metal-organic compounds

catena-Poly[bis[dimethyl(pyridine-κN)-indium(III)]-μ4-benzene-1,3-diolato-bis[dimethylindium(III)]-μ4-benzene-1,3-diolato]

Glen G. Briand,[a]* Andreas Decken[b] and Marshall R. Hoey[a]

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The title compound, $[In_2(CH_3)_4(C_6H_4O_2)(C_5H_5N)]$ or $[\{(CH_3)_2In\}(1,3-O_2C_6H_4)\{In(CH_3)_2(py)\}]_n$, (py = pyridine) contains two crystallographically unique In^{III} ions which are in distorted tetrahedral C_2O_2 and distorted trigonal-bipyramidal C_2O_2N coordination environments. The In^{III} coordination centers are bridged head-to-head *via* In—O bonds, yielding four-membered In_2O_2 rings and zigzag polymeric chains along [001].

Related literature

For background to dimethylindium aryloxides, see: Briand *et al.* (2010); Beachley *et al.* (2003); Hausslein *et al.* (1999); Blake *et al.* (2011); Bradley *et al.* (1988); Trentler *et al.* (1997). For dimethylindium compounds with bidentate imine-alkoxide ligands, see: Hu *et al.* (1999); Wu *et al.* (1999); Pal *et al.* (2013); Lewinski *et al.* (2003); Ghoshal *et al.* (2007).
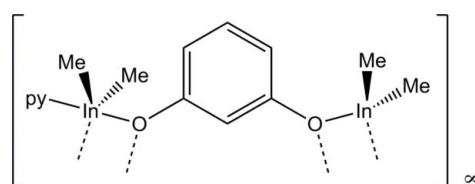
Experimental

Crystal data

$[In_2(CH_3)_4(C_6H_4O_2)(C_5H_5N)]$
$M_r = 476.97$

Monoclinic, $P2_1/n$
$a = 9.1584$ (17) Å

$b = 14.075$ (3) Å
$c = 13.856$ (3) Å
$\beta = 90.106$ (3)°
$V = 1786.1$ (6) Å^3
$Z = 4$

Mo $K\alpha$ radiation
$\mu = 2.58$ mm^{-1}
$T = 188$ K
$0.20 \times 0.03 \times 0.03$ mm

Data collection

Bruker P4/SMART 1000 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*a*)
$T_{min} = 0.626$, $T_{max} = 0.938$

12064 measured reflections
3967 independent reflections
2885 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.087$
$S = 1.16$
3967 reflections

185 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.02$ e Å^{-3}
$\Delta\rho_{min} = -0.72$ e Å^{-3}

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008*b*); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008*b*); molecular graphics: *DIAMOND* (Brandenburg, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008*b*).

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supporting information

catena-Poly[bis[dimethyl(pyridine-*κN*)indium(III)]-*μ*₄-benzene-1,3-diolato-bis-[dimethylindium(III)]-*μ*₄-benzene-1,3-diolato]

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S1. Comment

Dimethylindium aryloxides [Me$_2$InOR]$_2$ form dimeric structures in the solid state *via* intermolecular In—O coordinate bonding interactions (Briand *et al.*, 2010; Beachley *et al.*, 2003; Hausslein *et al.*, 1999; Blake *et al.*, 2011; Bradley *et al.*, 1988; Trentler *et al.*, 1997). These structures feature distorted tetrahedral geometries at In, distorted trigonal planar or slightly pyramidal geometries at O, and symmetric near planar In$_2$O$_2$ ring cores. Substitution of monodentate alkoxide (–OR) ligands with bidentate imine-alkoxide ligands additionally results in an intramolecular In—N coordination, yielding distorted trigonal bipyramidal In centres and asymmetric In$_2$O$_2$ rings (Hu *et al.*, 1999; Wu *et al.*, 1999; Pal *et al.*, 2013; Lewinski *et al.*, 2003; Ghoshal *et al.*, 2007). The molecular structure of (I) (Fig. 1) shows two crystallographically unique In atoms. In addition to the In1—O1 bond, In1 exhibits an intermolecular In1—O1^i interaction. This results in a distorted tetrahedral C$_2$O$_2$ bonding environment for indium [C1—In1—C2 = 144.3 (3), O1—In1—O1^i = 73.87 (14)°] and a symmetric In$_2$O$_2$ ring structure [In1—O1 = 2.172 (3), In1—O1^i = 2.174 (3) Å]. Similarly, In2 is coordinated to two methyl C atoms [C3 and C4] and two aryloxide O atoms [O2 and O2^{ii}], but is is also coordinated by the N atom of a pyridine molecule [2.486 (4) Å]. This results in a distorted trigonal bypyramidal C$_2$O$_2$N bonding environment for In, with the two methyl C atoms and a bridging O atom in equatorial positions [C3—In2—C4 = 142.5 (2), C3—In2—O2^{ii} = 107.8 (2), C4—In2—O2^{ii} = 109.25 (19)°], and the pyridine N atom and a bridging O atom in axial positions [O2—In2—N1 = 156.63 (13)°]. The axial In2—O2 bond distance [2.330 (3) Å] is longer than the equatorial In2—O2^{ii} bond distance [2.152 (3) Å], presumably as a result of the *trans* influence of the pyridine N atom, resulting in an asymmetric In$_2$O$_2$ ring. The two unique In$_2$O$_2$ rings are bridged by the 1,3-benzenediolate phenyl ring, giving a zigzag polymeric structure along [001] (Fig. 2).

S2. Experimental

Under an atmosphere of dinitrogen, InMe$_3$ (0.250 g, 1.56 mmol) was dissolved in diethyl ether (10 ml). Pyridine (0.125 g, 1.56 mmol) was added and the solution stirred for 30 min. Resorcinol (0.088 g, 0.78 mmol) was then added and the reaction mixture stirred for an additional 1 h. The reaction was then filtered and the filtrate allowed to sit at 296K. After 1 d, the solution was filtered to yield colourless crystals of [Me$_2$In(1,3-O$_2$C$_6$H$_4$)InMe$_2$(py)]$_\infty$ (0.122 g, 0.256 mmol, 33%). Anal. Calc. for C$_{15}$H$_{21}$In$_2$NO$_2$: C, 37.77; H, 4.44; N, 2.94. Found: C, 38.32; H, 4.47; N, 2.88. F T—IR (ATR, cm^{-1}): 618 w, 698 s, 748 m, 772 w, 829 w, 844 w, 968 s, 1003 w, 1034 w, 1142 s, 1171 s, 1213 w, 1249 m, 1299 m, 1427 w, 1441 w, 1482 m, 1467 m, 1573 s, 2283 w, 2475 w, 2881 m, 3004 m. FT-Raman (cm^{-1}): 487 vs [v_{sym} (Me—In—Me)], 524 w [v_{asym} (Me—In—Me)], 994 m, 1034 m, 1159 m, 1305 w, 1586 w, 2920 m, 2982 w, 3064 m.

S3. Refinement

Hydrogen atoms were included in calculated positions and refined using a riding model.
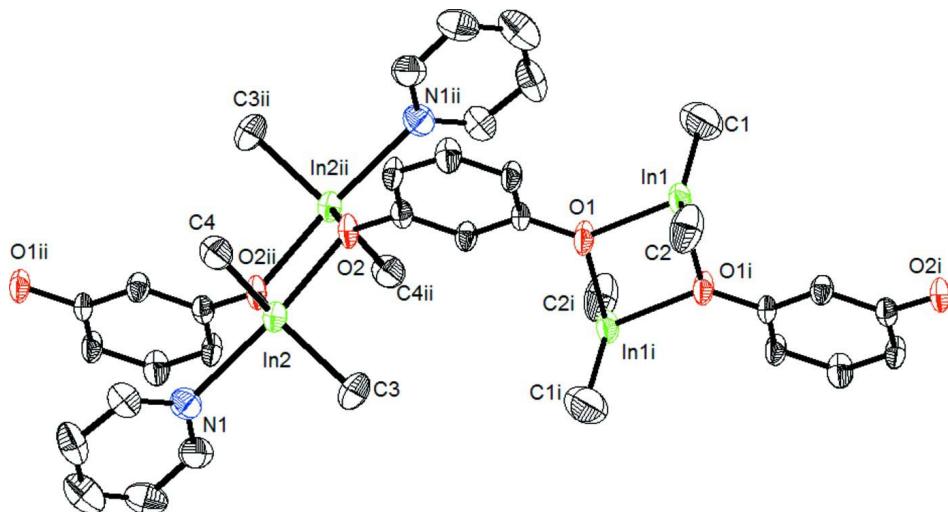

Figure 1

The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: (i) -x, 1 - y, 1 - z; (ii) -x, 1 - y, 2 - z.
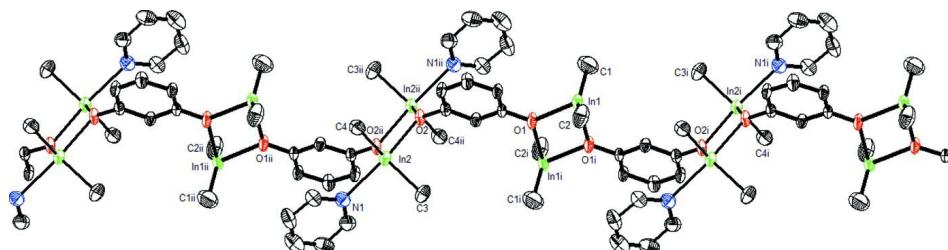
Figure 2

Part of the crystal structure of (I) showing the zigzag polymeric structure along [001], with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: (i) -x, 1 - y, 1 - z; (ii) -x, 1 - y, 2 - z.

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Crystal data

[In$_2$(CH$_3$)$_4$(C$_6$H$_4$O$_2$)(C$_5$H$_5$N)]
M_r = 476.97
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 9.1584 (17) Å
b = 14.075 (3) Å
c = 13.856 (3) Å
β = 90.106 (3)°
V = 1786.1 (6) Å^3
Z = 4

$F(000)$ = 928
D_x = 1.774 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5671 reflections
θ = 2.7–27.9°
μ = 2.58 mm^{-1}
T = 188 K
Rod, colourless
0.20 × 0.03 × 0.03 mm

Data collection

Bruker P4/SMART 1000 diffractometer	12064 measured reflections
Radiation source: fine-focus sealed tube, K760	3967 independent reflections
Graphite monochromator	2885 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.039$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*a*)	$\theta_{max} = 27.5°$, $\theta_{min} = 2.1°$
	$h = -10 \rightarrow 11$
	$k = -18 \rightarrow 18$
$T_{min} = 0.626$, $T_{max} = 0.938$	$l = -16 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.087$	
$S = 1.16$	H-atom parameters constrained
3967 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 1.2232P]$ where $P = (F_o^2 + 2F_c^2)/3$
185 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 1.02$ e Å^{-3}
	$\Delta\rho_{min} = -0.72$ e Å^{-3}

Special details

Experimental. Crystal decay was monitored by repeating the initial 50 frames at the end of the data collection and analyzing duplicate reflections.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Reflections were merged by *SHELXL* according to the crystal class for the calculation of statistics and refinement.
_reflns_Friedel_fraction is defined as the number of unique Friedel pairs measured divided by the number that would be possible theoretically, ignoring centric projections and systematic absences.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
In1	0.12136 (4)	0.57110 (3)	0.43640 (3)	0.03464 (12)
In2	0.11428 (4)	0.39665 (3)	1.01934 (3)	0.02955 (11)
O1	0.0623 (4)	0.5253 (3)	0.5809 (2)	0.0361 (8)
O2	0.0754 (3)	0.5316 (2)	0.9254 (2)	0.0300 (8)
N1	0.0635 (5)	0.2789 (3)	1.1488 (3)	0.0396 (11)
C1	0.0184 (8)	0.7054 (5)	0.4259 (6)	0.073 (2)
H1A	0.0580	0.7480	0.4755	0.109*
H1B	−0.0870	0.6980	0.4356	0.109*
H1C	0.0365	0.7325	0.3619	0.109*
C2	0.3108 (7)	0.4920 (5)	0.3979 (5)	0.0631 (19)
H2A	0.3153	0.4856	0.3276	0.095*
H2B	0.3060	0.4288	0.4275	0.095*
H2C	0.3981	0.5253	0.4211	0.095*
C3	0.0431 (7)	0.3018 (4)	0.9068 (4)	0.0562 (17)

H3A	0.1234	0.2910	0.8616	0.084*
H3B	−0.0397	0.3302	0.8724	0.084*
H3C	0.0130	0.2412	0.9353	0.084*
C4	0.3053 (6)	0.4553 (4)	1.0846 (4)	0.0454 (15)
H4A	0.3067	0.5242	1.0746	0.068*
H4B	0.3923	0.4269	1.0553	0.068*
H4C	0.3047	0.4417	1.1540	0.068*
C5	0.1383 (5)	0.5416 (3)	0.6650 (3)	0.0270 (10)
C6	0.0693 (5)	0.5259 (3)	0.7530 (3)	0.0277 (11)
H6	−0.0282	0.5029	0.7544	0.033*
C7	0.1435 (5)	0.5439 (3)	0.8395 (3)	0.0264 (10)
C8	0.2872 (5)	0.5754 (4)	0.8361 (4)	0.0314 (11)
H8	0.3395	0.5870	0.8941	0.038*
C9	0.3536 (6)	0.5897 (4)	0.7479 (4)	0.0371 (13)
H9	0.4518	0.6115	0.7462	0.044*
C10	0.2808 (5)	0.5731 (3)	0.6622 (3)	0.0311 (11)
H10	0.3282	0.5832	0.6022	0.037*
C11	−0.0627 (6)	0.2311 (4)	1.1471 (5)	0.0464 (14)
H11	−0.1250	0.2380	1.0927	0.056*
C12	−0.1062 (7)	0.1719 (4)	1.2216 (5)	0.0572 (17)
H12	−0.1960	0.1383	1.2176	0.069*
C13	−0.0192 (8)	0.1624 (5)	1.3002 (5)	0.066 (2)
H13	−0.0476	0.1223	1.3520	0.080*
C14	0.1099 (8)	0.2112 (5)	1.3044 (5)	0.0614 (18)
H14	0.1723	0.2061	1.3590	0.074*
C15	0.1467 (7)	0.2677 (4)	1.2274 (4)	0.0479 (15)
H15	0.2369	0.3010	1.2302	0.057*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
In1	0.0337 (2)	0.0504 (2)	0.0198 (2)	−0.00910 (16)	0.00038 (15)	0.00502 (16)
In2	0.0284 (2)	0.0370 (2)	0.02328 (19)	0.00222 (15)	0.00004 (14)	−0.00206 (15)
O1	0.035 (2)	0.058 (2)	0.0152 (17)	−0.0138 (17)	−0.0001 (15)	0.0008 (16)
O2	0.0281 (18)	0.047 (2)	0.0149 (17)	0.0054 (15)	0.0021 (14)	0.0016 (15)
N1	0.039 (3)	0.040 (3)	0.040 (3)	0.001 (2)	0.004 (2)	0.003 (2)
C1	0.080 (5)	0.058 (4)	0.081 (5)	−0.005 (4)	−0.005 (4)	0.018 (4)
C2	0.043 (4)	0.103 (6)	0.044 (4)	−0.001 (4)	0.004 (3)	−0.014 (4)
C3	0.078 (5)	0.054 (4)	0.037 (3)	−0.002 (3)	0.002 (3)	−0.018 (3)
C4	0.034 (3)	0.051 (4)	0.051 (4)	−0.007 (3)	−0.011 (3)	0.011 (3)
C5	0.035 (3)	0.032 (3)	0.014 (2)	−0.001 (2)	−0.001 (2)	0.0007 (19)
C6	0.022 (2)	0.040 (3)	0.022 (3)	−0.004 (2)	−0.001 (2)	0.000 (2)
C7	0.031 (3)	0.030 (3)	0.019 (2)	0.006 (2)	0.001 (2)	0.001 (2)
C8	0.028 (3)	0.048 (3)	0.018 (2)	−0.003 (2)	−0.004 (2)	−0.001 (2)
C9	0.025 (3)	0.058 (4)	0.029 (3)	−0.007 (2)	−0.001 (2)	0.004 (2)
C10	0.031 (3)	0.046 (3)	0.016 (2)	−0.007 (2)	0.003 (2)	−0.001 (2)
C11	0.049 (4)	0.040 (3)	0.050 (4)	−0.003 (3)	−0.002 (3)	0.001 (3)
C12	0.049 (4)	0.047 (4)	0.076 (5)	−0.010 (3)	0.009 (4)	0.009 (3)

C13	0.065 (5)	0.065 (5)	0.069 (5)	0.001 (4)	0.013 (4)	0.024 (4)
C14	0.073 (5)	0.069 (5)	0.042 (4)	0.011 (4)	−0.004 (3)	0.020 (3)
C15	0.050 (4)	0.048 (4)	0.046 (4)	0.001 (3)	0.002 (3)	0.008 (3)

Geometric parameters (Å, º)

In1—C1	2.118 (7)	C3—H3C	0.9800
In1—C2	2.130 (6)	C4—H4A	0.9800
In1—O1	2.172 (3)	C4—H4B	0.9800
In1—O1^i	2.174 (3)	C4—H4C	0.9800
In2—C4	2.134 (5)	C5—C10	1.379 (7)
In2—O2^{ii}	2.152 (3)	C5—C6	1.393 (6)
In2—C3	2.152 (5)	C6—C7	1.400 (6)
In2—O2	2.330 (3)	C6—H6	0.9500
In2—N1	2.486 (4)	C7—C8	1.390 (7)
O1—C5	1.376 (5)	C8—C9	1.380 (7)
O1—In1^i	2.174 (3)	C8—H8	0.9500
O2—C7	1.355 (5)	C9—C10	1.381 (7)
O2—In2^{ii}	2.152 (3)	C9—H9	0.9500
N1—C11	1.337 (7)	C10—H10	0.9500
N1—C15	1.338 (7)	C11—C12	1.385 (8)
C1—H1A	0.9800	C11—H11	0.9500
C1—H1B	0.9800	C12—C13	1.355 (9)
C1—H1C	0.9800	C12—H12	0.9500
C2—H2A	0.9800	C13—C14	1.368 (9)
C2—H2B	0.9800	C13—H13	0.9500
C2—H2C	0.9800	C14—C15	1.373 (8)
C3—H3A	0.9800	C14—H14	0.9500
C3—H3B	0.9800	C15—H15	0.9500
C1—In1—C2	144.3 (3)	H3A—C3—H3C	109.5
C1—In1—O1	102.5 (2)	H3B—C3—H3C	109.5
C2—In1—O1	106.3 (2)	In2—C4—H4A	109.5
C1—In1—O1^i	101.9 (2)	In2—C4—H4B	109.5
C2—In1—O1^i	106.1 (2)	H4A—C4—H4B	109.5
O1—In1—O1^i	73.87 (14)	In2—C4—H4C	109.5
C4—In2—O2^{ii}	109.25 (19)	H4A—C4—H4C	109.5
C4—In2—C3	142.5 (2)	H4B—C4—H4C	109.5
O2^{ii}—In2—C3	107.8 (2)	O1—C5—C10	120.5 (4)
C4—In2—O2	92.62 (17)	O1—C5—C6	119.0 (4)
O2^{ii}—In2—O2	72.15 (13)	C10—C5—C6	120.4 (4)
C3—In2—O2	93.2 (2)	C5—C6—C7	120.0 (4)
C4—In2—N1	96.11 (19)	C5—C6—H6	120.0
O2^{ii}—In2—N1	84.49 (13)	C7—C6—H6	120.0
C3—In2—N1	93.0 (2)	O2—C7—C8	120.5 (4)
O2—In2—N1	156.63 (13)	O2—C7—C6	120.3 (4)
C5—O1—In1	127.2 (3)	C8—C7—C6	119.1 (4)
C5—O1—In1^i	126.0 (3)	C9—C8—C7	119.8 (5)

In1—O1—In1[i]	106.13 (14)	C9—C8—H8	120.1
C7—O2—In2[ii]	128.7 (3)	C7—C8—H8	120.1
C7—O2—In2	121.6 (3)	C8—C9—C10	121.5 (5)
In2[ii]—O2—In2	107.85 (13)	C8—C9—H9	119.2
C11—N1—C15	116.4 (5)	C10—C9—H9	119.2
C11—N1—In2	119.1 (4)	C5—C10—C9	119.1 (4)
C15—N1—In2	124.0 (4)	C5—C10—H10	120.4
In1—C1—H1A	109.5	C9—C10—H10	120.4
In1—C1—H1B	109.5	N1—C11—C12	122.7 (6)
H1A—C1—H1B	109.5	N1—C11—H11	118.7
In1—C1—H1C	109.5	C12—C11—H11	118.7
H1A—C1—H1C	109.5	C13—C12—C11	119.2 (6)
H1B—C1—H1C	109.5	C13—C12—H12	120.4
In1—C2—H2A	109.5	C11—C12—H12	120.4
In1—C2—H2B	109.5	C12—C13—C14	119.5 (6)
H2A—C2—H2B	109.5	C12—C13—H13	120.3
In1—C2—H2C	109.5	C14—C13—H13	120.3
H2A—C2—H2C	109.5	C13—C14—C15	118.1 (7)
H2B—C2—H2C	109.5	C13—C14—H14	120.9
In2—C3—H3A	109.5	C15—C14—H14	120.9
In2—C3—H3B	109.5	N1—C15—C14	124.1 (6)
H3A—C3—H3B	109.5	N1—C15—H15	118.0
In2—C3—H3C	109.5	C14—C15—H15	118.0

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) −*x*, −*y*+1, −*z*+2.