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Synthesis of rare pure phase  $Ni_3S_4$  and  $Ni_3S_2$  nanoparticles in different primary amine coordinating solvents

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### ABSTRACT

Two nickel(II) complexes, namely piperidine (1) and tetrahydroquinoline (2) dithiocarbamate complexes were synthesized and characterized by infra-red spectroscopy, elemental analysis and thermogravimetric analyses. The single crystal X-ray structure of complex (1) was also elucidated. The as-synthesized complexes have been utilized as single source precursors to afford nickel sulfide nanoparticles  $Ni_3S_4$ ,  $Ni_3S_2$  and mixed phases via solvothermal decomposition in oleylamine (OLA), dodecylamine (DDA) and hexadecylamine (HDA) at different temperatures. Powder X-ray diffraction studies reveal that the temperature and capping agents play a significant role in determining the crystalline structure and chemical composition of the as-synthesized nanoparticles (NPs). Electron microscopy images showed formation of nanoparticles of various shapes ranging from spherical, tetrahedral and irregular shaped morphologies. Magnetization measurements indicated that  $Ni_3S_4$  nanoparticles prepared at 230 °C using DDA display ferromagnetic behaviour, while rhombohedral  $N_3S_2$  also prepared at 230 °C but using HDA, displayed paramagnetic property.

### **Keywords:**

Nickel sulfide, single source precursor, magnetic property, crystalline structure.

### 1. Introduction

The binary nickel sulfide system has raised interest because of its multiplicity of phases and stoichiometries which include NiS ( $\alpha$ -NiS and  $\beta$ -NiS), NiS<sub>2</sub>, Ni<sub>3</sub>S<sub>2</sub>, Ni<sub>3</sub>S<sub>4</sub>, Ni<sub>7</sub>S<sub>6</sub>, Ni<sub>6</sub>S<sub>5</sub> and Ni<sub>9</sub>S<sub>8</sub> [1-4]. The stability fields of naturally occurring mineral nickel-sulfur systems have been extensively studied and categorized as heazlewoodite (Ni<sub>3</sub>S<sub>2</sub>), polydymite (Ni<sub>3</sub>S<sub>4</sub>), millerite (Ni<sub>1</sub>. <sub>x</sub>S) and vaesite (NiS<sub>2</sub>) [1]. The phase diagram of the Ni-S system reveals that temperature, amount of nickel and/or sulfur present in the reaction system are key for the formation of a unique pure phase of nickel sulfide. Whilst a few of these phases have been identified as naturally occurring, others can be fabricated via laboratory protocols. The preparation of a specific Ni-S system is a challenge due not only to the existence of many phases within a single phase such as NiS ( $\alpha$ -NiS and  $\beta$ -NiS) but also to the co-existence of different phases making it difficult to extract a single pure phase [5].

The various phases of nickel sulfide nanomaterials are useful in many technological applications. NiS<sub>2</sub> has photocatalytic properties for hydrogen production and supercapacitors [6-8]. NiS has shown potential in dye-sensitized solar cells as counter electrodes, IR detectors and Li-ion storage applications [9-11]. Ni<sub>3</sub>S<sub>2</sub> has been reported as a potent catalyst for water splitting reactions [12-14] whereas Ni<sub>3</sub>S<sub>4</sub> has been reported to have applications in high performance supercapacitors [15, 16]. The low temperature heazlewoodite Ni<sub>3</sub>S<sub>2</sub>, NiS and Ni<sub>7</sub>S<sub>6</sub> phases have been reported to have common physical features of creamy bright yellow colour and are not easily distinguished from each other [1]. Ni<sub>3</sub>S<sub>2</sub> has two modifications namely a-Ni<sub>3</sub>S<sub>2</sub> (healzlewoodite) at low temperature ( $T \le 838$  °C) and  $\beta$ -Ni<sub>3</sub>S<sub>2</sub> at higher temperature (wide range of temperature) [17]. Reports have shown that at temperatures above 556 °C, Ni<sub>3</sub>S<sub>2</sub> changes into Ni<sub>3+x</sub>S with an fcc crystal structure [18]. Both Ni<sub>3</sub>S<sub>2</sub> and Ni<sub>7</sub>S<sub>6</sub> are non-magnetic whereas NiS is semi-metallic in nature, a p-type semiconductor whose paramagnetism is temperature independent [3]. Ni<sub>3</sub>S<sub>4</sub> polydymite has a cubic spinel crystal structure [19] which decomposes at higher temperatures (400 °C) to form NiS and NiS<sub>2</sub>.

Both nanocystalline NiS and Ni<sub>3</sub>S<sub>2</sub> can be prepared by various methods. Keigo *et al.* [20] reported the synthesis of NiS, Ni<sub>3</sub>S<sub>2</sub> and Ni<sub>9</sub>S<sub>8</sub> in high boiling point coordinating or non-coordinating solvents. The formation of pure phases was influenced by time, temperature and

boiling solvents. Salavati-Niasari *et al.* [21] were able to isolate NiS nanocrystals by using microwave irradiation from organometallic complexes. The same group reported the use of nickel dithiosemicarbazide as a new precursor to obtain nickel sulfide nanoparticles [21, 22]. Karthikeyan *et al.* [23] used hydrothermal method to prepare nickel sulfide with EDTA as a capping group. The obtained nanocrystals were mixed phases of Ni<sub>3</sub>S<sub>4</sub>, NiS<sub>2</sub>, NiS and Ni<sub>17</sub>S<sub>18</sub>. Ni<sub>3</sub>S<sub>4</sub> has been observed to co-exist with other forms of the Ni-S system i.e. NiS and NiS<sub>2</sub>. It is also a challenge to prepare this particular phase of nickel sulfide in the laboratory by a solid state reaction method, since at higher temperatures (360 °C) it is unstable [19]. The phase diagram of Ni-S system shows pure phase Ni<sub>3</sub>S<sub>4</sub> to be stable up to 356 °C [1, 14] and efforts to prepare it in laboratory have resulted in mixed phases [18]. Various researchers have reported the synthesis of Ni<sub>3</sub>S<sub>4</sub> by the colloidal route [5, 16, 24]. The solvent-less synthetic route produced mixed phases of NiS (millerite) and Ni<sub>3</sub>S<sub>4</sub> [18, 25].

Single source precursors (SSPs) have been widely used in the synthesis of different metal sulfides and various phases of nickel sulfide [25-28]. Dithiocarbamate complexes, in particular have been extensively used for the preparation of nickel sulfide nanoparticles with different phases [29-33]. The decomposition patterns of dithiocarbamates promote the formation of a particular pure phase of nickel sulfide [29, 33]. For example, Hogarth and co-workers [33] showed that temperature and solvents are key determinants of Ni-S phase obtained. Roffey *et al.* [29] reported the use of dithiocarbamate complexes for the preparation of a wide range of phase-pure nickel sulfide particles by the manipulation of different reaction conditions.

In this paper we report the use of bis(dipiperidinyldithiocarbamato) nickel(II) (1) and bis(ditetrahydroquinolinyldithiocarbamato) nickel (II) (2) complexes for the synthesis of pure phase of Ni<sub>3</sub>S<sub>4</sub>, Ni<sub>3</sub>S<sub>2</sub> and mixed phase of nickel sulfide nanoparticles. Magnetic measurements were showed to be phase dependent. An improved crystal structure of complex (1) is also elucidated [34].

#### 2. Experimental details

### 2.1. Materials

Hexadecyalamine (HDA) 98%, oleyamine (OLA) 99%, dodecylamine (DDA), tri-noctylphosphine (TOP) 90%, piperidine 99%, tetrahydroisoquinoline 99%, carbon disulfide 99 %, nickel acetate tetrahydrate (Sigma Aldrich), sodium hydroxide 98%, methanol 99.5%, chloroform, acetone and hexane were used as purchased without any further purification.

#### 2.2. Instrumentation

Microanalysis was performed on a Perkin-Elmer automated model 2400 series II CHNS/O analyser. Infrared spectra were recorded on a Bruker FT-IR Tensor 27 spectrophotometer directly on small samples of the compounds in the 200-4000 cm<sup>-1</sup> range Thermogravimetric analysis was carried out at 10 °C min<sup>-1</sup> heating rate using a Perkin Elmer Pyris 6 TGA up to 600 °C in a closed perforated aluminium pan under N<sub>2</sub> gas flow. The <sup>1</sup>H NMR spectra were recorded with a Bruker 400 spectrometer, using CDCl<sub>3</sub> as a solvent. Single crystal X-ray structure analyses: A green needle-like single crystal measuring about  $0.21 \times 0.04 \times 0.02$  mm for (1), mounted on the goniometer of a Bruker Apex II Duo CCD diffractometer using a 500 µm-long needle cryoloop (MiTeGen®) mount. After initial suspension and selection in Paratone® oil. Intensity data were collected using Mo Ka radiation from an Incoatec® microsource (IuS, Quazar mirror optics) at a temperature of 100(2) K. The structures were solved using direct methods with SHELXS [35] running in WinGX [36]. The structures were refined using leastsquares methods (SHELXL) [35]. All non-H-atoms were refined anisotropically; hydrogen atoms were included in calculated positions, assigned isotropic thermal parameters ( $U_{iso}$  for H atoms =  $1.2U_{iso}$  for the attached C atom) and allowed to ride on their parent carbon atoms using the standard HFIX parameters in SHELXL. Crystal data and structure refinement parameters are presented in ESI Table S1.

Optical absorption measurements were carried out using a Perkin-Elmer Lambda 1050 UV-Visible NIR spectrophotometer. The samples were placed in silica cuvettes (1 cm path length), using hexane as a reference solvent. A Perkin-Elmer, LS 55 Luminescence spectrophotometer was used to measure the photoluminescence of the particles. Samples were

placed in a quartz cuvette (1 cm path length). TEM and HRTEM analyses were performed using a JEOL 1010 TEM and JEOL 2100 HRTEM. Samples were prepared by placing a drop of dilute solution of nanoparticles on Formvar-coated Cu grids (150 mesh) for TEM and holey carbon grids for HRTEM. The samples were allowed to dry completely at room temperature and viewed at an accelerating voltage of 100 kV (TEM) and 200 kV (HRTEM), and images captured digitally using a Megaview III camera; stored and measured using Soft Imaging Systems iTEM software (TEM) and Gatan camera and Gatan software (HRTEM). Particle sizes were measured using ImageJ Tool 1.4.6r software (a total number of >10 particles). Powder X-ray diffraction (p-XRD) patterns were recorded in the high angle 2 $\theta$  range of 20 - 80° using a Bruker AXS D8 Advance X-ray diffractometer, equipped with nickel filtered Cu Ka radiation ( $\lambda = 1.5406$  Å) at 40 kV, 40 mA and at room temperature. The variation of room temperature hysteresis loops was investigated by using a Lakeshore model 735 vibrating sample magnetometer (VSM). In this case, the hysteresis loops were obtained in external applied magnetic fields of only up to 14 kOe.

### 2.3. Synthesis of ligands and nickel complexes

The piperidine and tetrahydroquinoline dithiocarbamate ligands and the corresponding nickel complexes were synthesized using the procedures described in our previous work [26]. The synthesis of complexes is detailed as follows; nickel acetate (4.1 g, 16.4 mmol) was dissolved in deionized water (25.0 mL), and then added drop-wise to the corresponding solution of the dithiocarbamate ligand (6.0 g, 32.8 mmol). The reaction mixture was stirred for 45 min, and the precipitate formed was vacuum filtered, washed with deionized water and dried in an oven at 70 °C overnight. Two complexes were prepared as follows:

[Ni(pip-dtc)<sub>2</sub>] (1), (where pip = piperidinyl and dtc = dithiocarbamate) yield: 79%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.29 (m, 8H, 3-CH<sub>2</sub>), 1.68 (t, 4H, 4-CH<sub>2</sub>), 3.75 (t, 8H, 2-CH<sub>2</sub>). Microanalysis: Calculated for C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>NiS<sub>4</sub>: C, 38.00; H, 5.32; N, 7.39. Found: C, 38.12; H, 5.78; N, 7.24. IR (cm<sup>-1</sup>, ATR): 998, *v* (C=S); 1438, *v* (C=N); 1507, *v* (C-N); 385-365, *v* (Ni–S).

[Ni(thq-dtc)<sub>2</sub>] (**2**), (where thq = tetrahydroquinyl and dtc = dithiocarbamate) yield: 67%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.99 (m, 4H, 3-CH<sub>2</sub>), 3.99 (t, 4H, 4-CH<sub>2</sub>), 4.99 (t, 4H, 2-CH<sub>2</sub>), 7.20–7.50 (m, 8H, Ar–H). Microanalysis; Calculated for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>NiS<sub>4</sub>: C, 50.54; H, 4.24; N,

5.89. Found: C, 50.34; H, 4.52; N, 5.56. IR (cm<sup>-1</sup>, ATR): 985, v (C=S); 1441, v (C=N); 1521, v(C-N); 385-365, v (Ni–S).

### 2.4. Preparation of nickel sulfide nanoparticles

In a typical procedure, 0.3 g of complex (1) or (2) was dissolved in 3.0 mL of tri-noctylphosphine (TOP) and injected in hot DDA in a three-necked flask at 190 °C. A drop in temperature of about 20 °C was observed and the solution turned to a blackish colour. The reaction temperature was maintained for 2 hours, after which the heating was stopped. Ethanol was then added to flocculate the nickel sulfide nanoparticles. The DDA capped nickel sulfide nanoparticles were separated by centrifugation followed by washing with ethanol and acetone. The reaction was repeated at a temperature 230 °C. The above reaction procedures were also repeated at temperatures 190 °C, 230 °C and 270 °C, using HDA and OLA as the capping groups.

#### 3. Results and discussion

### 3.1. Characterization of the ligands and complexes

The nickel dithiocarbamato complexes used in this work were synthesized from costeffective starting materials using relatively simple reaction protocols. They are stable in air similar to other complexes of dithiolates [32]. The ligands and the complexes were obtained in good yields and microanalysis confirmed their purity. The complexes were green microcrystalline powders soluble in most organic solvents. IR spectroscopy revealed a very broad band around 3324-3367 cm<sup>-1</sup> in the spectra of the ligands due to the v (O-H) of water. This band was absent in the spectra of the complexes. Both the ligands and complexes showed bands in the 1466–1485 cm<sup>-1</sup> region, corresponding to v (C=N) and v (C-N). The v (C=S) band was observed at 999-975 cm<sup>-1</sup> region in the spectra of the ligands. The upward shift of this band in the complexes compared to the free ligand, together with a strong band (or very close bands) attributed to v (C-S) was indicative of a bidentate or slightly anisobidentate dithiocarbamate. The TGA plots of both complexes displayed a single step decomposition pattern. The TGA plots showed a weight loss of 74.7% and 71.0% (calc = 76.0% and 80.1%) at 353.5 and 315.4 °C for complexes (1) and (2), respectively (Figure 1), corresponding to the loss of the organic moiety Dithiocarbamate metal complexes decompose in solid state either by and sulfur atoms.

volatilization, leaving behind almost no residue or decomposition via a number of steps to yield respective metal sulfides [37]. Our metal complexes are in the latter category as the final residues 25.3% and 21.0 % were close to the calculated values of 24.0% and 19.1%, for NiS from complexes (1) and (2), respectively.



Fig. 1. Thermogravimetric analysis (TGA) plots of complexes (1) and (2).

### 3.2. Single-crystal X-ray structure

The X-ray data for complex (1) was previously recorded at ambient temperature by Radha *et al.* [34]. The data presented herein shows improvement in data/parameter ratios as well as significant improvements in the R<sub>1</sub>, wR<sub>2</sub> and accuracy in the C–C bond lengths. Complex (1) crystallised in the monoclinic space group  $P2_1/c$  with a half molecule in the asymmetric unit and Z = 2. The molecule has crystallographically imposed inversion symmetry with a centre of inversion located at the Ni(II) ion (Figure 2).



**Fig. 2.** Displacement ellipsoid plot of complex (1) showing 50% probability surfaces. Hydrogen atoms have been rendered as spheres of arbitrary radius. The molecule has inversion symmetry with the centre of inversion located at the Ni(II) ion. Symmetry code: (i) -x, -y, -z (CCDC 1502999).

The d<sup>8</sup> Ni(II) ion has adopted a nominally square planar coordination geometry. The bond parameters are summarized in Table 1. The most notable deviation from an ideal square planar geometry lies in the intraligand S1–Ni1–S2 bond angle which measures 79.49(1)°, significantly more acute than the ideal bond angle of 90°. This acute bond angle is attributed to the small bite of the dithiocarbamate ligand and the associated 4-membered chelate ring. Consequently, the interligand S1–Ni1–S2 bond angle is obtuse, measuring 100.51(1)°. The S1-C1 and S2-C1 bond lengths measure 1.727(1) Å and 1.722(1) Å, respectively. These bond lengths are intermediate to those of a formal single or double C–S bond, highlighting the delocalisation of the dithiocarbamate ligand. Further, the C1-N1 bond length measures 1.321(2) Å. This is shorter than a typical sp<sup>2</sup> C–N single bond (1.377 Å) [38] suggesting a portion of double bond character and illustrating further delocalisation.

### Table 1

Selected bond parameters of (1).

Bond	Length	Bond	Angle (°)	
	(Å)			
Ni1–S1	2.2010(3)	S2–Ni1–S1	79.49(1)	$\mathbf{O}$
		(intraligand)		
Ni1–S2	2.2117(4)	S2–Ni1–S1	100.51(1)	
		(interligand)		
S1–C1	1.727(1)	S1C1N1	125.4(1)	
S2–C1	1.722(1)	S2-C1-N1	124.8(1)	
C1-N1	1.321(2)	~		

The four coordinating atoms and the metal ion are planar by definition; however, this planarity does not extend to the C–N bond which shows a significant out-of-plane distortion. The atoms C1 and N1 are displaced from the 5-atom mean plane defined by the coordination sphere by 0.132(1) Å and 0.346(1) Å, respectively. The piperidine rings are approximately perpendicular to the coordination sphere and are in a *trans*-configuration. This geometry leads to a herringbone pattern in the crystal lattice as shown in the packing diagram in Figure 3.

The structure does not show any signs of axial coordination by the sulfur atoms of adjacent dithiocarbamate ligands as is noted in previously reported copper (II) dithiocarbamate structures [39], seemingly the steric bulk of the piperidine rings preclude the formation of these interactions. The lattice is stabilized by weak C-H···S interactions between the C6 methylene CH and S1 of an adjacent molecule. The C-H···S distance measures 2.935(2) Å, only fractionally shorter than the sum of the van der Waals radii suggesting a weak interaction. The X-ray data for complex (**2**) were recorded at ambient temperature by Hogarth *et al.* [40].



Fig. 3. Packing diagram of (1) viewed down the a-axis. The packing diagram illustrates the trans-configuration of the piperidine rings and the resultant herringbone pattern. The lattice is stabilized by C-H<sup>...</sup>S interactions, shown as dashed purple tubes.

### 3.3. Nickel sulfide nanoparticles

The thermolysis of precursors in high boiling point primary amine solvents is a well reported route to high quality nanoparticles [3]. The size of the nanoparticles depends on the reaction time, temperature, precursors and capping agent. In particular, long chain amines are found to be suitable surfactants for II–VI semiconductor nanomaterials. In this work we decided to explore hexadecylamine (DDA), dodecylamine (HDA) and oleylamine (OLA) as capping groups for nickel sulfide nanoparticles. Both complexes (1) and (2) were thermolysed in coordinating solvents at temperatures of 190 °C, 230 °C for DDA and 190 °C, 230 °C and 270 °C for HDA and OLA for 2 hrs.

### 3.4. Structural and morphological characterization

The powder X-ray diffraction (p-XRD) pattern for both precursors using capping groups at different temperatures show a change of phases as the capping group is varied. DDA which is a shorter carbon chain (12 carbon) capping group gave pure phase of Ni<sub>3</sub>S<sub>4</sub> (Card No. 00-043-1469) when complex (1) and (2) were used as single source precursors at 190 and 230 °C (Figure 4 and ESI Fig. S1). All diffraction peaks with *hkl* values (022), (113), (004), (115), (044) and

(335) can be indexed to the sulfur rich pure phase of cubic  $Ni_3S_4$  (Card No. 00-043-1469). This is in good agreement with literature [4], where at temperatures lower than 250 °C the cubic phase  $Ni_3S_4$  is obtained. The results are in agreement with the decomposition pattern of other dithiocarbamate complexes reported elsewhere [33].



**Fig. 4.** Powder X-ray diffraction (p-XRD) pattern for DDA capped nickel sulfide nanoparticles from complex (1).

The primary amine with 16 carbon chain (HDA) gave pure phase of  $Ni_3S_2$  at temperatures of 190 °C, 230 °C and 270 °C (card no.00-002-0772) (Figure 5 and ESI Fig. S2). The XRD peaks were indexed to the (101), (012), (003), (202), (211), (122), (303), (214) and (401) mirror planes of rhombohedral a-Ni\_3S\_2. The diffraction patterns show an increase in crystallinity as the temperature is raised from 190 °C to 270 °C. Particle sizes as estimated by the Debye-Scherrer equation show average crystallite sizes of 3.1 nm, 7.1 nm and 11.9 nm for nanoparticles prepared at 190 °C, 230 °C and 290 °C respectively. These sizes were corroborated by the TEM studies.

When OLA was used as a capping agent, both complex (1) and (2) gave nanoparticles with mixed phases (Figure 6 and ESI Fig S3). The diffraction peaks show a dominant phase of hexagonal NiS at 270 °C (card number 03-065-3419) which is indexed to (100), (101), (102), and (110) planes. Unlabeled peaks could also be matched to a rhombohedral phase of nickel sulfide (card #; 00-012-0041). At lower temperatures (190 °C and 230 °C), a mixture of cubic phase of polydymite (Ni<sub>3</sub>S<sub>4</sub>) was identified labelled # (card number: 00-047-1739) which fits well in what has been reported on the formation of this phase at lower temperatures [33]. Phase transition in nickel sulfide due to an increase in temperature has been reported previously [30]. The results of the parameters and properties of the as-synthesized nickel sulfide nanoparticles are presented in Table 2.



**Fig. 5.** X-ray diffraction (p-XRD) pattern for HDA capped nickel sulfide nanoparticles from complex (1).



**Fig. 6.** X-ray diffraction (p-XRD) pattern of OLA capped Nickel sulfide nanoparticles synthesized using complex (1).

Figure 7 shows TEM images for DDA capped nickel sulfide nanoparticles from both complex (1) and (2) at various temperatures. The morphology and average particle sizes of the as synthesized nickel sulfide nanoparticles varied with temperature and precursor type. Nanoplates are observed at lower reaction temperature of 190 °C when complex (1) was used (Figure 7 (a)). These nanoplates with unusual cross-like shape have been reported previously by Wu *et al.* [41]. The nanoplates in our case have four seemingly equal wings, with each lateral wing having a dimension of approximately 65 nm. At 230 °C particles without a regular shape are observed (Figure 7(b)). Complex (2) at 190 °C gave spherical nanoparticles with a relatively smaller average size of 8.63 nm (Figure 7 (c)) while at 230 °C, short rods with average width of 8.68 nm and length of 53.89 nm were observed (Figure 7(d)). At higher magnification, the HRTEM image for nickel sulfide particles in Figure 7(d) shows lattice fringes with a d-spacing of 2.87 Å, assigned to the (311) plane of Ni<sub>3</sub>S<sub>4</sub> (ESI Fig.S.4 (c) ). A summary of the morphology, particle size and phase formation of nickel sulfide synthesized using different reaction parameters is shown in Table 2.

TEM images for HDA capped nickel sulfide nanoparticles from complex (1) and (2) are represented in Figure 8. Complex (2) gave slightly larger nanoparticles as compared to complex (1). The nickel sulfide synthesized from complex (1) were spherical with an average size of 2.9 nm, 7.4 nm and 12.1 nm at 190 °C, 230 °C and 270 °C, respectively. For complex (2), the estimated particle size for the spherical nanoparticles was 5.9 nm (190 °C), 9.8 nm (230 °C) whereas at 270 °C, irregular shaped particles were formed. The high resolution TEM image for Figure 8 (f) represented in ESI Fig S4 (a) and its corresponding SAED ESI Fig S4 (b) revealed the formation of crystalline Ni<sub>3</sub>S<sub>2</sub> nanoparticles.

 Table 2 Summary of the reaction conditions, sizes and shapes of the obtained nickel sulfide nanoparticles.

Complex	Capping group	Temp (°C)	Morphology	Particle	Phase
				size/aspect	
				ratio (nm)	
(1)	DDA	190	Nanoplates	67.71	Ni <sub>3</sub> S <sub>4</sub>
		230	Irregular shaped rods	7.67	Ni <sub>3</sub> S <sub>4</sub>
	HDA	190	Spherical	5.93	Ni <sub>3</sub> S <sub>2</sub>
		230	Spherical	9.80	Ni <sub>3</sub> S <sub>2</sub>
C		270	Irregular shape	-	Ni <sub>3</sub> S <sub>2</sub>
	OLA	190	Close to sphere	5.17	Mixed
		230	Irregular tetrahedral shape	8.96 length	Mixed
		270	Irregular shape	9.67 length	Hex. NiS
(2) DDA HDA OLA	DDA	190	Spherical	8.63	Ni <sub>3</sub> S <sub>4</sub>
		230	Short rods	6.21	Ni <sub>3</sub> S <sub>4</sub>
	HDA	190	Spherical	2.93	Ni <sub>3</sub> S <sub>2</sub>
		230	Spherical	7.39	Ni <sub>3</sub> S <sub>2</sub>
		270	Spherical	12.06	Ni <sub>3</sub> S <sub>2</sub>
	OLA	190	Spherical	4.21	Mixed
		230	Irregular tetrahedral shape	8.31	Mixed
		270	Spherical	9.83	Hex. NiS



**Fig. 7.** TEM images for DDA capped nickel sulfide nanoparticles from complex (1) synthesized at (a) 190 °C (b) 230 °C and complex (2) at (c) 190 °C and (d) 230 °C.



**Fig. 8.** TEM images for HDA capped nickel sulfide nanoparticles at (a) 190 °C, (b) 230 °C and (c) 270 °C from complex (1) and (d) 190 °C, (e) 230 °C and (f) 270 °C from complex (2).

TEM images for OLA capped nickel sulfide nanoparticles synthesized from precursor (1) and (2) are presented in Figure 9. The TEM images (Figure 9) for OLA capped nickel sulfide nanoparticles synthesized from precursor (1) and (2) show the formation of close to spherical nanoparticles and irregular shaped nanoparticles depending on the reaction parameters as presented in Table 2. The particle size increase with an increase in temperature for particles synthesized from both complexes. High resolution TEM for Figure 9 (c) shows fringes with a d-spacing of 2.86 Å which fit well with the data obtained from p-XRD results for the same in Figure 4 (ESI Fig. S4 (d)).



**Fig. 9.** TEM images for OLA capped nickel sulfide nanoparticles synthesized from complex (1) at (a) 190 °C, (b) 230 °C and (c) 270 °C and complex (2) at (d) 190 °C, (e) 230 °C, (f) 270 °C.

### 3.5. Magnetic properties

The magnetic properties of the samples annealed at 230 °C were recorded at 17 °C by a vibrating sample magnetometer. The hysteresis loops are presented in Figure 10. The sample (DDA PIPDTC) prepared in DDA using complex (1) presents the cubic-Ni<sub>3</sub>S<sub>4</sub> sample with magnetization at 2000 Oe of about 1.6 emu/g and a coercive field of 224 Oe. Similarly, the sample (DDA THQDTC) prepared in DDA using complex (2) showed cubic-Ni<sub>3</sub>S<sub>4</sub> exhibiting magnetization of about 3.2 emu/g and a coercive field of 93 Oe, with a saturation magnetization that is higher than that from complex (1) prepared under similar conditions. The coercive field of the sample prepared using complex (1) is higher than that from complex (2) both in DDA. Both samples prepared in DDA showed ferromagnetic behaviour, typical of Ni<sub>3</sub>S<sub>4</sub> phase [42]. It can be seen that the rhombohedral ( $\alpha$ -Ni<sub>3</sub>S<sub>2</sub>) sample (HDA THQDTC) prepared from complex (2) using

HDA shows an almost linear plot of magnetization against applied field with almost zero coercive field which corresponds to a paramagnetic phase. The magnetic properties of nanomaterials are believed to be highly dependent on the structure and particle sizes. The coercive fields tend to correlate well with particle sizes. From Figure 10 and Table 2, the DDA Ni<sub>3</sub>S<sub>4</sub> sample with higher coercive field has a relatively larger particle size. These results appear consistent with transformation from a single to multi-domain structure with increase in particle size [43]. The coercive fields  $H_c$  and particle sizes D are expected to vary as  $H_c = a_1 - b_1/D^2$  and  $H_c = a_2 + b_2/D$  for single domain and for multi-domain regions respectively where  $a_i$  and  $b_i$  are constants.



**Fig. 10.** Magnetic hysteresis curves of the nickel sulfide samples synthesized by the hot injection thermal decomposition of complexes at 230 °C. The hysteresis loops were recorded at 17 °C.

### 3.6. Optical properties

The absorption spectra of HDA capped nickel sulfide nanoparticles synthesized 270 °C displays an absorption onset at 327 nm (ESI Fig S5). Absorption (UV-Vis) spectra for nickel sulfide nanoparticles synthesized at various reaction conditions are presented in ESI Figs. S5 – S10. All spectra show absorption in the higher energy region ranging from 3.5 eV to 4.1 eV which is a blue shift in relation to bulk nickel sulfide (2.7 eV) affirming the size quantization effect of the nanoparticles.

### 4. Conclusion

Piperidine (1) and tetrahydroquinoline (2) nickel(II) dithiocarbamate complexes have been synthesized and characterized. An improved low temperature single X-ray crystal structure of complex (1) has also been elucidated. These complexes have been used as single source precursors to synthesize high quality nickel sulfide nanoparticles via a solvothermal route using dodecylamine, hexadecylamine and oleylamine as the coordinating solvents. Nickel sulfides of different mineral phases, namely NiS, Ni<sub>3</sub>S<sub>4</sub> and Ni<sub>3</sub>S<sub>2</sub> have been produced. The rare pure phases produced are in agreement with previous reports, where the formation of phase pure Ni-S systems is temperature dependent. In addition, the formation of mixed phases when oleylamine is used and the formation of Ni<sub>3</sub>S<sub>4</sub> for dodecylamine (at all temperatures) suggest further studies in the field. Nanoparticles can display a variety of magnetic properties near room temperature which are dependent on the crystalline phases. The coercive field data can therefore be investigated on the basis of transformation from single to multi-domain structure. This study provides a relatively reliable single source precursor route for preparing stoichiometric nickel sulfide nanocrystals with well-defined crystalline structures, compositions and morphologies.

### Appendix A.

Supplementary data CCDC 1502999 contains the supplementary crystallographic data for *bis*(dipiperidinyldithiocarbamato) nickel(II) (1). These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

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High temperature solution based thermolyis of single source precursors has been employed to synthesize phase pure magnetic nickel sulfide nanoparticles.

