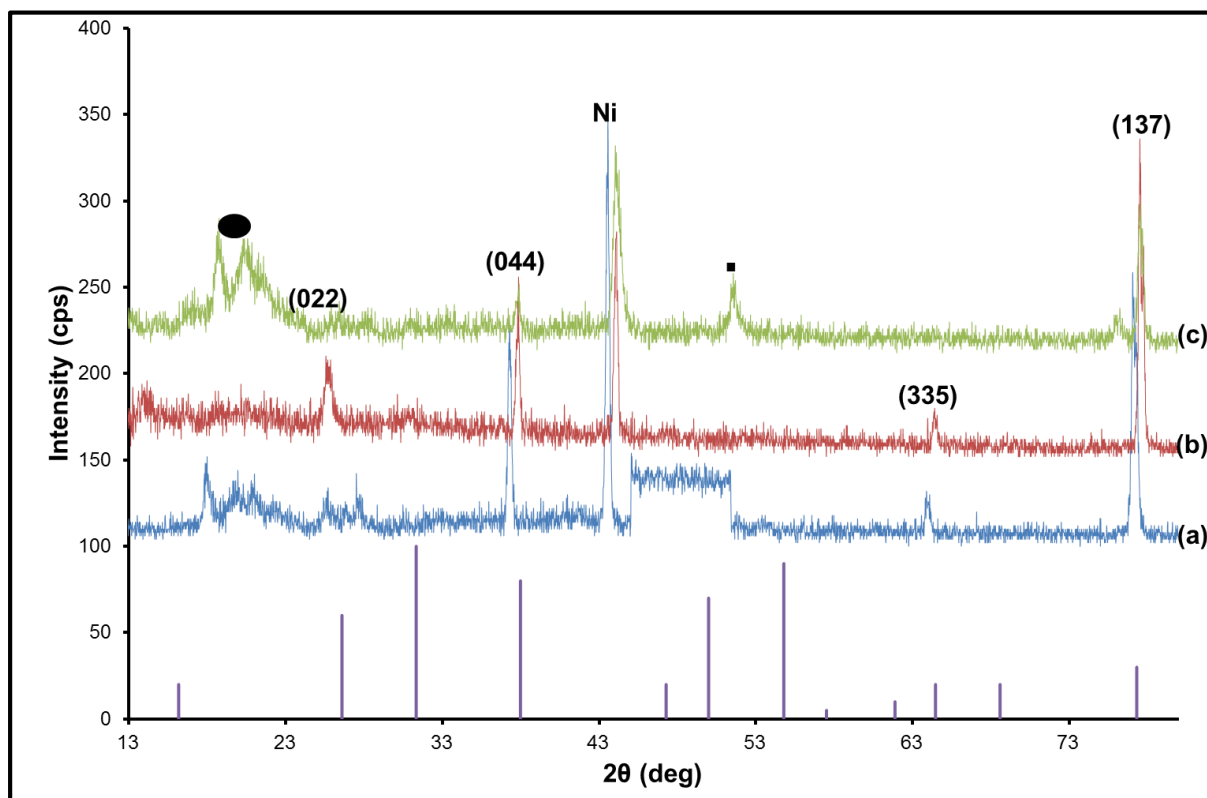


Figure 24: Powder X-ray diffractogram of Ni_3S_4 , $\blacksquare \text{Ni}_x\text{S}_6$ nanoparticles and $\bullet \text{C}_7\text{OS}_8$ synthesized from 0.3 g complex III in 6 g HDA at a) 140 °C, b) 160 °C and c) 180 °C.

(b) HDA- Ni_3S_4 Nanoparticles prepared using complex IV (Temperature variation)

The preparation of the HDA-capped Ni_3S_4 nanoparticles was done under similar conditions with complex III but in this case complex IV was used. The conditions are outlined in Table 7. The optical and morphological features were explored for the synthesized nanoparticles using UV/vis and PL spectroscopy, TEM and XRD techniques.

The absorption spectra for the nickel sulphide nanoparticles synthesized at different temperatures from complex IV are shown in Fig. 25(a-c)). Nickel sulphide nanoparticles show a blue shift in relative to bulk NiS (495 nm). It was observed that as the temperature was increased the size of the particles also increased and this could be due to Ostwald ripening

effect. The absorption band for the particles synthesized at lower temperature (Fig. 25(a)) was distinctly sharper and more pronounced than the absorption bands of the particles synthesized at higher temperatures. The spectra at high temperatures (Fig. 25(b) and (c)) shows some degree of tailing and this is due to a change of shape or anisotropic particles or the presence of larger elongated particles as seen on TEM images.

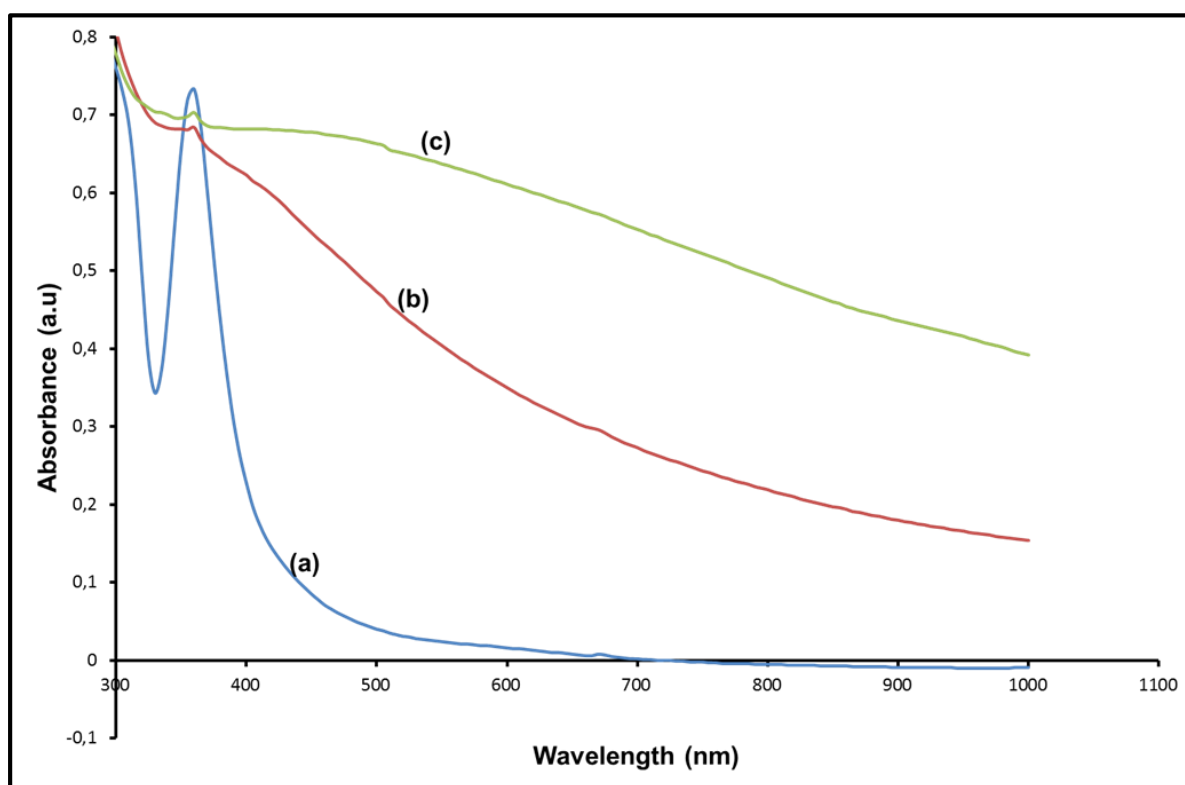


Figure 25: UV-VIS spectra of Ni_3S_4 nanoparticles prepared with 0.3 g of complex IV with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

The emission spectra for the nickel sulphide nanoparticles synthesized at different temperatures from complex IV is shown in Fig. 26(a-c). Photoluminescence spectra were observed with the strong emission peaks centred at 696 nm, 698 nm and 700 nm respectively (Table 9) when excited at 520 nm. The emission peaks were red shifted in relative to the absorption peaks. The broad emission peaks at higher temperatures are an indication of a broader size distribution shown by the distribution curves or the presence of anisotropic particles and this was confirmed by TEM. The emission maxima slightly shifts to the higher wavelength as the temperature was

increased or they are slightly red shifted to each other and this indicates that the particles are growing bigger as the temperature was increased.

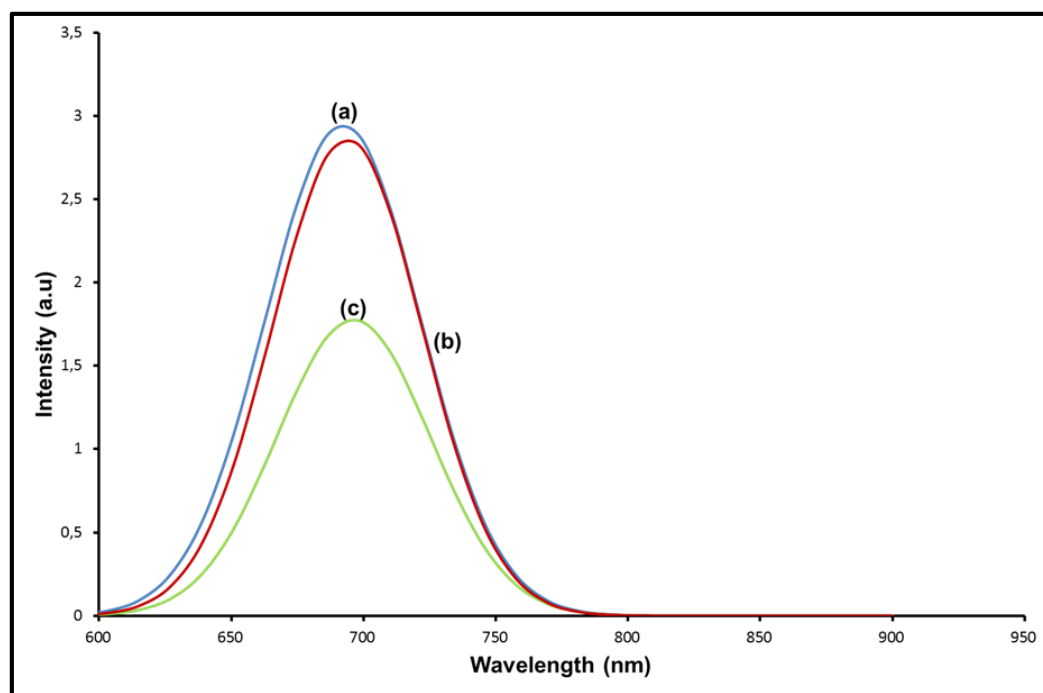


Figure 26: PL spectra of Ni_3S_4 nanoparticles prepared with 0.3 g of complex IV with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Table 8: Absorption bands and emission maxima of Ni_3S_4 nanoparticles prepared with 6 g HDA at 140 °C, 160 °C and 180 °C.

Reaction temperature (°C)	Absorption bands (nm)	Emission maximum (nm)
140	360	696
160	365	698
180	380	700

The TEM images of particles prepared from complex IV at different temperatures are shown in Fig. 27(a-c). The images show that as the temperature was increased the size of the particles also increased. There was a shape transformation from isotropic to anisotropic shaped particles and that means the reaction is favoured by kinetic growth regime. There is an evolution of shape from spherical particles Fig. 27(a) to a mixture of cubes, rods, spheres and triangles Fig.

27(b) shaped particles with an increase in temperature and this can be due to methyl group attached. Nair and Scholes reported that anisotropic particle growth could be due to oriented attachment (Nair and Scholes, 2006). As the temperature was increased to 180 °C the particles became aggregated. The estimated average size at 140 °C was 4.21 ± 1.33 nm and for cubes at 160 °C since they are dominant was 8.86 ± 1.48 nm. It was observed that the particles are well dispersed and well resolved at 160 °C.

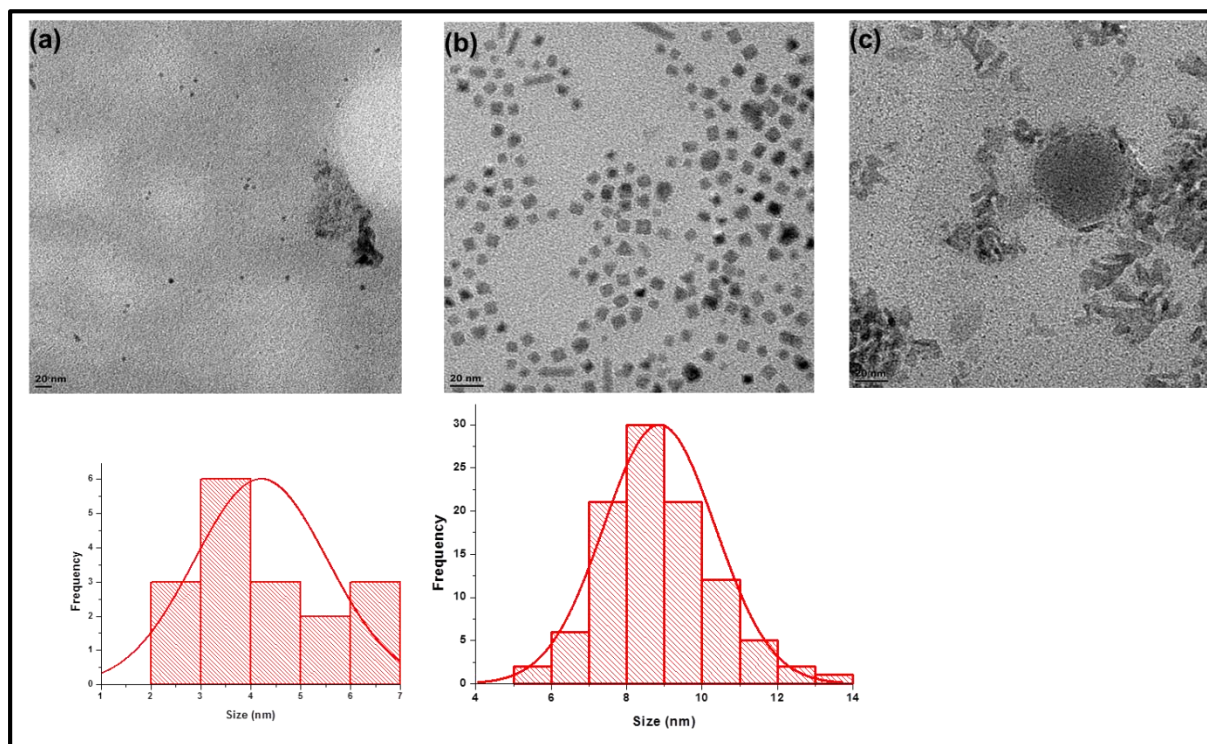


Figure 27: TEM images and their histograms of Ni_3S_4 nanoparticles prepared with 0.3 g of complex IV with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Fig. 28 shows XRD pattern of particles synthesized at different temperatures from complex IV. Low (140 °C) and high (180 °C) temperatures show some impurities of C_7OS_8 (peaks marked by a sphere) and pure nickel and this was confirmed by TGA final residue which showed the mixture of nickel and nickel sulphide. However middle temperature (160 °C) only shows Ni as an impurity. Five major peaks were observed and they were indexed to cubic Ni_3S_4 with 2θ values at 16 °, 26 °, 37 °, 64 °C and 77 °. These diffraction peaks matches well with the standard XRD pattern (JCPDS No. 00-043-1469). The wideness of the peaks indicates the presence of smaller particles and this was confirmed by TEM. At high temperature an introduction of

monoclinic Ni_xS_6 phase was observed (marked by a square) and this indicates that temperature does not only arrests the nanoparticle growth it also introduced phase change.

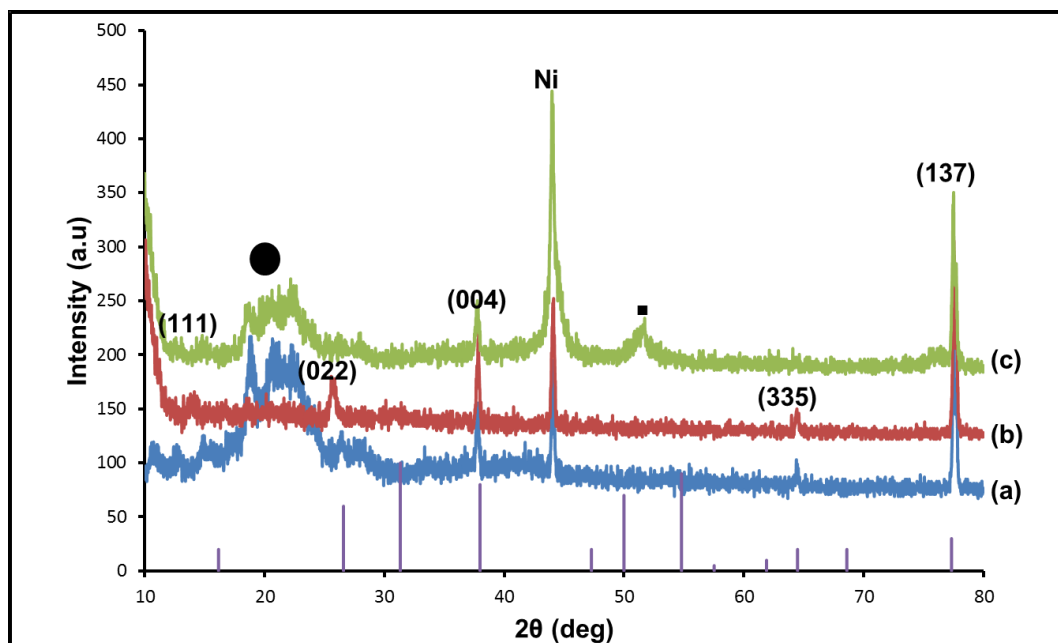


Figure 28: Powder X-ray diffractogram of Ni_3S_4 , $\blacksquare \text{Ni}_x\text{S}_6$ nanoparticles and $\bullet \text{C}_7\text{OS}_8$ nanoparticles synthesized from 0.3 g complex IV in 6 g HDA at a) 140 °C, b) 160 °C and C) 180 °C.

(c) HDA-nickel sulphide nanoparticles prepared using complex III (Conc variation)

Table 10 shows the reaction parameters for the preparation of nickel sulphide nanoparticles by using various concentrations of complex III, while no other parameters were changed.

Table 9: Variation of concentration in the preparation of HDA-nickel sulphide nanoparticles using complex III

Surfactant (HDA) mass (g)	Complex III mass (g)	Temperature (°C)	Time (Minutes)
6.0	0.3	160	60
6.0	0.35	160	60
6.0	0.4	160	60

The absorption spectra of nickel sulphide nanoparticles from complex III is shown in Fig. 29(a-c). The absorption bands were observed at a) 365 nm, b) 485 nm and c) 390 nm respectively and were blue shifted from the bulk nickel sulphide. The spectra show that as the concentration was increased the size of the particles also increased shown in Table 11. The first absorption peaks around 350 nm was due to instrumental error (the glass cuvettes were reading those peaks) at higher concentrations. The absorption band at low concentration was shifted to lower wavelength and that indicate the presence of smaller particles and this was confirmed by TEM.

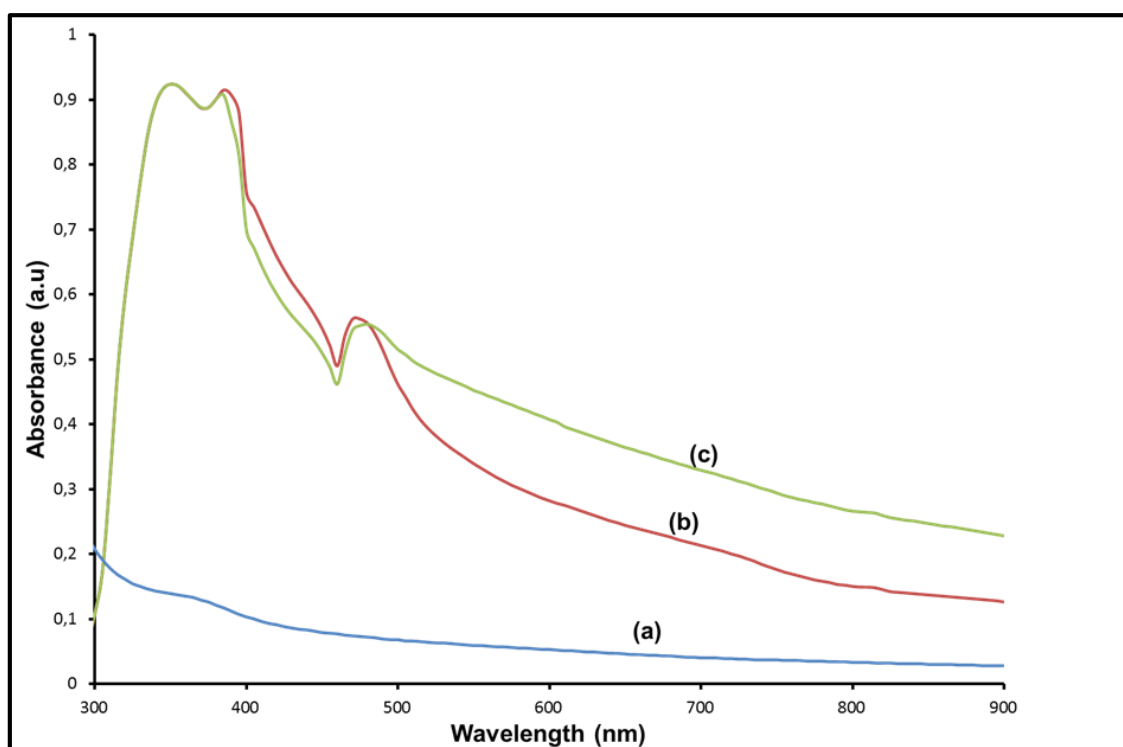


Figure 29: UV/Vis spectra of nickel sulphide nanoparticles prepared from (a) 0,3 g, (b) 0,35 g and (c) 0,4 g of complex III with 6 g of HDA at 160 °C.

The emission spectra of nickel sulphide nanoparticles from complex III is shown in Fig. 30 (a-c). The emission maxima of the samples were red shifted from their respective absorption bands. The emission maxima were observed at 677 nm, 688 nm and 657 nm from low concentration to high concentration. The emission peaks shows no specific trend and this can be due to change of shapes and this was confirmed by TEM. The emission peaks for the sample prepared at low concentration have a narrow shape which indicates good passivation of particles. However, for the nanoparticle prepared at high concentrations (Fig. 30(b) and c)), the

emission peaks are broad which indicate that the particles are polydispersed. The emission maximum shift to higher wavelength as the concentration of the precursor was increased however the emission maximum at higher concentration (Fig. 30(c)) was blue shifted from the others, this can be due to change in shape but the morphology was unclear.

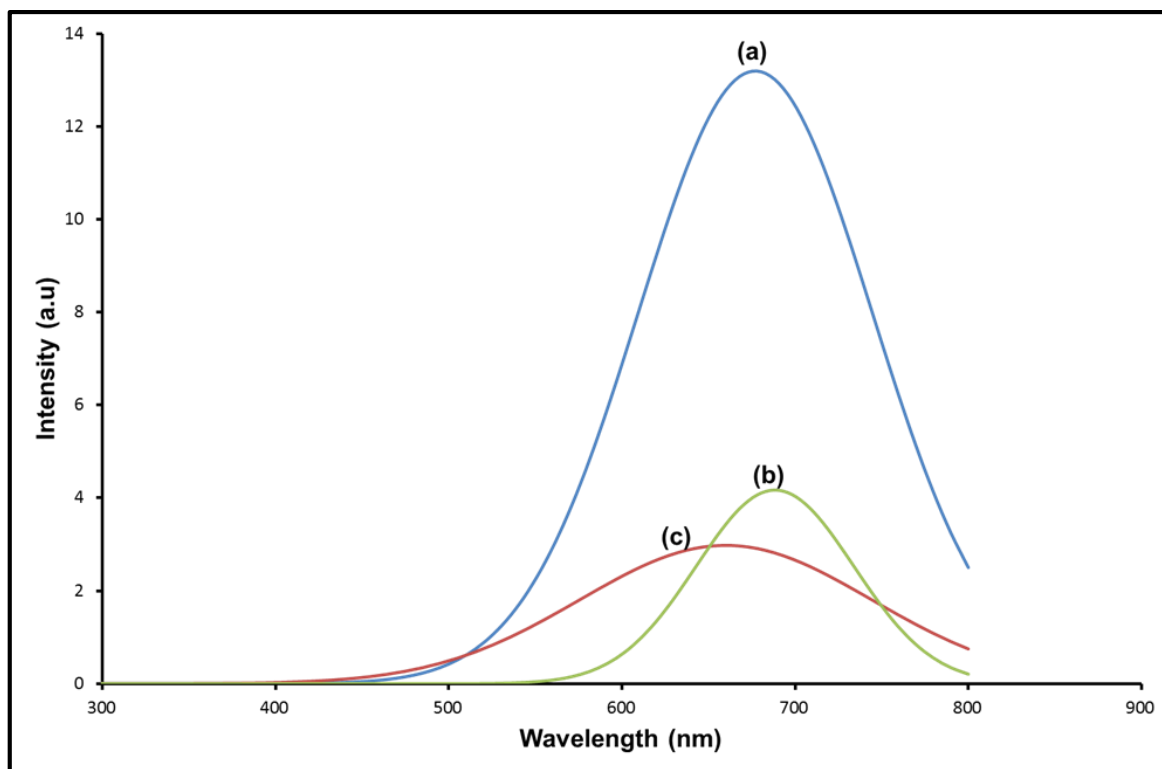


Figure 30: PL spectra of nickel sulphide nanoparticles prepared from (a) 0,3 g, (b) 0,35 g and (c) 0,4 g of complex III with 6 g of HDA at 160 °C.

Table 10: Absorption bands and emission maxima of the nickel sulphide nanoparticles prepared at 160 °C using various amount of precursor in HDA.

Precursor concentration (g)	Absorption bands (nm)	Emission maximum (nm)
0.3	365	677
0.35	485	688
0.4	490	657

Fig. 31(a-c) shows the TEM images for nickel sulphide nanoparticles synthesized from complexes III at different concentrations. These images show that as the concentration was increased the size of the particles also increased and this can be due to Ostwald ripening effect. The nanoparticles synthesized were dominated by cubes with an average size of 5.81 ± 1.31 nm.

at low concentration Fig. 31(a). By further increasing the concentration Fig. 31(b) under similar reaction conditions the shape of the particles changes to stacked sheets with small cubes on top with the average size of 11.21 ± 3.36 for cubes and 106.91 ± 29.22 nm for sheets. At a higher concentration the particles are agglomerated and the morphology is unclear.

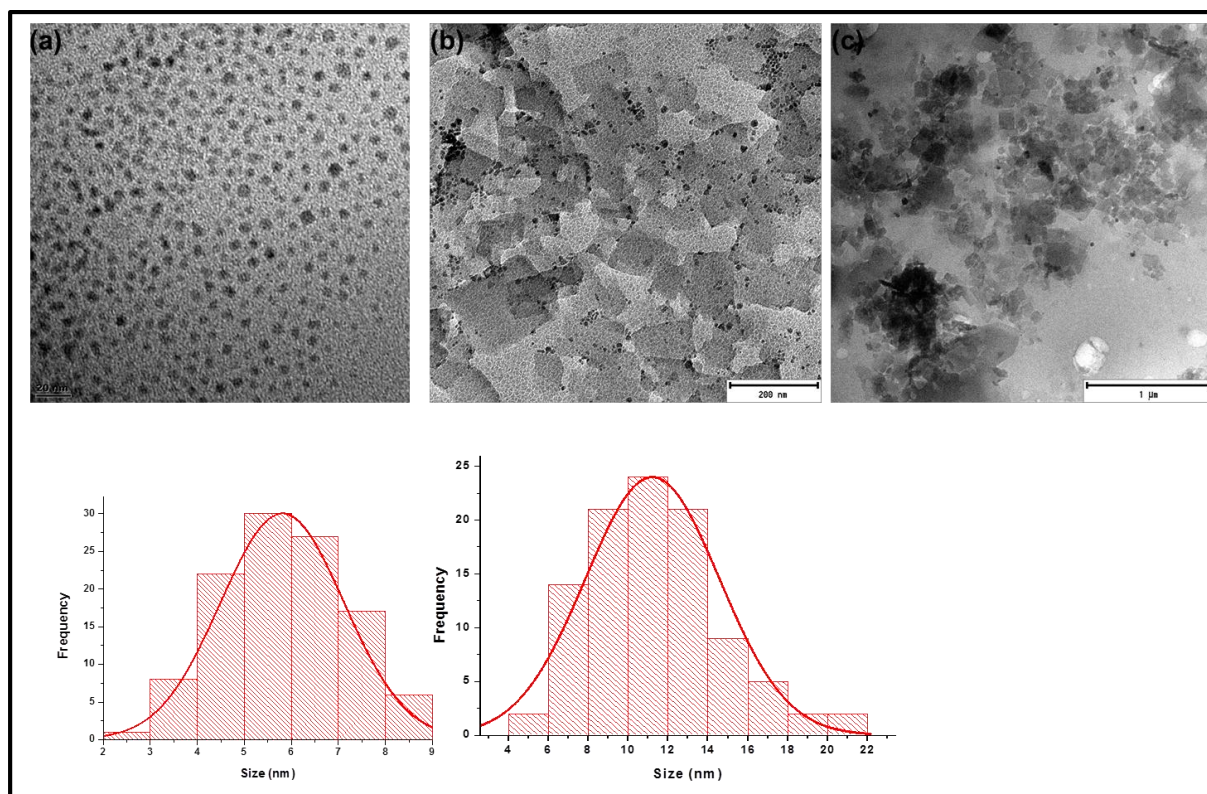


Figure 31: TEM images and their histograms of nickel sulphide nanoparticles prepared from (a) 0, 3 g, (b) 0, 35 g and (c) 0,4 g of complex III with 6 g of HDA at 160 °C.

Fig. 32 shows XRD pattern of particles synthesized from complex III (a-c) by varying concentration. The pattern shows side reactions of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (marked by a star) at high concentrations. However at 0.35 g a peak for hexagonal NiS was observed marked by a sphere. The miller index (044) was also observed and this indicates that there was a mixture of phases at 0.35 g. Four major peaks were observed at low concentration Fig. 32(a) and they were indexed to cubic Ni_3S_4 with 2θ values at 26° , 37° , 64° and 77° . The diffraction peaks match well with the standard XRD pattern (JCPDS No. 00-043-1469). Nickel peak was also observed as an impurity at low concentration.

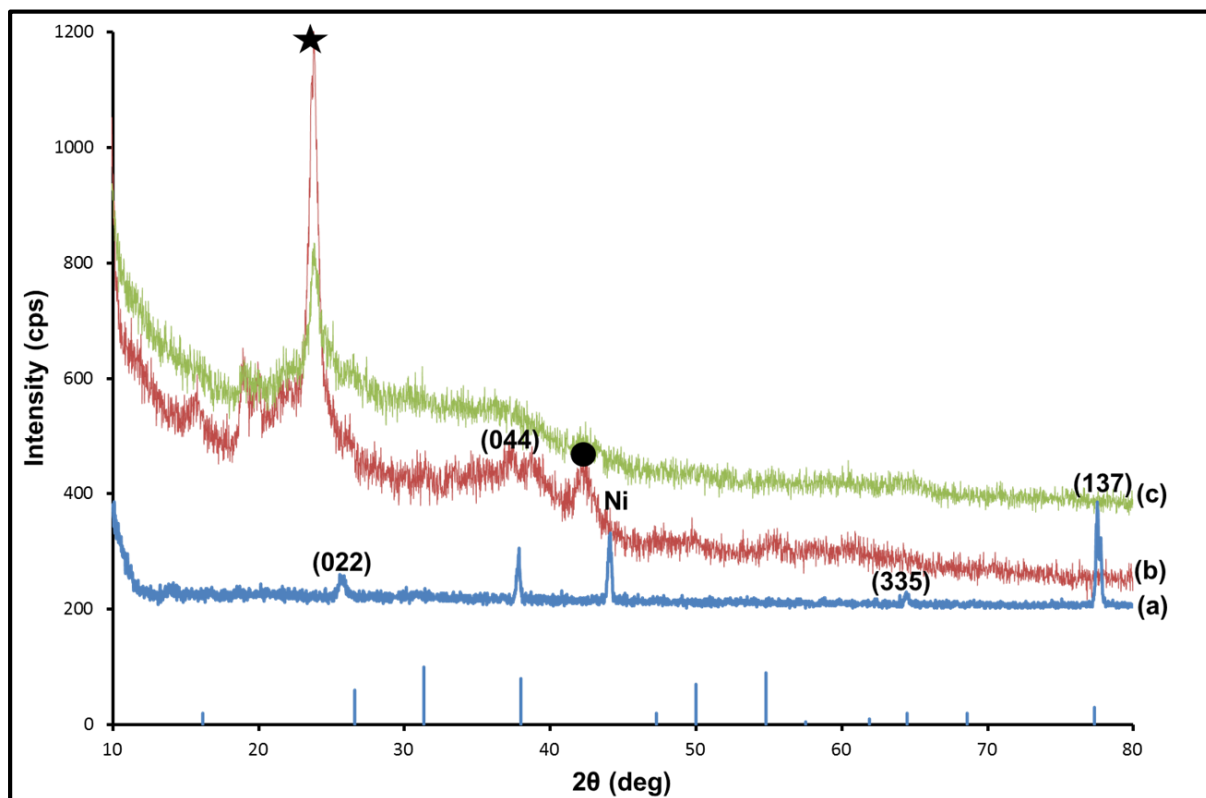


Figure 32: XRD patterns of nickel sulphide Ni_3S_4 , $\bullet$ NiS and $\star$ $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ prepared from (a) 0, 3 g, (b) 0, 35 g and (c) 0, 4 g of complex III with 6 g of HDA at 160 °C.

(d) HDA-nickel sulphide Nanoparticles prepared using complex IV (Conc variation)

Table 12 shows the reaction parameters for the preparation of Ni_3S_4 nanoparticles by using various concentrations of complex IV, while no other parameters were changed

Table 11: Variation of concentration in the preparation of HDA- Ni_3S_4 nanoparticles using complex IV

Surfactant(HDA)mass(g)	ComplexIV mass(g)	Temperature (°C)	Time (Minutes)
6	0.3	160	60
6	0.35	160	60
6	0.4	160	60

The absorption spectra of Ni_3S_4 nanoparticles from complex IV are shown in Fig. 33 (a-c). The absorption bands were blue shifted in relative to the bulk nickel sulphide of 495 nm. The

absorption bands at low and high concentrations were observed at a) 320 and c) 360 nm, the absorption spectrum at 0.35 g (b) was featureless. The tailing of absorption spectra at low and high concentrations indicates the presence of anisotropic particles and this was confirmed by TEM.

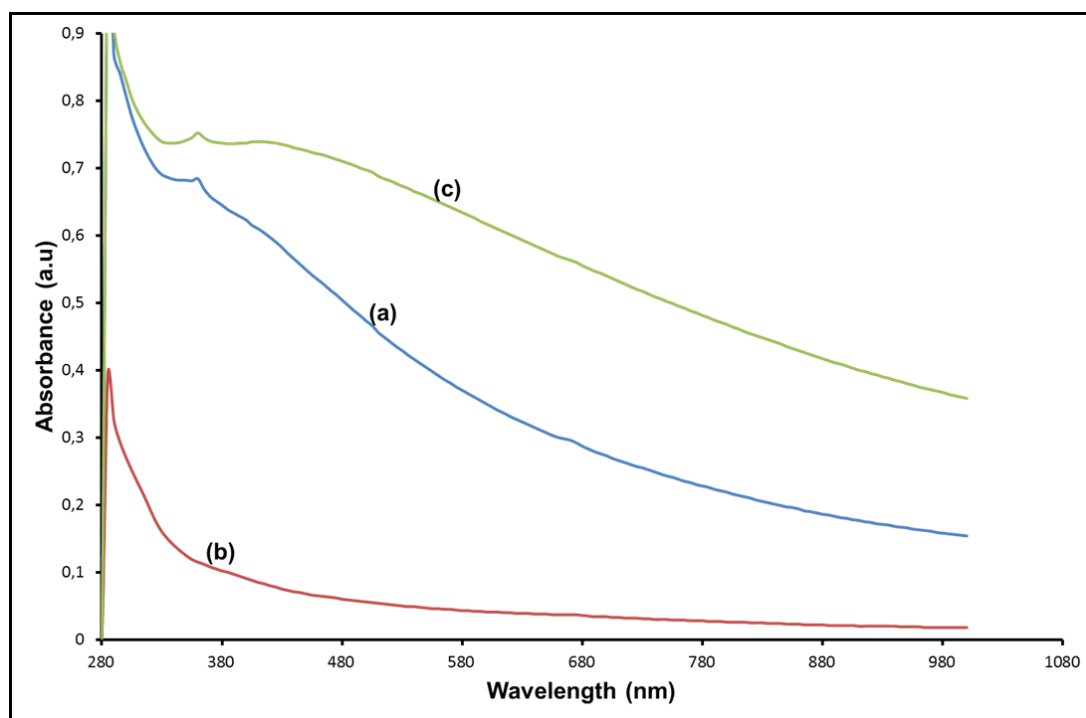


Figure 33: UV/Vis spectra of Ni_3S_4 nanoparticles prepared from (a) 0, 3 g, (b) 0, 35 g and (c) 0, 4 g of complex IV with 6 g of HDA at 160 °C.

The emission spectra of Ni_3S_4 nanoparticles from complex IV are shown in Fig. 34 (a-c). The emission maxima of the samples were red shifted from their respective absorption bands. The emission maxima were observed at 698 nm, 698 nm and 688 nm from low concentration to high concentration excited at 520 nm (Table 13). The photoluminescence spectra for complex IV show broad emissions peaks which are an indication of polydispersed particles. The emission maximum shift to lower wavelength at higher concentration and this can be due to change of shapes. The narrow emission peak at low concentration is an indication of smaller sizes.

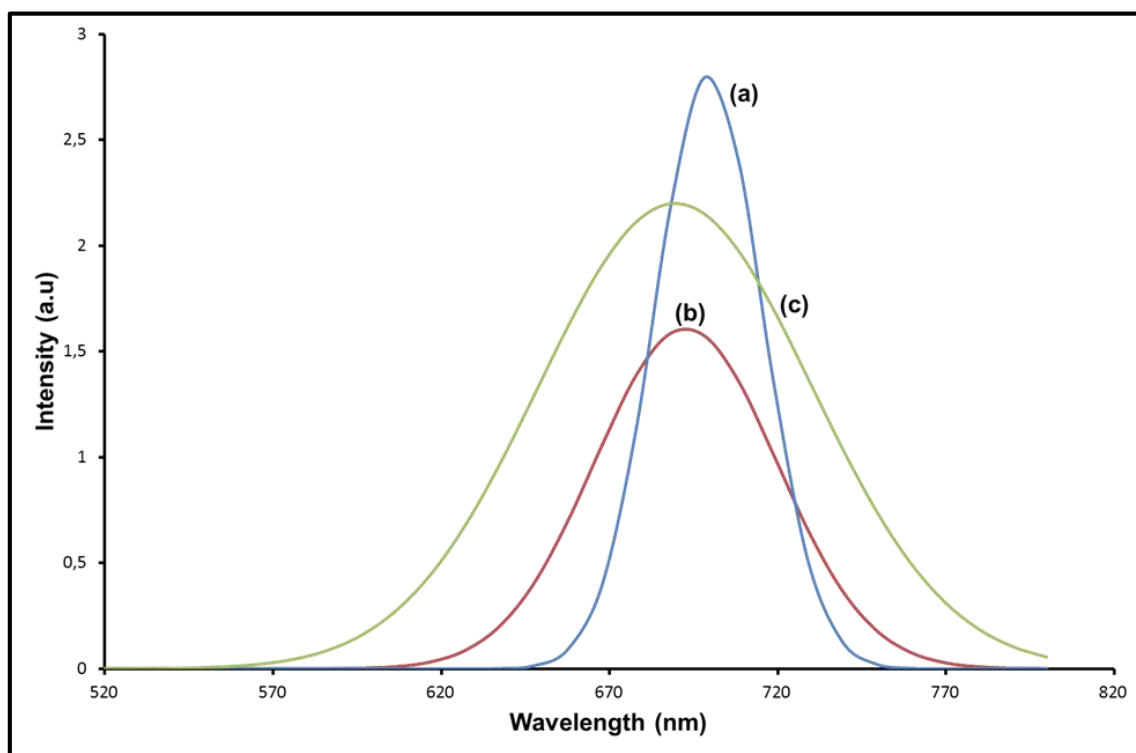


Figure 34: PL spectra of Ni_3S_4 nanoparticles prepared from (a) 0, 3 g, (b) 0, 35 g and (c) 0, 4 g of complex IV with 6 g of HDA at 160 °C.

Table 12: Absorption bands and emission maxima of the Ni_3S_4 nanoparticles prepared at 160 °C using various amount of precursor in HDA.

Precursor concentration (g)	Absorption bands (nm)	Emission maximum (nm)
0.3	320	698
0.35	-	698
0.4	360	688

Fig. 35 (a-c) shows the TEM images for nickel sulphide nanoparticles synthesized from complexes IV at different concentrations. The images show that as the concentration of the particles was increased the size of the particles also increased and this was promoted by the amount of precursor provided in the nucleation and growth of particles. The images show that particles were dominated by cubes and spheres moreover rods and triangles also present at all concentrations. At low concentration the particles were well resolved but as the concentration was increased the particles joined other forming long rods and bigger cubes, further increasing the concentration the particles were losing shapes forming squasi spheres. The average sizes

for the cubes and spheres were found to be 8.87 ± 1.48 nm, 10.26 ± 3.65 nm and 10.42 ± 5.18 nm respectively. The mixed morphology was promoted by the methyl group attached which caused the instability of particles.

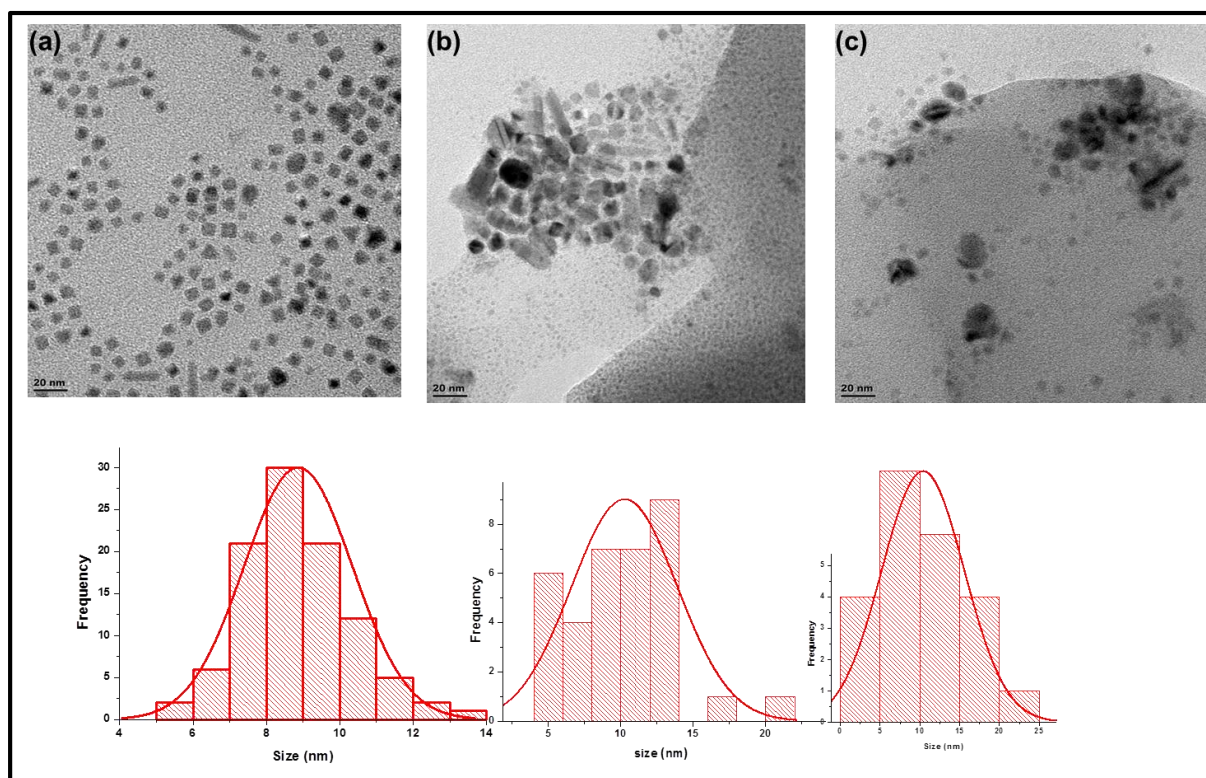


Figure 35: TEM images and their histograms of Ni_3S_4 nanoparticles prepared from (a) 0, 3 g, (b) 0, 35 g and (c) 0, 4 g of complex IV with 6 g of HDA at 160°C .

Fig. 36 shows XRD pattern of particles synthesized at different concentrations from complex IV. At high temperatures some impurities of C_7OS_8 (peaks marked by a sphere) and pure nickel are observed. However at low temperature (140°C) only Ni was observed as an impurity. Five major peaks were observed and they were indexed to cubic Ni_3S_4 with 2θ values at 16° , 26° , 37° , 64° and 77° at all temperatures. These diffraction peaks matches well with the standard XRD pattern (JCPDS No. 00-043-1469). The wideness of the peaks indicates the presence of smaller particles and this was confirmed by TEM.

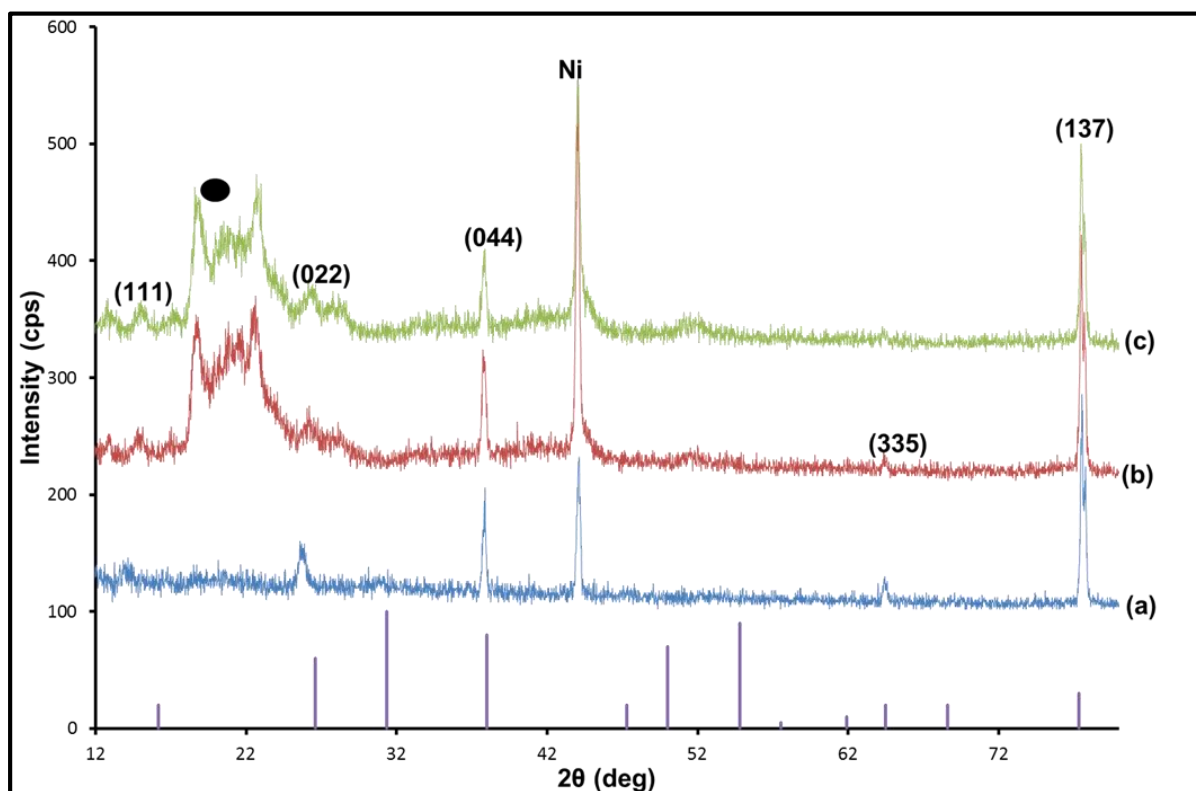


Figure 36: XRD patterns of Ni_3S_4 nanoparticles and $\bullet$ C_7OS_8 prepared from (a) 0, 3 g, (b) 0, 35 g and (c) 0, 4 g of complex IV with 6 g of HDA at 160 °C.

5.2 Conclusions

Nickel sulphide nanoparticles were synthesized by the thermal decomposition of benzimidazole and 2-methylbenzimidazole dithiocarbamate complexes (III and IV) in the presence of hexadecylamine capping agent. Optical properties and TEM revealed that the study of reaction temperature have more effect on the size and shape of the nanoparticles. This was confirmed by the increase in the band edges and the change in shape of the nanoparticle prepared when increasing the reaction temperature. The optical measurements also supported the presence of smaller particles for all complexes. TEM showed better dispersity of the particles at 160 °C for all complexes and it was considered as the best temperature. Complex III was considered as the best because it showed most stable shapes (spheres and cubes) of nanocrystals. Complex IV displayed a mixture of spheres, cubes, triangles and rods at 160 °C. All complexes at different temperatures exhibited anisotropic shapes of particles. XRD for both complexes exhibited cubic phase of Ni_3S_4 at all temperatures however there was an introduction of a monoclinic phase of Ni_xS_6 at 180 °C. Complex VI showed a mixture of more

than two shapes and this was due to the orientated attachment (methyl group). The nature of the precursor was found to have an influence on the shape of the nanoparticles particles.

Nickel sulphide nanoparticles were synthesized by thermal decomposition of benzimidazole and 2-methylbenzimidazole dithiocarbamate complexes (III and IV) in the presence of hexadecylamine capping agent by varying the amount of the precursor. The optical measurements supported the presence of smaller particles at all concentrations except for complex III at higher concentrations. This was confirmed by TEM which exhibited a mixture of cubes and bigger sheets at high concentrations and a mixture of spheres and cubes at low concentration. It was also in line with XRD which showed broad peak width. Complex IV exhibited a mixture of spheres, cubes, triangles, squasi spheres (0.4 g) and rods. TEM showed better dispersity of particles at low concentration (0.3 g) for all complexes and it was considered as the best concentration. XRD for complex III showed cubic Ni_3S_4 at low concentration, a mixture of cubic Ni_3S_4 and hexagonal NiS when the concentration was raised to 0.35 g and impurities of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ at higher concentrations. XRD for complex IV displayed cubic phase of Ni_3S_4 at all concentrations and impurities of C_7OS_8 at higher concentrations.

Chapter 6

Characterization of HDA capped cobalt sulphide nanoparticles using benzimidazole dithiocarbamate and 2-methyldithiocarbamate as ligands

6.1 HDA capped cobalt sulphide nanoparticles

The synthetic procedure followed was thermal decomposition of benzimidazole dithiocarbamate and 2-methyldithiocarbamate complexes of cobalt in an inert environment in the presence of trioctylphosphine (solvent) and hexadecylamine (capping agent). The reaction condition such as temperature was varied to determine its effect on size and shape of the nanoparticles. Complex V and VI were used in this chapter and temperature was varied from 140, 160 to 180 °C while keeping other parameters constant. The reaction parameter such as temperature of the reaction has showed a profound effect on the size and morphology.

6.1.1 (a) HDA- cobalt sulphide Nanoparticles prepared using complex V (Temperature variation)

Table 14 shows reaction conditions for the preparations of cobalt sulphide nanoparticles at different temperatures using complex V, while keeping all the other parameters the same.

Table 13: Variation of temperature in the preparation of HDA-Co₃S₄ nanoparticles using complex V

Surfactant (HDA) mass (g)	Complex V mass (g)	Temperature (°C)	Time (Minutes)
6	0.3	140	60
6	0.3	160	60
6	0.3	180	60

Figure 37(a-c) shows the absorption spectra of Co_3S_4 synthesized from complex V at different temperatures. The bulk band edge of cobalt sulphide was reported to 1127.27 nm with a cubic structure (Bao et al., 2008b). The absorption spectra displayed three excitonic peaks and they were blue shifted in relative to the bulk cobalt sulphide. Cobalt sulphide bulk is composed of a conduction bands and a continuous valence resulting in a fixed energy band with a single absorption peak. The discrete atomic-like states with energies that are determined by the properties of the nanoparticles ascend as the cobalt sulphide becomes quantized. Thus, the observed three peaks of cobalt sulphide nanoparticles in the absorption spectra were due to the 1S, 1P and 1D transition, with the third excitonic peak categorized as the band gap of the material. Cobalt sulphide nanoparticles prepared at low temperature (Fig. 37(a)) exhibited three major absorption peaks, two excitonic peaks at 610 nm, 430 nm and a maximum peak at 320 nm. A fourth absorption shoulder or absorption peak was observed at 880 nm. This peak maybe attributed to absorption from a subset of larger particles and this was confirmed by TEM which showed a mixture of small and bigger particles. At 160 °C the spectrum displayed three excitonic peaks positioned at 605 nm, 425 nm and a maximum peak at 305 nm. At high temperature, cobalt sulphide also displayed three absorption peaks positioned at 600 nm, 415 nm and a maximum peak at 310 nm respectively. Table 15 clearly shows that as the temperature was increased, the size of the particles decreased. The pronounced excitonic peaks at high temperatures as well as high energy absorption feature indicate a stable and narrow size distribution and this was confirmed by PL which showed narrow emission peaks at high temperatures.

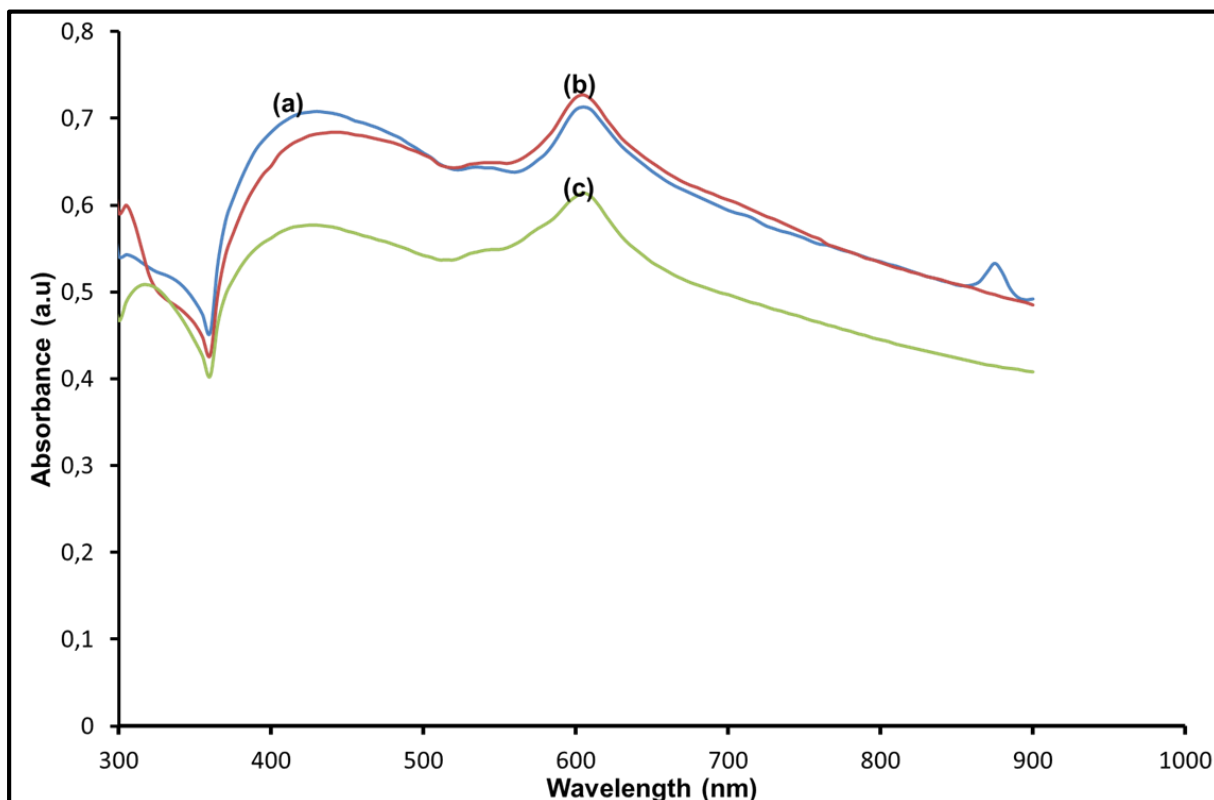


Figure 37: UV-VIS spectra of cobalt sulphide nanoparticles prepared with 0.3 g of complex V with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

The emission spectra of the samples prepared at different temperatures are given in Fig. 38. The emission maxima of the samples were red shifted from their respective absorption bands. This red shift in relation to the absorption bands was generally observed in II-VI semiconductor nanoparticles (Malik et al., 2000). The photoluminescence spectra at high temperatures (Fig. 38(b) and (c)) exhibited narrow emission peaks and this indicates narrow size distribution. The emission peak for the sample prepared at low temperature (Fig. 38(a)) has a broad shape, which indicates polydispersity of the particles and this was confirmed by TEM which showed a mixture of big and small particles. The emission maxima are shown in Table. 15. The samples were excited at 520 nm.

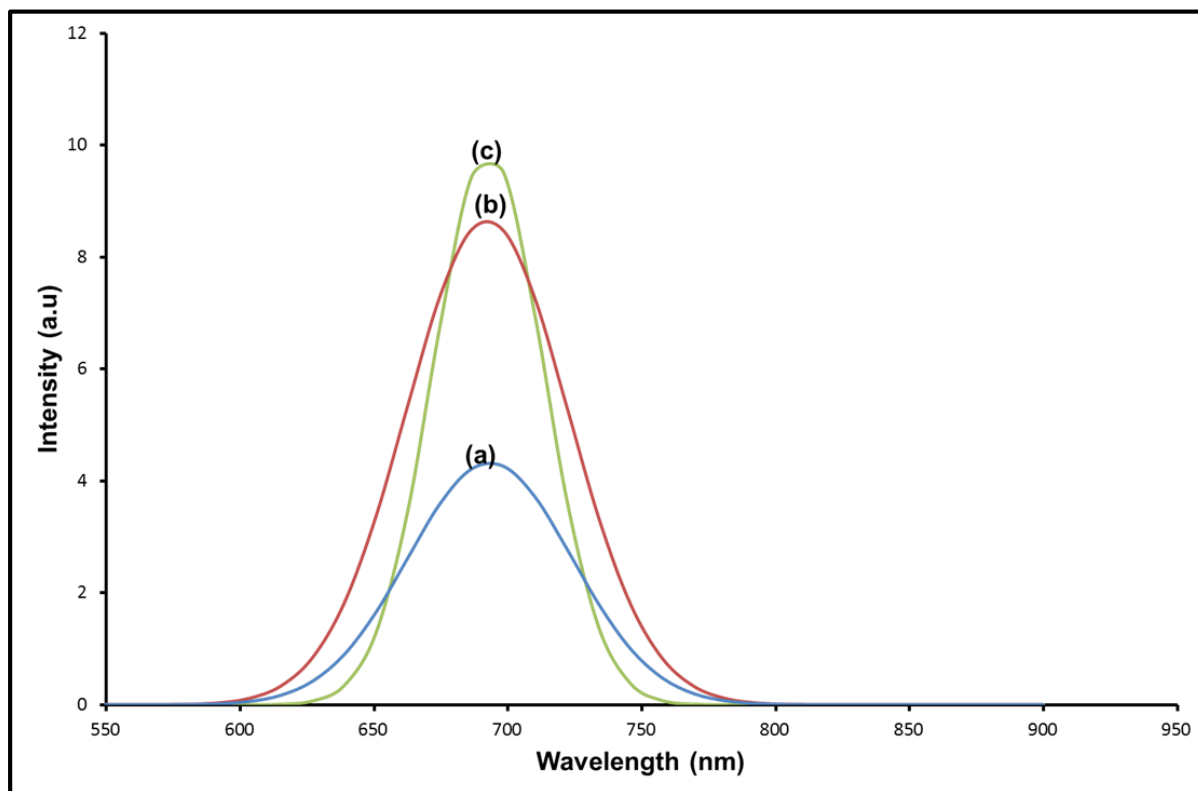


Figure 38: PL spectra of cobalt sulphide nanoparticles prepared with 0.3 g of complex V with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Table 14: Absorption bands and emission maxima of cobalt sulphide nanoparticles prepared with 6 g HDA at 140 °C, 160 °C and 180 °C.

Reaction temperature (°C)	Absorption bands (nm)	Emission maximum (nm)
140	430	698
160	425	698
180	415	698

Figure 39 (a-c) show TEM images of HDA capped cobalt sulphide nanoparticles prepared at different temperatures. The images show that as temperature was increased, the size of the particles decreased and this can be due to effect of decomposition rate. The morphology observed was close to spherical shapes. The average sizes were found to be 10 ± 3.89 nm, 5.45 ± 1.08 nm and 3.03 ± 1.90 nm respectively. Particles at low temperature were polydispersed

as shown by the histogram and this was confirmed by the broad emission peak in Fig. 38(a). Fig. 39(b) shows good passivation of Particles as shown by the histogram.

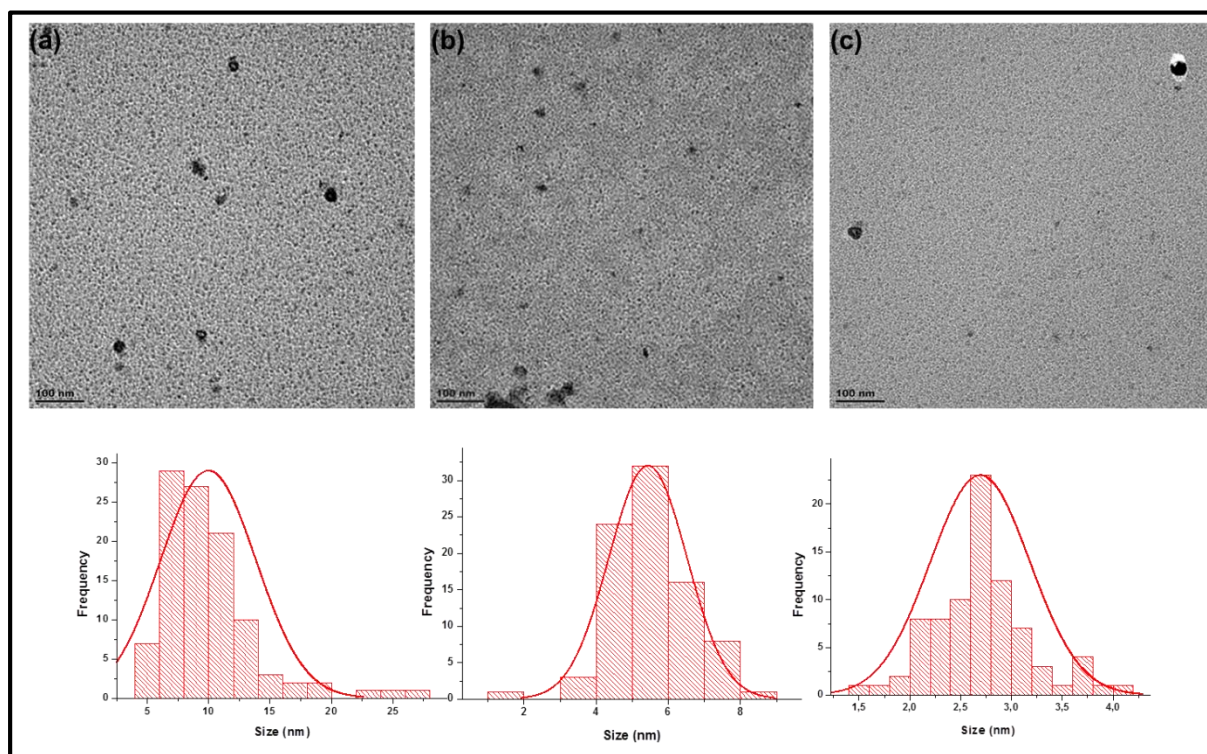


Figure 39: TEM images and their histograms of cobalt sulphide nanoparticles prepared with 0.3 g of complex V with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C

The X-ray diffraction patterns of the as-prepared cobalt sulphide nanoparticles capped by HDA synthesized from complex V at different temperatures for 1 h are shown in Fig. 40. All the main reflection peaks can be indexed as face-centred cubic Co_3S_4 (15.8° (111), 31.8° (222), 36.4° (400), 37.9° (331), 45.9° (422), 47.9° (551)), consistent with those reported values for bulk Co_3S_4 crystal (JCPDS Card 73-1703). The peak widths were found to be wide and this indicates that the particles have smaller sizes and it was confirmed by TEM. There were some impurities of C_7OS_8 (marked by a sphere) at all temperatures and this indicates that the nanoparticles prepared were not pure and this was confirmed by TGA which showed the presence of impurities. The XRD instrument that was used in this chapter did not have the zero background; therefore the peak marked with a star was for the empty sample holder.

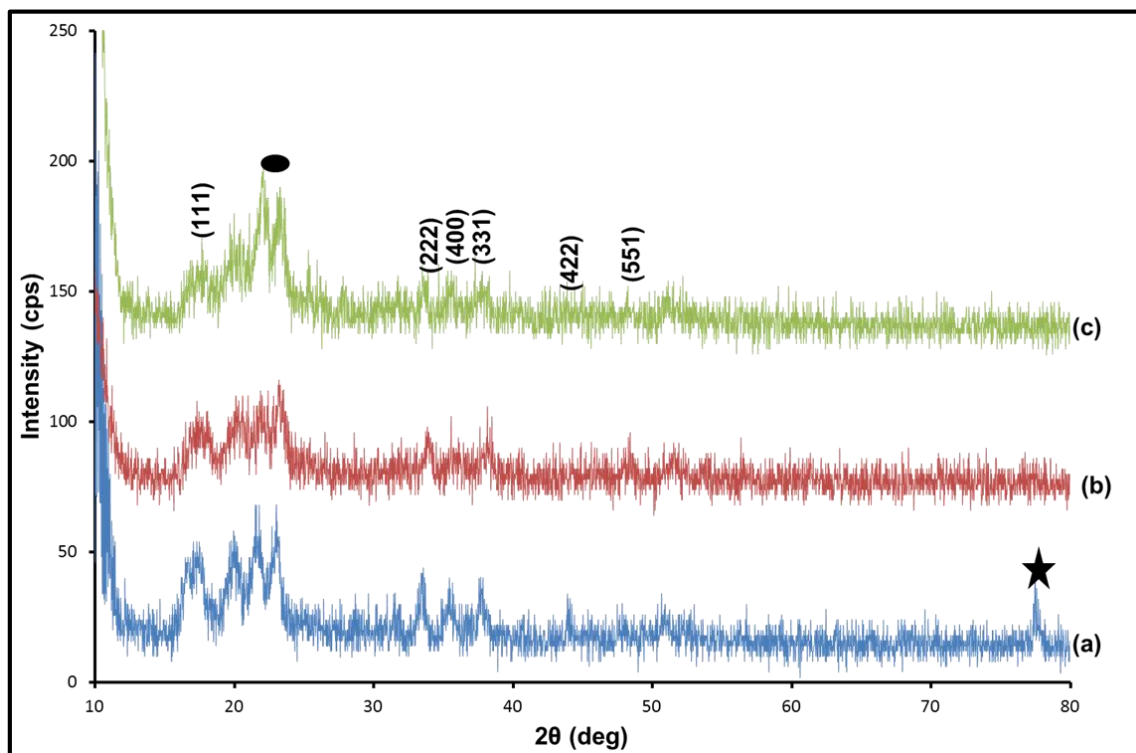


Figure 40: Powder X-ray diffractogram of Co_3S_4 nanoparticles, ● C_7OS_8 and ★ sample holder synthesized from 0.3 g complex V in 6 g HDA at a) 140 °C, b) 160 °C and c) 180 °C.

6.1.1 (b) HDA- cobalt sulphide Nanoparticles prepared using complex VI(Temp variation)

The preparation of the HDA-capped nanoparticles was done under similar conditions with complex V but in this case complex VI was used. The conditions are outlined in Table 14. The optical and morphological features were explored for the synthesized nanoparticles using UV/vis and PL spectroscopy, TEM and XRD techniques. Figure 41(a-c) shows the absorption spectra of nanoparticles synthesized from complex VI at different temperatures. The spectra are featureless and do not have any features of cobalt sulphide nanoparticles.

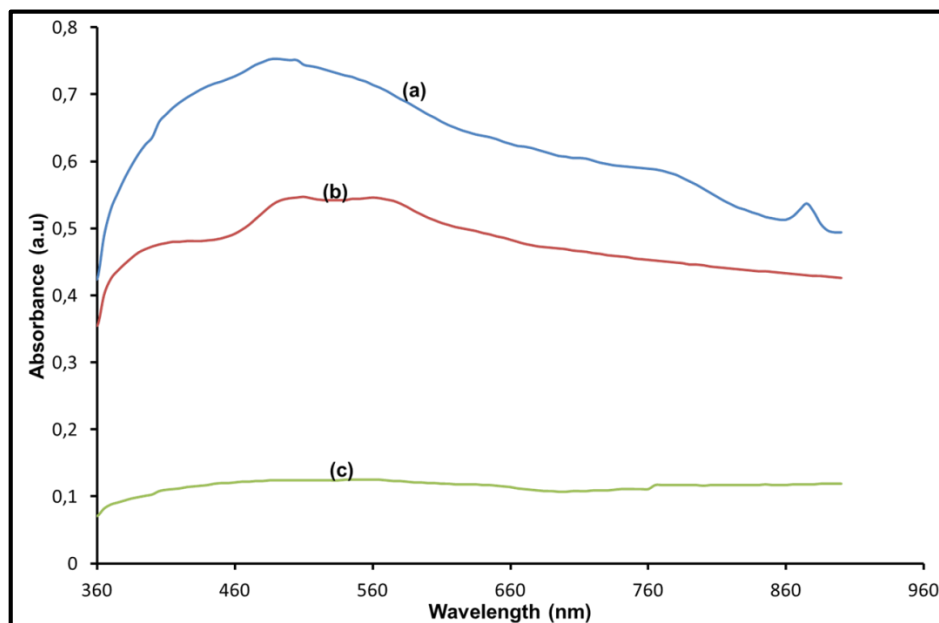


Figure 41: UV-VIS spectra of nanoparticles prepared with 0.3 g of complex VI with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

The emission spectra of the samples prepared at different temperatures are given in Fig. 42. The emission maxima of the samples were centred at 698 nm when excited at 520 nm. The emission peaks were broad and this is an indication of broad size distribution and this was confirmed by TEM which showed bigger particles.

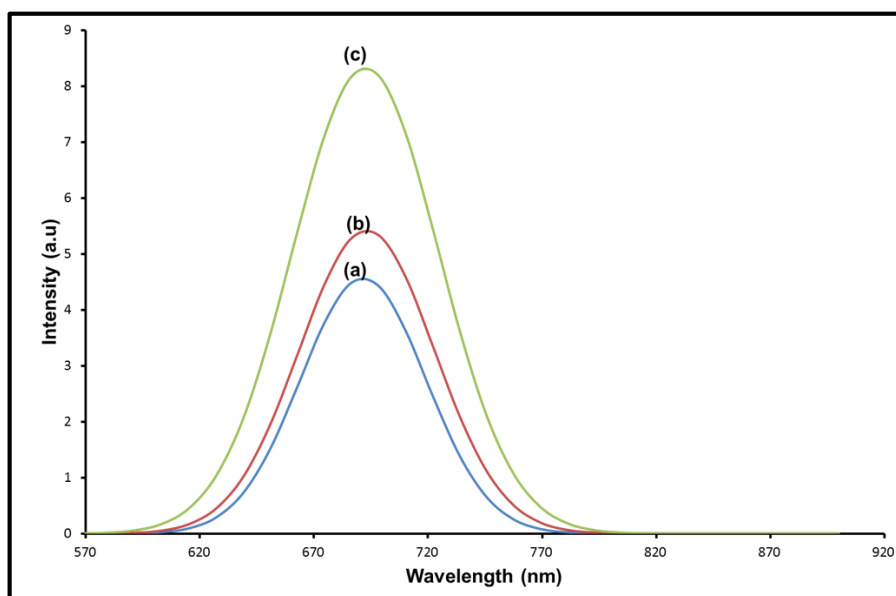


Figure 42: PL spectra of cobalt nanoparticles prepared with 0.3 g of complex VI with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

Figure 43(a-c) show TEM images of nanoparticles prepared at different temperatures. The images show that the morphology of the particles was undefined and the sizes were not calculated and this was confirmed by UV/vis spectra which also exhibited featureless spectra.

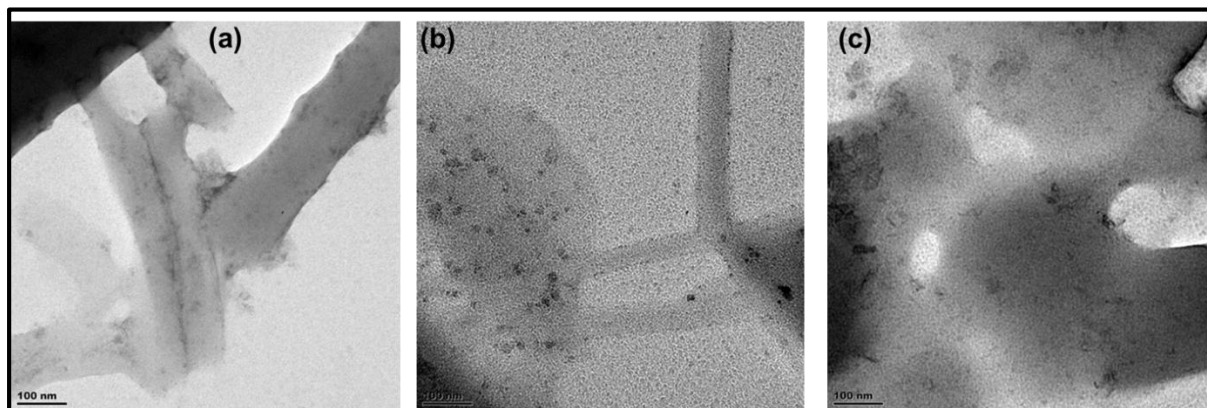


Figure 43: TEM images and their histograms of nanoparticles prepared with 0.3 g of complex VI with 6 g of HDA at (a) 140 °C, (b) 160 °C and 180 °C.

The X-ray diffraction patterns of the nanoparticles capped by HDA synthesized from complex VI at different temperatures for 1 h are shown in Fig. 6.1.8. The patterns exhibited some impurities of C_7OS_8 (marked by a sphere) at all temperatures. There was no any peak related to cobalt or cobalt sulphide and this could be due to that the time these nanoparticles were synthesized, the complexes had already decomposed. The peaks marked by triangles belong to the empty sample holder.

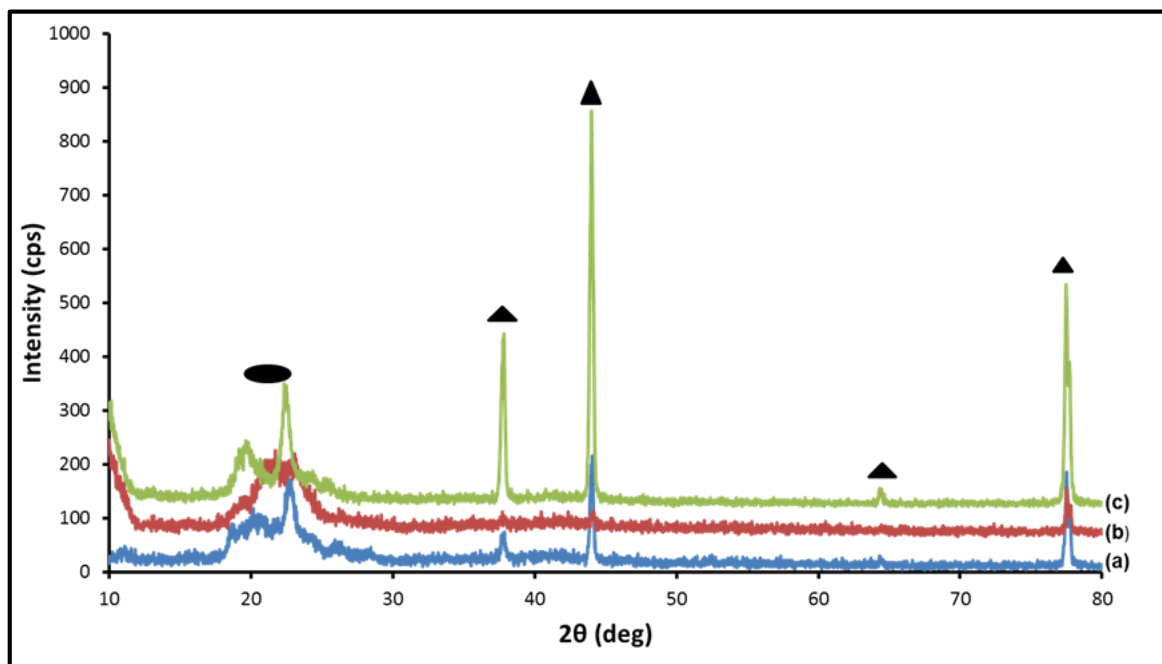


Figure 44: Powder X-ray diffractogram of ●C₇OS₈ and ▲sample holder synthesized from 0.3 g complex VI in 6 g HDA at a) 140 °C, b) 160 °C and c) 180 °C.

6.2 Conclusions

Cobalt sulphide nanoparticles were synthesized from complex V at different temperatures. Close to spherical shapes were observed at all temperatures for complex V. The absorption spectra showed a decrease in absorption maxima and band gap as the temperature was increased. This decrease in absorption maxima and band gap is associated to a decrease in particle size as the temperature was increased. At high temperatures (160 and 180 °C) smaller particles or good passivation of nanoparticles was observed and it was supported by optical measurements which showed narrow absorption and emission bands. Low temperature showed bigger particles which was supported by PL which showed broad emission peak. The XRD patterns confirmed face-centered cubic phase of Co₃S₄ and also confirmed the presence of smaller particles at higher temperatures with wide peak width. Complex VI showed featureless optical measurement, undefined bigger particles morphology and C₇OS₈ phase at all temperatures and it was concluded that the nanoparticles were synthesised using a decomposed complex.

Chapter 7

General conclusions and recommendations

7.1 Overall conclusions

Lead, nickel and cobalt sulphide nanoparticles were synthesized from lead, nickel and cobalt complexes of benzimidazole dithiocarbamate (I, III and V) and 2-methylbenzimidazole dithiocarbamate (II, IV and VI). The effect of nature of the precursor, temperature, amount of precursor concentration and type of capping agent were studied. Techniques such as microanalysis, FTIR spectroscopy and TGA were used to characterize the complexes. There was a percentage mismatch from elemental analysis for complexes I, III, IV and V. However complex II and VI calculated percentages were within the limits with the found percentages except for sulphur percentages which had low values. The found percentages on complexes I and III showed that the formed complexes were dimers and this was in line with FTIR spectroscopy which exhibited the doublet C=S band. Complexes IV and V showed that the leaving groups such as the sodium chlorides and hydroxides were still present in the complexes as impurities. FTIR spectroscopy confirmed the presence of $\nu(\text{C}=\text{S})$ singlet peak in all four complexes which indicates completely symmetrical bonding of the dithiocarbamate ligand to metal in a bidentate mode except for complex I and III which displayed a doublet peak which indicates monodentate coordination mode (dimeric molecules). The TGA curves decomposed to form a mixture of metal and metal sulphides for complex I, II, III and IV and this was confirmed by XRD which showed the presence of Pb and Ni metals in the patterns except for complexes V and VI. All benzimidazole complexes (I, III and V) decomposed at higher temperatures and were considered as the most stable complexes and this was confirmed by TEM which showed most stable shapes (spheres and cubes) of nanocrystals.

The effect of type of capping agent (HDA and TOPO) was studied by varying reaction temperature using complexes I and II on lead sulphide nanoparticles. From complexes I and II, HDA was found to be the stable capping agent with a larger capping density since it produced only cubic morphology and well resolved lead sulphide nanoparticles. TOPO capped lead sulphide nanoparticles from complexes I and II depicted anisotropic particles. The optical measurements supported the presence of smaller particles for both capping agents. TEM and

XRD for complex I showed that as the reaction temperature was increased the size of the particles decreased and this was due to effect of decomposition rate. The optical properties for TOPO capped PbS nanoparticles using complex I and II showed no specific trend and this was confirmed by TEM and XRD which also gave no specific trend. HDA capped PbS nanoparticles formed using complex I at 180 °C were monodispersed and it was considered as the best temperature. TOPO capped PbS nanoparticles formed using complex I at 160 °C were well resolved and the combination of optical and morphological properties proved that it was best temperature. HDA capped PbS nanoparticles formed using complex II at 140 °C were well resolved and it was considered as the best temperature. TOPO capped nanoparticle from complex II were agglomerated under all temperature conditions used. XRD patterns for all temperatures were well crystalline and matched cubic phase of PbS (Galena) except for HDA capped PbS from complex I at low temperature which matched face centred cubic phase. There was no significant change in the position of the peaks which means temperature only arrests the nanoparticle growth and does not introduce any phase change for both complexes except complex 1 at low temperature which introduced a new phase.

The temperature was observed to be affecting size, morphology and the composition of the nanoparticles on nickel sulphide nanoparticles. The study of temperature revealed the increase in band edges of nickel sulphide nanoparticles prepared by gradually increasing the reaction temperature. This suggests that the particles size of the nanoparticles was increasing in size with an increase in reaction temperature as a result of Oswald ripening. The TEM images confirmed a mixture of spheres and cubes with particle sizes increasing with an increase in temperature for complex III and a mixture of spheres, cubes, rods and triangles with cubes being dominant at 160 °C for complex IV. This is expected as the rate of the reaction increases with temperatures. XRD for both complexes exhibited cubic phase of Ni_3S_4 and impurities of C_7OS_8 at all temperatures however there was an introduction of a monoclinic phase of Ni_xS_6 at 180 °C. Complex III was considered as the best since it gave stable shapes of nanocrystals 160 °C was considered as the best temperature since it gave well resolved particles.

The study of the concentration depicted that an increase in the amount of precursor increases the size of the nanoparticles. But, the band edges of the nanoparticles did not show any specific trend hence they were blue shifted from their bulk. This was due to change in shapes and it was

also confirmed by PL spectra which did not show any trend. Complex III depicted a mixture of spheres and cubes at low concentrations, a mixture of cubes and sheets at high concentrations. Complex IV depicted a mixture of spheres, cubes, triangles and rods with cubes being dominant at all concentrations. XRD for complex III showed cubic Ni_3S_4 at low concentration, a mixture of cubic Ni_3S_4 and hexagonal NiS when the concentration was raised to 0.35 g and impurities of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ at higher concentrations. XRD for complex IV displayed cubic phase of Ni_3S_4 at all concentrations and impurities of C_7OS_8 at higher concentrations. And also nickel as a metal was observed and this observation was in line with the TGA which showed the residue of nickel sulphide plus nickel. The XRD pattern confirmed that the amount of the precursor has a significant effect on the composition of the nanoparticles as there were different phases observed as the amount of the precursor was varied. The capping molecule and the amount of the precursor have a profound effect on the growth of the nanoparticles.

Temperature was observed to be affecting size but did not have any significant effect on the morphology and the composition of the nanoparticles on cobalt sulphide nanoparticles. The absorption spectra from complex V showed a decrease in absorption maxima and band gap as the temperature was increased. This decrease in absorption maxima and band gap was associated to a decrease in particle size as the temperature was increased. At high temperatures (160 and 180 °C) smaller particles or good passivation of nanoparticles was observed and it was supported by optical measurements which showed narrow absorption and emission bands. Low temperature showed bigger particles which was supported by PL which showed broad emission peak. The morphology observed was close to spherical shapes. The XRD patterns confirmed face-centred cubic phase of Co_3S_4 and also confirmed the presence of smaller particles at higher temperatures with wide peak width. Complex VI showed featureless optical measurement, undefined bigger particles morphology and C_7OS_8 phase at all temperatures and it was concluded that the nanoparticles were synthesised using a decomposed complex. Nickel sulphide nanoparticles gave narrow size distribution at all concentrations and temperatures as compared to cobalt and lead sulphide nanoparticles.

7.2 Recommendations

Based on the results obtained and the conclusions provided in each section, the following recommendations were made;

1. The complexes based on both benzimidazole derivatives should be prepared using one-pot synthesis method and should be washed more than three times and then be recrystallized to remove impurities.
2. The more bulky ligands can be used and if successful they can also be explored using X-ray crystallography.
3. Dithiocarbamates complexes should be purchased to avoid the instability problems. Alternatively, the modification of the alkyl or aryl groups must be extended to relatively bulkiness to bring stability.
4. TOPO capped nickel and cobalt sulphide nanoparticles on the growth of nanoparticles should be investigated using complex III, IV, V and VI to understand their chemistry more.
5. Temperature above 200 °C should be investigated to understand the formation of anisotropic particles when TOPO was used as a capping agent and for the HDA capped nickel sulphide nanoparticles.
6. Variation of reaction time intervals is recommended in the preparation of nanoparticles.
7. During the synthesis of the ligands further organic separation techniques must be used such as column to understand fully the extent of the formation of the desired organic ligands.

7.3 References

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