Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Tetrameric indium trichloride, a new modification of a widely used compound

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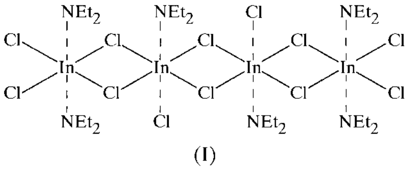
Received 27 March 2000
Accepted 25 July 2000

The title compound, hexa-μ-chloro-1:2κ^4*Cl*;2:3κ^4*Cl*;3:4κ^4*Cl*-hexachloro-1κ^2*Cl*,2κ*Cl*,3κ*Cl*,4κ^2*Cl*-hexakis(diethylamine)-1κ^2*N*,2κ*N*,3κ*N*,4κ^2*N*-tetraindium(III), $[(InCl_3)_4(Et_2NH)_6]$ or $[In_4Cl_{12}(C_4H_{11}N)_6]$, lies about an inversion centre and consists of four octahedrally coordinated In centres linked by bridging Cl atoms to form three four-membered In_2Cl_2 rings.

Comment

$InCl_3$ is a compound widely used as an educt in metal–organic chemistry. Its relatively good solubility in coordinating solvents such as tetrahydrofuran (THF) makes it easy to obtain crystals suitable for X-ray crystallography from almost any experiment in which it does not fully react to form a product. The orthorhombic adduct $InCl_3$·2THF, the best known modification, has been the subject of several structure determinations (*e.g.* Dias & Jin, 1996). The molecule described here, (I), can be regarded as a tetrameric species of $InCl_3$ which is coordinated to six molecules of Et_2NH.



(I)

Single-crystal X-ray structure analysis of (I) shows the molecule to crystallize in the triclinic space group $P\overline{1}$ with half a molecule in the asymmetric unit. The rest of the molecule is generated by an inversion centre. The core of the structure consists of four In atoms linked by six bridging Cl atoms forming three four-membered In_2Cl_2 rings. In addition, the inner In atoms are each connected to one, and the outer In atoms to two, terminal-bonded Cl atoms. To complete their distorted octahedral coordination sphere, the inner In atoms are coordinated by one and the outer by two molecules of diethylamine, as shown in Fig. 1.

The centre of the middle In_2Cl_2 ring lies on the crystallographic inversion centre, so this ring is planar. The outer four-membered rings are planar to within a maximum deviation of 0.0574 (2) Å from the best plane. As expected for octahedral coordination, the dihedral angle of 87.9 (3)° is close to 90°.

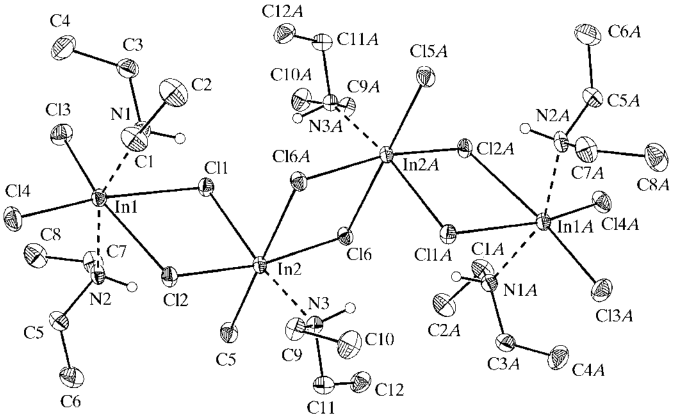


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. Only amino-H atoms are shown, as small spheres of arbitrary radii.

Two differently coordinated In centres exist in the structure: In1 and In1*A* are coordinated to four Cl atoms (two bridging and two terminal Cl atoms) and two diethylamine molecules, while In2 and In2*A* are linked to five Cl atoms (four bridging and one terminal Cl atoms) and only one diethylamine. The mean $In1-Cl_{terminal}$ and In1—N distances of 2.396 (2) and 2.160 (2) Å, respectively, are somewhat shorter than the corresponding In2—*X* bonds [2.4122 (8) and 2.267 (2) Å, respectively], while the mean $In1-Cl_{bridging}$ bonds [2.781 (2) Å] are longer than the $In2-Cl_{bridging}$ bonds [2.562 (2) Å].

The octahedral angle varies from 75.97 (4)° for Cl1—In1—Cl2 to 103.04 (5)° for Cl3—In1—Cl4. The ring tension in the four-membered rings tends to reduce the value for the endocyclic Cl—In—Cl angles, while it increases the exocyclic angles, and a net of five crystallographically independent weak hydrogen bonds between the H atoms of the diethylamine molecules and Cl atoms influences the N—In—Cl and N—In—N angles. The strongest hydrogen bond is 2.62 (2) Å, between Cl5 and the H atom bonded to N2, and the longest is 2.88 (2) Å, between Cl6*A* and the H atom bonded to N1.

Several structures of compounds containing two In centres that are linked *via* bridging Cl atoms can be found in the literature (*e.g.* Neumüller, 1991), but only one of them shows terminal-bonded Cl atoms as well (Su *et al.*, 1998). Only two such species with bridging Cl and more than two In centres (Self *et al.*, 1994; Beachley *et al.*, 1989) are deposited with the Cambridge Structural Database (Allen & Kennard, 1993).

Experimental

In the course of obtaining compound (I), the primary reaction was an elimination of Me_3SiCl from Et_2NSiMe_3 and $InCl_3$ to generate an InN precursor system for chemical vapour deposition. Traces of H_2O reacted with some of the Et_2NSiMe_3 to give the siloxane and diethylamine. Compound (I) was obtained as a by-product following the scheme given below:

$$6Et_2NH + 4InCl_3 \longrightarrow [(InCl_3)_4(Et_2NH)_6].$$

Suitable crystals grew directly in the reaction flask after a few weeks.

Crystal data

$[In_4Cl_{12}(C_4H_{11}N)_6]$
M_r = 1323.64
Triclinic, $P\overline{1}$
a = 10.962 (2) Å
b = 11.407 (2) Å
c = 11.674 (2) Å
α = 95.46 (3)°
β = 109.57 (3)°
γ = 114.20 (3)°
V = 1207.8 (4) $Å^3$

Z = 1
D_x = 1.820 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
θ = 1.9–25.0°
μ = 2.574 mm^{-1}
T = 133 (2) K
Block, colourless
0.3 × 0.3 × 0.1 mm

Data collection

Stoe–Siemens–Huber four-circle diffractometer
φ and ω scans
Absorption correction: semi-empirical (*SADABS*; Sheldrick, 1999)
T_{min} = 0.512, T_{max} = 0.783
45 298 measured reflections

5291 independent reflections
4871 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 27.06°
$h = -14 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 14$
Intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.023
$wR(F^2)$ = 0.054
S = 1.138
5291 reflections
223 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 0.4598P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.58 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.08 e $Å^{-3}$

H atoms connected to C atoms were set in geometrically calculated positions and were refined using a riding model. H atoms attached to N atoms were located in the difference electron-density map and were refined while restraining the N—O distances to 0.91 Å. The displacement parameters of the H atoms were constrained to be $1.2U_{eq}$ of their parent atoms for N—H and CH_2, and to be $1.5U_{eq}$ for CH_3 groups. The deepest electron-density hole is located 0.90 Å from the In1 atom.

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.88 (2)	2.75 (2)	3.258 (2)	118 (2)
N2—H2···Cl5	0.88 (2)	2.62 (2)	3.476 (2)	167 (2)
N2—H2···Cl2	0.88 (2)	2.76 (2)	3.158 (2)	110 (2)
N1—H1···$Cl6^i$	0.88 (2)	2.85 (2)	3.685 (2)	158 (2)
N3—H3···$Cl1^i$	0.89 (2)	2.78 (2)	3.653 (2)	168 (2)

Symmetry code: (i) $-x, 1-y, -z$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1146). Services for accessing these data are described at the back of the journal.

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