Reactions of the Alkylindium(I) Compound $In_4[C(SiMe_3)_3]_4$ with Sulfur and Tellurium: Syntheses of $In_4S_4[C(SiMe_3)_3]_4$ and $In_4Te_4[C(SiMe_3)_3]_4$ with Indium Chalcogen Heterocubane Structures

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Tetrahedro-Tetrakis[tris(trimethylsilyl)methyl]tetraindane(4) (**1**) with a tetrahedral In_4 molecular center reacts with an excess of elemental sulfur or tellurium in boiling *n*-hexane to give in an almost quantitative yield the appropriate In_4S_4 (**2**) or In_4Te_4 derivatives (**3**). Crystal structure determinations revealed distorted In_4X_4 (X = S, Te) heterocubane molecular centers for both compounds.

The alkylindium(I) derivative $In_4[C(SiMe_3)_3]_4$ (**1**) with a tetrahedral In_4 molecular core is synthesized by the reaction of InBr or InCl with $LiC(SiMe_3)_3 \cdot 2$ THF[1,2]. Compound **1** exhibits a remarkable chemical reactivity, and up to now we found three different types of reaction: (a) Electrochemical reduction leading to the reversible transfer of one electron, as shown by cyclovoltammetric experiments, probably with formation of a radicalic cluster anion which, however, could only be EPR-spectroscopically detected for the Ga_4 analog[3]. (b) Replacement of carbonyl groups by the monomeric fragment $In-C(SiMe_3)_3$ in transition metal carbonyl complexes with formation of e.g. a $Mn_2(CO)_8$ derivative containing two InR groups bridging the Mn–Mn bond[4]. (c) Formation of a cage compound ($In_4Se_4R_4$) with a heterocubane-type molecular structure by the reaction of **1** with an excess of elemental selenium[1]. The reactions of sulfur and tellurium with **1** completing the reactions with the heavier chalcogens are described in this article. Up to now we did not succeed in synthesizing an In_4O_4 derivative by reactions with oxygen donors; with moist air **1** gives $In_4O_4(OH)_6[C(SiMe_3)_3]_4$[2,5].

Reactions of $In_4[C(SiMe_3)_3]_4$ (1) with Sulfur and Tellurium

Compound **1** forms deep violet solutions in *n*-hexane which remain unchanged on treatment with an excess of sulfur or tellurium at room temperature for several days. However, the color of the In_4 compound completely disappears when the mixture with sulfur is heated at reflux for only 15 minutes. With tellurium in boiling hexane a much longer reaction time of 19 hours is required for the complete consumption of **1** (eq. 1), similar to the reaction of **1** with elemental selenium[1]. Probably, this difference is due to the higher solubility of sulfur in hot hydrocarbon solvents. Complete decomposition is observed in boiling toluene with quantitative formation of tris(trimethylsilyl)methane. Both indium-chalcogen derivatives were isolated in about 80% yield by recrystallization from cyclopentane/toluene mixtures (**2**; X = S) or from pure pentane (**3**; X = Te). The crystals of **2** include solvent molecules which are released under very mild conditions, and the crystals become amorphous immediately after they are separated from the solvent even at low temperatures and without evacuation. **3** crystallizes as a strongly intergrown solid with 1 to 1.5 molecules of pentane per formula unit.

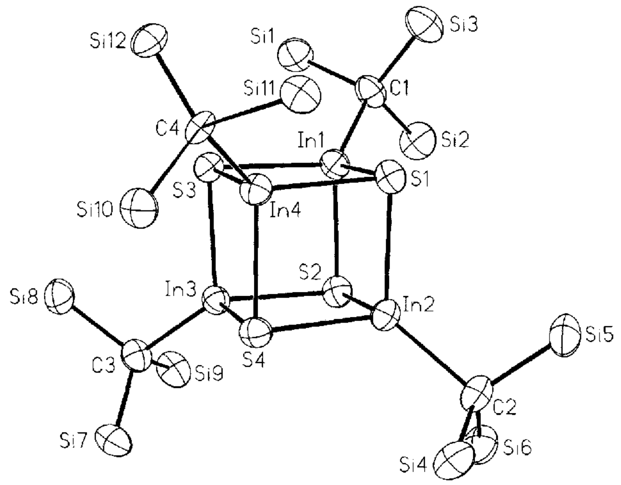
$$\underset{\mathbf{1}}{In_4[C(SiMe_3)_3]_4} + 4\,X \longrightarrow \underset{\mathbf{2}\ (X\,=\,S);\ \mathbf{3}\ (X\,=\,Te)}{In_4X_4[C(SiMe_3)_3]_4} \qquad (1)$$

The properties of **2** and **3** are nearly indistinguishable and very similar to those of the In_4Se_4 analog[1]. The compounds are sparingly soluble in benzene, and we did not succeed in determining the molar mass by cryoscopic methods. They show the same chemical shifts in the ^1H-NMR spectra with $\delta = 0.44$ for the $SiMe_3$ groups and exhibit very similar patterns in the IR spectra between 250 and 1500 cm^{-1}. The decomposition points decrease with increasing mass of the chalcogen from 375 °C for **2** (X = S) to 350 °C for X = Se[1] and 330 °C for **3** (X = Te). A remarkable difference results from the color of these compounds: The sulfur and selenium derivatives are both colorless, while the tellurium derivative **3** is bright yellow. The UV/Vis spectra exhibit two intensive absorptions at about 260 and 280 nm for all three indium chalcogenides, but only for **3** (X = Te) an additional absorption is observed at 378 nm. To our knowledge only two organoindium tellurolates were published[6], from which the phenyltellurol derivative is described as yellow, while an alkyl derivative is colorless. UV/Vis investigations were not carried out. Reactions of **1** with tellurium are described in a recent article[2], but the compound obtained differs significantly from **3**, and the In-to-Te ratio was given as 2:1. The constitution of the product could not be solved by a crystal structure determination. A similar reaction of the Al(I) compound $Al_4(C_5Me_5)_4$[7,8] with elemental tellurium yielding an Al_4Te_4 heterocubane derivative was recently published by Roesky et al.[8].

Crystal Structures of 2 and 3

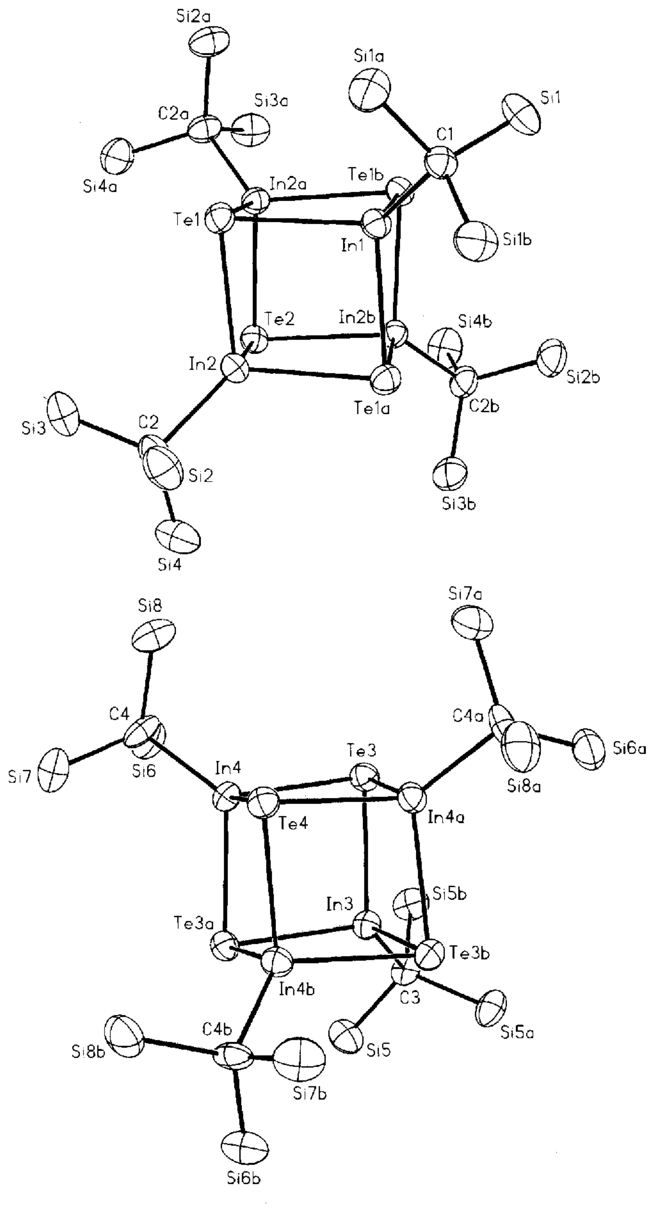
Although we tried a multitude of pure solvents and mixtures of solvents, we had enormous problems in growing single crystals suitable for an X-ray structure analysis with both derivatives; the experimental details are described in the experimental section. Figures 1 (**2**) and 2 (**3**) show the molecular structures of both compounds. They exhibit an In_4S_4 or In_4Te_4 heterocubane center with an alternating occupation of the vertices by indium and chalcogen atoms. The cubes are considerably distorted, and the inner cage angles at the In atoms (**2**: 93.1° and **3**: 95.6°) are larger on average than the angles In−S−In (86.8°) and In−Te−In (83.7°). These values are similar to those found with the selenium derivative[1] or in compounds with indium-chalcogen heterocubanes containing the $Fe(C_5H_5)(CO)_2$ or $Mo(C_5H_5)(CO)_2$ ligand[9] instead of the alkyl substituent in **2** and **3**.

Figure 1. Molecular structure of **2**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; only one position is drawn from the statistically disordered $C(SiMe_3)_3$ group. Selected bond lengths [pm] and angles [°]: In1−S1 255.3(2), In1−S2 253.6(2), In1−S3 256.0(2), In2−S1 255.4(2), In2−S2 253.8(2), In2−S4 255.1(2), In3−S2 254.0(2), In3−S3 255.3(2), In3−S4 255.1(2), In4−S1 255.4(2), In4−S3 254.6(2), In4−S4 254.8, In1−C1 220.3(8), In2−C2 219.4(8), In3−C3 219.5(8), In4−C4 223 (average); S1−In1−S2 93.04(7), S1−In1−S3 92.67(7), S2−In1−S3 93.09(7), S1−In2−S2 92.98(7), S1−In2−S4 93.11(7), S2−In2−S4 93.17(7), S2−In3−S3 93.16(7), S2−In3−S4 93.14(7), S3−In3−S4 93.06(7), S1−In4−S3 92.97(7), S1−In4−S4 93.15(7), S3−In4−S4 93.29(7), In1−S1−In2 86.57(7), In1−S1−In4 87.05(7), In2−S1−In4 86.69(7), In1−S2−In2 87.26(7), In1−S2−In3 87.20(7), In2−S2−In3 87.02(7), In1−S3−In3 86.42(7), In1−S3−In4 87.10(7), In3−S3−In4 86.74(7), In2−S4−In3 86.52(6), In2−S4−In4 86.88(7), In3−S4−In4 86.73(6)



The indium-chalcogen distances differ only slightly from the mean values (**2**: 254.9 and **3**: 286.4 pm) and are within the region usually observed in alkylthiolato or tellurolato compounds with In−S[10] or In−Te[6,9] bonds and tetracoordinated In atoms. Much shorter In−S bonds are observed in the case of a tri-*tert*-butylphenylthiolato compound with a tricoordinated In atom (239.8 pm)[11] or in the ether adduct of tris[tris(trifluoromethyl)phenylthiolato]indium (241.8 pm)[12]. The In···In distances are largest in the Te derivative **3** (382.9 pm) and correspond to twice the In van der Waals radius (380 pm[13]). They become shorter with the lighter chalcogen atoms showing values of 362.1 pm (X = Se[1]) and 350.4 pm (**2**, X = S), respectively. In contrast, the chalcogen-chalcogen distances of all three cage compounds are larger than the sum of the van der Waals

Figure 2. Molecular structures and numbering schemes of the two independent molecules of **3**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity. Selected bond lengths [pm] and angles [°]: Te1−In1 287.4(1), Te1−In2 286.6(2), Te1−In2a 285.3(1), Te2−In2 286.5(2), Te3−In3 287.2(1), Te3−In4 285.4(1), Te3−In4a 286.5(2), Te4−In4 286.2(2), In−C1 227(3), In2−C2 221(1), In3−C3 220(2), In4−C4 220(1); In1−Te1−In2 84.15(4), In1−Te1−In2a 84.37(4), In2−Te1−In2a 83.66(5), In2−Te2−In2 83.46(5), In3−Te3−In4 84.34(4), In3−Te3−In4a 84.14(4), In4−Te3−In4a 83.56(5), In4−Te4−In4 83.45(5), Te1−In1−Te1 95.13(5), Te1−In2−Te1a 95.78(5), Te1a−In2−Te2 96.25(4), Te1−In2−Te2 95.96(4), Te3−In4−Te3a 95.74(5), Te3−In4−Te4 96.29(4), Te4−In4−Te3a 96.03(4)



radii[13]: Te–Te 425.2 in comparison with 420 pm, Se–Se 392.1[1] to 380 pm, and S–S 370.0 to 360 pm. This can be attributed to the charge separation between the electronegative chalcogen atoms and the more electropositive indium atoms leading to a repulsion between the negatively charged chalcogen atoms. The difference between indium-indium and chalcogen-chalcogen distances grows significantly from the sulfur (**2**, 20 pm) to the tellurium derivative (**3**, 42 pm) and indicates that the In_4Te_4 cage is the most distorted one, as can also be seen from Figures 1 and 2. Similar structural relations exist between an In_4N_4[14] and an In_4P_4 heterocubane compound[15]. The In–C bond lengths amount to 221 (**2**) and 222 pm (**3**), which is the region normally observed for compounds with tetracoordinated indium atoms[16]. These values are smaller than those found for the starting compound tetraindane(4) **1**, which exhibits an In–C bond length of 225 pm[1].

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Experimental

All procedures were carried out under purified argon in dried solvents (*n*-hexane, *n*-pentane, and cyclopentane with $LiAlH_4$, toluene and *o*-xylene with Na/benzophenone). Compound **1** was prepared as described in ref.[1]; S and Te powders from Ventron GmbH were used without further purification.

Synthesis of **2** ($In_4S_4R_4$): 0.63 g (0.46 mmol) of **1** and 0.23 g (7.2 mmol) of sulfur powder were suspended in 50 ml of *n*-hexane, and the suspension was heated at reflux for 20 min. The color of the mixture changed from deep violet for **1** to pale yellow, and a small amount of a grey powder of probably elemental indium precipitated, which was filtered off. The filtrate was cooled to −20 °C to crystallize excess sulfur. The supernatant solution was separated, the solvent removed in vacuo and the residue recrystallized from mixtures of cyclopentane and toluene. Yield: 0.61 g of **2** (81%); colorless, fairly air-stable crystals; m.p. (closed capillary, argon): 375 °C (dec.). – ^1H NMR (C_6D_6; 300 MHz): $\delta = 0.44$. – ^{13}C NMR (C_6D_6; 75.5 MHz): $\delta = 6.82$ ($SiMe_3$), 24.1 (InC). – IR (paraffine, CsBr): $\tilde{\nu} = 1298$ w cm^{-1}, 1260 s, 1250 s δCH_3; 1169 w, 1157 vw, 1108 vw, 1040 w, 970 vw; 858 vs, 841 vs, 777 m, 721 m $\rho CH_3(Si)$; 679 m, 656 m $\nu_{as}SiC$; 608 m ν_sSiC; 521 w, 465 w νInC. – $C_{40}H_{108}In_4S_4Si_{12} \cdot C_5H_{10}$ (1584.0): calcd. C 34.1, H 7.5, In 29.0, S 8.1; found C 33.9, H 7.6, In 28.5, S 7.8.

Synthesis of **3** ($In_4Te_4R_4$): 0.89 g (0.64 mmol) of **1** and 0.40 g (3.13 mmol) of tellurium powder were suspended in 100 ml of *n*-hexane, and the suspension was heated at reflux for 19 h. After cooling to room temp. excess Te was allowed to settle, and the supernatant solution was cautiously decanted. The solvent was evaporated at room temp. and the residue recrystallized from *n*-pentane or cyclopentane. The crystals were thoroughly vacuum-dried. Yield: 1.06 g of **3** (83%); yellow, fairly air-stable crystals with 1 to 1.5 molecules of pentane per formula unit; m.p. (closed capillary, argon): 330 °C (dec.). – ^1H NMR (C_6D_6; 300 MHz): $\delta = 0.44$. – ^{13}C NMR (C_6D_6; 75.5 MHz): $\delta = 6.84$ ($SiMe_3$); InC not detectable. – IR (paraffine, CsBr): $\tilde{\nu} = 1269$ cm^{-1} s, 1254 s δCH_3; 1169 w, 1074 w, 1059 w, 1044 w; 957 w, 858 vs, 841 sh, 775 m, 754 w, 721 m $\rho CH_3(Si)$; 679 m, 654 m $\nu_{as}SiC$; 617 w, 594 m ν_sSiC; 465 w νInC; 363 w δSiC. – UV (*n*-pentane), λ_{max} (lg ε): 240 (4.6), 266 (4.5), 310 (sh, 4.0), 378 (3.1). – $C_{40}H_{108}In_4Si_{12}Te_4 \cdot 1.5\ C_5H_{10}$ (2001.2): calcd. C 28.5, H 6.2, In 23.0, Te 25.5; found C 28.2, H 6.1, In 23.2, Te 24.7.

Crystal Structure Determination of **2**: Crystals of **2** by crystallization from *o*-xylene; only twinned crystals were obtained, from which one single crystal was cut under a polarizing microscope; $C_{40}H_{108}In_4S_4Si_{12} \cdot 1.5\ C_6H_4Me_2$; crystal size 0.8 × 0.5 × 0.4 mm; four-circle diffractometer AED2; ω-2Θ scan; temperature 20 °C; monoclinic; $P2_1/n$ (Nr. 14[17]); $a = 1674.41(9)$, $b = 2306.3(1)$, $c = 2373.5(1)$ pm, $\beta = 90.95(1)°$; $V = 9164 \cdot 10^{-30}$ m^3; $d_{calcd.} = 1.202$ g/cm^3; $Z = 4$ (four independent cage molecules and twelve *o*-xylene fragments refined with an occupancy factor of 0.5 with restraints of bond lengths and angles giving 1.5 molecules of the solvent per formula unit; the integration of the signals of the ^1H-NMR spectrum reveals 2.5 molecules of the solvent per formula unit); 2Θ range $3 \leqslant 2\Theta \leqslant 50°$; μ(Mo-K_α) = 1.27 mm^{-1}; 16102 independent reflections; 700 parameters; programs SHELXTL PLUS and SHELXL-93[18]; structure solution by direct methods; refinement by the full-matrix least-squares method with all independent structure factors; $wR^2 = 0.199$; $R_1 = 0.064$ for 9176 $F > 4\sigma(F)$; max./min. residual electron density 1.49 (in the region of the solvent molecules)/−0.56 · 10^{30} e/m^3; the $C(SiMe_3)_3$ group with the central carbon atom C4 is statistically disordered with C4 and the silicon atoms Si10, Si11, and Si12 in two positions, while the methyl carbon atoms of the disordered groups occupy identical positions[19].

Crystal Structure Determination of **3**: Crystals of **3** by crystallization from cyclopentane of a toluene-containing solid precipitated from pure toluene; $C_{40}H_{108}In_4Si_{12}Te_4 \cdot$ 1.5toluene; crystal size 0.4 × 0.4 × 0.1 mm; four-circle diffractometer AED2; ω-2Θ scan; temperature 20 °C; trigonal; $P3$ (Nr. 143[17]); $a = 1607.9(2)$, $c = 1841.1(2)$ pm; $V = 4122 \cdot 10^{-30}$ m^3; $d_{calcd.} = 1.615$ g/cm^3; $Z = 2$ (two independent cage molecules on different crystallographic threefold axes of rotation and three toluene molecules disordered around threefold axes with the methyl groups not detectable); 2Θ range $3.7 \leqslant 2\Theta \leqslant 50°$; μ(Mo-K_α) = 2.69 mm^{-1}, empirical absorption correction; 5003 independent reflections; 411 parameters; programs SHELXTL PLUS and SHELXL-93[18]; structure solution by direct methods; refinement by the full-matrix least-squares method with all independent structure factors; $wR^2 = 0.116$; $R_1 = 0.039$ for 3901 $F > 4\sigma(F)$; max./min. residual electron density 0.85/−0.53 · 10^{30} e/m^3; the $C(SiMe_3)_3$ groups located on crystallographic threefold axes of rotation are disordered similar to the structure of **2**, but the ratio of the occupancy factors is 9:1[19].

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