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Heavy-Metal π Complexes. 13.† Trichloro-(1,2,3-trimethylbenzene)bismuth(III)

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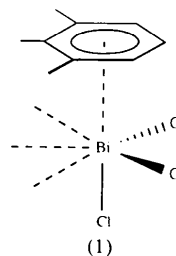
Abstract

The title compound, [BiCl₃(1,2,3-Me₃C₆H₃)], contains quasi-dimeric units of arene-coordinated BiCl₃ fragments that are further associated *via* additional Bi—Cl contacts to form coordination-polymeric layers. The re-

sulting coordination number of Bi is 3 + 3 + 1 (primary + secondary Cl contacts + arene). The Bi–arene bonding is characterized by Bi—C distances in the range 3.168 (7)–3.751 (8) Å.

Comment

The ability of liquid arenes to dissolve BiCl₃ and the isolation of arene solvates from the corresponding solutions was first reported in 1968 (Peyronel *et al.*, 1968). During the last three decades the crystal structures of compounds derived from the most important monocyclic arenes have been elucidated: [BiCl₃(arene)], where arene is C₆H₆ (Frank *et al.*, 1993); MeC₆H₅, 1,2-, 1,3- and 1,4-Me₂C₆H₄ (Müller-Becker *et al.*, 1993); 1,3,5-Me₃C₆H₃ (Schmidbaur, Wallis *et al.*, 1987); [(BiCl₃)₂(C₆Me₆)] (Schmidbaur, Nowak *et al.*, 1987). As part of a systematic study of the dependency of arene basicity on the strength of Bi–arene π bonding, we prepared the hitherto unknown compound [BiCl₃(1,2,3-Me₃C₆H₃)], (1), and determined its solid-state structure at ambient temperature.



In contrast to unsolvated BiCl₃, which has eight Cl atoms in the Bi coordination sphere (Nyburg *et al.*, 1971), the Bi atom in (1) has only six Cl neighbours, suggesting that 1,2,3-trimethylbenzene solvation in a formal sense replaces two weak Bi—Cl interactions. In this respect, 1,2,3-trimethylbenzene behaves like benzene or mesitylene, which both solvate BiCl₃ to give related layer polymers, and unlike the three isomeric xylenes, which all give chain coordination polymers characterized by three strong and two weak Cl contacts and the arene interaction of Bi. With respect to the different strengths of the six Bi—Cl contacts, (1) is best interpreted as a layer coordination compound, built up from quasi-dimeric units of arene-coordinated BiCl₃ fragments.

As documented by the lengths of the three short Bi—Cl bonds [Bi1—Cl1 2.5226 (17), Bi1—Cl2 2.4684 (17) and Bi1—Cl3 2.4680 (14) Å] and the corresponding Cl—Bi—Cl angles [Cl1—Bi1—Cl2 93.13 (6), Cl1—Bi1—Cl3 92.30 (6) and Cl2—Bi1—Cl3 86.24 (6)°], the geometry of the BiCl₃ fragment is closely related to that found in the crystal structure of solid BiCl₃ [Bi—Cl 2.468 (4)–2.518 (7) Å and Cl—Bi—Cl 84.45 (14)–94.9 (3)°]. As shown by the Bi—C distances [Bi—

† Part 12: Frank & Wittmer (1997).

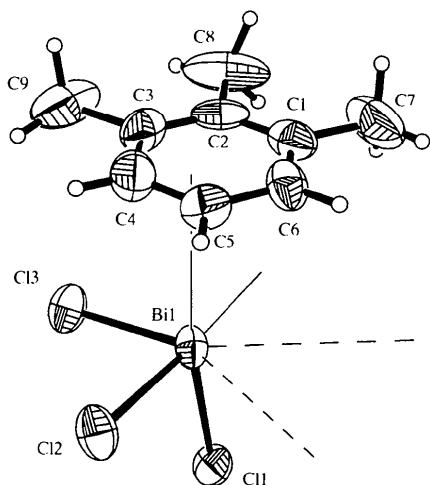


Fig. 1. Diagram of the monomeric fragment defining the asymmetric unit of the crystal structure of (1) with displacement ellipsoids at the 50% probability level. The radii of H atoms are chosen arbitrarily, their atom labels are omitted for clarity and one H atom is covered by C9. Dashed lines indicate the directions of layer-forming interactions between quasi-dimeric units.

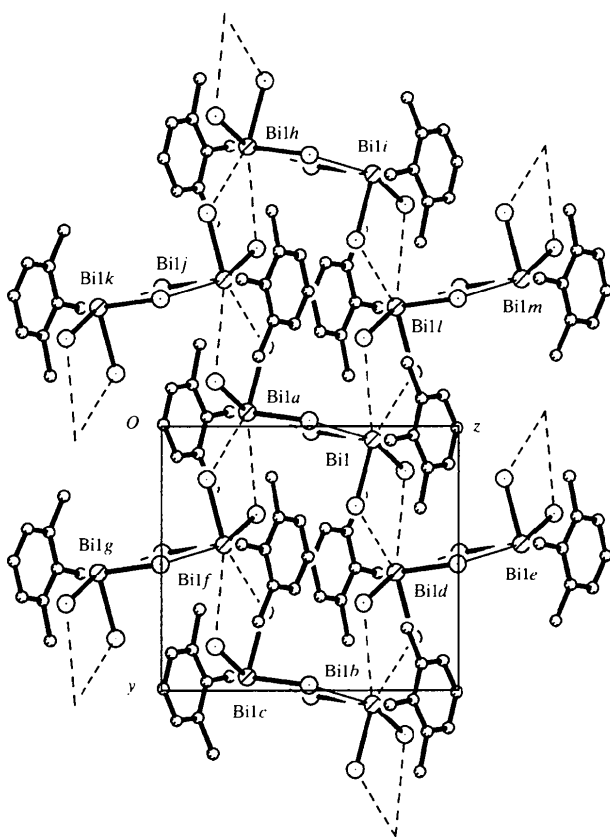


Fig. 2. Diagram of an arbitrarily chosen segment of one of the layers building up the crystal of (1) viewed down the a axis. [Bond lengths: Bi1—Cl1 a 3.2926 (18), Bi1—Cl2 l 3.5939 (16) and Bi1—Cl3 l 3.4062 (18) Å; selected symmetry codes: (a) $-x, -y, 1-z$; (d) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (l) $-x, -\frac{1}{2} + y, \frac{3}{2} - z$.]

C1 3.686 (8), Bi1—C2 3.751 (8), Bi1—C3 3.544 (8), Bi—C4 3.244 (8), Bi1—C5 3.168 (7) and Bi1—C6 3.401 (7) Å], the Bi–arene interaction shows a significant deviation from the ideal η^6 coordination mode. Since two of the Bi—C distances are only slightly shorter than the sum of the corresponding van der Waals radii (about 3.8 Å), one could also describe the arene coordination as η^4 -like. A quantitative measure of the asymmetry of the π interaction is given by the ring slippage of 0.75 Å. Further characterizing structural parameters are the distances Bi—COR (COR = centre of ring) [3.1833 (4) Å] and Bi—LSP (LSP = least-squares plane of the C1–C6 ring) [3.094 (4) Å], as well as the angle between LSP and the plane defined by atoms Cl2, Bi1 and Cl3 [6.0 (4)°]. Comparison of Bi—LSP values shows the Bi–arene bonding in (1) to be stronger than in the benzene analogue, slightly weaker than in the mesitylene derivative and much weaker than in the cationic complexes [Bi(C₆Me₆)Cl₂][AlCl₄] (2.62 Å; Frank *et al.*, 1987) and [BiCl₂(C₅H₅)] (2.33 Å; Frank, 1990). Three weak bonds from Bi to Cl atoms of neighbouring moieties and one bond from each Cl atom to neighbouring Bi atoms connect the fragments described above to give layers with the Bi atoms arranged at the nodes of a hexagon net.

Between adjacent [$\{\text{BiCl}_3[1,2,3\text{-(CH}_3)_3\text{C}_6\text{H}_3]\}_2$] $_{\infty}$ layers only non-bonding arene–arene contacts are observed, showing that the structure can be strictly divided into regions of inorganic and organic components.

Experimental

The clear yellow solution obtained by dissolving sublimed BiCl₃ (0.273 g) in absolutely dry 1,2,3-Me₃C₆H₃ (10 ml) at 343 K gave crystals of (1) upon slow cooling to room temperature. Analysis calculated for C₉H₁₂BiCl₃: C 24.82, H 2.78%; found C 24.86, H 2.67%. As the compound is very moisture sensitive, the crystal used for the structure determination was enclosed in a thin-walled glass capillary.

Crystal data

[BiCl₃(C₉H₁₂)]
 $M_r = 435.52$
 Monoclinic
 $P2_1/c$
 $a = 12.7462 (10)$ Å
 $b = 9.1967 (5)$ Å
 $c = 11.4950 (9)$ Å
 $\beta = 114.977 (7)^\circ$
 $V = 1221.46 (15)$ Å³
 $Z = 4$
 $D_x = 2.368$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 5000 reflections
 $\theta = 2.83\text{--}25.97^\circ$
 $\mu = 15.046$ mm⁻¹
 $T = 293 (2)$ K
 Prismatic
 $0.62 \times 0.48 \times 0.22$ mm
 Clear pale yellow

Data collection

Stoe IPDS diffractometer
 Area-detector measurements

1862 reflections with
 $I > 2\sigma(I)$

Absorption correction: $R_{\text{int}} = 0.097$
 by integration (Stoe & Cie, 1996d) $\theta_{\text{max}} = 25.24^\circ$
 $T_{\text{min}} = 0.010$, $T_{\text{max}} = 0.083$ $h = -15 \rightarrow 15$
 6843 measured reflections $k = -10 \rightarrow 11$
 2131 independent reflections $l = -13 \rightarrow 13$
 Intensity decay: none

Refinement

Refinement on F^2 Weighting scheme: see below
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.063$ $(\Delta/\sigma)_{\text{max}} = 0.002$
 $S = 1.006$ $\Delta\rho_{\text{max}} = 1.049 \text{ e } \text{Å}^{-3}$
 2131 reflections $\Delta\rho_{\text{min}} = -0.709 \text{ e } \text{Å}^{-3}$
 121 parameters Extinction correction: none
 H atoms treated by a Scattering factors from
 mixture of independent *International Tables for*
 and constrained refinement *Crystallography* (Vol. C)

Data are 90.3% complete to $\theta = 25.24^\circ$. The faces of the forms {111} and {001} were developed. Their distances from the centre of gravity were determined microscopically. For the face-indexed numerical absorption correction, the Gaussian integration routine implemented in X-RED (Stoe & Cie, 1996d) was applied. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques. Weights $w = \{1 - \exp[-9.0(\sin\theta/\lambda)^2]\}/[\sigma^2(F_o^2) + (0.014P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$, were used. All but two H-atom positions could be located in a difference Fourier map after refining positions and anisotropic displacement parameters of the heavier atoms. In the final stages of refinement, the H atoms were included in idealized positions. H atoms of the C—H groups were situated 0.93 Å from the parent C atom on the external bisector of the corresponding C—C—C angle (quasi-idealized positions neglecting a very small out-of-plane tilt due to Bi—arene bonding) and a riding model was applied. C—H distances of the methyl groups were set to 0.96 Å, and C—C—H and H—C—H angles to 109.5°. The H atoms of each group were allowed to ride on the parent C atom and to rotate around the C—C bond direction. The isotropic displacement parameters were kept equal to 120 and 150% of the equivalent isotropic displacement parameters of the ring and of the methyl-group C atoms, respectively. Only one significant electron-density maximum ($1.05 \text{ e } \text{Å}^{-3}$ at 0.90 Å from Bi1) was found in the final difference Fourier map.

Data collection: EXPOSE (Stoe & Cie, 1996b). Cell refinement: CELL (Stoe & Cie, 1996a). Data reduction: INTEGRATE (Stoe & Cie, 1996c). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997b). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a). Molecular graphics: SHELXTL-Plus (Sheldrick, 1991). Software used to prepare material for publication: SHELXL97.

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1,3-Propanediammonium Tetrachloromercurate

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Abstract

The title compound, (C₃H₁₂N₂)[HgCl₄], contains layers of tilted corner-sharing chloromercurate octahedra, with Hg—Cl distances ranging from 2.397 (2) to 2.839 (2) Å. These layers are interconnected by N—H···Cl bonds to the cations, building a three-dimensional network. The cation has a disordered propane chain.