Synthesis and Structural Characterization of Dimeric and Trimeric Indium Thiolates

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Received June 14, 1994[®]

Reaction of Mes_3In (Mes = 2,4,6-trimethylphenyl) with *tert*-butyl mercaptan, *tert*-amyl mercaptan, 2-*tert*-butylthiophenol, and triphenylsilanethiol yields $[Mes_2In(\mu\text{-}SR)]_2$ (R = *t*-Bu (**1**), *tert*-amyl (**2**), 2-*t*-BuC_6H_4 (**3**), and $SiPh_3$ (**4**)). A trimeric indium thiolate, $[Me_2In(\mu\text{-}SSiPh_3)]_3$ (**5**), is isolated from the reaction of Me_3In with $HSSiPh_3$. The first structures of di- and trimeric indium thiolato species, **1**, **2**, **4**, and **5**, have been determined. The structure of **1** was determined in the space group *C*2/*c* (No. 15) with cell constants $a = 28.809(6)$ Å, $b = 9.041(2)$ Å, $c = 18.156(5)$ Å, $\beta = 110.24(2)°$, $V = 4437(2)$ Å^3, and $Z = 8$; $R = 5.40\%$, $R_w = 5.67\%$. **2** and **4** crystallize as dimers in the space group $P\bar{1}$ (No. 2). For **2**: $a = 11.631(7)$ Å, $b = 12.866(3)$ Å, $c = 15.767(5)$ Å, $\alpha = 90.09(2)°$, $\beta = 93.70(4)°$, $\gamma = 105.13(3)°$, $V = 2273(1)$ Å^3, $Z = 4$, $R = 8.1\%$, $R_w = 7.4\%$. For **4**: $a = 12.423(3)$ Å, $b = 13.019(3)$ Å, $c = 14.126(2)$ Å, $\alpha = 91.50(1)°$, $\beta = 113.23(1)°$, $\gamma = 117.72(2)°$, $V = 1795.8(6)$ Å^3, $Z = 2$, $R = 3.75\%$, $R_w = 4.3\%$. In **1**, **2**, and **4**, the $(InS)_2$ core is planar with the alkyl groups on S oriented in a transoid fashion. **5** exists as a trimer in the space group $P\bar{1}$ (No. 2): $a = 15.012(5)$ Å, $b = 17.784(5)$ Å, $c = 24.838(8)$ Å, $\alpha = 76.23(2)°$, $\beta = 83.03(3)°$, $\gamma = 69.84(2)°$, $V = 6040(3)$ Å^3, $Z = 4$ (trimers), $R = 5.99\%$, $R_w = 5.34\%$.

Introduction

The current interest in the synthesis of new organometallic compounds containing group13 and 16 elements as precursors for MOCVD preparation of new materials is well established.[1] Rapid progress in this area is demonstrated, for example, by the recent preparation and characterization of thiolato species of aluminum[2] and gallium.[3,4] The metal−sulfur chemistry of these two metals has yielded many surprising results with respect to structural features, method of preparation, and degree of aggregation; similar features can be uncovered by examining the chemistry associated with the heavier group 13 elements.

In this paper we report the synthesis of new mesityl- and methylindium thiolates by the reaction of thiols with Mes_3In (Mes = 2,4,6-trimethylphenyl) and Me_3In. These reactions proceed via hydrocarbon elimination to produce $[Mes_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_2$ (**1**), $[Mes_2In(\mu\text{-}S\text{-}t\text{-}amyl)]_2$ (**2**), $\{Mes_2In[\mu\text{-}S(2\text{-}t\text{-}BuC_6H_4)]\}_2$ (**3**), $[Mes_2In(\mu\text{-}SSiPh_3)]_2$ (**4**), and $[Me_2In(\mu\text{-}SSiPh_3)]_3$ (**5**) in high yield. X-ray crystallographic studies of **1**, **2**, **4**, and **5** are the first reported structures of cyclic organoindium thiolates. **1**, **2**, and **4** have planar $(InS)_2$ cores. **5** has a six-membered $(InS)_3$ ring in a skew-boat conformation in the solid state. The temperature dependence of the ^{1}H NMR spectra of **1** and **3** was examined.

Experimental Section

General Data. All solvents were purified and dried according to established procedures.[5] Argon gas was purified by passing it through a series of columns containing Deox catalyst (Alfa), phosphorus pentoxide, and sodium hydroxide. Mes_3In[6] and $HSSiPh_3$[7] were prepared according to the published procedures. Me_3In was prepared by a modified procedure initially described by Dennis[8] by reacting Me_2Hg with In metal at 130 °C in a sealed tube. The thiols, *tert*-butyl mercaptan, 2-*tert*-butylthiophenol, and *tert*-amyl mercaptan (Aldrich) were used as received. All of the glassware used in the synthetic work was oven and/or flame dried. The compounds are both air and water sensitive so standard Schlenk line and glovebox techniques were employed. ^{1}H and ^{13}C NMR spectra were recorded on either a QE-300 or a GN-300 NMR General Electric spectrometer. The ^{1}H and ^{13}C chemical shifts were referenced to benzene ($\delta = 7.15$ ppm for ^{1}H; $\delta = 128.00$ ppm for ^{13}C). Variable temperature ^{1}H NMR spectra were obtained on the GN-300 NMR spectrometer equipped with a computer-controlled variable temperature accessory. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were recorded on a Haake-Buchler apparatus in sealed capillaries and are uncorrected. Mass spectrometry data were obtained on a Kratos MS80 RFA mass spectrometer with electron impact ionization at 70 eV.

Preparation of $[Mes_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_2$ (1). The addition of *tert*-butyl mercaptan (0.25 mL, 2.22 mmol) to a solution of Mes_3In (1.05 g, 2.22 mmol) in pentane led to a white precipitate within 10 min. The mixture was stirred for 24 h and then filtered, giving a product identified as $[Mes_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_2$. The supernatant liquid yielded X-ray quality crystals on standing overnight at 4 °C. Yield: 90%. Mp: 234−235 °C. ^{1}H NMR (C_6D_6; δ, ppm): 1.26 (s, 9H, $C(CH_3)_3$), 2.14 (s, 6H, *p*-CH_3 of Mes), 2.72 (s, 12H, *o*-CH_3 of Mes), 6.83 (s, 4H, aryl H). ^{13}C NMR (C_6D_6; δ, ppm): 21.2 (*p*-CH_3 of Mes), 27.6 (*o*-CH_3 of Mes), 34.3 ($C(CH_3)_3$), 50.8 ($C(CH_3)_3$), 128.3, 137.8, 144.4, 152.8 (aryl). Anal. Calcd (found) for Mes_2InS-*t*-Bu ($C_{22}H_{31}InS$): C, 59.73 (59.00); H, 7.06 (7.19).

Preparation of $[Mes_2In(\mu\text{-}S\text{-}t\text{-}amyl)]_2$ (2). *tert*-Amyl mercaptan (0.26 mL, 2.12 mmol) was added dropwise to a stirred pentane solution of Mes_3In (1.00 g, 2.12 mmol). A white precipitate formed and was removed by filtration. The supernatant solution yielded X-ray quality crystals on standing at 4 °C. Spectroscopic characterization of both the precipitate and the crystalline material confirmed that they are the same compound. Yield: 88%. Mp: 222 °C. ^{1}H NMR (C_6D_6; δ,

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[®] Abstract published in *Advance ACS Abstracts,* November 15, 1994.

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0020-1669/94/1333-6307$04.50/0

ppm): 0.80 (t, $J_{\mathrm{H-H}} = 7.6$ Hz, 3H, $-\mathrm{SC(CH_3)_2CH_2}\mathbf{CH_3}$), 1.20 (s, 6H, $-\mathrm{SC}(\mathbf{CH_3})_2\mathrm{CH_2CH_3}$), 1.49 (q, $J_{\mathrm{H-H}} = 7.5$ Hz, 2H, $-\mathrm{SC(CH_3)_2}\mathbf{CH_2}\mathrm{CH_3}$), 2.14 (s, 6H, *p*-$\mathrm{CH_3}$ of Mes), 2.73 (s, 12H, *o*-$\mathrm{CH_3}$ of Mes), 6.84 (s, 4H, aryl H). ^{13}C NMR($\mathrm{C_6D_6}$; δ, ppm): 9.9 ($\mathrm{SC(CH_3)_2CH_2}\mathbf{CH_3}$), 21.1 (*p*-$\mathrm{CH_3}$ of Mes), 27.5 (*o*-$\mathrm{CH_3}$ of Mes), 31.6 ($\mathrm{SC}(\mathbf{CH_3})_2\mathrm{CH_2CH_3}$), 40.4 ($\mathrm{S}\mathbf{C}\mathrm{(CH_3)_2CH_2CH_3}$) 127.3, 137.7, 144.4, 153.1 (aryl).

Preparation of $\{\mathrm{Mes_2In}[\mu\text{-S(2-}t\text{-BuC_6H_4)}]\}_2$ (3). Dropwise addition of a pentane solution of 2-*tert*-butylthiophenol (0.347 g, 2.12 mmol) to a pentane solution of $\mathrm{Mes_3In}$ (1.00 g, 2.12 mmol) results in a white precipitate within 1 min of the addition. Recrystallization of this precipitate from toluene results in a colorless crystalline material. Yield: 85%. Mp: 259 °C. ^{1}H NMR ($\mathrm{C_6D_6}$; δ, ppm): 1.66 (s, 9H, $\mathrm{C(CH)_3}$), 2.02 (s, 6H, *p*-$\mathrm{CH_3}$ of Mes), 2.65 (s, 12H, *o*-$\mathrm{CH_3}$ of Mes), 6.62 (s, 4H, aryl of Mes), 6.21 (t, $J_{\mathrm{H-H}} = 8$ Hz, 1H, aryl of 2-*t*-$\mathrm{BuC_6H_4}$), 6.56 (t, $J_{\mathrm{H-H}} = 8$ Hz, 1H, aryl of 2-*t*-$\mathrm{BuC_6H_4}$), 7.01 (d, $J_{\mathrm{H-H}} = 8$ Hz, 1H, aryl of 2-*t*-$\mathrm{BuC_6H_4}$), 7.21 (d, $J_{\mathrm{H-H}} = 8$ Hz, 1H, aryl of 2-*t*-$\mathrm{BuC_6H_4}$). ^{13}C NMR ($\mathrm{C_6D_6}$; δ, ppm): 21.0 (*p*-$\mathrm{CH_3}$ of Mes), 26.6 (*o*-$\mathrm{CH_3}$ of Mes), 31.4 ($\mathrm{C}(\mathbf{CH})_3$), 36.6 ($\mathbf{C}\mathrm{(CH)_3}$), 124.6, 126.6, 127.1, 127.7, 128.5, 137.6, 140.9, 144.2, 148.8, 149.8 (aryl). Anal. Calcd (found) for $\mathrm{Mes_2InS}$-(2-*t*-$\mathrm{BuC_6H_4}$) ($\mathrm{C_{28}H_{35}InS}$): C, 64.87 (64.36); H, 6.80 (7.01). MS (EI, *m/e*): 399 (MesInS-*t*-$\mathrm{BuC_6H_4^+}$), 353 $\mathrm{Mes_2In^{+\bullet}}$.

Preparation of $[\mathrm{Mes_2In}(\mu\text{-SSiPh_3})]_2$ (4). Trimesitylindium (0.600 g, 1.27 mmol) and triphenylsilanethiol (0.370 g, 1.27 mmol) were combined in a flask, and toluene was added to the two reagents. The reaction mixture was stirred overnight and then warmed slightly to dissolve the precipitate that had formed. The solution was cooled to 4 °C, yielding a crystalline product. Yield: 90%. Mp: 237 °C. ^{1}H NMR ($\mathrm{C_6D_6}$; δ, ppm): 2.12 (s, 6H, *p*-$\mathrm{CH_3}$ of Mes), 2.32 (s, 12H, *o*-$\mathrm{CH_3}$ of Mes), 6.68 (s, 4H, aryl of Mes), 6.96 (m, 9H, Ph), 7.51 (m, 6H, Ph). ^{13}C NMR ($\mathrm{C_6D_6}$; δ, ppm): 21.1 (*p*-$\mathrm{CH_3}$ of Mes), 26.6 (*o*-$\mathrm{CH_3}$ of Mes), 127.9, 128.1, 130.0, 135.1, 136.3, 137.9, 144.0, 152.3 (aryl). Anal. Calcd (found) for $[\mathrm{Mes_2InSSiPh_3}]_2$ ($\mathrm{C_{72}H_{76}In_2S_2Si_2}$): C, 67.07 (67.37); H, 5.98 (6.01).

Preparation of $[\mathrm{Me_2In}(\mu\text{-SSiPh_3})]_3$ (5). A toluene solution of $\mathrm{Me_3In}$ (0.32 g, 2.0 mmol) was added to $\mathrm{Ph_3SiSH}$ (0.57 g, 1.95 mmol) in pentane. The evolution of gas was noted upon the addition. The colorless solution was stirred for 2 h, the volatiles were removed under vacuum, and the white residue was washed with cold pentane, leaving a white powder. This was dissolved in toluene, pentane was added, and the material crystallized from this mixture at room temperature. Yield: 80%. Mp: 160 °C. ^{1}H NMR ($\mathrm{C_6D_6}$; δ, ppm): 0.00 (s, 6H, $\mathrm{In(CH_3)_2}$), 7.10 (m, 9H, $\mathrm{SiPh_3}$), 7.79 (m, 6H, $\mathrm{SiPh_3}$). ^{13}C NMR ($\mathrm{C_6D_6}$; δ, ppm): 0.9 ($\mathrm{In(CH_3)_2}$), 128.3, 130.3, 135.9, 136.1 (aryl). Anal. Calcd (found) for $[\mathrm{Me_2In}(\mu\text{-SSiPh_3})]$ ($\mathrm{C_{20}H_{21}InSSi}$): C, 55.05 (54.22); H, 4.85 (4.77). MS (EI, *m/e*): 550−553 ($\mathrm{In_2S_2SiPh_3^+}$, $\mathrm{Me_4In_2SSiPh_2^+}$), 471−475 ($\mathrm{In_2S_2SiPh_2^+}$), 394−398 ($\mathrm{In_2S_2SiPh}$).

Synthesis of $\mathrm{In_2S_3}$ from the Reaction of $\mathrm{Mes_3In}$ and $\mathrm{H_2S}$. Trimesitylindium (0.750 g, 1.58 mmol) was placed in a Schlenk flask containing approximately 60 mL of toluene. The flask was evacuated and then filled with $\mathrm{H_2S}$. An orange precipitate formed immediately and was collected. It was found to be insoluble in all organic solvents including THF and did not diffract. This material was heated at 400 °C for 1.5 h under argon. It turned brown but underwent no weight loss. Analysis of this product by powder X-ray diffraction confirmed the formation of $\mathrm{In_2S_3}$ (JCPDS No. 25-390).

X-ray Structure Determination. Crystals of $[\mathrm{Mes_2In}(\mu\text{-S-}t\text{-Bu})]_2$ (1), $[\mathrm{Mes_2In}(\mu\text{-S-}t\text{-amyl})]_2$ (2), $[\mathrm{Mes_2In}(\mu\text{-SSiPh_3})]_2$ (4), and $[\mathrm{Me_2In}(\mu\text{-SSiPh_3})]_3$ (5) were grown as described earlier. Suitable samples were sealed in X-ray capillary tubes under an argon atmosphere, mounted on a goniometer head, and placed on a Nicolet $\mathrm{P2_1}$ diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å). The initial orientation matrices were obtained from 15 reflections chosen from rotation photographs. The final cell dimensions and orientation matrices were determined from 20−25 high-angle reflections. Rotation photographs around each axis were consistent with the monoclinic cell system for 1. Systematic absences indicated the space group $C2/c$ or Cc for this molecule. For 2, 4, and 5, the triclinic system with space group $P1$ or $P\bar{1}$ was indicated. Successful refinement of 1 in the space group $C2/c$ and 2, 4, and 5 in $P\bar{1}$ confirmed the space group assignments. No absorption correction was applied to 1 and 2; ψ-scan corrections were applied to 4 and 5. Three standard reflections were recorded every 197 (1) and every 97 (2, 4, and 5) reflections, revealing only small degrees of decay for the crystals.

For 1, data reduction, solution, and refinement were carried out using the SHELXTL PC program.[9] For 2, 4, and 5, data reduction was carried out using SHELXTL[10] programs, and data refinement was performed with SHELX-76.[11] Scattering factors[12] for neutral non-hydrogen atoms were used, and the data were corrected for Lorentz and polarization effects. Direct methods were used to solve the structures. Any non-hydrogen atoms not located in the initial solution were located from successive difference Fourier maps. Full-matrix, least-squares refinement of positional and thermal parameters for the non-hydrogen atoms of 1 and 4 was carried out by minimizing the function $\sum(w|F_o| - |F_c|)^2$, while 2 and 5 were refined with blocked matrices. The hydrogen atoms were placed in calculated positions with C−H bond distances of 0.96 Å (2, 4) and 1.08 Å (5); their isotropic thermal parameters were fixed at 0.08 (1 and 5), 0.10 (2), and 0.09, 0.10, and 0.15 (4). All hydrogen atom positional parameters were allowed to ride with their parent carbon atoms during subsequent refinement.

In the final cycles of refinement for 1, the indium and sulfur atoms were refined anisotropically, the *t*-Bu groups were refined isotropically, and the mesityl rings were treated as rigid bodies with regular hexagons with C−C bond lengths of 1.395 Å. For 2, all non-hydrogen atoms except C10 and C42 and, in 4, all non-hydrogen atoms were refined anisotropically. In 5, the In, Si, and S atoms were refined anisotropically with the remaining atoms refined isotropically. The asymmetric units for 1, 2, 4, and 5 contain a $\mathrm{Mes_2InS}$-*t*-Bu group, two independent $\mathrm{Mes_2InS}$-*t*-amyl groups, a $\mathrm{Mes_2InSSiPh_3}$ group, and two independent $[\mathrm{Me_2In}(\mu\text{-SSiPh_3})]_3$ trimers, respectively. The unit cell of 4 also contains one molecule of toluene (verified by ^{1}H NMR spectroscopy) located near the inversion center. All observed reflections were used for the refinement of 1, 2, and 4, but five reflections for 5 were omitted due to secondary extinctions. The residual electron densities are of no chemical significance. Selected crystal structure parameters are given in Table 1. Atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms are listed in Tables 2−5. Selected bond distances and angles are given in Table 6. A complete listing of crystal and X-ray data collection parameters, bond distances and angles, hydrogen atom coordinates and isotropic thermal parameters, and anisotropic thermal parameters for the non-hydrogen atoms are deposited as supplementary material.

Results and Discussion

Addition of either an alkyl or aryl mercaptan to a pentane solution of $\mathrm{Mes_3In}$ or $\mathrm{Me_3In}$ in a 1:1 ratio at room temperature results in the rapid formation of colorless precipitate with concomitant generation of mesitylene or methane as shown in eq 1. This represents an efficient, established route to indium

$$n\mathrm{R_3In} + n\mathrm{R'SH} \rightarrow [\mathrm{R_2In}(\mu\text{-SR}')]_n + n\mathrm{RH} \qquad (1)$$

$$\mathrm{R} = \mathrm{Mes};\ \mathrm{R'} = t\text{-Bu}\ (\mathbf{1}),\ t\text{-amyl}\ (\mathbf{2}),$$
$$2\text{-}t\text{-BuC_6H_4}\ (\mathbf{3}),\ \mathrm{SSiPh_3}\ (\mathbf{4});\ n = 2$$

$$\mathrm{R} = \mathrm{Me};\ \mathrm{R'} = \mathrm{SSiPh_3}\ (\mathbf{5});\ n = 3$$

thiolato species.[13] Other routes include the reaction of organoindium halides with disulfides[14] and salt elimination.[15,16] The salt elimination reactions may result in formation of anionic

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Table 1. Selected Experimental Parameters for the X-ray Diffraction Study of [$Mes_2In(\mu$-S-*t*-Bu)]$_2$ (**1**), [$Mes_2In(\mu$-S-*t*-amyl)]$_2$ (**2**), [$Mes_2In(\mu$-$SSiPh_3$)]$_2$·toluene (**4**), and [$Me_2In(\mu$-$SSiPh_3$)]$_3$ (**5**)

	1	**2**	**4**	**5**
empirical formula	$C_{22}H_{31}SIn$	$C_{23}H_{33}SIn$	$C_{79}H_{82}S_2Si_2In_2$	$C_{20}H_{21}SSiIn$
fw	442.37	456.40	1381.47	436.36
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	28.809(6)	11.631(7)	12.423(3)	15.012(5)
b (Å)	9.041(2)	12.866(3)	13.019(3)	17.784(5)
c (Å)	18.156(5)	15.767(5)	14.126(2)	24.838(8)
α (deg)		90.09(2)	91.50(1)	76.23(2)
β (deg)	110.24(2)	93.70(4)	113.23(1)	83.03(3)
γ (deg)		105.13(3)	117.72(2)	69.84(2)
vol (Å^3)	4437(2)	2273(1)	1795.8(6)	6040(3)
D_{calcd} (g/cm^3)	1.325	1.334	1.277	1.439
Z	8 monomers	4 monomers	2 monomers	4 trimers
radiation type (λ (Å))	Mo K$\bar{\alpha}$ (0.710 73)	Mo K$\bar{\alpha}$ (0.710 73)	Mo K$\bar{\alpha}$ (0.710 73)	Mo K$\bar{\alpha}$ (0.710 73)
μ (cm^{-1})	11.6	11.2	7.6	12.5
F(000)	1824	944	714	2640
no. of refined variables	194	394	343	643
R^a	0.054	0.081	0.038	0.060
$R_w{}^b$	0.057	0.074	0.043	0.053
residual electron dens (e/Å^3)	−0.50 to 1.12 (C23)	−1.9 to 1.9 (In)	−0.34 to −.44 (In,S)	0.76 (In3)

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (×10^3) for the Non-Hydrogen Atoms of [$Mes_2In(\mu$-S-*t*-Bu)]$_2$ (**1**)

atom	*x*	*y*	*z*	U_{eq},^{a} Å^2
In	1789(1)	2528(2)	4610(1)	58(1)
S	2493(2)	545(3)	5100(3)	57(1)
C1	1324(3)	2661(11)	3361(3)	60(5)
C2	1385(3)	1759(11)	2778(3)	66(6)
C3	1084(3)	1954(11)	1997(3)	68(6)
C4	721(3)	3050(11)	1798(3)	74(6)
C5	659(3)	3952(11)	2381(3)	78(7)
C6	961(3)	3757(11)	3163(3)	62(6)
C7	1739(6)	473(19)	2972(8)	90(8)
C8	416(7)	3308(23)	939(8)	119(9)
C9	873(7)	4822(17)	3745(9)	86(8)
C11	1326(3)	2386(11)	5359(4)	60(5)
C12	1392(3)	3295(11)	6008(4)	64(6)
C13	1097(3)	3100(11)	6470(4)	67(6)
C14	737(3)	1996(11)	6282(4)	69(7)
C15	671(3)	1088(11)	5632(4)	74(7)
C16	966(3)	1283(11)	5171(4)	66(6)
C17	1749(6)	4587(17)	6192(9)	84(8)
C18	432(7)	1738(22)	6805(11)	110(10)
C19	864(6)	279(18)	4464(9)	87(8)
C21	2493(5)	−409(16)	6012(8)	66(4)
C22	2499(5)	735(16)	6628(8)	79(6)
C23	2026(5)	−1339(18)	5797(9)	85(7)
C24	2955(5)	−1365(18)	6308(9)	94(7)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.

complexes under some conditions.[17] Reaction of sulfur with *t*-Bu_3Ga[4,18] or with *t*-Bu_3Al[18] yields cubanes, although when (*t*-Bu)$_3$Al is reacted with sulfur, selenium, or tellurium under ambient conditions, dimers can be isolated.[18] Attempts to prepare the analogous trimethylbenzenethiolato compound, [$Mes_2In(\mu$-SMes)]$_2$, by reaction of Mes_3In with elemental sulfur resulted in formation of a white flocculent material, not soluble in aromatic solvents, which was not further characterized.

The ^{1}H NMR spectra of **1**−**5** are consistent with the empirical formula $R_2In(\mu$-SR′) (R = Mes, Me; R′ = *t*-Bu, *t*-amyl, 2-*t*-BuC_6H_4, $SiPh_3$). The resonances associated with the *o*- and *p*-Me groups of the Mes ligands occur in the ranges of 2.32−2.73 and 2.02−2.14 ppm, respectively. The *o*-Me group is shifted 0.1−0.4 ppm to lower field; the *p*-Me group and the aryl protons (6.62−6.84 ppm) are similar to those of the starting material, Mes_3In (2.34 (*o*-Me), 2.17 (*p*-Me), and 6.81 ppm (aryl protons)).[6] In the case of **1**, the *t*-Bu group displays only one proton resonance at 1.26 ppm and two carbon-13 resonances at 34.26 and 50.80 ppm. These fall within the expected range and are readily compared with those of the *t*-BuS-bridged compound [(*t*-Bu)$_2$Ga(μ-S-*t*-Bu)]$_2$.[4] The ^{1}H and ^{13}C resonances found for **2** and **3** show no unusual features and are consistent with the spectra observed for similar indium thiolates.[13] Variable-temperature NMR studies on compounds **1** and **3** over the temperature range 27−80 °C show only small shift as a function of temperature, moving to higher field with increasing temperature. At temperatures of 80 °C, some line broadening was observed for the *o*-methyl region of the spectrum. This may indicate that species with different degrees of aggregation are present in solution, but the data are insufficient to permit the determination of the equilibria involved.

The mass spectra of compounds with stable bridge bonds, for example [*i*-Pr(Cl)In(NH-*t*-Bu)]$_2$, are dimeric in solution and in the solid state and show mass fragments assigned to dimeric species in the gas phase.[19] The thiolate derivatives [R_2In(S-*t*-Bu)] (R = Me, *n*-Bu, *t*-Bu)[20] show peaks associated with the dimers. In the compounds described here, the mass spectra show fragments of the parent molecules containing indium, sulfur, and organic groups but not the molecular ion. The failure to observe molecular ions or larger aggregates in the gas phase likely results from the heated (200 °C) inlet system used to vaporize the compounds.

The aluminum and gallium thiolates which have been structurally characterized exist as dimers, trimers, or tetramers. Notable exceptions are the monomeric species $Al(SR)_3$ and $Ga(SR)_3$ where R is the supermesityl group, 2,4,6-*t*-$Bu_3C_6H_2$.[15] Molecular weight studies indicate that mononuclear species predominate for $Ph_2Ga(SR)$ (R = Ph, Bz) in solution.[21] However, the indium derivative [$Ph_2In(SEt)$]$_2$ is dimeric in benzene.[13] Changes in the substituent on the indium or the sulfur lead to weaker association; thus for [$R_2In(SR^-)$]$_n$ (R =

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Table 3. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[Mes_2In(\mu\text{-S-}t\text{-amyl})]_2$ (**2**)

atom	x	y	z	U_{eq},[a] Å^2
In1	0.0155(1)	−0.1426(1)	0.46943(9)	0.0630(7)
S1	0.0910(5)	0.0552(4)	0.4217(3)	0.063(2)
C1	−0.097(1)	−0.2433(9)	0.3647(7)	0.07(1)
C2	−0.219(1)	0.2529(9)	0.3495(7)	0.07(1)
C3	−0.284(1)	−0.3211(9)	0.2846(7)	0.07(1)
C4	−0.228(1)	−0.3798(9)	0.2348(7)	0.06(1)
C5	−0.106(1)	−0.3703(9)	0.2500(7)	0.06(1)
C6	−0.041(1)	−0.3020(9)	0.3150(7)	0.06(1)
C7	−0.281(2)	−0.190(2)	0.403(2)	0.15(2)
C8	−0.302(2)	−0.457(1)	0.166(1)	0.08(1)
C9	0.094(2)	−0.295(2)	0.325(1)	0.07(1)
C10	0.152(1)	−0.215(1)	0.5324(8)	0.046(5)
C11	0.275(1)	−0.172(1)	0.5333(8)	0.07(1)
C12	0.352(1)	−0.233(1)	0.5627(8)	0.08(1)
C13	0.306(1)	−0.337(1)	0.5911(8)	0.11(2)
C14	0.183(1)	−0.381(1)	0.5901(8)	0.09(1)
C15	0.106(1)	−0.320(1)	0.5608(8)	0.07(1)
C16	0.325(2)	−0.064(2)	0.503(2)	0.10(1)
C17	0.398(3)	−0.400(2)	0.618(1)	0.13(2)
C18	−0.023(2)	−0.379(2)	0.560(1)	0.09(1)
C19	0.061(2)	0.077(2)	0.307(1)	0.07(1)
C20	−0.076(3)	0.073(2)	0.290(2)	0.14(2)
C21	0.091(2)	−0.011(2)	0.256(1)	0.10(1)
C22	0.133(4)	0.187(2)	0.286(2)	0.14(2)
C23	0.263(4)	0.206(3)	0.298(2)	0.19(2)
In2	0.3905(1)	−0.1297(1)	0.02910(9)	0.0547(6)
S2	0.4070(5)	0.0743(4)	0.0398(3)	0.053(2)
C24	0.407(1)	−0.221(1)	0.1474(7)	0.051(9)
C25	0.388(1)	−0.332(1)	0.1356(7)	0.063(9)
C26	0.377(1)	−0.399(1)	0.2057(7)	0.057(9)
C27	0.384(1)	−0.355(1)	0.2875(7)	0.07(1)
C28	0.402(1)	−0.245(1)	0.2993(7)	0.07(1)
C29	0.414(1)	−0.177(1)	0.2292(7)	0.056(9)
C30	0.379(2)	−0.385(1)	0.049(1)	0.069(9)
C31	0.368(2)	−0.426(2)	0.366(1)	0.09(1)
C32	0.436(2)	−0.058(1)	0.245(1)	0.08(1)
C33	0.229(1)	−0.2157(9)	−0.048(1)	0.045(8)
C34	0.127(1)	−0.2531(9)	−0.003(1)	0.052(9)
C35	0.026(1)	−0.3236(9)	−0.042(1)	0.07(1)
C36	0.026(1)	−0.3567(9)	−0.127(1)	0.07(1)
C37	0.128(1)	−0.3193(9)	−0.172(1)	0.07(1)
C38	0.229(1)	−0.2488(9)	−0.132(1)	0.07(1)
C39	0.116(2)	−0.223(2)	0.089(1)	0.066(9)
C40	−0.084(2)	−0.436(2)	−0.167(1)	0.09(1)
C41	0.332(2)	−0.209(2)	−0.181(1)	0.09(1)
C42	0.282(2)	0.112(1)	−0.029(1)	0.053(5)
C43	0.283(2)	0.075(2)	−0.120(1)	0.10(1)
C44	0.166(2)	0.056(2)	0.007(2)	0.11(1)
C45	0.313(2)	0.235(2)	−0.025(1)	0.08(1)
C46	0.312(3)	0.284(2)	0.061(2)	0.12(1)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.

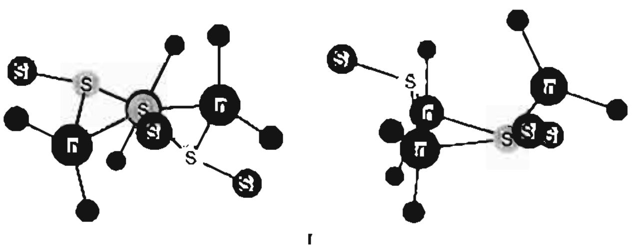
n-Bu, *i*-Bu; R′ = *n*-Pr, *i*-Pr, c-C_6H_{11}), an equilibrium between monomer and dimer is observed in solution,[22] and $[Mes_2In(\mu\text{-}I)]_2$ is monomeric in benzene and CH_2Cl_2.[23]

With this moderate tendency toward aggregation, we chose to examine the solid state structures of compounds **1**, **2**, **4**, and **5**. Of the four In/S compounds structurally characterized in this work, **1**, **2**, and **4** are dimeric while **5** is trimeric. The unit cells of **2** and **5** contain two independent molecules. Deviations between the individual molecules in each structure are minor, typically within 3 standard deviations, and can be accounted for by the uncertainty in measurement and by crystal packing forces. Molecules of **1**, **2**, and **4** contain planar $(InS)_2$ rings with the organothiolate ligands oriented in a transoid fashion. These are shown in Figures 1−3. Analogous structures for aluminum and gallium thiolates such as $[Me_2Al(\mu\text{-SMe})]_2$,[24] $[Ph_2Ga(\mu\text{-SEt})]_2$,[21] $[Me_2Al(\mu\text{-SC}_6F_5)]_2$,[25] and $[I_2Ga(\mu\text{-S-}i\text{-Pr})]_2$[26] are known, but this is the first report of structurally-characterized dimeric indium thiolates. The trimeric indium derivative $[Me_2In(\mu\text{-SSiPh}_3)]_3$ (**5**) is shown in Figure 4 with an $(InS)_3$ ring in a skew-boat conformation as shown in **I**. While no other indium−sulfur trimers are known, a number of structurally similar

Table 4. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[Mes_2In(\mu\text{-SSiPh}_3)]_2$ (**4**)

atom	x	y	z	U_{eq},[a] Å^2
In1	−0.14160(3)	0.03511(3)	0.00921(3)	0.0415(2)
S1	0.0524(1)	0.1111(1)	−0.05711(9)	0.0405(6)
Si1	0.0697(1)	0.1873(1)	−0.1872(1)	0.0400(7)
C1	−0.0781(5)	0.1557(4)	0.1548(4)	0.043(3)
C2	0.0585(5)	0.2223(4)	0.2347(4)	0.047(3)
C3	0.0911(6)	0.2855(4)	0.3331(4)	0.058(3)
C4	−0.0080(7)	0.2867(5)	0.3544(5)	0.067(4)
C5	−0.1406(7)	0.2253(5)	0.2758(5)	0.066(4)
C6	−0.1786(5)	0.1593(4)	0.1756(4)	0.055(3)
C7	0.1753(5)	0.2339(5)	0.2164(4)	0.060(3)
C8	0.0321(8)	0.3591(6)	0.4620(5)	0.097(5)
C9	−0.3271(6)	0.0963(5)	0.0933(5)	0.077(4)
C10	−0.3312(4)	−0.0408(4)	−0.1391(3)	0.043(2)
C11	−0.4280(5)	−0.1643(4)	−0.1824(4)	0.046(3)
C12	−0.5366(5)	−0.2050(5)	−0.2861(4)	0.059(3)
C13	−0.5506(6)	−0.1248(6)	−0.3466(4)	0.067(4)
C14	−0.4604(6)	−0.0032(6)	−0.2997(5)	0.067(4)
C15	−0.3498(5)	0.0418(5)	−0.1966(4)	0.054(3)
C16	−0.4246(5)	−0.2570(4)	−0.1207(4)	0.058(3)
C17	−0.6651(7)	−0.1731(7)	−0.4618(5)	0.096(5)
C18	−0.2546(6)	0.1770(5)	−0.1504(5)	0.075(4)
C19	−0.0623(3)	0.0808(3)	−0.3217(2)	0.045(3)
C20	−0.1896(3)	−0.0120(3)	−0.3369(2)	0.058(3)
C21	−0.2867(3)	−0.0897(3)	−0.4379(2)	0.079(4)
C22	−0.2566(3)	−0.0746(3)	−0.5236(2)	0.086(4)
C23	−0.1293(3)	0.0182(3)	−0.5084(2)	0.077(4)
C24	−0.0322(3)	0.0959(3)	−0.4074(2)	0.063(3)
C25	0.2459(3)	0.2355(3)	−0.1716(3)	0.045(3)
C26	0.2756(3)	0.1491(3)	−0.1926(3)	0.054(3)
C27	0.4072(3)	0.1840(3)	−0.1769(3)	0.072(4)
C28	0.5091(3)	0.3053(3)	−0.1402(3)	0.089(4)
C29	0.4794(3)	0.3917(3)	−0.1193(3)	0.084(4)
C30	0.3478(3)	0.3568(3)	−0.1350(3)	0.064(3)
C31	0.0550(4)	0.3235(3)	−0.1715(3)	0.047(3)
C32	0.1123(4)	0.3976(3)	−0.0710(3)	0.057(3)
C33	0.1003(4)	0.4983(3)	−0.0617(3)	0.076(4)
C34	0.0312(4)	0.5250(3)	−0.1529(3)	0.093(5)
C35	−0.0261(4)	0.4509(3)	−0.2534(3)	0.107(6)
C36	−0.0142(4)	0.3501(3)	−0.2627(3)	0.080(4)
C37	0.521(3)	0.534(3)	0.389(2)	0.31(2)
C38	0.554(1)	0.458(2)	0.467(2)	0.20(1)
C39	0.551(1)	0.436(1)	0.569(3)	0.29(2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i{\cdot}\mathbf{a}_j$.



I

Molecule 2 viewed along the S5 - In5 vector and along the S5 - S6 vector to show the twist-boat configuration of the ring and the orientation of the substituents on In and S. The phenyl groups have been omitted for clarity.

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Table 5. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[Me_2In(\mu\text{-}SSiPh_3)]_3$ (**5**)

atom	x	y	z	U_{eq},[a] Å^2	atom	x	y	z	U_{eq},[a] Å^2
In4	1.87567(5)	0.06411(4)	0.24051(3)	0.0557(3)	In1	0.89845(5)	0.63424(4)	0.23927(3)	0.0489(3)
In5	1.63794(6)	0.07022(5)	0.35452(3)	0.0663(4)	In2	0.60422(5)	0.77686(4)	0.19593(3)	0.0481(3)
In6	1.58402(5)	0.23993(4)	0.19182(3)	0.0512(3)	In3	0.67150(5)	0.55313(5)	0.34081(3)	0.0518(3)
S4	1.7703(2)	0.1377(2)	0.31550(9)	0.046(1)	S1	0.7627(2)	0.6671(1)	0.17015(9)	0.042(1)
S5	1.7542(2)	0.1490(2)	0.16519(9)	0.047(1)	Si1	0.8637(2)	0.6005(2)	0.3976(1)	0.038(1)
S6	1.5720(2)	0.1051(2)	0.2562(1)	0.048(1)	S2	0.7802(2)	0.6438(1)	0.32590(9)	0.043(1)
Si4	1.8551(2)	0.1188(2)	0.3835(1)	0.046(1)	S3	0.5526(2)	0.6756(2)	0.2773(1)	0.052(1)
Si5	1.8223(2)	0.2060(2)	0.0960(1)	0.043(1)	Si2	0.8086(2)	0.7238(2)	0.0906(1)	0.046(1)
Si6	1.4242(2)	0.1189(2)	0.2655(1)	0.049(1)	Si3	0.4443(2)	0.6351(2)	0.2604(1)	0.045(1)
C7	1.5924(7)	0.3177(6)	0.2432(4)	0.068(3)	C1	0.9745(7)	0.5072(6)	0.2423(4)	0.064(3)
C8	1.5037(8)	0.2587(7)	0.1221(4)	0.077(3)	C2	0.6384(7)	0.8487(6)	0.2423(4)	0.063(3)
C9	1.5520(9)	0.1528(7)	0.4044(5)	0.094(4)	C3	0.6131(7)	0.5545(6)	0.4224(4)	0.073(3)
C10	1.8614(9)	−0.0533(8)	0.2515(5)	0.105(4)	C4	0.9405(7)	0.7404(6)	0.2235(4)	0.072(3)
C11	1.690(1)	−0.0599(9)	0.3728(6)	0.120(5)	C5	0.7287(8)	0.4631(7)	0.2929(4)	0.078(3)
C12	2.0030(7)	0.0945(6)	0.2221(4)	0.065(3)	C6	0.5105(7)	0.7974(6)	0.1312(4)	0.064(3)
C67	1.7797(7)	0.1748(6)	0.4365(4)	0.057(3)	C13	0.7452(6)	0.8370(6)	0.0767(4)	0.051(2)
C68	1.7952(8)	0.1446(7)	0.4934(5)	0.088(4)	C14	0.7541(7)	0.8843(7)	0.1113(4)	0.069(3)
C69	1.738(1)	0.1920(9)	0.5318(6)	0.108(4)	C15	0.7073(8)	0.9696(7)	0.1017(5)	0.079(3)
C70	1.675(1)	0.2581(9)	0.5134(6)	0.107(4)	C16	0.6544(8)	1.0039(7)	0.0571(5)	0.083(4)
C71	1.7115(8)	0.2505(7)	0.4198(5)	0.085(4)	C17	0.6400(8)	0.9630(7)	0.0232(5)	0.079(3)
C72	1.657(1)	0.2960(9)	0.4611(6)	0.117(5)	C18	0.6864(8)	0.8778(7)	0.0316(4)	0.072(3)
C73	1.9526(7)	0.1629(6)	0.3576(4)	0.054(3)	C19	0.9839(6)	0.6103(6)	0.3752(4)	0.048(2)
C74	1.9457(8)	0.2249(7)	0.3117(4)	0.073(3)	C20	1.0641(8)	0.5425(6)	0.3716(4)	0.072(3)
C75	2.105(1)	0.1743(9)	0.3721(6)	0.114(5)	C21	0.9897(8)	0.6882(7)	0.3584(4)	0.074(3)
C76	2.0293(9)	0.1375(7)	0.3912(5)	0.087(4)	C22	1.1485(9)	0.6320(9)	0.3340(5)	0.092(4)
C77	2.094(1)	0.2328(9)	0.3266(6)	0.105(4)	C23	1.1535(9)	0.5577(8)	0.3490(5)	0.092(4)
C78	2.0196(9)	0.2599(7)	0.2957(5)	0.091(4)	C24	1.080(1)	0.6973(8)	0.3368(5)	0.102(4)
C79	1.7391(6)	0.2433(5)	0.0373(3)	0.043(2)	C25	0.8736(6)	0.4919(5)	0.4284(3)	0.040(2)
C80	1.7291(7)	0.1916(6)	0.0068(4)	0.058(3)	C26	0.8582(6)	0.4638(5)	0.4846(4)	0.049(2)
C81	1.6837(7)	0.3241(6)	0.0261(4)	0.059(3)	C27	0.8969(6)	0.4344(6)	0.3949(4)	0.056(3)
C82	1.6152(8)	0.3535(7)	−0.0171(5)	0.080(3)	C28	0.8634(7)	0.3830(6)	0.5064(4)	0.061(3)
C83	1.6126(8)	0.2981(7)	−0.0454(5)	0.080(3)	C29	0.9003(7)	0.3546(7)	0.4174(4)	0.071(3)
C84	1.6653(8)	0.2204(7)	−0.0366(5)	0.078(3)	C30	0.8825(7)	0.3307(6)	0.4726(4)	0.064(3)
C85	1.9347(6)	0.1254(6)	0.0811(4)	0.050(2)	C31	0.3354(6)	0.7275(6)	0.2452(4)	0.052(3)
C86	1.9373(9)	0.0451(8)	0.0866(5)	0.086(4)	C32	0.190(1)	0.8054(9)	0.1963(6)	0.105(4)
C87	2.0183(8)	0.1422(6)	0.0659(4)	0.071(3)	C33	0.3143(8)	0.7877(7)	0.2742(5)	0.081(3)
C88	2.1025(9)	0.0775(8)	0.0563(5)	0.096(4)	C34	0.2744(8)	0.7354(7)	0.2053(4)	0.075(3)
C89	2.0989(9)	0.0065(8)	0.0610(5)	0.099(4)	C35	0.229(1)	0.8575(8)	0.2654(6)	0.108(4)
C90	2.022(1)	−0.0177(9)	0.0777(6)	0.118(5)	C36	0.174(1)	0.8601(9)	0.2257(6)	0.108(4)
C91	1.3517(6)	0.2288(6)	0.2587(4)	0.054(3)	C37	0.4236(6)	0.5637(5)	0.3262(4)	0.046(2)
C92	1.2839(8)	0.2676(7)	0.2191(4)	0.069(3)	C38	0.3797(6)	0.5929(6)	0.3739(4)	0.054(3)
C93	1.3091(9)	0.3598(8)	0.2863(5)	0.088(4)	C39	0.4413(8)	0.4259(7)	0.3802(5)	0.079(3)
C94	1.3645(8)	0.2761(7)	0.2917(4)	0.076(3)	C40	0.4553(7)	0.4814(6)	0.3292(4)	0.062(3)
C95	1.2448(9)	0.3943(7)	0.2464(5)	0.088(4)	C41	0.3682(7)	0.5394(6)	0.4218(4)	0.065(3)
C96	1.2309(8)	0.3507(8)	0.2144(5)	0.087(4)	C42	0.3968(8)	0.4591(7)	0.4242(4)	0.075(3)
C97	1.3920(7)	0.0777(6)	0.2118(4)	0.054(3)	C43	0.5607(7)	0.5623(6)	0.1734(4)	0.056(3)
C98	1.2736(9)	0.0407(8)	0.1737(5)	0.098(4)	C44	0.4749(6)	0.5759(5)	0.2032(4)	0.047(2)
C99	1.3005(9)	0.0719(7)	0.2139(5)	0.091(4)	C45	0.5808(7)	0.5148(6)	0.1328(4)	0.063(3)
C100	1.4518(7)	0.0524(6)	0.1686(4)	0.069(3)	C46	0.5165(8)	0.4830(6)	0.1229(4)	0.066(3)
C101	1.335(1)	0.0156(8)	0.1344(5)	0.101(4)	C47	0.4330(8)	0.4956(6)	0.1510(4)	0.069(3)
C102	1.4217(9)	0.0219(7)	0.1297(5)	0.087(4)	C48	0.4124(7)	0.5404(6)	0.1920(4)	0.059(3)
C103	1.4053(7)	0.0569(6)	0.3336(4)	0.061(3)	C49	0.8063(6)	0.6625(5)	0.4506(3)	0.042(2)
C104	1.3652(8)	0.0882(8)	0.3793(5)	0.090(4)	C50	0.7236(9)	0.7349(8)	0.5386(5)	0.094(4)
C105	1.361(1)	0.032(1)	0.4321(6)	0.120(5)	C51	0.8575(7)	0.6543(6)	0.4961(4)	0.062(3)
C106	1.393(1)	−0.043(1)	0.4358(6)	0.122(5)	C52	0.8132(9)	0.6929(7)	0.5401(5)	0.083(4)
C107	1.431(1)	−0.080(1)	0.3945(9)	0.167(7)	C53	0.7121(7)	0.7101(6)	0.4495(4)	0.066(3)
C108	1.437(1)	−0.025(1)	0.3399(7)	0.133(5)	C54	0.6692(8)	0.7488(7)	0.4955(5)	0.087(4)
C109	1.8478(6)	0.2956(5)	0.1081(4)	0.049(2)	C55	0.9822(7)	0.7617(6)	0.0754(4)	0.060(3)
C110	1.8347(7)	0.3134(6)	0.1602(4)	0.063(3)	C56	0.9400(6)	0.6998(6)	0.0888(4)	0.049(2)
C111	1.8913(9)	0.4195(8)	0.0705(6)	0.101(4)	C57	1.0994(8)	0.6031(7)	0.1032(5)	0.080(3)
C112	1.877(1)	0.4355(8)	0.1215(6)	0.106(4)	C58	1.1342(8)	0.6643(7)	0.0903(4)	0.076(3)
C113	1.8505(9)	0.3856(8)	0.1657(5)	0.094(4)	C59	1.0805(8)	0.7421(7)	0.0764(4)	0.073(3)
C114	1.8758(8)	0.3494(7)	0.0632(4)	0.077(3)	C60	0.9989(7)	0.6211(6)	0.1023(4)	0.066(3)
C115	1.9032(7)	0.0061(6)	0.4129(4)	0.063(3)	C61	0.7800(7)	0.6808(6)	0.0370(4)	0.060(3)
C116	1.8490(8)	−0.0325(8)	0.4505(5)	0.088(4)	C62	0.7031(8)	0.6565(7)	0.0403(4)	0.076(3)
C117	1.885(1)	−0.121(1)	0.4656(6)	0.120(5)	C63	0.8408(9)	0.6718(8)	−0.0098(5)	0.098(4)
C118	1.958(1)	−0.1590(9)	0.4436(6)	0.119(5)	C64	0.816(1)	0.6434(9)	−0.0538(6)	0.122(5)
C119	1.985(1)	−0.0409(9)	0.3902(5)	0.102(4)	C65	0.6807(9)	0.6257(8)	−0.0031(6)	0.099(4)
C120	2.015(1)	−0.129(1)	0.4070(7)	0.139(6)	C66	0.738(1)	0.6209(8)	−0.0486(6)	0.111(5)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

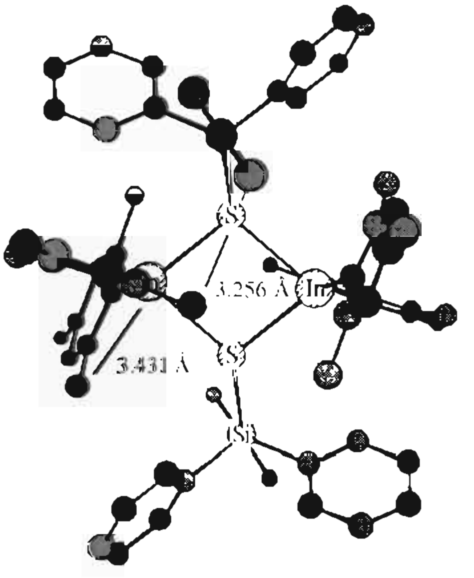
compounds have been reported. These include $[t\text{-}BuGa(\mu\text{-}S)\text{-}Py]_3$,[27] $[Me_2Al(\mu\text{-}OMe)]_3$,[28] $[t\text{-}Bu_2Al(\mu\text{-}OH)]_3$,[29] $[t\text{-}Bu_2Ga(\mu\text{-}OH)]_3$,[30] $[(Me_3SiCH_2)Zn(\mu\text{-}SR)]_3$ (R = i-Pr, t-Bu),[31] and $[Me_2Al(\mu\text{-}SR)]_3$ (R = 2-t-BuC_6H_4, 2-i-PrC_6H_4, 2-$(Me_3Si)C_6H_4$) and

Table 6. Selected Bond Distances (Å) and Angles (deg) for [$Mes_2In(\mu$-S-*t*-Bu)$]_2$ (**1**), [$Mes_2In(\mu$-S-*t*-amyl)$]_2$ (**2**), [$Mes_2In(\mu$-$SSiPh_3)]_2$ (**4**), and [$Me_2In(\mu$-$SSiPh_3)]_3$ (**5**)

[$Mes_2In(\mu$-S-*t*-Bu)$]_2$ (**1**)		[$Mes_2In(\mu$-S-*t*-amyl)$]_2$ (**2**)				[$Mes_2In(\mu$-$SSiPh_3)]_2$ (**4**)		$Me_2In(\mu$-$SSiPh_3)]_3$ (**5**)			
		mol 1		mol 2				mol 1		mol 2	
atoms	dist	atoms	dist	atoms	dist	atoms	dist	atoms	dist	atoms	dist
In−S	2.622(5)	In1−S1	2.595(4)	In2−S2	2.587(3)	In1−S1	2.698(1)	In2−S1	2.627(3)	In4−S4	2.589(3)
In−Sa	2.615(5)	In1−S1′	2.598(4)	In2−S2′	2.586(3)	In1−S1′	2.172(3)	In2−S3	2.604(4)	In4−S5	2.586(3)
In−C1	2.201(6)	In1−C1	2.23(1)	In2−C24	2.23(1)	In1−C1	2.179(4)	In3−S2	2.604(3)	In5−S4	2.637(3)
In−C11	2.213(10)	In1−C10	2.22(1)	In2−C33	2.20(1)	In1−C10	2.5973(7)	In3−S3	2.605(3)	In5−S6	2.603(3)
								In1−S1	2.644(3)	In6−S6	2.596(4)
								In1−S2	2.617(3)	In6−S5	2.614(3)
								In1−C1	2.14(1)	In4−C10	2.12(2)
								In1−C4	2.13(1)	In4−C12	2.13(1)
								In2−C2	2.13(1)	In5−C9	2.13(2)
								In2−C6	2.15(1)	In5−C11	2.12(2)
								In3−C3	2.11(1)	In6−C7	2.13(1)
								In3−C5	2.10(1)	In6−C8	2.12(1)

[$Mes_2In(\mu$-S-*t*-Bu)$]_2$ (**1**)		[$Mes_2In(\mu$-S-*t*-amyl)$]_2$ (**2**)				[$Mes_2In(\mu$-$SSiPh_3)]_2$ (**4**)		$Me_2In(\mu$-$SSiPh_3)]_3$ (**5**)			
		mol 1		mol 2				mol 1		mol 2	
atoms	angle	atoms	angle	atoms	angle	atoms	angle	atoms	angle	atoms	angle
C1−In−C11	110.8(3)	C1−In1−C10	114.3(4)	C24−In2−C33	109.1(4)	C1−In1−C10	128.3(1)	C1−In1−C4	133.4(4)	C7−In6−C8	133.8(5)
In−S−Ina	94.5(1)	In1−S1−In1′	97.6(2)	In2−S2−In2′	94.1(2)	In1−S1−In1′	102.18(2)	C2−In2−C6	137.2(5)	C9−In5−C11	129.9(7)
S−In−Sa	85.5(1)	S1−In1−S1′	82.4(3)	S1−In1−S1′	85.9(2)	S1−In1−S1′	77.82(2)	C3−In3−C5	135.3(6)	C10−In4−C12	127.3(5)
								In1−S1−In2	112.6(1)	In4−S4−In5	109.4(1)
								In1−S2−In3	116.1(1)	In4−S5−In6	120.9(1)
								In2−S3−In3	123.7(1)	In5−S6−In6	120.9(1)
								S1−In2−S3	95.0(1)	S4−In4−S5	92.03(9)
								S2−In3−S3	86.7(1)	S5−In6−S6	84.76(9)
								S1−In1−S2	93.21(9)	S4−In5−S6	91.3(1)

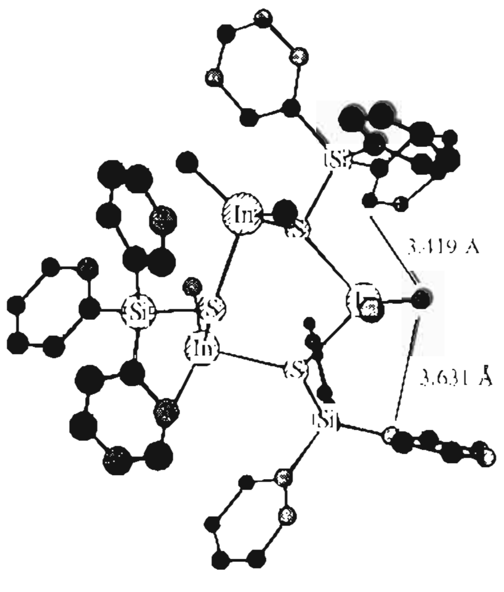
[$I_2B(\mu$-SMe)$]_3$.[32] The factors which determine the degree of aggregation have not been established, but it seems likely that steric factors, as opposed to electronic effects, are largely responsible for determining the degree of association. In the present systems, this is seen in the change from dimer for [$Mes_2In(\mu$-$SSiPh_3)]_2$ (**4**) to trimer for [$Me_2In(\mu$-$SSiPh_3)]_3$ (**5**) with a change in the ligand on the metal from mesityl to methyl. The shortest nonbonded distance in **4** is between the *ortho* methyl groups on the mesityl moieties and the indium atom, but this interaction likely has limited impact on the degree of aggregation. The next nonbonded interaction is between one of the *ortho* methyl groups and the *ortho* carbon atom in one of the adjacent phenyl groups shown in **II**. A second relatively short (3.666 Å) nonbonded interaction occurs between the *ortho* methyl groups of the two mesityl moieties bound to the same indium atom. This interaction is minimized by rotation of the mesityl groups so that they are approximately orthogonal.



II

A view of **4** perpendicular to the $(InS)_2$ ring showing the shortest C-C distances.

In **5**, the shortest nonbonded interactions which may influence the aggregation state are between the methyl groups bound to the indium and one of the *ortho* carbon atoms in the adjacent phenyl group (**III**). A second short distance is observed between the methyl group and a phenyl ring attached to the silicon on the other side of the methyl group so that the methyl group is nearly equidistant from these two rings.



III

A diagram of **5** showing the orientation of the methyl groups bound to In and the closest phenyl groups.

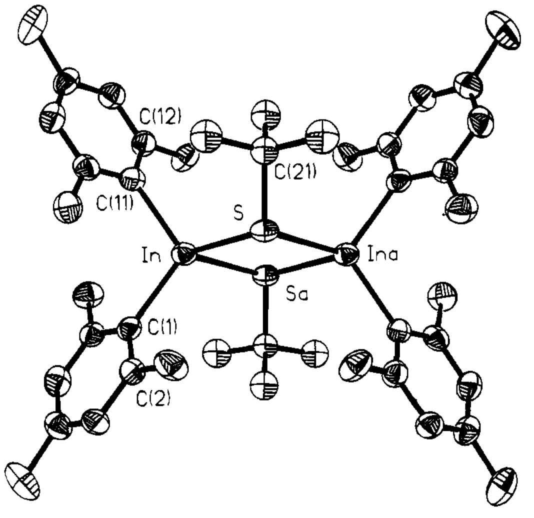


Figure 1. Thermal ellipsoid diagram (30%) of $[Mes_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_2$ (**1**). Hydrogen atoms have been omitted for clarity.

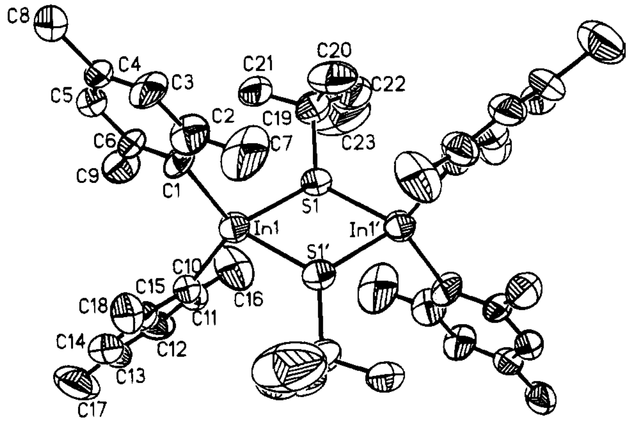


Figure 2. Thermal ellipsoid diagram (50%) of one of the dimers in the unit cell of $[Mes_2In(\mu\text{-}S\text{-}t\text{-}amyl)]_2$ (**2**). Hydrogen atoms have been omitted for clarity.

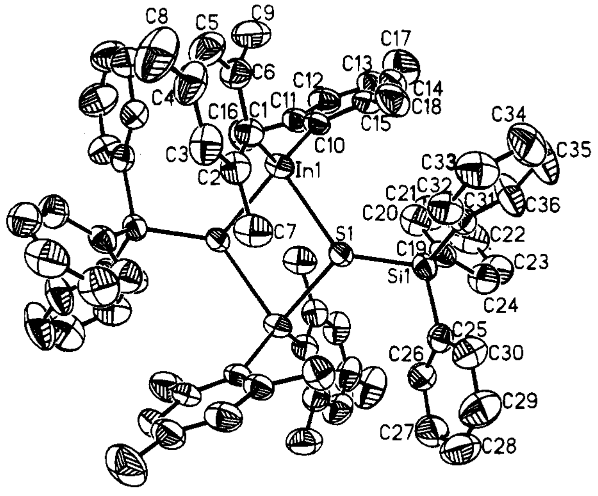


Figure 3. Thermal ellipsoid diagram (50%) of $[Mes_2In(\mu\text{-}SSiPh_3)]_2$ (**4**). Hydrogen atoms have been omitted for clarity.

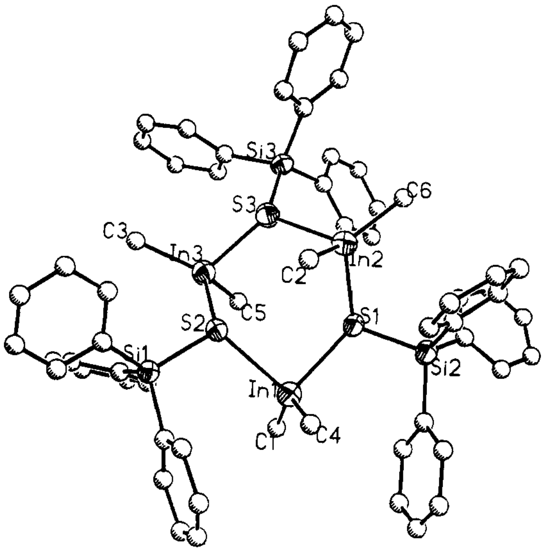


Figure 4. Thermal ellipsoid diagram (50%) of one of the trimers in the unit cell of $[Me_2In[(\mu\text{-}SSiPh_3)]_3$ (**5**). Hydrogen atoms have been omitted for clarity.

Table 7. Selected In−S and In−C Bond Distances (Å)

compound	In−S	In−C
$[Mes_2In(\mu\text{-}Cl)]_2$[a]		2.146, 2.174
$[Mes_2In(\mu\text{-}I)]_2$[b]		2.173, 2.164
$[MesIn(\mu\text{-}I)_2]_\infty$[b]		2.137
$[Me_2In(\mu\text{-}CN)]_\infty$[c]		2.128−2.146
Mes_3In[a]		2.163−2.170
Me_3In (gas phase)[d]		2.161
Me_3In (solid)[e]		2.121, 2.179
$[(n\text{-}Bu)_4N]_2\{[S_2C_2(CN)_2]_2InCl\}$[f]	2.509−2.590	
$[2,4,6\text{-}(CF_3)_3C_6H_2S]_3In{\cdot}OEt_2$[g]	2.410−2.425	
$[Me_3In{\cdot}1,4\text{-}S_2C_4H_8]_\infty$[h]	2.970, 3.134	2.167−2.172
$In(SC_6H_2\text{-}t\text{-}Bu_3\text{-}2,4,6)_3$[i]	2.389−2.403	
$Ph_4P[BrIn(SPh)_3]$[j]	2.435−2.470	
$In(SPh)_3{\cdot}2Py$[k]	2.458	
$K_8(In_4S_{10})$[l]	2.453−2.479	
$(Ph_3P)_2{\cdot}Cu(\mu\text{-}SEt)_2In(SEt)_2$[m]	2.49 (bridge) 2.419 (terminal)	
$[Cp_2Mo(\mu\text{-}SEt)_2InCl_2][BPh_4]{\cdot}Me_2CO$[n]	2.58−2.72	
$\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$[o]	2.551	2.141−2.149
$Mes_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_2$ (**1**)[p]	2.622−2.615	2.201, 2.213
$[Mes_2In(\mu\text{-}S\text{-}t\text{-}amyl)]_2$ (**2**)[p]	2.586−2.598	2.20−2.23
$[Mes_2In(\mu\text{-}SSiPh_3)]_2$ (**4**)[p]	2.597−2.644	2.172−2.179
$[Me_2In(\mu\text{-}SSiPh_3)]_3$ (**5**)[p]	2.589−2.644	2.10−2.14

[a] Reference 6. [b] Reference 23. [c] Reference 35. [d] Fjeldberg, T.; Haaland, A.; Seip, R.; Shen, Q.; Weidlein, J. *Acta Chem. Scand.* **1982**, *A36*, 495. [e] Blake, A. J.; Cradock, S. *J. Chem. Soc., Dalton Trans.* **1990**, 2393. [f] Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 2379. [g] Bertel, N.; Noltemeyer, M.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1990**, *588*, 102. [h] Blank, J.; Hausen, H.-D.; Schwarz, W.; Weidlein, J. *J. Organomet. Chem.* **1993**, *443*, 145. [i] Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 3478. [j] Reference 17. [k] Annan, T.; Kumar, R.; Mabrouk, H. E.; Tuck, D. G.; Chadha, R. K. *Polyhedron* **1989**, *8*, 865. [l] Krebs, B.; Voelker, D.; Stiller, K.-O. *Inorg. Chim. Acta* **1982**, *65*, L101. [m] Reference 37. [n] Reference 36. [o] Reference 38. [p] This work.

The important bond distances and angles for **1**, **2**, **4**, and **5** are listed in Table 6. The $In{-}C_{Mes}$ bond lengths fall between 2.11 and 2.21 Å and are in the range expected for In−C bond lengths. Similar bond distances are found in other organoindium compounds, and a number of these are listed in Table 7. In the dimeric compounds, the C−In−C angles are 110.8(3)° for **1**, 114.3(4) and 109.1(4)° for **2**, and considerably larger at 128.3(1)° for **4**. In the trimeric derivative, **5**, the C−In−C angles fall in the range 127.3(5)−137.2(5)° with an average value of 132.8(3)°. The average values for the analogous angles in $[Mes_2InI]_2$,[23] $[Mes_2In(\mu\text{-}SeMes)]_2$, and $[Mes_2In(\mu\text{-}TePh)]_2$[33] are

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127.7(1), 119.7(9), and 121.9(2)°. A value of 135.8(5)° is found for $[Me_2In(\mu\text{-}\eta^2\text{-CN})]_n$.[34] These observations indicate that the C−In−C angles are very sensitive to the substituents on the bridging moiety and on the degree of aggregation as well as on the substituents bound to the indium. Additional data will be required to develop relationships among the angle, the substituents, and the observed degree of aggregation.

The In−S bond distances observed (Table 6) fall between those found in In−S single bonds and those in the In$\leftarrow$S adducts and are comparable to those observed in the In−S(Et)−Mo,[35] In−S(Et)−Cu,[36] and $In{-}S[Sn(c\text{-}C_6H_{11})_3]{-}In$[37] bridged systems (Table 7). The asymmetry observed in the In−S−In bridge bonds in **4** (2.698(1) and 2.5973(7) Å) may indicate a tendency toward the dissociation in solution that has been noted for the asymmetrically-bridged, mesityl complex $[Mes_2In(\mu\text{-I})]_2$, which is monomeric in solution.[23] For the trimer, **5**, the In−S distances are in the range 2.586(3)−2.644(3) Å and average 2.611(14) Å.

The internal S−In−S angles for **1**, **2**, and **4** (Table 6) are 82.4(3), 85.9(2), and 77.82(2)°. The only comparable system is $\{Ph_2In[\mu\text{-}SSn(c\text{-}C_6H_{11})]_3\}_2$, recently reported by our group,[37] which has a planar, four-membered ring with an S−In−S angle of 90.72(5)°. For $[Ph_2Ga(\mu\text{-SEt})]_2$ the S−Ga−S angle in the planar core is 93.58(4)°.[21] For the six-membered ring in **5** where the angles are not constrained, the S−In−S angles range from 84.76(9) to 95.0(1)° with an average of 90.5(3.2)°; the In−S−In angles range from 109.4(1) to 123.7(1)° and average 116.4(4)°. The larger internal angles observed at both the sulfur and indium atoms within the $(InS)_3$ ring, as compared to those of the $(InS)_2$ ring, result from the relaxation of the constraints on the system and from the change in the steric interactions that are responsible for the formation of the higher-aggregate species.

The sum of the angles around sulfur provide a measure of the geometry at the S atom and lie between 270°, which would correspond to a system primarily used for bonding with *p* orbitals to 360°, which corresponds to a planar sulfur with sp^2 hybridized orbitals. For **1** and **2**, these sums range from 317 to 330°, representing a fairly pyramidal structure. In **4**, the sum is 352°, corresponding to a nearly planar sulfur atom. The shift in geometry results from either steric or electronic effects. For **5**, four S atoms lying in the plane of the ring have sums between 324.5 and 330.1°, and the other two S atoms at the peak of the ring have sums of 345.5 and 347.1°. The changes in geometry at sulfur may be influenced by steric and electronic effects, but from the observations here and from an extensive study of organoaluminum thiolate derivatives,[38] it appears that the steric factors predominate. It is also clear that, in six-membered rings, the sulfur atoms in the plane of the ring are more pyramidal than those at the apex.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Complete listings of crystal and X-ray data collection parameters, bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates and isotropic thermal parameters for the hydrogen atoms (33 pages). See any current masthead page for ordering information.

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