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Short Communication

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Synthesis and structure of three molecular arylindium phosphinates

Abstract: Reported here are the syntheses and molecular structures of three novel arylindium phosphinates, \([\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{In}](\text{O})_2\text{PMe}_2\text{H})_2\] (1), \([\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{In}](\text{O})_2\text{PMe}_2\text{H})_2\] (2), and \([\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{In}](\text{O})_2\text{PMe}_2\text{H})_2\] (3), which were obtained by condensation reaction of the \(m\)-terphenylindium dihydroxide \([\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{In}(\text{OH})_2]\)_1 with dimethylphosphinic acid, diphenylphosphinic acid, and 2,2,3,4,4-pentamethylyphosphinic acid, respectively. We now describe the reactions of \([\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{In}(\text{OH})_2]\)_1 with dimethylphosphinic acid, diphenylphosphinic acid, and 2,2,3,4,4-pentamethylyphosphinic acid, respectively, which gave rise to the formation of the arylindium phosphinates \([\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{In}(\text{OH})_2]\)_1 with dimethylphosphinic acid, diphenylphosphinic acid, and 2,2,3,4,4-pentamethylyphosphinic acid, respectively, as sole products regardless of the stoichiometric ratio of the reactants applied (Scheme 1).

Compounds 1–3 were obtained as colorless high-melting crystalline solids that are reasonably soluble in quite polar solvents, such as CHCl₃, CH₂Cl₂, and THF. The In/P ratios of 1 (1:1), 2 (2:3), and 3 (1:2) were determined by integration of ¹H NMR resonances (see Experimental) and confirmed by elemental analysis. The ³¹P NMR spectra (CDCl₃) and ³¹P MAS NMR spectra of 1–3 reveal signals at \(\delta=40.5\) and \(\delta=49.4\) for 1, \(\delta=31.8\), 28.0 (integral ratio 1:2) and \(\delta=28.8\), 23.6 (integral ratio 1:2) for 2, and \(\delta=49.4\) and \(\delta=49.7\) for 3, which shifted significantly upfield from those of the parent phosphinic acids Me₂P(O)OH (\(\delta=54.1\)), Ph₂P(O)OH (\(\delta=38.7\)), and Me(C₆H₄)₂P(O)OH (\(\delta=60.2\)), respectively. The molecular structures of 1–3 established by single crystal X-ray diffraction are depicted in Figures 1–3, respectively, and selected bond parameters are collected in the caption of the figures.

The degree of aggregation of the indium phosphinates 1–3 is smaller than in the tetranuclear starting material. While 1 and 2 are dimeric, 3 is even mononuclear presumably due to the fact that 1,1,2,3,3-pentamethyllumethylenephosphinato (Chandrasekhar et al., 2004; Chandrasekhar and Thirumoothir, 2009) is bulkier than the dimethyl- and diphenylphosphinato.

In the crystal structure of 1, the two In atoms are bridged via two μ-OH groups and two μ-O₂PMe₂ groups. In the crystal structure of 2, the two In atoms are bridged via one μ-OH group and three μ-O₂PMe₂ groups. The spatial arrangement of the In atoms is trigonal bipyramidal and defined by a CO₄ donor set.
The In-O bond lengths vary between 2.104(8) and 2.247(4) Å and compare well with those of the starting compound [(2,6-Mes₂C₆H₃In(OH))₈]₈ (Ahmad and Beckmann, 2009), the previously reported indium phosphinates (Arif and Barron, 1988; Hahn et al., 1990), and the recently published indium phosphonates.
Figure 3  Molecular structure of 3 showing 30% probability ellipsoids and the crystallographic numbering scheme.

Selected bond lengths [Å]: In1-O1 2.121(5), In1-O2 2.126(5), In1-O3 2.225(4), In1-O4 2.240(4), In1-C10 2.141(6), P1-O4 1.508(4), P1-O6 1.529(5), P1-C80 1.831(7), P1-C82 1.842(7), In2-O7 2.134(5), In2-O8 2.129(5), In2-O9 2.215(5), In2-O10 2.237(5), In2-C40 2.125(6), P3-O9 1.514(5), P3-O11 1.517(4), P3-C100 1.847(8), P3-C102 1.804(8), P4-O10 1.480(5), P4-O12 1.513(4), P4-C90 1.816(8), P4-C92 1.832(8), O1···O5 2.647(6), O2···O6 2.659(7).

(Chandrasekhar et al., 2013). The structures of 1 and 2 contain \( \mu \)-OH groups, whereas that of 3 possesses two \( \text{H}_2\text{O} \) molecules that coordinate to the In atom and engage in hydrogen bonding with the \( \text{P} = \text{O} \) groups of the phosphinate moieties [O···O 2.647(6) and 2.659(7) Å]. Consistently, the IR spectra (KBr) show absorptions at \( \nu(\text{OH}) = 3624 \text{ cm}^{-1} \) for 1, \( \nu(\text{OH}) = 3587 \text{ cm}^{-1} \) for 2, and \( \nu(\text{OH}) = 3626 \text{ cm}^{-1} \) for 3 that are indicative of O-H stretching vibrations.

### Experimental

#### General

The \( m \)-terphenylindium dihydroxide \( [(2,6-\text{Mes}_2\text{C}_6\text{H}_3\text{In(OH)}_2)_4] \) (Ahmad and Beckmann, 2009) and the \( 2,2,3,4,4\)-pentamethylphosphonic acid \( \text{Me}_2\text{C}_3\text{HPO(OH)} \) (Emsley et al., 1984) were prepared according to literature procedures. The other two phosphinic acids \( \text{Me}_2\text{P(O)}\text{OH} \) and \( \text{Ph}_2\text{P(O)}\text{OH} \) were obtained commercially and used as received. The \( ^1\text{H}, ^{13}\text{C}, \text{and} ^{31}\text{P NMR spectra were recorded in CDCl}_3 \) using Jeol GX 270 and Varian 300 Unity Plus spectrometers and are referenced to SiMe_4 (1H, 13C) and aqueous H_3PO_4 (31P). The \( ^{31}\text{P MAS NMR spectra were obtained using a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a 6-mm rotor operating at spinning frequencies between 8 and 10 kHz. Infrared (IR) spectra were recorded using a Nexus FTIR spectrometer with a Smart DuraSampler. Microanalyses were obtained from a Vario EL elemental analyzer.

#### Synthesis of \( [(2,6-\text{Mes}_2\text{C}_6\text{H}_3\text{In})_2\text{(OH)}_2(\text{O}_2\text{PM}_{\text{Me}_2})_2] \) (1)

A mixture of \( [(2,6-\text{Mes}_2\text{C}_6\text{H}_3\text{In(OH)}_2)_4 \) (200 mg, 0.11 mmol) and \( \text{Me}_2\text{P(O)}\text{OH} \) (40 mg, 0.40 mmol) in THF (25 mL) was stirred overnight at r.t. The solvent was completely removed in vacuum and the solid residue recrystallized from THF to give 1 (153 mg, 0.14 mmol, 64%; Mp. 290–292°C).

#### Synthesis of \( [(2,6-\text{Mes}_2\text{C}_6\text{H}_3\text{In})_2\text{(OH)}_2(\text{O}_2\text{PPh}_{\text{Me}_2})_3] \) (2)

A mixture of \( [(2,6-\text{Mes}_2\text{C}_6\text{H}_3\text{In(OH)}_2)_4 \) (190 mg, 0.10 mmol) and \( \text{Ph}_2\text{P(O)}\text{OH} \) (140 mg, 0.64 mmol) in THF (25 mL) was stirred overnight at r.t. The solvent was completely removed in vacuum and the solid residue recrystallized from CH_2Cl_2/hexane (1:3) to give 2 (0.27 mg, 0.17 mmol, 87%; Mp. 330°C [dec.]).

#### Synthesis of \( [(2,6-\text{Mes}_2\text{C}_6\text{H}_3\text{In})(\text{O}_2\text{PPh}_{\text{Me}_2})_2(\text{H}_2\text{O})_2] \) (3)

A mixture of \( [(2,6-\text{Mes}_2\text{C}_6\text{H}_3\text{In(OH)}_2)_4 \) (110 mg, 0.06 mmol) and \( \text{Ph}_2\text{P(O)}\text{OH} \) (100 mg, 0.64 mmol) in THF (25 mL) was stirred overnight at r.t. The solvent was completely removed in vacuum and the solid residue recrystallized from CH_2Cl_2/hexane (1:3) to give 3 (167 mg, 0.20 mmol, 86%; Mp. 330°C [dec.]).
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. 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 $F^2$ were performed using all data. All nonhydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model and were refined isotropically.

Disorder was resolved in for C12, C13, C32, and C33 of 1 as well as C71 of 3 and refined with occupancy ratios of 50:50. The crystal lattice of 3 contained larger voids, the diffuse electron density of which was accounted by Platon’s Squeeze routine (Van der Sluis and Spek, 1990; Spek, 2003). Crystal and refinement data are collected in Table 1. Figures were created using DIAMOND (Brandenburg and Putz, 2006). 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: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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