Synthesis and crystal structure
of pentabenzylcyclopentadienylindium(I)

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Abstract

$(PhCH_2)_5C_5In^I$ (**1**) is formed in the reaction between InCl and $(PhCH_2)_5C_5Li$. **1** crystallizes in the space group $P2_1/c$ with a 1022.8(1), b 1575.3(2), c 1871.3(3) pm, β 91.01(1)°, and V 3014.6×10^{-30} m³. The crystal and molecular structure was solved to final values of $R = 0.025$ for 5545 observed reflections with $F_0 \geq 4\sigma(F_0)$. The association of two single molecules, via a center of symmetry between the two In atoms, gives the impression of quasi-"dimeric" units with an In–In distance of 363.1 pm and predominantly covalent In–C bonds. ^1H NMR, ^{13}C NMR, infrared, and mass spectroscopic data are reported.
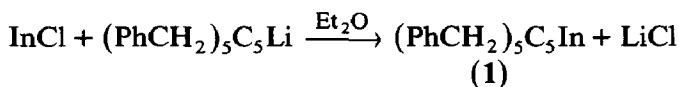
Introduction

As one aspect of the considerable interest in low-valent main-group organometallic species cyclopentadienyl-indium(I) [1–3] and -thallium(I) [4–14] complexes have been investigated in respect of their synthesis and structure and the theoretical understanding of the η^5-C_5–In and η^5-C_5–Tl interactions [15,16]. X-Ray structural studies reveal zig-zag polymeric chains of alternating E (E = In, Tl) and C_5 units for most of the indium(I) and thallium(I) cyclopentadienides, with long E–C_5 distances [1,7,9,17–19] indicating a highly ionic character of the E–C_5 bond [16]. Exceptions to this type of structure are found for $\{(PhCH_2)_5C_5Tl\}_\infty$ (linear chains of covalently bonded monomers) [4], $\{1,3\text{-}(Me_3Si)_2C_5H_3Tl\}_6$ (cyclic hexameric "doughnut" molecules) [7], $\{(PhCH_2)_5C_5Tl\}_2$ (quasi-"dimeric" units of covalently bonded monomers) [8], $\{Me_5C_5In\}_6$ (hexameric octahedral clusters) [3], and for $C_5H_5Co[\mu\text{-}Me_2C_2(Me_2B)CH]Tl$ (discrete, monomeric molecules) [13]. It is evident that the substituents on the C_5 ring strongly influence the physical properties and structures of the indium or thallium complexes. Bulky ligands tend to reduce the intermolecular interactions, leading to oligomeric or monomeric molecules with an increase in

the covalency of the E–C$_5$ bond. In the gas phase, however, probably all C$_5$–E compounds exist as discrete monomers [1–4,6–9,11,20,21], with In–C or Tl–C distances significantly shorter than those in the polymeric solids [1,16,20,21], thus proving that monomer formation and increasing covalency go hand-in-hand.

The pentabenzylcyclopentadienyl ligand, (PhCH$_2$)$_5$C$_5$$^-$, has been successfully employed in thallium(I), germanium(II), tin(II) and lead(II) organometallic chemistry. It gives complexes of much greater stability than the related compounds containing less-substituted cyclopentadienyl ligands. The complexes also have very interesting structures [4,8,22,23]. Thus (PhCH$_2$)$_5$C$_5$$^-$ promise to be a suitable ligand also for the synthesis of a comparatively stable and, so well-characterizable indium(I) derivative. Furthermore, the structure of (PhCH$_2$)$_5$C$_5$In (1) should provide a better understanding of the bonding situation in the quasi-"dimeric" {(PhCH$_2$)$_5$C$_5$Tl}$_2$ [8] and the hexameric {Me$_5$C$_5$In}$_6$ cluster [3].

Synthesis and properties

Pentabenzylcyclopentadienylindium(I) (1) is easy to prepare from InCl [24] and (PhCH$_2$)$_5$C$_5$Li [22] in diethyl ether at room temperature. Reduction of InCl is observed as a side-reaction, leading to a precipitate of grey indium metal.

$$InCl + (PhCH_2)_5C_5Li \xrightarrow{Et_2O} (PhCH_2)_5C_5In + LiCl$$
$$(1)$$

Complex 1 crystallizes from hexane as white parallelepipeds, or from a more concentrated hexane solution as needle-shaped crystals, which, upon addition of a little toluene are converted into the parallelepipeds. The analogous thallium compound shows the same allotropy [4,6,8]. The crystals of 1 are air-stable for some hours, and show no light sensitivity. However, there is some darkening of the crystals after some weeks even when they are stored in the dark under nitrogen at 5°C, and this is due to separation of indium metal. An attempt to recrystallize the parallelepipeds from toluene/hexane or to dissolve them in tetrahydrofuran (all the solvents were dried over liquid sodium/potassium alloy) resulted in an almost immediate decomposition to give black indium metal.

The ^{13}C NMR spectrum of 1 shows six signals, thus indicating free rotation and equilibration of the benzyl groups in solution, as previously observed for the thallium analogue [6] and for the decabenzylmetallocenes of germanium, tin, and lead [22] and iron [25].

Molecular structure

The molecular structure of 1 was determined by X-ray diffraction. The compound is isostructural with the analogous thallium complex. Two monomeric species (Fig. 1, showing the atom numbering scheme) are associated to a "quasi-dimer" via an inversion center between the two In atoms. Three of the five benzyl groups of each cyclopentadienyl ring are oriented toward the In atoms, thus enveloping the two metal atoms (Fig. 2). The unit cell packing of 1 is shown in Fig. 3.

The distance of 363.1 pm between the two In atoms of a "dimeric" unit is like that between the two Tl atoms (363.2 pm) in the "dimeric" unit of the correspond-
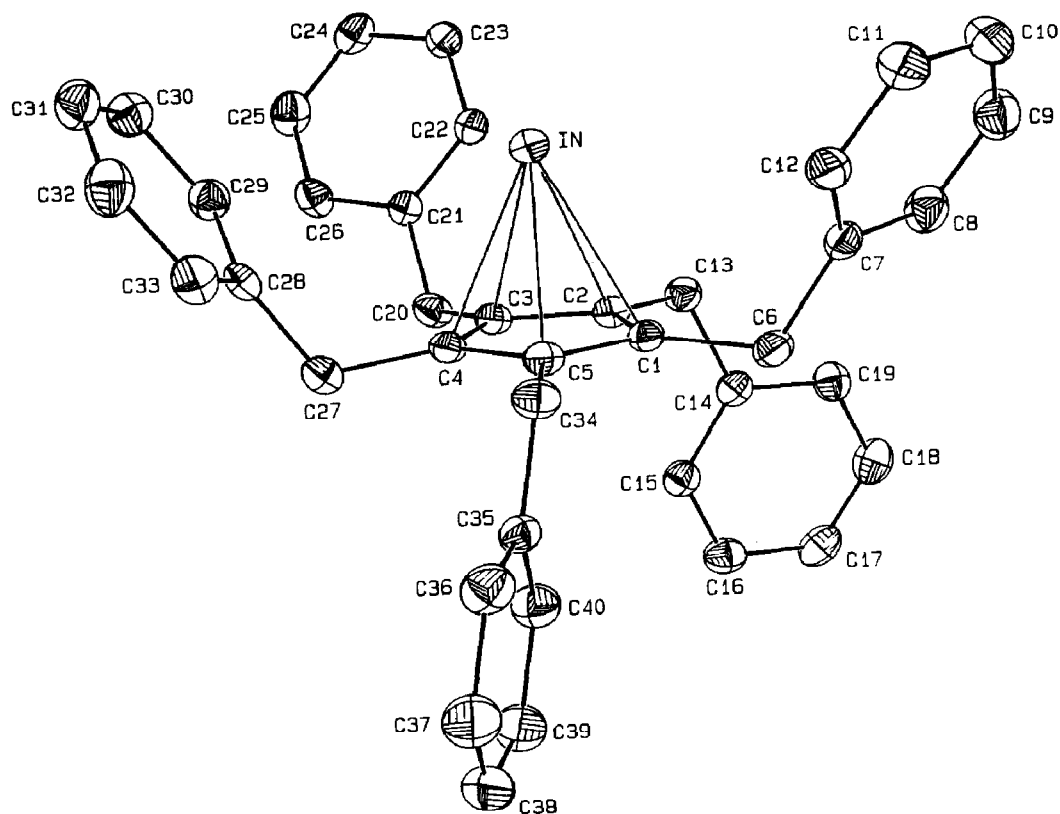
Fig. 1. ORTEP drawing [33] of **1**, with the numbering scheme. Thermal ellipsoids scaled at 50% probability level. Hydrogen atoms omitted for clarity.

ing Tl compound. However, this In–In distance is significantly shorter than the interchain In $\cdots$ In distances of 398.6(1) pm in $\{C_5H_5In\}_\infty$ and $\{MeC_5H_4In\}_\infty$ [1,19], or the intraclusteral In $\cdots$ In distances of 396.3(1) and 394.3(1) pm in $\{Me_5C_5In\}_6$, which are interpreted in terms of weak In–In interactions. Since the metal–metal distances are the same in the indium and thallium derivative, we suggest that the packing effect of the ligand enforces dimerization of these molecules by organic-envelope interaction rather than by metal–metal interaction. We also think that similar packing effects are responsible for the comparatively long interchain and intraclustural distances in the above-mentioned polymeric or hexameric In complexes.

The indium–carbon distances, ranging from 262.1(2) to 271.8(2) pm, (In–ring center 238.2(2)) (Table 2), are indicative of a high degree of covalent bonding even in the solid state [16,20], when compared with those for monomeric C_5H_5In (gas phase, average 262.1(5) pm) [20] and polymeric $\{C_5H_5In\}_\infty$ (solid state, range 285(2)–309(2) pm) [1], or monomeric MeC_5H_4In (gas phase, average 260.7(5) pm) [1] and polymeric $\{MeC_5H_4In\}_\infty$ (solid state, range 280.0(5)–292.4(5) pm) [1]. The In–C distances in the hexameric $\{Me_5C_5In\}_6$ are even shorter (range 258.1(4)–261.3(4) pm) [3]. The angle of 136.46(5)° at the indium (ring center–In–In′) is larger than the Cp–In–Cp angle in the polymeric $\{C_5H_5In\}_\infty$ (128.02° [1]), and is in same range as the Cp–Tl–Tl angle in the corresponding Tl′ compound

(131.8°). The smallest phenyl carbon–indium distance is between the *meta*-C atom C23 and the indium of the quasi-dimeric unit (In′ ⋯ C23) (3.475(2) pm). The atomic coordinates are given in Table 1. Relevant bond distances and angles for **1** are summarized in Table 2.

The protective shield around the In–In unit build up by the phenyl rings of six benzyl groups accounts for the air-stability of **1**. The solubility properties of **1**,

Table 1

Final atomic coordinates for **1** with estimated standard deviations in parentheses and equivalent isotropic thermal parameters ($\mathring{A}^2$)

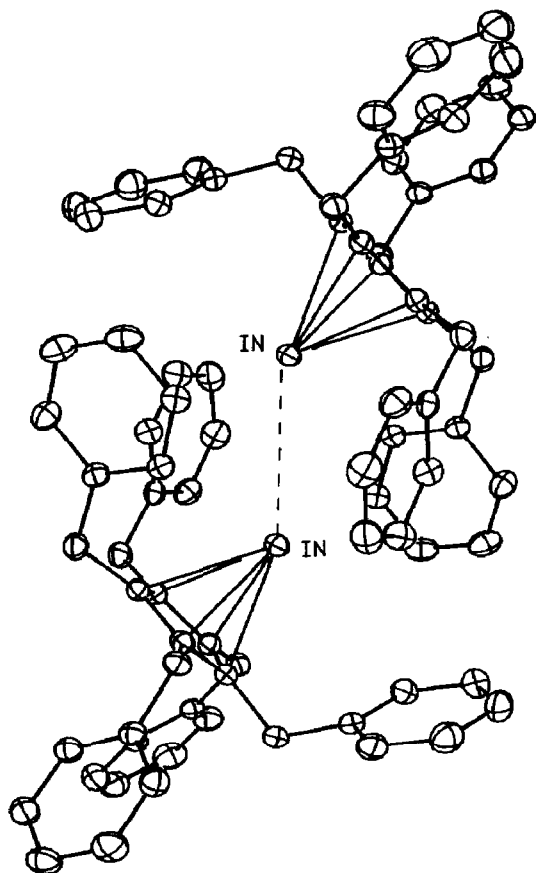| Atom	x	y	z	B_{eq}
In	0.0108(0)	0.0706(0)	0.5766(0)	1.63
C1	0.0875(2)	0.1978(1)	0.6617(1)	1.52
C2	0.1334(2)	0.2225(1)	0.5936(1)	1.53
C3	0.2322(2)	0.1642(1)	0.5734(1)	1.55
C4	0.2471(2)	0.1032(1)	0.6292(1)	1.54
C5	0.1569(2)	0.1240(1)	0.6839(1)	1.61
C6	−0.0083(2)	0.2481(1)	0.7057(1)	1.81
C7	−0.1518(2)	0.2393(1)	0.6848(1)	1.73
C8	−0.2202(2)	0.3060(1)	0.6537(1)	2.38
C9	−0.3534(2)	0.3000(2)	0.6383(1)	2.88
C10	−0.4207(2)	0.2270(2)	0.6544(1)	2.74
C11	−0.3536(2)	0.1594(2)	0.6855(1)	2.51
C12	−0.2203(2)	0.1650(1)	0.6997(1)	2.00
C13	0.0941(2)	0.3015(1)	0.5536(1)	1.83
C14	0.1517(2)	0.3839(1)	0.5837(1)	1.70
C15	0.2783(2)	0.3870(1)	0.6119(1)	1.88
C16	0.3328(2)	0.4640(1)	0.6333(1)	2.20
C17	0.2604(2)	0.5383(1)	0.6284(1)	2.45
C18	0.1337(2)	0.5354(1)	0.6021(1)	2.63
C19	0.0795(2)	0.4585(1)	0.5793(1)	2.15
C20	0.3149(2)	0.1721(1)	0.5080(1)	1.93
C21	0.2616(2)	0.1382(1)	0.4370(1)	1.63
C22	0.1315(2)	0.1476(1)	0.4147(1)	1.62
C23	0.0894(2)	0.1197(1)	0.3480(1)	1.87
C24	0.1765(2)	0.0825(1)	0.3014(1)	2.30
C25	0.3059(2)	0.0736(1)	0.3227(1)	2.58
C26	0.3475(2)	0.1003(1)	0.3897(1)	2.20
C27	0.3488(2)	0.0336(1)	0.6348(1)	1.95
C28	0.3083(2)	−0.0541(1)	0.6097(1)	1.67
C29	0.2962(2)	−0.0725(1)	0.5369(1)	2.03
C30	0.2655(2)	−0.1536(1)	0.5137(1)	2.40
C31	0.2445(2)	−0.2181(1)	0.5625(1)	2.66
C32	0.2550(2)	−0.2007(1)	0.6345(1)	2.74
C33	0.2878(2)	−0.1194(1)	0.6581(1)	2.29
C34	0.1450(2)	0.0789(1)	0.7541(1)	1.86
C35	0.2491(2)	0.1013(1)	0.8105(1)	1.64
C36	0.2601(2)	0.0524(1)	0.8722(1)	2.38
C37	0.3524(3)	0.0706(2)	0.9249(1)	2.99
C38	0.4369(2)	0.1382(2)	0.9161(1)	2.87
C39	0.4271(2)	0.1875(2)	0.8555(1)	2.82
C40	0.3330(2)	0.1696(1)	0.8026(1)	2.21

Fig. 2. An ORTEP plot emphasizing the quasi-dimeric association of two molecules of 1. Hydrogen atoms are omitted for clarity.

Table 2

Selected inter- and intra-molecular distances, angles, and torsion angles for 1 with estimated standard deviations in parentheses

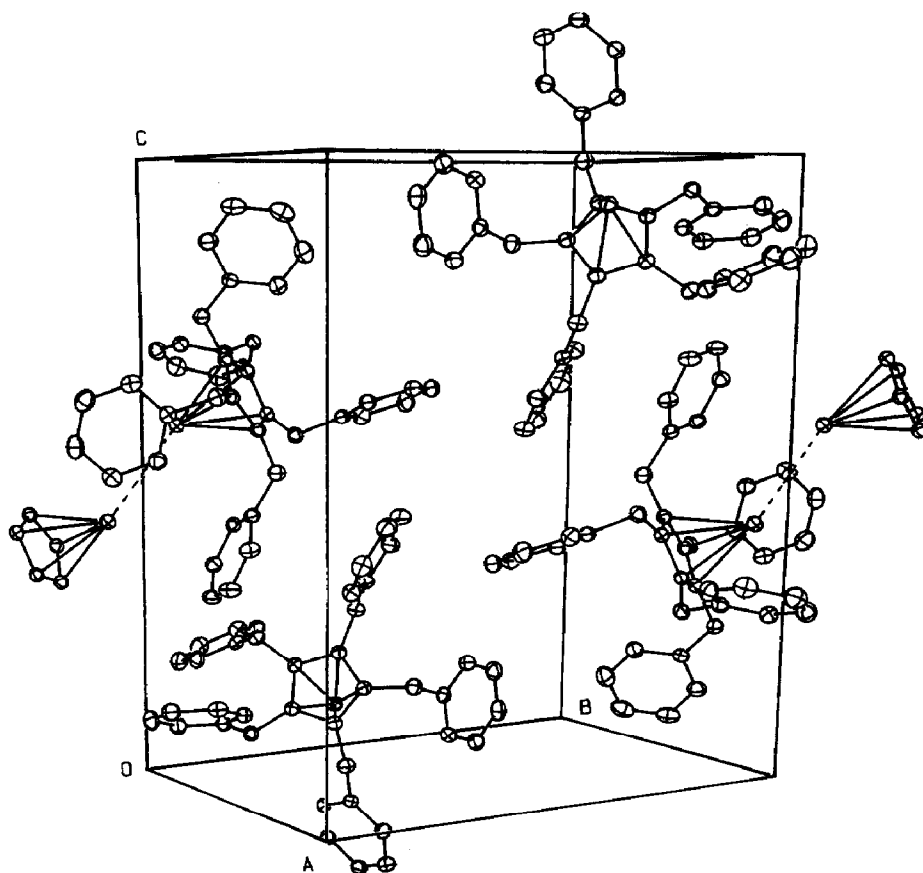| Distances [pm]					
In...In	363.1(2)	In–Cp [a]	238.2(2)	In...C22	350.7(2)
In...C12	364.8(2)	In'...C23	347.5(2)	In'...C30	352.0(2)
In–Cl	266.9(2)	In–C2	271.8(2)	In–C3	270.4(2)
In–C4	264.5(2)	In–C5	262.1(2)	In–$C_\eta s$(mean)	267.1
Angles [°]					
In'–In–Cp [a]	136.46(5)	C1–C6–C7	116.4(2)	C2–C13–C14	114.9(2)
C3–C20–C21	118.8(2)	C4–C27–C28	117.2(2)	C5–C34–C35	115.3(2)
Torsion angles [°]					
C5–C1–C6–C7	− 107.2(2)	C1–C2–C13–C14	73.3(2)		
C2–C3–C20–C21	− 84.9(2)	C3–C4–C27–C28	− 97.1(2)		
C4–C5–C34–C35	78.0(2)				

[a] Cp denotes the centroid of the cyclopentadienyl ring.

Fig. 3. A view of the molecular packing of 1 in the unit cell. Hydrogen atoms are omitted for clarity. The quasi-dimeric association with neighbouring molecules (only the cyclopentadienylindium unit is shown for clarity) is indicated by broken line.

especially its rapid decomposition upon redissolution, a behaviour apparently not observed to such extent with $\{C_5H_5In\}_\infty$ and $\{MeC_5H_4In\}_\infty$, cannot yet be explained.

Experimental

All experiments were carried out under purified nitrogen by use of flame-dried glassware and solvents distilled from liquid sodium/potassium alloy. Manipulations were performed by use of standard Schlenk and vacuum techniques. NMR tubes and melting-point capillaries were sealed under vacuum.

Pentabenzylcyclopentadienylindium (1). A pink solution of $(PhCH_2)_5C_5Li$, freshly prepared from $(PhCH_2)_5C_5H$ [26] (1.38 g, 2.66 mmol) and n-butyllithium (1.74 ml, 1.53 molar in hexane) in diethyl ether (20 ml) at $0\,^\circ C$, was added dropwise to the yellow slurry of InCl [24] (0.40 g, 2.66 mmol) in 20 ml of ether at $-78\,^\circ C$. The first drops produced a grey precipitate of some indium metal. When addition was complete mixture was allowed to warm to room temperature. Since much of the InCl was evidently still present rapid stirring was continued at room temperature for 15 h, after which the grey precipitate was allowed to settle and the light yellow

solution decanted. The volume of the solution was reduced to about 15 ml but ice cooling did not lead to crystallization, and so the ether was removed in vacuo and the white sticky residue taken up in hexane (30 ml) but with a small amount of solid left undissolved to induce crystallisation, which took place when the solution was cooled in ice. The product was obtained as white parallelepipeds (yield 0.86 g, 51%; m.p. 110–113°C, partial dec.). ^{1}H NMR [27*] (C_6D_6, conc. 200 mg/ml): δ (ppm) 3.88 (s, 10 H, CH_2), 7.19 ("s", 25 H, C_6H_5-). ^{13}C NMR [27*] (C_6D_6, conc. 200 mg/ml): δ (ppm) 31.78 (CH_2–C), 120.33 (C_5–C), 125.96 (para-Ph–C), 128.57 (meta-Ph–C), 128.99 (ortho-Ph–C), 144.44 (quaternary-Ph–C). MS [28*] (70 eV, 220°C): m/e (%) = 630 (65) [$(PhCH_2)_5C_5In$]$^+$ = M^+, 516 (20) [$(PhCH_2)_5C_5$ + H]$^+$, 515 (17) mostly ^{13}C isotope peak of 514, 514 (33) [$(PhCH_2)_5C_5$ – H]$^+$, 425/423 (11/8) [516/514 – $PhCH_2$ (= 91)]$^+$, 345 (5) [514 – $PhCH_2$ – PhH]$^+$, 331 (7) [514 – $PhCH_2$ – $PhCH_3$]$^+$, 255/254 (10/10) [514 – 2$PhCH_2$ – Ph/H]$^+$, 241 (7) [514 – 3$PhCH_2$]$^+$, 167 (10) [$C_{13}H_{11}$]$^+$, 115 (44) [In]$^+$, 91 (100) [$PhCH_2$ = C_7H_7]$^+$. IR [29] 3100(vw), 3080(w), 3055(m), 3020(m), 2995(vw), 2920(m), 2840(w), 1950(w,br), 1870(w,br), 1820(w,br), 1600(m), 1580(w), 1490(s), 1451(sh), 1420(w), 1325(w), 1290(w,br), 1275(w), 1260(w), 1195(vw), 1182(w), 1150(w), 1120(vw), 1075(m), 1030(m), 1000–800(w/vw), 750(m), 745(m), 730(m), 720(m), 700(s), 665(w), 650(vw), 633(w), 620(vw), 590(vw), 570(w), 470(w), 460(m), 320(m). Found: C, 76.35; H, 5.73; In, 18.19. $C_{40}H_{35}In$ (630.54) calc.: C, 76.20; H, 5.59; In, 18.21%.

X-ray structural analysis

Complex 1 crystallizes as white cubes. A crystal of dimensions 0.29 × 0.36 × 0.29 mm^3 was used; monoclinic, $P2_1/c$ from intensity statistics and structure refinement; cell parameters from 56 reflections (2θ range 46–53°); a 1022.8(1), b 1575.3(2), c 1871.3(3) pm, β 91.01(1); Mo-K_α radiation (graphite monochromator); 6992 unique reflections; intensities of all reflections with $1° \leq 2\theta \leq 54°$ measured at 140(5) K; $-13 \leq h \leq 13$, $0 \leq k \leq 20$, $0 \leq l \leq 23$; ω–2θ scan technique, variable scan width $(0.85 + 0.30 \tan \theta)°$, variable horizontal receiving aperture 2.00 mm; three standard reflections measured every 1.5 h of X-ray exposure time, maximal fluctuation 1%; three orientation control reflections measured every 100 data, and a new orientation matrix computed from a list of 25 reflections if angular change of the control reflections was more than 0.07°; 155 h of X-ray exposure time; no decay correction, Lorentz and polarization correction, empirical absorption correction (μ 7.28 cm^{-1}, psi scan method, max. transmission 99.9%, min. transmission 96.0%); 5545 observed structure factors with $F_0 \geq 4$ $\sigma(F_0)$; structure determined by Patterson method and succesive difference Fourier syntheses; refinement by block-diagonal least squares in which the quantity $\Sigma w(|F_0| - |F_c|)^2$ was minimized; non-hydrogen atoms refined anisotropically, all hydrogen atoms located and refined isotropically; R 0.025, R_w 0.033 for 510 parameters and 5545 reflections ($F_0 \geq 4$ $\sigma(F_0)$); maximum ratio of shift to error $(\Delta/\sigma) = 0.002$; maximum electron density in final difference Fourier map 0.71 e Å^{-3} close to the indium position.

All X-ray measurements were made with an Enraf–Nonius CAD-4 automatic diffractometer fitted with a low temperature set up; scattering factors and anomalous dispersion terms for C and In were taken from International Tables of X-Ray

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* Reference number with asterisk indicates a note in the list of references.

Crystallography [30], and scattering factors for H from Stewart, Davidson and Simpson [31]; all calculations were by SHELX76 [32]. The final atomic parameters are given in Table 1. Further details of the structure determination are available on request from the Fachinformationszentrum Energie, Physik and Mathematik, D-5714 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-53499, the names of the authors, and the journal citation.

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