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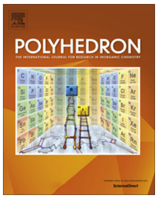

Symmetrical and unsymmetrical nickel(II) complexes of *N*-(dialkylcarbamothioyl)-nitro substituted benzamide as single-source precursors for deposition of nickel sulfide nanostructured thin films by AACVD

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ABSTRACT

The nickel(II) complexes of various *N*-(dialkylcarbamothioyl)-nitro substituted benzamides [dialkyl═di-propyl (**2a**); hexyl, methyl (**2b**); butyl, ethyl (**2c**); ethyl, isopropyl (**2d**)] have been synthesized and characterized by elemental analysis, I.R. spectroscopy, ^{1}H NMR and atmospheric pressure chemical ionization-mass spectrometry. The molecular structures of the complexes **2a** and **2d** were determined by single-crystal X-ray diffraction. Thermogravimetric analysis shows that complexes **2a**–**c** decompose in a single step and complex **2d** decomposes in two-steps to give a final residue corresponding to nickel sulfides. These complexes were used as single-source precursors for the deposition of nickel sulfide thin films by aerosol assisted chemical vapor deposition at 723 K. Powder X-ray diffraction patterns of the thin films deposited from complexes **2a** and **2c** showed the deposition of the hexagonal NiS phase with spherical crystallites. The films deposited from complex **2b** showed hexagonal and rhombohedral systems of the millerite NiS phase. The degree of the surface roughness of the films was determined by atomic force microscopy. Scanning electron microscopy and energy dispersive X-ray analysis results showed a uniform distribution of nickel sulfide in the films, which makes them potentially useful semiconducting materials on a structured surface.

1. Introduction

The phase diagram of the Ni–S system is more complex than those of 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 [1–3]. Some compounds, *e.g.* NiS and NiS_2, have been studied extensively, whilst for others only more limited information is available. NiS_2 (vaesite) is a *p*-type semiconductor with a band gap of 0.5 eV [4]. It is potentially useful in photo electrochemical solar devices [5,6], I.R. detectors [7], catalysis [8] and sensors [9]. It is also used as a hydrodesulfuration catalyst and as a cathode material in rechargeable lithium batteries [10]. There are relatively few reports on the deposition of nickel sulfide thin films from single source precursors by chemical vapor deposition. Nomura et al. studied the growth of $NiS_{1.03}$ from $[Ni(S_2CNEt_2)_2]$ on silicon (1 1 1) substrates by low pressure chemical vapor deposition [11]. Earlier, O'Brien and co-workers have reported the deposition of nickel sulfide films from dithiocarbamato compounds of the type $[Ni(S_2CNRR')_2]$ where RR′ = Et_2, MeEt, Me^{n}Bu or Me^{n}Hex, by AA [12]and LP-CVD methods [13], and also from xanthate compounds of the type $[Ni(S_2COR)_2]$ where R = Et or ^{i}Pr by AACVD [14]. 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 AACVD [15].

Substituted acylthiourea ligands exhibit various coordination modes: O and S bonded to M (monobasic bidentate) [16], only S bonded to M (neutral monodentate) [17], O and N bonded to M (neutral bidentate)[18], and O and S bonded to M and N bonded to M′ (monobasic bridging ligand) [19]. It has been shown in the literature that substituted acylthiourea ligands which do not form an intramolecular hydrogen bond tend to coordinate predominately in a bidentate (S, O) fashion to transition metal ions through the sulfur and acyl oxygen atoms [19]. Examples of this type of

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coordination are mononuclear complexes of the type [ML_2], where M = Ni(II), Cu(II), Co(II), Zn(II), Cd(II), Pt(II) and Pd(II) and L = substituted acylthiourea derivatives [20]. It has been suggested that intramolecular hydrogen bonding exists between the thiourea N–H moiety (where R/R′ = H) and the amidic O-donor atom to form a six-membered ring, with the consequence that the ligands coordinate to metal centers in a monodentate fashion through the sulfur donor atom [19].

In the last decade, there has been a significant interest in metal sulfide materials that have potential for use in the electronics industry or photovoltaic applications. Keeping in view the requirement of new semiconducting nanostructured materials for photovoltaic applications, we have tried to develop symmetrical and unsymmetrical single-source precursors for the deposition of nickel sulfide semiconducting nanostructured thin films by aerosol assisted chemical vapor deposition.

2. Experimental section

2.1. Materials and reagents

3,5-Dinitrobenzoyl chloride, ammonium thiocyanate, 4-nitrobenzoyl chloride, nickel acetate, di-*n*-propylamine, *N*-ethylbutylamine, *N*-ethylisopropylamine and *N*-hexylmethylamine were used as obtained from Sigma–Aldrich. The symmetrical and unsymmetrical ligands *N*-(dipropylcarbamothioyl)-3,5-dinitrobenzamide (**1a**), *N*-[hexyl(methyl)carbamothioyl]-3,5-dinitrobenzamide (**1b**), *N*-[ethyl(butyl)carbamothioyl]-3,5-dinitrobenzamide (**1c**) and *N*-[ethyl(propan-2-yl)carbamothioyl]-4-nitrobenzamide (**1d**) were synthesized and re-crystallized according to the literature methods [21–26].

2.2. Preparation of the nickel(II) complexes

2.2.1. Synthesis of bis[1-(3, 5-dinitrobenzoyl)-3, 3-dipropyl thiourea]nickel(II) (*2a*)

A solution of nickel acetate (0.005 mol) in methanol (35 cm^3) was added drop-wise to a solution of the ligand **1a** in a 1:2 ratio, with a small excess of the ligand, in ethanol (35 cm^3) at room temperature, and the resulting mixture was stirred for 3 h. The reaction mixture was filtered, washed with ethanol and re-crystallized from a THF/acetonitrile mixture (1:1). Brown. Yield: 3.8 g (81%). IR (ν_{max}/cm^{-1}): 2928, 2856 (Ar—H), 1501 (C—O), 1536 (C—N), 1128 (C—S). ^1H NMR (400 MHz, $CDCl_3$) in δ (ppm): 9.06 (t, 2H, Ar—H), 8.87 (d, 4H, Ar—H), 3.80 (m, 8H, —C$\underline{H}_2$), 1.59 (m, 8H, —C$\underline{H}_2$), 0.96 (t, 12H, C$\underline{H}_3$). *Anal.* Calc. for $C_{28}H_{34}N_8O_{10}S_2Ni$: C, 43.94; H, 4.48; N, 14.64; S, 8.38; Ni, 7.67. Found: C, 43.64; H, 4.29; N, 14.48; S, 8.35; Ni, 7.41%. Mass (MS-APCI) (major fragment, *m*/*z*): 765 [M+, $C_{28}H_{34}N_8O_{10}S_2Ni$].

2.2.2. Synthesis of bis[N-[hexyl(methyl)carbamothioyl]-3,5-dinitrobenzamide]nickel(II) (*2b*)

Complex **2b** was synthesized by the method described for complex **2a**. The quantities used were 3.68 g (0.01 mol) ligand **1b** and 1.24 g (0.005 mol) nickel acetate tetrahydrate in ethanol. Yellowish golden. M.p.: 283–284 K. Yield: 3.3 g (68%). IR (ν_{max}/cm^{-1}): 2927, 2855 (Ar—H), 1502 (C—O), 1537 (C—N), 1153 (C—S). ^1H NMR (400 MHz, $CDCl_3$) in δ (ppm): 9.09 (t, 2H, Ar—H), 8.77 (d, 4H, Ar—H), 3.84 (m, 4H, N—C$\underline{H}_2$), 3.04 (s, 6H, C$\underline{H}_3$), 2.59 (m, 4H, —C$\underline{H}_2$—), 1.84 (m, 4H, —C$\underline{H}_2$—), 1.62 (m, 4H, —C$\underline{H}_2$—), 1.31 (m, 4H, —C$\underline{H}_2$—), 0.94 (t, 6H, C$\underline{H}_3$). *Anal.* Calc. for $C_{30}H_{38}N_8O_{10}S_2Ni$: C, 45.41; H, 4.83; N, 14.12; S, 8.08; Ni, 7.40. Found: C, 44.62; H, 4.42; N, 14.07; S, 8.07; Ni, 7.24%. Mass (MS-APCI) (major fragment, *m*/*z*): 793 [M+, $C_{30}H_{38}N_8O_{10}S_2Ni$].

2.2.3. Synthesis of bis[N-[ethyl(butyl)carbamothioyl]-3,5-dinitrobenzamide]nickel(II) (*2c*)

Complex **2c** was synthesized by the method described for complex **2a**. The quantities used were 3.54 g (0.01 mol) ligand **1c** and 1.24 g (0.005 mol) nickel acetate tetrahydrate in ethanol. Yellowish golden. Yield: 3.3 g (70%). IR (ν_{max}/cm^{-1}): 2928, 2855 (Ar—H), 1503 (C—O), 1536 (C—N), 1154 (C—S). ^1H NMR (400 MHz, $CDCl_3$) in δ (ppm): 9.18 (t, 2H, Ar—H), 8.84 (d, 4H, Ar—H), 3.83 (m, 8H, N—C$\underline{H}_2$), 3.45 (m, 4H, —C$\underline{H}_2$), 1.71 (m, 4H, —C$\underline{H}_2$—), 1.20 (t, 6H, C$\underline{H}_3$), 0.91 (t, 6H, C$\underline{H}_3$). *Anal.* Calc. for $C_{28}H_{34}N_8O_{10}S_2Ni$: C, 43.94; H, 4.48; N, 14.64; S, 8.38; Ni, 7.67. Found: C, 43.93; H, 4.19; N, 14.54; S, 8.39; Ni, 7.30%. Mass (MS-APCI) (major fragment, *m*/*z*): 765 [M+, $C_{28}H_{34}N_8O_{10}S_2Ni$].

2.2.4. Synthesis of bis[N-[ethyl(propan-2-yl)carbamothioyl]-4-nitrobenzamide]nickel(II) (*2d*)

Complex **2d** was synthesized by the method described for complex **2a**. The quantities used were 3.09 g (0.01 mol) ligand **1d** and 1.24 g (0.005 mol) nickel acetate tetrahydrate in methanol. The reaction mixture was filtered, washed with ethanol and re-crystallized from a THF/acetonitrile mixture (1:1). Yellowish golden crystals. M.p.: 431–432 K. Yield: 3.5 g (82%). IR (ν_{max}/cm^{-1}): 2927, 2853 (Ar—H), 1508 (C—O), 1533 (C—N), 1142 (C—S); *Anal.* Calc. for $C_{26}H_{32}N_6O_6S_2Ni$: C, 48.24; H, 4.98; N, 12.98; S, 9.91; Ni, 9.07. Found: C, 48.51; H, 4.95; N, 12.87; S, 9.94; Ni, 8.98%. ^1H NMR (400 MHz, $CDCl_3$) in δ (ppm): 8.28 (d, $4H_{meta}$, *p*-nitrophenyl), 8.01 (d, $4H_{ortho}$, *p*-nitrophenyl), 4.05 (m, 4H, N-C$\underline{H}_2$), 3.70 (m, 2H, N—C$\underline{H}$), 1.35 (t, 6H, —C$\underline{H}_3$), 1.28 (s, 12H, —C$\underline{H}_3$). Mass (MS-APCI) (major fragment, *m*/*z*): 647 [M+, $C_{26}H_{32}N_6O_6S_2Ni$].

2.3. Physical measurements

The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on Bruker 400 MHz spectrophotometers using tetramethylsilane as an internal reference. The apparent resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet) and m (multiplet). Infrared measurements were recorded in the range 400–4000 cm^{-1} on a Spectrum 2000 spectrometer by Perkin Elmer and on a Specac single reflectance ATR instrument. Elemental analysis of the complexes was performed by a Flash 2000 elemental analyzer from the University of Manchester. All results were within 0.3% of the theoretical values. Metals analysis of the complexes was carried out by Thermo iCap 6300 Inductively Coupled Plasma Optical Emission Spectroscopy. Mass spectra of the complexes were recorded on a Micromass Platform II instrument. All the complexes were studied by thermogravimetry in an inert atmosphere, at a sample heating rate of 283 K min^{-1}, with a DuPont 2000 ATG. Thin films of nickel sulfide were carbon coated using Edward's E306A coating system before carrying out SEM and EDX analysis. SEM analysis was performed using a Philips XL 30FEG and EDX was carried out using a DX4 instrument. AFM analysis was carried out using a Veeco CP2 instrument. The p-XRD studies were performed on an Xpert diffractometer using Cu Kα radiation. The diffraction patterns were then compared to the documented patterns in the ICDD index.

2.4. X-ray structure determination

Single crystal X-ray diffraction data for compound **2a** were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Bruker SMART 1000 CCD diffractometer. A crystal for each of **1d** and **2d** was mounted on a loop and placed in a -373 K compressed air stream on an Agilent Gemini-EOS Single Crystal Auto diffractometer. The crystallographic data were integrated and corrected for absorption using *CrysAlisRed* (Oxford