A range of bismuth(III) dithiocarbamato complexes were prepared and characterized. The X-ray crystal structures of the compounds $[\text{Bi}\{S_2\text{CN}(\text{CH}_3)(\text{C}_6\text{H}_{13})\}_3]$ (1) and $[\text{Bi}\{S_2\text{CN}(\text{CH}_3)(\text{C}_6\text{H}_{13})\}_3(\text{C}_3\text{H}_6\text{N}_2)]$ (2) are reported. The preparation of Bi$_2$S$_3$ particulates using a wet chemical method and involving the thermalysis of Bi(III) dithiocarbamato complexes is described. The influence of several experimental parameters on the optical and morphological properties of the Bi$_2$S$_3$ powders was investigated. Nanosized Bi$_2$S$_3$ colloids were obtained having long-term stability and showing a blue shift on the optical band edge; the presence of particles exhibiting quantum size effects is discussed. Morphological well-defined Bi$_2$S$_3$ particles were obtained in which the fiber-type morphology is prevalent.

1. Introduction

Synthetic methods and physical properties of semiconducting nanocrystals (or quantum dots) have been the subject of active research during the past decade. In such materials, the charge carriers are confined within what is effectively a small portion of the bulk crystalline lattice. In this size regime, quantum confinement effects are observed and the band gap of the crystalline lattice widens as the particle size decreases to dimensions comparable to the exciton Bohr radius.

Band gap tuning in nanophase semiconductors, among other properties such as the capability for surface derivatization, has been a possibility by using a plethora of chemical methods. Most of such synthetic methods have focused on II/VI semiconductors and on III/V semiconductors. Semiconductors having more complex structures, such as bismuth sulfide (Bi$_2$S$_3$, bismuthinite), which crystallizes in a lamellar structure, have received less attention.

Macromeristalline Bi$_2$S$_3$ has been investigated as a material for photodiode arrays and photovoltaic devices. Besides its technological interest, it has been suggested that because of its anisotropic structure, layers of lamellar semiconductors may be regarded as colloidal analogues of quantum well structures. Therefore, quantum confinement of the charge carriers would occur, provided at least one dimension of the particles is located within the nanosize regime. Studies reporting such behavior for Bi$_2$S$_3$ have been scarce because of the lack of theoretical data and also of reliable synthetic methods that give Bi$_2$S$_3$ particulates with well-defined morphologies.

We have been interested in the preparation of nanocrystalline semiconductors using single-molecule precursors that is, molecular compounds containing

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To whom correspondence should be addressed. E-mail: ttrindade@dq.ua.pt. Fax: +351 213 370 084.

both elements of the semiconductor within a single molecule, for example, metal dithiocarbamate complexes. The use of tris(benzylthiolato)bismuth to produce pure polycrystalline Bi2S3 is reported in the literature.20 Recently, we showed that the compound bismuth(III) methyl-n-hexyl-dithiocarbamate, [Bi(S2CN(CH3)(C6H13))] is a useful single-molecule precursor to produce fiber-type Bi2S3 particles, either in organic solution21 or by a CVD method.22 Here, we report a more detailed study using other single-molecule precursors to prepare nanocrystalline Bi2S3 powders by thermal analysis in high boiling point solvents. The influence of several synthetic parameters on the final morphological and optical properties of the powders is reported.

Moreover, our interest in the production of Bi2S3 materials using such compounds led us to investigate some structural features inherent to bismuth(III) dithiocarbamate complexes, in particular, the asymmetric structural features of several elements of the semiconductor within a single molecule, for example, metal dithiocarbamate complexes. The use of tris(benzylthiolato)bismuth to produce pure polycrystalline Bi2S3 is reported in the literature.20 Recently, we showed that the compound bismuth(III) methyl-n-hexyl-dithiocarbamate, [Bi(S2CN(CH3)(C6H13))] is a useful single-molecule precursor to produce fiber-type Bi2S3 particles, either in organic solution21 or by a CVD method.22 Here, we report a more detailed study using other single-molecule precursors to prepare nanocrystalline Bi2S3 powders by thermal analysis in high boiling point solvents. The influence of several synthetic parameters on the final morphological and optical properties of the powders is reported.

2. Experimental Section

All chemicals were supplied by Aldrich except Bi2O3 and dry methanol (Merck), and toluene and 2-ethoxyethanol (Riedel & Haan). All chemicals were used as received.

2.1. Synthesis of Bismuth(III) Dialkylidithiocarbamate Complexes. The complexes [Bi(S2CNMeBu)3], [Bi(S2CNEt2)3], and [Bi(S2CNBu)3], in which Me = methyl, Et = ethyl, Bu = n-butyl, and Hex = n-hexyl, were prepared by adaptation of the literature method.29 The synthetic method consists of the insertion of CS2 into the secondary amine in the presence of Bi2O3. In a typical synthesis, [Bi(S2CNMeBu)3] was obtained by adding dropwise N-methylhexylamine, 98% (40 mmol), and then CS2 (40 mmol) to a methanol solution (50 mL) containing [Bi(S2CNMe

\[\text{[Bi(S2CNMeBu)3]} \] is a useful single-molecule precursor to produce fiber-type Bi2S3 particles, either in organic solution21 or by a CVD method.22 Here, we report a more detailed study using other single-molecule precursors to prepare nanocrystalline Bi2S3 powders by thermal analysis in high boiling point solvents. The influence of several synthetic parameters on the final morphological and optical properties of the powders is reported.

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methanol and then dispersed in solvents such as dichloromethane or pyridine. When 4-ethylpyridine was used as the solvent, the powder obtained was washed with n-hexane and dispersed in dichloromethane. The decomposition of the bismuth complexes in p-xylene resulted in the formation of a powder that did not disperse in organic solvents.

### 2.3. Instruments and Characterization

Crystallography. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation (λ = 0.71069 Å) with an ω-2θ scan at 180 K. The unit cell parameters were determined by least-squares refinement on diffractometer 9.38° ≤ θ ≤ 12.15° (1) and 8.411° ≤ θ ≤ 12.72° (2) for 25 automatically centered reflections in each case. Crystal data are summarized in Table 1. All data were corrected for absorption by semiempirical methods (ψ scan)31 and for Lorentz-polarization effects by XCAD4.32 The structure was solved by the Patterson method using SHELXS-9733 and refined anisotropically (non-hydrogen atoms) by full-matrix least-squares on F2.

| Table 1. Crystal Data and Structure Refinement of [Bi(S2CNMe-Hex)3] and [Bi(S2CNMe-Hex)3(C2H8N2)] |
|---------------------------------|---------------------------------|
| empirical formula               | C8H14BiN3S6                    |
| formula weight                  | 779.99                         |
| temperature                     | 293(2) K                       |
| wavelength                      | 0.71073 Å                      |
| crystal system                  | monoclinic                     |
| space group                     | P21/c                          |
| unit cell dimensions            | a = 19.833(3) Å, α = 90°       |
|                                 | b = 17.423(3) Å, β = 104.57(2)°|
|                                 | c = 10.145(2) Å, γ = 90°       |
| volume                          | 3392.9(10) Å                   |
| Z                               | 4                              |
| density (calculated)            | 1.527 Mgm⁻³                    |
| absorption coefficient          | 5.583 mm⁻¹                     |
| F(000)                          | 1568                           |
| crystal size                    | 0.2 × 0.2 × 0.1 mm³            |
| θ range for data collection     | 1.58°–24.98°                   |
| index ranges                    | 0 ≤ h ≤ 23, 0 ≤ k ≤ 20, –12 ≤ l ≤ 11 |
| reflections collected           | 6119                           |
| independent reflections         | 5940 [R(int) = 0.0527]          |
| completeness to θ = 24.98°      | 99.8%                          |
| refinement method               | full-matrix least-squares on F² |
| data/restraints/parameters      | 5940/90/313                    |
| goodness-of-fit on F²           | 1.007                          |
| final R indices (| > 2σ(]) | R1 = 0.0591, wR2 = 0.1720     |
| R indices (all data)            | R1 = 0.1414, wR2 = 0.2364      |
| largest d peak and hole         | 2.668 and –2.754 e Å⁻³         |

Transmission electron microscopy (TEM) was carried out on a Hitachi H-9000 microscope operating at 300 kV. An aliquot containing the nanodispersed sample was placed on a copper grid coated with an amorphous carbon film and then the solvent was evaporated.

Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDAX) measurements results were obtained using a FEG-SEM Hitachi S4100 microscope operating at 25 kV. The samples were prepared by deposition of an aliquot of the sample on aluminum pieces.

### 3. Results and Discussion

#### 3.1. Crystal Structures

The molecular structure of [Bi(S2CNMe-Hex)3] (1) is shown in Figure 1. The complex comprises a bismuth atom coordinated by three bidentate asymmetric methyl-n-hexyl dithiocarbamato ligands. Selected bond lengths and angles for this...
a pseudorotation 3-fold axis. Such an arrangement
bonds (2.679 Å). Coordination polyhedron defined by the three Bi


As, and Sb.23,36,37 Comparative bond distances for metal
structures for diethyldithiocarbamato complexes of Bi,

This asymmetry is not so accentuated as in the reported
for each dithiocarbamato ligand are asymmetric but
59.4°–87.2°). It must be emphasized

As described for the complex [As(S2CNEt2)3],37

results in a distorted coordination environment around
the metal center, which is best described as a distorted
triangular antiprism. The distortion on the coordination
polyhedron by elongation of the Bi–S bonds of one of
the triangular faces of the triangular antiprism may result
from the presence of a stereochemically active
electron lone pair along the pseudo-3-fold axis and
directed to the larger triangular face. The presence of
the stereochemically active electron lone pair is also
suggested by the bigger angles S–Bi–S involving the
three Bi–S longer bonds (107.99°–117.82°), when
compared to the S–Bi–S angles involving the three Bi–S
short bonds (81.94°–87.27°). It must be emphasized
that, in such a case, the electronic repulsion effects of
the electron lone pair on the coordination geometry of
the metal center are less pronounced than those
described for [Bi(S2CNETe2)3]23 and for [As(S2CNETe2)3].37
A comparison of the molecular structures of [Bi(S2-
CNETe2)3]23 and [Bi(S2CNMeHex)3] is elucidative with
respect to the observation of different coordination
geometries for the bismuth by introducing subtle
differences in the ligands as it is the case of replacing the
ethyl groups by an asymmetric set formed by short-
chain (methyl) and long-chain (n-hexyl) alkyl groups.
In the compound [Bi(S2CNMeHex)3],23 the bismuth
coordination sphere is completed by the close proximity of a
S atom from a neighboring molecule at a distance (3.210 Å)
less than the sum of the van der Waals radii.30 The
bismuth stereochemistry has been described for such
compounds as a distorted dodecahedron by taking
in account the presence of an active electron lone pair.23
It is apparent from Figure 1 that a distinct stereochem-
istry is present for bismuth in compound 1. Unlike the
complex [Bi(S2CNETe2)3], compound 1 consists of discrete
units in which intermolecular contacts, comprising the
metal center, within adjacent molecules are not present.
This can be associated with the lengthening of a
substituent alkyl group from a two-carbon chain to a
six-carbon chain, resulting in a distinct molecular
packing to accommodate the longer hexyl chain.
The nonexistence of intermolecular contacts involving the
metal center favors in this case a less distorted
coordination geometry.
A few bismuth N,N-diethylthiocarbamato complexes
containing nitrogen donors in the coordination sphere
have been reported by Raston et al.27,28 Because of the
Lewis acidic character and large size of bismuth, the
expansion of the coordination number of dithiocarba-
amo bismuth complexes in the presence of Lewis bases is
favored. However, there are no reports on the
structural characterization of such types of complexes
in which the alkyl chains of the dithiocarbamato ligands
are asymmetric. Figure 2 shows the molecular structure
of the compound [Bi(S2CNMeHex)3(C12H8N2)]2 (2). Bismuth
is coordinated by three asymmetric bidentate dithiocar-amato ligands and the coordination sphere is expanded
in this case by chelation of an α-phenantronine
molecule leading to a complex with coordination number
8. The Bi–S distances are within the typical values
found for this type of compound. The Bi–N interactions
are inferior to the sum of the van der Waals radii (< 4 Å)
and within the range found for Bi–N distances in

| Compound | M–S1 Å | M–S2 Å | Δ (|M–S1| – |M–S2|) Å |
|----------|--------|--------|-------------------|
| [As(S2CNETe2)3] | 2.350 | 2.904 | 0.554 |
| [Sb(S2CNETe2)3] | 2.344 | 2.819 | 0.475 |
| [Sb(S2CNETe2)3] | 2.354 | 2.812 | 0.458 |
| [Bi(S2CNETe2)3] | 2.631 | 2.886 | 0.255 |
| [Bi(S2CNETe2)3] | 2.487 | 2.965 | 0.478 |
| [Bi(S2CNETe2)3] | 2.626 | 2.895 | 0.269 |
| [Bi(S2CNMeHex)3] | 2.595 | 2.956 | 0.361 |
| [Bi(S2CNMeHex)3] | 2.775 | 2.964 | 0.189 |
| [Bi(S2CNMeHex)3] | 2.730 | 2.908 | 0.178 |
| [Bi(S2CNMeHex)3] | 2.679 | 2.885 | 0.206 |
| [Bi(S2CNMeHex)3] | 2.694 | 2.886 | 0.174 |
| [Bi(S2CNMeHex)3] | 2.741 | 2.889 | 0.148 |
| [Bi(S2CNMeHex)3] | 2.794 | 2.900 | 0.106 |
| [Bi(S2CNMeHex)3] | 2.779 | 2.848 | 0.069 |

a Data from ref 36. b Data from ref 23.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Bi(S2CNMeHex)3] and [Bi(S2CNMeHex)3(C12H8N2)]

Table 3. Comparative Bond Distances for Group 15 Metal Dithiocarbamato Complexes: M–Sa and M–Sb Refer to
the Shorter and Longer Distances, Respectively


molecule in complex 2 due to the presence of an additional o
ligand trans to the phenantroline molecule in relation
to the plane defined by the remaining S donor ligands. The
shortest secondary bond, that is, the Bi-N bond, is
opposite the primary bond, that is, the Bi-S bond.

When compared to compound 1, sterical hindrance
due to the presence of an additional o-phenanthroline
molecule in complex 2 forces the donor atoms to define
early two planes containing the bismuth atom, which
are almost orthogonal in relation to each other. The
presence of the o-phenanthroline molecule as a relative
trans position to a dithiocarbamato ligand induces an
increase in the asymmetry of the bismuth dithiocarba-
mato bond distances. In fact, the higher difference in
the Bi-S distances is observed for the dithiocarbamato
ligand trans to the phenanthroline molecule in relation
to the plane defined by the remaining S donor ligands.
Also, in compound 2, the coordination number of bis-
muth has increased to 8 in relation to the parent
compound 1 and the stereochemistry is best described
as a distorted dodecahedron defined by the S and N
donor atoms. The distortion on the coordination geometry
could also be due to the presence of an electron lone-
pair stereochemically active on bismuth. The influence
of the electron lone pair on the coordination geometry
of bismuth is not so evident as that in the previous
compound, 1, which can be related to the expansion of
the coordination number by introducing a bidentate
ligand with a higher bite angle such as o-phenantrho-
line.38 In this case, the distortion from a regular geometry is possibly due mainly to stereochemical
restrictions imposed by both types of bidentate ligands
with distinct bite angles.

3.2. Preparation of Bi2S3 Nanocrystals. The molec-
ular precursors 1 and 2 and the complexes [Bi(S2-
CNMe2Bu)3], [Bi(S2CNMe2Et)3], and [Bi(S2CNBu2)3] ther-
mal decompose into pure Bi2S3 under a N2 stream. This
led us to investigate in detail the use of such compounds
as single-molecule precursors to prepare Bi2S3 particulates. In a preliminary report we have
described the preparation of Bi2S3 nanofibers in 2-ethoxy-
ethanol using [Bi(S2CNMe2Hex)3] as a single-molecule precursor.21 Here, a more detailed study of the solution
phase thermalysis of bismuth(III) dithiocarbamato com-
plexes is reported. Moreover, the preliminary results21
suggested that the solvent used had a strong influence
on the final properties of the Bi2S3 powders. In this
work, the solution thermalysis of bismuth complexes
was investigated using other solvents with higher boiling points and also thermally more stable than 2-ethoxyethanol.39

The results obtained from the solution thermal treat-
ment of the complex [Bi(S2CNMe2Hex)3] in several solvents are summarized in Table 4. The treatment
of [Bi(S2CNMe2Hex)3] in p-xylene led to Bi2S3 powders
that were not dispersible in any of the organic solvents tested. This result suggested that the particles in this case were not nanosized, a result confirmed later by SEM. A possible explanation for this fact is that the
Bi2S3 primary particles formed during the thermalysis
of the precursor do not have a capped surface because
p-xylene is not a coordinating solvent. Absence of
protective agents at the surface of the Bi2S3 nanopar-
ticles formed facilitates the growth into larger particles
at the high temperature used.

The thermalysis of [Bi(S2CNMe2Hex)3] and [Bi(S2-
CNMe2Hex)3(C12H8N2)] in TOP led to a mixture of
Bi2S3 and elemental bismuth. The latter was detected
in the powder as a secondary phase from XRD analysis.
The other solvents tried (2-ethoxyethanol, 4-ethylpyri-
dine, and ethyleneglycol) led to pure Bi2S3 which
disperses in hydrocarbons. The amount of nanomaterial

<table>
<thead>
<tr>
<th>solvent</th>
<th>temp/°C</th>
<th>solid phasea</th>
<th>observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ethoxyethanol</td>
<td>132</td>
<td>Bi2S3</td>
<td>brown powder which disperses easily in hydrocarbons such as CH2Cl2 (leading to long-term stable dispersions)</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>197</td>
<td>Bi2S3</td>
<td>brown powder which disperses easily in hydrocarbons such as CH2Cl2 (leading to long-term stable dispersions)</td>
</tr>
<tr>
<td>4-ethylpyridine</td>
<td>168</td>
<td>Bi2S3</td>
<td>brown powder which disperses in hydrocarbons</td>
</tr>
<tr>
<td>p-xylene</td>
<td>140</td>
<td>Bi2S3</td>
<td>brown powder which does not disperse in organic solvents</td>
</tr>
<tr>
<td>TOPO/TOP</td>
<td>150</td>
<td>Bi2S3 and Bi</td>
<td>gray powder which disperses in hydrocarbons (leading to short-term stable dispersions)</td>
</tr>
</tbody>
</table>

a Reflux except for TOPO/TOP. b As determined by XRD data.

Figure 2. Molecular structure of [Bi(S2CNMe2Hex)3(C12H8N2)].

Table 4. Relevant Experimental Data for the 2-h Thermalysis of [Bi(S2CNMe2Hex)3] in High Boiling Point Solvents

prepared in 2-ethoxyethanol was higher than those with other solvents. At room temperature, the molecular precursor [Bi(S2CNMenHex)3] also decomposes in a 2-ethoxyethanol solution. However, the powders prepared in such conditions showed a low crystallinity degree and were obtained by stirring the solution over several days.

The optical spectra of the nanoparticulates prepared using 4-ethylpyridine, ethyleneglycol, and 2-ethoxyethanol (at 132 °C for all solvents) are shown in Figure 3. The subtle differences observed on the band profiles of the optical spectra (Figure 3) can be associated with different particle size distributions for the Bi2S3 particles, depending on the solvent used in their preparation. The optical band edge of Bi2S3 for all the samples is considerably shifted to high energy (ca. 0.6 eV) from the typical direct band gap of 1.3 eV (952 nm). As will be discussed later, this shift may be explained by the presence of Bi2S3 nanocrystals in which at least one linear dimension of the crystallites is nanosized.\(^{18}\)

No meaningful distinct features were observed in the optical spectra of Bi2S3 prepared using distinct bismuth(III) dithiocarbamato complexes. This result suggests that the nature of the alkyl chain of the precursors reported here does not have a strong influence on the optical properties of the Bi2S3 that results from the thermalysis. A red shift on the optical absorption onset was clearly observed with the increase of the temperature of thermalysis, in agreement with an increase in the mean particle size, and suggesting a growth process driven by the reduction of the total surface energy of the particulates (Ostwald ripening).

### 3.3. Structural and Morphological Characterization of Bi2S3 Powders

X-ray powder diffraction performed on the powders obtained in this work showed that bismuthinite was the crystalline phase present in all the samples, except for those prepared in TOPO in which elemental bismuth was also detected. The IR spectra of the powders did not show organic vestiges either from the solvent or from the molecular precursor. EDAX measurements performed on the powders showed peaks for Bi and S.
To establish the morphological properties of the Bi$_2$S$_3$ nanoparticulates, TEM was performed on samples collected from a CH$_2$Cl$_2$ solution containing Bi$_2$S$_3$, which were deposited on carbon-coated copper grids. Figure 4 shows that the Bi$_2$S$_3$ powders prepared in 2-ethoxyethanol are composed of nanoparticles with a fiberlike morphology and with an average linear cross-section dimension of ca. 6 nm. The low contrast of the TEM images also suggests that the sample consists of very thin particles of Bi$_2$S$_3$. As reported by others for several colloidal layered semiconductors,\textsuperscript{17,18,40,41} it is reasonable to suggest that because of the lamellar-like structure of Bi$_2$S$_3$, such particles are in fact layers of the semiconductor. In this case, and as suggested in Figure 4, the TEM images agree with the presence of Bi$_2$S$_3$ nanocrystals with a linear dimension for which quantum size effects are expected to be observed. It also seems that such quantum size effects are observed, even though the length of the particles, the largest linear dimension, surpasses the nanosize regime. In this context it is noteworthy that quantum size effects have also been reported by Variano et al. for Bi$_2$S$_3$ disklike-shaped particles prepared in microemulsions, for which the anisotropic particle-in-a-box model has been applied.\textsuperscript{12} Compared to nanocrystals of other semiconductors (e.g., II/VI materials) in which quantum confinement occurs in a three-dimension box,\textsuperscript{42} the charge carriers in anisotropic lamellar nanostructures are confined in a quantum structure defined by two (disk-type) or one (fiber-type) linear dimensions.\textsuperscript{12,18}

Although the fiber-type morphology predominates for Bi$_2$S$_3$ particles prepared using the method reported here, it was observed that the particle dimensions were strongly dependent on the synthetic parameters used in their preparation, in particular, the type of solvent used and the growth temperature. Typically, larger fibers were obtained in ethylene glycol and the dimensions of the fibers increased as the temperature was raised. For example, the TEM image in Figure 5 shows Bi$_2$S$_3$ nanoparticles (ca. 24-nm linear cross section) prepared in ethylene glycol (197 °C) using the single-molecule precursor [Bi(S$_2$CNMe$_6$Hex)$_3$(C$_{12}$H$_8$N$_2$)] (2). Longer fibers were obtained using this precursor, when compared to the use of precursor 1, although a similar morphology was observed, providing the solvent and the temperature were maintained. The thermal analysis of the molecular precursors 1 and 2 showed that both compounds thermally decompose in one step. The lower temperature of decomposition of 2 (280 °C), when

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\textsuperscript{40} Peterson, M. W.; Micic, O. I.; Nozik, A. J. J. Phys. Chem. 1988, 92, 4160.  
compared to 1 (300 °C), may account for such slight differences in the particles size, although the precursors’ thermal stabilities are not so pronounced as to lead to a strong influence on the final morphology of the Bi$_2$S$_3$ nanocrystals. On the other hand, the influence of the solvent and temperature on the morphology of the powders was also clearly evident by SEM performed on the nondispersible solid phases collected from the thermalysis of the molecular precursors. Figure 6 shows the SEM images of such powders, which have been prepared in p-xylene (a), 2-ethoxyethanol (b), 4-ethylpyridine (c), and TOPO (d). The predominance of fiber-type particles is again observed in all the samples with the exception of the one prepared in TOPO in which elemental bismuth was also present. For this sample, the elemental bismuth particles were also analyzed by TEM and transmission electron diffraction, performed on the dispersible powders (nanophase material), showing either a hexagonal or spherical shape. When p-xylene is used, which is a noncoordinating solvent, steric hindrance of the particles is less effective and hence agglomerates of smaller particles have been formed, as discussed above (Figure 6a).

Bismuth(III) sulfide crystallizes in a layer structure formed from threadlike molecules. The crystallization occurs in a two-dimensional array forming infinite bands, which are connected via weaker van der Waals interactions. The Bi$_2$S$_3$ fiber-type morphology observed for the powders may result from the cleavage of larger particles from the van der Waals planes of the crystalline structure or/and from preferential directional growth of the particles. In fact, both processes have been reported to occur for Bi$_2$S$_3$ particles grown using distinct synthetic methods.\textsuperscript{43,44} Temperature exerts a strong influence on the morphology of particles in which preferential growth is a relevant process and this experimental parameter was investigated for the solvent ethyleneglycol. As shown in Figure 7, distinct morphologies for micrometric Bi$_2$S$_3$ particles were obtained depending on the temperature used, 132 and 197 °C. Such SEM images suggest that the morphological evolution of the particles is to obtain longer fibers as the temperature increases, which may result from a higher growth rate along the c axis. Solvent thermalysis of commercial Bi$_2$S$_3$ over 2 h, using similar conditions to those used in the synthesis of the nanocrystalline counterpart, did not lead to fiber-type particles. It has been reported that treatment of macromolecular semiconductors (e.g., MoS$_2$, WS$_2$, Bi$_2$Se$_3$) in acetonitrile results in stable nanodispersed systems.\textsuperscript{45} The breakup of crystallites due to interpenetration of acetonitrile molecules within the van der Waals planes has been suggested as the underlying mechanism. The Bi – S interatomic distance at the van der Waals planes is ca. 300 pm; hence, an exfoliation process by intercalation of larger molecules, such as those of the solvents used in this work, seems unlikely. Moreover, the fiber-type morphology has been observed by us for Bi$_2$S$_3$ particles prepared using several chemical strategies, including a chemical vapor deposition method in which the molecular precursors used were similar to those employed in this work.\textsuperscript{22} Therefore, it is suggested that the Bi$_2$S$_3$ fiber-type morphology for particles prepared from the decomposition of bismuth(III) dithiocarbamato complexes is mainly a result of preferential directional growth along the c axis, the shortest distance of the unit cell of bismuthinite.

4. Conclusions

It was shown that crystalline Bi$_2$S$_3$ nano- and microparticles showing well-defined morphologies can be prepared using the solution-phase thermalysis of bismuth(III) alkylidithiocarbamato complexes. The tem-
perature and chemical nature of the solvent used have a strong influence on the final properties of the powders. Particle growth along the c axis appears to be a preferential process leading to Bi$_2$S$_3$ particulates in which the fiber-type morphology is predominant.

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**Supporting Information Available:** Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and structures of compounds 1 and 2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.