

The Complex $\text{BiCl}_3 \cdot \text{CH}_3\text{C}_6\text{H}_5$

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Single crystals of $\text{BiCl}_3 \cdot \text{CH}_3\text{C}_6\text{H}_5$ (**1**) formed from BiCl_3 and toluene have been analysed by X-ray crystallography (triclinic, $P\bar{1}$, $Z = 4$, $a = 7.308(2)$, $b = 12.013(3)$, $c = 12.284(2)$ Å, $\alpha = 75.02(2)$, $\beta = 84.23(2)$, $\gamma = 88.86(2)^\circ$, $T = 173(2)$ K).

Key words: Bismuth, Arene Complex, X-Ray Crystallography

Introduction

The first crystal structures of arene complexes of bismuth trichloride were reported by Schmidbaur *et al.* for $\text{BiCl}_3 \cdot 1,3,5\text{-(CH}_3)_3\text{C}_6\text{H}_3$ [1,2] and $\text{BiCl}_3 \cdot (\text{CH}_3)_6\text{C}_6$ [1,3]. Crystal structures were also determined for complexes of BiCl_3 with C_6H_6 [4], 1,2- $(\text{CH}_3)_2\text{C}_6\text{H}_4$, 1,3- $(\text{CH}_3)_2\text{C}_6\text{H}_4$, 1,4- $(\text{CH}_3)_2\text{C}_6\text{H}_4$ [5], and 1,2,3- $(\text{CH}_3)_3\text{C}_6\text{H}_3$ [6]. An overview of the structural chemistry of the bismuth analogues of the Menshutkin complexes of antimony trihalides and arenes has been included in a review article [7].

We report here the molecular structure of $\text{BiCl}_3 \cdot \text{CH}_3\text{C}_6\text{H}_5$ (**1**), a new member in the family of BiCl_3 complexes with arenes $(\text{CH}_3)_{6-n}\text{C}_6\text{H}_n$ ($n = 1-6$).

Results and Discussion

Needle-shaped crystals of **1** are formed in 86.5% yield by slowly cooling a solution of freshly sublimed BiCl_3 in toluene. The crystals are stable up to 103 °C, beyond which temperature they melt with decomposition. When exposed to air the crystals lose toluene and become colourless powders.

An X-ray crystal structure analysis revealed that crystals of **1** belong to space group $P\bar{1}$ with two crystallographically independent molecular units $\text{BiCl}_3 \cdot$

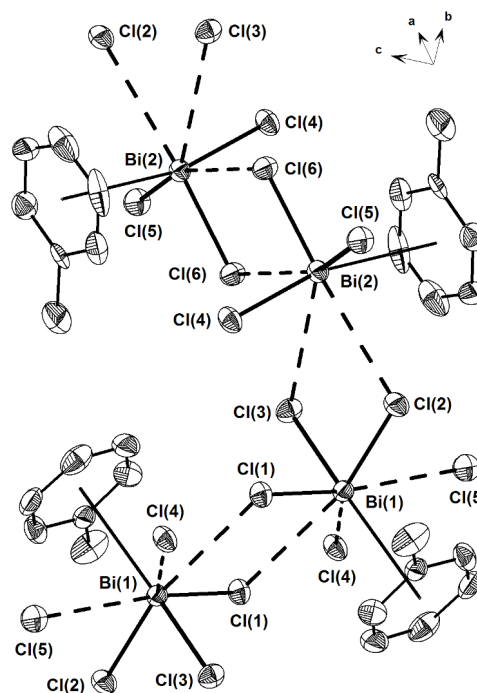


Fig. 1. Thermal ellipsoid representation (50 %) of a section of the structure of $\text{BiCl}_3 \cdot \text{CH}_3\text{C}_6\text{H}_5$ (**1**). Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Bi(1)–Cl(1) 2.500(2), Bi(1)–Cl(2) 2.518(3), Bi(1)–Cl(3) 2.471(2), Bi(2)–Cl(4) 2.461(2), Bi(2)–Cl(5) 2.517(2), Bi(2)–Cl(6) 2.513(2), Bi(1)···C₆(centre) 3.04, Bi(2)···C₆(centre) 3.09, Bi(1)···Cl(1) 3.290(3), Bi(1)···Cl(4) 3.535(2), Bi(1)···Cl(5) 3.504(3), Bi(2)···Cl(2) 3.439(3), Bi(2)···Cl(3) 3.524(2), Bi(2)···Cl(6) 3.243(3); Cl(1)–Bi(1)–Cl(2) 90.18(9), Cl(1)–Bi(1)–Cl(3) 93.13(8), Cl(2)–Bi(1)–Cl(3) 87.40(9), Cl(4)–Bi(2)–Cl(5) 88.76(9), Cl(4)–Bi(2)–Cl(6) 93.23(9), Cl(5)–Bi(2)–Cl(6) 89.48(8), Cl(3)–Bi(1)···C₆(centre) 168.1, Cl(4)–Bi(2)···C₆(centre) 166.4.

$\text{CH}_3\text{C}_6\text{H}_5$. A section of the structure of **1** is shown in Fig. 1.

Both molecular units consist of pyramidal BiCl_3 moieties and toluene ligands in an almost ideal η^6 -coordination. The distance between the bismuth atoms and the respective C₆ ring centre is 3.04 Å for Bi(1) and 3.09 Å for Bi(2). The Bi···C distances vary from 3.261(11) to 3.562(13) Å. The toluene ligands occupy positions *trans* to Bi–Cl bonds (angles Cl(3)–Bi(1)···C₆(centre) 168.1°, Cl(4)–Bi(2)···C₆(centre) 166.4°). The angles between the normals on the centres of the C₆-rings and the lines connecting to the bismuth atoms are 3.56° for Bi(1) and 7.88° for Bi(2). These values indicate a ring slip-

page of 0.19 and 0.42 Å, respectively, towards the methyl groups. The Bi–Cl bond lengths are in the range between 2.461(2) and 2.518(3) Å, with the shorter values for the bonds *trans* to the arene ring. The coordination around the bismuth centres is completed by three Bi···Cl contacts (3.243(3)–3.535(2) Å) to neighbouring molecular units to give distorted pentagonal bipyramidal (3 + 3 + 1) environments with the toluene molecules in apical positions.

Bi···Cl contacts between the molecules lead to a bidimensional arrangement, ${}^2[\text{BiCl}_3 \cdot \text{CH}_3\text{C}_6\text{H}_5]_2$, with alternating inorganic and organic double layers. The thickness of a double layer, *i. e.* the distance between the planes containing the outermost carbon atoms of the toluene molecules, is 9.2 Å. The distance between carbon atoms of neighbouring layers is 2.4 Å.

In all aspects the crystal structure of **1** is very similar to that of $\text{BiCl}_3 \cdot \text{C}_6\text{H}_6$ (Bi–Cl 2.444–2.486 Å; Bi···C₆(centre) 3.10, 3.21 Å; Cl–Bi···C₆(centre) 167.6, 166.4° [4], layer thickness 9.47 Å, inter layer distance 2.02 Å), although the toluene ligand is more tightly bound to the bismuth centre than the benzene molecule in $\text{BiCl}_3 \cdot \text{C}_6\text{H}_6$. Bi···C₆(centre) distances similar to those found in the structure of **1** were reported for $\text{BiCl}_3 \cdot 1,4\text{-(CH}_3)_2\text{C}_6\text{H}_4$ (3.05, 3.08 Å) [5].

Experimental Section

The manipulations of the compounds were carried out in an argon atmosphere and with dry toluene. BiCl_3 was sublimed before use.

Synthesis of $\text{BiCl}_3 \cdot \text{CH}_3\text{C}_6\text{H}_5$ (**1**)

1.12 g (3.6 mmol) of BiCl_3 was dissolved in 60 mL of boiling toluene. Upon cooling to r. t. and further to –10 °C, **1**

was obtained as colourless needles. M. p.: 103–104 °C (decomp). Yield: 1.25 g (86.5 %).

X-Ray structure determination

A crystal of **1** mounted on a glass fiber using Kelf oil was investigated under a cold nitrogen stream on a Siemens P4 diffractometer. Crystal data: $\text{C}_7\text{H}_8\text{BiCl}_3$, $M_r = 407.46$, crystal size $0.6 \times 0.4 \times 0.1 \text{ mm}^3$, triclinic, $P\bar{1}$, $Z = 4$, $a = 7.308(2)$, $b = 12.013(3)$, $c = 12.284(2)$ Å, $\alpha = 75.02(2)$, $\beta = 84.23(2)$, $\gamma = 88.86(2)^\circ$, $V = 1036.5(4) \text{ Å}^3$, $D_{\text{calcd}} = 2.611 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 17.72 \text{ cm}^{-1}$, $T = 173(2) \text{ K}$. Data collection and refinement: graphite monochromator, $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ Å}$, $F(000) = 736 \text{ e}$, 5880 measured reflections, 4684 independent reflections, 3923 reflections with $I \geq 2\sigma(I)$ ($R(\text{int}) = 0.027$), hkl range $-9/+8$, ± 15 , ± 15 , $\theta_{\text{max}} = 27.5^\circ$, empirical (DIFABS) absorption correction [8], $T_{\text{min}} = 0.033$, $T_{\text{max}} = 0.270$. The structure was solved using Patterson Methods [9] and refined using full-matrix least-squares methods on F^2 . The hydrogen atoms were included in riding positions with isotropic thermal parameters set at 1.2 times those of the carbon atoms to which they are directly attached. Final R values for $I \geq 2\sigma(I)$: $R(F) = 0.0439$, $wR(F^2) = 0.1162$; all data: $R(F) = 0.0552$, $wR(F^2) = 0.1232$, extinction coefficient 0.0013(3), $\text{Gof}(F^2) = 1.049$, residual electron densities: 2.784/–2.748 e Å^{-3} . Structure refinements were carried out with SHELXL-97 [10] as included in the WINGX software package [11]. The ring centroids and the angles were calculated using the PLATON software [12] according to the description of Cremer [13].

CCDC 646194 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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