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Trichlorobis(tetrahydrofuran)indium(III)

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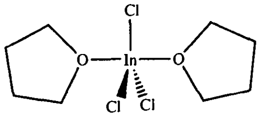
Abstract

The coordination geometry about the In atom in trichlorobis(tetrahydrofuran)indium(III), [InCl$_3$(C$_4$H$_8$O)$_2$], approximates a trigonal bipyramid, with three Cl atoms in equatorial positions and two axial tetrahydrofuran ligands. The molecule lies on a crystallographic twofold axis that is coincident with one of the In—Cl bonds.

Comment

Recent interest in the preparation of semiconducting materials has led to widespread activity in the synthesis of new compounds of indium. A common starting material for these preparations is indium trichloride and the reactions are often carried out with tetrahydrofuran as the solvent. In the course of our synthetic investigations we were able to isolate crystals of the complex InCl$_3$(thf)$_2$ (I) (thf = tetrahydrofuran). Indium complexes exhibit a wide range of coordination numbers and geometries, and the empirical formula of the complex is not always a reliable indicator of its structure. The InCl$_5^{2-}$ ion has a square-pyramidal configuration (Brown, Einstein & Tuck, 1969), whereas InCl$_3$(PPh$_3$)$_2$ has trigonal bipyramidal geometry (Veidis & Palenik, 1969). In the case of InI$_3$(Me$_2$SO)$_2$ the crystal structure determination revealed that the compound is actually the ionic complex [InI$_2$(Me$_2$SO)$_4$][InI$_4$] (Einstein & Tuck, 1970). We decided, therefore, to undertake a single-crystal X-ray diffraction study of InCl$_3$(thf)$_2$ in order to determine the exact structure of this synthetic intermediate. The parameters obtained from the structure determination also provide a benchmark for comparison with similar structural elements in other complexes in which Cl or thf ligands are attached to In.



(I)

A colorless crystal of InCl$_3$(thf)$_2$ was obtained from a solution of indium trichloride in dry tetrahydrofuran and was sealed in a 0.5 mm glass capillary tube under a thf-saturated atmosphere of dry nitrogen. The structure determination revealed that the coordination geometry about the In atom approximates a trigonal bipyramid, with the three Cl atoms in equatorial positions and two axial thf ligands. The molecule lies on a crystallographic twofold axis that passes through the In and Cl(1) atoms. Both of the symmetry-related thf ligands are oriented so that the C$_4$O rings are tilted toward the In—Cl(1) bond and are rotated slightly about the oxygen–centroid axis, with ring-centroid—O—In—Cl(1) torsion angles of 3.1°. Each In—O bond axis makes an angle of 112.5° with respect to the mean plane of the ring, the In—O—centroid angle is 155.8° and the sum of the angles about the O atom is 351.2 (7)°. The relationship of the two O atoms to the In is virtually linear, with a O—In—O′ angle of 179.0 (3)°. The In—O distance is 2.265 (5) Å.

The orientations of the thf ligands cause very little distortion from idealized local D_{3h} symmetry at the In atom. The Cl(2)—In—Cl(2′) angle of 118.1 (1)° and the value of 120.9 (1)° for the two identical Cl(1)—In—Cl(2) angles are very close to the idealized value of 120°, and the In—Cl(1) bond distance of 2.314 (3) Å is only slightly shorter than the value of 2.339 (2) Å observed for the bonds to the two symmetry-related Cl atoms.

Coordination geometry and electronic factors appear to have a significant effect upon the In—Cl bond length. Higher coordination numbers and bulky ligands are expected to give longer bonds as a result of steric crowding at the In atom. Greater negative charge and increased electron donation from ligands should also increase the In—Cl distance. The average In—Cl distance of 2.331 (3) Å for InCl$_3$(thf)$_2$ is virtually the same as the value of 2.33 (3) Å found for the InCl$_4^-$ anion, which has a lower coordination number but a higher negative charge (Trotter, Einstein & Tuck, 1969). The effects of increasing coordination number and increasing negative charge are evident when comparing these values to those found for the anionic complexes InCl$_5^{2-}$ [square-pyramidal geometry, average In—Cl

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= 2.448 (12) Å (Brown, Einstein & Tuck, 1969)] and $InCl_5(OH_2)^{2-}$ [octahedral, average In—Cl = 2.58 Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1958, 1965)]. It is interesting to note that the average In—Cl distance in $InCl_3(thf)_2$ is significantly shorter than the corresponding average of 2.383 (5) Å found for the related complex $InCl_3(PPh_3)_2$, which also has a trigonal bipyramidal coordination environment (Veidis & Palenik, 1969). When one of the thf ligands of $InCl_3(thf)_2$ is removed and two of the Cl atoms are replaced by two more electron-donating $Mo(\eta^5\text{-}C_5H_5)(CO)_3$ groups to give $[\mu\text{-}InCl(thf)][Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$, the In—Cl bond lengthens from 2.331 (3) to 2.437 (2) Å and the distance between In and the O atom of the tetrahydrofuran changes from 2.265 (5) to 2.301 (5) Å (Clarkson, Norman & Farrugia, 1990).

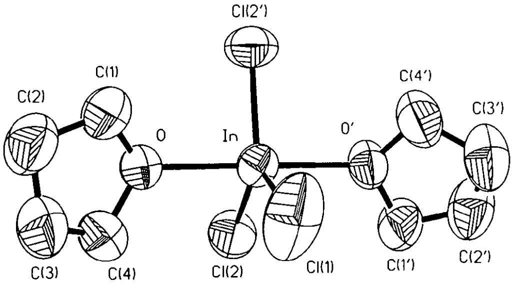

Fig. 1. An *ORTEP*II drawing of $InCl_3(thf)_2$ with 50% probability ellipsoids. H atoms are omitted for clarity.

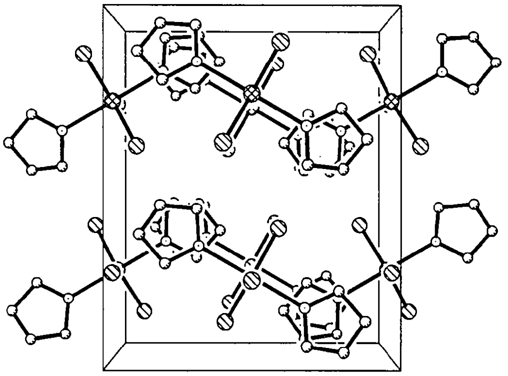

Fig. 2. The contents of one unit cell shown in projection down the *b* axis. H atoms are omitted for clarity.

Experimental

Crystal data

$[InCl_3(C_4H_8O)_2]$
M_r = 365.39
Orthorhombic
Pbcn
a = 10.805 (1) Å
b = 10.114 (1) Å
c = 13.110 (1) Å
V = 1432.8 (2) Å^3
Z = 4
D_x = 1.694 Mg m^{-3}

Mo *Kα* radiation
λ = 0.71073 Å
Cell parameters from 43 reflections
θ = 5.437-12.476°
μ = 2.140 mm^{-1}
T = 296 K
Plate
0.38 × 0.36 × 0.14 mm
Colorless

Data collection

Siemens *P*4 diffractometer
ω/2θ scans
Absorption correction: empirical
T_{min} = 0.775, T_{max} = 0.963
1400 measured reflections
1016 independent reflections
618 observed reflections [$F > 4\sigma(F)$]

R_{int} = 0.0151
θ_{max} = 23.15°
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 11$
$l = -14 \rightarrow 1$
3 standard reflections monitored every 97 reflections intensity variation: within counting statistics

Refinement

Refinement on *F*
R = 0.0347
wR = 0.0330
S = 1.52
618 reflections
65 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
In	1/2	0.1029 (1)	3/4	0.068 (1)
Cl(1)	1/2	−0.1259 (3)	3/4	0.153 (2)
Cl(2)	0.5929 (2)	0.2218 (2)	0.6175 (2)	0.102 (1)
O	0.3187 (5)	0.1009 (6)	0.6633 (4)	0.084 (2)
C(1)	0.2038 (8)	0.0733 (10)	0.7117 (7)	0.108 (5)
C(2)	0.1170 (9)	0.0419 (11)	0.6299 (9)	0.126 (5)
C(3)	0.1926 (10)	−0.0152 (10)	0.5493 (9)	0.127 (5)
C(4)	0.3130 (10)	0.0524 (10)	0.5603 (7)	0.117 (5)

Table 2. *Selected geometric parameters* (Å, °)

In—Cl(1)	2.314 (3)	In—Cl(2)	2.339 (2)
In—O	2.265 (5)	O—C(1)	1.421 (10)
O—C(4)	1.439 (11)	C(1)—C(2)	1.460 (15)
C(2)—C(3)	1.455 (16)	C(3)—C(4)	1.476 (15)
Cl(1)—In—Cl(2)	120.9 (1)	Cl(1)—In—O	89.5 (2)
Cl(2)—In—O	90.2 (1)	Cl(2)—In—Cl(2′)	118.1 (1)
O—In—Cl(2′)	90.3 (1)	O—In—O′	179.0 (3)
In—O—C(1)	122.2 (5)	In—O—C(4)	120.7 (5)
C(1)—O—C(4)	108.3 (7)	O—C(1)—C(2)	106.0 (8)
C(1)—C(2)—C(3)	105.0 (8)	C(2)—C(3)—C(4)	103.9 (9)
O—C(4)—C(3)	106.7 (8)		

H atoms were placed in calculated positions but were not refined. The computer program used was *SHELXTL-IRIS* (Sheldrick, 1978) provided by Siemens Analytical X-ray Instruments Inc. Molecular graphics were produced using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71698 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1063]

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$(C_{18}H_{36}N_2O_6Na)_2[Ta_6Cl_{12}(CH_3O)_6]$.-$6CH_3OH$ with Partial Substitution of CH_3O^- by OH^-

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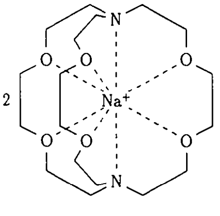
Abstract

Bis[(4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane-κ^2N,κ^6O)sodium] dodeca-μ-chlorohexamethoxy-1κO,2κO,3κO,4κO,5κO,6κO-*octahedro*-hexatantalate–methanol (1/6), $[Na(C_{18}H_{36}N_2O_6)]_2$-$[Ta_6Cl_{12}(CH_3O)_{5.4}(OH)_{0.6}].6CH_3OH$, is built of $(C_{18}H_{36}N_2O_6Na)^+$ cations, $[Ta_6Cl_{12}(OCH_3/1OH)_6]^{2-}$ anions and solvating methanol molecules linked by hydrogen bridges to the anions. The octahedral $[Ta_6Cl_{12}]^{4+}$ cluster unit exhibits two slightly different Ta—Ta distances of 2.978 (1) and 2.987 (1) Å. All four crystallographically distinct Ta—Cl distances are identical within one standard deviation [2.447 (3) – 2.449 (3) Å]. For the terminal methoxy ligand a Ta—O distance of 2.05 (1) Å is observed. Because of the preparation procedure employed, we expected a partial substitution of OCH_3^- by OH^-, which was supported by the structure refinement as only 90% occupancy of the position of the C atom was observed.

Comment

In the course of experiments aimed at the preparation of $[Ta_6Cl_{12}]^{4+}$ clusters with the anions of thermally labile alcohols as outer ligands we attempted to adapt the method developed by Perchenek & Simon (1993) for $[Mo_6Cl_8]^{4+}$ systems to the redox labile $[Ta_6Cl_{12}]^{n+}$ unit ($2 \leq n \leq 4$). We prepared the title compound (I) as a starting material and determined its structure by single-crystal X-ray diffraction for proper characterization.



$[Ta_6Cl_{12}(OCH_3)_{5.4}(OH)_{0.6}]^{2-} \cdot 6CH_3OH$

(I)

The centre of the $[Ta_6Cl_{12}(OCH_3/OH)_6]^{2-}$ anion occupies position 3(*b*) with site symmetry $\bar{3}$ in the hexagonal setting of space group $R\bar{3}$ (No. 148). The octahedron is slightly elongated along the $\bar{3}$ axis passing through the triangles Ta-Ta^{i}-Ta^{ii} and Ta^{iii}-Ta^{iv}-Ta^{v}. The Ta—Ta distance of 2.978 (1) Å within the regular triangles compares with a distance of 2.987 (1) Å between these triangles. Twelve Cl atoms generated from two crystallographically different positions bridge all the edges of the Ta_6 octahedron. Despite the small distortion of the octahedron, all Ta—Cl distances are identical (2.448 ± 0.001 Å) within the precision of the structure determination. Six methanol molecules are connected to the anion *via* O(1)···H(9)—O(2) hydrogen bonds [O(1)···O(2) = 2.684 (15) Å], as similarly observed in the structure of $(C_{18}H_{36}N_2O_6Na)_2[Mo_6Cl_8(CH_3O)_6]$.-$6CH_3OH$, which contains an $[Mo_6Cl_8(CH_3O)_6]^{2-}$ anion (Perchenek & Simon, 1993). The anionic unit is, in certain details, *e.g.* point symmetry and degree of distortion, very similar to that in $[Na_2(CH_3OH)_9]$-$[Ta_6Cl_{12}(CH_3O)_6]$.$3CH_3OH$ (Brničević, McCarley, Hilsenbeck & Kojić-Prodić, 1991), where methanol molecules are also coordinated to each OCH_3^- ligand by hydrogen bonds.