Synthesis and Structural Characterization of the Molecular Complex Between Bismuth Trichloride and Pyrene†

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The preparation of a bismuth charge-transfer molecular complex with pyrene, $2BiCl_3$·pyrene, and the determination of its structure by single-crystal *X*-ray analysis is described. Crystals are monoclinic, with a = 10.564(3), b = 12.564(3), c = 7.220(1) Å, β = 90.33(7)°, Z = 4, space group $P2_1/c$, and R = 0.0669. The structure contains two pyramidal $BiCl_3$ units interacting with one centrosymmetrical pyrene molecule. Two chlorine atoms are bridging with Bi ••• Cl distances of 3.154(12) and 3.347(12) Å, which connect the $BiCl_3$ units in zig-zag chains interlayered by the organic molecules.

The application and uses of charge-transfer (c.t.) molecular complexes cover a wide field, from medicine to chemistry in its widest aspects. Studies of these systems provide direct information on the charge-transfer mechanism and on the nature of the excited state. Several interesting new acceptor and donor molecules have recently emerged, increasing the interest in c.t. complexes and their possible applications in electrically conducting devices, including photoconductors.[1] It is known that many hydrocarbons form molecular complexes with electron acceptors both in the solid phase and in solution.[2] In previous work, we have investigated complexes of many hydrocarbons, ranging from benzene through molecules of increasing complexity to polycondensed aromatic rings, with metal halide acceptors in the solid and solution state.[3–5] Among the complexes obtained in the solid state some *X*-ray crystal and molecular structures of the compounds formed by $SbCl_3$,[6–9] $SbBr_3$,[5,10] and $BiCl_3$[11,12] and aromatic hydrocarbons were determined; now we have studied the structure of $2BiCl_3$·pyrene with the aim of contributing to a greater understanding of these last systems.

Experimental

Preparation of $2BiCl_3$·pyrene.—Because of the very high hygroscopicity of $BiCl_3$ and its molecular complexes, all manipulations were performed in a dry-box in a P_4O_{10} dried N_2 atmosphere. The $BiCl_3$ was dehydrated over P_4O_{10} and recrystallized from toluene. Pyrene, in cyclohexane solution, was purified by chromatography on neutral alumina. All solvents were dehydrated and kept over metallic sodium wire. The solid complex was prepared by adding (at 100 °C) a *p*-xylene solution of $BiCl_3$ to one of pyrene (both 5.4×10^{-2} mol dm^{-3}) with metal-to-ligand molar ratios ranging from 2:1 to 1:2.

Red-purple cube shaped crystals separated after a few days (Found: C, 22.85; H, 1.20; Cl, 25.35. Calc. for $C_{16}H_{10}Bi_2Cl_6$: C, 23.05; H, 1.20; Cl, 25.55%).

Table 1. Experimental data for the crystallographic analysis

Formula	$C_8H_5BiCl_3$
M	416.5
Space group	$P2_1/c$
a/Å	10.564(3)
b/Å	12.564(3)
c/Å	7.220(1)
β/°	90.33(7)
U/Å^3	958.3(4)
Z	4
D_c/Mg m^{-3}	2.887
Reflections for lattice parameters: number	15
Reflections for lattice parameters: θ range/°	10—12
F(000)	748
T/K	293
Crystal size/mm	0.49 × 0.65 × 0.78
μ/cm^{-1}	191.28
Absorption correction (min.—max.)	1.000—1.695
Scan speed/° min^{-1}	4.8
Scan width/°	1.4
Radiation	Mo-K_α (λ = 0.7093 Å)
θ range/°	3—21
h range	−12 to 12
k range	−10 to 10
l range	0 to 7
Standard reflection	−3 −2 1
Intensity variation/%	4.8
Scan mode	ω—2θ
No. of measured reflections	2 048
No. of reflections used in the refinement [$I > 3\sigma(I)$]	673
$R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I$	0.112
No. of refined parameters	109
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0669
$R' = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}$	0.0662
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$*	2.30
k, g $\{w = k/[\sigma^2(F_o) + gF_o^2]\}$	2.2, 0.001 57

* N = Number of observations, P = number of parameters.

X-Ray Data Collection.—A crystal, sealed in a glass capillary under nitrogen, was mounted on a Phillips PW 1100 diffractometer in a random orientation: the resulting crystal data and other structural details are quoted in Table 1. The intensities of the half-reflection sphere were collected, measuring a reflection every hour as a check of the crystal alignment and instrument stability. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and converted to an absolute scale by least squares; in addition a correction for absorption was applied.[13]

Solution and Refinement of the Structure.—The structure was solved by the heavy-atom technique and refined by full-matrix isotropic and then anisotropic least squares: the final R indices obtained were R = 0.0669 and R' = 0.0662; during the final

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 2. Fractional atomic co-ordinates (× 10^4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Bi	1 505(2)	1 280(1)	269(2)
Cl(1)	54(11)	2 732(8)	−504(15)
Cl(2)	669(12)	37(9)	−2 178(14)
Cl(3)	3 059(12)	1 973(9)	−2 057(15)
C(1)	4 539(33)	−31(27)	742(54)
C(2)	3 553(50)	−772(34)	468(62)
C(3)	2 638(45)	−931(33)	1 936(78)
C(4)	2 791(53)	−305(55)	3 573(58)
C(5)	3 697(53)	358(40)	3 681(63)
C(6)	4 632(42)	602(42)	2 332(58)
C(7)	5 635(39)	1 242(34)	2 521(54)
C(8)	6 434(46)	1 443(33)	1 154(60)

Table 3. Bond distances (Å) and angles (°) with their estimated standard deviations in parentheses

Bi–Cl(1)	2.445(11)	Cl(1)–Bi–Cl(2)	94.9(4)
Bi–Cl(2)	2.514(11)	Cl(1)–Bi–Cl(3)	90.0(4)
Bi–Cl(3)	2.511(12)	Cl(2)–Bi–Cl(3)	88.5(4)
Bi–Cl(2^{iii})	3.154(12)		
Bi–Cl(3^{iv})	3.347(12)		
C(1)–C(1^{i})	1.45(5)	C(5)–C(6)	1.42(7)
C(1)–C(2)	1.41(6)	C(6)–C(1)	1.40(6)
C(2)–C(3)	1.45(7)	C(6)–C(7)	1.34(6)
C(3)–C(4)	1.43(7)	C(7)–C(8)	1.33(6)
C(4)–C(5)	1.28(8)	C(8)–C(2^{i})	1.44(6)
C(1^{i})–C(1)–C(6)	122(3)	C(3)–C(4)–C(5)	120(4)
C(1^{i})–C(1)–C(2)	115(3)	C(4)–C(5)–C(6)	129(5)
C(2)–C(1)–C(6)	123(4)	C(5)–C(6)–C(1)	113(4)
C(1)–C(2)–C(8^{i})	119(4)	C(5)–C(6)–C(7)	128(4)
C(1)–C(2)–C(3)	119(4)	C(1)–C(6)–C(7)	119(4)
C(3)–C(2)–C(8^{i})	121(4)	C(6)–C(7)–C(8)	123(4)
C(2)–C(3)–C(4)	117(4)		

Contacts less than 3.70 Å

Bi ··· C(1)	3.62(3)	Cl(3) ··· C(5^{ii})	3.46(5)
Bi ··· C(2)	3.37(5)	Cl(3) ··· C(6^{ii})	3.50(5)
Bi ··· C(3)	3.25(4)	Cl(3) ··· C(7^{ii})	3.54(4)
Bi ··· C(4)	3.39(5)	C(1) ··· Cl(3^{ii})	3.58(4)
Bi ··· C(5)	3.56(5)		

i, $1 - x, \bar{y}, \bar{z}$; ii, $x, y - \frac{1}{2}, \frac{1}{2} - z$; iii, $\bar{x}, \bar{y}, \bar{z}$; iv, $x, \frac{1}{2} - y, \frac{1}{2} + z$.

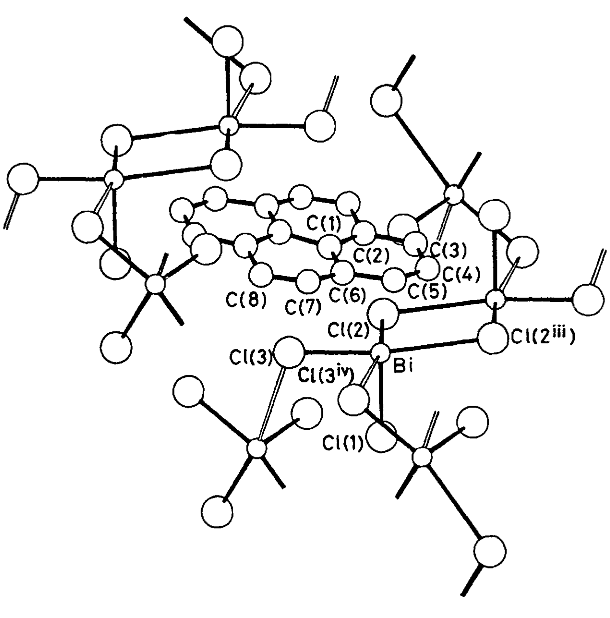

Figure. Perspective view of the structure of $2BiCl_3$·pyrene

refinement zero weight was assigned to 30 reflections which may be affected by counting errors or extinction; hydrogen atoms were not located.

The small diffracting power of the crystals, in spite of their dimensions, and the presence of the very heavy bismuth atom, justifies the relevant uncertainties affecting the carbon atoms. The atomic scattering factors used, corrected for anomalous dispersion, were taken from ref. 14. Major calculations were performed using the CRAY X/MP computer of the Centro di Calcolo dell'Italia Nord-Orientale, Casalecchio (Bologna) with the SHELX 76 program package[15] and the ORTEP plotting program;[16] the final atomic parameters are given in Table 2.

Results and Discussion

Description of the Structure.—The asymmetric unit of $2BiCl_3$·pyrene (Figure) contains one centrosymmetric hydrocarbon molecule, the centre being localized at $\frac{1}{2}\,0\,0$ at the mid-point between C(1) and C(1^{i}) (i, $1 - x, \bar{y}, \bar{z}$), and two $BiCl_3$ units, linked in the same way, on opposite sides of the hydrocarbon molecule. The two bond distances, Bi–Cl(2) = 2.514(11) and Bi–Cl(3) = 2.511(12) Å (Table 3), are comparable and significantly different from Bi–Cl(1) [2.445(11) Å] ($\Delta/\sigma = 4.24$*), in a way very similar to that found in the structure of the bismuth trichloride[17] [Bi–Cl = 2.518(7), 2.513(7), and 2.468(4) Å]. The interbond angles at bismuth, having a similar trend to that above, are much less than the tetrahedral angle because of lone pair–bond pair electron repulsions.[6] The Cl(2) atom of one adjacent molecule at $\bar{x}, \bar{y}, \bar{z}$ is bridging, at 3.154(12) Å from the bismuth [Bi ··· Bi 4.538(3) Å], and a longer contact Bi ··· Cl(3) at $x, \frac{1}{2} - y, \frac{1}{2} + z$ of 3.347(12) Å [Bi ··· Bi 4.736(3) Å] which connect in zig-zag chains the $BiCl_3$ units interlayered by the organic molecules. The line passing through the Bi–Cl(1) bond is approximately normal to the pyrene plane [deviation 8.0(1)°], the other two Bi–Cl bonds are roughly parallel to it with angles between Bi–Cl(2), and Bi–Cl(3), and the pyrene plane of 2.1(8) and 7.7(8)° respectively, so that the plane Bi, Bi^{iii}, Cl(2), Cl(2^{iii}) (iii = $\bar{x}, \bar{y}, \bar{z}$) forms an angle of 8.4(8)° with the pyrene plane, *i.e.* nearly parallel to it. The relevant Bi–pyrene contacts range from 3.25(4) for Bi ··· C(3) (Table 3) to 3.71(4) Å for Bi ··· C(6) and these distances, much greater than the sum of the covalent radii, 1.46 + 0.77 = 2.23 Å, indicate an appreciable interaction with the C(1)—C(6) ring, with the shorter contacts at the C(2), C(3), and C(4) atoms. The donation of electrons from the π system to bismuth explains the lengthening of the bismuth–halogen bond opposite to it as found in $2SbCl_3$·naphthalene, $2SbCl_3$·*p*-xylene, and $2SbCl_3$·phenanthrene, but in the present structure the shorter Bi–Cl(1) bond is nearly perpendicular to the pyrene plane, as also found in $[C_6H_3(CH_3)_3]BiCl_3$[11] [Bi–Cl(normal) = 2.465(5); Bi–Cl-(parallel) = 2.489(4) and 2.483(5) Å]. The co-ordination at the metal can be described as very distorted octahedral with the *trans* angles Cl(1)–Bi–C(3) 161.9(8)°, Cl(3)–Bi–Cl(2^{iii}) 162.7(8)°, and Cl(2)–Bi–Cl(3^{iv}) (iv, $x, \frac{1}{2} - y, \frac{1}{2} + z$) 169.0(3)°, and this structure shows many analogies with that found for the molecular structures of $2SbBr_3$·pyrene[6] and $2SbCl_3$·naph-

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* $\Delta/\sigma = |x_1 - x_2|/(\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}}$ where σ_1 and σ_2 are the e.s.d.s of the values x_1 and x_2 respectively.

thalene,[7] in which the aromatic molecule is centrosymmetric and bonded to two antimony atoms, related by symmetry.

The C–C bond distances in the pyrene molecule range from 1.28(8) to 1.45(7) Å and in spite of the large differences ($\Delta_{max.}$ = 0.17 Å) the relevant uncertainties affecting these bond distances preclude any discussion of the significance of these variations (Δ/σ = 1.80) and the same is true for the bond angles [113(4)—129(5)°, Δ/σ = 2.50]. The planarity analysis confirms that the aromatic molecule is planar; the shorter pyrene–pyrene contacts, C(4) $\cdots$ C(7^{i}) 3.47(6), C(5) $\cdots$ C(6^{i}) 3.58(7), C(5) $\cdots$ C(5^{i}) 3.46(7), and C(5) $\cdots$ C(7^{i}) 3.47(6) Å, indicate attractive interactions between the rings which are responsible for the packing in the crystal, with the other van der Waals contacts quoted in Table 3.

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