Two molecular stannaindoxanes and one molecular indium hydrogen carbonate cluster comprising trinuclear oxygen-bridged structures

Syed Usman Ahmad[1] and Jens Beckmann[1,2,*]

[1] Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstr. 34/36, D-14195 Berlin, Germany
[2] Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Str. NW2, D-28359 Bremen, Germany

* Corresponding author
 e-mail: j.beckmann@uni-bremen.de

Abstract

Two trinuclear stannaindoxanes $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})(t\text{-Bu}_2\text{Sn})_2$ $(\mu_3\text{-O})(\mu\text{-OH})_2(\mu\text{-Cl})\text{Cl}$ (**1**) and $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})_2(t\text{-Bu}_2\text{Sn})$ $(\mu_3\text{-O})\text{O}(\mu\text{-OH})_2$ (**2**) were obtained by the reaction of $(t\text{-Bu}_2\text{SnO})_3$ with $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-Cl})\text{Cl}]_2$ and $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-OH})_2]_4$, respectively. Attempts at crystallizing **2** by slow evaporation of a CHCl_3 solution proceeded with the advantageous absorption of CO_2 from the air and yielded the trinuclear indium hydrogen carbonate cluster $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})_3(\text{CO}_3\text{H})_2(\mu\text{-OH})_4$ (**3**). More rationally, **3** was prepared when a CHCl_3 solution of $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-OH})_2]_4$ was purged with gaseous CO_2.

Keywords: carbonate; indium; indium tin oxide (ITO); tin.

Introduction

Thin films of transparent conducting oxides based on tin-doped indium oxide (ITO) have found numerous applications as transparent electrodes including display devices (flat-panel technology), light-emitting diodes, and photovoltaics (solar cells) (Chopa et al., 1983; Tahar et al., 1998). Thin films of ITO were conventionally applied by methods such as sputtering techniques, chemical vapor deposition, and sol-gel processes as well as spray pyrolysis. However, molecular compounds containing Sn-O-In linkages are rare. Veith and Kunze (1991) reported the dinuclear In(I)/Sn(II) alkoxide $\text{In}(t\text{-BuO})_3\text{Sn}$ (ITBO), which undergoes smooth reactions with chromium and molybdenum hexacarbonyls to give the transition metal complexes $(\text{CO})_5\text{MIn}$ $(t\text{-BuO})_3\text{SnM}'(\text{CO})_5$ (M, M'=Cr, Mo). The same group reported on the related In(III)/Sn(II) alkoxides $\text{X}_2\text{In}(t\text{-BuO})_3\text{Sn}$ [X=Cl, Br (Veith et al., 2001), Me (Veith et al., 2011)] and assessed the utility of the dimethylindium compound as precursor for the preparation of ITO by the sol-gel approach. Aksu and coworkers used ITBO as single-source precursor to prepare

tin-rich ITO coatings by thermal decomposition at low temperatures (Aksu and Driess, 2009), most recently even for thin layers with mesoporous structures (Aksu et al., 2011).

Dakternieks et al. (1997) introduced di-*tert*-butyltin oxide $[(t\text{-Bu}_2\text{SnO})_3]$ (Puff et al., 1984) as mild transfer reagent for oxide ions, which is soluble in a variety of solvents and reacts under virtually neutral, proton-free conditions with the only by-product being volatile, low-melting $t\text{-Bu}_2\text{SnCl}_2$ that can be easily removed (Dakternieks et al., 1994). Scope and limitations of the oxide transfer reagent were probed by the reaction with a number of chloro- and fluorosilanes (Beckmann et al., 1998a,c). In those cases in which the silane contained bulky substituents, the oxide transfer remained incomplete, and stannasiloxanes featuring Sn-O-Si linkages formed (Beckmann and Jurkschat, 2001).

Recently, we studied the base hydrolysis of the bulky dinuclear arylindium dichloride $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-Cl})\text{Cl}]_2$, which gave rise to the formation of the corresponding tetranuclear arylindium dihydroxide $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-OH})_2]_4$, a heavier congener of the more common arylboronic acids (Ahmad and Beckmann, 2009). In preceding work, we disclosed that $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-OH})_2]_4$ has a distinctive reactivity toward carbon dioxide and ethylene glycol in tetrahydrofuran (THF) yielding three oxygen-bridged products, namely, $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})_4(\text{CO}_3)_2(\mu\text{-OH})_4(\text{H}_2\text{O})_2$, $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})_4(\mu\text{-OCH}_2\text{CH}_2\mu\text{-O})_2(\mu\text{-OH})_4$, and $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})_4(\text{CO}_3)_2(\mu\text{-OCH}_2\text{CH}_2\mu\text{-OH})_2(\mu\text{-OH})_2$, respectively, which show the same nuclearity as the starting material (Ahmad et al., 2012).

We have now studied the reactivity of $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-Cl})\text{Cl}]_2$ and $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-OH})_2]_4$ toward $(t\text{-Bu}_2\text{SnO})_3$ and obtained two trinuclear stannaindoxanes containing Sn-O-In bonds, namely, $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})(t\text{-Bu}_2\text{Sn})_2(\mu_3\text{-O})$ $(\mu\text{-OH})_2(\mu\text{-Cl})\text{Cl}$ (**1**) and $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})_2(t\text{-Bu}_2\text{Sn})(\mu_3\text{-O})$ $\text{O}(\mu\text{-OH})_2$ (**2**). Attempts at recystallizing **2** at the air afforded the trinuclear indium hydrogen carbonate cluster $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})_3(\text{CO}_3\text{H})_2(\mu\text{-OH})_4$ (**3**). More rationally, **3** was prepared by the reaction of $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-OH})_2]_4$ with CO_2 in CHCl_3.

Results and discussion

The reaction of $(t\text{-Bu}_2\text{SnO})_3$ with $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-Cl})\text{Cl}]_2$ and $[2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In}(\mu\text{-OH})_2]_4$, respectively, gave the trinuclear stannaindoxanes $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})(t\text{-Bu}_2\text{Sn})_2(\mu_3\text{-O})$ $(\mu\text{-OH})_2(\mu\text{-Cl})\text{Cl}$ (**1**) and $(2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{In})_2(t\text{-Bu}_2\text{Sn})(\mu_3\text{-O})$ $\text{O}(\mu\text{-OH})_2$ (**2**) as sole products that were isolated as colorless microcrystalline compounds in good yields (Scheme 1).
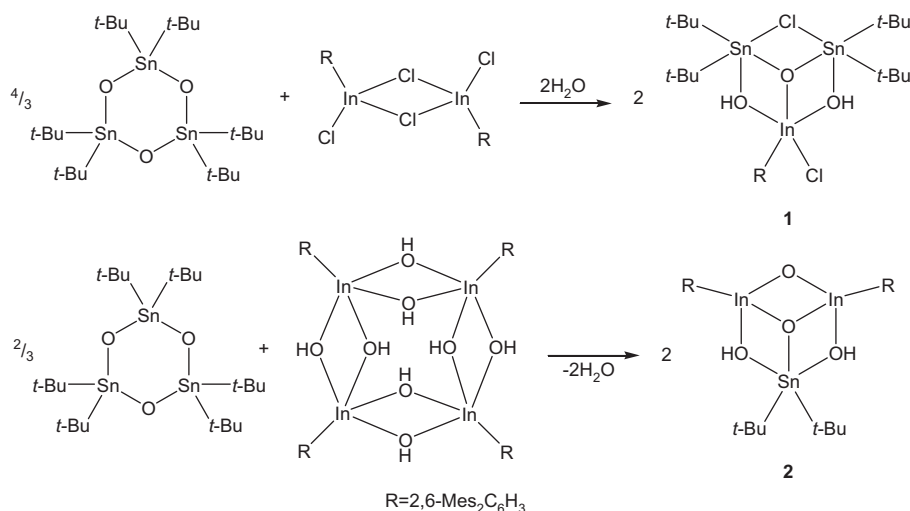
Scheme 1   Synthesis of the stannaindoxanes **1** and **2**.

The formation of **1** required the presence of water. No effort was made to exclude water from the reaction, which was carried out in an open flask. Thus, sufficient water was present either from the solvent or the atmosphere. Variation of the reaction conditions (e.g., stoichiometric ratio of the reactants and temperature) gave no indication of other products than **1** and **2**. The selective formation of **1** and **2** was attributed to the kinetic lability of the M-O and M-Cl bonds (M=Sn and In) within these compounds on the laboratory time scale and the low activation barrier for the oxide/chloride transfer (Beckmann et al., 2001a).

The Sn/In ratios of 2:1 (**1**) and 1:2 (**2**) were determined by ^{1}H-NMR spectroscopy and confirmed by elemental analysis. The trinuclear tricyclic structures was established for **1** by X-ray crystallography and resembles the structural motif of the so-called ¾ ladder $(R_2Sn)_3(\mu\text{-O})(\mu_3\text{-O})(\mu\text{-Cl})_2$ proposed by Dakternieks et al. (1997). Similar trinuclear stannoxane motifs were also reported for the fully characterized compounds $[M(t\text{-}Bu_2Sn)_3(\mu_3\text{-O})(\mu\text{-OH})_2]$ [M=Ph$_2$Si (Beckmann et al., 1998b), Me$_2$Si (Cervantes-Lee et al., 1998), OC (Ballivet-Tkatchenko et al., 2006), MesB (Brown et al., 1992), Ph$_2$P$^+$ (Beckmann et al., 2003)] and $[(n\text{-}Bu_2Sn)_3(\mu_3\text{-O})(\mu\text{-O})_2(\mu\text{-OH})_2(H_2O)_2]^{2+}$ (Plasseraud et al., 2012). Both compounds feature pentacoordinated Sn atoms, which was unambiguously confirmed by the ^{119}Sn-NMR chemical shifts (CDCl$_3$) of δ=-202 (**1**) and -278 ppm (**2**) that are significantly shifted from that of $(t\text{-}Bu_2SnO)_3$ (-84 ppm) having tetracoordinated Sn atoms. While the coordination number of the pentacoordinated In atoms remains unchanged, the increase of the coordination number at the Sn atoms (i.e., the formation of a hypercoordinated complex) might be associated with the thermodynamic driving force of both reactions. The molecular structure of **1** (as CHCl$_3$ solvate) is shown in Figure 1 and selected bond parameters are collected in the caption. It features a tricyclic inorganic core with an almost planar Sn$_2$In(μ_3-O)(μ-OH)(μ-Cl) structural motif [largest deviation of the mean plane 0.127(4) Å for O1] excluding only the Cl1 atom that is singly bond to the In atom.

The spatial arrangement of the Sn and In atoms is strongly distorted trigonal bipyramidal and defined by C$_2$O$_2$Cl (Sn) and CO$_3$Cl (In) donor sets. The μ-Cl2 atom rests between the two Sn atoms and adopts an axial position in the coordination
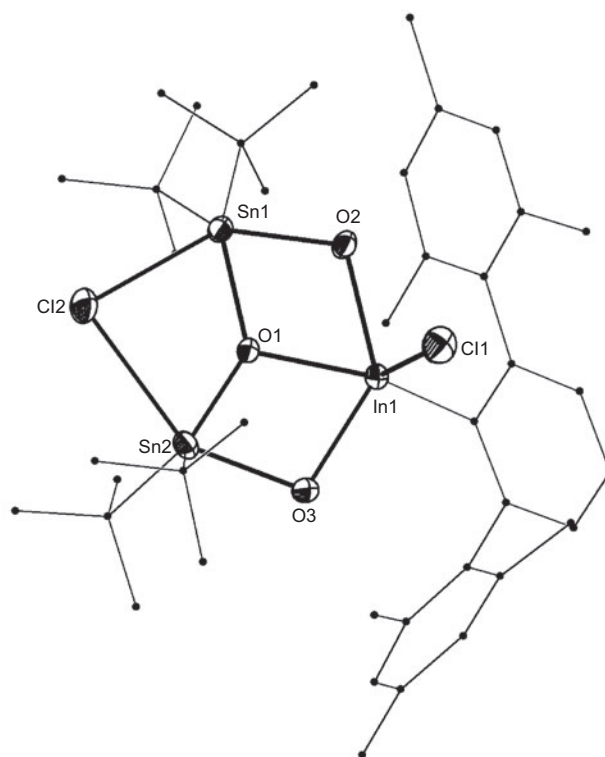
Figure 1   Molecular structure of **1** showing 20% probability ellipsoids and the crystallographic numbering scheme.
Selected bond lengths [Å, °]: In1-O1 2.131(5), In1-O2 2.233(5), In1-O3 2.252(5), In1-Cl1 2.417(3), In1-C10 2.204(8), Sn1-O1 1.996(5), Sn1-O2 2.103(5), Sn1-Cl2 2.756(3), Sn1-C40 2.180(9), Sn1-C50 2.18(1), Sn2-O1 1.990(5), Sn2-O3 2.094(6), Sn2-Cl2 2.765(3), Sn2-C60 2.172(9), Sn2-C70 2.188(9).

sphere of both Sn atoms, while the Cl1 atom is situated in an equatorial position of the In atom. The co-crystallized $CHCl_3$ molecule (not shown) forms a weak hydrogen bond with the Cl1 atom [donor acceptor distance C1⋯Cl1 3.55 (6) Å]. Electroneutrality requires that two of the three O atoms are related to hydroxyl groups. The presence of hydroxyl groups is confirmed by an IR spectrum (KBr) that shows vibrations at $\tilde{\nu}(OH)$=3599 and 3450/cm, which were tentatively assigned to symmetric and asymmetric O-H stretching vibrations of the O2 and O3 atoms not being involved in hydrogen bonding. The average Sn-O and Sn-Cl bond lengths of **1** being 2.045(6) and 2.761(3) Å compare well with those of related dimeric tetraorganodistannoxanes (Beckmann et al., 2001b). The (average) In-O and In-Cl bond lengths of **1** being 2.205(3) and 2.417(3) Å resemble those of the starting materials (Ahmad and Beckmann, 2009). All efforts to grow single crystals suitable for X-ray diffraction of **2** failed. Therefore, the structure determination remains incomplete at this time. During one attempt at crystallizing **2** from hexane/$CHCl_3$ at the air provided a small crop of single crystals that turned out to be the trinuclear indium hydrogen carbonate cluster $(2,6\text{-}Mes_2C_6H_3In)_3(CO_3H)_2(\mu\text{-}OH)_4$ (**3**), which had formed upon an advantageous absorption of CO_2 from the atmosphere. The deliberate synthesis of **3** was achieved by passing CO_2 through a solution of $[2,6\text{-}Mes_2C_6H_3In(OH)_2]_4$ in $CHCl_3$ (Equation 1). Compound **3** was isolated as colorless crystals in very good yield. To the best of our knowledge, **3** is the first organoelement hydrogen carbonate of a heavy *p*-block element. It is to note that the latter reaction performed in THF afforded the tetranuclear indium carbonate $(2,6\text{-}Mes_2C_6H_3In)_4(CO_3)_2(\mu\text{-}OH)_4(H_2O)_2$ (Ahmad et al., 2012), which precipitates from the reaction solvent.
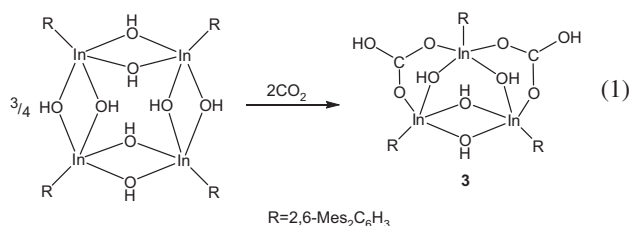
We attribute the formation of **3** to the greater solubility in $CHCl_3$, which enables a longer reaction time with CO_2. The molecular structure of **3** is shown in Figure 2 and selected bond parameters are collected in the caption. It contains a central six-membered $In_3(\mu\text{-}OH)_3$ ring, whereby two of the three In-μ-OH-In linkages are overcapped by hydrogen carbonate moieties. The spatial arrangement of the In atom is strongly distorted trigonal bipyramidal and defined by a CO_4 donor set. The average In-O bond lengths of **3** being 2.169(6) Å is similar to **1** and the starting material. The two crystallographically independent hydrogen carbonate moieties are characterized by two short C-O bond lengths [1.238(9) and 1.257(8) Å for C1], [1.250(9) and 1.266(9) Å for C2], and one longer C-O bond length [1.55(1) Å for C1 and 1.55(1) for C2]. The presence of the hydrogen carbonate moieties is confirmed by the ^{13}C-NMR chemical shift ($CDCl_3$) of δ=176.3 ppm, which allows the spectroscopic

discrimination from carbonate moieties of related *p*-block element carbonates that resonate at about δ=165 ppm (Beckmann et al., 2010 and references cited therein). The KBr of **3** shows two absorptions at $\tilde{\nu}(OH)$=3636 and 3570/cm, which were assigned to O-H stretching vibrations not affected by hydrogen bonding.

Experimental

General

The starting materials $(t\text{-}Bu_2SnO)_3$ (Puff et al., 1984), $[2,6\text{-}Mes_2C_6H_3In(\mu\text{-}Cl)Cl]_2$, and $[2,6\text{-}Mes_2C_6H_3In(\mu\text{-}OH)_2]_4$ (Ahmad and Beckmann, 2009) were prepared according to literature procedures. The ^1H, ^{13}C, and ^{119}Sn-NMR spectra were recorded using a Jeol Lambda 400 spectrometer and are referenced to $SiMe_4$ (^1H and ^{13}C) and Me_4Sn (^{119}Sn). Microanalyses were obtained from a Vario EL elemental analyzer. Infrared spectra were recorded using a Nexus FT-IR spectrometer with a Smart DuraSamplIR.

Synthesis of $(2,6\text{-}Mes_2C_6H_3In)(t\text{-}Bu_2Sn)_2(\mu_3\text{-}O)(\mu\text{-}OH)_2$ $(\mu\text{-}Cl)Cl$ (1)

A solution of $[2,6\text{-}Mes_2C_6H_3In(\mu\text{-}Cl)Cl]_2$ (499 mg) and $(t\text{-}Bu_2SnO)_3$ (498 mg) in THF (30 ml) was stirred for 12 h at room temperature in an open flask. After removing the solvent in vacuum, the solid residue was recrystallized in chloroform/hexane at the air to give **1**·$CHCl_3$ as colorless crystals. The analytical sample was dried in vacuum at 50°C to give **1** as microcrystalline solid [750 mg, 74%; Mp. 276°C dec. (sweats at 188°C)].

^{1}H-NMR (399.65 MHz, $CDCl_3$): δ=7.41 (t, 1H; *p*-C_6H_3), 7.00 (d, 2H; *m*-C_6H_3), 6.95 (s, 4H; *m*-Mes), 2.27 (s, 6H; *p*-CH_3), 2.12 (s, 12H; *o*-CH_3), 1.27 (s, 18H; *t*-Bu) 1.24 (s, 18H; *t*-Bu). ^{13}C-{^{1}H}-NMR (100.40 MHz, $CDCl_3$): δ=149.6, 142.6, 137.1, 136.3, 129.0, 128.2, 128.0, 127.8 (Ar), 44.0, 41.0, 30.0, 29.9, 21.3, 20.1 (Me). ^{119}Sn-{^{1}H}-NMR (149.06 MHz, $CDCl_3$): δ=-202. IR (KBr): $\tilde{\nu}$(OH)=3599, 3450/cm. Anal. Calcd. for $C_{40}H_{61}Cl_2InO_3Sn_2$ (1013.07): C 47.42; H 6.07; Found: C 47.53; H 6.10.

Synthesis of $(2,6\text{-}Mes_2C_6H_3In)_2(t\text{-}Bu_2Sn)$ $(\mu_3\text{-}O)O(\mu\text{-}OH)_2$ (2)

A suspension of $[2,6\text{-}Mes_2C_6H_3In(\mu\text{-}OH)_2]_4$ (925 mg) and $(t\text{-}Bu_2SnO)_3$ (249 mg) in $CHCl_3$ (50 ml) was dissolved using an ultrasonic bath at ambient temperature. The solution stirred for 12 h before the solvent was removed in vacuum to give **2** as microcrystalline colorless solid [603 mg, 53%; Mp. 250°C dec. (sweats at 230°C)].

^{1}H-NMR (399.65 MHz, $CDCl_3$): δ=7.35, 7.34 (t, 2H; *p*-CH_3), 6.97–6.88 (m, 4H; *m*-C_6H_3, 8H; *m*-Mes), 2.45, 2.42 (s, 12H; *p*-CH_3), 2.04, 2.00 (s, 24H; *o*-CH_3), 0.84 (s, 18H; *t*-Bu). ^{13}C-{^{1}H}-NMR (100.40 MHz, $CDCl_3$): δ=149.5, 149.0, 142.8, 142.5, 136.4, 136.2, 135.8, 135.4, 135.3, 135.2, 128.3, 128.1, 128.0, 127.8, 126.7, 126.6 (Ar), 30.5, 30.3, 21.6, 21.5, 21.4, 21.2 (Me). ^{119}Sn-{^{1}H}-NMR (149.06 MHz, $CDCl_3$): δ=-278. IR (KBr): $\tilde{\nu}$(OH)=3636, 3570/cm. Anal. Calcd. for $C_{56}H_{70}In_2O_3Sn$ (1137.48): C 59.13; H 6.03; Found: C 59.05; H 5.97.

Synthesis of $(2,6\text{-}Mes_2C_6H_3In)_3(CO_3H)_2(\mu\text{-}OH)_4$ (3)

A solution of $[2,6\text{-}Mes_2C_6H_3In(\mu\text{-}OH)_2]_4$ (463 mg) in $CHCl_3$ (35 ml) was purged with CO_2 (generated from dry ice) for 8 h. During the time, fresh $CHCl_3$ was constantly added to replace the amount lost by
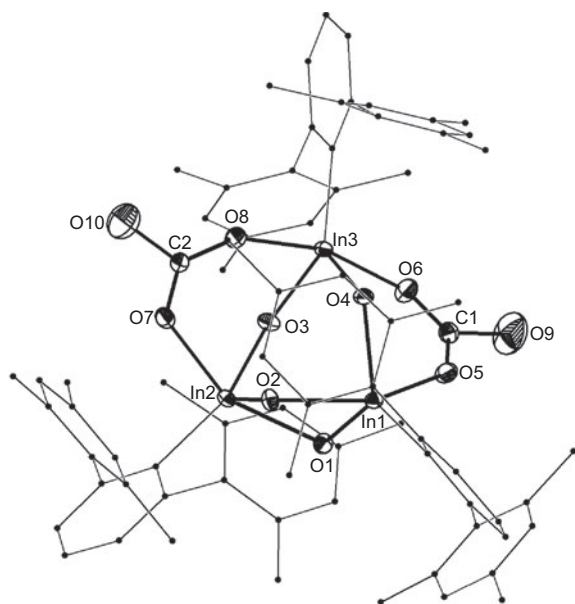
Figure 2 Molecular structure of **3** showing 20% probability ellipsoids and the crystallographic numbering scheme.
Selected bond lengths [Å, °]: In1-O1 2.095(5), In1-O2 2.204(5), In1-O4 2.168(4), In1-O5 2.205(6), In1-C10 2.155(5), In2-O1 2.218(5), In2-O2 2.099(5), In2-O3 2.132(5), In2-O9 2.224(5), In2-C40 2.151(6), In3-O3 2.121(5), In3-O4 2.103(4), In3-O6 2.215(5), In3-O8 2.247(5), In3-C70 2.145(6), C1-O5 1.238(9), C1-O6 1.257(8), C1-O7 1.55(1), C2-O9 1.250(9), C2-O8 1.266(9), C2-O10 1.55(1).

evaporation. The solvent was slowly evaporated at the air to give **3** as colorless crystals (295 mg, 60%; Mp. 265–267°C).

^{1}H-NMR (399.65 MHz, CDCl$_3$): δ=7.42, 7.37 (t, 1H; *p*-CH$_3$), 7.07, 6.98 (d, 2H; *m*-C$_6$H$_3$), 6.89, 6.81 (s, 4H; *m*-Mes), 2.36, 2.27 (s, 6H; *p*-CH$_3$), 1.97, 1.90 (s, 12H; *o*-CH$_3$). ^{13}C-{^{1}H}-NMR (100.40 MHz, CDCl$_3$): δ=176.3 (CO$_3$) 149.2, 148.9, 141.70, 141.2, 136.8, 136.5, 135.8, 135.7, 129.3, 128.6, 128.0, 127.5, 127.4, 127.3, 126.2, 126.1 (Ar), 23.2, 21.2, 20.1, 20.5 (Me). IR: $\tilde{v}$(OH)=3636, 3570/cm. Anal. Calcd. for C$_{74}$H$_{81}$In$_3$O$_{10}$ (1474.85): C 60.24; H 5.48; Found: C 60.36; H 5.33.

X-ray crystallography

Intensity data were collected on a STOE IPDS 2T diffractometer at 150 K with graphite-monochromated Mo-Kα (0.7107 Å) radiation and corrected for absorption. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 and SHELXL-97 implemented in the program WinGX 2002 (Farrugia, 1999). Full-matrix least-squares refinements on F^2, using all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Compound **3** contains rather large voids in the crystal lattice that are most likely filled by disordered CHCl$_3$ molecules, which have been accounted for by Platon's SQUEEZE routine (Farrugia, 1999). Crystal and refinement data are collected in Table 1. Figures were created using DIAMOND (Brandenburg and Putz, 2002). Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-

Table 1   Crystal data and structure refinement of **1** and **3**.

	1·CHCl$_3$	**3**
Formula	C$_{41}$H$_{62}$Cl$_5$InO$_3$Sn$_2$	C$_{74}$H$_{81}$In$_3$O$_{10}$
Formula weight, g/mol	1132.36	1474.85
Crystal system	Monoclinic	Monoclinic
Crystal size, mm	0.39×0.20×0.14	0.18×0.17×0.12
Space group	P2$_1$/c	P2$_1$/n
a, Å	19.71(1)	13.74(1)
b, Å	11.427(7)	22.70(2)
c, Å	22.20(1)	24.07(3)
α, °	90	90
β, °	92.31(5)	95.40(8)
γ, °	90	90
V, Å^3	4995(5)	7472(1)
Z	4	4
ρ$_{calcd}$, Mg/m^3	1.506	1.311
μ (Mo Kα), /mm	1.750	0.970
F(000)	2264	3008
θ range, deg	1.84–25.25	1.79–24.00
Index ranges	-23≤h≤23	-15≤h≤15
	0≤k≤12	-23≤k≤25
	0≤l≤26	-27≤l≤27
No. of reflections collected	22 361	51 309
Completeness to θ$_{max}$	99.6%	99.1%
No. of independent reflections	9006	11 622
No. of observed reflections with [$I>2\sigma(I)$]	5838	6224
No. of refined parameters	469	784
GooF (F^2)	0.922	0.784
R_1 (F) [$I>2\sigma(I)$]	0.0441	0.0450
wR_2 (F^2) (all data)	0.1416	0.1021
Largest difference peak/hole, e/Å^3	0.951/-1.087	0.478/-0.590
CCDC number	874 868	874 869

Acknowledgments

References

Ahmad, S. U.; Beckmann, J. Synthesis and structure of polynuclear indoxanes and thalloxanes containing bulky *m*-terphenyl substituents. *Organometallics* **2009**, *28*, 6893–6901.

Ahmad, S. U.; Beckmann, J.; Duthie A. The concomitant reactivity of the *m*-terphenylindium dihydroxide [2,6-Mes$_2$C$_6$H$_3$In(OH)$_2$]$_4$ toward carbon dioxide and ethylene glycol. *Organometallics* **2012**, *31*, dx.doi.org/10.1021/om3001857.

Aksu, Y.; Driess, M. A. Low-temperature molecular approach to highly conductive indium tin oxide thin films with durable electro-optical performance. *Angew. Chem. Int. Ed.* **2009**, *48*, 7778–7782.

Aksu, Y.; Frasca, S.; Wollenberger, U.; Driess, M.; Thomas, A. A molecular precursor approach to tunable porous tin-rich indium tin oxide with durable high electrical conductivity for bioelectronic devices. *Chem. Mater.* **2011**, *23*, 1798–1804.

Ballivet-Tkatchenko, D.; Burgat, R.; Chambrey, S.; Plasseraud, L.; Richard, P. Reactivity of di-*tert*-butyldimethoxystannane with carbon dioxide and methanol: X-ray structure of the resulting complex. *J. Organomet. Chem.* **2006**, *691*, 1498–1504.

Beckmann, J.; Jurkschat, K. Stannasiloxanes: from rings to polymers. *Coord. Chem. Rev.* **2001**, *215*, 267–300.

Beckmann, J.; Biesemans, M.; Hassler, K.; Jurkschat, K.; Martins, J. C.; Schürmann, M.; Willem, R. Reactions of (*t*-Bu$_2$SnO)$_3$ with (*t*-BuX$_2$Si)$_2$ (X=F, Cl). Syntheses and structures of novel stannasiloxanes and of [(*t*-Bu$_2$FSn)$_2$O]$_2$, the first fluorine-containing tetraorganodistannoxane. *Inorg. Chem.* **1998a**, *37*, 4891–4897.

Beckmann, J.; Jurkschat, K.; Mahieu, B.; Schürmann, M. On the reaction of diorganodihydroxysilanes with (*t*-Bu$_2$SnO)$_3$. Synthesis and characterization of a novel stannasiloxane complex and its dissociation in solution. *Main Group Met. Chem.* **1998b**, *21*, 113–122.

Beckmann, J.; Mahieu, B.; Nigge, W.; Schollmeyer, D.; Schürmann, M.; Jurkschat, K. Reaction of (*t*-Bu$_2$SnO)$_3$ with organohalosilanes. Simple formation of open-chain and cyclic stannasiloxanes. *Organometallics* **1998c**, *17*, 5697–5712.

Beckmann, J.; Jurkschat, K.; Rabe, S.; Schürmann, M. Hexakis(2,4,6-triisopropylphenyl)cyclotristannoxane – a molecular diorganotin oxide with kinetically inert Sn-O bonds. *Z. Anorg. Allg. Chem.* **2001a**, *627*, 2413–2419.

Beckmann, J.; Jurkschat, K.; Rabe, S.; Schürmann, M.; Dakternieks, D. New insights in asymmetric tetraorganodistannoxane ladder formation. A NMR-spectroscopic and crystallographic study. *Z. Anorg. Allg. Chem.* **2001b**, *627*, 458–464.

Beckmann, J.; Dakternieks, D.; Duthie, A.; Jurkschat, K.; Mehring, M.; Mitchell, C.; Schürmann, M. The isoelectronic replacement of E=P⁺ and Si in the trinuclear organotin-oxo clusters [Ph$_2$E(OSn*t*-Bu$_2$)$_2$O·*t*-Bu$_2$Sn(OH)$_2$]. *Eur. J. Inorg. Chem.* **2003**, 4356–4360.

Beckmann, J.; Bolsinger, J.; Duthie, A. Carbon dioxide fixation with dialkyltellurium(IV) dihydroxides. *Z. Anorg. Allg. Chem.* **2010**, *636*, 765–769.

Brandenburg, K.; Putz, H. DIAMOND V2.id, Crystal Impact, GbR, **2002**.

Brown, P.; Mahon, M. F.; Molloy, K. C. Sterically hindered organotin compounds. Part 3. The reaction between di-*tert*-butyltin oxide and organoboronic acids. *J. Chem. Soc., Dalton Trans.* **1992**, 3503–3509.

Cervantes-Lee, F.; Sharma, H. K.; Haiduc, I.; Pannell, K. H. A unique self-assembled tricyclic stannasiloxane containing a planar Sn$_3$SiO$_5$ fused 6.4.4 tricyclic ring system. *J. Chem. Soc., Dalton Trans.* **1998**, 1–2.

Chopa, K. L.; Major, S.; Pandya, D. K. Transparent conductors – a status review. *Thin Solid Films* **1983**, *102*, 1–46.

Dakternieks, D.; Jurkschat, K.; Schollmeyer, D.; Wu, H. Synthesis and structure of the first alkyl-bridged double ladder: {[R(Cl)Sn(CH$_2$)$_3$Sn(Cl)R]O}$_4$ (R=Me$_3$SiCH$_2$). *Organometallics* **1994**, *13*, 4121–4123.

Dakternieks, D.; Jurkschat, K.; van Dreumel, S.; Tiekink, E. R. T. Molecular dynamics within diorganotin systems: solution and solid state studies of new mixed distannoxane dimers [ᵗBu$_2$(Cl)SnOSn(Cl)R$_2$]$_2$. *Inorg. Chem.* **1997**, *36*, 2023–2029.

Farrugia, L. J. WinGX suite for single crystal small molecule crystallography. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

Plasseraud, L.; Therrien, B.; Růžička, A.; Cattey, H. Organotin(IV) trifluoromethanesulfonates chemistry: isolation and characterization of a new di-*n*-butyl derivate presenting a Sn$_3$O$_3$ core. *Inorg. Chim. Acta* **2012**, *380*, 50–56.

Puff, H.; Schuh, W.; Sievers, R.; Wald, W.; Zimmer, R. Niedermolekulare Diorganozinn-Sauerstoff-Verbindungen: Di-*t*-Butyl- und di-*t*-Amylzinnoxid. *J. Organomet. Chem.* **1984**, *260*, 271–280.

Tahar, R. B. H.; Ban, T.; Ohya, Y.; Takahasi, Y. Tin doped indium oxide thin films: electrical properties. *J. Appl. Phys.* **1998**, *83*, 2631–2645.

Veith, M.; Kunze, K. Alkoxystannate chemistry. 6. Different Lewis basicity of indium(I) versus tin(II) in molecular indium-tin and thallium-tin alkoxides. *Angew. Chem.* **1991**, *103*, 92–94; *Angew. Chem. Int. Ed.* **1991**, *30*, 95–97.

Veith, M.; Hill, S.; Huch, V. Synthese und Charakterisierung von InIII-SnII-Halogenido-Alkoxiden und von Indiumtri-*tert*-butoxid. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1495–1504.

Veith, M.; Bubel, C.; Zimmer, M. A novel precursor system and its application to produce tin doped indium oxide. *Dalton Trans* **2011**, *40*, 6028–6032.