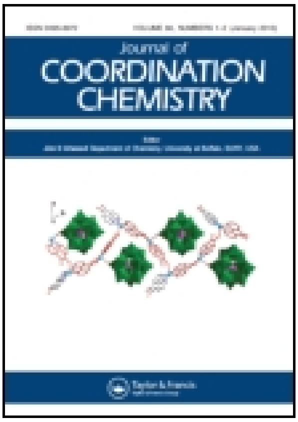

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Nickel(II) complexes of *N*-(dialkylcarbamothioyl)-4-nitrobenzamide as single-source precursors for the deposition of nanostructured nickel sulfide thin films by chemical vapor deposition

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Nickel(II) complexes of *N*-(di-alkyl-carbamothioyl)-4-nitrobenzamide (alkyl = ethyl or *n*-propyl) have been synthesized and characterized by infrared spectroscopy, elemental analysis, nuclear magnetic resonance spectroscopy, and mass spectrometry. The structures of *bis*[*N*-(diethylcarbamothioyl)-4-nitrobenzamide]nickel(II) (**2a**) and *bis*[*N*-(dipropylcarbamothioyl)-4-nitrobenzamide]nickel(II) (**2b**) have been determined by X-ray crystallography. FTIR and NMR of the nickel complexes showed the absence of the N–H proton resonance and the N–H stretch and shift of $v_{C=O}$ and $v_{C=S}$ as expected. Both complexes have been used as single-source precursors for the deposition of nickel sulfide nanostructured thin films by aerosol-assisted chemical vapor deposition. The nanostructured thin films were characterized by X-ray powder diffraction, scanning electron microscopy, energy dispersive X-ray analysis, and atomic force microscopy.

Keywords: Nickel complexes; Crystal structure; *cis*-Configuration; Thin films; AACVD; SEM

1. Introduction

There is growing interest in nanostructured and thin film materials and the design of the metal coordination complexes to be used for the synthesis of these materials [1–7]. The coordination chemistry and potential applications of such precursors have only been explored in the last few decades. Acylthiourea ligands with presence of O, N, N′, and S donors exhibit various coordination modes: (a) O and S bonded to M (monobasic bidentate) [8], (b) only S bonded to M (neutral monodentate) [9], (c) O and N bonded to M (neutral bidentate) [10], and (d) O and S bonded to M and N is bonded to M′ (monobasic bridging ligand) [11]. Substituted acylthiourea ligands, which do not form an intramolecular hydrogen bond, tend to coordinate predominately in bidentate (S, O) fashion to transition-metal ions through sulfur and acyl oxygen [11]. Examples for this

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*Corresponding author. Email: paul.obrien@manchester.ac.uk type of coordination are mononuclear complexes [ML_2], where M = Ni(II), Cu(II), Co(II), Zn(II), Cd(II), Pt(II), and Pd(II) and L = substituted acylthiourea derivatives [12]. Coordination solely through sulfur is rare and so far only known for complexes with Au(I) [13], Ag(I) [14], Hg(II) [15], and Cu(I) [16]. It has been suggested that intramolecular hydrogen bonding exists between the thiourea N–H (where R/R′ = H) and the amidic O-donor to form a six-membered ring, with the consequence that the ligands coordinate to metal centers in a monodentate fashion through sulfur [11].

There are relatively few reports on the deposition of nickel sulfide thin films from single-source precursors by CVD. The phase diagram of the Ni–S system is more complex than that of the Fe or Co sulfides. In this system, many crystalline phases and stoichiometries have been reported including: $Ni_{3+x}S_2$, Ni_3S_2, $Ni_{4+x}S_2$, Ni_6S_5, Ni_7S_6, Ni_9S_8, NiS, Ni_3S_4, and NiS_2 [17–19]. Some compounds, for example, NiS and NiS_2, have been studied extensively, while for others only more limited information is available. NiS_2 (Vaesite) is a *p*-type semiconductor with a band gap of 0.5 eV [20]. It is potentially useful in photo electrochemical solar cells [21, 22], I.R detectors [23], catalysis [24], and sensors [25]. It is also used as a hydrodesulfuration catalyst and as a cathode material in rechargeable lithium batteries [26]. Nomura *et al.* studied the growth of $NiS_{1.03}$ from [$Ni(S_2CNEt_2)_2$] on silicon (111) substrates by low-pressure chemical vapor deposition (LP-CVD) [27]. Earlier, O'Brien *et al.* have reported the deposition of nickel sulfide films from dithiocarbamate compounds of the type [$Ni(S_2CNRR')_2$], where RR′ = Et_2, MeEt, Me^{n}Bu, or Me^{n}Hex, by AA [28] and LP-CVD methods [29] and also from xanthate compounds of the type [Ni ($S_2COR)_2$], where R = Et or ^{i}Pr by AACVD [30]. Recently, Alam *et al.* have used pyridine adducts of nickel(II) xanthates as single-source precursors for the deposition of nickel sulfide thin films by aerosol-assisted chemical vapor deposition (AACVD) [31].

Our team has focused on synthesis, characterization, crystal structures, biological activities, and material applications of new thiourea derivatives and their metal complexes [32–36]. In this manuscript, two acylthiourea derivatives, *N*-(diethylcarbamothioyl)-4-nitrobenzamide (**1a**) and *N*-(di-n-propylcarbamothioyl)-4-nitrobenzamide (**1b**), and their Ni (II) complexes were synthesized, characterized by spectroscopic techniques and crystal structures of both complexes were determined by X-ray crystallography. In addition, these metal complexes have been used as single-source precursors for deposition of nickel sulfide semiconducting nanostructured thin films by AACVD.

2. Experimental

2.1. *Materials and reagents*

Analytical grade 4-nitrobenzoyl chloride (⩾98.0%), dipropylamine (99%), diethylamine (⩾98%), sodium thiocyanate (99%), nickel(II) acetate tetrahydrate (99%), and tetrabutylammonium bromide (TBAB) (⩾98%) were purchased from Sigma–Aldrich. Analytical grade solvents such as tetrahydrofuran (THF), toluene, acetonitrile, n-hexane, dichloromethane, ethanol, methanol, chloroform, ethyl acetate, and others were purchased from Sigma–Aldrich and Riedel-de Haën (Germany), whereas ethanol and acetone were dried using standard procedures [37]. All manipulations were carried out in air except the AACVD.

2.2. *Physical measurements*

Elemental analysis was carried out by the University of Manchester micro-analytical laboratory. The ^{1}H NMR was recorded in $CDCl_3$ solvent on Bruker 400 MHz spectrophotometers using tetramethylsilane as an internal reference. All the complexes were studied by thermogravimetry in an inert atmosphere, at sample heating rate of 283 K/min, with a DuPont 2000 ATG. Infrared spectra were recorded on a Specac single reflectance ATR instrument (4000–400 cm^{-1}, resolution 4 cm^{-1}). Mass spectra of complexes (MS-APCl) were recorded on a Micromass Platform II instrument. Melting points were recorded on the Barloworld SMP10 Melting Point Apparatus. Deposited thin films of nickel sulfide were carbon coated using Edward's E306A coating system before carrying out SEM and EDX analysis. SEM analysis was carried out using a Philips XL 30FEG and EDX was carried out using a DX4 instrument. AFM analysis was carried out using a Veeco CP2 instrument. p-XRD studies were carried out on a Bruker SMART 1000 CCD diffractometer using Cu-Kα radiation.

2.3. *Synthesis of the ligands*

A solution of p-nitrobenzoyl chloride 1.85 gm (0.01 M) in anhydrous acetone (80 mL) and TBAB0.678 gm (0.3 M%) in acetone was added dropwise to a suspension of sodium thiocyanate 0.81 gm (0.01 M) in acetone (50 mL) and the reaction mixture was refluxed for 45 min. After cooling to room temperature, a solution of diethylamine 0.73 gm (0.01 M) or di-n-propylamine 0.101 gm (0.01 M) in acetone (25 mL) was added and the resulting mixture refluxed for 2 h. The reaction mixture was poured into five times its volume of cold water, whereupon the acylthiourea precipitated. The solid product was washed with water and purified by re-crystallization from an ethanol-dichloromethane mixture (1 : 2) or ethyl acetate.

2.3.1. *N*-(Diethylcarbamothioyl)-4-nitrobenzamide (1a). Yellow crystals. M.p.: 437–439 K. Yield: 3.0 g (91%). IR (ν_{max}/cm^{-1}): 3282 (NH), 2942, 2855 (C–H), 1645(C=O), 1231 (C=S). ^{1}H NMR (400 MHz, $CDCl_3$) in δ (ppm): 8.43 (br s, 1H, CONH), 8.32 (d, $2H_{meta}$, p-nitrophenyl), 8.06 (d, $2H_{ortho}$, p-nitrophenyl), 4.07 (q, 2H, N–$C\underline{H}_2$), 3.59 (q, 2H, N-$C\underline{H}_2$), 1.38 (t, 3H, –$C\underline{H}_3$), 1.30 (t, 3H, –$C\underline{H}_3$); ^{13}C–NMR (300 MHz, $CDCl_3$) in δ (ppm): 178.9, 163.2, 141.5, 138.3, 129.2, 125.1, 49.1.7, 13.9, 12.1. Anal. Calcd for $C_{12}H_{15}N_3O_3S$: C, 51.23; H, 5.37; N, 14.94; S, 11.40. Found: C, 51.89; H, 5.41; N, 14.82; S, 11.42.

2.3.2. *N*-(Dipropylcarbamothioyl)-4-nitrobenzamide (1b). Pale yellow. M.p.: 389–390 K. Yield: 3.2 g (88%). IR (ν_{max}/cm^{-1}): 3202 (NH), 2929, 2863 (C–H), 1681 (C=O), 1252 (C=S). ^{1}H NMR (400 MHz, $CDCl_3$) in δ (ppm) and J (Hz): 8.45 (s, 1H, CONH), 8.12 (d, $2H_{meta}$, $J = 8.3$ Hz, p-nitrophenyl), 7.35 (d, $2H_{ortho}$, $J = 8.8$ Hz, p-nitrophenyl), 3.82 (t, 2H, N–$C\underline{H}_2$), 3.53 (m, 2H, $C\underline{H}_2$), 1.81 (m, 2H, $C\underline{H}_2$), 1.60 (m, 2H, $C\underline{H}_2$), 0.98 (t, 3H, $C\underline{H}_3$), 0.91 (t, 3H, $C\underline{H}_3$). Anal. Calcd for $C_{14}H_{19}N_3O_3S$: C, 54.35; H, 6.19; N, 13.58; S, 10.36. Found: C, 54.32; H, 6.35; N, 13.57; S, 10.37.

2.4. *Synthesis of the complexes*

A solution of nickel acetate (0.005 M) in methanol (35 mL) was added dropwise to a solution of the ligand in a 1 : 2 ratio with a small excess of ligand in ethanol (35 mL) at room temperature, and the resulting mixture was stirred for 3 h. The reaction mixture was filtered, washed with ethanol, and re-crystallized from THF/acetonitrile mixture (1 : 1).

2.4.1. *Bis*[*N*-(diethylcarbamothioyl)-4-nitrobenzamide]nickel(II) (2a). Quantities used were 2.81 g (0.01 M) ligand (**1a**) and 1.24 g (0.005 M) nickel acetate tetrahydrate in ethanol. Golden crystals. Yield: 3.5 g (88%). IR (ν_{max}/cm^{-1}): 2929, 2852 (Ar–H), 1506 (C–O), 1532 (C–N), 1139 (C–S). ^{1}H NMR (400 MHz, CDCl$_3$) in δ (ppm) and J (Hz): 8.01 (d, 4H, Ar–H), 7.32 (d, 4H, Ar–H), 3.51 (m, 8H, N–C$\underline{H_2}$), 1.32 (t, 12H, –C$\underline{H_3}$). Anal. Calcd for $C_{24}H_{28}N_6O_6S_2Ni$: C, 46.54; H, 4.56; N, 13.57; S, 10.35; Ni, 9.48. Found: C, 46.23; H, 4.53; N, 13.50; S, 10.26; Ni, 9.95. Mass (MS-APCI) (major fragment, *m/z*): 619 [M+, $C_{24}H_{28}N_6O_6S_2Ni$].

2.4.2. *Bis*[*N*-(di-n-propylcarbamothioyl)-4-nitrobenzamide]nickel(II) (2b). Quantities used were 3.09 g (0.01 M) ligand (**1b**) and 1.24 g (0.05 M) nickel acetate tetrahydrate in ethanol. Dark brown. Yield: 3.6 g (85%). IR (ν_{max}/cm^{-1}): 2930, 2857(Ar–H), 1503 (C–O), 1535 (C–N), 1142 (C–S). ^{1}H NMR (400 MHz, CDCl$_3$) in δ (ppm) and J (Hz): 8.03 (d, 4H, Ar–H), 7.37 (d, 4H, Ar–H), 3.73 (t, 8H, N–C$\underline{H_2}$), 1.70 (m, 8H, C$\underline{H_2}$), 0.90 (t, 12H, –C$\underline{H_3}$). Anal. Calcd for $C_{28}H_{36}N_6O_6S_2Ni$: C, 47.79; H, 5.37; N, 12.44; S, 9.49; Ni, 8.69. Found: C, 49.55; H, 5.34; N, 12.37; S, 9.46; Ni, 8.34. Mass (MS-APCI) (major fragment, *m/z*): 675 [M+, $C_{28}H_{36}N_6O_6S_2Ni$].

2.5. *X-ray structure determination*

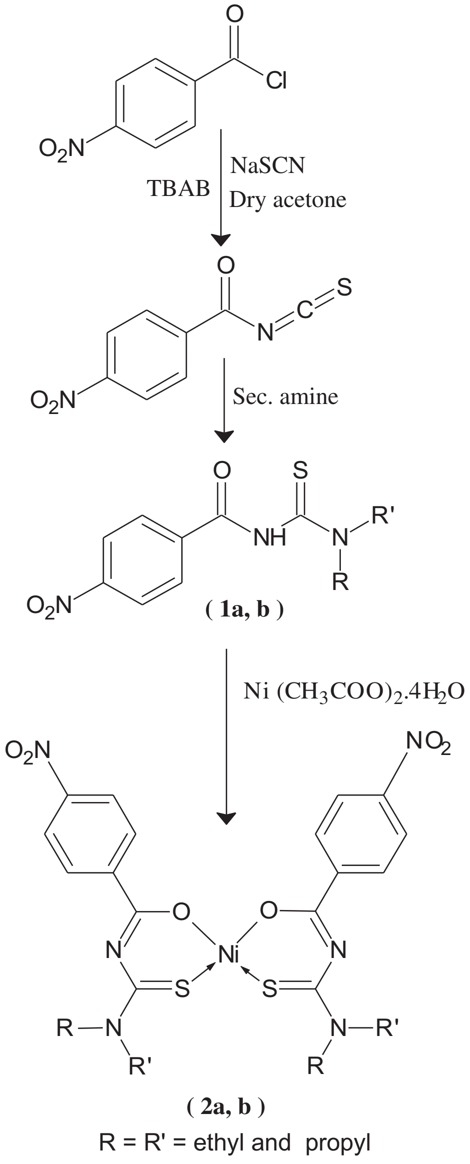
Single-crystal X-ray diffraction (XRD) data for both the nickel complexes (**2a**, **2b**) were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Bruker SMART 1000 CCD diffractometer. The structures were solved by Patterson methods *DIRDIF-99* [38] and expanded using Fourier techniques. All non-H atoms were refined anisotropically. The programs used for data collection and cell refinement were *SMART* and *SAINT* v7.34A, respectively [39, 40]. The software used to solve and refine the structures was *SHELXL97* [41].

2.6. *Deposition of nickel sulfide thin films by AA-CVD*

Experiments were carried out as described by us previously [42]. In a typical deposition, 0.25 g of the precursor was dissolved in 15 mL THF in a two-necked 100 mL round-bottom flask with a gas inlet that allowed the carrier gas (argon) to pass into the solution to aid the transport of the aerosol. This flask was connected to the reactor tube by a piece of reinforced tubing. The argon flow rate was controlled by a Platon flow gauge. Seven soda glass substrates (approx. 1 × 2 cm) were placed inside the reactor tube, which is placed in a CARBOLITE furnace. The precursor solution in a round-bottom flask was kept in a water bath above the piezoelectric modulator of a PIFCO ultrasonic humidifier (Model No. 1077). The aerosol droplets of the precursor thus generated were transferred into the hot wall zone of the reactor by carrier gas. Both the solvent and the precursor were evaporated and the precursor vapor reached the heated substrate surface where thermally induced reactions and film deposition took place.

3. Results and discussion

The acylthiourea derivatives and their nickel complexes were synthesized according to reported procedures [43–47] with minor modifications as presented in scheme 1. The use of phase transfer catalyst (PTC) as a method of agitating a heterogeneous reaction system



Scheme 1. Preparation of **1a**, **b** and their metal complexes (**2a**, **b**).

is gaining recognition [48, 49]. In search of improving methods to prepare the target acylthiourea by reacting isothiocyanates with nucleophiles, we have found that use of TBAB as phase transfer catalyst can produce isothiocyanates in good yield. The reaction proceeds via nucleophilic addition of the secondary amine to the isothiocyanate. We have conducted our reaction using TBAB as PTC to synthesize the acylthiourea derivatives.

3.1. *Spectroscopic characterization*

Solid state IR spectra of acylthiourea derivatives and the metal complexes from 4000 to 400 cm^{-1} were compared and assigned on careful comparison. Tentative assignments are

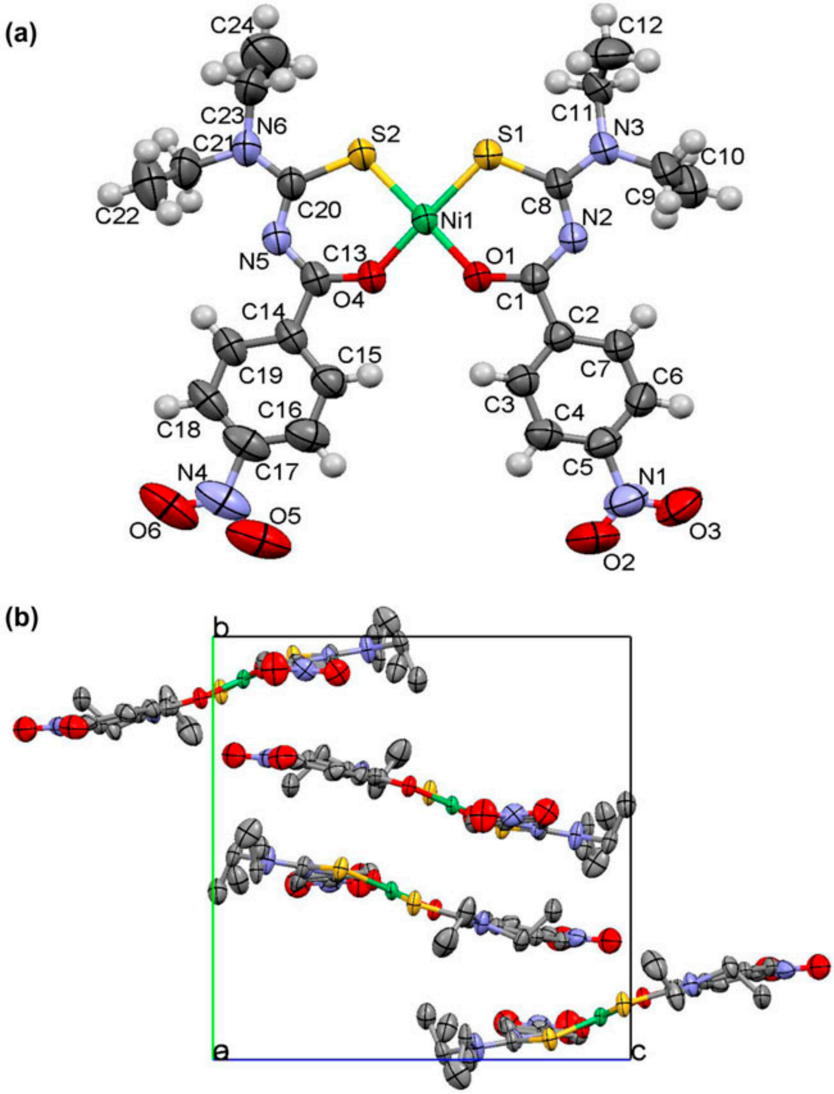


Figure 1. (a) The molecular structure of *bis*[*N*-(diethylcarbamothioyl)-4-nitrobenzamide]nickel(II) (**2a**). (b) Unit cell diagram of **2a**.

made according to the literature [50]. *N,N′*-disubstituted thioureas behave both as monodentate and bidentate ligands, depending upon the reaction conditions. The characteristic bands of *N,N′*-disubstituted thioureas are (cm^{-1}): 3202–3282 (NH), 2855–2942 Ph (CH), 1645–1681 (C=O), and 1231–1252 (C=S), and there is a slight shift of (C=O) and (C=S) groups stretching frequencies due to coordination of the ligands to nickel.

Acythioureas usually are bidentate to transition-metal ions through the acyl oxygen and sulfur [43, 51–53]. FT-IR spectra of the complexes show significant changes when

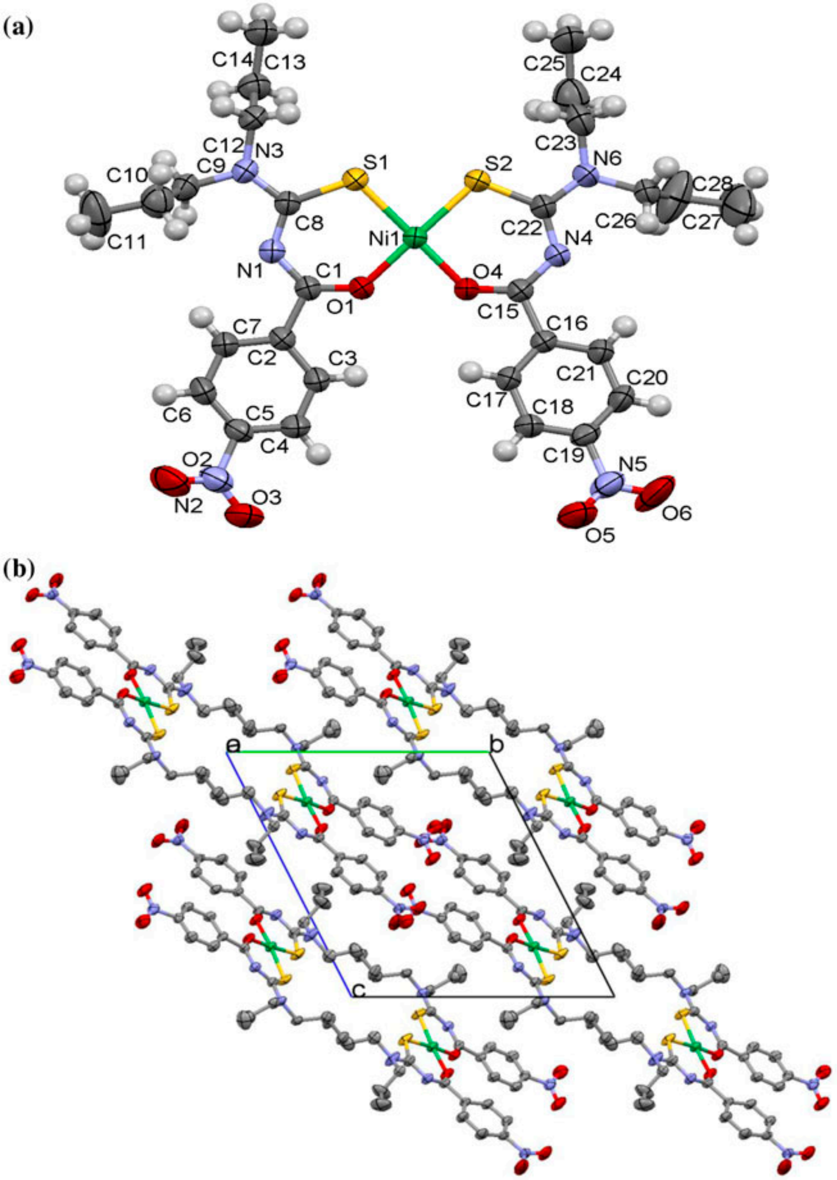


Figure 2. (a) The molecular structure of *bis*[1-(4-nitrobenzoyl)-3,3-dipropylthiourea]nickel(II) (**2b**). (b) Packing diagram of **2b**.

compared with FT-IR spectra of the corresponding ligands. The IR spectra of complexes show absorption bands at υ_{max}/cm^{-1}: 2852–2929 Ph (CH), 1503–1506 (C–O), 1531–1575 (C–N), and 1139–1142 (C–S). The most striking changes are the N–H stretching frequency at $\sim$3200 cm^{-1} in the free ligands disappears, in agreement with both ligand and complex structure and the complexation reaction, indicating loss of proton originally bonded to nitrogen of the (NH–CO) amide. Another striking change is observed for the carbonyl stretching vibrations. The vibrational frequencies due to carbonyl (1645–1681 cm^{-1}) in the free ligands shift to lower frequencies upon complexation, confirming ligands are coordinated to nickel(II) through oxygen and sulfur [54–57]. A comparative absorption pattern of the complexes with the values of the free ligands demonstrates that the coordination of acylthiourea ligands to nickel has a significant effect on υ(NH), υ(CO), and υ(CS) frequencies.

^{1}H NMR data for *N,N′*-disubstituted thioureas show that the NH resonates considerably downfield from other resonances in the spectra. The proton chemical shifts are 8.43–8.45 for free NH protons and aromatic protons between 7.35 and 8.32 ppm. It has also been observed that coordinating or highly polar solvents like DMSO-*D6* have profound effect on the free NH chemical shift and appear more downfield as compared with C_6D_6, $CDCl_3$, and CD_2Cl_2. This shift can be attributed to hydrogen bonding between NH and sulfoxide (S=O). ^{1}H NMR data for the metal complexes describe the existence of aromatic protons at 7.32–8.01 ppm as reported earlier [58, 59]. Resonances due to NH of CONH moiety in the ligands completely disappear in both **2a** and **2b**. This indicates loss of the proton originally bonded to nitrogen of (NH–CO) amide in the ligands and confirms the formation of

Table 1. Crystal data and structure refinement for **2a** and **2b**.

	2a	**2b**
CCDC	879,351	879,353
Empirical formula	$C_{24}H_{28}N_6NiO_6S_2$	$C_{28}H_{36}N_6NiO_6S_2$
Formula weight	619.35	675.46
Crystal size	0.50 × 0.35 × 0.12 mm	0.35 × 0.32 × 0.18 mm
Temperature	299 K	300 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions	$a = 13.2407(13)$ Å $b = 14.8611(14)$ Å $c = 14.2608(14)$ Å $\beta = 91.928(1)°$	$a = 8.9483(8)$ Å $b = 13.3915(12)$ Å $c = 14.9970(13)$ Å $\alpha = 65.229(1)°$ $\beta = 87.987(1)°$ $\gamma = 79.441(1)°$
Volume	2804.5(5) $Å^3$	1602.4(2) $Å^3$
Density (calculated)	1.467 $Mg\,m^{-3}$	1.400 $Mg\,m^{-3}$
Theta range of data collection	2.7–25.0°	2.6–25.0°
Max. and min. transmission	0.6646, 0.9007	0.7707, 0.8716
No. of reflections measured	15,272	8906
No. of independent reflections	4924	5515
F (0 0 0)	1288	708
Refinement method	Least-squares matrix on F^2	Least-squares matrix on F^2
Z	4	2
R indices (all data)	0.0674	0.0460
Goodness-of-fit on F^2	1.05	1.04
$(\Delta/\rho)_{max}$	0.74 e $Å^{-3}$	0.69 e $Å^{-3}$
$(\Delta/\rho)_{min}$	−0.86 e $Å^{-3}$	−0.48 e $Å^{-3}$

nickel complexes. Thus, all the characteristic chemical shifts were identified by their intensity and multiplicity patterns.

3.2. *Single-crystal X-ray crystallography*

The molecular structures of *bis*[*N*-(diethylcarbamothioyl)-4-nitrobenzamide]nickel(II) (**2a**) and *bis*[*N*-(di-n-propylcarbamothioyl)-4-nitrobenzamide]nickel(II) (**2b**) with their packing

Table 2. Selected bond lengths (Å) and angles (°) for **2a** and **2b**.

2a		**2b**	
Ni1–S2	2.1331(10)	Ni1–O4	1.854(17)
Ni1–S1	2.1439(10)	Ni1–O1	1.859(17)
S1–C8	1.727(3)	Ni1–S2	2.136(8)
S2–C20	1.739(4)	Ni1–O4	1.854(17)
O1–C1	1.273(4)	Ni1–O1	1.859(17)
O4–C13	1.273(4)	Ni1–O4	1.854(17)
O4–Ni1–S2	94.90(8)	O4–Ni1–O1	84.42(7)
O1–Ni1–S2	178.52(8)	O4–Ni1–S2	94.57(6)
O4–Ni1–S1	178.16(7)	O1–Ni1–S2	176.16(7)
O1–Ni1–S1	94.43(7)	O4–Ni1–S1	174.64(8)
S2–Ni1–S1	86.91(4)	O1–Ni1–S1	94.98(6)

Table 3. Thermogravimetric analysis of **2a** and **2b**.

	2a	**2b**
1st stage decomposition temperature range (K)	506–598	511–802
2nd stage decomposition temperature range (K)	601–848	–
Maximum degradation temperature range (K)	553–593	553–603
Weight loss at 1st stage decomposition (%)	61	77
Weight loss at 2nd stage decomposition (%)	17	–
Residual weight at 873 K (%)	18.64	18.18

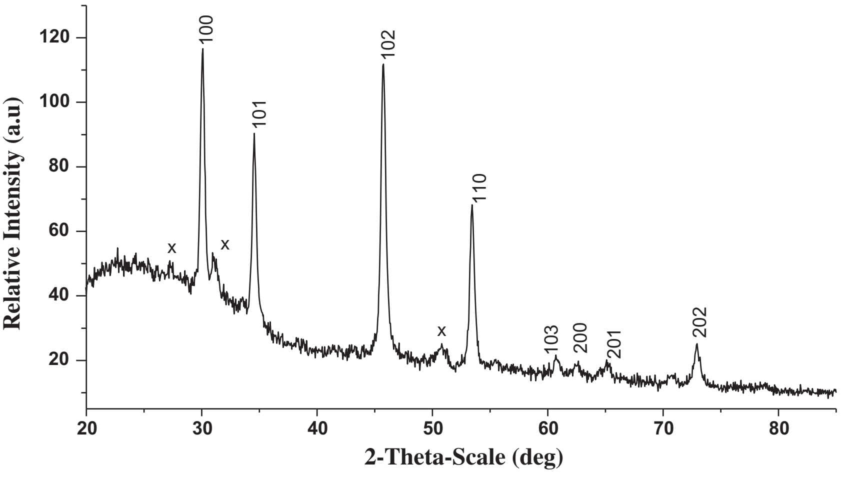
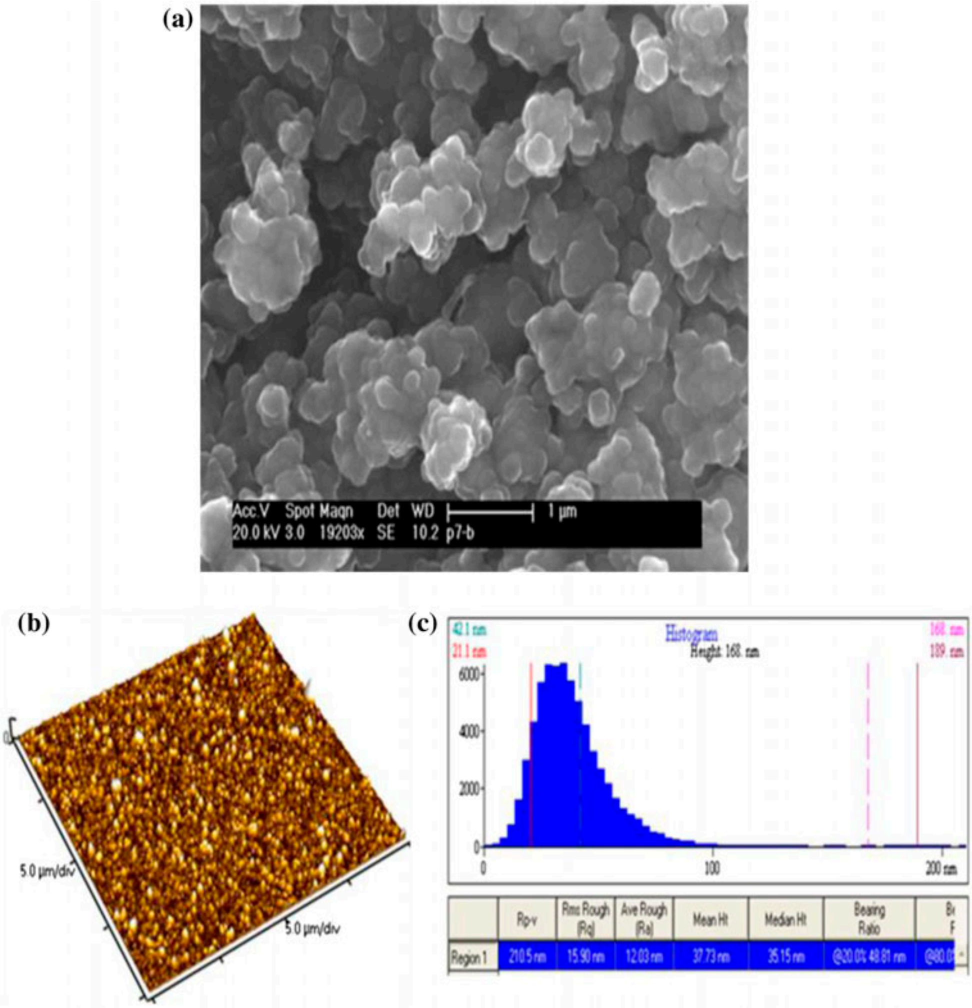


Figure 3. XRD pattern of the nickel sulfide thin film obtained from **2a**.

diagrams are shown in figures 1 and 2, respectively; crystal data and refinement and selected bond lengths and angles are listed in tables 1 and 2, respectively. In both of these structures, the nickels are coordinated to two *N*-(di-R-carbamothioyl)-4-nitrobenzamide (R = ethyl and *n*-propyl) ligands in *cis*-configuration. Nickels are in slightly distorted square planar geometry coordinated by two oxygens and two sulfurs forming *cis*-[NiL$_2$]. The angle between the planes (Ni, S1, O1) and (Ni, S2, O4) is 0.67(1)° for **2a** and 6.21 (1)° for **2b**. There is no significant difference between Ni–S bonds, 2.1331(10)-2.1439(10) Å in both complexes. The Ni–O bonds are 1.852(2)–1.8591(17) Å. The bond lengths are also comparable with those of square planar nickel(II)-β-thioxoketonates [8, 59–61].

The C–S, 1.720(3)–1.740(3) Å, and C–O, 1.265(3)–1.273(4) Å, bonds are longer than the free ligand (**1a**) C=S (1.6632(14) Å) and C=O (1.2228(17) Å) bonds. However, C–N bonds in the complexes, 1.308(4)–1.351(3) Å, were shorter than in the free ligand (1.3423 (17)–1.43431(16) Å). Lengthening of C–S and C–O bonds and shortening of C–N bonds



	Rp-v	Rms Rough (Rq)	Ave Rough (Ra)	Mean Ht	Median Ht	Bearing Ratio	B F
Region 1	210.5 nm	15.90 nm	12.03 nm	37.73 nm	35.15 nm	@20.0% 48.81 nm	@80.0

Figure 4. (a) SEM image of nickel sulfide thin film deposited from **2a** at 723 K, (b) AFM image in 3D view of film, and (c) shows average roughness and Rms roughness of thin film deposited at 723 K.

suggest delocalization of the π-electrons over the chelate rings. The chelate rings are almost planar, with maximum deviation from the mean plane less than 0.156(1) Å. The dihedral angles between the chelate rings are 5.9(1)° for **2a** and 7.3(1)° for **2b**. Both complexes also show short interchelate distances between S1 and S2, 2.942(4) Å for **2a** and 2.926(4) Å for **2b**, which are also within the usual S–S interchelate distance of analogous square planar nickel(II)-β-thioxoketonates (2.85(1)–2.95(1) Å). Unlike analogs reported earlier [60], both Ni complexes are not stacked into dimers, and the Ni···Ni distances in both complexes are > 6.30(1) Å. No close Ni···Ni interactions were observed.

3.3. *Thermal decomposition studies and characterization of thin films deposited from single-source precursors*

Thermal behavior of **2a** and **2b** has been examined by TGA, performed under an inert atmosphere of flowing nitrogen (20 mL min^{-1}) and a heating rate of 283 K/min. Thermal decomposition data of complexes are given in table 3. TGA of **2a** shows two-step decomposition with a rapid weight loss between 406 and 598 K and the second step between 601 and 848 K. The major part of the complex degraded sharply at 553–593 K leaving the approximate residual amount of 18.63%, close to the accumulative mass of decomposed product NiS (Calcd 19.04%). TGA of **2b** shows single-step decomposition of the complex starts at 511 K and accomplished by 802 K. The major part of the complex degraded sharply at 553–603 K leaving the approximate residual weight of 21.31%, close to the accumulative mass of decomposed product NiS (Calcd 18.18%).

Thin films of nickel sulfide were prepared as described in the experimental section and were studied and characterized by XRD, SEM, energy dispersion X-ray analysis (EDXA), and AFM. The XRD pattern of as deposited film from **2a** at 723 K is shown in figure 3. At 723 K, the XRD pattern from this film shows that there are two phases of nickel sulfide. The diffraction pattern of the dominant phase is nickel sulfide in hexagonal ($NiS_{1.19}$) with major diffraction peaks of (1 0 0), (1 0 1), (1 0 2), (1 1 0), and (2 0 2) planes (ICDD: 002-1277). The second phase is orthorhombic nonanickeloctasulfide (Ni_8S_9). The peaks of

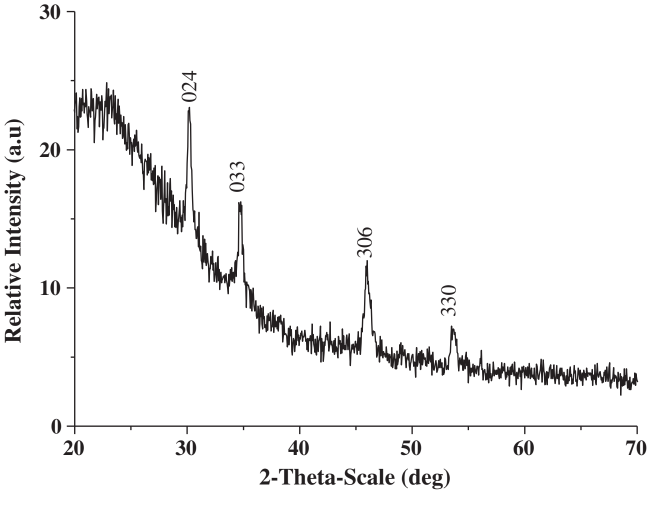
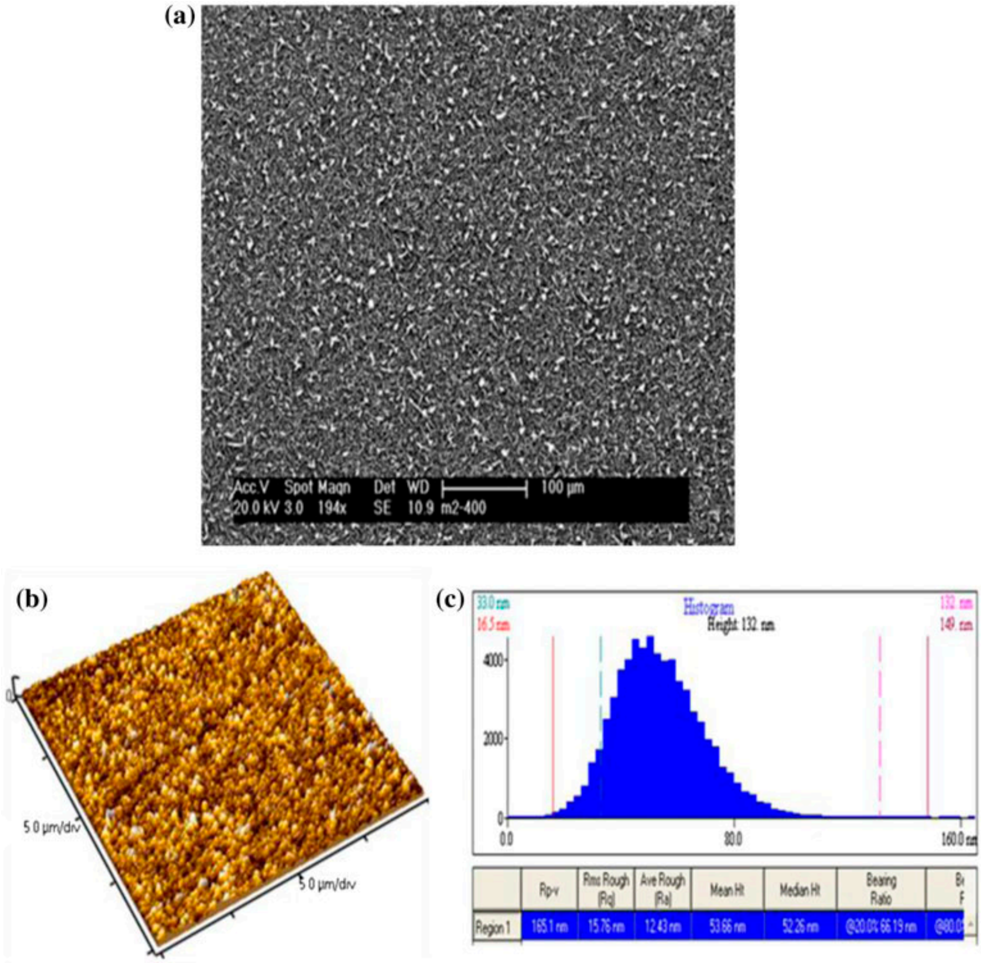


Figure 5. p-XRD pattern of the nickel sulfide thin films obtained from **2b** by AACVD.

the second phase are shown with "x". The SEM image of the film (figure 4(a)) shows that the film morphology is porous structure formed by the network of interlinked or agglomerated NiS crystals. EDX analysis of the film shows the composition Ni : S ratio: 61.67 : 44.57. The AFM image of the film (figure 4(b)) shows the growth of closely packed crystallites onto a glass substrate with an average roughness of 12.0 nm (figure 4 (c)). The XRD pattern of as deposited film from **2b** at 723 K is shown in figure 5. At 723 K, the XRD pattern from this film shows diffractions of hexagonal $Ni_{17}S_{18}$ in the space group P3121 (152) with major diffraction peaks of (0 2 4), (0 3 3), (3 0 6), and (3 3 0) planes (ICDD: 007-1010). The SEM image of the nickel sulfide thin film (figure 6(a)) shows compact and smooth film morphology with homogeneously dispersed particles. The particles with irregular appearance have good orientation and clearly well-defined grain boundaries. The EDXA of film indicates the composition as Ni : S ratio: 64.67 : 47.57. The AFM image of the film (figure 6(b)) shows the growth of closely packed crystallites onto a glass substrate with an average roughness of 12.4 nm (figure 6(c)).



	Rp-v	Rms Rough (Rq)	Ave Rough (Ra)	Mean Ht	Median Ht	Bearing Ratio	B F
Region 1	165.1 nm	15.76 nm	12.43 nm	53.66 nm	52.26 nm	@20.0% 66.19 nm	@80.0

Figure 6. (a) SEM image of nickel sulfide thin film deposited from **2b** at 723 K, (b) AFM image in 3D view of film, and (c) shows average roughness and Rms roughness of thin film deposited at 723 K.

4. Conclusions

Nickel(II) complexes of thiourea ligands, *N*-(diethylcarbamothioyl)-4-nitrobenzamide (**1a**) and *N*-(dipropylcarbamothioyl)-4-nitrobenzamide (**1b**), have been synthesized and the structures of the complexes determined by single-crystal X-ray crystallography. AACVD from **2a** and **2b** deposited nickel sulfide thin films at 450 °C. AFM studies showed the average roughness of the deposited films as 12 nm.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with Cambridge Crystallographic Data Center, CCDC 879,351 (**2a**) and 879,353 (**2b**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ IEZ, UK. Facsimile 44 01223 336 033, E-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.com.ac.uk/deposit.

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