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The Structure of an Indium Trichloride Trimethylarsine Oxide Complex, $2InCl_3 \cdot 3Me_3AsO$

A. G. GROVES, WARD T. ROBINSON and C. J. WILKINS*

Chemistry Department, University of Canterbury, Christchurch, New Zealand

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Indium trihalides show well-developed electron-acceptor properties with the metal atom usually becoming five- or six-coordinated [1]. Work in this laboratory has shown that the ligands Me_3MY (M = P, As; Y = O, S) commonly form complexes of composition $InX_3 \cdot 2L$. However, the product from indium trichloride and trimethylarsine oxide is exceptional in having the composition $2InCl_3 \cdot 3Me_3AsO$. The conductivity of the compound in acetone is almost zero, so that any ionic formulation is excluded. Moreover, the simplicity of the infrared spectrum in the 500–200 cm^{-1} region (440vs, 810m, 281vs) suggested a rather symmetrical molecular species. The ν(As–O) band showed a large displacement to lower frequency, from 887 cm^{-1} in the free ligand to 796 in the complex. It has been suggested that, for Me_3AsO complexes, large shifts of this band are indicative of ligand bridging, although this rested on analogy rather than on more direct evidence [2]. Nevertheless, this interpretation in terms of arsine oxide bridging is fully confirmed by the X-ray structure determination which we now report.

Experimental

Acetone solutions of indium trichloride (1 mmol in 10 ml) and ligand (2 mmol in 10 ml) were brought together under anhydrous conditions. The crystalline adduct separated on addition of petroleum ether and was recrystallised from acetone. It was stable in air. *Anal.* Calc. for $C_9H_{27}O_3As_3Cl_6In_2$: C, 12.7; H, 3.2; Cl, 25.0. Found: C, 12.9; H, 3.3; Cl, 24.6%.

X-ray Analysis

Data collection

The tetrahedral crystal used was truncated at its apices and had an average dimension 0.2 mm. Intensities were recorded at room temperature using a Nicolet R3M diffractometer with Mo Kα radiation (λ = 0.7107 Å). Cell parameters from 25 accurately-centred reflections; θ–2θ scans; 2θ max = 42°; *h*, *k* and *l*, $0 \rightarrow 14$; three standard reflections monitored but no significant variations; 1829 reflections measured, 586 unique reflections [$I > 0.5\sigma(I)$] used in the analysis; corrections applied for isotropic extinction and absorption (transmission range 0.186–0.203).

Crystal data

$2InCl_3 \cdot 3Me_3AsO$; cubic, space group $P2_13$ from preliminary photographs; $M = 850.4$; $a = 13.846(3)$ Å; $V = 2654.4(7)$ Å^3; $Z = 4$; $D_c = 2.128$ g cm^{-3}; μ(Mo Kα) = 60.4 cm^{-1}; $F(000) = 1616$.

Structure solution and refinement

The Patterson function showed a strong vector through two heavy atom positions, parallel to a cube diagonal, and surrounded by a trigonally symmetric atom array. The atoms defining the vector were assigned as indium, and the identity of the surrounding atoms became evident from electron density maps. Temperature factors were refined anisotropically and hydrogen atoms were inserted at idealised positions. The final refinement of 81 parameters gave $R = 0.0268$ and $R_w = 0.0259$, with $w = [\sigma^2F + 0.00059F^2]^{-1}$. All computations were done using the SHELXTL (revision 4) programs [3]. Atomic coordinates are listed in Table I and bond lengths and angles in Table II*.

Results and Discussion

The structure shows the compound to be a molecular complex of simple, but unusual, type with three equivalent oxygen atom bridges linking the two terminal $InCl_3$ groups (Fig. 1). Each indium centre is thus in six-fold coordination with the In– –In vector coincident with a C_3 symmetry axis. The In–O–In bridges are symmetrical, and the three sets

TABLE I. Atomic Coordinates

Atom	*x*	*y*	*z*
In(1)	0.4632(1)	0.4632(1)	0.4632(1)
In(2)	0.6002(1)	0.6002(1)	0.6002(1)
Cl(1)	0.4535(2)	0.2907(2)	0.4935(3)
Cl(2)	0.6887(2)	0.5241(2)	0.7302(2)
O	0.6190(4)	0.4702(4)	0.5065(4)
As	0.7066(1)	0.3834(1)	0.5123(1)
C(1)	0.7013(9)	0.3114(8)	0.3969(9)
C(2)	0.8291(7)	0.4441(8)	0.5216(9)
C(3)	0.6880(9)	0.2967(8)	0.6182(9)

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*Author to whom correspondence should be addressed.

*See also 'Supplementary Material'.

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TABLE II. Bond Lengths and Bond Angles

Bond lengths (Å)			
In(1)–Cl(1)	2.429(4)	As–O	1.710(6)
In(2)–Cl(2)	2.419(4)	As–C(1)	1.884(12)
In(1)–O	2.241(6)	As–C(2)	1.897(11)
In(2)–O	2.234(6)	As–C(3)	1.931(12)
In(1)– –In(2)	3.286(4)	(non-bonded distance)	
O– –O	2.631(10)	(non-bonded distance)	
Bond angles (deg)[a]			
In(1)–In(2)–Cl(2)	118.1(1)	O–In(1)–O	71.9(2)
In(2)–In(1)–Cl(1)	120.0(1)	O–In(2)–O	72.1(2)
Cl(1)–In(1)–Cl(1)	97.2(1)	In(1)–O–As	131.7(3)
Cl(2)–In(2)–Cl(2)	99.7(1)	In(2)–O–As	128.4(3)
O^i–In(1)–Cl(1^i)	92.9(2)	O–As–C(1)	107.7(4)
O^i–In(2)–Cl(2^i)	93.9(2)	O–As–C(2)	109.0(4)
O^i–In(1)–Cl(1^{iii})	162.5(2)	O–As–C(3)	112.4(4)
O^i–In(2)–Cl(2^{iii})	160.8(2)	C(1)–As–C(2)	109.1(5)
In(1)–O–In(2)	94.5(2)	C(1)–As–C(3)	108.2(5)
In(1)–In(2)–O	42.8(2)	C(2)–As–C(3)	110.3(5)
In(2)–In(1)–O	42.7(2)		

[a] The inter-plane angle Cl(1^i)–In(1)–In(2)–Cl(2^i)/In(1)–In(2)–O^i is 57.4°.

of O, As and C(3) atoms are almost coplanar, so that the molecule has near C_{3h} symmetry.

In the unit cell (Fig. 2) the C_3 axis of the unique molecule, **A**, lies on a cube diagonal. The other molecules contributing to the cell (e.g. **B**, **C** and **D**) are oriented with their C_3 axes parallel to the other body diagonals of the cube. The centres of mass of the molecules are 0.760 Å from the cube centre, or from the mid-point of a cube edge.

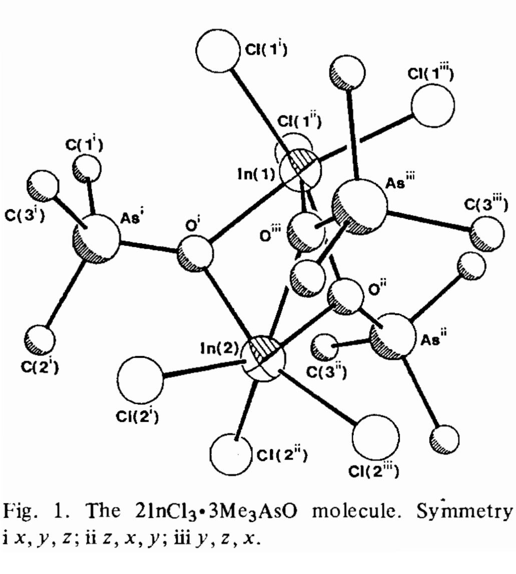

Fig. 1. The $2InCl_3 \cdot 3Me_3AsO$ molecule. Symmetry code: i *x*, *y*, *z*; ii *z*, *x*, *y*; iii *y*, *z*, *x*.

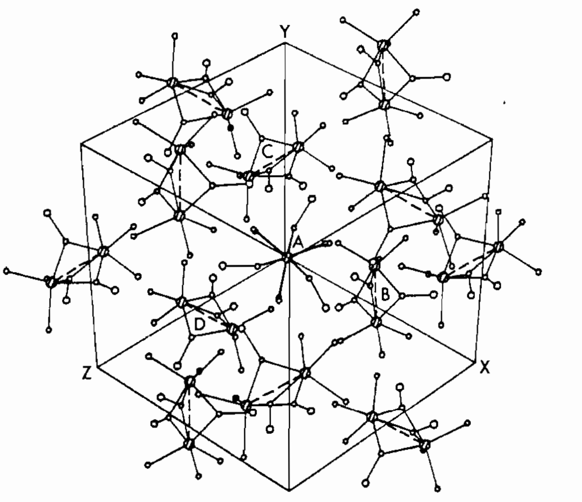

Fig. 2. A perspective view of the unit cell looking along a cube diagonal towards the origin (but with methyl groups omitted). For the indium atoms of the labelled molecules, symmetry codes are: **A** *x*, *y*, *z*; **B** 1 – *x*, *y* – 1/2, 1/2 – *z*; **C** 1/2 – *x*, 1 – *y*, *z* – 1/2; **D** *x* – 1/2, 1/2 – *y*, 1 – *z*.

The development of the face-sharing bi-octahedral structure with this particular oxo-ligand may be ascribed to its high electron-donor activity, which enables the formation of a pair of rather strong dative bonds. For the Me_3MY free ligands the charge transfer in the As–O bond, estimated at 0.51 e [4], is greater than for As–S (0.43 e) or P–O (0.45 e). Complex formation by these molecules reduces the M–Y bond order, and presumably enhances the already high polarisation. It seems clear, however, that this does not alter the position of Me_3AsO, as the pre-eminent electron donor in this series of ligands. In the present complex, the As–O bond length increases from 1.631(3) in the free ligand [4] to 1.710(6) Å. This corresponds to a Pauling bond order reduction from 2.3 to 1.75 [4, 5]. The As–O bond thus remains strong. At the same time, the bond length data enable assessment of the strength of the In–O bridging linkages. The In–O average bond length, 2.238 Å, may be compared with that in $In(OH)_3$, 2.17 Å[≠], where there are six In–O–In hydroxyl bridges (between corner-sharing octahedra) to each indium centre [6]. Taking 2.17 Å as the length, l_1, of a bond of order $n = 1.0$, the relationship $l_n = l_1 - 0.6 \log n$ [5] gives $n = 0.75$ for the bridging links.

The O–In–O coordination angle is 72.0°, and the In–O–In bridging angle is 94.5°[†]. The low O–In–O angles would not in themselves favour stability of a bridged structure, apart from increasing the

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[≠] This value, moreover, almost identifies with the sum of the Pauling covalent radii, 2.16 Å [7].

[†] For a four-membered ring with equivalent bonds, the geometrical relationship between these two angles, 2θ and 2ϕ respectively, is $\sin\theta = \cos\phi \sin\alpha$, where 2$\alpha$ is the angle between the 'bridge planes', in this case 120°.

TABLE III. Indium Coordination Angles (average values)

Angle[a]	$In_2Cl_9^{3-}$ (deg)	$2InCl_3 \cdot 3Me_3AsO$ (deg)
Cl_b–In–Cl_b(O_b–In–O_b)	78.7[b], 78.0[c]	72.0
Cl_b–In–Cl_t(O_b–In–Cl_t)	89.3[b], 88.7[c]	93.4
Cl_t–In–Cl_t	100.7[b], 102.2[c]	98.5

[a] The subscript b indicates a bridging atom, and t a terminal atom. [b] For $Cs_3[In_2Cl_9]$, ref. 8a. [c] For $In_3^I[In_2Cl_9]$, ref. 8b.

In– –In separation. However, comparison with bond angles in the triply-bridged $In_2Cl_9^{3-}$ anion [8] shows that any effects from this small angle do not extend over the whole indium coordination sphere (see Table III), as might have been expected on the basis of VSEPR theory [9]. In fact, the Cl_t–In–Cl_t angles in the arsine oxide complex are smaller than in $In_2Cl_9^{3-}$ (Cl_t = terminal Cl). The effect cannot be attributed to dissimilarity of the In–Cl_t bonds, for they are of closely similar length (2.416 Å in $In_2Cl_9^{3-}$, and 2.424 Å in the complex). We suggest there is outwards 'bending' of the In–O bonds, which means that the effective O–In–O valence angles are larger than the measured values.

The destabilising effects of face-sharing have been pointed out by Pauling [10], and oxo-ligands coordinating through a single oxygen atom generally form no more than two bridge linkages [11]. In the present case, the high electron-donor activity of the ligands enables formation of sufficiently strong bonds to permit face-sharing through three bridging ligands. Charge withdrawal from indium to chlorine enhances the donor–acceptor interaction, and the capacity of the structure for charge dispersion would reduce the otherwise destabilising influence of O– –O repulsions in the four-membered rings.

Supplementary Material

Tables of structure factors and thermal parameters have been deposited with the Editor-in-Chief.

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