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Selenide and selenolate compounds of indium: a comparative study of In–Se bond-forming reactions

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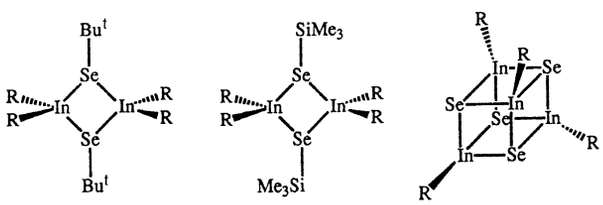
A range of In–Se bond-forming reactions have been investigated, including insertion of selenium into either an In–C or In–S bond, reaction of an indium halide with a magnesium selenolate and *via* chlorosilane elimination. The reaction of $InBu^t_3$ with Se yielded $[Bu^t_2In(\mu\text{-}SeBu^t)]_2$ and $[Bu^tIn(\mu_3\text{-}Se)]_4$. In contrast, $In(CMe_2Et)_3$ and $InBu^n_3$ with Se preferentially formed $[(Me_2EtC)In(\mu_3\text{-}Se)]_4$ and $[Bu^nIn(\mu_3\text{-}Se)]_4$, respectively. The reaction of $In(CMe_2Et)_3$ with Te yielded $[(Me_2EtC)In(\mu_3\text{-}Te)]_4$. The compound $[Bu^tIn(\mu_3\text{-}Se)]_4$ is also formed from the reaction of $[Bu^t_2In(\mu\text{-}SBu^t)]_2$ with either Se or $Se{=}PPh_3$, while both it and $[Bu^tIn(\mu\text{-}SeBu^t)]_2$ may be prepared from $[Bu^t_2In(\mu\text{-}Cl)]_n$ and $(Bu^tSe)MgCl$. Similarly, $[Bu^n_2In(\mu\text{-}SeBu^t)]_2$ may be prepared from $[Bu^n_2In(\mu\text{-}Cl)]_2$. However, the reaction of $[(Me_2EtC)_2In(\mu\text{-}Cl)]_2$ with $(Bu^tE)MgCl$ (E = S, Se or Te) yielded $[(Me_2EtC)In(\mu_3\text{-}E)_4]$. Reaction of $[Bu^t_2M(\mu\text{-}Cl)]_n$ (M = In or Ga) with $Se(SiMe_3)_2$ yielded the silylselenolate compounds $[Bu^t_2M(\mu\text{-}SeSiMe_3)]_2$. The various In–Se bond-forming reactions are compared. The molecular structures of $[Bu^t_2In(\mu\text{-}EBu^t)]_2$ (E = S or Se) have been determined by X-ray crystallography.

Since our first reports of the synthesis of the *tert*-butyl substituted gallium chalcogenide cubane compounds $[Bu^tGa(\mu_3\text{-}E)]_4$ (E = S, Se or Te),[1,2] and their potential application as precursors for the metal–organic chemical vapour deposition (MOCVD) of gallium chalcogenide thin films,[3,4] there has been a number of reports of Group 13–16 (III–VI) cubane molecules,[5] as well as a large number of thiolate,[6] selenolate[7] and tellurolate[8] compounds. This renaissance in the chalcogenide compounds of the Group 13 metals (in particular gallium and indium) is largely due to interest in their application as potential single-source precursors for the MOCVD growth of semiconductor thin films.[9]

While the growth of Group 13 sulfide thin films has generally been well studied, reports of the MOCVD growth of gallium and indium selenides are limited.[9,10] In part this is most likely due to the smaller range of precursor compounds known relative to comparable thiolates.[11] Despite this limitation, the deposition properties of mono- and di-meric organoindium selenolate compounds have been published,[12] and we have studied the MOCVD growth of GaSe and GaTe using the cubane precursors, $[RGa(\mu_3\text{-}E)]_4$ (R = Bu^t or CMe_2Et, E = Se or Te).[13,14]

We have demonstrated several systems where the combination of deposition conditions (substrate temperature, flow rate, *etc.*) and molecular precursor structure determines the composition, phase and morphology of films formed by MOCVD.[3,13] In order to extend these studies it is important to have a homologous series of compounds that contain a range of alkyl substituent (influencing the precursor volatility[15] and film quality), stoichiometry (*i.e.* M to E ratio in the precursor and deposited film[16]), as well as the size and geometry of the molecular core (*i.e.* monomer *versus* oligomer, which can influence the phase of the deposited film[3]). In this regard our interest in preparing the indium analogues of our *tert*-butyl- and *tert*-pentyl-gallium chalcogenide compounds has been driven by the desire to probe their application as CVD precursors,[13] and completion of the homologous series of compounds, *e.g.* $[RM(\mu_3\text{-}E)]_4$ (M = Al, Ga or In; E = S, Se or Te). Herein we report the synthesis and characterization of dialkylindium selenolate dimers (**I** and **II**) and cubane alkylindium selenides (**III**).

By analogy to known thiolate complexes [equation (1)] the



$$MR_3 + n\text{RSH} \longrightarrow R_{3-n}M(SR)_n + n\text{RH} \quad (1)$$

most logical approach to the synthesis of organometallic compounds of the heavier chalcogenides involves alkane-elimination reactions. Unfortunately, the corresponding selenols (RSeH) are malodorous, toxic and often unstable.[17] Given the greater stability and hence availability of dialkyl diselenides (RSeSeR), alternative methodologies involving their reaction with MR_3 [equation (2)] or directly with indium metal [equation (3)] have been employed for the synthesis of Group 13 seleno-

$$MR_3 + R'\text{SeSe}R' \longrightarrow [R_2M(\text{SeR}')]_n + \text{RSeR}' \quad (2)$$

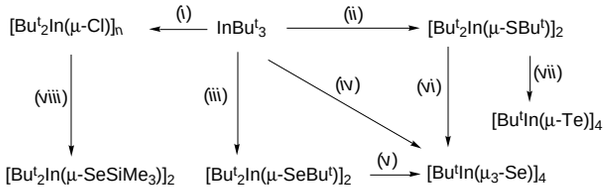
$$\text{In} + \text{RSeSeR} \longrightarrow [\text{In(SeR)}_3]_n \quad (3)$$

lates.[18] These methods are still less than ideal because the dialkyl diselenides are oils, highly toxic, and also equally difficult to work with due to their noxious odours. In contrast, the diaryl diselenides are solids, less toxic and with their lower volatility do not smell as bad, but they are slow to react,[19] and the presence of aromatic groups is deleterious to film growth due to incorporation of carbon (a dopant) into the films. Other approaches used to prepare indium selenolates include: ligand-redistribution reactions [*e.g.* equation (4)],[20] and the use of

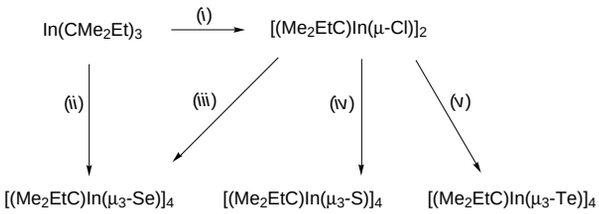
$$\text{In(SePh)}_3 + 2\ \text{In}(CH_2CMe_3)_3 \longrightarrow \tfrac{3}{2}[(Me_3CCH_2)_2\text{In}(\mu\text{-SePh})]_2 \quad (4)$$

lithium or sodium salts of selenols derived from large bulky ligands such as the mesityl (2,4,6-trimethylphenyl),[21] tris(trimethylsilyl)silyl $[Si(SiMe_3)_3]$ or tris(trimethylsilyl)methyl $[C(SiMe_3)_3]$ groups.[17]

In addition to the goal of preparing a range of In–Se contain-



Scheme 1 Synthetic routes to *tert*-butylindium selenolate, selenide and telluride compounds. (*i*) $InCl_3$; (*ii*) Bu^tSH; (*iii*) grey Se; (*iv*) excess of grey Se; (*v*) heat; (*vi*) grey Se or $Se{=}PPh_3$; (*vii*) elemental Te; (*viii*) $Se(SiMe_3)_2$



Scheme 2 Synthetic routes to *tert*-pentyl indium selenolate and chalcogenide compounds. (*i*) $InCl_3$; (*ii*) grey Se; (*iii*) (Bu^tSe)MgCl; (*iv*) (Bu^tS)MgCl; (*v*) (Bu^tTe)MgCl

ing structures for MOCVD studies, we are interested in a comparative study of the various routes for In–Se bond formation, to allow for optimization of large-scale synthesis. Thus, three types of reactions were used to synthesize new alkylindium dimers and cubanes: (*a*) the insertion of selenium into In–C and In–S bonds, (*b*) the reaction of (*tert*-butylchalcogenido)-magnesium chloride, (Bu^tE)MgCl (E = S, Se or Te), with indium chlorides and (*c*) *via* the trimethylsilyl chloride elimination reaction.

Results and Discussion

tert-Pentyl compounds of indium

Our initial studies in the chemistry of gallium chalcogenides concentrated on the *tert*-butyl compounds,[3] in part due to the ability to prepare multigram quantities of $GaBu^t_3$. However, $InBu^t_3$, a yellow crystalline solid, is extremely light sensitive both in solution and solid state, decomposing to indium metal.[22] This hinders the practicality of any compound prepared from $InBu^t_3$, especially with regard to scale-up. We have recently reported that the sterically more demanding *tert*-pentyl (CMe_2Et) compounds of gallium[5d] and aluminium[5e] show enhanced stability as compared to their *tert*-butyl analogues and have therefore investigated the synthesis of their indium homologues.

The parent trialkylindium compound, $In(CMe_2Et)_3$ **1**, may be prepared from the reaction of $InCl_3$ with 3 equivalents of the appropriate Grignard reagent [equation (5)]. Similar syn-

$$InCl_3 + 3(Me_2EtC)MgCl \longrightarrow \underset{\mathbf{1}}{In(CMe_2Et)_3} + 3MgCl_2 \quad (5)$$

thesis have been employed for the aluminium and gallium analogues.[5d,5e] Compound **1** is a clear, pyrophoric, straw-yellow liquid that has been characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. Unlike $InBu^t_3$, $In(CEtMe_2)_3$ is only moderately light sensitive and fumes in air. The dimeric monochloride compound, $[(Me_2EtC)_2In(\mu\text{-}Cl)]_2$ **2**, is prepared by the disproportionation reaction commonly employed for Group 13 alkyl halide compounds, equation (6).[23] Compound **2** is a white crystalline, moderately air-stable solid.

$$InCl_3 + 2\,In(CMe_2Et)_3 \longrightarrow \tfrac{3}{2}[(Me_2EtC)_2In(\mu\text{-}Cl)]_2 \quad (6)$$

Insertion reactions

We have previously reported that the reaction of a gallium trialkyl with elemental chalcogenide is a convenient method for the synthesis of gallium chalcogenide and alkyl chalcogenate compounds.[3,5b,5e] Reaction of $InBu^t_3$ with 1 molar equivalent of metallic selenium yields a mixture of $[Bu^t_2In(\mu\text{-}SeBu^t)]_2$ **3** and $[Bu^tIn(\mu_3\text{-}Se)]_4$ **4**, Scheme 1 [(*iii*) and (*iv*)] which may be separated by fractional crystallization. Both compounds have been isolated and characterized by mass and NMR spectroscopy (see Experimental section). The molecular structure of **3** has been confirmed by X-ray crystallography, as has that of the previously reported sulfur analogue $[Bu^t_2In(\mu\text{-}SBu^t)]_2$ (see below).[16] While the yield of compound **4** may be optimized by the use of an excess of metallic (grey) selenium, extended reaction times and higher temperatures, attempts to optimize the yield of **3** were unsuccessful. Theremolysis of **3** results in its conversion into **4**, even in the absence of an excess of selenium.

In contrast to the *tert*-butyl derivatives, reaction of InR_3 (R = CMe_2Et or Bu^n) with elemental selenium does not allow for the isolation of the dimeric selenolate, however the cubane compounds $[RIn(\mu_3\text{-}Se)]_4$ (R = CMe_2Et **5** or Bu^n **6** (*cf.* **III**) are formed in modest yield, see Scheme 2 and Experimental section. The reaction of $In(CMe_2Et)_3$ with elemental tellurium yields only the cubane $[(Me_2EtC)In(\mu_3\text{-}Te)]_4$ **7**. Compounds **5**–**7** have been characterized by NMR spectroscopy and mass spectrometry. X-Ray analysis of **7** showed it to be isostructural to the aluminium and gallium analogues,[5e] however due to severe disorder of the *tert*-pentyl groups no satisfactory solution was obtained.[24] It is interesting that $[Bu^nIn(\mu_3\text{-}Se)]_4$ is essentially insoluble in non-polar solvents despite the presence of long-chain aliphatic alkyl substituents.

In addition to the insertion of a chalcogen into a M–C bond (M = Al, Ga or In), previous work has shown that such insertion into a M–E bond (E = S, Se or Te) is also possible.[3] We have reported that the gallium thiolate compound, $[Bu^t_2Ga(\mu\text{-}SBu^t)]_2$ reacts with elemental sulfur to yield the sulfide cubane *via* an alkyldisulfide, equation (7). In a similar manner,

$$[Bu^t_2Ga(\mu\text{-}SBu^t)]_2 \xrightarrow{+\,S_8} [Bu^t_2Ga(\mu\text{-}SSBu^t)]_2 \xrightarrow[-Bu^t(S)_nSBu^t]{+\,S_8} [Bu^tGa(\mu_3\text{-}S)]_4 \quad (7)$$

$[Bu^t_2Ga(\mu\text{-}SBu^t)]_2$ reacts with elemental selenium or tellurium to give the appropriate cubane compounds, *e.g.* equation (8).

$$2\,[Bu^t_2Ga(\mu\text{-}SBu^t)]_2 + 8\,E \xrightarrow{E = Se \text{ or } Te} [Bu^tGa(\mu_3\text{-}E)]_4 + 4\,Bu^tSEBu^t \quad (8)$$

The complex nature of the reaction of $InBu^t_3$ with elemental selenium and the difficulties in the synthesis of $InBu^t_3$ compared to the stability and ease of synthesis of $[Bu^t_2In(\mu\text{-}SBu^t)]_2$,[16,25] prompted the investigation of a similar series of reactions for $[Bu^t_2In(\mu\text{-}SBu^t)]_2$. With Se or $Se{=}PPh_3$, *i.e.* Scheme 1(*vi*) $[Bu^t_2In(\mu\text{-}SBu^t)]_2$ cleanly yields compound **4**.

(*tert*-Butylchalcogenido)magnesium chloride reactions

The reactions of alkali-metal thiolates with transition- or main group-metal halides has been a major route to metal thiolate compounds. Recently, researchers have reported the formation of Group 13 selenolate and tellurolate compounds by this method,[26] however these have been limited to aromatic or sterically hindered derivatives. The enhanced stability of the dialkylindium chloride compounds, $[R_2In(\mu\text{-}Cl)]_n$, with respect to the homologous trialkyls suggests that this approach should provide a convenient route to the formation of In–Se bonds.

Although lithium selenolates may be prepared by the reaction of an alkyllithium with selenium,[27] the (alkylchalcogenido)-

magnesium halide derivatives, (RE)MgX, prepared in an analogous manner,[28] appear to be of more general applicability due to the wide range of stable selenolate derivatives that have been isolated. In fact, hydrolysis of these species has been commonly employed as a convenient route to the appropriate selenol.[29] As solids (RSe)MgX are stable and may be stored in an inert-atmosphere dry-box for several months.

Reaction of $[Bu^t_2In(\mu\text{-}Cl)]_2$[22,30] with $(Bu^tSe)MgCl$ yields a mixture of compounds **3** and **4**. In contrast, $[Bu^n_2In(\mu\text{-}SeBu^t)]_2$ **8** may be prepared from $[Bu^n_2In(\mu\text{-}Cl)]_2$, in high yield without significant formation of the cubane, equation (9).

$$[Bu^n_2In(\mu\text{-}Cl)]_2 + 2\,(Bu^tSe)MgCl \longrightarrow [Bu^n_2In(\mu\text{-}SeBu^t)]_2 + 2\,MgCl_2 \quad (9)$$

In the case of the reaction of $[(Me_2EtC)_2In(\mu\text{-}Cl)]_2$ with $(Bu^tSe)MgCl$ only the cubane **5** was formed, Scheme 2(*ii*). In fact, both $[(Me_2EtC)In(\mu_3\text{-}S)]_4$ **9** and **7** are prepared in modest yields by the use of the appropriate *tert*-butylchalcogenide, see Scheme 2 (*iv*) and (*v*). Presumably, an unstable Bu^tSe-bridged dimer is formed, but under the reaction conditions employed rapidly converts into the cubane. It is possible that the driving force for this conversion is the greater steric hindrance around indium in $[R_2In(\mu\text{-}SeBu^t)]_2$ for the *tert*-pentyl *versus tert*-butyl *versus n*-butyl.

Chlorosilane-elimination reactions

The use of the chloro–silyl elimination method [*i.e.* equation (10)] for the formation of bonds to the Group 13 metals was

$$L_nM{-}Cl + Me_3Si{-}X \longrightarrow L_nM{-}X + Me_3SiCl \quad (10)$$

originally developed by Wells[31] for the synthesis of Ga–As bonds. Subsequently, this reaction has been utilized for a wide range of applications, and most recently extended to include the formation of Group 13 chalcogenide compounds, prepared from the reaction of the bis(trialkylsilyl) chalcogenides, $E(SiMe_3)_2$ (E = S, Se or Te), with Group 13 dihalides.[32]

Reaction of $[Bu^t_2In(\mu\text{-}Cl)]_n$ with $Se(SiMe_3)_2$ yielded the silyl-selenolate compound $[Bu^t_2In(\mu\text{-}SeSiMe_3)]_2$ **10** as the major isolable product, see Scheme 1. However, a second product is formed, which based on the ^1H NMR and mass spectra of the reaction mixture we propose to be $[Bu^t(Me_3Si)In(\mu\text{-}Cl)]_2$ formed as a result of alkyl–silyl elimination. Silyl-substituted selenolates have been previously prepared by the reaction of silylselenols with either InR_3 or $InCl_3$. However, while chloro–silyl elimination is thermodynamically favoured over alkyl–silyl elimination there are prior eamples of the latter taking precendent, *e.g.* equation (11). The gallium analogue of compound

$$R'InX_2 + (Me_3Si)SeR \longrightarrow X_2InSeR + Me_3SiR' \quad (11)$$

10, *i.e.* $[Bu^t_2Ga(\mu\text{-}SeSiMe_3)]_2$ **11**, may be prepared cleanly in an analogues manner, see Experimental section.

Comparison of In–Se bond-forming reactions

As mentioned in the Introduction, one of the goals of this work was to compare various synthetic methodologies for the formation of In–Se bonds. A number of routes have been studied: insertion of selenium into either an In–C or In–S bond, reaction of an indium halide with a magnesium selenolate, and *via* chlorosilane elimination. We note that while all the compounds reported herein have an In : Se ratio of 1 : 1, the core geometry (*i.e.* dimer *versus* cubane) is controlled by both the identity of the alkyl substituent and the reaction methodology employed. The following general points that can be made. First, the In–Se bond-forming reactions are not as 'clean' as their Ga–Se analogues.[3,5d] Secondly, alkyl substituents on indium sterically more demanding than *tert*-butyl are required to inhibit the formation of multiple products. This latter issue has been clearly the concept employed by the groups of Uhl,[5b,c,7] Power[21] and Arnold,[11,17] for the high-yield isolation of indium selenolates and selenides.

Ostensibly the insertion of elemental selenium into an In–C bond has practical advantage over a salt-elimination reaction, since there is no filtering of the reaction mixture required prior to isolation of the product. Unfortunately, reactions where the dimeric selenolate is stable, *i.e.* $[Bu^t_2In(\mu\text{-}SeBu^t)]_2$ make it difficult to isolate the cubane product pure. This may be overcome by the use of larger alkyl groups, *e.g. tert*-pentyl. Alternatively, since indium thiolates, $[R_2In(\mu\text{-}SR')]_2$, may be prepared in high yield from the reaction of the trialkylindium with the thiol, and the thiolate acts as a 'sacrificial ligand' during the reaction with elemental selenium (or tellurium), the formation of the cubane compounds can be accomplished irrespective of the steric size of the indium alkyl substituent. Unfortunately, in each of the above cases the formation of low-volatility RSeSeR (or RSeSR') moieties as a side product hinders purification of the indium-containing species. The use of bis(trimethylsilyl) selenide is attractive for the ease in removing the volatile silyl by-product, although the unpredictability of Me_3SiR or Me_3SiCl elimination, limits its efficacy as a general approach. In addition, the potential dopant property of silicon to Group 13–16 compound semiconductors makes the use of silicon-containing alkyl substituents, or any silicon methodology, highly undesirable.

By choice of appropriate reaction conditions the magnesium selenolate reagents have several advantages for synthesizing In–Se containing compounds, in particular the cubane derivatives. First, the magnesium selenolates are stable for even a wide range of alkyl substituents (as opposed to the sterically demanding trialkylsilyl groups used previously[17]). Secondly, reaction of (RSe)MgCl with dialkylindium halides occurs readily without requiring forcing conditions. Thirdly, since during the formation of the cubane compounds the alkyl of (RSe)MgCl is sacrificial, almost any convenient (alkylchalcogenido)magnesium halide may be employed for Group 13 chalcogenide cubane compounds inaccessible by any other route. For example, we have used the tellurium Grignard as the chalcogenide source for the synthesis of $[(Et_3C)Ga(\mu_3\text{-}Te)]_4$, equation (12), where the parent trialkyl cannot be prepared.[33]

$$2\,[(Et_3C)_2Ga(\mu\text{-}Cl)]_2 \xrightarrow{+\,(MeTe)MgBr} [(Et_3C)Ga(\mu_3\text{-}Te)]_4 \quad (12)$$

Crystallographic studies

The molecular structures of $[Bu^t_2In(\mu\text{-}SeBu^t)]_2$ **3** and $[Bu^t_2In(\mu\text{-}SBu^t)]_2$ are shown in Figs. 1 and 2, respectively; selected bond lengths and angles are given in Table 1. The In–Se bonds in **3** [2.704(4) and 2.699(7) Å] are typical for bridging selenolate compounds of indium [2.611(2)–2.75(1) Å],[34,35] and may be compared to the value of 2.61 Å for the sum of the covalent radii of In (1.44) and Se (1.17 Å).[36] Similarly, the In–S bonds [2.601(2) and 2.594(2) Å] are within the range reported for indium thiolates [2.551(2)–2.622(5) Å].[37] The In–C bond lengths are within experimental error identical for the two compounds. As is commonly observed, the In_2E_2 cyclic cores are both nearly planar. Comparing $[Bu^t_2In(\mu\text{-}EBu^t)]_2$, the E–In–E bond angles are larger and the In–E angles smaller for E = Se relative to E = S. This trend is consistent with the increased covalent radius of selenium (1.17 Å) with respect to sulfur (0.95 Å).

As with other thiolate- and selenolate-bridged Group 13 compounds,[6–8] the geometry about the chalcogen itself is pyramidal (see Fig. 3), not planar as is found in their oxygen analogues, *i.e.* Σ(M–E–C) = 333(2) (E = Se), 339.9(3) (S) and

Table 1 Selected bond lengths (Å) and angles (°) for $[Bu^tIn(\mu\text{-}EBu^t)]_2$ (E = S or Se **3**)*

	E = Se	E = S
In(1)–E(1)	2.704(4)	2.601(2)
In(1)–E(1a)	2.699(7)	2.594(2)
In(1)–C(11)	2.22(3)	2.201(5)
E(1)–C(1)	1.89(4)	1.830(6)
E(1a)–C(1)	1.86(3)	1.817(6)
E(1)–In(1)–E(1′)	86.9(2)	82.3(1)
E(1a)–In(1)–E(1a′)	86.7(3)	81.9(1)
E(1)–In(1)–C(11)	124.5(7)	122.7(1)
E(1a)–In(1)–C(11)	96.7(8)	100.6(1)
E(1)–In(1)–C(11′)	96.7(8)	100.6(1)
E(1a)–In(1)–C(11′)	125.3(6)	123.1(1)
C(11)–In(1)–C(11′)	123(1)	122.5(1)
In(1)–E(1)–In(1′)	93.1(2)	97.7(1)
In(1)–E(1a)–In(1′)	93.3(3)	98.1(1)
In(1)–E(1)–C(1)	119.0(8)	121.9(1)
In(1)–E(1a)–C(1)	120(1)	122.9(1)

* E(1a) and C(11a) denote disordered *tert*-butylchalcogenide postions; E(1′) the symmetry equivalent position.

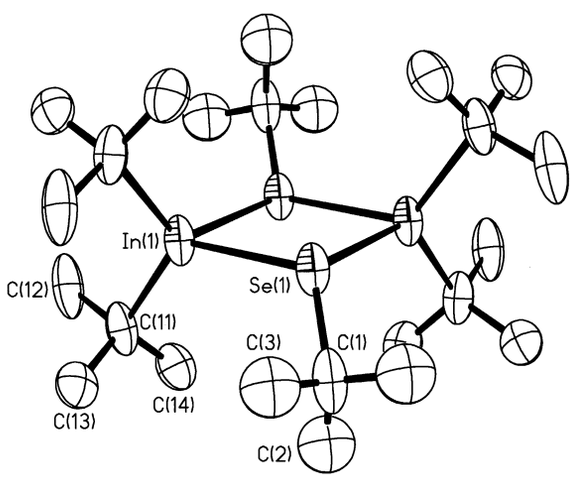


Fig. 1 Molecular structure of $[Bu^t_2In(\mu\text{-}SeBu^t)]_2$ **3**. Thermal ellipsoids are drawn at the 30% level. Only one of the positions for the disorder of the $SeBu^t$ groups is shown, and hydrogen atoms are omitted for clarity

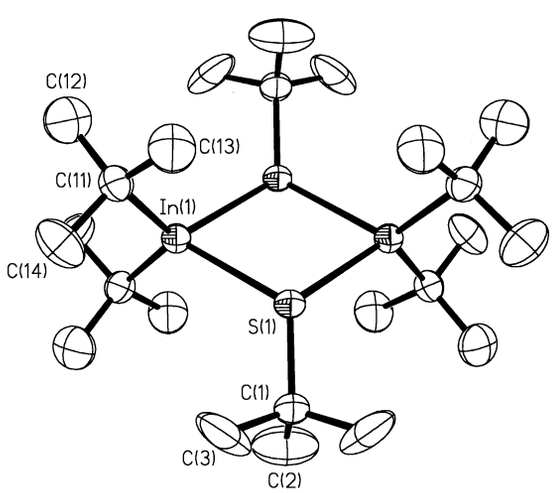


Fig. 2 Molecular structure of $[Bu^t_2In(\mu\text{-}SBu^t)]_2$. Only one of the positions for the disorder of the SBu^t groups is shown; other details as in Fig. 1

360° (O[38]). A consequence of the non-planar geometry of the selenium and sulfur is that there is significant distortion of the indium centre from ideal tetrahedral. A wide range of dimeric

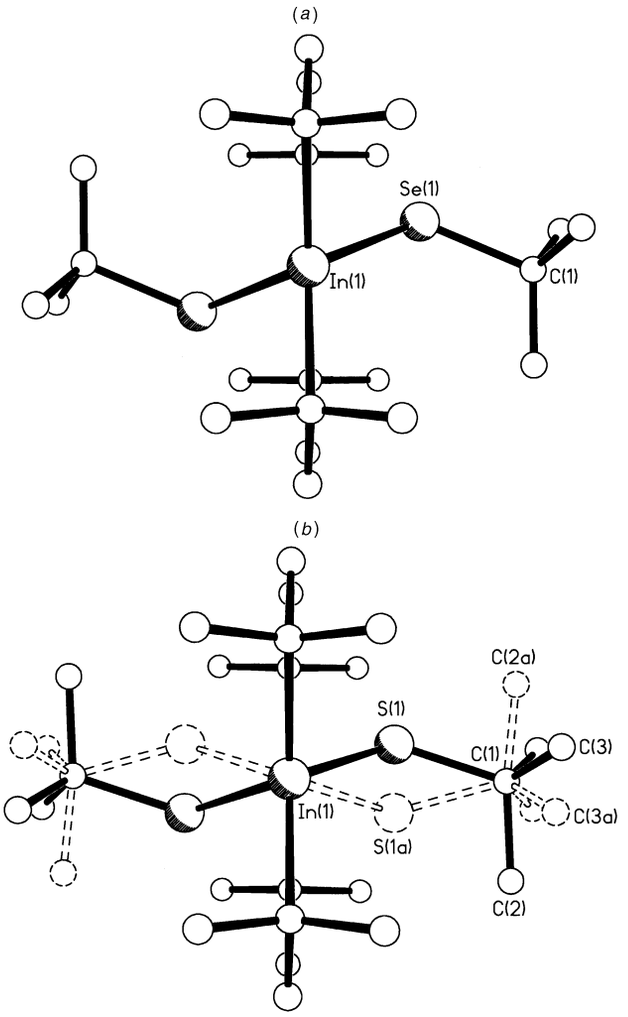


Fig. 3 Molecular structures of (*a*) compound **3** and (*b*) $[Bu^t_2In(\mu\text{-}SBu^t)]_2$ viewed along the In(1)–In(1′) vector, showing the distortion about the indium centres. The view in (*b*) also shows the disordered thiolate ligand. A similar disorder is found for **3** but is omitted for clarity

di-*tert*-butyl Group 13 compounds has now been structurally characterized, $[Bu^t_2M(\mu\text{-}X)]_2$ (X = OR, O_2R, NR_2, PR_2 or AsR_2).[34] In each case the torsion angle between the MC_2 and M_2X_2 planes has been approximately, or crystallographically equal to, 90°. In the case of **3** the InC_2 planes are pitched at 68.7° with respect to the In_2E_2 plane, as compared to 71.9° for $[Bu^t_2In(\mu\text{-}SBu^t)]_2$, see Fig. 3. Similar distortions have been observed in the molecular structures of $[Bu^t_2M(\mu\text{-}OPh)]_2$ (M = Al[38] or Ga),[39] $[Bu^t_2Al\{\mu\text{-}OAl(Bu^t)_2\}]_2$,[40] $[(2,4,6\text{-}Me_3C_6H_2)_2In(\mu\text{-}Cl)]_2$[41] and $[Ph_2In\{\mu\text{-}SSn(C_6H_{11})_3\}]_2$.[37a] The greater distortion from tetrahedral about indium in **3** as compared to that in $[Bu^t_2In(\mu\text{-}SBu^t)]_2$ is consistent with increased $Bu^t\cdots Bu^t$ steric interaction because of the greater pyramidalization of Se *versus* S.

The selenolate and thiolate ligands in $[Bu^t_2In(\mu\text{-}EBu^t)]_2$ exhibit crystallographic disorder, *e.g.* Fig. 3(*b*). The disorder may be rationalized by placing the chalcogen above or below a plane defined by the indium atoms and the *α*-carbons [C(1) and C(1′)] of the *tert*-butyl groups attached to the chalcogens. The β-carbons are also disordered and suitably positioned to retain the tetrahedral geometry about C(1) and C(1′). Since a crystal-packing diagram (Fig. 4) indicates no close intermolecular contacts this disorder is not due to crystal twinning, but random orientation of the thiolate/selenolate ligands. The disorder is not due to the symmetry of the structure. Indeed, it is present when attempting to solve the structure in either *C*2 or *Cm*.

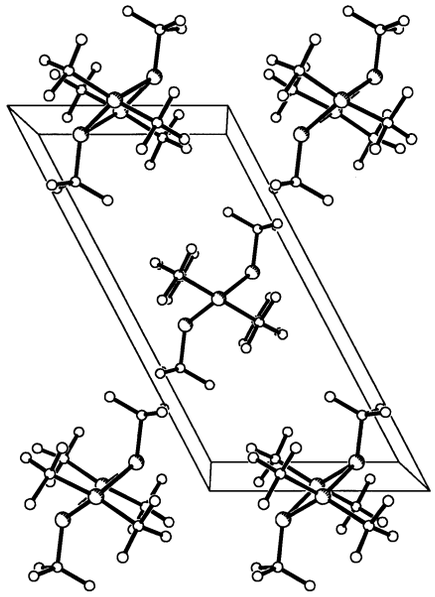


Fig. 4 Crystal-packing view of compound **3**. All hydrogens have been omitted for clarity

Experimental

Electron-impact (EI) mass spectra were obtained using Finnigan MAT 95 and JEOL AX-505 H spectrometers operating with an electron-beam energy of 70 eV (*ca.* 1.42×10^{-17} J), IR spectra on a Perkin-Elmer 1600 Series FT-IR spectrometer using KBr plates and NMR spectra on Bruker AM-200 (^{1}H, ^{13}C) and WM-300 (^{77}Se) spectrometers using (unless otherwise stated) C_6D_6 solutions. Chemical shifts are reported relative to internal solvent resonances (^{1}H and ^{13}C) and external Me_2Se (^{77}Se).

The compounds $(Me_2EtC)MgCl$, $[R_2In(\mu\text{-}Cl)]_2$ (R = Bu^t or Bu^n) and $[Bu^t_2In(\mu\text{-}SBu^t)]_2$ were prepared according to published procedures,[16,25] (Bu^{t}E)MgCl (E = S, Se or Te) were prepared by a modification of literature procedures[28] and Bu^{t}MgCl, $InCl_3$, elemental S, Se and Te, were obtained from commercial sources and used as received. All manipulations were carried out under an inert atmosphere using Schlenk techniques or a VAC atmospheres dry-box. All solvents were dried, distilled and degassed prior to use. **CAUTION**: selenium compounds are highly toxic by inhalation and have dangerous cumulative effects.

Preparations

$In(CMe_2Et)_3$ 1. A solution of $(Me_2EtC)MgCl$ (375 cm^3 of 0.8 mol dm^{-3} Et_2O solution, 0.3 mol) was added dropwise to an Et_2O (200 cm^3) suspension of $InCl_3$ (22.2 g, 0.10 mol). Heat was liberated and the $InCl_3$ dissolved. After addition was complete and the reaction was stirred for 60 min, the solvent was removed under vacuum. The bright yellow residue was extracted in hexane (400 cm^3) and the resulting solution filtered through Celite®. This solution may be used directly, or the hexane removed under vacuum and the yellow oil distilled [110 °C, 10^{-2} mmHg (*ca.* 1.33 Pa)]. Yield: 50%. EI mass spectra: *m*/*z* 257 ($M^+ - CMe_2Et$, 100%). NMR: ^{1}H, δ 1.41 [6 H, q, *J* (H–H) = 7.4, CH_2CH$_3$], 1.12 (18 H, s, C(CH$_3$)$_2$] and 0.92 [9 H, t, *J*(H–H) = 7.4 Hz, CH$_2$CH_3]; ^{13}C, δ 37.1 (CH$_2$*C*H$_3$), 28.1 [C(*C*H$_3$)$_2$] and 15.0 (*C*H$_2$CH$_3$).

$[(Me_2EtC)_2In(\mu\text{-}Cl)]_2$ 2. To a hexane suspension (80 cm^3) of $InCl_3$ (4.21 g, 0.019 mol) was added a hexane (80 cm^3) solution of $In(CMe_2Et)_3$ (12.5 g, 0.038 mol) and stirred for 3 d. The solvent was removed under vacuum and the solid extracted with CH_2Cl_2 (50 cm^3). Filtration through Celite® followed by cooling to −20 °C yielded white needle-like crystals. Yield: 90%. El mass spectrum: *m*/*z* 513 ($M^+ - CMe_2Et$, 5), 292 [InCl-$(CMe_2Et)_2$, 10], 257 [$In(CMe_2Et)_2$, 45], 221 [$InCl(CMe_2Et)$, 10], 150 (InCl, 15) and 71 (CMe_2Et, 100%). IR (cm^{-1}): 1325m, 1269m, 1163w, 1146s, 1049m, 1032m, 1007m, 992w, 941w, 907w, 801m, 771m and 459w. NMR: ^{1}H, δ 1.60 [4 H, q, *J* (H–H) = 7.3, CH_2CH$_3$], 1.44 [12 H, s, C(CH$_3$)$_2$] and 0.99 [6 H, t, *J*(H–H) = 7.3 Hz, CH$_2$CH_3]; ^{13}C, δ 49.31 (InC), 38.09 (CH$_2$*C*H$_3$), 29.60 (CH$_3$) and 14.63 (CH_2CH$_3$).

$[Bu^t_2In(\mu\text{-}SeBu^t)]_2$ 3. *Method* 1. A freshly prepared pentane solution (200 cm^3) of $InBu^t_3$ (*ca.* 0.01 mol) was added to grey selenium (1.0 g, 0.01 mol). Over 24 h, the solution turned bright yellow and a white powder formed. All volatiles were removed *in vacuo* and the residue was extracted in hexane (50 cm^3). Reduction in the volume and cooling to −25 °C resulted in the formation of X-ray-quality crystals. Yield: 20%.

Method 2. The solids $[Bu^t_2In(\mu\text{-}Cl)]_n$ (1.79 g, 6.8 mmol) and (Bu^{t}Se)MgCl (1.34 g, 6.8 mmol) were mixed and Et_2O (50 cm^3) added. The resulting solution was stirred overnight. The solvent was removed under vacuum and the solid extracted with pentane (40 cm^3). Reduction in volume and cooling (−25 °C) gave a white solid. Yield: 45%. M.p. = 176–180 °C (decomp.). EI mass spectrum: *m*/*z* 732 (M^+, 8), 675 ($M^+ - Bu^t$, 60), 618 ($M^+ - 2Bu^t$, 10), 561 ($M^+ - 3Bu^t$, 18), 504 ($M^+ - 4Bu^t$, 18), 447 ($M^+ - 5Bu^t$, 10), 396 (In_2Se_2, 15), 366 ($InSeBu^t_3$, 45), 309 ($InSeBu^t_2$, 75), 263 [InSe(Bu^t)H, 40] and 229 ($InBu^t_2$, 47%). NMR: ^{1}H, δ 1.52 [36 H, s, SeC(CH$_3$)$_3$] and 1.51 [18 H, s, InC(CH$_3$)$_3$]. ^{13}C, δ 38.31 [SeC(*C*H$_3$)$_3$] and 33.09 [InC(*C*H$_3$)$_3$]; ^{77}Se, δ 180.9 (s).

$[Bu^tIn(\mu_3\text{-}Se)]_4$ 4. *Method* 1. A freshly prepared pentane solution (200 cm^3) of $InBu^t_3$ (*ca.* 0.01 mol) was added to grey selenium (1.0 g, 0.01 mol). Over 2 d, the solution turned bright yellow and a white powder formed. The solvent was removed under vacuum and the product extracted with toluene (50 cm^3). Reduction in volume and cooling to −25 °C yielded a white solid. Yield: 10%.

Method 2. The solids $[Bu^t_2In(\mu\text{-}Cl)]_n$ (1.79 g, 6.8 mmol) and (Bu^{t}Se)MgCl (1.34 g, 6.8 mmol) were mixed and Et_2O (50 cm^3) added. The resulting solution was stirred for 3 d. The solvent was removed under vacuum and the solid extracted with pentane or toluene. Cooling of the resulting solution (−25 °C) yielded a white solid. Yield: 40%. EI mass spectrum: *m*/*z* 1006 (M^+, 18), 949 ($M^+ - Bu^t$, 100), 892 ($M^+ - 2Bu^t$, 45), 835 ($M^+ - 3Bu^t$, 38) and 778 ($M^+ - 4Bu^t$, 43%). IR (cm^{-1}): 1730s, 1649m, 1558m, 1287s and 1240s. NMR: ^{1}H, δ 1.37 [36 H, s, InC(CH$_3$)$_3$]; ^{13}C, δ 32.11 [InC(*C*H$_3$)$_3$]; ^{77}Se, δ −109.7 (s).

$[(Me_2EtC)In(\mu_3\text{-}Se)]_4$ 5. *Method* 1. A hexane solution (200 cm^3) of $In(CMe_2Et)_3$ (*ca.* 0.10 mol) was added to grey selenium (7.8 g, 0.10 mol) and allowed to react for 3 d. It turned yellow and a white precipitate formed at the bottom. The supernatant was filtered off and the volume reduced and cooled to −25 °C. Additional product was obtained by extraction of the white solid in hexane. The solution was then filtered, concentrated and cooled to −25 °C, yielding a white crystalline solid. Yield: 65%.

Method 2. To a Et_2O solution (50 cm^3) of $[(Me_2EtC)_2In(\mu\text{-}Cl)]_2$ (2.00 g, 6.84 mmol) was added a Et_2O solution of (Bu^{t}Se)MgCl (6.84 mmol). The resulting solution was stirred for 3 d. The solvent was removed under vacuum and the solid extracted with pentane or toluene. Cooling of the resulting solution (−25 °C) yielded a white solid. Yield: 20%. EI mass spectrum: *m*/*z* 1059 (M^+, 10), 991 ($M^+ - CMe_2Et$, 50), 920 ($M^+ - 2\ CMe_2Et$, 40), 849 ($M^+ - 3\ CMe_2Et$, 20) and 778 (In_4Se_4, 25%). IR (cm^{-1}): 1260s, 1092m, 1019m, 800s and 456w cm^{-1}. NMR: ^{1}H, δ 1.50 [8 H, q, *J*(H–H) = 7.5, CH_2CH$_3$], 1.19 [24 H, s, C(CH$_3$)$_2$] and 1.10 [12 H, t, *J*(H–H) = 7.5 Hz, CH$_2$CH_3]; ^{13}C, δ 13.78 (CH$_2$*C*H$_3$), 27.77 [C(*C*H$_3$)$_2$] and 37.43 (*C*H$_2$CH$_3$); ^{77}Se, δ −146.5 (s).

[Bu^{n}In(μ$_3$-Se)]$_4$ 6. A hexane solution (300 cm^3) of InBu$^n_3$ (10.0 g, 0.035 mol) was added to grey selenium (2.8 g, 0.035 mol). The solution was stirred for 3 d and the supernatant filtered. The resulting white solid was sufficiently soluble in C_6D_6 for low signal-to-noise ^{1}H NMR spectroscopy, however insufficient material could be dissolved in toluene, tetrahydrofuran (thf) or Et_2O to further purify by recrystallization. Yield: 70%. M.p. = 230–240 °C (decomp.). EI mass spectrum: *m*/*z* 1006 (M^+, 10), 949 ($M^+ - Bu^t$, 60), 892 ($M^+ - 2Bu^t$, 5), 835 ($M^+ - 3Bu^t$, 15) and 778 ($M^+ - 4Bu^t$, 2%). IR (cm^{-1}): 1413w, 1259s, 1093m, 1018m, 958w, 920w, 798s, 642m, 575m and 460w. ^{1}H NMR: δ 0.79 [3 H, t, *J*(H–H) = 7.3, $CH_2(CH_2)_2CH_3$], 1.23 [2 H, m, *J*(H–H) = 7.3, $(CH_2)_2CH_2CH_3$], 1.49 [2 H, m, *J*(H–H) = 7.4, $(CH_2)_2CH_2CH_3$] and 2.37 [2 H, t, *J*(H–H) = 7.3 Hz, $CH_2(CH_2)_2CH_3$].

[(Me$_2$EtC)In(μ$_3$-Te)]$_4$ 7. A hexane solution (100 cm^3) of In(CMe$_2$Et)$_3$ (*ca.* 0.01 mol) was added to elemental tellurium (0.78 g, 0.01 mol). After 6 d the solution turned brandy coloured and white crystals formed which were filtered off and dried under vacuum. Yield: 20%. EI mass spectrum: *m*/*z* 1256 (M^+, 5), 1185 ($M^+ - CMe_2Et$, 30), 1114 ($M^+ - 2\ CMe_2Et$, 10), 1043 ($M^+ - 3\ CMe_2Et$, 10) and 972 (In_4Se_4, 12%). ^{1}H NMR: δ 1.73 [8 H, q, *J*(H–H) = 7.5, CH_2CH_3], 1.33 [24 H, s, $C(CH_3)_2$] and 0.89 [12 H, t, *J*(H–H) = 7.5 Hz, CH_2CH_3].

[Bu$^n_2$In(μ-SeBu^t)]$_2$ 8. The solids [Bu$^n_2$In(μ-Cl)]$_2$ (1.0 g, 0.004 mol) and (Bu^{t}Se)MgCl (0.78 g, 0.004 mol) were mixed and Et_2O (150 cm^3) added. After stirring for 1 d the solvent was removed under vacuum and the residue extracted with pentane. Removal of the volatiles yielded a viscous oil. Yield: 10%. EI mass spectrum: *m*/*z* 675 ($M^+ - Bu$, 80), 61 ($M^+ - Bu - C_4H_8$, 15), 561 ($M^+ - 3$ Bu, 20), 505 ($M^+ - 3$ Bu $- C_4H_8$, 55), 481 (In_2SeBu, 100), 447 ($M^+ - 5$ Bu, 20), 366 (InSeBu$^t_3$, 45) and 309 (InSeBu$^t_2$, 70%). NMR: ^{1}H, δ 1.02 [12 H, t, *J* (H–H) = 7.3, $CH_2(CH_2)_2CH_3$], 1.30 [8 H, t, *J*(H–H) = 8.0, $CH_2(CH_2)_2CH_3$], 1.51 [8 H, m, *J*(H–H) = 7.6, $(CH_2)_2CH_2CH_3$], 1.91 [8 H, m, *J*(H–H) = 8.0 Hz, $(CH_2)_2CH_2CH_3$] and 1.53 [18 H, s, SeC(CH$_3$)$_3$]: ^{13}C, δ 37.3 [SeC(CH_3)$_3$], 30.84, 28.67 ($InCH_2CH_2CH_2$), 19.11 [In(CH$_2$)$_3$CH$_3$] and 14.07 ($InCH_2$).

[(Me$_2$EtC)In(μ$_3$-S)]$_4$ 9. To [(Me$_2$EtC)$_2$In(μ-Cl)]$_2$ (1.11 g, 3.8 mmol) was added (Bu^{t}Se)MgCl (0.51 g, 3.8 mmol) in Et_2O and the mixture stirred for 2 d, resulting in a clear solution and a white precipitate ($MgCl_2$). The supernatant was filtered and the solvent removed under vacuum to give a white solid. Yield: *ca.* 20%. EI mass spectrum: *m*/*z* 872 (M^+, 20), 801 ($M^+ - CMe_2Et$, 40) and 731 ($M^+ - CMe_2Et - C_5H_{10}$, 60%). ^{1}H NMR: δ 1.63 [8 H, q, *J*(H–H) = 7.3, CH_2CH_3], 1.44 [24 H, s, $C(CH_3)_2$] and 0.99 [12 H, t, *J*(H–H) = 7.3 Hz, CH_2CH_3].

[Bu$^t_2$In(μ-SeSiMe$_3$)]$_2$ 10. To a toluene solution (50 cm^3) of [Bu$^t_2$In(μ-Cl)]$_n$ (0.40 g, 7.6 mmol) was added Se(SiMe$_3$)$_2$ in thf (540 μl, 0.76 mmol) by syringe. The solution was stirred for several hours and a white solid formed with a yellow supernatant. The solution was filtered and the white solid washed with pentane (20 cm^3) and dried under vacuum. Yield: 10%. ^{1}H NMR: δ 1.38 [18 H, s, $C(CH_3)_3$] and 0.09 [9 H, s, $Si(CH_3)_3$].

[Bu$^t_2$Ga(μ-SeSiMe$_3$)]$_2$ 11. To a toluene solution (50 cm^3) of [Bu^{t}Ga(μ-Cl)]$_2$ (0.165 g, 7.60 mmol) was added Se(SiMe$_3$)$_2$ in thf (540 μl, 0.76 mmol) by syringe. The solution was stirred for several hours and a white solid formed, which was filtered off. Yield: 30%. EI mass spectrum: *m*/*z* 556 (M^+, 40) and 501 ($M^+ - Bu^t$). ^{1}H NMR: δ 1.36 [18 H, s, $C(CH_3)_3$] and 0.08 [9 H, s, $Si(CH_3)_3$].

(Bu^{t}S)MgCl. An Et_2O solution of Bu^{t}MgCl (10 cm^3, 1.0 mmol dm^{-3}, 0.01 mol) was added to elemental sulfur (0.64 g, 0.02 mmol) suspended in Et_2O (50 cm^3). After stirring overnight the mixture was filtered and the solvent removed under vacuum to give a white powder. Yield: 90%. M.p. = 280 °C (decomp.). IR (cm^{-1}): 1256s, 1238m, 1198m, 1161s, 1091s, 1039s, 951s, 892m, 796s, 719m, 582vs and 498s. ^{1}H NMR: δ 1.21 [s, $C(CH_3)_3$].

(Bu^{t}Se)MgCl. An Et_2O solution of Bu^{t}MgCl (10 cm^3, 1.0 mol dm^{-3}, 0.01 mol) was added to grey selenium (7.0 g, 0.09 mol). After 2 h the mixture was filtered and the solvent removed yielding a white solid. Additional product was extracted from the excess of Se using thf (50 cm^3). Yield: 90%. M.p. = 220–240 °C (decomp.). EI mass spectrum: *m*/*z* 161 (Bu^{t}SeMg, 10) and 138 (Bu^{t}SeH, 25%). IR (cm^{-1}): 1256m, 1146s, 1024s, 962w, 918w, 877m, 796m, 763w, 722w, 675w, 597m, 498m and 479w. ^{1}H NMR: δ 1.36 [s, $C(CH_3)_3$].

(Bu^{t}Te)MgCl. An Et_2O solution of Bu^{t}MgCl (10 cm^3, 1.0 mol dm^{-3}, 0.01 mol) was added to elemental tellurium (1.54 g, 0.012 mol) suspended in Et_2O (20 cm^3). After 2 h the solvent was removed under vacuum and the solid was extracted with thf and filtered through Celite®. Yield: 90%. ^{1}H NMR: δ 1.51 [s, $C(CH_3)_3$].

Table 2 Summary of X-ray diffraction data*

	[Bu$^t_2$In(μ-SeBu^t)]$_2$ **3**	[Bu$^t_2$In(μ-SBu^t)]$_2$
Empirical formula	$C_{24}H_{54}In_2Se_2$	$C_{24}H_{54}In_2S_2$
Crystal size/mm	0.11 × 0.24 × × 0.24	0.31 × 0.34 × 0.41
a/Å	17.398(5)	17.4100(9)
b/Å	11.951(4)	11.9143(6)
c/Å	8.784(1)	8.8137(6)
β/°	117.490(1)	118.840(5)
U/Å^3	1620.0(8)	1601.5(2)
D_c/g cm^{-3}	1.497	1.320
μ/mm^{-1}	13.67	15.52
2θ Range/°	4.0–40.0	2.0–44.0
No. data collected	834	1074
No. independent data	801	1040
No. observed data ($\|F_o\| > 6.0\sigma\|F_o\|$)	705	991
Weighting scheme, w^{-1}	$\sigma^2(\|F_o\|)$	$\sigma^2(\|F_o\|) + 0.04(\|F_o\|)^2$
R	0.095	0.024
R′	0.095	0.025
Largest difference peak/e Å^{-3}	1.36	0.33

* Details in common: monoclinic, space group *C*2/*m*; *Z* = 2; Mo-Kα radiation (λ = 0.710 73 Å); 298 K.

Crystallography

A crystal of [Bu$^t_2$In(μ-SeBu^t)]$_2$ **3** was mounted in a glass capillary attached to the goniometer head of a Nicolet R3m/V four-circle diffractometer. The data collection, unit cell and space group determination were all carried out in a manner previously described in detail.[42] The structure was solved using the direct methods program XS[43] which readily revealed the positions of the In and Se atoms. Subsequent Fourier-difference maps revealed the positions of all the non-hydrogen atoms. The selenolate ligands exhibit crystallographic (50:50) disorder due to inversion of the selenium above or below a plane defined by the indium atoms and the *α*-carbons [C(1) and C(1′)] of the *tert*-butyl groups attached to the selenium. Attempts to solve the structure in either *C*2 or *Cm* space group symmetry resulted in retention of the disorder. Subsequently, full refinement with 50% site occupancy of the selenium atom and associated *tert*-butyl methyl groups was successful. All the hydrogen atoms were placed in calculated positions [U_{iso} = 0.08 Å^2, *d*(C–H) = 0.96 Å] for refinement. Neutral-atom scattering factors were taken from the usual source.[44] Refinement of positional and anisotropic thermal parameters led to convergence (see Table 2).

A crystal of $[Bu^t_2In(\mu\text{-}SBu^t)]_2$ was sealed in a glass capillary under argon and mounted on the goniometer of an Enraf-Nonius CAD-4 automated diffractometer. Data collection and cell determinations were performed in a manner previously described.[40] The indium was located by using a Patterson map while the remaining atomic coordinates were determined through the generation of Fourier-difference maps using MOLEN.[45] The thiolate ligands were shown to have an analogous disorder to that found in compound **3**, see above and Results and Discussion. Hydrogen atoms were included and constrained to 'ride' upon the appropriate atoms [d(C−H) = 0.95 Å, U(H) = 1.3 B_{eq}(C)]. Scattering factors were taken from ref. 44.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/386.

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