Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Synthesis and crystal structure of bis(μ-2-methylbenzenethiolato-κ^2S:S)bis[methyl(2-methylbenzenethiolato-κS)indium(III)]

Glen G. Briand,[a]* Andreas Decken,[b] Courtney M. Dickie[a] and Gregory MacNeil[a]

[a]Department of Chemistry and Biochemistry, Mount Allison University, 63C York Street, Sackville, NB, E4L 1G8, Canada, and [b]Department of Chemistry, University of New Brunswick, Fredericton, NB, E3B 5A3, Canada. *Correspondence e-mail: gbriand@mta.ca

Received 17 February 2017
Accepted 3 March 2017

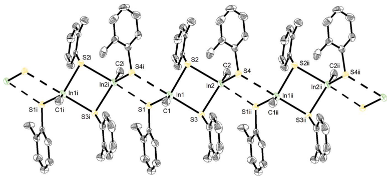
Edited by A. J. Lough, University of Toronto, Canada

Keywords: crystal structure; indium; thiolate; dinuclear; coordination polymer.

CCDC reference: 1535922

Supporting information: this article has supporting information at journals.iucr.org/e

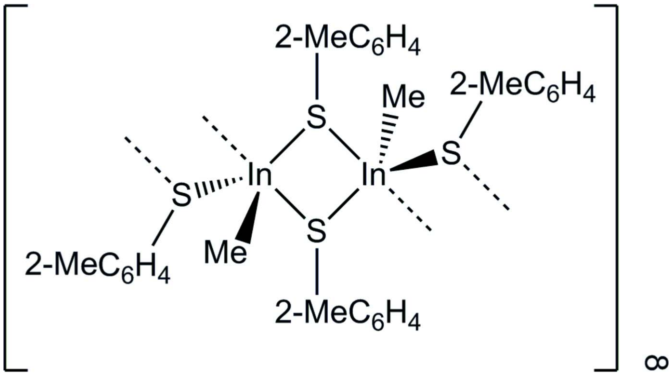
The dinuclear title compound, $[In_2(CH_3)_2(C_7H_7S)_4]$ or $[Me(2\text{-}MeC_6H_4S)In\text{-}\mu\text{-}(2\text{-}MeC_6H_4S)_2InMe(2\text{-}MeC_6H_4S)]$, was prepared from the 1:2 reaction of Me_3In and $2\text{-}MeC_6H_4SH$ in toluene. Its crystal structure exhibits a four-membered In_2S_2 ring core *via* bridging $(2\text{-}MeC_6H_4S)$ groups. The dimeric units are further associated into a one-dimensional polymeric structure extending parallel to the *a* axis *via* intermolecular In$\cdots$S contacts. The In atoms are then in distorted trigonal–bipyramidal CS_4 bonding environments.



1. Chemical context

Methylindium dithiolates $[MeIn(S_2R)]$ have been shown to be useful compounds for the ring-opening polymerization (ROP) of cyclic esters to produce biodegradable polymers (Allan *et al.*, 2013; Briand *et al.*, 2016). These compounds are prepared from the stoichiometric reaction of $InMe_3$ with polydentate amino/oxo-dithiols. However, the 1:2 reaction of triorganylindium (R_3In) with simple monothiols ($R'SH$) often results in isolation of the diorganylindium thiolate $R_2In(SR')$ (Hoffmann, 1988; Nomura *et al.*, 1989). The favourable formation of the organylindium dithiolate $RIn(SR')_2$ was reported to be determined by the steric bulk of the thiolate ligand and the *R*-In group, and the acidity of the thiol reactant. The 1:2 reaction of nBu$_3$In or iBu$_3$In and PhSH afforded the dithiolate $RIn(SPh)_2$ ($R = n$Bu, iBu) as solids, although the compounds were poorly soluble in organic solvents, precluding crystallization. All compounds in these studies were primarily characterized by NMR. The only structurally characterized example of such a compound is $[(Me_3Si)_3C](PhS)In\text{-}\mu\text{-}(PhS)_2In[C(Me_3Si)_3](SPh)$, which is prepared from the redox reaction of the indium(I) compound $[(Me_3Si)_3CIn]_4$ and the disulfide $(SPh)_2$ (Peppe *et al.*, 2009). The 1:2 reaction of Me_3In and $2\text{-}MeC_6H_4SH$ in toluene affords $[Me(2\text{-}MeC_6H_4S)In\text{-}\mu\text{-}(2\text{-}MeC_6H_4S)_2InMe(2\text{-}MeC_6H_4S)]$, (I), in high yield. The modest steric bulk afforded by the $2\text{-}MeC_6H_4$ group moderates intermolecular bonding and increases solubility in organic solvents without preventing formation of the $RIn(SR')_2$ species. The observation of only one signal for the *Me*In and 2-*Me*C_6H_4S groups in the ^1H NMR study suggests that the compound dissociates into $MeIn(2\text{-}MeC_6H_4S)_2$ monomers in tetrahydrofuran solution.

https://doi.org/10.1107/S2056989017003498



2. Structural commentary

The asymmetric unit comprises the dinuclear compound, [Me(2-MeC$_6$H$_4$S)In-μ-(2-MeC$_6$H$_4$S)$_2$InMe(2-MeC$_6$H$_4$S)], (I) (Fig. 1). The two unique indium atoms are each bonded to a methyl carbon atom, and one terminal and one bridging (2-MeC$_6$H$_4$S) group, generating a nearly square-planar four-membered In$_2$S$_2$ ring core [S2—In1—S3 = 88.28 (6), In1—S2—In2 = 91.86 (6), S2—In2—S3 = 87.02 (6), In1—S3—In2 = 92.58 (7)°]. The In atoms are in distorted trigonal–pyramidal CS$_3$ bonding environments [C1—In1—S1 = 127.3 (2), C1—In1—S2 = 113.1 (3), S1—In1—S2 = 114.66 (7), C1—In1—S3 = 105.7 (2), S1—In1—S3 = 96.94 (6), S2—In1—S3 = 88.28 (6), C2—In2—S3 = 118.2 (3), C2—In2—S4 = 124.1 (3), S3—In2—S4 = 115.00 (7), C2—In2—S2 = 102.4 (2), S2—In2—S3 = 87.02 (6), S2—In2—S4 = 95.87 (6)°]. Bond lengths and angles are similar at each indium atom.

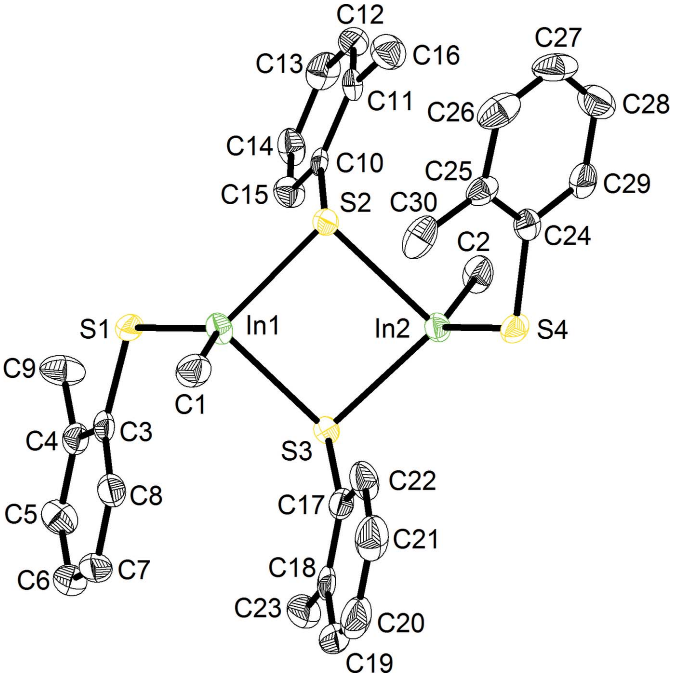


Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

3. Supramolecular features

The dimeric structures are further associated into one-dimensional polymers extending parallel to the *a* axis *via* intermolecular In$\cdots$S contacts [In1$\cdots$S4(x − 1, y, z) = 3.091 (2), In2$\cdots$S1(x + 1, y, z) = 2.920 (2) Å] (sum of metallic/van der Waals radii = 3.52 Å; Bondi, 1964) (Fig. 2). Such contacts are common for indium and other heavy main group metal chalcogenolates due to their large metal radii and potential for high coordination numbers (Briand *et al.*, 2010, 2011, 2012; Appleton *et al.*, 2011). This leads to the formation of insoluble materials for *i*BuIn(SPh)$_2$ (Nomura *et al.*, 1989). The steric bulk provided by the Me group of the (2-MeC$_6$H$_4$S) ligand is sufficient to moderate intermolecular contacts and afford solubility in organic solvents (*e.g.* toluene and tetrahydrofuran).

4. Database survey

The dinuclear structure of (I) is similar to that of [Me(MeO$_2$CCH$_2$CH$_2$S)In-μ-(MeO$_2$CCH$_2$CH$_2$S)$_2$InMe(MeO$_2$CCH$_2$CH$_2$S)] (Allan *et al.*, 2013). However, the ester carbonyl oxygen atoms of the terminal MeO$_2$CCH$_2$CH$_2$S groups occupy the coordination site *trans* to the axial bridging thiolate sulfur atom. This precludes intermolecular In$\cdots$S bonding and yields discrete dimeric units. The structure of (I) is also similar to that of the structure of dimeric [(Me$_3$Si)$_3$C](PhS)In-μ-(PhS)$_2$In[C(Me$_3$Si)$_3$](SPh) (Peppe *et al.*, 2009). However, the steric bulk of the (Me$_3$Si)$_3$C precludes further intermolecular In$\cdots$S bonding and the indium atoms are restricted to a four-coordinate distorted tetrahedral bonding environment. Other reported methylindium dithiolates employ polydentate dithiolate ligands, some of which possess dimeric and trimeric structures (Briand *et al.*, 2016).

5. Synthesis and crystallization

2-Methylbenzenethiol (0.300 g, 2.42 mmol) in toluene (2 ml) was added dropwise to a stirred solution of InMe$_3$ (0.193 g, 1.21 mmol) in toluene (5 ml). The solution was stirred for 18 h and concentrated *in vacuo* to 4 ml. After sitting at 296 K for 1 d, the solution was filtered to yield colourless, needle-like

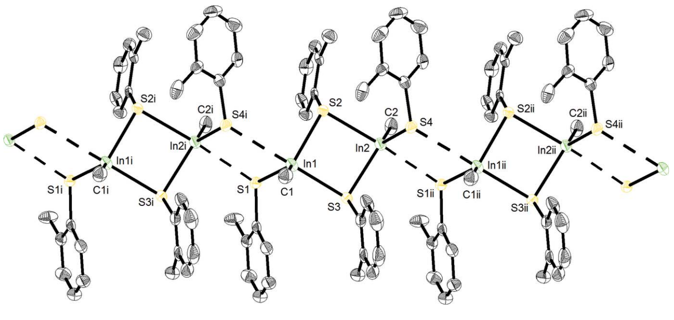


Figure 2
Part of the crystal structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) −1 + x, y, z; (ii) 1 + x, y, z.]

Table 1
Experimental details.

Crystal data	
Chemical formula	$[In_2(CH_3)_2(C_7H_7S)_4]$
M_r	752.45
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	173
a, b, c (Å)	7.4441 (15), 14.625 (3), 14.074 (3)
β (°)	99.693 (3)
V (Å^3)	1510.4 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.82
Crystal size (mm)	0.45 × 0.08 × 0.03
Data collection	
Diffractometer	Bruker *SMART1000*/P4
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2008*a*)
T_{min}, T_{max}	0.495, 0.956
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	10442, 5591, 4742
R_{int}	0.041
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.074, 1.04
No. of reflections	5591
No. of parameters	332
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.49, −1.01
Absolute structure	Flack (1983), 2079 Friedel pairs
Absolute structure parameter	0.41 (3)

Computer programs: *SMART* (Bruker, 1999), *SAINT* (Bruker, 2006), *SHELXS97* and *SHELXTL* (Sheldrick, 2008*b*), *SHELXL2013* (Sheldrick, 2015) and *DIAMOND* (Brandenburg, 2012).

crystals of (I). Yield: 0.317 g (0.421 mmol, 70%). Analysis calculated for $C_{30}H_{34}S_4In_2$: C, 47.88; H, 4.55; N, 0.00. Found: C, 46.88; H, 4.55; N, <0.3. M.p 421–422 K.

FT−IR (cm^{-1}): 672 *s*, 705 *s*, 741 *s*, 800 *w*, 846 *w*, 861 *w*, 939 *w*, 978 *w*, 1041 *m*, 1055 *m*, 1280 *w*, 1378 *w*, 1451 *m*, 1464 *m*, 1585 *w*, 2913 *w*, 3056 *w*. FT–Raman (cm^{-1}): 121 *vs*, 158 *s*, 244 *w*, 322 *m*, 443 *w*, 508 *s*, 552 *w*, 675 *w*, 800 *m*, 1043 *s*, 1128 *w*, 1148 *w*, 1204 *m*, 1465 *w*, 1565 *w*, 1586 *m*, 2916 *w*, 3047 *m*. ^{1}H NMR (200 MHz, thf-d_8, p.p.m.): δ = 0.23 [*s*, 3H, *Me*In], 2.60 [*s*, 6H, (S-2-*Me*C_6H_4)], 7.06–7.11 [*m*, 4H, (S-2-MeC_6*H_4*)] 7.23–7.28 [*m*, 2H, (S-2-MeC_6*H_4*)], 7.62–7.66 [*m*, 2H, (S-2-MeC_6*H_4*)]. ^{13}C{^{1}H} NMR (101 MHz, thf-d_8, p.p.m.): δ = −5.1 (*Me*In), 21.7 (S-2-*Me*C_6H_4), 124.1, 125.2, 129.4, 134.6, 138.4, 139.7 (S-2-Me*C_6*H_4)].

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms were included in calculated positions and refined using a riding model.

Funding information

Funding for this research was provided by: Natural Sciences and Engineering Research Council of Canada; Canada Foundation for Innovation; New Brunswick Innovation Foundation; Mount Allison University.

References

Allan, L. E. N., Briand, G. G., Decken, A., Marks, J. D., Shaver, M. P. & Wareham, R. G. (2013). *J. Organomet. Chem.* **736**, 55–62.

Appleton, S. E., Briand, G. G., Decken, A. & Smith, A. S. (2011). *Acta Cryst.* E**67**, m714.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Brandenburg, K. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Briand, G. G., Cairns, S. A., Decken, A., Dickie, C. M., Kostelnik, T. I. & Shaver, M. P. (2016). *J. Organomet. Chem.* **806**, 22–32.

Briand, G. G., Decken, A. & Hamilton, N. (2010). *Dalton Trans.* **39**, 3833–3841.

Briand, G. G., Decken, A., Hunter, N. M., Lee, G. M., Melanson, J. A. & Owen, E. M. (2012). *Polyhedron*, **31**, 796–800.

Briand, G. G., Decken, A., Hunter, N. M., Wright, J. A. & Zhou, Y. (2011). *Eur. J. Inorg. Chem.* pp. 5430–5436.

Bruker (1999). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2006). *SAINT*. Bruker AXS inc., Madison, Wisconsin, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hoffmann, G. G. (1988). *J. Organomet. Chem.* **338**, 305–317.

Nomura, R., Inazawa, S., Kanaya, K. & Matsuda, H. (1989). *Polyhedron*, **8**, 763–767.

Peppe, C., Molinos de Andrade, F. & Uhl, W. (2009). *J. Organomet. Chem.* **694**, 1918–1921.

Sheldrick, G. M. (2008*a*). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008*b*). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

supporting information

Acta Cryst. (2017). E**73**, 481-483 [https://doi.org/10.1107/S2056989017003498]

Synthesis and crystal structure of bis(μ-2-methylbenzenethiolato-κ^2S:S)bis[methyl(2-methylbenzenethiolato-κS)indium(III)]

Glen G. Briand, Andreas Decken, Courtney M. Dickie and Gregory MacNeil

Computing details

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008b); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008b).

Bis(μ-2-methylbenzenethiolato-κ^2S:S)bis[methyl(2-methylbenzenethiolato-κS)indium(III)]

Crystal data

$[In_2(CH_3)_2(C_7H_7S)_4]$
$M_r = 752.45$
Monoclinic, $P2_1$
$a = 7.4441$ (15) Å
$b = 14.625$ (3) Å
$c = 14.074$ (3) Å
$\beta = 99.693$ (3)°
$V = 1510.4$ (5) Å^3
$Z = 2$
$F(000) = 752$
$D_x = 1.655$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5877 reflections
$\theta = 2.8$–27.8°
$\mu = 1.82$ mm^{-1}
$T = 173$ K
Rod, colourless
0.45 × 0.08 × 0.03 mm

Data collection

Bruker SMART1000/P4 diffractometer
Radiation source: fine-focus sealed tube, K760
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)
$T_{min} = 0.495$, $T_{max} = 0.956$
10442 measured reflections
5591 independent reflections
4742 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 27.5$°, $\theta_{min} = 1.5$°
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 19$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.074$
$S = 1.04$
5591 reflections
332 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.49$ e Å^{-3}
$\Delta\rho_{min} = -1.01$ e Å^{-3}

Absolute structure: Flack (1983), 2079 Friedel pairs

Absolute structure parameter: 0.41 (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 esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin

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

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
In1	0.60776 (7)	0.80291 (3)	0.26699 (4)	0.02518 (14)
In2	1.05764 (7)	0.69727 (3)	0.23677 (4)	0.02406 (14)
S1	0.4196 (2)	0.70588 (16)	0.35474 (14)	0.0268 (4)
S2	0.7227 (3)	0.72420 (11)	0.12869 (14)	0.0218 (4)
S3	0.9290 (3)	0.76607 (13)	0.37732 (15)	0.0232 (4)
S4	1.2193 (2)	0.80568 (17)	0.14747 (13)	0.0268 (4)
C1	0.5973 (11)	0.9472 (6)	0.2527 (7)	0.036 (2)
H1A	0.6958	0.9746	0.2988	0.054*
H1B	0.4796	0.9694	0.2656	0.054*
H1C	0.6115	0.9641	0.1870	0.054*
C2	1.0874 (11)	0.5515 (5)	0.2317 (7)	0.034 (2)
H2A	1.2104	0.5364	0.2206	0.051*
H2B	0.9975	0.5265	0.1792	0.051*
H2C	1.0678	0.5249	0.2931	0.051*
C3	0.4643 (10)	0.7328 (5)	0.4795 (6)	0.0235 (17)
C4	0.4170 (10)	0.6667 (5)	0.5433 (6)	0.0269 (18)
C5	0.4608 (11)	0.6852 (6)	0.6420 (6)	0.0346 (19)
H5	0.4308	0.6413	0.6865	0.042*
C6	0.5449 (11)	0.7639 (6)	0.6763 (6)	0.035 (2)
H6	0.5751	0.7736	0.7439	0.042*
C7	0.5863 (11)	0.8296 (5)	0.6137 (6)	0.034 (2)
H7	0.6436	0.8850	0.6376	0.040*
C8	0.5435 (10)	0.8145 (6)	0.5147 (5)	0.0297 (18)
H8	0.5687	0.8604	0.4711	0.036*
C9	0.3221 (13)	0.5794 (6)	0.5076 (6)	0.041 (2)
H9A	0.2848	0.5467	0.5618	0.061*
H9B	0.4054	0.5410	0.4780	0.061*
H9C	0.2143	0.5937	0.4597	0.061*
C10	0.6499 (9)	0.6072 (5)	0.1171 (5)	0.0196 (16)
C11	0.6429 (10)	0.5650 (5)	0.0265 (6)	0.0254 (17)
C12	0.6019 (10)	0.4720 (5)	0.0215 (6)	0.0307 (19)
H12	0.5984	0.4414	−0.0383	0.037*
C13	0.5667 (11)	0.4229 (5)	0.0989 (6)	0.035 (2)
H13	0.5361	0.3599	0.0918	0.042*

C14	0.5755 (11)	0.4651 (5)	0.1872 (6)	0.0305 (19)
H14	0.5540	0.4311	0.2417	0.037*
C15	0.6163 (11)	0.5583 (5)	0.1957 (6)	0.0285 (18)
H15	0.6208	0.5881	0.2560	0.034*
C16	0.6849 (12)	0.6168 (6)	−0.0591 (6)	0.037 (2)
H16A	0.8122	0.6372	−0.0464	0.056*
H16B	0.6045	0.6701	−0.0708	0.056*
H16C	0.6656	0.5770	−0.1159	0.056*
C17	1.0334 (10)	0.8758 (5)	0.4071 (6)	0.0281 (18)
C18	1.0799 (11)	0.8983 (6)	0.5038 (7)	0.038 (2)
C19	1.1513 (12)	0.9872 (7)	0.5242 (8)	0.050 (3)
H19	1.1826	1.0054	0.5897	0.060*
C20	1.1768 (12)	1.0467 (7)	0.4554 (9)	0.058 (3)
H20	1.2259	1.1055	0.4727	0.070*
C21	1.1315 (12)	1.0226 (6)	0.3587 (8)	0.049 (3)
H21	1.1498	1.0646	0.3097	0.059*
C22	1.0589 (11)	0.9361 (5)	0.3345 (7)	0.037 (2)
H22	1.0272	0.9187	0.2688	0.044*
C23	1.0596 (12)	0.8356 (7)	0.5848 (6)	0.045 (2)
H23A	1.1387	0.7822	0.5831	0.068*
H23B	0.9325	0.8154	0.5782	0.068*
H23C	1.0941	0.8677	0.6462	0.068*
C24	1.1434 (10)	0.7751 (5)	0.0239 (6)	0.0267 (18)
C25	1.0177 (10)	0.8323 (5)	−0.0341 (5)	0.0276 (18)
C26	0.9738 (11)	0.8081 (7)	−0.1314 (6)	0.042 (2)
H26	0.8901	0.8452	−0.1730	0.050*
C27	1.0464 (13)	0.7330 (6)	−0.1693 (6)	0.045 (2)
H27	1.0144	0.7192	−0.2360	0.054*
C28	1.1654 (12)	0.6781 (6)	−0.1103 (7)	0.044 (2)
H28	1.2144	0.6253	−0.1359	0.053*
C29	1.2146 (10)	0.6990 (6)	−0.0141 (6)	0.0334 (17)
H29	1.2980	0.6608	0.0263	0.040*
C30	0.9353 (11)	0.9151 (6)	0.0057 (7)	0.040 (2)
H30A	1.0317	0.9593	0.0289	0.060*
H30B	0.8745	0.8965	0.0593	0.060*
H30C	0.8462	0.9432	−0.0451	0.060*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
In1	0.0262 (3)	0.0223 (2)	0.0294 (3)	−0.0009 (2)	0.0116 (2)	−0.0015 (3)
In2	0.0220 (3)	0.0244 (3)	0.0273 (3)	−0.0018 (2)	0.0085 (2)	−0.0032 (2)
S1	0.0209 (9)	0.0376 (11)	0.0221 (10)	−0.0070 (10)	0.0047 (8)	−0.0036 (10)
S2	0.0205 (10)	0.0232 (9)	0.0225 (10)	−0.0030 (7)	0.0057 (8)	−0.0025 (8)
S3	0.0218 (10)	0.0283 (9)	0.0203 (10)	−0.0009 (8)	0.0062 (9)	−0.0015 (8)
S4	0.0204 (9)	0.0356 (10)	0.0244 (10)	−0.0058 (11)	0.0039 (8)	0.0023 (11)
C1	0.033 (5)	0.031 (5)	0.042 (5)	−0.004 (4)	0.003 (4)	−0.006 (4)
C2	0.027 (5)	0.021 (4)	0.053 (6)	0.006 (3)	0.005 (4)	−0.004 (4)

C3	0.016 (4)	0.026 (3)	0.029 (4)	0.007 (3)	0.006 (3)	0.000 (3)
C4	0.021 (4)	0.033 (4)	0.027 (4)	0.005 (3)	0.004 (3)	0.002 (3)
C5	0.044 (5)	0.033 (4)	0.027 (4)	0.005 (4)	0.008 (4)	0.005 (4)
C6	0.035 (5)	0.044 (4)	0.025 (5)	0.001 (4)	0.005 (4)	−0.002 (4)
C7	0.033 (5)	0.032 (4)	0.037 (5)	−0.008 (4)	0.008 (4)	−0.014 (4)
C8	0.027 (4)	0.032 (4)	0.032 (4)	0.001 (4)	0.010 (3)	−0.002 (4)
C9	0.059 (6)	0.039 (5)	0.022 (5)	−0.011 (4)	0.004 (4)	0.002 (4)
C10	0.010 (4)	0.024 (4)	0.025 (4)	0.002 (3)	0.005 (3)	−0.002 (3)
C11	0.017 (4)	0.031 (4)	0.030 (4)	0.006 (3)	0.009 (3)	−0.003 (3)
C12	0.027 (4)	0.029 (4)	0.036 (5)	0.003 (4)	0.002 (4)	−0.012 (4)
C13	0.032 (5)	0.021 (4)	0.052 (6)	−0.009 (4)	0.008 (4)	0.000 (4)
C14	0.029 (5)	0.026 (4)	0.040 (5)	0.000 (3)	0.016 (4)	0.001 (4)
C15	0.031 (5)	0.030 (4)	0.025 (4)	−0.004 (4)	0.009 (4)	0.001 (3)
C16	0.040 (5)	0.041 (5)	0.032 (5)	−0.001 (4)	0.010 (4)	0.000 (4)
C17	0.018 (4)	0.029 (4)	0.038 (5)	−0.002 (3)	0.007 (4)	−0.008 (4)
C18	0.013 (4)	0.046 (5)	0.054 (6)	0.008 (4)	0.007 (4)	−0.022 (5)
C19	0.026 (5)	0.066 (7)	0.058 (7)	−0.005 (5)	0.005 (5)	−0.037 (6)
C20	0.026 (5)	0.054 (6)	0.096 (10)	−0.011 (5)	0.015 (6)	−0.036 (7)
C21	0.036 (5)	0.035 (5)	0.081 (8)	−0.008 (4)	0.021 (5)	−0.012 (5)
C22	0.034 (5)	0.029 (4)	0.052 (6)	−0.007 (4)	0.023 (4)	−0.009 (4)
C23	0.037 (5)	0.071 (6)	0.027 (5)	0.012 (5)	0.003 (4)	−0.007 (4)
C24	0.023 (4)	0.035 (4)	0.024 (4)	−0.007 (3)	0.011 (3)	0.003 (3)
C25	0.024 (4)	0.033 (4)	0.025 (4)	−0.010 (3)	0.002 (3)	0.005 (3)
C26	0.039 (5)	0.049 (5)	0.034 (5)	−0.013 (5)	−0.006 (4)	0.015 (5)
C27	0.053 (6)	0.061 (6)	0.020 (5)	−0.028 (5)	0.004 (4)	−0.002 (4)
C28	0.048 (6)	0.044 (6)	0.043 (6)	−0.011 (5)	0.017 (5)	−0.017 (4)
C29	0.022 (4)	0.042 (4)	0.038 (5)	−0.003 (4)	0.009 (3)	0.000 (5)
C30	0.027 (5)	0.035 (4)	0.055 (6)	0.004 (4)	−0.002 (4)	0.015 (4)

Geometric parameters (Å, º)

In1—C1	2.119 (9)	C12—C13	1.366 (12)
In1—S1	2.466 (2)	C12—H12	0.9500
In1—S2	2.531 (2)	C13—C14	1.379 (11)
In1—S3	2.678 (2)	C13—H13	0.9500
In1—S4$^{\rm i}$	3.0910 (19)	C14—C15	1.398 (10)
In2—C2	2.146 (8)	C14—H14	0.9500
In2—S4	2.460 (2)	C15—H15	0.9500
In2—S3	2.546 (2)	C16—H16A	0.9800
In2—S2	2.722 (2)	C16—H16B	0.9800
In2—S1$^{\rm ii}$	2.9201 (19)	C16—H16C	0.9800
S1—C3	1.776 (8)	C17—C22	1.386 (12)
S1—In2$^{\rm i}$	2.9201 (19)	C17—C18	1.386 (12)
S2—C10	1.794 (7)	C18—C19	1.415 (12)
S3—C17	1.802 (8)	C18—C23	1.491 (13)
S4—C24	1.792 (8)	C19—C20	1.339 (15)
C1—H1A	0.9800	C19—H19	0.9500
C1—H1B	0.9800	C20—C21	1.391 (14)

C1—H1C	0.9800	C20—H20	0.9500
C2—H2A	0.9800	C21—C22	1.395 (11)
C2—H2B	0.9800	C21—H21	0.9500
C2—H2C	0.9800	C22—H22	0.9500
C3—C8	1.386 (10)	C23—H23A	0.9800
C3—C4	1.404 (10)	C23—H23B	0.9800
C4—C5	1.398 (11)	C23—H23C	0.9800
C4—C9	1.504 (11)	C24—C29	1.379 (11)
C5—C6	1.361 (11)	C24—C25	1.409 (10)
C5—H5	0.9500	C25—C26	1.399 (11)
C6—C7	1.373 (11)	C25—C30	1.508 (11)
C6—H6	0.9500	C26—C27	1.371 (13)
C7—C8	1.393 (11)	C26—H26	0.9500
C7—H7	0.9500	C27—C28	1.368 (13)
C8—H8	0.9500	C27—H27	0.9500
C9—H9A	0.9800	C28—C29	1.376 (11)
C9—H9B	0.9800	C28—H28	0.9500
C9—H9C	0.9800	C29—H29	0.9500
C10—C15	1.374 (10)	C30—H30A	0.9800
C10—C11	1.409 (10)	C30—H30B	0.9800
C11—C12	1.393 (10)	C30—H30C	0.9800
C11—C16	1.500 (11)		

C1—In1—S1	127.3 (2)	C12—C11—C10	116.6 (7)
C1—In1—S2	113.1 (3)	C12—C11—C16	121.7 (8)
S1—In1—S2	114.66 (7)	C10—C11—C16	121.6 (7)
C1—In1—S3	105.7 (2)	C13—C12—C11	122.9 (8)
S1—In1—S3	96.94 (6)	C13—C12—H12	118.6
S2—In1—S3	88.28 (6)	C11—C12—H12	118.6
C1—In1—S4$^{\rm i}$	85.4 (2)	C12—C13—C14	119.8 (7)
S1—In1—S4$^{\rm i}$	73.86 (6)	C12—C13—H13	120.1
S2—In1—S4$^{\rm i}$	89.64 (6)	C14—C13—H13	120.1
S3—In1—S4$^{\rm i}$	168.67 (6)	C13—C14—C15	119.3 (8)
C2—In2—S4	124.1 (3)	C13—C14—H14	120.4
C2—In2—S3	118.2 (3)	C15—C14—H14	120.4
S4—In2—S3	115.00 (7)	C10—C15—C14	120.4 (8)
C2—In2—S2	102.4 (2)	C10—C15—H15	119.8
S4—In2—S2	95.87 (6)	C14—C15—H15	119.8
S3—In2—S2	87.02 (6)	C11—C16—H16A	109.5
C2—In2—S1$^{\rm ii}$	88.3 (2)	C11—C16—H16B	109.5
S4—In2—S1$^{\rm ii}$	77.21 (6)	H16A—C16—H16B	109.5
S3—In2—S1$^{\rm ii}$	88.45 (6)	C11—C16—H16C	109.5
S2—In2—S1$^{\rm ii}$	169.21 (6)	H16A—C16—H16C	109.5
C3—S1—In1	109.9 (3)	H16B—C16—H16C	109.5
C3—S1—In2$^{\rm i}$	125.0 (3)	C22—C17—C18	122.0 (8)
In1—S1—In2$^{\rm i}$	106.71 (7)	C22—C17—S3	120.2 (6)
C10—S2—In1	111.6 (2)	C18—C17—S3	117.8 (6)
C10—S2—In2	98.4 (2)	C17—C18—C19	116.1 (9)

In1—S2—In2	91.86 (6)	C17—C18—C23	124.3 (8)
C17—S3—In2	109.2 (3)	C19—C18—C23	119.6 (8)
C17—S3—In1	105.3 (3)	C20—C19—C18	123.0 (9)
In2—S3—In1	92.58 (7)	C20—C19—H19	118.5
C24—S4—In2	103.5 (2)	C18—C19—H19	118.5
In1—C1—H1A	109.5	C19—C20—C21	120.1 (9)
In1—C1—H1B	109.5	C19—C20—H20	120.0
H1A—C1—H1B	109.5	C21—C20—H20	120.0
In1—C1—H1C	109.5	C20—C21—C22	119.2 (10)
H1A—C1—H1C	109.5	C20—C21—H21	120.4
H1B—C1—H1C	109.5	C22—C21—H21	120.4
In2—C2—H2A	109.5	C17—C22—C21	119.5 (9)
In2—C2—H2B	109.5	C17—C22—H22	120.2
H2A—C2—H2B	109.5	C21—C22—H22	120.2
In2—C2—H2C	109.5	C18—C23—H23A	109.5
H2A—C2—H2C	109.5	C18—C23—H23B	109.5
H2B—C2—H2C	109.5	H23A—C23—H23B	109.5
C8—C3—C4	120.1 (7)	C18—C23—H23C	109.5
C8—C3—S1	122.8 (6)	H23A—C23—H23C	109.5
C4—C3—S1	117.0 (6)	H23B—C23—H23C	109.5
C5—C4—C3	117.4 (7)	C29—C24—C25	121.0 (7)
C5—C4—C9	120.9 (7)	C29—C24—S4	119.9 (6)
C3—C4—C9	121.6 (7)	C25—C24—S4	119.0 (6)
C6—C5—C4	122.2 (8)	C26—C25—C24	116.1 (8)
C6—C5—H5	118.9	C26—C25—C30	121.7 (8)
C4—C5—H5	118.9	C24—C25—C30	122.2 (7)
C5—C6—C7	120.2 (8)	C27—C26—C25	122.8 (8)
C5—C6—H6	119.9	C27—C26—H26	118.6
C7—C6—H6	119.9	C25—C26—H26	118.6
C6—C7—C8	119.5 (7)	C28—C27—C26	119.4 (8)
C6—C7—H7	120.3	C28—C27—H27	120.3
C8—C7—H7	120.3	C26—C27—H27	120.3
C3—C8—C7	120.4 (7)	C27—C28—C29	120.3 (9)
C3—C8—H8	119.8	C27—C28—H28	119.8
C7—C8—H8	119.8	C29—C28—H28	119.8
C4—C9—H9A	109.5	C28—C29—C24	120.3 (8)
C4—C9—H9B	109.5	C28—C29—H29	119.8
H9A—C9—H9B	109.5	C24—C29—H29	119.8
C4—C9—H9C	109.5	C25—C30—H30A	109.5
H9A—C9—H9C	109.5	C25—C30—H30B	109.5
H9B—C9—H9C	109.5	H30A—C30—H30B	109.5
C15—C10—C11	121.1 (7)	C25—C30—H30C	109.5
C15—C10—S2	121.1 (6)	H30A—C30—H30C	109.5
C11—C10—S2	117.7 (6)	H30B—C30—H30C	109.5

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