

The synthesis and characterisation of tris(*N,N'*-diethylmonothiocarbamato)indium(III) [In(SOCNEt₂)₃] **1** and diethyl(*N,N'*-diethylmonothiocarbamato)indium(III) [Et₂In(SOCNEt₂)₂]**2**: potential precursors for the growth of indium sulfide by low pressure metal organic chemical vapour deposition

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Received 24th August 1998, Accepted 30th October 1998

The indium complexes [In(SOCNEt₂)₃] **1** and [Et₂In(SOCNEt₂)₂]**2**, containing the *N,N'*-diethylmonothiocarbamato ligand, have been prepared. Complex **1** is a colourless crystalline solid. Complex **2** was prepared by the comproportionation of **1** with triethylindium. The tris(diethylmonothiocarbamate) complex **1** is a distorted trigonal prismatic polymer with the unusual meridional configuration. The mixed alkyl diethylmonothiocarbamate **2** is a colourless polymeric solid, where the metal centre is found in a distorted trigonal bipyramidal geometry. Chain propagation occurs through In–O bonds. Both complexes have been characterised by their single-crystal X-ray structure determinations. Complex **1** can be used for the deposition of highly oriented films of β-In₂S₃ by low pressure metal-organic chemical vapour deposition (LPMOCVD) at temperatures ranging from 350–500 °C on borosilicate glass substrates.

Introduction

The carbamato family of ligands have been known for many years. Dithio- and diseleno-carbamates have found extensive technological applications,¹ whereas monothiocarbamates have received much less attention. Dichalcogenocarbamates have recently found application in the single-source approach to the preparation of semiconducting materials.² In continuing the development of such precursors, we now report on some novel monothiocarbamato complexes of indium; the first such complexes to be crystallographically characterised.

Single-source precursors may have considerable advantages over conventional sources (e.g. a metal alkyl and a main group hydride) and have been extensively studied in the past ten years.^{2–7} Such precursors have little or no tendency to take part in unwanted homogeneous reactions (pre-reactions). The complexes are often easy to handle and store, and toxic hazards are minimised as no permanent toxic gases are employed. A possible disadvantage of such precursors is that often their volatility is rather low, however assisted delivery methods such as aerosol assisted CVD or flash evaporation can overcome this difficulty.

The majority of work has been aimed at the growth of II/VI (II = Zn, Cd; VI = S, Se)^{2–5} or III/V (III = Al, Ga, In; V = N, P, As)^{3,6–7} materials, with much less attention given to III/VI materials. However, such materials have properties which are suitable for the design of optoelectronic and photovoltaic devices,⁸ and have intermediate band-gaps e.g. InS and β-In₂S₃ have band-gaps of 2.44⁹ and 2.07 eV¹⁰ respectively. These values may be compared to wide band-gap materials such as ZnS (3.68 eV)³ and narrow band-gap materials such as InAs (0.35 eV).³ Other applications of III/VI films include their use in the passivation of III/V materials.¹¹ Complexes involving indium and/or gallium with copper yield the important class of ternary materials of the form CuME₂ [E = S, Se, Te; M = In, Ga] or quaternary materials, CuM_{1–x}M'_xE₂ or CuME_{2–x}E'_x, which have been used in solar cells.^{12,13}

A variety of single-source organometallic precursors have

been employed in the preparation of III/VI films by metal-organic chemical vapour deposition (MOCVD). One particular group of complexes which have been extensively studied are the dithio- and diseleno-carbamates. The ligands, of the form R₂NCE₂[–] (E = S, Se), are 3-electron donors, capable of stabilising metal centres in a variety of oxidation states.¹ Complexes with the general formula RME₂CNR'₂ [M = Zn, Cd; E = S, Se] have been employed to grow thin films of II/VI materials by MOCVD techniques.^{2,14,15} Other work has involved precursors with asymmetric dithiocarbamate groups, e.g. complexes of the type M(E₂CNR'R'')₂ [M = Zn; R' = Me; R'' = Et, ⁿPr, ⁿBu], and have improved characteristics for deposition.¹⁶

Dithio- and diseleno-carbamates have also been used to prepare III/VI materials. Although complexes of the form M(E₂CNR₂)₃ have been known for some years,¹⁷ it was not until recently that complexes of this type were used in growth. Mixed alkyl dithiocarbamates [R₂MS₂CNEt₂; R = Me, Et, Me₃CCH₂; M = In, Ga] yielded films of β-In₂S₃ and In₆S₇ by low pressure metal-organic chemical vapour deposition (LPMOCVD) at temperatures ranging from 325 to 425 °C.¹⁸ A series of tri-alkylpropylenediaminedithiocarbamates [R₂MS₂CNMe(CH₂)₃-NMe₂; R = Me, Et, Me₃CCH₂, C₅H₁₁; M = Ga, In] have also been prepared, though no growth work has been reported.¹⁹ Highly oriented films of α-In₂S₃ have been prepared from a range of asymmetric tris(dialkyl)dithiocarbamates [In(E₂CNRR')₃; R = Me; R' = ⁿBu, ⁿHex (*n*-hexyl)] where best results are observed at substrate temperatures of 450–500 °C.²⁰ Thin films of cubic In₂Se₃ have been deposited from an asymmetric dialkyldiselenocarbamate precursor, In(Se₂CNMeⁿHex)₃, at temperatures of 450–500 °C.²¹ In addition, the ternary complex CuInSe₂, has been prepared from a stoichiometric mixture of In(Se₂CNMeⁿHex)₃ and Cu(Se₂CNMeⁿHex)₂, held at 250 °C with the substrate at 450 to 470 °C.²²

The monothiocarbamato [(R)₂NCOS[–]] ligand, an analogue of the dithio- or diseleno-carbamato ligands referred to above, has not been extensively investigated as a precursor for the preparation of semiconductor films. The Group 12 monothiocarbamates have been known for some time,²³ and bis(diethyl-

monothiocarbamato)cadmium(II), Cd(SOCNEt₂)₂, has recently been employed for the growth of CdS by LPMOCVD.²⁴ Oxygen incorporation in films grown by complexes of this type might be expected to be a problem, however studies of the thermal decomposition of carbonyl sulfide (COS) show that in static systems, between 350 and 600 °C, a heterogeneous reaction, generating CO and S, accompanies the homogeneous process, yielding CO₂ and CS₂.²⁵ Hence it is not surprising that Wright *et al.*²⁶ used mixtures of COS and dimethylcadmium to grow thin films of CdS by MOCVD, which show no oxygen contamination. An example of a III/VI complex where the metal is bonded to both oxygen and sulfur has been presented by Bessergenev *et al.*,²⁷ an indium(III) alkyl dithiocarbonate, In(S₂CO'Pr)₃, which was used to prepare the α-phase of In₂S₃, deposited at temperatures below 250 °C.

There have been a number of other approaches to the preparation of III/VI thin films by single-source methods. Nomura *et al.*^{28,29} have used alkylindium dithiolates [RInSR'] to grow tetragonal β-In₂S₃ thin films, highly oriented in the (103) direction, at substrate temperatures of 300–400 °C, and have also used Bu₂InS'Pr to grow In₂O₃ using an oxygenated carrier gas in the MOCVD process.³⁰ Barron *et al.*³¹ have used dialkylindium thiolates [(R₂InSR')₂; R = Me, 'Bu, "Bu; R' = 'Bu] to grow InS films at temperatures above 400 °C which yield In₂S₃ upon annealing. Below 400 °C, indium rich films are observed. The structures of the analogous dialkylindium selenolates have also been reported.³²

A different approach has been developed by Hampden-Smith *et al.*,³³ which involves the indium thiocarboxylate salt [HL]⁺-[In(SCOCH₃)₄]⁻ (L = 3,5-dimethylpyridine), prepared by the reaction of indium alkyls with thioacetic acid and the dialkylamine. Growth is achieved by aerosol-assisted chemical vapour deposition (AACVD), in which the precursor is dissolved in tetrahydrofuran before injection into the atomisation chamber. This method yields crystalline films of β-In₂S₃ at substrate temperatures as low as 210 °C.

Gysling *et al.*³⁴ have prepared InSe and In₂Se₃ thin films from the precursors Me₂InSePh and In(SePh)₃ by a spray MOCVD technique. Different phases of InSe were observed at different substrate temperatures, with a cubic phase observed at temperatures between 310 and 365 °C. Pyrolysis of In(SePh)₃ yielded hexagonal films of In₂Se₃ at substrate temperatures between 470 and 530 °C. Gallium sulfide has been prepared by Barron *et al.*,³⁵ from a gallium chalcogenide cubane complex, [(^tBu)-GaS]₄. GaS films were prepared on a variety of substrates, at temperatures between 380 and 550 °C. The same author³⁶ has recently prepared GaSe from similar cubane complexes at 325 to 370 °C using an atmospheric pressure MOCVD approach. Schulz *et al.*³⁷ have prepared Ga₂S₃ and Ga₂Se₃ from similar cubane precursors, where the alkyl groups are replaced by cyclopentadienyl derivatives. These complexes deposited III/VI films at temperatures at around 300 °C.

Here, we report the preparation and characterisation of some novel indium(III) complexes, the first example of such complexes involving the monothiocarbamate ligand. A tris(dialkylmonothiocarbamate) {[In(SOCNEt₂)₃] **1**} and a mixed alkyl monothiocarbamate {[Et₂In(SOCNEt₂)_n] **2**} are reported. The complexes are fully characterised, and the single crystal structures are discussed herein. Furthermore, we have prepared films of indium sulfide by LPMOCVD from **1** at a range of growth temperatures on borosilicate glass substrates. The films have been examined by various methods.

Experimental

Sodium diethylmonothiocarbamate was prepared by the literature method.²³ Indium(III) chloride and triethylindium (adduct purified) were gifts from Epichem Ltd. Toluene (BDH) was distilled over Na-benzophenone and degassed prior to use. All manipulations and reactions were carried out in an inert

atmosphere using Schlenk techniques and a vacuum line. Low pressure growth experiments (10⁻² Torr) were carried out using an Edwards model E2M8 vacuum pump system.

Preparation of tris(*N,N'*-diethylmonothiocarbamato)indium(III), [In(SOCNEt₂)₃] **1**

Indium(III) chloride (0.26 g, 1.18 mmol) was suspended in dry toluene (≈10 ml). Sodium diethylmonothiocarbamate (0.64 g, 4.11 mmol) was then added slowly to the suspension at room temperature, and the mixture was allowed to stir overnight. The toluene solution was transferred to another flask by filtration, and the solvent was removed *in vacuo* yielding a white powder. The powder was dissolved in toluene and placed in a freezer for 48 hours, where clear, plate-like crystals were obtained: white crystalline solid (mp 98.5 °C, 70% yield based on InCl₃). ¹H NMR (C₆D₆, 400 MHz): δ 0.72 [3 H, t, CH₂, ³J_{H-H} 7.0]; 0.80 [3 H, t, CH₂, ³J_{H-H} 7.0]; 2.97 [2 H, q, C-CH₃, ³J_{H-H} 7.0]; 3.09 [2 H, q, C-CH₃, ³J_{H-H} 7.0 Hz]. ¹³C NMR (C₆D₆, 100 MHz): δ 12.97 (CH₃); 41.88 (CH₂); 48.68 (CH₂); 182.37 (N-C-O-S). IR (Nujol mull): 669, 723, 877, 1078, 1140, 1211, 1262, 1302, 1379, 1462, 1537, 2047, 2355, 2720, 2857, 2922 cm⁻¹. Mass spectrum: *m/z* significant peaks include (L = SOCNEt₂) 512, 88% [InL₃]⁺; 379, 46% [InL₂]⁺; 248, 72% [InL]⁺; 233, 88% [In(SOCNEt-CH₂)₂]⁺; 132, 87% [L]⁺; 115, 25% [In]⁺; 74, 100% [SOCN]⁺ (Calc. for C₁₅H₃₀InO₃S₃N₃: C, 35.23; H, 5.91; N, 8.22. Found: C, 35.11; H, 5.58; N, 8.06%).

Preparation of diethyl(*N,N'*-diethylmonothiocarbamato)indium(III), [Et₂In(SOCNEt₂)_n] **2**

Triethylindium (0.67 g, 3.32 mmol) was sublimed under vacuum at 75 °C into a flask held at -196 °C. Dry toluene (≈10 ml) was then added to the Et₃In. Complex **1** (0.84 g, 1.67 mmol) was dissolved in dry toluene (≈10 ml) and added slowly to the triethylindium solution at 0 °C. The mixture was allowed to stir at room temperature for 90 minutes, then the solution was concentrated under vacuum and placed in a refrigerator overnight. A white crystalline product was observed which was collected by filtration. Some of this product was recrystallised in toluene to give clear, rectangular crystals: white crystalline solid (mp 53 °C, 82% yield based on Et₃In). ¹H NMR (C₆D₆, 400 MHz): δ 0.94 [3 H, t, N-CH₂, ³J_{H-H} 7.1]; 1.46 [3 H, t, In-CH₂, ³J_{H-H} 7.0]; 3.02 [2 H, q, CH₃, ³J_{H-H} 7.1]; 3.32 [2 H, q, CH₃, ³J_{H-H} 7.0 Hz]. ¹³C NMR (C₆D₆, 100 MHz): δ 12.28 (CH₃); 12.98 (CH₃); 13.11 (CH₃); 41.87 (CH₂); 46.56 (CH₂); 181.71 (N-C-O-S) [Calc. for (C₉H₂₀InOSN)_n: C, 35.42; H, 6.61; N, 4.59. Found: C, 35.05; H, 6.24; N, 4.22%].

Physical measurements

NMR spectra were recorded using a Bruker AM400 pulsed Fourier-transform spectrometer. Infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer as Nujol mulls between potassium bromide plates. Optical absorption measurements were carried out using a Philips PU 8710 UV/Vis spectrophotometer. Electron microscopy and energy dispersive analytical X-ray analysis (EDAX) was carried out with a JEOL J535CM scanning electron microscope. Microanalyses were carried out by the service at Imperial College. Melting points were recorded in sealed tubes with an electrothermal melting point apparatus. Mass spectra were recorded between 100 and 600 u with a scan speed of 0.9 u s⁻¹.

Single-crystal X-ray diffraction study

Table 1 provides a summary of the crystal data, data collection and refinement parameters for complexes **1** and **2**. The structures were solved by direct methods and all the non-hydrogen atoms were refined anisotropically by full-matrix least squares based on *F*². In both structures the hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters,

Table 1 Crystal data, data collection and refinement parameters of **1** and **2**^a

	1	2
Formula	C ₁₅ H ₃₀ N ₃ O ₃ S ₃ In	C ₉ H ₂₀ NOSIn
<i>M</i>	511.4	305.1
Colour, habit	Colour, thin plates	Colour, platy needles
Crystal size/mm	1.00 × 0.60 × 0.03	0.90 × 0.67 × 0.13
Lattice type	Triclinic	Monoclinic
Space group symbol, number	<i>P</i> $\bar{1}$, 2	<i>P</i> 2 ₁ / <i>c</i> , 14
<i>a</i> /Å	9.588(5)	8.477(1)
<i>b</i> /Å	9.740(5)	7.992(1)
<i>c</i> /Å	13.790(6)	18.154(1)
<i>a</i> /°	80.46(3)	—
<i>β</i> /°	78.58(3)	95.29(1)
<i>γ</i> /°	63.55(3)	—
<i>U</i> /Å ³	1125.7(9)	1224.6(2)
<i>Z</i>	2	4
<i>D</i> _c /g cm ⁻³	1.509	1.655
<i>F</i> (000)	524	616
<i>μ</i> /mm ⁻¹	1.35	2.07
<i>θ</i> range/°	2.3–25.0	2.4–27.5
No. of unique reflections		
measured	3788	2678
observed, $ F_o > 4σ(F_o)$	3208	2240
Absorption correction	Semi-empirical	Semi-empirical
Max., min. transmission	0.96, 0.63	0.84, 0.40
No. of variables	226	119
<i>R</i> ₁ ^b	0.033	0.033
<i>wR</i> ₂ ^c	0.066	0.076
Weighting factors, <i>a</i> , <i>b</i> ^d	0.032, 0.000	0.046, 0.000
Largest diff. peak and hole/e Å ⁻³	0.62, -0.42	0.97, -0.58

^a Details in common: graphite monochromated Mo-K α radiation, ω scans, Siemens P4/PC diffractometer, 203 K, refinement based on *F*². ^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}$. ^d $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

U(H) = 1.2*U*_{eq}(C) [*U*(H) = 1.5*U*_{eq}(C–Me)], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system.³⁸

CCDC number 186/1226.

See <http://www.rsc.org/suppdata/dt/1998/4205/> for crystallographic files in .cif format.

Results and discussion

The complex [In(SOCNET₂)₃] **1** was prepared by the stoichiometric reaction of indium(III) chloride and sodium diethylmonothiocarbamate in toluene. The white powdered product was isolated after filtration and removal of solvent *in vacuo*. Complex **1** is soluble in toluene, benzene, hexane and other organic solvents. The complex was recrystallised from a concentrated toluene solution to give thin, colourless crystals. When left in contact with air, **1** showed no appreciable tendency to decompose over an extended time period.

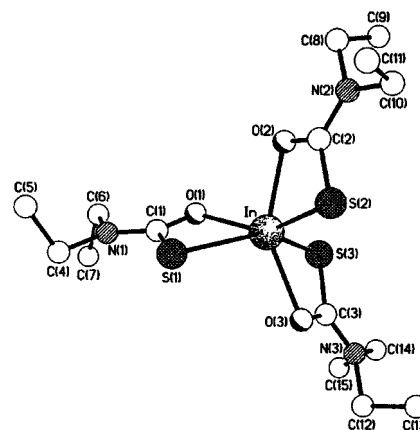
[Et₂In(SOCNET₂)₃] **2** was prepared by the comproportionation of **1** and triethylindium in toluene, and isolated as thin, rectangular clear crystals from the concentrated reaction mixture. Complex **2** is soluble in toluene and benzene, and sparingly soluble in hexane. When left in contact with air, **2** decomposes slowly, becoming yellow after some time.

Single-crystal X-ray structures of [In(SOCNET₂)₃] **1** and [Et₂In(SOCNET₂)₃] **2**

The X-ray analysis of **1** confirmed the formation of the anticipated tris-chelate complex shown in Fig. 1. The arrangement of the ligands is meridional (*mer*) in contrast to the facial (*fac*) geometry observed in the related iron(III) complex.³⁹ It is interesting to compare the co-ordination geometry of the iron complex and **1**, especially as both complexes have few if any

Table 2 Selected interatomic distances (Å) and angles (°) for **1**

In–O(2)	2.243(3)	In–O(3)	2.290(3)
In–O(1)	2.318(3)	In–S(1)	2.486(2)
In–S(3)	2.502(2)	In–S(2)	2.533(2)
S(1)–C(1)	1.752(4)	S(2)–C(2)	1.750(4)
S(3)–C(3)	1.753(4)	O(1)–C(1)	1.260(5)
O(2)–C(2)	1.273(5)	O(3)–C(3)	1.261(5)
O(2)–In–O(3)	147.6(1)	O(2)–In–O(1)	89.1(1)
O(3)–In–O(1)	117.8(1)	O(2)–In–S(1)	109.94(9)
O(3)–In–S(1)	98.39(9)	O(1)–In–S(1)	64.96(8)
O(2)–In–S(3)	100.3(8)	O(3)–In–S(3)	65.12(8)
O(1)–In–S(3)	88.61(8)	S(1)–In–S(3)	138.59(4)
O(2)–In–S(2)	65.38(8)	O(3)–In–S(2)	92.66(9)
O(1)–In–S(2)	148.61(8)	S(1)–In–S(2)	105.45(5)
S(3)–In–S(2)	112.69(5)		

**Fig. 1** The molecular structure of [In(SOCNET₂)₃] **1**.

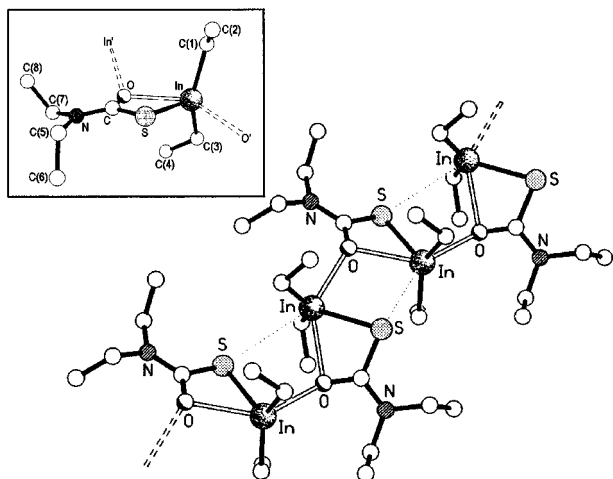
significant intermolecular interactions. The differences in the geometries observed for the two complexes can be rationalised in terms of the differences between the bonding for a Group 13 main group element and a transition metal. In the case of the iron complex, there will be some covalent character, and so overlap of the d-orbitals of the Fe centre with the bonding electrons of the monothiocarbamate ligands will be an important factor. The complex hence adopts a structure close to octahedral and in the statistically preferred facial geometry.

In the case of the indium complex, the ligand–metal interactions are those of a sphere of +3 charge with negative charge on the ligand donors; directional bonding is likely to be of little importance. The negative charge on the ligands resides predominantly at the sulfur atoms. An isolated molecule would adopt a trigonal planar geometry, were there no donor groups. However, in this system, the pendant oxygen atoms, with a small net negative charge, approach the positive charge on the indium. This contrast is achieved by two of the oxygen atoms being associated with one side of the trigonal plane and the third oxygen atom associated with the other side. The result of this is that the geometry observed for **1** is a distorted trigonal prism, with the sulfur atoms meridionally arranged. The co-ordination planes of the monothiocarbamate ligands are inclined by 84, 57 and 82° to the In/C(1)/C(2)/C(3) molecular plane. The In–S and In–O bond lengths are in the ranges 2.486(2)–2.533(2) Å and 2.243(3)–2.318(3) Å respectively, the long In–O distances being consistent⁴⁰ with only a small negative charge on the oxygen atoms, all of which retain a distinctive C=O character [bond lengths in the range 1.260(5)–1.273(5) Å, Table 2]. Thus, the dominant metal–ligand interaction is between indium and sulfur, an ideal scenario for its utilisation as an indium sulfide single source precursor. Although Fig. 1 depicts the Λ configuration the complex crystallises in a centrosymmetric space group and thus there are equal numbers of Λ and $\bar{\Lambda}$ forms.

The single-crystal X-ray study of the product of the compro-

Table 3 Selected interatomic distances (Å) and angles (°) for **2**

In–C(3)	2.155(4)	In–C(1)	2.158(4)
In–O'	2.501(3)	In–S	2.567(1)
In–O	2.607(3)	S–C	1.750(4)
O–C	1.265(5)	O–In'	2.501(3)
C(3)–In–C(1)	141.6(2)	C(3)–In–O'	87.7(1)
C(1)–In–O'	99.3(1)	C(3)–In–S	114.9(1)
C(1)–In–S	103.3(1)	O'–In–S	84.1(1)
C(3)–In–O	93.1(1)	C(1)–In–O	103.6(1)
O'–In–O	141.4(1)	S–In–O	60.7(1)
In–O–In'	112.9(1)		

**Fig. 2** The polymeric structure of $[\text{Et}_2\text{In}(\text{SOCNEt}_2)]_n$, **2**. Inset: the repeat unit of **2** indicating the geometry around the metal centre.

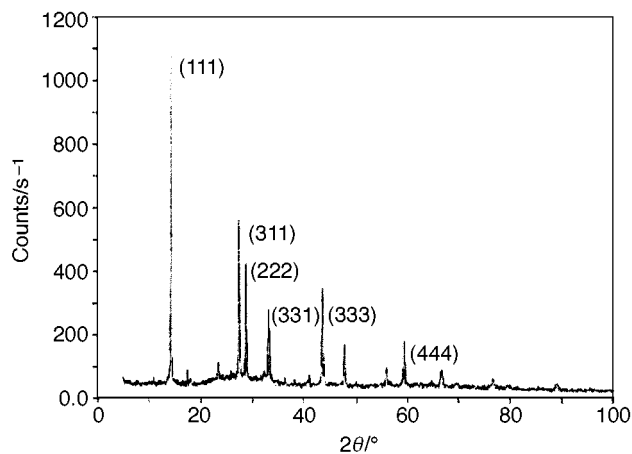
portionation of **1** with triethylindium reveals the formation of a polymeric complex with a 1:1:2 indium:monothioacetate:ethyl stoichiometry. The geometry at indium can probably be best described as severely distorted trigonal bipyramidal with the strongly co-ordinated sulfur atom and the two carbon atoms C(1) and C(3) forming the equatorial plane. The In–S distance of 2.567(1) Å is slightly longer than those seen in **1** whilst the chelating In–O distance is significantly increased [2.607(3) Å, Table 3]. This latter increase is probably in part due to the additional binucleating role of the oxygen atom which serves to bridge [2.501(3) Å] adjacent metal centres; the non-bonded In...In separation is 4.26 Å.

The polymer chain propagates *via* the crystallographic 2_1 screw axis, the indium atoms being arranged to form a zigzag chain (Fig. 2). The alternating pattern of monothioacetate ligands as one progresses along the polymer direction results in the sulfur atom attached to one indium atom being directed into the “vacant” co-ordination site of the next in the chain, *i.e.* adopting a pseudo-bridging role analogous to that of the oxygen atom. The S...In distance of 3.51 Å, however, is long and any internuclear interaction must be very weak. Adjacent chains are arranged parallel to each other, and with their exteriors being dominated by ethyl groups, there are no interchain interactions other than normal van der Waals.

Complex **2** is similar to a dimethylindium thioacetate complex reported by Hausen and Guder.⁴¹ In both structures, the indium atom has a 5-co-ordinate geometry, and a similar indium–oxygen bridging character. However, **2** has shorter In–S bonds [2.567(1) *vs.* 2.632(6) Å] and a longer In–O bond length [2.607(3) *vs.* 2.582(15) Å], suggesting a greater affinity for sulfur in this complex. Interestingly, the thioacetate complex decomposes at between 132 and 140 °C, a much higher temperature than the melting point of **2** (53 °C).

Deposition of thin films

Thin films of indium sulfide have been grown using $[\text{In}(\text{SOC-$

**Fig. 3** XRD pattern of $\beta\text{-In}_2\text{S}_3$ grown from **1** at 400 °C.

NEt_2]**1** as a single source precursor. The films were grown on borosilicate glass substrates by MOCVD. Growth experiments were carried out using a cold wall low-pressure MOCVD reactor, which has been described in detail elsewhere. In brief, the reactor consists of a furnace for heating the precursor, a tungsten filament lamp, which is used to heat a graphite susceptor, holding the substrate, a thermocouple which is used to control the temperature at the substrate, and a high-vacuum pump which holds the system at 10^{-2} Torr throughout the experiments.⁴²

Films were grown at substrate temperatures ranging from 350 to 500 °C, while the volatilisation temperature for the precursor was kept constant at 150 °C. At 350 °C the growth of indium sulfide is very slow, with very poor films observed after several hours growth. At higher temperatures however, the quality of the films is improved greatly. At 400 °C, bright orange-red films are grown over *ca.* 2 hours. At a substrate temperature of 500 °C slightly darker reddish-brown films are observed after one hour of growth.

Powder diffraction analysis of the films prepared at temperatures of 400 °C and higher showed that the cubic β -phase of In_2S_3 had been deposited (Fig. 3). The films are highly oriented in the (111) direction, especially for the case for growth at 500 °C. EDAX profiles of the films show peaks for indium and sulfur, as well as a peak for silicon, due to the glass substrate. The indium/sulfur ratio was found to be approximately 2:3. Similarities in the EDAX profiles at 400 and 500 °C suggest that the stoichiometry of the films is not affected greatly by the temperature of growth.

Scanning electron microscopy (SEM) was used to analyse the thin films of indium sulfide. Poor coverage of the substrate is observed for deposition at 350 °C, with individual crystallites of In_2S_3 discernible (Fig. 4a). The crystallites are cubic, consistent with the results of X-ray powder diffraction. Full coverage of the substrate is observed for films grown at 400 °C, but the films were not uniform in terms of the orientation of the crystallites and their size (Fig. 4b). However, the degree of uniformity is markedly increased in films deposited at 500 °C. The crystallites appear much more strongly oriented, as suggested by X-ray analysis, and there is a much narrower range of particle dimensions, with crystallites of *ca.* 2–3 μm observed (Fig. 4c). SEM images of the side profile of the films grown at 500 °C, show that the film is approximately 1 μm thick, thus giving a growth rate of approximately 1 $\mu\text{m h}^{-1}$ (Fig. 4d). The band-gap of the film deposited at 500 °C, determined by the direct band-gap method⁴³ was found to be 2.12 eV, which compares favourably with the literature figure of 2.07 eV.¹⁰

Conclusions

Novel indium complexes incorporating the monothioacetate

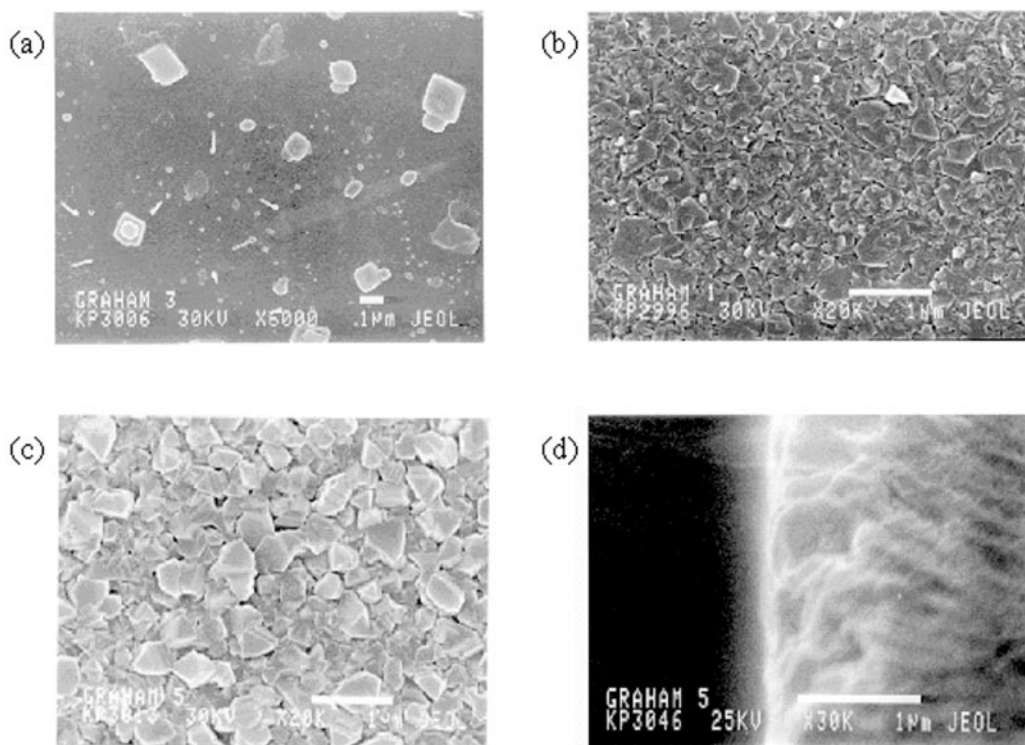


Fig. 4 SEM images of films grown from **1** on glass substrates at (a) 350 °C, (b) 400 °C, (c) 500 °C, and a side profile (d) at 500 °C.

ligand have been prepared. $[\text{In}(\text{SOCNET}_2)_3]$ **1** is a colourless, crystalline complex and the structure has been shown to be monomeric. The complex exhibits relatively short In–S contacts, and corresponding short C–O bond lengths. $[\text{Et}_2\text{In}(\text{SOCNET}_2)]_n$ **2** is also a colourless, crystalline solid but exists as a polymer, with the chain propagated through In–O bonds. The shortened In–S contacts are also observed in this structure.

Preliminary growth studies suggest that these complexes may be useful single-source precursors for the preparation of indium sulfide by MOCVD. Complex **1** has been used to prepare thin films of indium sulfide at growth temperatures ranging from 350–500 °C. At the higher end of this range, the films are well-ordered, and highly oriented $\beta\text{-In}_2\text{S}_3$. Growth has not yet been attempted using complex **2**.

Further work in this area is in hand. Other indium tris(dialkylmonothiocarbamates) with either longer alkyl chains or asymmetric alkyl units will be prepared, with an aim to increase the volatility of the precursors. In addition, the mixed alkyl-indium monothiocarbamates, analogous to complex **2**, can be investigated to see if the polymeric character of the complex reported here is maintained with bulkier alkyl substituents. Further investigation into the gallium analogues of all of the complexes mentioned above will also be carried out.

Acknowledgements

P. O. B. thanks the EPSRC and Leverhulme Trust for their support of work on single-molecular precursors. P. O. B. is the Sumitomo/STS Professor of Materials Chemistry at Imperial College, and the Royal Society Amersham International Research Fellow (1997/98). G. A. H. would like to thank the EPSRC for a CASE award with Epichem Ltd. M. C. thanks the EPSRC for a studentship. We thank Mr Keith Pell of the Biomedical Science Department, Queen Mary and Westfield College, London, for SEM and EDAX analysis, and Mr Richard Sweeney of the Materials Department, Imperial College, for thin film X-ray analysis.

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Paper 8/06622A