

mer-Triiodotripyridineindium(III)

Jennifer A. J. Pardoe,^a Andrew R. Cowley,^a Anthony J. Downs^{a*} and Timothy M. Greene^b

^aInorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, England, and ^bDepartment of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, England

Correspondence e-mail: tony.downs@chem.ox.ac.uk

Received 27 January 2005

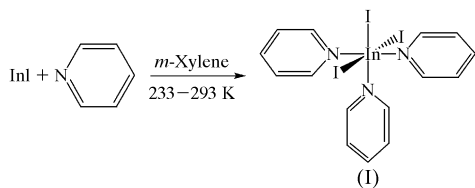
Accepted 1 March 2005

Online 18 March 2005

Crystals of the title compound, $[\text{InI}_3(\text{C}_5\text{H}_5\text{N})_3]$, consist of discrete molecules lying on a twofold axis running parallel to the crystallographic *b* axis. The molecules exhibit meridional octahedral stereochemistry, with In—I bond lengths of 2.8390 (6) and 2.8676 (3) Å, and In—N bond lengths of 2.323 (5) and 2.309 (4) Å.

Comment

In an attempt to extend the chemistry of subvalent indium compounds, we have been investigating the feasibility of producing solutions in which an indium(I) halide is acceptably stable to disproportionation at temperatures between 190 and 300 K. One strategy has involved co-condensation of the vapours of the halide and an excess of a potential solvent (*e.g.* toluene or toluene/ether), followed by warming of the mixture to see whether a solution of practical use in synthesis can be formed. Although ready dissolution without disproportionation is rare, indium(I) iodide has proved to be the halide most prone to dissolve in organic solvents, of which pyridine or pyridine-containing mixtures have been among the most promising. Solutions of indium(I) iodide in a pyridine/*m*-xylene (2:1) mixture are lastingly stable below 243 K but undergo slow disproportionation at room temperature, giving a mixture of indium metal and triiodotripyridineindium(III), (I). Crystallographic studies of (I) at 150 K have afforded a rare structural characterization of a neutral six-coordinate indium(III) iodide complex.



The orthorhombic crystals of (I) (Fig. 1) consist of neutral molecules with indium in a pseudo-octahedral environment and with the meridional stereochemistry suggested in a

preliminary report (Small & Worrall, 1982) but different from that deduced on the basis of IR measurements (Adams *et al.*, 1968). Unlike the corresponding chloride (Jefferies *et al.*, 1984) and bromide (Small & Worrall, 1982) adducts, the iodo compound takes up no additional pyridine molecules of solvation, presumably as a result of the extra bulk of the iodide ligands.

The In—I bond lengths [2.8390 (6) and 2.8676 (3) Å] are comparable to those found in the related complex $[\text{InI}_3(4\text{-MeC}_5\text{H}_4\text{N})_3]$, (II) [2.803 (4), 2.848 (4) and 2.893 (4) Å; Brown & Tuck, 1996], there being a less pronounced but still distinct shortening of the unique In—I bond *trans* to a pyridine ring. For these two neutral six-coordinate InI_3 complexes, the In—I distances occur in the range 2.80–2.90 Å. As expected, the corresponding distances are shorter in similar five-coordinate complexes (2.66–2.80 Å), and shorter still in four-coordinate complexes (2.50–2.74 Å), as revealed by the 19 hits in a search of the Cambridge Structural Database (Version 5.26; Allen, 2002). The terminal and bridging In—I distances of the In_2I_6 molecules of solid indium(III) iodide are 2.644 (2) and 2.842 (2) Å, respectively (Kniep *et al.*, 1982).

The In—N bond lengths in (I), with an average of 2.316 Å, are not significantly different from those in (II) (2.31 Å), $[\text{InCl}_3(\text{C}_5\text{H}_5\text{N})_3] \cdot \text{C}_5\text{H}_5\text{N}$ (2.327 Å) and $[\text{InBr}_3(\text{C}_5\text{H}_5\text{N})_3] \cdot \text{C}_5\text{H}_5\text{N}$ (2.30 Å). In every case, the longest In—N bond is that *trans* to a halogen, *viz.* 2.323 (5) *versus* 2.309 (4) Å in (I), 2.34 (2) *versus* 2.28 (3)/2.30 (3) Å in (II), 2.377 (21) *versus* 2.302 (7) Å in $[\text{InCl}_3(\text{C}_5\text{H}_5\text{N})_3] \cdot \text{C}_5\text{H}_5\text{N}$ and 2.32 (2) *versus* 2.28 (3)/2.31 (2) Å in $[\text{InBr}_3(\text{C}_5\text{H}_5\text{N})_3] \cdot \text{C}_5\text{H}_5\text{N}$, even if the difference is not always statistically significant. Any systematic dependence on the nature of the halogen is, at best, small,

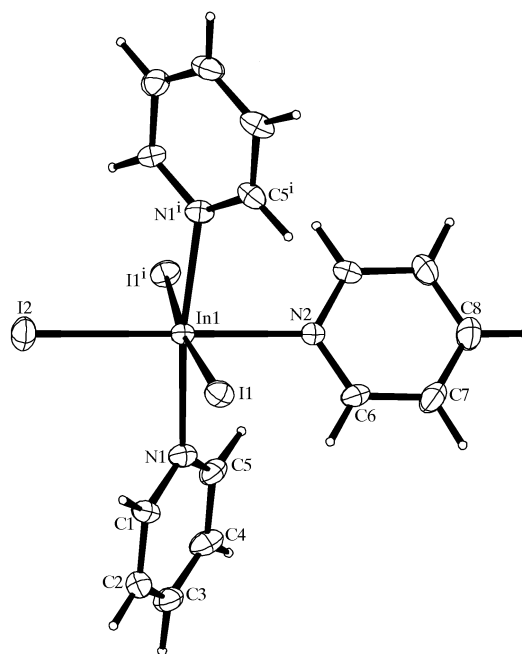


Figure 1

The molecular structure of (I), showing the atom-labelling scheme (ORTEP; Burnett & Johnson, 1996). Displacement ellipsoids are drawn at the 40% probability level. [Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.]

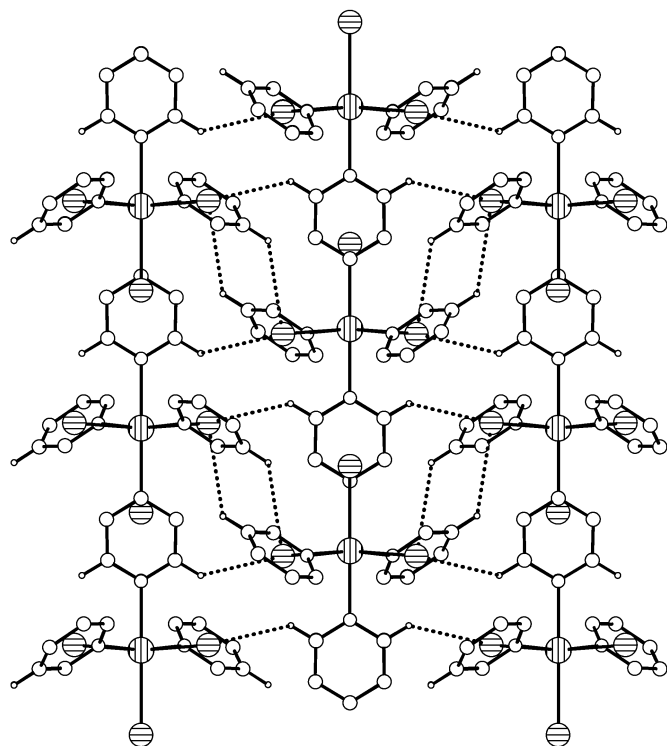


Figure 2

A packing diagram of (I), viewed along the *a* axis, with the *b* axis aligned vertically. Dotted lines indicate relatively short H...I distances, which may be indicative of weak hydrogen bonding. Key: In atoms are vertically hatched, I atoms are horizontally hatched, and N, C and H atoms are unfilled white circles.

although no strict comparison can be made in view of the diversity of the data (most of which relate to crystals at room temperature).

The molecules in (I) each lie on a twofold rotation axis running through the I2–In–N2 group and parallel to the crystallographic *b* axis. As in (II), the I1–In–I1ⁱ and N1–In–N1ⁱ angles (symmetry code as in Table 1) depart from linearity, and each pyridine ring is tilted out of the appropriate plane by an average of 40 (2)°, in keeping with both the stronger non-bonded repulsion exerted by atom I2, as compared with N2, and minimization of the interaction between the iodide and pyridine functions. Analysis of the dimensions of the coordinated pyridine molecules indicate no unusual features. The packing of the molecules of (I) (Fig. 2) gives little evidence of specific interactions. At 3.17 Å, for example, the shortest H...I distance is consistent with a normal van der Waals contact, although the existence of weak hydrogen bonding is not precluded (Table 2). Likewise, short I...I contacts are evidently disfavoured (there are none below 5 Å), which could imply that the I atoms carry a substantial negative charge.

Experimental

Crystals of (I) were grown from a solution initially containing InI in pyridine/*m*-xylene (2:1) over a period of one month at room temperature.

Crystal data

[InI₃(C₅H₅N)₃]
M_r = 732.84
 Orthorhombic, *Pbcn*
a = 9.6622 (2) Å
b = 14.9139 (4) Å
c = 13.9850 (4) Å
V = 2015.25 (9) Å³
Z = 4
D_x = 2.415 Mg m⁻³

Data collection

Nonius KappaCCD diffractometer
 ω scans
 Absorption correction: multi-scan
 (DENZO/SCALEPACK;
 Otwinowski & Minor, 1997)
T_{min} = 0.53, *T_{max}* = 0.71
 13 983 measured reflections
 2293 independent reflections

Refinement

Refinement on *F*
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.029$
S = 1.01
 1670 reflections
 102 parameters
 H-atom parameters constrained
 Weighting scheme: part 1,
 Chebyshev polynomial (Watkin,
 1994; Prince, 1982), [weight] =

Mo *K* α radiation
 Cell parameters from 13 983
 reflections
 $\theta = 5\text{--}28^\circ$
 $\mu = 5.77\text{ mm}^{-1}$
T = 150 K
 Block, colourless
 0.11 × 0.09 × 0.06 mm

1670 reflections with *I* > 3 σ (*I*)
 $R_{\text{int}} = 0.038$
 $\theta_{\text{max}} = 27.5^\circ$
h = -12 → 12
k = -19 → 19
l = -18 → 18

$1/[A_0T_0(x) + A_1T_1(x) + \dots + A_{n-1}T_{n-1}(x)]$, where *A_i* are the Chebyshev coefficients 0.403, 0.231 and 0.196, and $x = F/F_{\text{max}}$; robust weighting (Prince, 1982), $W = [\text{weight}][1 - (\Delta F/6\sigma F)^2]^2$
 $(\Delta\sigma)_{\text{max}} = 0.006$
 $\Delta\rho_{\text{max}} = 0.60\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.86\text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

In1–I1	2.8676 (3)	In1–N1	2.309 (4)
In1–I2	2.8390 (6)	In1–N2	2.323 (5)
I1–In1–I1 ⁱ	173.079 (18)	N1–In1–N1 ⁱ	172.52 (18)
I1–In1–I2	93.460 (9)	I1–In1–N2	86.540 (9)
I1–In1–N1	89.64 (9)	I2–In1–N2	179.995
I2–In1–N1	93.74 (9)	N1–In1–N2	86.26 (9)
I1–In1–N1 ⁱ	89.91 (9)		

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C2–H21...I1 ⁱⁱ	1.00	3.17	3.904 (5)	131
C6–H61...I1 ⁱⁱⁱ	1.00	3.18	3.946 (4)	135

Symmetry codes: (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$.

H atoms were positioned geometrically and treated using a riding model, with C–H distances assumed to be 1.00 Å. The $U_{\text{iso}}(\text{H})$ values were taken to be $1.2U_{\text{eq}}(\text{C})$.

Data collection: COLLECT (Nonius, 2000); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: DENZO; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: CRYSTALS; software used to prepare material for publication: CRYSTALS.

The authors thank the EPSRC for the award of a research grant including the funding of a postdoctoral assistantship for JAJP.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1705). Services for accessing these data are described at the back of the journal.

References

- Adams, D. M., Carty, A. J., Carty, P. & Tuck, D. G. (1968). *J. Chem. Soc. A*, pp. 162–164.
- Allen, F. H. (2002). *Acta Cryst. B***58**, 380–388.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
- Brown, M. A. & Tuck, D. G. (1996). *Inorg. Chim. Acta*, **247**, 135–138.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Jeffs, S. E., Small, R. W. H. & Worrall, I. J. (1984). *Acta Cryst. C***40**, 1329–1331.
- Knier, R., Bles, P. & Poll, W. (1982). *Angew. Chem. Int. Ed. Engl.* **21**, 386.
- Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.
- Small, R. W. H. & Worrall, I. J. (1982). *Acta Cryst. B***38**, 932–934.
- Watkin, D. (1994). *Acta Cryst. A***50**, 411–427.