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AN ALKYL-SUBSTITUTED INDIUM(I) TETRAMER

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NOTE

AN ALKYL-SUBSTITUTED INDIUM(I) TETRAMER

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The first indium(I) alkyl, $[\text{InC}(\text{SiMe}_3)_3]_4$ (**1**), has been prepared by treatment of InCl with $\text{LiC}(\text{SiMe}_3)_3 \cdot 2\text{THF}$ in Et_2O solution. Compound **1** crystallizes in the space group $Pnma$ with $a = 30.465(2)$, $b = 13.855(2)$, $c = 17.824(2)\text{\AA}$, and $Z = 4$. Individual molecules of **1** feature a tetrahedral In_4 core with an average indium-indium distance of $3.09(2)\text{\AA}$.

KEY WORDS: Indium(I), tetramer, structure, reactivity.

INTRODUCTION

Examples of organometallic indium(I) compounds are confined to cyclopentadienyl and aryl derivatives.¹ At low degrees of steric loading, the cyclopentadienyl-substituted compounds adopt polymeric zigzag structures in the solid state. However, use of the bulky C_5Me_5 and $\text{C}_5(\text{PhCH}_2)_5$ ligands results in novel hexameric² and dimeric³ structures, respectively. Recent interest in these species has been sparked by the question of indium-indium bonding.⁴ In this communication we report the first alkyl-substituted indium(I) compound, the first indium(I) tetramer, and significantly shortened indium(I)-indium(I) distances.

EXPERIMENTAL

*Preparation of $[\text{InC}(\text{SiMe}_3)_3]_4$ (**1**)*

Compound **1** was prepared by the addition of $\text{LiC}(\text{SiMe}_3)_3 \cdot 2\text{THF}$ ⁵ (0.64 g, 1.6 mmol) in 50 cm^3 of Et_2O *via* cannula to a slurry of InCl (0.25 g, 1.6 mmol) in 20 cm^3 of Et_2O at -78°C . The stirred reaction mixture was allowed to warm slowly to ambient temperature, during which time the color changed from red to purple. After removal

of the Et₂O under reduced pressure, the residue was extracted with hexane. Following filtration, the filtrate was concentrated and cooled to -20°C , thereby affording 0.28 g (51% yield) of dark purple crystalline **1** (mp 185°C). ¹H NMR (300.15 MHz, C₆D₆, 295 K, TMS ext.): δ 0.45 (s). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 295 K, TMS ext.): δ 7.14 (s). CIMS (CH₄): *m/e* 692, [$\{\text{InC}(\text{SiMe}_3)\}_2$]⁺; 677, [$\{\text{InC}(\text{SiMe}_3)_2\text{-Me}\}$]⁺; 346, [$\text{InC}(\text{SiMe}_3)_3$]⁺; 331, [$\text{InC}(\text{SiMe}_3)_3\text{-Me}\}$]⁺. UV-VIS: (hexane): $\lambda(\text{\AA})$ ($9.25 \times 10^{-4} \text{ M}$) = 486 (ϵ 700), 326 (ϵ 3700), 286 (ϵ 3050). Anal. Calcd for C₄₀H₁₀₈In₄Si₁₂: C, 34.67; H, 7.86%. Found: C, 34.60; H, 7.21%.

For compound **3**: CIMS (CH₄): *m/e* 772 (M⁺). ¹H NMR (300.15 MHz, C₆D₆, 295 K, TMS ext.): δ 0.32 (s). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 295 K, TMS ext.): δ 6.18 (s).

For compound **4**: CIMS (CH₄): *m/e* 822 (M⁺). ¹H NMR (300.15 MHz, C₆D₆, 295 K, TMS ext.): δ 0.36 (s). ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 295 K, TMS ext.): δ 6.21 (s).

X-ray Crystal Structure Analysis of [InC(SiMe₃)₃]₄ (1)

Single crystals of **1** suitable for X-ray analysis were grown by cooling a hexane solution to -20°C for 24 h. The X-ray crystal structure of **1** was complicated by disorder problems. Nevertheless, the study established that, in the solid state, **1** consists of a tetramer with a tetrahedral In₄ core (Figure 1). Molecules of **1** crystallize in the orthorhombic space group *Pnma* with four molecules per unit cell. In the structure solution, indium atoms (1)–(3) were found to lie on a mirror plane with $y=0.25$. This leads to a disordered In(4) (50% occupancy) which is reflected through the In(1)–In(2)–In(3) plane to an equivalent position (50% occupancy). The indium atoms were refined with anisotropic thermal parameters. The C and Si atoms associated with In(4) were found from difference maps and allowed to refine isotropically with 50% occupancy. The C and Si atoms associated with indiums (1)–(3) were found to be disordered. The data set was not of sufficient quality to model the disorder effectively and hence these atoms were included in the refinement with fixed positional and thermal parameters. The final cycle of refinement converged at an *R* value of 15%. Crystal data: (C₄₀H₁₀₈In₄Si₁₂): orthorhombic, space group *Pnma* with

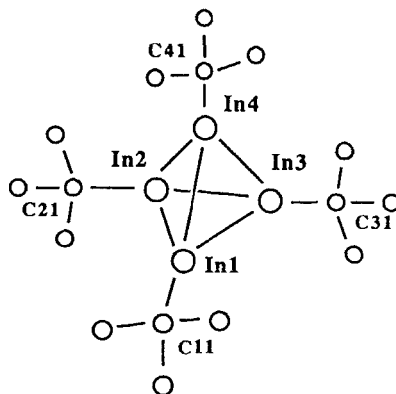


Figure 1 Idealized drawing of the structure of [InC(SiMe₃)₃]₄ (**1**) in the solid state. See text for a discussion of disorder problems. Important internuclear distances (Å): In(1)–In(2) 3.02 (2), In(1)–In(3) 2.98 (2), In(1)–In(4) 3.16 (2), In(2)–In(3) 3.02 (2), In(2)–In(4) 3.17 (2), In(3)–In(4) 3.18 (2).

$a = 30.465(2)$, $b = 13.855(2)$, $c = 17.824(2)$ Å, $V = 7523.4(4)$ Å³, $Z = 4$, $d_{\text{calcd}} = 1.228$ g cm⁻³, $\mu(\text{MoK}\alpha) = 14.072$ mm⁻¹. A total of 4762 independent reflections (1149 with $I > 3.0\sigma(I)$) was collected at 298 K on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.71069$ Å). All calculations were performed on a MICROVAX 3100 computer using the SHELX programs.

RESULTS AND DISCUSSION

As pointed out by Janiak and Hoffmann,^{4a} the ligand environment in In(I) and Tl(I) complexes plays a decisive role in the observed solid state structure. The only previous non-polymeric In(I) organometallics are the hexamer $[\text{In}(\text{C}_5\text{Me}_5)]_6$ ² and the dimer $[\text{In}\{\text{C}_5(\text{CH}_2\text{Ph})_5\}]_2$.³ The fact that **1** is a tetramer presumably related to the distinctive packing requirements of the $(\text{Me}_3\text{Si})_3\text{C}$ ligand. A further noteworthy feature of **1** concerns the short In-In distances, which average 3.09(2) Å. The average In-In distances in $[\text{In}(\text{C}_5\text{Me}_5)]_6$ (3.952(1) Å)² and $[\text{In}\{\text{C}_5(\text{CH}_2\text{Ph})_5\}]_2$ (3.631(2) Å)³ are considerably longer and comparable to the interchain contacts in, e.g., polymeric $[\text{In}(\text{C}_5\text{H}_5)]_\infty$ (3.986(1) Å).⁶ In the absence of calculations on a representative alkylindium(I) tetramer, it is difficult to ascribe the shortened In(I)/In(I) distances in **1** to enhanced indium-indium bonding. We note, however, that **1** exhibits an absorption in the visible region at 486 Å and that this might be associated with metal-metal bonding.

Preliminary investigations reveal that **1** is quite reactive. Thus, exposure to moist air at 25°C results in slow conversion of **1** to the known⁷ cage compound $[\text{O}\{(\text{Me}_3\text{Si})_3\text{CIn}\}_4(\text{OH})_6]$ (**2**). The reaction of **1** with elemental selenium and tellurium in refluxing hexane affords the chalcogenide derivatives $[\text{In}_2\{\text{C}(\text{SiMe}_3)_3\}_2\text{Se}]$ (**3**) and $[\text{In}_2\{\text{C}(\text{SiMe}_3)_3\}_2\text{Te}]$ (**4**), respectively. So far, we have not obtained crystals of **3** and **4** suitable for X-ray analysis. However, on the basis of spectroscopic data, and by analogy with the lighter congeneric species $[\text{B}_2\{\text{C}(\text{SiMe}_3)_3\}_2\text{O}]$,⁸ they can be assigned three-membered In_2Se and In_2Te ring structures.

Acknowledgements

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Supplementary Data

Full lists of atomic coordinates, bond lengths and angles, thermal parameters and observed and calculated structure factors are available from the authors on request. Full details concerning crystal data and refinement parameters are also available.

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