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Aerosol-assisted metallo-organic chemical vapour deposition of Bi$_2$Se$_3$ films using single-molecule precursors. The crystal structure of bismuth(III) dibutyldiselenocarbamate

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The complexes [Bi{Se$_2$CN(C$_2$H$_5$)$_2$}$_3$], [Bi{Se$_2$CN(C$_4$H$_9$)$_2$}$_3$], [Bi{Se$_2$CN(CH$_3$)(C$_4$H$_9$)}$_3$] and [Bi{Se$_2$CN(CH$_3$)(C$_6$H$_{13}$)}$_3$] have been synthesized and characterized structurally using IR, ^{1}H and ^{13}C NMR. In addition, the crystal structure of [Bi{Se$_2$CN(C$_4$H$_9$)$_2$}$_3$] was determined by single-crystal X-ray diffraction, showing the bismuth centre coordinated to three dialkyldiselenocarbamate ligands through the selenium donor atoms. The Bi(III) compounds were used as precursors for the deposition of Bi$_2$Se$_3$ films on glass substrates through aerosol-assisted metallo-organic chemical vapour deposition (AA-MOCVD).

Introduction

Single-molecule precursors have been widely used to prepare metal chalcogenides as thin films or nanopowders.[1–4] Thus, both elements needed for the final product come from a single molecule, allowing one-step preparation of the metal chalcogenide phase and avoiding the use of hazardous compounds such as hydrogen sulfide or hydrogen selenide. Compounds used as sources of metal selenides include metal diselenocarbamates (ZnSe, CdSe, PbSe),[5–8] (CH$_3$)$_2$InSe(C$_6$H$_5$) and In{Se(C$_6$H$_5$)}$_3$ (InSe and In$_2$Se$_3$),[9] bulky selenolate complexes of the type M(SeC$_6$H$_2$R$_3$-2,4,6)$_3$,[10] and diselenoimidodiphosphinate compounds (CdSe, As$_2$Se$_3$, Sb$_2$Se$_3$, Bi$_2$Se$_3$).[11,12] The paper by Crouch et al.[12] is the only report of chemical vapour deposition (CVD) of Bi$_2$Se$_3$ films using a single source approach. Bi$_2$Se$_3$, a narrow band gap semiconductor with E_g = 0.24 eV,[13] crystallizes with a rhombohedral lattice and, together with the analogous isomorphic compounds Bi$_2$Te$_3$ and Sb$_2$Te$_3$, is of interest for solid-state thermoelectric devices. These narrow band-gap semiconductors and their alloys have been used for cooling and for power generating devices operating near room temperature (e.g., Peltier coolers).[14]

The aim of the present work is to assess the potential of Bi(III) dialkyldiselenocarbamato complexes as single sources for the preparation of Bi$_2$Se$_3$ films using the AA-MOCVD method. We report the synthesis and characterization by IR, ^{1}H and ^{13}C NMR of a series of Bi(III) dialkyldiselenocarbamato complexes, [Bi(Se$_2$CNRR')$_3$] [where R = C$_2$H$_5$ (Et), ^{n}C$_4$H$_9$ (Bu^n) or CH$_3$ (Me), and R' = C$_2$H$_5$ (Et), ^{n}C$_4$H$_9$ (Bu^n) or ^{n}C$_6$H$_{13}$ (Hex^n)], with the crystal structure of [Bi{Se$_2$CN(C$_4$H$_9$)$_2$}$_3$]. This is the first reported Bi(III) diselenocarbamate, confirmed by a search of the Cambridge Structural Database.[15] As observed for the analogous Bi compound containing S$_2$CNBu^n$_2$,[16,17] [Bi(Se$_2$CN-Bu^n$_2$)$_3$] has three diselenocarbamate anions coordinated to the Bi^{3+} centre in a bidentate-chelating fashion, leading to a coordination environment best described as a distorted triangular antiprism.

Experimental

Preparation and identification of the compounds [Bi(Se$_2$CNRR^1)$_3$]

All chemicals were of at least reagent grade and were used as supplied by Aldrich. CSe$_2$ was prepared following reported methods.[18] **CAUTION**: carbon diselenide is a malodorous and very toxic liquid which should only be handled in a well-ventilated fume hood under strict safety conditions.

All the [Bi(Se$_2$CNRR')$_3$] compounds were prepared in a similar way, with CSe$_2$ reacting with the respective secondary amine in a methanolic solution and also in the presence of Bi$_2$O$_3$ in suspension. [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] was typically obtained as follows. Dibutylamine (5.17 g, 40 mmol) and then CSe$_2$ (4 g, 50 mmol) were added to a stirred suspension of Bi$_2$O$_3$ (2.80 g, 6 mmol) in methanol (20 cm^3). The mixture was stirred at room temperature for 48 h, and the orange precipitate collected by vacuum filtration. Recrystallization from a hot mixture of chloroform and methanol (3 : 1) followed by mechanical centrifugation yielded an orange solid which was manually harvested and kept in a flask under a nitrogen atmosphere. Single-crystals suitable for X-ray studies were obtained by recrystallization from acetone.

All the compounds were characterized by elemental analysis (theoretical values are given in parentheses), IR, ^{1}H and ^{13}C NMR spectroscopy. The elemental analyses were performed twice for the recrystallized compounds. The difference between the calculated and experimental values observed for [Bi{Se$_2$CN(C$_4$H$_9$)$_2$}$_3$] may be due to slight degradation of the analyzed sample.

[Bi{Se$_2$CN(C$_2$H$_5$)$_2$}$_3$]. ^{1}H NMR: δ 1.38 (6H, t, CH$_2$CH_3), 3.91 (4H, q, CH_2CH$_3$); ^{13}C NMR: δ 12.04 (CH$_2$$CH_3$), 51.56 (C$H_2CH_3$), 191.95 (Se$_2$CN); selected IR data (cm^{-1}): 1493 v(C–N), 820 v(C–Se); mp 176 °C; elemental composition: C 19.31 (19.13), H 3.29 (3.21), N 3.64 (4.47)%.

[Bi{Se$_2$CN(C$_4$H$_9$)$_2$}$_3$]. ^{1}H NMR: δ 0.95 (3H, t, (CH$_2$)$_3$CH_3), 1.38 (2H, m, (CH$_2$)$_2$CH_2CH$_3$), 1.81 (2H, m, CH$_2$CH_2CH$_2$CH$_3$), 3.84 (2H, t, CH_2CH$_2$CH$_2$CH$_3$); ^{13}C NMR: δ 13.72 ((CH$_2$)$_3$CH_3), 20.13 ((CH$_2$)$_2$CH_2CH$_3$), 28.79 ((CH$_2$)CH_2(CH$_2$)CH$_3$), 57.16 (CH_2(CH$_2$)$_2$CH$_3$), 192.34 (Se$_2$CN); selected IR data (cm^{-1}): 1487 ν(C–N), 851 ν(C–Se); mp 118 °C; elemental composition: C 25.59 (29.22), H 4.19 (4.91), N 3.17 (3.79)%.

[Bi{Se$_2$CN(CH$_3$)(C$_4$H$_9$)}$_3$]. ^{1}H NMR: δ 0.96 (3H, t, (CH$_2$)$_3$CH_3), 1.37 (2H, m, (CH$_2$)$_2$CH_2CH$_3$), 1.79 (2H, m, CH$_2$CH_2CH$_2$CH$_3$), 3.43 (3H, s, CH$_3$), 3.88 (2H, t, CH_2CH$_2$CH$_2$CH$_3$); ^{13}C NMR: δ 13.76 ((CH$_2$)$_3$CH_3), 20.03 ((CH$_2$)$_2$CH_2CH$_3$), 28.75 ((CH$_2$)CH_2(CH$_2$)CH$_3$), 45.02 (CH$_3$), 59.66 (CH_2(CH$_2$)$_2$CH$_3$), 193.37 (Se$_2$CN); Selected IR data (cm^{-1}): 1493 ν(C–N), 865 ν(C–Se); mp 132 °C; elemental composition: C 21.60 (21.98), H 3.54 (3.69), N 3.94 (4.28)%.

[Bi{Se$_2$CN(CH$_3$)(C$_6$H$_{13}$)}$_3$]. ^{1}H NMR: δ 0.89 (3H, t, (CH$_2$)$_5$CH_3), 1.31 (6H, m, (CH$_2$)$_2$(CH_2)$_3$CH$_3$), 1.80 (2H, m, CH$_2$CH_2(CH$_2$)$_3$CH$_3$), 3.42 (3H, s, CH$_3$), 3.87 (2H, t, CH_2(CH$_2$)$_4$CH$_3$); ^{13}C NMR: δ 14.00 ((CH$_2$)$_5$CH_3), 22.54 ((CH$_2$)$_4$CH_2CH$_3$), 26.39 ((CH$_2$)$_3$CH_2CH$_2$CH$_3$), 26.66 ((CH$_2$)$_2$-CH_2(CH$_2$)$_2$CH$_3$), 31.39 ((CH$_2$)CH_2(CH$_2$)$_3$CH$_3$), 45.00 (CH$_3$), 59.89 (CH_2(CH$_2$)$_4$CH$_3$), 193.32 (Se$_2$CN); Selected IR data (cm^{-1}): 1496 ν(C–N), 857 ν(C–Se); mp 112 °C; elemental composition: C 26.57 (26.99), H 4.37 (4.53), N 3.69 (3.94)%.

Crystallography

A suitable single crystal of [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] **I** was mounted on a glass fibre using perfluoropolyether oil.[19] Data were collected on a Nonius Kappa CCD diffractometer with Mo-Kα graphite-monochromated radiation (λ = 0.7107 Å). The structure was solved by the direct methods of SHELXS 97,[20] and refined by full-matrix least squares on F^2 using SHELXL 97,[21] with anisotropic displacement parameters for non-hydrogen atoms and common bond length restraints for the alkyl chains [–(CH$_2$)$_3$CH$_3$] of {Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$^-$. Multi-scan absorption corrections were also applied.[22] Thermal ellipsoids of terminal carbon atoms from four of the alkyl chains showed large displacements in more than one direction, suggesting that they are affected by thermal disorder. These atoms were modelled with common isotropic displacement parameters (one for the –CH$_2$– groups and one for the terminal –CH$_3$ groups) (Fig. 1). One terminal –CH$_3$ group [atom C(42)] from one alkyl chain was located in two alternative positions, and it was modelled with variable occupancy factors in order to ensure the best possible fit for the distribution of electron

Table 1 Crystal data and structure refinement information for [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] **I**

Formula	C$_{27}$H$_{54}$BiN$_3$Se$_6$
M_r	1103.47
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	11.39620(10)
b/Å	11.97520(10)
c/Å	28.0596(4)
α/°	81.8236(5)
β/°	86.7661(4)
γ/°	86.6659(8)
V/Å^3	3779.51(7)
Z	2
D_c/g cm^{-3}	1.939
μ(Mo-Kα)/mm^{-1}	10.463
$F(000)$	2096
Crystal size/mm	0.23 × 0.12 × 0.10
Crystal type	Orange blocks
θ Range/°	3.52–27.49
Index ranges, hkl	−14 to 14, −15 to 15, −33 to 36
Reflections collected	34123
Independent reflections (R_{int})	16822 (0.0633)
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0585$, $wR2 = 0.1305$
Final R indices (all data)	$R1 = 0.0867$, $wR2 = 0.1477$
Largest diff. peak and hole/e Å^{-3}	2.287 and −2.767

density [occupancies of 31 and 69% for C(42) and C(42′), respectively] (Fig. 1). Hydrogen atoms from {Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$^-$ anionic ligands were placed in calculated positions, and refined using a riding model with an isotropic thermal displacement parameter fixed at x times U_{eq} for the atom to which it is attached (x = 1.2 for –CH$_2$ groups, and x = 1.5 for the –CH$_3$ groups). The last difference Fourier map synthesis showed a residual electron density with the highest peak (2.287 e Å^{-3}) located at 0.93 Å from Bi(2), and the deepest hole (−2.767 e Å^{-3}) located at 0.94 Å from Bi(1). Information concerning crystallographic data collection and structure refinement for [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] is summarised in Table 1. Selected bond lengths and angles for the two identical molecular units present in the asymmetric unit are given in Table 2.

CCDC reference number 211911.

See http://www.rsc.org/suppdata/jm/b3/b306662m/ for crystallographic data in CIF or other electronic format.

Instrumentation

IR spectra were measured from KBr pellets on a Mattson 7000 FT instrument. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.4 MHz)
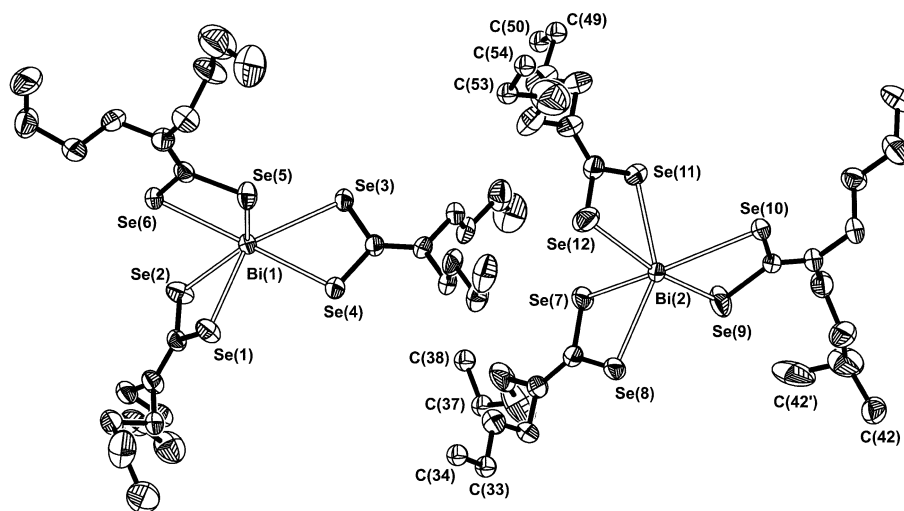

Fig. 1 Asymmetric unit of **I** showing the two independent [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] units represented with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for the two [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] molecular units present in **I**

1		2	
Bi(1)–Se(1)	2.8058(10)	Bi(2)–Se(7)	2.8487(10)
Bi(1)–Se(2)	3.0324(11)	Bi(2)–Se(8)	2.9436(10)
Bi(1)–Se(3)	3.0836(10)	Bi(2)–Se(9)	2.8440(12)
Bi(1)–Se(4)	2.9202(10)	Bi(2)–Se(10)	3.1084(9)
Bi(1)–Se(5)	2.8220(11)	Bi(2)–Se(11)	2.9093(11)
Bi(1)–Se(6)	2.9089(10)	Bi(2)–Se(12)	2.9723(12)
Se(1)–Bi(1)–Se(2)	67.28(3)	Se(7)–Bi(2)–Se(8)	67.03(3)
Se(1)–Bi(1)–Se(3)	141.15(3)	Se(7)–Bi(2)–Se(10)	142.65(3)
Se(1)–Bi(1)–Se(4)	80.13(3)	Se(7)–Bi(2)–Se(11)	83.35(3)
Se(1)–Bi(1)–Se(5)	95.29(3)	Se(7)–Bi(2)–Se(12)	91.89(4)
Se(1)–Bi(1)–Se(6)	87.79(3)	Se(8)–Bi(2)–Se(10)	134.07(3)
Se(2)–Bi(1)–Se(3)	119.40(3)	Se(8)–Bi(2)–Se(12)	94.69(3)
Se(4)–Bi(1)–Se(2)	124.57(3)	Se(9)–Bi(2)–Se(7)	83.66(4)
Se(4)–Bi(1)–Se(3)	64.76(3)	Se(9)–Bi(2)–Se(8)	96.95(4)
Se(5)–Bi(1)–Se(2)	141.83(3)	Se(9)–Bi(2)–Se(10)	65.40(3)
Se(5)–Bi(1)–Se(3)	95.77(3)	Se(9)–Bi(2)–Se(11)	98.42(4)
Se(5)–Bi(1)–Se(4)	82.08(3)	Se(9)–Bi(2)–Se(12)	164.76(4)
Se(5)–Bi(1)–Se(6)	68.02(3)	Se(11)–Bi(2)–Se(8)	144.71(3)
Se(6)–Bi(1)–Se(2)	77.27(3)	Se(11)–Bi(2)–Se(10)	81.20(3)
Se(6)–Bi(1)–Se(3)	130.77(3)	Se(11)–Bi(2)–Se(12)	66.52(3)
Se(6)–Bi(1)–Se(4)	146.55(3)	Se(12)–Bi(2)–Se(10)	112.35(3)

Fig. 2 Ball-and-stick and polyhedral representation of one [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] unit, emphasizing the distorted triangular antiprismatic coordination environment around each Bi^{3+} centre [only Bi(1) is represented].

referenced to SiMe$_4$. X-Ray diffraction studies were performed using Cu-Kα radiation on a Bruker AXS D8 Advance diffractometer. The sample was mounted flat and scanned from 5 to 90° in steps of 0.02° with a count time of 2.5 s. Films were carbon-coated using Edward's E306A coating system before SEM and EDAX analyses. SEM was carried out using a Philips XL30 FEG and EDAX using a DX4 instrument.

AA-MOCVD studies

Approximately 0.2 g of the precursor was dissolved in 30 ml THF in a round-bottomed flask. Six glass substrates (1 × 3 cm) were placed inside the reactor tube. The carrier gas flow rate was controlled by Platon flow gauges. The solution in the flask was placed in a water-bath above the piezoelectric modulator of a humidifier, where aerosol droplets were generated and transferred by the carrier gas into a hot-wall zone. Both the solvent and the precursor evaporated and the precursor vapour reached the heated substrate surface where thermally induced reactions and film deposition took place. This homemade aerosol-assisted chemical vapour deposition kit consists of a two-neck flask, a PIFCO ultrasonic humidifier (Model No. 1077) and a Carbolite furnace.

Results and discussion

Crystal structure of [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$]

The reaction between CSe$_2$ and dibutylamine in the presence of Bi$_2$O$_3$ (see Experimental section), yielded crystals which were analysed using single-crystal X-ray diffraction and formulated as [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] **I** (Table 1). The X-ray powder diffraction analyses are in good agreement with the theoretical calculations based on single-crystal data, confirming the phase purity and homogeneity of the bulk. The asymmetric unit of **I** comprises two independent, yet approximately similar [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] molecular units, orientated so as to maximize close packing between neighbouring butyl chains from different {Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$^-$ anionic ligands (Fig. 1).

The polyhedron describing the coordination environment around each Bi^{3+} cation arises from six Se-donor atoms from three different {Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$^-$ ligands, {BiSe$_6$}, each forming an asymmetrical η^2-syn,syn-chelate with bite angles ranging between 64.76(3) and 68.02(3)° (Figs. 1 and 2, Table 2). As observed for [As(S$_2$CNEt$_2$)$_3$],[23] and analogous Bi compounds
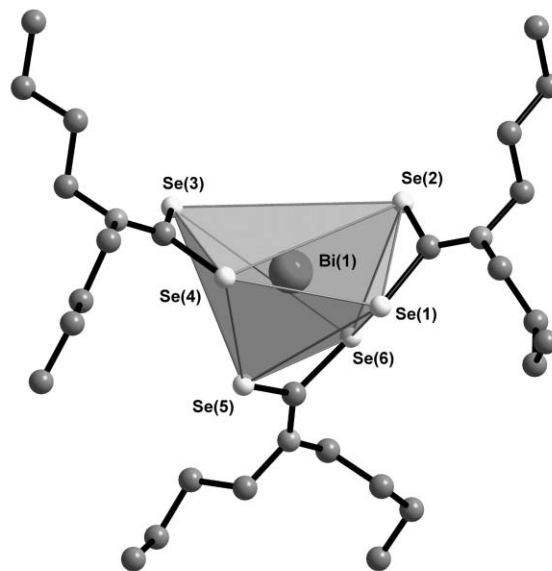
containing {S$_2$CN(^{n}C$_4$H$_9$)$_2$}$^-$,[16] the coordination polyhedron for the cation clearly shows two distinct triangular faces: one formed by the shorter Bi–Se bonds [2.80–2.91 and 2.84–2.91 Å for Bi(1) and Bi(2), respectively], and the other by the longer Bi–Se bonds [2.92–3.08 and 2.94–3.11 Å for Bi(1) and Bi(2), respectively]. Such an arrangement results in a coordination geometry which is best described as a distorted triangular antiprism.

The Bi–Se bonds for **I** [in the 2.81–3.08 and 2.84–3.11 Å ranges for the molecular units containing Bi(1) and Bi(2), respectively; see Table 2] are very similar to those observed in related compounds,[24–26] with the markedly longer Bi–Se bonds in **I** [Bi(1)–Se(2) 3.0324(11) Å; Bi(1)–Se(3) 3.0836(10) Å; Bi(2)–Se(10) 3.1084(9) Å] reflecting, in part, the influence of the lone-pair of electrons in Bi^{3+}. Sawyer and Gillespie have noted that the weakest interactions form along the vector of the maximum electron density of the lone pair of Bi^{3+}, although not directly over it.[27] In fact, the final difference Fourier map synthesis for **I** clearly shows that the most intense Q peaks are located very close to the Bi^{3+} centres, generally pointing away from any existent bonds in the structure. For example, the Q2–Bi(1) vector (peak intensity of ca. 2.24 e Å^{-3}, located at ca. 0.93 Å from the metal centre) is situated exactly between the Bi(1)–Se(2) and Bi(1)–Se(3) bonds. Thus, the structural arrangement of the three {Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$^-$ ligands for both molecular units suggests the presence of a small gap in the coordination sphere of each Bi^{3+} (most probably located in the triangular faces which arise from the longer Bi–Se bonds), indicating that the lone pair of electrons could be stereochemically active (Fig. 2).

The presence of long-chain alkyl substituent groups (*n*-butyl) in the diselenocarbamate anionic ligand has direct consequences in the crystal structure of **I**. On the one hand, close interactions (mostly of the weak C–H···C type) between neighbouring *n*-butyl chains facilitates the close packing of [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] molecular units (Fig. 1). On the other hand, the terminal –CH$_2$CH$_3$ groups are largely affected by thermal disorder (see section on crystal solution refinement; Fig. 1) even at very low temperatures [180(2) K], giving rise to two identical [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] complexes in the asymmetric unit. In fact, the two complexes could be related by a pseudo-two-fold rotation axis.
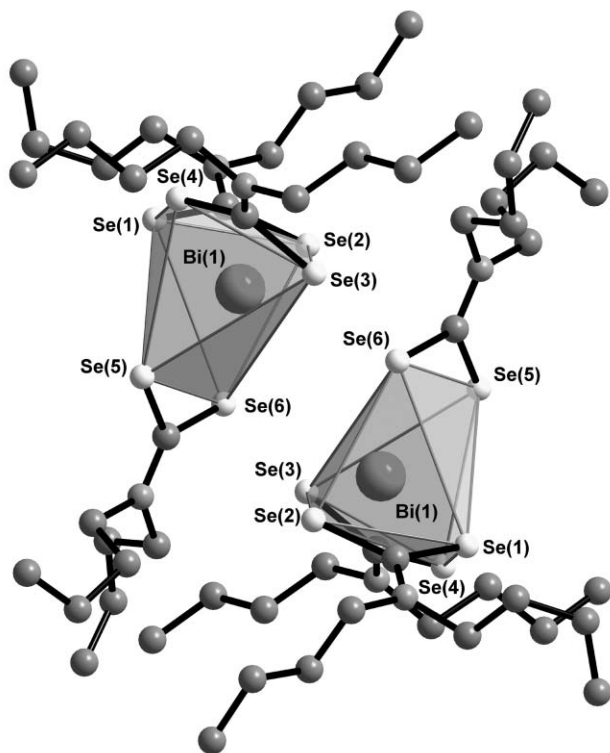
Fig. 3 Ball-and-stick and polyhedral representation of two [Bi{Se$_2$CN(^{n}C$_4$H$_9$)$_2$}$_3$] units related by inversion. The two Bi(1) centres are separated by 4.9859(7) Å.

An interesting feature of the crystal packing in **I** arises from the proximity between crystallographically related Bi^{3+} centres. Each is located near an inversion centre, imposing separations of Bi(1)···Bi(1)^i 4.9859(7) Å and Bi(2)···Bi(2)^{ii} 5.1842(7) Å [symmetry operations: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $2 - x$, $1 - y$, $2 - z$]. Even though these distances are greater then the sum of van der Waals radii for bismuth, the molecular orientation could suggest that the electron lone pairs may interact with each other. This does not occur in the structure, since the lone pairs are, in fact, pointing in opposite directions (Fig. 3) [for the Bi(1)/Bi(1)^i pair of units; symmetry operation: (i) $1 - x$, $1 - y$, $1 - z$].

AA-MOCVD studies

The [Bi(Se$_2$CNRR′)$_3$] compounds [where R = C$_2$H$_5$ (Et), ^{n}C$_4$H$_9$ (Bu^n) or CH$_3$ (Me), and R′ = C$_2$H$_5$ (Et), ^{n}C$_4$H$_9$ (Bu^n) or ^{n}C$_6$H$_{13}$ (Hex^n)] were investigated as precursors for the deposition of Bi$_2$Se$_3$ films on glass substrates using AA-MOCVD techniques. The XRD patterns of the deposited films
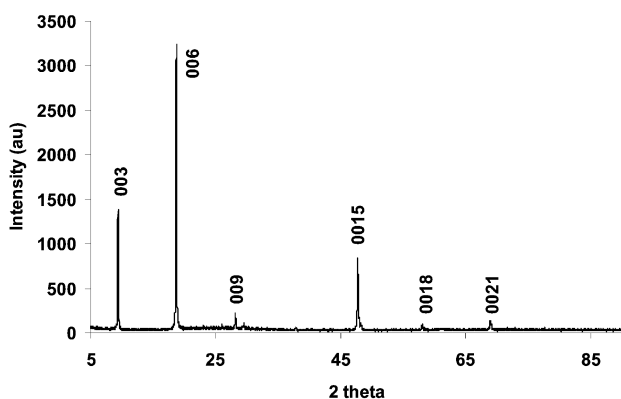

Fig. 4 Powder X-ray diffraction pattern of a Bi$_2$Se$_3$ film deposited on glass using as source the single-molecule precursor [Bi(Se$_2$CNEt$_2$)$_3$] (T_{growth} = 475 °C).

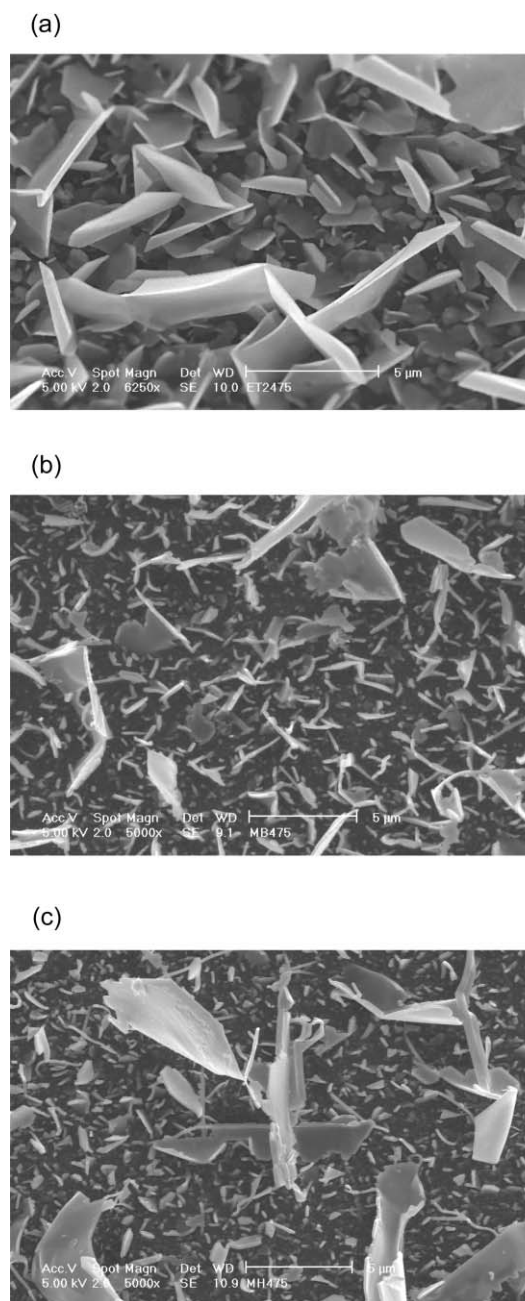**Fig. 5** SEM images of Bi$_2$Se$_3$ films deposited (T_{growth} = 475 °C) on glass using as sources the single-molecule precursors: (a) [Bi(Se$_2$CNEt$_2$)$_3$]; (b) [Bi(Se$_2$CNMe^{n}Bu)$_3$]; (c) [Bi(Se$_2$CNMe^{n}Hex)$_3$].

matched the pattern of rhombohedral Bi$_2$Se$_3$ (JCPDS: 33–214). No other phases were detected. These results were confirmed by EDAX measurements performed on several films deposited under different conditions. Fig. 4 shows the XRD pattern of a Bi$_2$Se$_3$ film in which strongly oriented growth has occurred along the *c*-axis of the unit cell of the semiconductor. In fact all the observed peaks are assigned to the (001) reflections of pure Bi$_2$Se$_3$.

Morphologically homogeneous Bi$_2$Se$_3$ films, containing thin flake-like particles evenly dispersed on the glass substrates, were deposited at 475 °C using [Bi(Se$_2$CNEt$_2$)$_3$], [Bi(Se$_2$CN-MeBu^n)$_3$] and [Bi(Se$_2$CNMeHex^n)$_3$] as precursors (Fig. 5). The SEM images suggest that the dialkyl-symmetric precursor [Bi(Se$_2$CNEt$_2$)$_3$] leads to larger Bi$_2$Se$_3$ particles (Fig. 5(a)) than the asymmetric counterparts (Fig. 5(b) and (c)).

We have found that the growth temperature is of crucial importance to the morphological characteristics of the Bi$_2$Se$_3$ films. [Bi(Se$_2$CNMe^{n}Bu)$_3$] was used as the single-molecule
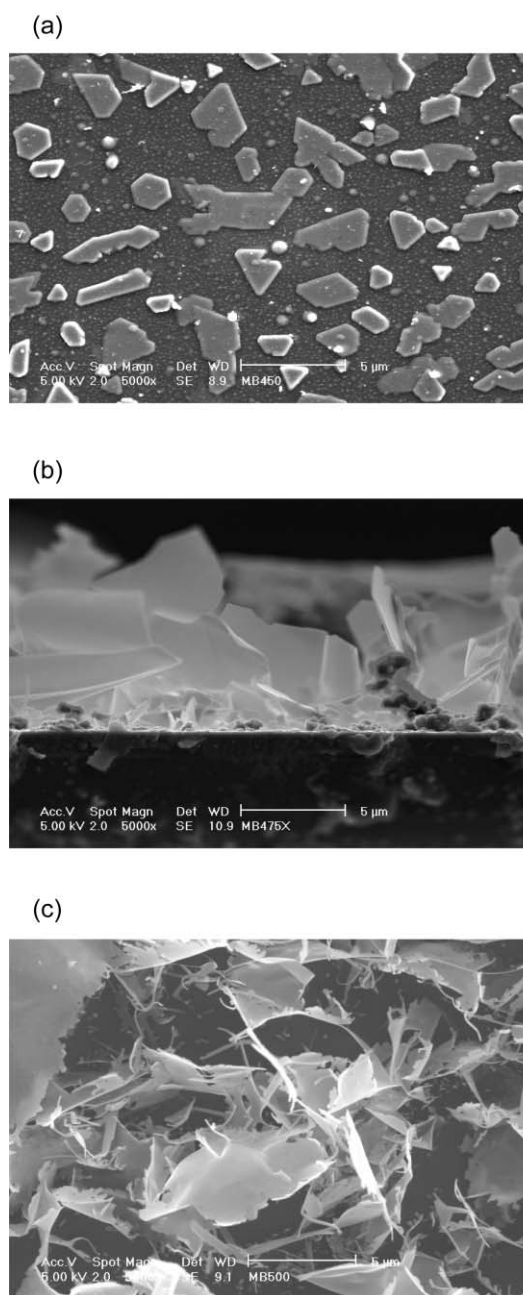
(a)

(b)

(c)

Fig. 6 SEM images of Bi_2Se_3 films deposited on glass using as source the single-molecule precursor $[Bi(Se_2CNMe^nBu)_3]$, at growth temperatures: (a) 450 °C (top view); (b) 475 °C (cross view) and (c) 500 °C (top view).

precursor to produce films at 450, 475 and 500 °C, with the results clearly showing that the flake-like deposited particles become predominant as the growth temperature increases (Fig. 6). At 450 °C the films are characterized by a dense layer containing nanosized spheroids on the top of which dispersed flake-like particles have grown (Fig. 6(a)). A direct comparison

between the SEM images for a Bi_2Se_3 film deposited at 475 °C using the precursor $[Bi(Se_2CNMeBu^n)_3]$ [Fig. 6(b) (cross view), and Fig. 5(b) (top view)], clearly shows that the films are formed by an under layer of nanosized Bi_2Se_3 particles from which the bigger flake-like crystallites protrude.

Acknowledgements

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