

# The Layer Polymer $\{[\text{Bi}(\text{C}_6\text{H}_6)\text{Cl}_3]_2\}_\infty$ : Very Weak Bismuth–Arene Bonding in the Parent Compound of the Bismuth Analogue of Menshutkin Complexes

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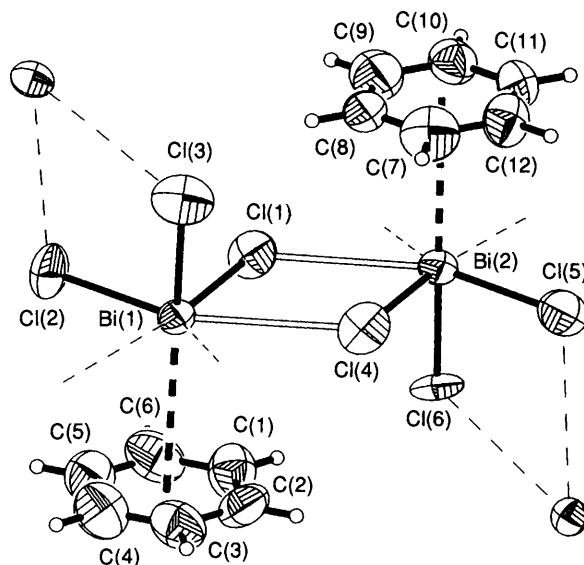
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$[\text{Bi}(\text{C}_6\text{H}_6)\text{Cl}_3]$ , obtained from a benzene solution of  $\text{BiCl}_3$ , has been shown by X-ray crystallography to be a layer polymer with very weak bismuth–benzene  $\pi$ -bonding.

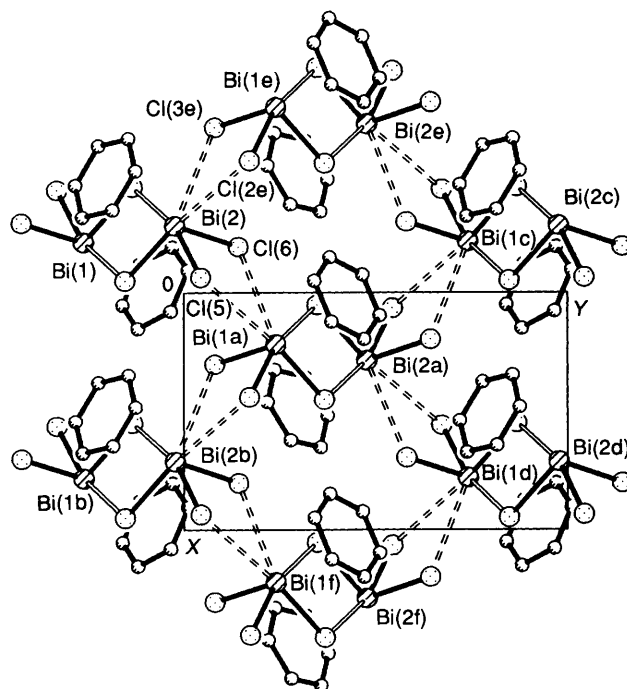
In the course of our studies on the interaction of bismuth with aromatic  $\pi$  systems we succeeded in the preparations and X-ray structure determinations of several compounds exhibiting bismuth aromatic  $\pi$ -bonding of different strengths and geometries:  $[\text{Bi}(\text{C}_5\text{H}_5)\text{Cl}_2]$ ,<sup>1</sup>  $[\text{Bi}(\text{C}_6\text{Me}_6)\text{Cl}_2][\text{AlCl}_4]$ ,<sup>2</sup>  $[\text{Bi}(\text{PhMe})\text{Cl}_2][\text{MCl}_4]$  ( $\text{M} = \text{Al}, \text{Ga}$ ),<sup>2,3</sup>  $[\text{Bi}(\text{PhMe})\text{Cl}_3]$ . We now report the X-ray crystal structure of  $[\text{Bi}(\text{C}_6\text{H}_6)\text{Cl}_3]$ , a new addition to the above list and the compound with the weakest bismuth– $\pi$ -system interaction.

The ability of  $\text{BiCl}_3$  to coordinate arenes was first reported by Peyronel *et al.*,<sup>4</sup> but further characterization of the resulting compounds was restricted to the determination of the chlorine content. Especially in the case of less basic arenes like benzene, evidence from structural investigations is needed to determine, whether metal arene bonding is present.<sup>5</sup> On cooling saturated  $\text{BiCl}_3$  benzene solutions to  $-15^\circ\text{C}$  we obtained single crystals of the 1:1 compound  $[\text{Bi}(\text{C}_6\text{H}_6)\text{Cl}_3]$  **1**.<sup>†</sup> This observation is in contrast to the system  $\text{SbCl}_3$ – $\text{C}_6\text{H}_6$ , where the 1:2 compound  $(\text{SbCl}_3)_2\text{C}_6\text{H}_6$  **2** is obtained on cooling or evaporation.<sup>6</sup> Metal–arene bonding is not comparable in these compounds owing to their entirely different nature: **1** is of the half-sandwich type, **2** of the inverse sandwich type with the benzene molecule coordinated at both faces. Compound **1** is unstable *in vacuo* and rapidly loses benzene, especially if finely powdered.

According to the different strengths of the six Bi–Cl contacts of each of two crystallographically independent bismuth atoms, **1** is best interpreted as a layer coordination polymer, built up from quasi-molecular  $\text{BiCl}_3$  units by weak chlorine bridges (Figs. 1 and 2).<sup>‡</sup> The geometries of these  $\text{BiCl}_3$  units are similar to those in the crystal structure of  $[\text{BiCl}_3]_3$ .<sup>7</sup> The three short Bi–Cl bonds in these fragments, three further layer forming Bi–Cl contacts and the benzene ligand give both Bi atoms a distorted pentagonal bipyramidal



**Fig. 1** Dimeric arrangement defining the asymmetric unit of the crystal structure (50% thermal ellipsoids, radii of hydrogen atoms are chosen arbitrarily); two molecular fragments are linked to each other by chlorine bridges; dashes show the further connection in layers; bond lengths (pm): Bi(1)–Cl(1) [–Cl(2), –Cl(3), –Cl(4)] 247.3(9) [248.6(11), 244.4(8), 324.6(12)], Bi(2)–Cl(1) [–Cl(4), –Cl(5), –Cl(6)] 321.9(12) [248.1(9), 246.1(11), 247.3(8)], Bi(1)–C(1) [–C(2), –C(3), –C(4), –C(5), –C(6)] 344(2) [349(2), 355(2), 356(2), 350(2), 344(2)], Bi(2)–C(7) [–C(8), –C(9), –C(10), –C(11), –C(12)] 325(2) [333(2), 348(2), 355(2), 347(2), 333(2)]



**Fig. 2** Arbitrarily chosen segment of one of the layers building up the crystal structure of **1** viewed along the  $c$ -axis; bond lengths (pm): Bi(2)–Cl(2e) 341.5(11), Bi(2)–Cl(3e) 362.1(8), Bi(1a)–Cl(5) 357.8(11), Bi(1a)–Cl(6) 348.3(8)

<sup>†</sup> M.p.  $140^\circ\text{C}$  (decomp.); great care is needed to get satisfactory elemental analyses; crystals cannot be dried *in vacuo* and even trying to remove excess benzene with a slow stream of dry argon results in a significant loss of coordinated benzene at room temperature. The crystal used for the X-ray structure determination was enclosed in a glass capillary.

<sup>‡</sup> Crystal data for **1**: space group  $P2_12_12_1$ ,  $a = 734.3(3)$ ,  $b = 1163.1(4)$ ,  $c = 2307.2(7)$  pm,  $V = 1.970$  nm<sup>3</sup>,  $Z = 8$ ,  $D_x = 2.652$  g cm<sup>-3</sup>,  $\mu = 18.64$  mm<sup>-1</sup>, crystal dimensions  $0.7 \times 0.3 \times 0.1$  mm<sup>3</sup>. The data set was collected at  $20^\circ\text{C}$  on an Enraf-Nonius CAD4 diffractometer using Mo-K $\alpha$  radiation. Semiempirical absorption corrections were applied. The structure was solved by Patterson and difference Fourier methods. 160 parameters including anisotropic thermal parameters for all atoms heavier than hydrogen were refined using 1925 reflections with  $F > 2\sigma(F)$  and a weighting scheme [ $w^{-1} = \sigma^2(F)$ ] was applied. The best result ( $R = 0.058$ ,  $R_w = 0.036$ ) has been obtained by treating the benzene ligands including the hydrogen atoms as rigid groups with  $D_{6h}$  point group symmetry (C–C 139.5, C–H 96 pm). The results of an unconstrained refinement agreed with this model within the limits of experimental error. The structural model has been proved to have the correct handedness by the Rogers  $\eta$  method. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

coordination with the arene molecule in an axial position. The distances of the atoms Bi(1) and Bi(2) from the ring planes are 320(2) and 308(2) pm, respectively, whereas the corresponding mean Bi–C distances are 340 and 345 pm. Comparison of the individual Bi–C distances shows that the  $\pi$  bonding is of the  $\eta^6$  mode at both Bi atoms. The bismuth–carbon contacts are only slightly shorter than the sum of the van der Waals radii of Bi and C (about 380 pm) and are significantly longer than those in [Bi(1,3,5-Me<sub>3</sub>C<sub>6</sub>H<sub>3</sub>)Cl<sub>3</sub>],<sup>8</sup> the only other structurally characterized BiCl<sub>3</sub> arene 1:1 compound published so far. These structural parameters reflect the instability of the title compound.

Unlike the unsolvated BiCl<sub>3</sub> with ten chlorine contacts in the coordination sphere of bismuth, the bismuth atoms in **1** have only six chlorine neighbours, suggesting that benzene solvation replaces four weak Bi–Cl bonds in a formal sense. Like in the crystal structures of Menshutkin complexes (SbCl<sub>3</sub>)<sub>x</sub>arene ( $x = 1, 2$ )<sup>6,9</sup> and in a small number of other structurally characterized BiCl<sub>3</sub> arene complexes<sup>8,10</sup> two metal halogen bonds are oriented nearly parallel to the plane of the aromatic molecule [angles of 8.3 and 6.2° between the ring plane and the plane through atoms Bi(1), Cl(1), Cl(2) and Bi(2), Cl(4), Cl(5), respectively], while the third one is almost perpendicular to it. Between adjacent [ $\{\text{Bi}(\text{C}_6\text{H}_6)\text{Cl}_3\}_2\]_\infty$  layers only nonbonding Cl–Cl contacts are observed, showing that solid state association in the third dimension is achieved by van der Waals forces only.

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