Organometallics **2000,** *19,* 865−871

Organoindium Thiolate Oligomers: An X-ray Structural Study

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Received November 4, 1999

The reaction of R_3In (R = methyl, *tert*-butyl, xylyl) with bis(tricyclohexyltin) sulfide, 2-methylpropane-2-thiol, 4,6-dimethyl-2-mercaptopyrimidine, cyclopentanethiol, cyclohexanethiol, 2,5-dimethylbenzenethiol, or 2,6-methylbenzenethiol has yielded seven new indium−sulfur complexes: $\{m\text{-}Xyl_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ (**2**), $[t\text{-}Bu_2In(\mu\text{-}S\text{-}C_5H_9)]_2$ (**3**), $[t\text{-}Bu_2In(\mu\text{-}S\text{-}C_6H_{11})]_2$ (**4**), $\{t\text{-}Bu_2In[\mu\text{-}S(2,5\text{-}Me_2)C_6H_3]\}_2$ (**5**), $[Me_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_3$ (**6**), $\{t\text{-}Bu_2In[\mu\text{-}S(4,6\text{-}Me_2)C_4N_2H]\}_3$ (**7**), and $\{Me_2In[\mu\text{-}S(2,6\text{-}Me_2)C_6H_3]\}_4$ (**8**). These complexes have been studied by ^1H and ^{13}C NMR spectroscopy, and their structures have been determined by single-crystal X-ray diffraction techniques. **2**−**5** form dimeric species with planar $(In{-}S)_2$ cores, **6** forms a trimer which adopts a skew-boat conformation, **7** forms a trimer with a planar six-membered $(InS)_3$ ring with a secondary In−N interaction, giving rise to a pseudo-five-coordinate In atom, and **8** forms a tetramer in an extended chair conformation, the first known indium tetramer. Several of the factors of importance to the structures of these compounds, and especially those which lead to the unusual planar derivative **7**, will be discussed.

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Published on February 9, 2000 on http://pubs.acs.org | doi: 10.1021/om990887b

Introduction

With the continuing interest in the use of group 13−16 organometallic compounds for the preparation of thin films or other materials, there have been extensive studies in the structures and dynamic properties of aluminum and gallium compounds.[1−8] This research has resulted in the discovery of various aggregation states and structures for complexes of these metals. While it is known that thin films of the type In_xS_y have interesting, and potentially useful, electrical, optical, and photovoltaic properties, little work has been done on the characterization of potential precursors for these materials. It is the behavior of the compounds in the gas phase, in solution, or in the solid state which frequently determines the reactions of these derivatives and the nature of the products obtained. Reported synthetic methods for the preparation of indium complexes have included the insertion of a chalcogen into an In−In bond,[9] preparation of complexes by stoichiometric ligand redistributions,[10] the reaction of R_3In with R_2Te_2,[6] and the reactions of X_2InR (where X = Cl, Br, I) with REH,[11] $(R_3Si)_2E$,[12] and R_2S_2.[13] On the basis of successful techniques employed in the synthesis of gallium−chalcogenide oligomers, we have attempted to extend these procedures to the synthesis of indium−chalcogenide oligomers.[3,7] The few structural studies reported show most of these compounds are dimers with $(InE)_2$ central rings.[3,4,6,10,14] Polymers[14,15] and one trimer[4] have also been reported. With this information in hand we have started a search for other aggregation states and structure types by studying the effects of the organic moiety on the molecules.

In this paper, we report the synthesis of $m\text{-}Xyl_3In$ (**1**) and the synthesis and X-ray studies of seven new indium−sulfur compounds: $\{m\text{-}Xyl_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ (**2**), $[t\text{-}Bu_2In(\mu\text{-}S\text{-}C_5H_9)]_2$ (**3**), $[t\text{-}Bu_2In(\mu\text{-}S\text{-}C_6H_{11})]_2$ (**4**), $\{t\text{-}Bu_2In[\mu\text{-}S(2,5\text{-}Me_2)C_6H_3]\}_2$ (**5**), $[Me_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_3$ (**6**), $\{t\text{-}Bu_2In[\mu\text{-}S(4,6\text{-}Me_2)C_4N_2H]\}_3$ (**7**), and $\{Me_2In[\mu\text{-}S(2,6\text{-}Me_2)C_6H_3]\}_4$ (**8**). The synthesis of **3**−**8** utilizes R_3In, with the elimination of RH upon addition of a ligand. The synthesis of **2** was accomplished by the reaction of bis(tricyclohexyltin) sulfide with Xyl_3In.

Experimental Section

General Procedures. All solvents were purified and dried by standard techniques.[16] Argon gas was purified by passing

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10.1021/om990887b CCC: $19.00 © 2000 American Chemical Society
Publication on Web 02/09/2000

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on February 9, 2000 on http://pubs.acs.org | doi: 10.1021/om990887b

it through a series of columns containing Deox catalyst (Alfa), phosphorus pentoxide, and sodium hydroxide. Bis(tricyclohexyltin) sulfide (Aldrich), 2-methylpropane-2-thiol (Aldrich), 4,6-dimethyl-2-mercaptopyrimidine (Aldrich), cyclopentanethiol (Aldrich), cyclohexanethiol (Aldrich), 2,5-dimethylbenzenethiol (Aldrich), and 2,6-methylbenzenethiol (Aldrich) were purchased and used as received. Trimethylindium etherate and tri-*tert*-butylindium were prepared according to the published procedures.[17,18] The compounds are both water- and oxygen-sensitive; therefore, standard Schlenk line and glovebox techniques were employed. All of the glassware used in the synthetic work was oven- and/or flame-dried. ^{1}H and ^{13}C NMR spectra were recorded on General Electric QE-300 or QN-300 or Varian Unity 500 NMR spectrometers. The ^{1}H and ^{13}C chemical shifts were referenced to benzene (δ 7.15 ppm for ^{1}H and δ 128.00 ppm for ^{13}C). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were recorded on a Haake-Buchler apparatus in sealed capillaries and are uncorrected.

Preparation of m-Xyl$_3$In (1). Indium metal (1.0 g, 8.70 mmol) was added to dixylylmercury (5.37 g, 13.06 mmol) in 100 mL of toluene. The mixture was placed under conditions of reflux for 72 h. After this time, no observable indium remained. The solution was transferred while still hot to a flask with use of a cannula. When the solution was cooled to room temperature, colorless crystals were deposited. Yield: 96%. Mp: 187 °C. Anal. Calcd (found) for $C_{24}H_{27}In$: C, 66.99 (64.48); H, 6.32 (6.21). ^{1}H NMR (C_6D_6; δ, ppm): 7.50 (s, 6H) $[C_6H_3(CH)_2]_3$, 6.88 (s, 3H) $[C_6H_3(CH)_2]_3$, 2.17 (s, 18H) $[C_6H_3(CH)_2]_3$. Mass spectrum (EI mode): *m/e* 430 Xyl_3In^+ , 325 Xyl_2In^+, 211 Xyl_2^+.

Preparation of $\{m\text{-}Xyl_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ (2). Bis(tricyclohexyltin) sulfide (0.62 g, 0.81 mmol) was added to **1** (0.35 g, 0.81 mmol) in pentane (ca. 60 mL). The mixture was stirred until all the reactants were dissolved and a precipitate was formed (ca. 3 min). The precipitate was dissolved by adding toluene (10 mL) and warming the mixture to 70 °C. The solution was cooled to 4 °C and allowed to remain at that temperature for 24 h, after which time the crystals formed were isolated at 0 °C, washed with pentane, and dried under vacuum. Yield: 75%. Mp: 187 °C. Anal. Calcd (found) for $C_{34}H_{51}SInSn$: C, 56.30 (56.08); H, 7.09 (7.12). ^{1}H NMR (C_6D_6; δ, ppm): 7.81 (s, 4H) [*o*-H, *m*-Xyl]; 6.91 (s, 2H) [*p*-H, *m*-Xyl]; 2.33 (m, 12H) [CH_3 of *m*-Xyl]; 1.09−2.18 (m, 33H) $[SSn(C_6H_{11})_3]$. $^{13}C\{^{1}H\}$ NMR (C_6D_6, δ, ppm) 137.0, 136.9, 136.5, 130.1 [*m*-Xyl]; 33.7, 33.3, 32.7, 32.5, 29.8, 29.4, 27.5, 27.2 $[SSn(C_6H_{11})_3]$; 21.6 [CH_3 of *m*-Xyl]. Mass spectrum (EI mode): *m/e* 363 $(C_6H_{11})_3Sn^+$, 281 $(C_6H_{11})_2Sn^+$, 196 $C_6H_{11}Sn^+$, 120 Sn^+.

Preparation of $[t\text{-}Bu_2In(\mu\text{-}S\text{-}C_5H_9)]_2$ (3). Cyclopentanethiol (0.19 mL,1.75 mmol) was added to a yellow solution of *t*-Bu_3In (0.50 g, 1.75 mmol) in a mixture of toluene and hexane (40 mL, 80:20). The solution became colorless on addition of the thiol. The solution was stirred for 24 h and then placed at −20 °C for 1 week. The solvent layer was removed under vacuum, leaving behind a white crystalline precipitate. This solid was recrystallized from toluene. The solid was identified as **3** from X-ray, MS, NMR, and elemental analysis. Yield: 85%. Mp: 148 °C. Anal. Calcd (found) for $C_{13}H_{27}SIn$: C, 47.28 (47.24); H, 8.24 (8.52). ^{1}H NMR (C_6D_6; δ, ppm): 1.33 (4H, m, SC_5H_9); 1.45 (18H, s, $In(C(CH_3)_3)_2$); 1.48 (2H, m, SC_5H_9); 1.83 (2H, m, SC_5H_9); 3.69 (1H, m, SC_5H_9). $^{13}C\{^{1}H\}$ NMR (C_6D_6; δ, ppm): 25.06 (C3, C4 of CypS); 33.15 ($C(CH_3)_3)_2$); 36.07 ($(C(CH_3)_3)_2$); 40.02 (C2, C5 of CypS); 41.83 (C1 of CypS). Mass spectrum (EI mode): *m/e* 603 $[C_{22}H_{45}In_2S_2]^{\bullet+}$ (dimer − *t*-Bu), 559 $[C_{21}H_{45}In_2S]^{\bullet+}$, 330 $[C_{13}H_{27}InS]^{\bullet+}$, 228 $[C_8H_{17}In]^{\bullet+}$.

Compounds **4**−**8** were also synthesized by this general procedure. Therefore, only essential information is provided for these syntheses.

Preparation of $[t\text{-}Bu_2In(\mu\text{-}S\text{-}C_6H_{11})]_2$ (4). Cyclohexanethiol (0.21 mL, 1.75 mmol) was added to *t*-Bu_3In (0.50 g, 1.75 mmol) in toluene/hexane (40 mL, 80:20). The crystalline solid was identified as **4** from X-ray, MS, NMR, and elemental analysis. The NMR of the crystalline solid was identical with that of the white solid initially formed. Yield: 85%. Mp: 190−192 °C. Anal. Calcd (found) for $C_{14}H_{29}SIn$: C, 48.84 (48.00); H, 8.49 (8.74). ^{1}H NMR (C_6D_6; δ, ppm): 1.10 (4H, m, SC_6H_{11}); 1.35 (2H, m, SC_6H_{11}); 1.47 (18H, s, $In(C(CH_3)_3)_2$); 1.59 (2H, m, SC_6H_{11}); 1.90 (2H, m, SC_6H_{11}); 3.31 (1H, m, SC_6H_{11}). $^{13}C\{^{1}H\}$ NMR (C_6D_6; δ, ppm): 25.7 (C4 of SC_6H_{11}); 26.7 (C3, C5 of SC_6H_{11}); 33.1 ($C(CH_3)_3)_2$); 39.5 (C2, C6 of SC_6H_{11}); 41.5 (C-1 of SC_6H_{11}). Mass spectrum (EI mode): *m/e* 631 $[C_{24}H_{49}In_2S_2]^{\bullet+}$ (dimer − *t*-Bu), 574 $[C_{20}H_{40}In_2S_2]^{\bullet+}$, 344 $[C_{14}H_{29}InS]^{\bullet+}$.

Preparation of $\{t\text{-}Bu_2In[\mu\text{-}S(2,5\text{-}Me_2)C_6H_3]\}_2$ (5). 2,5-Dimethylbenzenethiol (0.19 mL, 1.40 mmol) was added to *t*-Bu_3In (0.400 g, 1.40 mmol) in hexane (40 mL). The crystalline solid was identified as **5** by X-ray, MS, and NMR. Yield: 77%. Mp: 179−181 °C. ^{1}H NMR (C_6D_6; δ, ppm): 1.32 (18H, s, $In(C(CH_3)_3)_2$); 2.20 (3H, s, 2-CH_3 of C_6H_3); 2.25 (3H, s, 5-CH_3 of C_6H_3); 6.50 (1H, m, H6 of C_6H_3); 6.65 (2H, m, H3, H4 of C_6H_3). $^{13}C\{^{1}H\}$ NMR (C_6D_6; δ, ppm): 21.1 (2-CH_3); 22.2 (5-CH_3); 33.2 ($C(CH_3)_3)_2$); 127−128 (C_6H_3). Mass spectrum (EI mode): *m/e* 675 $[C_{28}H_{45}In_2S_2]^{\bullet+}$ (dimer − *t*-Bu), 618 $[C_{24}H_{36}In_2S_2]^{\bullet+}$, 603 $[C_{23}H_{33}In_2S_2]^{\bullet+}$, 329 $[C_{14}H_{14}InS]^{\bullet+}$, 314 $[C_{13}H_{11}InS]^{\bullet+}$, 277 $[C_{10}H_{10}InS]^{\bullet+}$. Exact mass of monomer $[C_{16}H_{27}InS]^{\bullet+}$ calcd (obsd): 366.2736 (366.2744).

Preparation of $[Me_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_3$ (6). 2-Methylpropanethiol (0.60 mL, 5.30 mmol) was added to 5.00 mL of trimethylindium etherate (20% Me_3In, 5.30 mmol of Me_3In) in pentane (ca. 35 mL). The solid was identified as **6** by X-ray, MS, and NMR. Yield: 81.9%. Mp: 90−91 °C. ^{1}H NMR (21 °C, C_6D_6; δ, ppm): 0.276 (6H, s, broad, Me_2In); 1.278 (9H, s, $SC(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR (C_6D_6; δ, ppm): 1.04 (Me_2In); 35.6 ($SC(CH_3)_3$); 94.8 ($SC(CH_3)_3$). Mass spectrum (EI mode): *m/e* 687 $[C_{17}H_{42}In_3S_3]^{\bullet+}$ (trimer − Me), 453 $[C_{11}H_{27}In_2S_2]^{\bullet+}$ (dimer − Me), 234 $[C_6H_{15}InS]^{\bullet+}$, 163 $[MeInSH]^{\bullet+}$.

Preparation of $\{t\text{-}Bu_2In[\mu\text{-}S(4,6\text{-}Me_2)C_4N_2H]\}_3$ (7). 4,6-Dimethyl-2-mercaptopyrimidine (2-mpym = 2-mercaptopyrimidine; 0.132 g, 0.944 mmol) was added to *t*-Bu_3In (0.270 g, 0.944 mmol) in 30 mL of toluene. The crystals were identified as **7** from X-ray, MS, NMR, and elemental analysis. Yield: 80%. Mp: 181−183 °C. Anal. Calcd (found) for $C_{14}H_{25}N_2SIn$: C, 45.66 (44.37); H, 6.84 (6.63). ^{1}H NMR (C_6D_6; δ, ppm): 1.33 (18H, s, $In(C(CH_3)_3)_2$); 1.73 (6H, s, 4-CH_3, 6-CH_3 of 2-mpym); 5.66 (1H, s, 2mpym *H*). $^{13}C\{^{1}H\}$ NMR (C_6D_6; δ, ppm): 22.78 (2-mpym CH_3), 32.20 ($In(C(CH_3)_3)_2$); 35.08 ($C(CH_3)$), 113.12 (C2 and C4 of mpym). Mass spectrum (EI mode): *m/e* 382 $[C_{15}H_{27}InN_2S]^{\bullet+}$. Exact mass of monomer $[C_{14}H_{25}InN_2S]^{\bullet+}$ calcd (obsd): 368.077 (368.077).

Preparation of $\{Me_2In[\mu\text{-}S(2,6\text{-}Me_2)C_6H_3]\}_4$ (8). 2,6-Dimethylbenzenethiol (0.71 mL, 5.3 mmol) was added to 5.00 mL of trimethylindium etherate (20% Me_3In, 5.3 mmol of Me_3In) in pentane (ca. 35 mL). The product was washed twice with pentane (40 mL), dried under a vacuum, and identified as **8** by X-ray, MS, NMR, and elemental analysis. Yield: 51.7%. Mp: 142−143 °C. Anal. Calcd (found) for $C_{10}H_{15}SIn$: C, 42.58 (42.10); H, 5.36 (5.32). ^{1}H NMR (C_6D_6; δ, ppm): 0.046 (6H, s, broad, Me_2In); 2.51 (6H, s, 2-CH_3, 6-CH_3); 6.87 (3H, s, C_6H_3). $^{13}C\{^{1}H\}$ NMR (C_6D_6; δ, ppm): −3.1 (Me_2In); 24.07 (2,6-Me_2); 127−128 (C_6H_3). Mass spectrum (EI mode): *m/e* 549 $[C_{19}H_{27}In_2S_2]^{\bullet+}$ (dimer − Me), 534 $[C_{18}H_{24}In_2S_2]^{\bullet+}$, 282 $[C_{10}H_{15}InS]^{\bullet+}$ (monomer), 267 $[C_9H_{12}InS]^{\bullet+}$.

X-ray Structure Determination of 2−8. Crystals were obtained as described above. A suitable crystal of each compound was chosen and mounted in a thin-walled capillary tube within a drybox. This tube was thermally sealed, mounted upon a goniometer head, and placed on either a Nicolet P2$_1$

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Published on February 9, 2000 on http://pubs.acs.org | doi: 10.1021/om990887b

Table 1. Selected Experimental Parameters for the X-ray Diffraction Study of the Compounds [*m*-$Xyl_2In(\mu\text{-}SSn(C_6H_{11})_3)]_2$ (2), [*t*-$Bu_2In(\mu\text{-}S\text{-}C_5H_9)]_2$ (3), [*t*-$Bu_2In(\mu\text{-}S\text{-}C_6H_{11})]_2$ (4), {*t*-$Bu_2In[\mu\text{-}S(2,5\text{-}Me_2)C_6H_3]\}_2$ (5), [$Me_2In(\mu$-S-*t*-Bu)]$_3$ (6), {*t*-$Bu_2In[\mu\text{-}S(4,6\text{-}Me_2)C_4N_2H]\}_3$ (7), and {$Me_2In[\mu\text{-}S(2,6\text{-}Me_2)C_6H_3]\}_4$ (8)

	2	**3**	**4**	**5**	**6**	**7**	**8**
formula	$C_{34}H_{51}SInSn$	$C_{13}H_{27}SIn$	$C_{14}H_{29}SIn$	$C_{16}H_{27}SIn$	$C_6H_{15}SIn$	$C_{14}H_{25}N_2SIn$	$C_{10}H_{15}SIn$
mol wt	725.3	330.22	344.25	366.26	234.06	368.24	282.10
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P6_3m$ (No. 176)	$P\bar{1}$ (No. 2)
a (Å)	16.365(3)	9.1128(3)	9.8763(6)	8.6360(5)	9.834(3)	15.9535(3)	10.795(2)
b (Å)	11.890(2)	17.8423(7)	11.9433(8)	11.0135(7)	19.108(4)	15.9535(3)	11.374(2)
c (Å)	18.339(2)	20.5846(8)	15.1396(10)	11.2653(9)	15.812(2)	13.1476(3)	11.652(2)
α (deg)	90	90	76.5370(10)	114.053(2)	90	90	100.23(3)
β (deg)	105.440(1)	100.2280(10)	78.2090(10)	107.9190(10)	102.74	90	115.02(3)
γ (deg)	90	90	87.8110(10)	97.0860(10)	90	120	106.09(3)
V (Å^3)	3432.2(2)	3293.7(2)	1700.0(2)	892.00(10)	2898.1(11)	2897.94(10)	1172.0(4)
calcd density (g/cm^3)	1.404	1.332	1.345	1.364	1.609	1.266	1.599
temp (K)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)	181(2)
linear abs coeff (μ) (mm^{-1})	1.480	1.537	1.492	1.427	2.584	1.320	2.145
R1 ($I > 2\sigma(I)$)	3.57	4.67	4.42	2.41	5.48	5.23	9.98
wR2 ($I > 2\sigma(I)$)	3.60	10.05	8.27	5.46	9.95	13.59	32.01

diffractometer (**2**, **6**), a Siemens R4/CCD SMART/SAINT system[19] (**3**−**5**, **7**), or a Siemens R3 diffractometer (**8**). For **2**, **3**, and **6**, the crystals were assigned to the monoclinic system on the basis of systematic absences, space group $P2_1/n$ (No. 14) for **2** and $P2_1/c$ (No. 14) for **3** and **6**. **7** was assigned to the hexagonal system, space group $P6_3/m$ (No. 176), and **4**, **5**, and **8** were assigned to the triclinic system and were successfully solved in space group $P\bar{1}$ (No. 2). No corrections for secondary extinction were made. Absorption corrections were semiempirical from Ψ-scans for **2**, **6**, and **8** and were performed by multiscan techniques with Sheldrick's program SADABS[20] for **3**−**5** and **7**.

Data reductions and full-matrix least-squares refinements were carried out using the SHELXTL PC[21] program for **2**, **6**, and **8**. Data reductions and full-matrix least-squares refinements were carried out using the SHELX-86[22] and SHELXL-93[23] programs for **3**−**5** and **7**. The direct methods routines produced solutions for the structures, yielding positions for some of the non-hydrogen atoms, while other atoms were located during subsequent refinements. Hydrogen atoms were observed or placed in calculated positions and allowed to ride on the carbon atoms to which they were bound. For **3** there was disorder in the cyclopentyl rings. Partial occupancy factors were used for carbon atoms 3, 4, 8, and 9 to resolve this, with occupancy factors set to 50%. For **7** there was disorder in the *tert*-butyl groups which did not improve when the space group was lowered. Partial occupancy factors were used for carbon atoms 8, 9, and 10 to resolve this, with occupancy factors set to 50%. Selected parameters from the crystal structure determination are shown in Table 1.

Results and Discussion

The structures of compounds **2**−**5** are dimeric with a central four-membered $(In-S)_2$ planar ring which is essentially square. This is shown in Figure 1 for **2**. In each case the SR groups are oriented so that the substituents on the S atoms are in the *anti* configuration. Selected bond distances and angles for **2**−**5** are listed in Table 2 and are in the normal range for indium thiolates. In all cases the In atoms are four-coordinate surrounded by two sulfur atoms and two carbon atoms, forming a distorted tetrahedron. The angles around the In atom range from approximately 130° for C−In−C to approximately 87° for S−In−S and In−S−In. The angles around the S atom range from 89 to 116° in **2**−**5** (Table 2). A comparison of the bond distances and angles of **2**−**5** with those of other dimeric group 13 derivatives is given in Table 3. The sum of the angles around S is nearly equivalent, with an average value of 316.9° in **2**−**5** (Table 3), which clearly indicates the pyramidal nature of the sulfur atom. The sum of these angles is similar to those reported for the majority of indium, as well as aluminum and gallium, thiolate dimers and serves as a sensitive measure of the pyramidal character of the sulfur or other chalcogen atom in the bridging site.

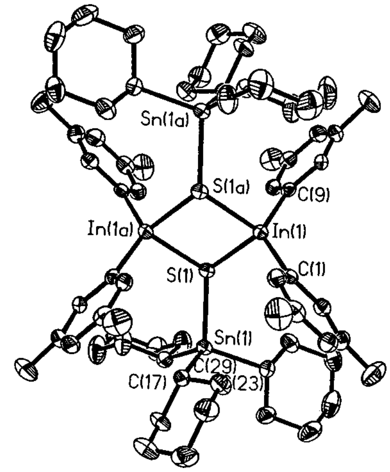

Figure 1. Diagram of [*m*-$Xyl_2In(\mu\text{-}SSn(C_6H_{11})_3)]_2$ (**2**; 0% thermal ellipsoids) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

The internal angles in the ring are all near 90°, and all the bond distances are similar, giving essentially square systems. The only indium thiolates for which this is not the case are $[Me_2In(\mu\text{-}SSiPh_3)]_3$, where the S−In−S angle is 77.8° with an In−S−In angle of 102.2°, and [$Mes_2In(\mu$-S-*t*-amyl)]$_2$,[4] where the corresponding angles are 84.2 and 95.9°. In these cases very bulky groups are attached to both the In and the S atoms and appear to distort the central square, elongating it along the In−In axis.

Examination of the In−S bond distances indicates that they are slightly altered by the substituents bound

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[m\text{-Xyl}_2\text{In}(\mu\text{-SSn}(\text{C}_6\text{H}_{11})_3)]_2$ (2), $[t\text{-Bu}_2\text{In}(\mu\text{-S-C}_5\text{H}_9)]_2$ (3), $[t\text{-Bu}_2\text{In}(\mu\text{-S-C}_6\text{H}_{11})]_2$ (4), and $\{t\text{-Bu}_2\text{In}[\mu\text{-S}(2,5\text{-Me}_2)\text{C}_6\text{H}_3]\}_2$ (5)

2		3		4		5	
Bond Distances							
In(1)−S(1)	2.557(2)	In(1)−S(2)	2.5930(14)	In(1)−S(1)	2.602(2)	In(1)−S(1)#1	2.6212(6)
In(1)−S(1A)	2.576(1)	In(1)−S(1)	2.5992(13)	In(1)−S(1)#1	2.6081(13)	In(1)−S(1)	2.6460(5)
		In(2)−S(2)	2.5950(13)	In(2)−S(2)	2.606(2)		
		In(2)−S(1)	2.5956(14)	In(2)−S(2)#2	2.6079(12)		
In(1)−C(1)	2.141(5)	In(1)−C(11)	2.189(6)	In(1)−C(7)	2.186(6)	In(1)−C(13)	2.202(2)
In(1)−C(9)	2.143(5)	In(1)−C(15)	2.200(5)	In(1)−C(11)	2.208(6)	In(1)−C(9)	2.217(2)
		In(2)−C(19)	2.193(5)	In(2)−C(25)	2.197(6)		
		In(2)−C(23)	2.206(5)	In(2)−C(21)	2.197(7)		
Sn(1)−S(1)	2.448(2)	S(1)−C(1)	1.838(5)	S(1)−C(1)	1.838(6)	S(1)−C(1)	1.786(2)
Sn(1)−C(17)	2.168(6)	S(2)−C(6)	1.829(5)	S(2)−C(15)	1.843(6)		
Sn(1)−C(23)	2.170(5)						
Sn(1)−C(29)	2.161(5)						
Bond Angles							
S(1)−In(1)−S(1A)	91.4(5)	S(2)−In(1)−S(1)	87.31(4)	S(1)−In(1)−S(1)#1	88.74(4)	S(1)#1−In(1)−S(1)	87.67(2)
		S(2)−In(2)−S(1)	87.35(4)	S(2)−In(2)−S(2)#2	88.50(4)		
In(1)−S(1)−In(1A)	88.6(1)	In(2)−S(1)−In(1)	92.59(4)	In(1)−S(1)−In(1)#1	91.26(4)	In(1)#1−S(1)−In(1)	92.33(2)
		In(1)−S(2)−In(2)	92.75(4)	In(2)−S(2)−In(2)#2	91.50(4)		
C(1)−In(1)−C(9)	130.5(2)	C(11)−In(1)−C(15)	124.7(2)	C(7)−In(1)−C(11)	125.2(2)	C(13)−In(1)−C(9)	123.96(9)
				C(27)−In(2)−C(21)	125.9(3)		
Sn(1)−S(1)−In(1)	116.0(1)	C(1)−S(1)−In(2)	111.1(2)	C(1)−S(1)−In(1)	115.6(2)		
Sn(1)−S(1)−In(1A)	114.1(1)	C(1)−S(1)−In(1)	113.7(2)	C(1)−S(1)−In(1)#1	108.4(2)		
				C(15)−S(2)−In(2)	114.3(2)		
				C(15)−S(2)−In(2)#2	110.23(14)		

Table 3. Selected Bond Distances (Å) and Angles (deg) Observed in $[m\text{-Xyl}_2\text{In}(\mu\text{-SSn}(\text{C}_6\text{H}_{11})_3)]_2$ (2), $[t\text{-Bu}_2\text{In}(\mu\text{-S-C}_5\text{H}_9)]_2$ (3), $[t\text{-Bu}_2\text{In}(\mu\text{-S-C}_6\text{H}_{11})]_2$ (4), $\{t\text{-Bu}_2\text{In}[\mu\text{-S}(2,5\text{-Me}_2)\text{C}_6\text{H}_3]\}_2$ (5), and Other Selected Group 13 Thiolate Derivatives

compd	M−E (Å)	E−M−E (deg)	M−E−M (deg)	sum of angles around E (deg)	M−C (Å)	C−M−C (deg)
$[m\text{-Xyl}_2\text{In}(\mu\text{-SSn}(\text{C}_6\text{H}_{11})_3)]_2$ (**2**)[a]	2.57	91.4	88.6	318.7	2.14	130.5
$[t\text{-Bu}_2\text{In}(\mu\text{-S-C}_5\text{H}_9)]_2$ (**3**)[a]	2.60	87.3	92.7	316.5	2.20	124.6
$[t\text{-Bu}_2\text{In}(\mu\text{-S-C}_6\text{H}_{11})]_2$ (**4**)[a]	2.61	88.7	91.3	315.3	2.20	125.5
$[t\text{-Bu}_2\text{In}[\mu\text{-S}(2,5\text{-Me}_2)\text{C}_6\text{H}_3]\}_2$ (**5**)[a]	2.63	87.7	92.3	317.2	2.21	124.0
$\{\text{Ph}_2\text{In}[\mu\text{-SSn}(\text{C}_6\text{H}_{11})_3]\}_2$[b]	2.55	90.7	89.3	311.9	2.15	116.3
$[\text{Mes}_2\text{In}(\mu\text{-SSiPh}_3)]_2$[c]	2.50	77.8	102.2	352.1	2.18	128.3
$[\text{Mes}_2\text{In}(\mu\text{-S-}t\text{-amyl})]_2$[c]	2.59	84.2	95.9	324.0	2.23	111.8
$[\text{Mes}_2\text{In}(\mu\text{-SePh})]_2$[d]	2.73	90.2	89.8	292.5	2.17	121.5
$[\text{Mes}_2\text{In}(\mu\text{-SeMes})]_2$[d]	2.72	90.5	88.7	292.3	2.18	119.5
$[\text{Np}_2\text{In}(\mu\text{-SePh})]_2$[e]	2.74	89.6	86.1	295.2	2.16	133.6
$[\text{Mes}_2\text{In}(\mu\text{-TePh})]_2$[f]	2.92	92.5	87.5	285.7	2.18	121.9
$[\text{Mes}_2\text{In}(\mu\text{-Te-}n\text{-Pr})]_2$[f]	2.91	92.2	87.8	274.4	2.16	122.1
$[\text{Mes}_2\text{Al}(\mu\text{-SBz})]_2$[g]	2.38	89.1	90.9	306.0	1.98	119.6
$[\text{Me}_2\text{Al}(\mu\text{-SSiPh}_3)]_2$[g]	2.36	87.6	92.2	330.5	1.93	120.0
$[\text{Mes}_2\text{Al}(\mu\text{-SPh})]_2$[g]	2.39	86.4	92.0	316.5	1.97	120.2
$[\text{Me}_2\text{Ga}(\mu\text{-SC}_5\text{H}_9)]_2$[h]	2.39	93.8	86.2	300.2	1.95	126.3
$\text{Ph}_2\text{Ga}(\mu\text{-S-SiMe}_3)]_2$[h]	2.38	90.8	89.2	313.4	1.96	118.2
$[\text{Ph}_2\text{Ga}(\mu\text{-SC}_5\text{H}_9)]_2$[h]	2.39	92.05	87.05	297.9	1.96	121.0
$\{\text{Ph}_2\text{Ga}[\mu\text{-SSn}(\text{C}_6\text{H}_{11})_3]\}_2$[b]	2.34	93.5	86.5	313.0	1.96	114.5
$\{\mu\text{-Xyl}_2\text{Ga}[\mu\text{-SSi}(\text{C}_6\text{H}_{11})_3]\}_2$[h]	2.38	88.6	91.4	322.1	1.97	124.6

[a] This work. [b] Reference 3. [c] Reference 4. [d] Reference 14. [e] Reference 10. [f] Reference 6. [g] Reference 7. [h] Reference 25.

to the sulfur atom. The In−S distances lie in the range 2.59−2.61 Å when the substituent bound to the S atom is aliphatic. For the one aromatic derivative reported, the distance is 2.63 Å, while for the two derivatives with the S bound to an Sn atom, the values are 2.57 Å in **2** and 2.55 Å in $[\text{Ph}_2\text{In}(\mu\text{-SSn}(\text{C}_6\text{H}_{11})_3)]_2$.[3] These data are summarized in Table 3.

We also see modest changes in the S−C bond distances. As we go from **3** and **4** to **5**, the hybridization of the carbon atom bound to the sulfur atom changes from sp^3 to sp^2. With this change, the S−C bond distance decreases from 1.84 to 1.79 Å, which can be associated with an increase in the bond strength. Along with this decrease in the S−C bond distance, there is also an increase in the In−S bond distance from 2.61 to 2.63 Å, which can be thought of as a decrease in the bond strength. One would expect that use of an ethynyl substituent bound to the sulfur would show a further decrease in the S−C bond distance and a corresponding increase in the In−S bond distance. If the suggestion is that these changes are related to bond strengths, then one would expect decreased stability for the $(\text{In}-\text{S})_2$ ring as a function on the substituent bound to S. This remains to be tested experimentally.

The C−M−C exocyclic angle appears to be determined primarily by the organic substituent bound to the indium. For compounds **3**−**5** with *tert*-butyl substituents, this angle varies over the narrow range of 124−125.5°. In **2**, where both substituents are changed, the angle increases to 130.5°. If we examine the eight mesityl derivatives listed in Table 3, six have exocyclic angles that fall in the very narrow range 119.6−122.1°. The two which fall outside of this are the SSiPh_3 derivative, with a 128.3° angle, and $[\text{Mes}_2\text{In}(\mu\text{-amyl})]_2$,

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with an angle of 111.8°. Two of the four phenyl derivatives listed also fall in this range, with the other two having slightly smaller C−M−C angles. This indicates that the primary concern is the organic substituent but also shows additional steric effect from the bridging ligands influencing this angle.

If we now examine the trends that occur as the chalcogen or the group 13 metal is changed, we find that the general structures remain the same. The dominant species remains dimeric with a planar or near-planar central four-membered ring. For the indium−selenium derivatives, there are two compounds with planar structures ($[Mes_2In(\mu\text{-}SePh)]_2$ and $[Mes_2In(\mu\text{-}SeMes)]_2$)[14] and two which have slightly puckered $(In-Se)_2$ rings ($[Np_2In(\mu\text{-}SePh)]_2$[10] and $Np_2In(\mu\text{-}SePh)(\mu\text{-}P\text{-}t\text{-}Bu_2)InNp_2$),[24] with the planar systems adopting a square configuration. For the indium−tellurium dimers $[Mes_2In(\mu\text{-}TePh)]_2$ and $[Mes_2In(\mu\text{-}Te\text{-}n\text{-}Pr)]_2$ these again show a planar $(In-Te)_2$ core, which is slightly distorted with a Te−In−Te angle of 92.2−92.5°.[6] For the dimeric indium compounds, it is easily seen that the normal trend is observed with the pyramidal character of the chalcogen increasing in the order S < Se < Te. For comparison some aluminum and gallium derivatives are also shown in Table 3.

$\{m\text{-}Xyl_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ has the same general structural features as **2** with a planar ring slightly skewed from square (the S−Ga−S angle is 91.4°), and shorter S bond distances (2.38 Å) as a result of the smaller metal radius.[25] The C−Ga−C angle is tighter (126.6°), and the sum of the angles around the sulfur is 322.1°. Although there is no directly relatable aluminum complex, by examining a variety of aluminum−sulfur dimeric complexes, one sees very similar overall geometries, with a shortening of the expected bond distances (metal−carbon and metal−sulfur).

Few structural studies have been reported for *tert*-butyl derivatives of Al or Ga, but the structure of one, $[t\text{-}Bu_2Al(\mu\text{-}S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)]_2$, with bridging sulfur atoms, has appeared.[26] In this system the $(Al-S)_2$ ring is planar, with the ligands in the *anti* arrangement. Other structural parameters appear to be altered by the very bulky groups on both the metal and the chalcogen.

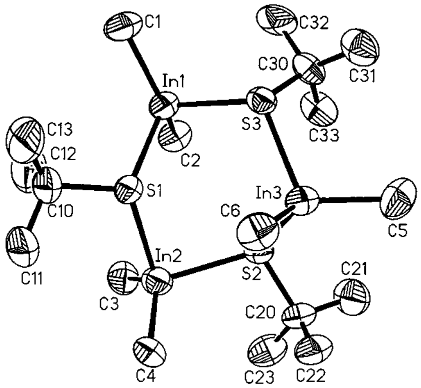

Figure 2. Diagram of $[Me_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_3$ (**6**; 50% thermal ellipsoids) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Me_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_3$ (6) and $\{t\text{-}Bu_2In[\mu\text{-}S(4,6\text{-}Me_2)C_4N_2H]\}_3$ (7)

6		**7**	
Bond Distances			
In(1)−S(1)	2.563(4)	In(1)−S(1)#2	2.623(2)
In(1)−S(3)	2.576(4)	In(1)−S(1)	2.712(2)
In(2)−S(2)	2.591(4)	S(1)−In(1)#3	2.623(2)
In(2)−S(1)	2.595(3)		
In(3)−S(3)	2.562(4)		
In(3)−S(2)	2.584(3)	In(1)−C(7)#1	2.185(5)
In(1)−C(1)	2.166(12)	In(1)−C(7)	2.185(5)
In(1)−C(2)	2.155(12)		
In(3)−C(6)	2.137(12)		
In(3)−C(5)	2.177(14)	N(2)−In(1)#3	2.922(5)
		In(1)−N(2)#2	2.922(5)
S(1)−C(10)	1.86(2)	S(1)−C(1)	1.735(6)
S(2)−C(20)	1.839(13)		
S(3)−C(30)	1.869(13)		
Bond Angles			
C(2)−In(1)−C(1)	129.5(5)	C(7)#1−In(1)−C(7)	139.4(4)
C(4)−In(2)−C(3)	126.4(5)	S(1)#2−In(1)−S(1)	79.78(7)
C(6)−In(3)−C(5)	122.0(6)	In(1)#3−S(1)−In(1)	160.22(7)
		C(7)#1−In(1)−N(2)#2	91.58(14)
		C(7)−In(1)−N(2)#2	91.58(14)
S(1)−In(1)−S(3)	92.30(12)	S(1)#2−In(1)−N(2)#2	55.39(9)
		S(1)−In(1)−N(2)#2	135.17(11)
		C(1)−S(1)−In(1)#3	94.9(2)
		C(1)−S(1)−In(1)	104.9(2)
		C(1)−N(1)−C(5)	117.7(6)
		N(2)−C(1)−N(1)	126.4(6)
		N(2)−C(1)−S(1)	116.5(4)
		N(1)−C(1)−S(1)	117.1(5)
S(3)−In(3)−S(2)	96.89(11)	C(1)−N(2)−C(2)	117.6(6)
In(1)−S(1)−In(2)	110.12(13)	C(1)−N(2)−In(1)#3	93.3(3)
In(3)−S(2)−In(2)	109.39(12)	C(2)−N(2)−In(1)#3	149.1(5)
In(3)−S(3)−In(1)	114.08(12)		
C(10)−S(1)−In(1)	107.1(6)		
C(10)−S(1)−In(2)	108.0(5)		
C(20)−S(2)−In(3)	106.6(5)		
C(20)−S(2)−In(2)	106.7(5)		
C(30)−S(3)−In(3)	109.7(5)		
C(30)−S(3)−In(1)	107.2(5)		

Compound **6**, $[Me_2In(\mu\text{-}S\text{-}t\text{-}Bu)]_3$, is the second reported example of an indium trimer, the first being $[Me_2In(\mu\text{-}SSiPh_3)]_3$.[4] Both of these systems show the same geometry, a skew-boat conformation, shown for **6** in Figure 2. Selected bond distances and angles for **6** are listed in Table 4. The In−C bond distances for **6** and the C−In−C exocyclic angles are similar to those for $[Me_2In(\mu\text{-}SSiPh_3)]_3$ and the other reported trimeric group 13 derivatives listed in Table 5. Bond distances and excocyclic C−M−C angles are also similar to those reported for the dimers listed in Table 3. For comparison, the aluminum trimeric derivatives have been included. The aluminum derivatives have been shown to form either a skew-boat or chair conformation, depending upon the substituents bound to the metal and the ligand. More sterically demanding substituents on the metal appear to favor the skew-boat conformation. It was also shown that when the sum of the angles around the sulfur approaches 360°, the conformation becomes skew-boat. For the aluminum−thiolate trimer systems, these angles ranged between 322.3 and 338.5° for the chair conformations, and the sum of the angles was 357.9° for the skew-boat conformation. The indium systems do not follow this trend, since the sum of the

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Table 5. Selected Bond Distances (Å) and Angles (deg) Observed in $[Me_2In(\mu\text{-S-}t\text{-Bu})]_3$ (6), $\{t\text{-}Bu_2In[\mu\text{-S}(4,6\text{-}Me_2)C_4N_2H]\}_3$ (7), and Selected Group 13 Trimeric Derivatives

compd	av M–E (Å)	E–M–E (deg)	M–E–M (deg)	sum of angles around E (deg)	av M–C (Å)	av C–M–C (deg)
$[Me_2In(\mu\text{-S-}t\text{-Bu})]_3$ (**6**)[a]	2.58	94.4	111.2	326.1	2.15	126.0
$\{t\text{-}Bu_2In[\mu\text{-S}(4,6\text{-}Me_2)C_4N_2H]\}_3$ (**7**)[a]	2.67	71.8	160.2	359.9	2.19	139.5
$[Me_2In(\mu\text{-SSiPh}_3)]_3$[b]	2.61	90.5	117.3	351.8	2.13	132.8
$\{Me_2Al[\mu\text{-S}(2\text{-}t\text{-BuC}_6H_4)]\}_3$[c]	2.35	100.6	115.1	323.9	1.94	120.6
		88.8	123.2	338.5		
		99.1	114.6	324.6		
$\{Me_2Al[\mu\text{-S}(2\text{-}Me_3Si)C_6H_4]\}_3$[c]	2.36	110.8	116.8	324.5	1.94	119.6
		89.4	114.2	337.1		
		99.2	122.5	320.0		
$\{i\text{-}Bu_2Al[\mu\text{-S}(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]\}_3$[c]	2.37	89.1	127.6	360.0	1.96	129.7
		93.2	126.8	357.4		
		96.1	131.5	356.3		
$[t\text{-}Bu_2Ga(\mu\text{-OH})]_3$ (planar)[d]	1.94	96.3	143.7		2.00	121.9

[a] This work. [b] Reference 4. [c] Reference 7. [d] Naiini, A. A.; Young, V.; Han, Y.; Akinc, M.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 3781.

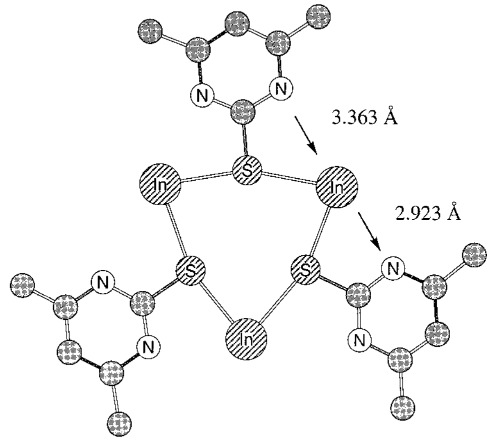

Figure 3. Diagram showing the distances between the In and N atoms in $\{t\text{-}Bu_2In[\mu\text{-S}(4,6\text{-}Me_2)C_4N_2H]\}_3$ (**7**).

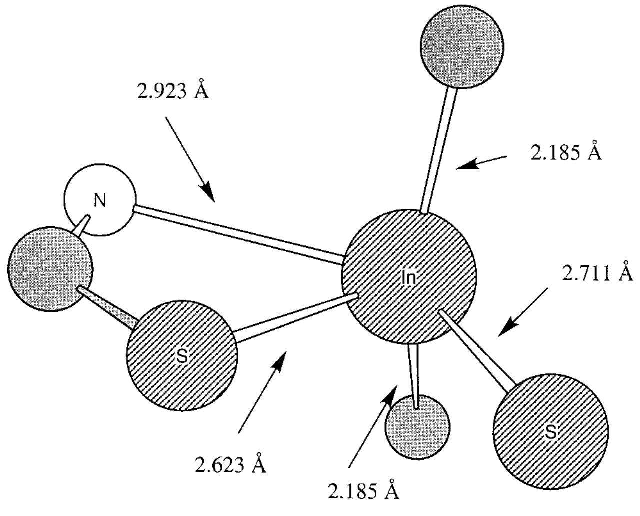

Figure 4. Diagram showing the coordination around indium in $\{t\text{-}Bu_2In[\mu\text{-S}(4,6\text{-}Me_2)C_4N_2H]\}_3$ (**7**).

angles around sulfur is 326.1° for **6** and 351.8° for $[Me_2In(\mu\text{-SSiPh}_3)]_3$ and both adopt the skew-boat conformation.

It was suggested previously that the small energy changes associated with the shift from the dimeric to the trimeric aggregation state may be due to interaction between nonbonded atoms.[4] In $[Mes_2In(\mu\text{-SSiPh}_3)]_2$, the two shortest interatomic distances are 3.419 and 3.631 Å between a methyl carbon atom attached to the indium atom and an *ortho* carbon atom of one of the phenyl rings. In the dimeric $[Mes_2In(\mu\text{-SSiPh}_3)]_2$ system, the equivalent distances are 3.256 and 3.431 Å. If $Me_2InS\text{-}t\text{-}Bu$ formed a dimeric species, these distances would likely be shorter, but in the trimeric molecule **6**, the equivalent distances are 3.740 and 3.751 Å. This provides further evidence that the substituents on the metal and the chalcogen affect the degree of aggregation, an observation which has been commented upon before with respect to the bulk of the groups bound to the metal.[8] The aggregate formed is dependent on the fine balance between steric and electronic effects in these systems, and small changes often lead to changes in the observed structure.

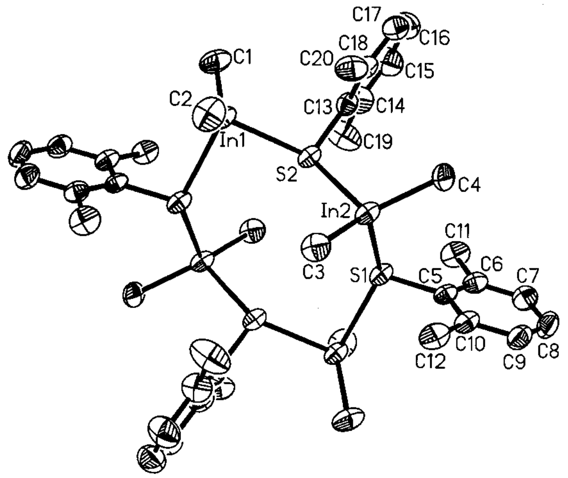

Figure 5. Diagram of $\{Me_2In[\mu\text{-S}(2,6\text{-}Me_2)C_6H_3]\}_4$ (**8**; 50% thermal ellipsoids) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $\{Me_2In[\mu\text{-S}(2,6\text{-}Me_2)C_6H_3]\}_4$ (8)

bond distances		bond angles	
In(1)–S(2)	2.584(2)	S(2)–In(2)–S(1)	92.82(6)
In(1)–S(1)#1	2.602(2)	S(2)–In(1)–S(1)#1	90.03(6)
In(2)–S(2)	2.581(2)	In(2)–S(1)–In(1)#1	130.47(7)
In(2)–S(1)	2.591(2)	In(2)–S(2)–In(1)	123.33(7)
		C(17)–In(2)–C(18)	135.0(4)
In(1)–C(19)	2.159(8)	C(19)–In(1)–C(20)	131.2(4)
In(1)–C(20)	2.154(7)		
In(2)–C(17)	2.135(7)	C(1)–S(1)–In(2)	105.0(2)
In(2)–C(18)	2.134(8)	C(1)–S(1)–In(1)#1	103.4(2)
S(1)–C(1)	1.788(6)		
S(2)–C(9)	1.794(7)	C(9)–S(2)–In(2)	104.0(2)
		C(9)–S(2)–In(1)	105.2(2)

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Table 7. Selected Bond Distances (Å) and Angles (deg) Observed in $\{Me_2In[\mu\text{-}S(2,6\text{-}Me_2)C_6H_3]\}_4$ (8) and Other Tetrameric Species

compd	av M−E (Å)	E−M−E (deg)	M−E−M (deg)	sum of angles around S (deg)	av M−C (Å)	av C−M−C (deg)
$\{Me_2In[\mu\text{-}S(2,6\text{-}Me_2)C_6H_3]\}_4$ (**8**)[a]	2.59	92.8	130.5	338.9	2.15	135.0
		90.0	123.3			131.2
$\{Me_2Al[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$[b]	2.36	99.5	126.9	342.8	1.94	126.0
		94.6	130.7	348.3		120.3
$\{Me_2Ga[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$[b]	2.40	93.1	126.2	340.7	1.94	129.5
		96.6	129.8	346.0		124.2
$[Me_2Ga(\mu\text{-}OH)]_4$[c]	1.96	98.7	133.0		1.95	124.5
		98.9	133.2			133.8

[a] This work. [b] Reference 7. [c] Smith, G. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 3907.

The trimer **7**, $\{t\text{-}Bu_2In[\mu\text{-}S(4,6\text{-}Me_2)C_4N_2H]\}_3$, differs significantly from **6** and the other trimeric species discussed above. The indium and pyrimidene ligands lie in a plane with 3-fold symmetry. Only the *tert*-butyl groups attached to the indium lie above and below this plane. A diagram showing a portion of the molecule is shown in Figure 3. The central ring is distorted substantially from a regular hexagon. The internal In−S−In angles of 160.2° and S−In−S angles of 79.8° represent extremely large deviations from those that have been reported previously, with the In−S−In angle significantly larger, and the S−In−S angle significantly smaller, than those seen in other group 13−chalcogen trimers. The average In−S bond length is 2.67 Å, which is within the range of previously reported bond distances, but the two individual In−S bond distances differ with values of 2.712 and 2.623 Å. The In−C bond lengths are in the normal range (Tables 3 and 5), but the C−In−C angle is 139.5°, which is somewhat wider than other reported values.

Figure 3 shows another unusual feature of this molecule. The pyrimidene moiety is tipped toward one In atom, giving rise to a very short In−N distance of 2.923 Å and a correspondingly long distance for the other In−N separation of 3.362 Å. This unusual geometry indicates an interaction between In and N which leads to both the planar geometry and the distorted structure. One can, in fact, consider that the indium atoms have gone from the common four-coordinate tetrahedral geometry to a distorted pentacoordinate trigonal prism, as illustrated in Figure 4.

The indium tetramer **8** has a geometry very similar to that of the aluminum and gallium tetramers $\{Me_2Al[\mu\text{-}S(2,6\text{-}Me_2)C_6H_3]\}_4$,[7] $\{Me_2Ga[\mu\text{-}S(2,6\text{-}Me_2)C_6H_3]\}_4$,[7] and $[Me_2Ga(\mu\text{-}OH)]_4$,[27] with each displaying an eight-membered ring in an extended chair configuration as shown in Figure 5. Selected bond distances and angles are listed in Table 6. The average bond distances and angles are well within the normal range for the dimers and trimers listed in Tables 3 and 5. Of more interest is the similarity of the four group 13 tetramers listed in Table 7. There is little change in the geometry of these species, except for the bond distances, which are dependent on the radii of the atoms involved.

Conclusions

We have been able to demonstrate that it is possible to extend current synthetic strategies used in the preparation of group 13 chalcogenide derivatives to yield new and unique systems. The dimers **2**−**5** show a planar four-membered ring with the ligands in an *anti* arrangement, and the trimer **6** crystallizes in the skew-boat six-membered-ring configuration; however, the trimer **7** forms a planar six-membered ring which displays a unique geometry as a result of the secondary interaction of the nitrogen atoms in the pyrimidene moieties bound to the bridging sulfur atom. Compound **8** is the first reported tetramer for a diorganoindium derivative.

We have also gathered more evidence supporting the suggestion that steric interactions play an inportant role in determining the C−M−C exocyclic angle and appear to be the driving force in the determination of the aggregation state for group 13−chalcogen complexes. Further, we have shown that secondary interactions which may occur when additional coordination sites are present, either in the ligand bound to the metal or in the bridging chalcogen, can substantially alter the structure of these derivatives. Finally, there is some evidence that it may be possible to control the In−S bond length with careful selection of the organosulfur moiety.

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

Supporting Information Available: Thermal ellipsoid diagrams for compounds **3**−**5** and **7** and complete listings of bond distances and angles, atomic coordinates and isotropic and anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates and isotropic thermal parameters for the hydrogen atoms for the four compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Smith, G. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 3907.