Oxidative Addition to Sn(II) Guanidinate Complexes: Precursors to Tin(II) Chalcogenide Nanocrystals.

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Abstract: SnS, SnSe and SnTe are a potentially important semiconductor materials. Here, we described the application of chalcogen containing Sn(IV) guanidinate precursors, for the production of tin(II) chalcogenide nano-crystals. Reaction of the stannylene (II) guanidinate complex \([\{\text{Me}_2\text{NC(NCy)}_2\} \cdot \text{Sn}\] (1) with \(\text{Ph}_2\text{E}_2\) (E = S, Se, Te), and \(\text{CBr}_6\) forms the Sn(IV) complexes \([\{\text{Me}_2\text{NC(NCy)}_2\} \cdot \text{Sn(Ch-Ph)}_2\] (2-4) and \([\{\text{Me}_2\text{NC(NCy)}_2\} \cdot \text{SnBr}_6\] (5) respectively. Complex 5 has been subsequently used for the synthesis of the corresponding Sn(IV) mono chalcogenide complexes, \([\{\text{Me}_2\text{NC(NCy)}_2\} \cdot \text{Sn} = \text{E}\] (6-8) by the reaction of 5 with Li_xE systems. Isolated tin complexes have characterized by elemental analysis, NMR spectroscopy, and the molecular structures of complexes 2-5 determined by single crystal X-ray diffraction. TG analysis showed complexes 2-4 and 6-8 all to have residual masses close to those expected for the formation of the corresponding ‘SnE’ systems. Complexes 6-8 were assessed for their utility in the formation of nano-crystalline materials. The materials obtained were characterized by powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray analysis (EDX). Analysis showed formation of SnSe and SnTe from complexes 7 and 8, respectively.

Introduction

The family of IV-VI mono-chalcogenide semiconducting materials, and in particular SnS, SnSe and SnTe, have attracted significant attention over the past decade.[1] The mono-chalcogenides ‘SnE’ (E = S, Se and Te) all display intense absorption across the electromagnetic spectrum, with narrow band gaps (E = S, 1.1 eV (direct), 1.3 eV (indirect); E = Se, 0.9 eV (direct), 1.3 eV (indirect); E = Te, 0.18 eV),[2] and therefore have potential as materials for thermoelectric devices, field effect transistors, superconducting crystals, rechargeable batteries, solar cells and near infrared detectors. Significant properties such as charge transfer and charge transport depends strongly on the morphology and crystallinity of the materials i.e. thin films vs nanocrystals, size and surface quality.[3]

Over the past two decades research has shown unmistakably, that the most relevant aspect to controlling the morphology of both thin films and nanocrystals is the precise selection of starting molecular precursors,[4] and it is this choice of precursor which determines features such as reaction solvent/temperature, and in the case of nanocrystal/thin film formation deposition/production temperatures.[5]

Lewis et al. have recently reviewed routes to both thin film and nanoparticle of IV-VI chalcogenide materials.[6] A key feature in the development of successful precursors for Sn(II) chalcogenide materials is the ability to control the oxidation state of the tin during the deposition process, so as to suppress the production of materials with variable oxidation states (i.e. Sn_xS_y Sn_2S_3, SnSe_2, SnSe_3 and SnSe_4) the presence of which can be detrimental to the performance binary Sn(II) chalcogenide materials.[7, 6] Therefore the ability to control the formation of these materials is paramount and to this end a large number of ligand systems have been developed in an attempt to do so.

As part of an ongoing exploration into the chemistry of group 14 semiconductor materials, and their application in the formation of IV-VI semiconducting materials, such as SnS and SnO,[4, 7] we have previously reported the chemistry of the homoleptic Sn(II) guanidinate system \([\{\text{Me}_2\text{NC(NCy)}_2\} \cdot \text{Sn}\] (1). Complex 1, readily formed in quantitative yields by the insertion of dicyclohexyl-carbodiimide into the \(\{\text{Sn-NMe}_2\}_2\) bonds of \([\text{Sn(NMe}_2]\) (Scheme 1), has proved to be an intriguing departure point for the synthesis of a range of Sn(IV) guanidinate complexes by reaction with elemental chalcogens (S, Se and Te) as well as single atom chalcogen transfer reagents such as \(\text{Bu}_2\text{P=Te}\).[8] While selected tin chalcogen products have found utility in AAS/CVD of Sn, SnS, SnSe and SnTe thin films,[11] the product distribution form direct reaction between stannylenes and elemental chalcogens are difficult to control and reaction with single atom transfer reagents, such as \(\text{Et}_3\text{PSe}\), often results in contamination with phosphine by-products.[9]

![Scheme 1](image-url)

**Scheme 1.** Synthesis of the homoleptic Sn(II) Guanidinate complexes 1.
In these systems, the unprecedented oxidative control over the resulting thermal decomposition products is such that we have been able to show selective, and exclusive, formation of thin films of Sn, SnS, SnSe and SnTe from an isoreticular series of complexes.

**Results and Discussion**

Reaction of di-cyclohexylcarbodiimide, in THF, with Sn(NMe₂)₂ in 2:1 molar ratio readily affords the homoleptic stannylene complex \([\{\text{Me}_2\text{NC(NCy)}_2\}_2\text{Sn}\} \text{ (1)}\]. Similar stannylenes have been reported previously. For the purposes of reference, and relevant to our discussion, the molecular structure of complex 1 has been reproduced here and is shown in Figure 1. Complex 1 has previously been fully characterized by solution state NMR (\(^1\)H, \(^{13}\)C and \(^{119}\)Sn) spectroscopy and elemental analysis. \(^{119}\)Sn NMR spectra of 1 shows the presence of a single resonance at \(\delta = -380.9\) ppm.

Subsequent reaction of 1 at ambient temperature, with the diphenyl dichalcogenide reagents Ph₂E₂ (E = S, Se and Te) results in the rapid oxidative addition of the {E-E} bond across the stereo-active lone pair of the stannylene, and formation of the Sn(IV) bis-phenylchalcogenide complexes, 2-3 as shown in Scheme 2.

Progress of the reaction could be easily followed since a color change from yellow to colorless (2), yellow to orange (3) and yellow to red (4), respectively were clearly observable. The resulting products were isolated in high yields (63%-89%). \(^1\)H and \(^{13}\)C NMR spectra of the resulting products showed the presence two resonances associated with the (CH) moieties of the bis-cyclohexyl guanidinate ligand, indicating a degree of asymmetry in the products. An inspection of the \(^1\)H NMR spectra for 2-4 indicates a 1:1 ratio of the \{Me₂NC(NCy)₂\} ligands and {Ph} groups indicative of the formation of complexes of the general form \([\{\text{Me}_2\text{NC(NCy)}_2\}_2\text{Sn(E-Ph)}_2\}]\). This asymmetry is further confirmed with the presence of 12 resonances associated with the \{CH\} and \{CH₂\} groups on the bis-cyclohexyl guanidinate ligand in the \(^{13}\)C NMR spectra for 2-4. \(^{119}\)Sn NMR spectra for complexes 2 and 3 show the presence of single resonances for each of the complexes at \(\delta = -578\) ppm (2) and -742 ppm (3), with additional coupling to the selenium atoms in complex 3 \([1J_{\text{SnSe}} = 1410 \text{ Hz}]\). Not unsurprisingly, the \(^{77}\)Se NMR spectrum for 3 shows the presence of singlet resonance \(\delta_{\text{Se}} = 267\) ppm accompanied by satellites generated by coupling to the neighbouring \(^{119}\)Sn centre \([1J_{\text{SnSe}} = 1411 \text{ Hz}]\). Unfortunately, intensive investigation of compound 4 by \(^{119}\)Sn and \(^{125}\)Te NMR spectroscopy failed to reveal the anticipated Sn and Te resonances.
Elemental analysis of the complexes similarly suggest the formation of the expected Sn(IV) bis-phenylchalcogenide complexes. Single crystals, suitable for X-ray diffraction studies, of complexes 2-3 were obtained upon storage of concentrated hexane solutions at -28 °C for 12 to 24 hrs. While all three complexes are fundamentally isostructural, complex 2 crystallises in the monoclinic space group P2₁/n with one full molecule in the asymmetric unit, whereas complexes 3 and 4 crystallise in the triclinic space group P-1 again with one molecule per asymmetric unit. The molecular structures for the three complexes are shown in figure 2. Selected bond lengths and angles are provided in table 1.

As noted previously, all three complexes, 2-4, are isostructural, with analogous gross structural features, i.e. the presence of a central hexa-coordinated pseudo-octahedral Sn atom, with the two phenyl chalcogenide groups occupying cisdial equatorial positions. The remaining four coordination sites are occupied by the nitrogen atoms of the two bi-dentate guanidine ligands which occupy equatorial and axial coordination sites. The differences between the three structures therefore lie in the relative orientation of the phenyl chalcogenide substituents as well as the relative orientation of both the cyclohexyl derivatives and the [NMe₂] moieties. Inspection of the complexes reveal Sn-N bond lengths in 2-4 are comparable with related Sn(IV) guanidinate and amidinate complexes in the literature. In all three complexes there is a slight lengthening of the axial and equatorial Sn-N bonds as the atomic number of the chalcogen atom attached the tin centre increases. The significant contraction of the axial Sn-N bonds, in 1, upon oxidation [ave. ~2.42Å to 2.17-2.19 Å] we presume is due the change in oxidation state of the central tin atom. Perhaps unsurprisingly, the average Sn-E bond length increase with the increasing atomic number of the chalcogen atom, and are in good agreement with both comparable Sn-E single bonds within the Cambridge Structural Database (CSD), specifically the related aryl and alkyl-halogenane compounds such as [[Me₃Si]₂Sn(Ph-E)₂] [17] and [[Me₃Si]₂N₃Sn(Ph-E)₂] [18] as well as theoretical values for single bonds calculated from the sum of the single bond covalent radii. [17]
Despite the increase in steric demands of the (E-Ph) groups in 2-4 respectively, which is reflected in the lengthening of the Sn-E bonds, there is no accompanying change in the (E-Sn-E) angle (θ) or the interplanar (N₂Sn) x (SnN₂) angles (ψ)\(^\text{[18]}\) (see table 2). (Cf. interplanar angles observed in 1 [108.25°]). Although there is a general increase in the [E-θ-E] distance. By the same token, the bite angle of the guanidinate ligands remain similar throughout 2: ave. 60.68°, 3: ave. 60.40°, 4: ave. 60.2°. One striking feature is the increasing deviation away from linearity of the axial N-Sn-N angle from 157.8° (2), to 146.4° (3) and 143.8° (4), respectively, as the cisoidal chalcogen atoms increase in size.

As part of our study we also wished to investigate an alternative route to the mono-chalcogenide products [(Me₆NC)(NCy)₂Sn=E] (E = S, Se or Te). We have previously described the synthesis of these complexes via the di-direct reaction of the stannylene 1 with suitable single chalcogen atom transfer reagents. However, we wished to improve the synthetic route by investigating the reactivity of dihalo-Sn(V) guanidinate complexes with LiE (E = S, Se and Te). Reaction of the stannylene 1 with CBr₄ results in the clean oxidation of the Sn(II) center and formation of the dibromo Sn(V) complex 5 (Scheme 3). Similar reactivity has been observed with plumbene systems,\(^\text{[18]}\) although this is, we believe, the first reported example of the reaction of CBr₄ with a stannylene.

**Scheme 3.** Synthesis of the Sn(IV) bis-Guanidinate di-bromo complexes 5.

Reaction of 1 with equimolar amounts of CBr₄ in THF, results in an immediate color change from pale yellow to red/purple. Removal of the solvent followed by recrystallisation from toluene results in formation of red crystals of 5 in almost quantitative yield (98%). The precise mechanism by which CBr₄ reacts with the stannylene 1 is unknown. However, it is most probable that the mechanism is comparable to similar reactions between stannenes and alkyl halides.\(^\text{[19]}\) With initial insertion across the Br-C bond, followed by elimination of a putative (CBr₄) fragment. As anticipated, ¹H and ¹³C NMR spectra of complex 5 reveal the presence of resonances associated with both the cyclohexyl (CH) and (NMe₃) groups [¹H δ = 3.30 (CH), 3.45 (CH) and 2.44 ppm (NMe₃)]. The ¹⁹Sn NMR spectrum for 5 shows the presence of a single resonance at δ = -567 ppm, which is comparable to related Sn(IV) di-halogen systems in the literature.\(^\text{[15b]}\) Elemental analysis of 5 closely matched the predicted carbon, nitrogen and hydrogen percentage masses expected for the complex. Figure 3 shows the molecular structure of complex 5, with selected bond lengths and angles reported in the figure caption. Crystallisation in the monoclinic space group P₂₁, complex 5 is a C₂ symmetric dibromo-stannene at the centre of which resides a six-coordinate tin atom with a distorted pseudo octahedral geometry (Br(1), Br(2), N(12) and N(21) atoms in equatorial positions).

**Figure 3.** Molecular structure of the Sn(IV) dibromo bis-guanidinate complex 5. Hydrogen atoms have been fully omitted, and the cyclohexyl groups have been partially omitted for clarity. Selected bond lengths (Å) and selected bond angles (°): Sn(1)-Br(1) 2.5696(8), Sn(1)-Br(2) 2.5702(9), Sn(1)-N(11) 2.140(6), Sn(1)-N(12) 2.1675(7), Sn(1)-N(21) 2.206(6), Sn(1)-N(22) 2.192(6), Br(1)-Sn(1)-Br(2) 92.74(3), N(11)-Sn(1)-N(22) 152.62(6), N(12)-Sn(1)-N(21) 106.7(2), N(11)-Sn(1)-N(12) 61.6(2), N(21)-Sn(1)-N(22) 61.7(2).

The Sn-N bond lengths are again comparable with other Sn(IV) bis-guanidinate systems described ibid. Similarly, the interatomic Sn-Br distances are comparable to the only other bis-guanidinate stannene system containing a Sn-Br interaction reported in the literature.\(^\text{[20]}\) In contrast to the [E-Sn-E] angles in complexes 2-4, the Br-Sn-Br angle in 5 is notably smaller. Concomitantly, the interplanar (N₂Sn) x (SnN₂) angle [F = 84.3°] only slightly smaller than that observed in complexes 2-4.

Direct reaction of 5 with either Li₂S, Li₂Se or Li₂Te (made in-situ in THF from elemental chalcogens and the super hydride, Li[BEt₃H])\(^\text{[21]}\) (Scheme 4), resulted in the formation of the corresponding mono-chalcogenide complexes, which after extraction away from THF and LiBr, could be isolated as microcrystalline powders in higher yields [6: 81%, 7: 96%, 8: 92%] than corresponding reaction between the stannylene 1, and suitable chalcogenide transfer reagents mentioned previously.\(^\text{[11]}\) The reactions of 5 with the dithio-chalcogenides resulted in obvious colour changes from a brown/red solution (5) to a pale yellow (6) and orange solution (7), respectively, alongside the formation of a cream coloured suspension.

**Scheme 4.** Salt metathesis synthesis of the Sn(IV) bis-Guanidinate mono-chalcogenide complexes 6-8.
For complex 8, very little colour change was observed and the reaction was worked-up after a 48hr. In all cases, characterisation data (1H, 13C and 119Sn NMR spectroscopy and elemental analysis) for complexes 6-8 was identical to that previously reported for these complexes.[11]

Thermogravimetric analyses (TGA) of complexes 2-4 and 6-8 were performed in order to gain insight into relative volatilities and thermal stabilities of the compounds (Figure 4). Table 3 gathers relevant data, relating to % mass residues, expected % mass residues, onset temperatures and melting points for these complexes. Analyses were carried out with an instrument housed in a nitrogen filled purge-box in order to minimize reaction with atmospheric moisture/air.

Compounds 2-4 (Figure 4A) were found to undergo mass loss to yield stable residues of between 24-25.5% over the temperature range 289-405 °C. In the case of complex 2 and 3 respectively, the % mass of the non-volatile residues, 25.1% and 25.5%, are both higher than residual masses expected for the formation of the appropriate mono-chalcogenide (i.e. 18.1% for SnS and 21.4% for SnSe). However, it should be noted that the formation of the corresponding di-chalcogenide systems SnS₂ (21.9%) and SnSe₂ (29.94%) cannot be ruled out in these systems. In the case of complex 4 the TGA trace reveals a significantly cleaner single decomposition process with a stable % mass residues of 24.2% formed around 348 °C which corresponds directly to the mass residue expected for the formation of SnTe. Contrastingly, the mono-chalcogen derivatives 6, 7 and 8 all show multi-step decomposition pathways (Fig. 4B) over differing temperature ranges. However, in all three cases the final mass residue is found to be less than that expected, respectively, for “SnS”, “SnSe” or “SnTe” formation, possibly indicating a small degree of volatility. It should be noted, however, that the solid state decomposition process monitored in thermogravimetric analysis is probably very different to any solvothermal decomposition process, and can only be used as a general guide.

Table 3: Expected % residue, % of non-volatile residue and onset of volatilisation/decomposition temperature for 2-4 and 6-8.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Expected % for Residue (Temp.)</th>
<th>% Non-volatile Residue</th>
<th>Onset Temp.</th>
<th>Melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>28.3 (289 °C)</td>
<td>25.5 (348 °C)</td>
<td>152 °C</td>
<td>133 °C</td>
</tr>
<tr>
<td>3</td>
<td>23.1 (349 °C)</td>
<td>25.1 (405 °C)</td>
<td>121 °C</td>
<td>149 °C</td>
</tr>
<tr>
<td>4</td>
<td>23.3 (289 °C)</td>
<td>24.2 (289 °C)</td>
<td>150 °C</td>
<td>101 °C</td>
</tr>
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</table>

Tin Chalcogenide Nanocrystals

In a typical procedure for the preparation of tin chalcogenide nanocrystals, the precursor was dissolved in a minimum volume of hexane. To this solution oleylamine was added and the hexane was removed in vacuo. The reaction mixture was then heated at 210 °C for 40 min before being cooled to room temperature. Excess ethanol was added and the precipitate was collected by ethanol washing and centrifugation three times.

Figure 4. Thermogravimetric analysis data for complexes (A) 2-4 and (B) 6-8.

Figure 5. TEM images of nano-crystal synthesised from A - 6, B - 7 and C - 8.
The tin chalcogenide precursors 2–4 and 6–8, were used in the nanocrystal preparation procedure with varying degrees of success: Compounds 2–4 failed to make identifiable chalcogenide containing materials.

While EDX analysis of the materials isolated did show the presence of Sn & S, Sn & Se and Sn & Te respectively, all the materials were Sn rich and contained a high carbon content consistent with an incomplete decomposition and formation of the desired materials. Analysis by PXRD revealed the isolated products to be amorphous.

In contrast, the mono-chalcogen systems 6–8 were more successful. After workup, the resulting nanoparticles were analyzed by TEM, the images of the resulting particles are shown in Figure 4. The particles produced over the 40 min reaction time varied considerably in size between ca. 0.4 μm (Figure 5 A), 0.5–20-50 nm (Figure 5 B) and 50–100 nm (Figure 5 C).

EDX spectra for nanocrystals formed from compounds 6, 7 and 8 respectively all show presence of both Sn and Chalcogen (S, Se or Te) in the approx. 1:1 atom-%, Sn/E ratio for materials synthesised over both the 40 min reaction time [Sn:S 49:51; Sn:Se 50:50; Sn:Te 44:56]. It should also be noted that the EDX spectra also showed the presence of trace amounts of Fe, Cu and C, the former arising from the TEM grid used to support the samples (See Supplementary Information).

Conclusions

This work documents the synthesis and characterization of a series of tin(IV) bis-guanidinate complexes 2–4 and 6–9, and initial investigations into their utility as precursors for the solvothermal synthesis of tin(II) chalcogenide nano-crystals. However, while it should be noted that related complexes have been used in the deposition of thin films of tin(VI) chalcogenides, by spin coating,[25] the work reported here, to the best of our knowledge, represents the first reported use of Sn=E containing systems as single source precursors for SnS, SnSe and SnTe nanoparticle synthesis, with control over the oxidation state of the products. The synthesis for the bis-phenyl chalcogenide complexes 2–4 involves the straight forward reaction of the easily prepared stannylene 1, with commercially available diphenyl dichalcogenides Ph₂E₂ (E = S, Se & Te). The molecular structures of all three complex [{Me₂NC(NCy)₂]₂SnE₂} (E = S (2), Se (3) or Te (4)) have been determined by single crystal X-ray diffraction experiments, revealing a family of isoreticular complexes, all of which pose a distorted pseudo octahedral geometry about the central Sn(IV) center. As part of our study we wished to access an alternative synthetic pathway to the mono-chalcogen complexes of the general form [{Me₂NC(NCy)₂]₂Sn=E} (E = S, Se or Te). To this end, we investigated the reactivity of the stannylene complex 1 with CBr₄, in which the bromoalkane is capable of the oxidative addition of “Br₂” to the Sn(II) centre, resulting in the high yielding formation of the dibromo bis-guanidinate complex [{Me₂NC(NCy)₂]₂SnBr₂} (5), which has been fully structurally characterised. Subsequent reaction of the dibromo species (5) with the Li₂S, Li₂Se or Li₂Te respectively results in a new high yielding synthesis of complexes 6–8.

The potential of complexes 2–4 and 6–8 respectively, as single source precursors for nano-crystal formation (un-optimised) has been evaluated. PXRD and EDX analysis provide clear evidence that under our reaction conditions, the phenyl chalcogenide precursors 2–4 fail to form the desired SnE materials, due to incomplete decomposition under our initial reaction conditions. In contrast precursors 6–8 all appear (by EDX and PXRD analysis) to produce the desired SnE materials. In the case of precursor 6 PXRD analysis was unable to unequivocally confirm the presence of crystalline SnS. In this case of precursors 7 and 8, the production of SnSe and SnTe could be confirmed. In the case of precursor 8, PXRD analysis suggests the possible presence of...
additional hexagonal Te to be present in the nano-crystalline product. Our future efforts in this area are directed towards the finding the optimised reaction conditions for the SnTe nano-crystal formation, as well as investigating these materials for other thin film and nanomaterial production.

**Experimental Section**

General Procedures: Elemental analyses were performed using an Exeter Analytical CE 440 analyzer. $^{1}H$, $^{13}C$, $^{79,81}$Se and $^{119,121}$Te NMR spectra were recorded on a Bruker Advance 300 or 500 MHz FT–NMR spectrometers, as appropriate, as saturated solutions at room temperature, unless stated otherwise; chemical shifts are in ppm with respect to Me$_2$Si($H$, $^{13}C$). TGA and PXRD were performed using a Perkin Elmer TGA7 or Bruker D8 instrument (CuK$\alpha$ radiation), respectively.

All reactions were carried out under an inert atmosphere using standard Schlenk techniques. Solvents were dried and degassed under an argon atmosphere over activated alumina columns using an Innovative Technology solvent purification system (SPS). The Sn(Ii) bis-guanidinate, [Me$_6$N(CN)$_2$]$_2$Sn(1), was prepared by literature method. The reagents Ph$_2$S$_2$, Se$_2$Ph$_2$, Te$_2$Ph$_2$, and CBr$_4$ were purchased from Aldrich chemicals. Stoichiometric amounts of the dithiol chalcogenides Li$\equiv$ (E = S, Se or Te) were synthesized in-situ via using a slightly modified literature method.$^{(21)}$

**Synthesis of [Me$_6$N(CN)$_2$]$_2$Sn(SPh)$_2$**

Under inert conditions, complex 1 (0.65 g, 1 mmol) and phenyl disulphide (0.23 g, 1 mmol) were dissolved in THF (20 ml). After stirring for 3 hours the solution was dried in vacuo to provide a pale yellow solid. The solid was extracted with hot hexane, and filtered through Celite™.

Concentration and storage of the filtrate at -28 °C yielded red brown crystals which were isolated by filtration and dried in vacuo. Yield: 0.98 g, 98%; $^{1}H$ NMR (CD$_2$Cl$_2$) $\delta$ 0.77-2.36 (m, 40 H, cyclohexyl), 2.44(s, 12H, N-C(=H)), 3.19 (m, 2H, N-C(=H)), 3.37 (m, 2H, N-C(=H)) 6.92-7.13 (m, 6H, ortho and para-CH$_2$), 7.83-7.92 (m, 4H, meta-CH$_2$), 7.95 (m, 2H, C(=H)). TGA and PXRD were performed using a Perkin Elmer TGA7 or Bruker D8 instrument (CuK$\alpha$ radiation), respectively.

**Synthesis of [Me$_6$N(CN)$_2$]$_2$Sn(SPh)$_2$**

Under inert conditions, compound 1 (0.80 g, 1.3 mmol) and CBr$_4$ (0.43 g, 1.3 mmol) were dissolved in THF (20 ml). After stirring for 3 hours the solution was dried in vacuo to provide a pale yellow solid. The solid was extracted with 20 ml of toluene, and filtered through Celite™. Concentration and storage of the filtrate at -28 °C yielded red brown crystals which were isolated by filtration and dried in vacuo. Yield: 0.98 g, 98%; $^{1}H$ NMR (CD$_2$Cl$_2$) $\delta$ 0.77-2.36 (m, 40 H, cyclohexyl), 2.44(s, 12H, N-C(=H)), 3.30 (m, 2H, N-C(=H)), 3.45 (m, 2H, N-C(=H)), 3.19 (m, 2H, N-C(=H)), 3.37 (m, 2H, N-C(=H)) 6.92-7.13 (m, 6H, ortho and para-CH$_2$), 7.83-7.92 (m, 4H, meta-CH$_2$), 7.95 (m, 2H, C(=H)). TGA and PXRD were performed using a Perkin Elmer TGA7 or Bruker D8 instrument (CuK$\alpha$ radiation), respectively.

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[1H] NMR (75.8 MHz, CdCl2): δ(H): -818 ppm (s); 129Te[1H] NMR (157.98 MHz, CdCl2): δ(0) = -1259 ppm.

General preparation of tin chalcogenide nanoparticles from precursors 2-4 and 6-9.

Under inert conditions, excess dry oleylamine (20 ml) was added to a hexane (10 ml) solution of the tin chalcogenide precursor (0.5 mmol). The hexane was removed in vacuo. The reaction mixture was heated at 210 °C for 40 mins (16 also heated for 20 mins and 2 hours). Once cooled to room temperature, excess ethanol was added. The precipitate was collected by centrifugation then purified by ethanol washing and centrifugation a further three times. The powder was dried in vacuo.

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in the supplementary information (ESI: Table S4). Crystallographic data were collected at 150 K on a Nonius Kappa-CCD Diffractometer [2/MoKα] = 0.71073 Å), and solved by direct methods (SIR-92) [23] and refined against all F² using SHELXL-97 [23]. All hydrogen atoms were included in idealised positions and refined using the riding model. Structure solution was followed by full-matrix least squares refinement and was performed using the WinGX [24] matrix least squares refinement and E. de Bettignies, B., Springer, Berlin ; Natural. 2005, 437, 664-670.

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Keywords: Tin(II) • Guanidine • sulphur • selenium • tellurium • Precursors


SnS, SnSe and SnTe are a potentially important semiconductor materials. Here, we have described the application of mono chalcogen Sn(IV) guanidinate precursors, containing either Sn-Ch or Sn=Ch bonds (Ch = S, Se and Te) derived from the oxidative addition of elemental chalcogenides (S, Se and Te) and Diphenyl dichalogenides to Sn(II) guanidinate complexes, for the production of tin(II) chalcogenide nano-crystals.

**Key Topic**
Nanocrystal Precursors, Tin(II) Chalcogenides
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Oxidative Addition to Sn(II) Guanidinate Complexes: Nanocrystal Precursors.