Characterization of the Bismuth(III) Bromide–[2.2]-Paracyclophane (2/1) Adduct†

Ida Maria Vezzosi,[*,a] **Luigi Pietro Battaglia**[b] **and Anna Bonamartini Corradi**[b]
[a] *Dipartimento di Chimica, Università di Modena, via Campi 183, 41100 Modena, Italy*
[b] *Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Università di Parma, Viale delle Scienze, 43100 Parma, Italy*

The 2:1 charge-transfer molecular complex between bismuth bromide and [2.2]paracyclophane has been prepared and investigated by means of thermogravimetric, electronic and IR spectra and resistivity measurements. The X-ray structure was also determined: monoclinic, space group $P2_1/c$, a = 7.896(3), b = 14.198(6), c = 10.803(8) Å, β = 101.27(5)°, Z = 2 and R = 0.0457. The structure is built up by polymeric linear chains of $BiBr_3$ units interlayered by centrosymmetric hydrocarbon molecules. Two bromine atoms bridge adjacent metal atoms so that the co-ordination is very distorted octahedral with three short [2.595(3)–2.676(3) Å] and two longer bridging [3.325(3), 3.402(2) Å] Bi–Br bonds; the sixth site is occupied by a benzene ring of the [2.2]paracyclophane molecule. The complex shows high stability and characteristic electrical properties of a semiconductor at 25 °C.

Cyclophanes, with their unusual structures containing benzene rings held rigidly in close proximity, are bridged aromatic hydrocarbons with unique steric and electronic properties.[1] The distortions of the benzene rings from planarity and transannular π-electronic interactions are of particular interest. The chemical reactivity and π basicity of these molecules have been studied by examining the formation of charge-transfer (c.t.) complexes with different organic molecules[2,3] and metal atoms.[4–9] In addition the molecular complexes between bismuth halides and arenes, interesting both from structural and theoretical points of view, have recently received further attention.[8,10] In connection with our previous studies on bismuth(III) halide complexes with arenes[11–13] we have now examined the complex between bismuth bromide and [2.2]-paracyclophane to elucidate the role of the intramolecular steric and electronic interactions in the formation and stability of such complexes.

Experimental

All the reagents were of the best commercial grade. The bismuth bromide was recrystallized from ethylbenzene and dried over P_4O_{10}; [2.2]paracyclophane (Aldrich Chemical) was used as received. Dichloromethane was dehydrated over calcium chloride and purified by distillation, collecting the fraction boiling at 40 °C. All the other solvents were dehydrated and kept over metallic sodium wire. The manipulations were performed in a dry-box over dry nitrogen.

Synthesis of the Complex.—The complex was obtained by adding, under stirring, a dichloromethane solution of the hydrocarbon to a warm (70 °C) toluene solution of bismuth bromide with metal-to-ligand ratios ranging from 2:1 to 1:1. After 2–3 d single yellow crystals of bismuth bromide–[2.2]paracyclophane (2/1) were formed (Found: C, 17.30; H, 1.45; Bi, 37.70. Calc. for $C_{16}H_{16}Bi_2Br_6$: C, 17.40; H, 1.45; Bi, 37.80%).

Physical Measurements. The thermogravimetric analysis was performed at a rate of 10° min^{-1} with a NETZ SCH STA 409 thermobalance. The electronic spectrum of the solid sample, in Nujol mull with Polythene as support, was recorded at room temperature with a Shimadzu MPS 50-L spectrophotometer. Infrared spectra were recorded at room temperature on a Bruker FT-IR-113V spectrophotometer in KBr pellets (400–4000 cm^{-1}) or in Polythene pellets (50–500 cm^{-1}). Electrical resistivity measurements were performed on a compressed pellet (diameter 12 mm, thickness 0.45 mm) using the two-probe method at 25 °C.

Crystallography.—The crystal was sealed in a glass capillary under dry nitrogen and mounted in a random orientation on an Enraf Nonius CAD4 single-crystal diffractometer: the resulting crystal data and the relevant details of the data collection and refinements are reported in Table 1. The intensity data were collected using the five-points technique and variable speed. The intensity of a standard reflection was measured every 200 reflections; no significant changes or decay were detected. After the usual data reduction the structure amplitudes were put on an absolute scale first by the Wilson method and then by least squares. The data were also corrected for absorption by Walker and Stuart's method.[14]

The structure was solved by Patterson and Fourier methods and refined by full matrix least squares with anisotropic thermal parameters for Bi and Br atoms. The final indexes were R = 0.0457 and R' = 0.0476. The final atomic parameters are reported in Table 2. All calculations were performed using a Gould 32/77 computer and SHELX 76,[15] ORTEP[16] and PARST[17] programs. Atomic scattering factors corrected for anomalous dispersion were taken from ref. 18.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Thermal gravimetric data indicate that the complex is stable up to 180 °C and then it undergoes complete decomposition. The room-temperature solid-state electronic spectrum shows a broad band centred about 375 nm due to a c.t. transition from

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† [2.2]Paracyclophane = tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

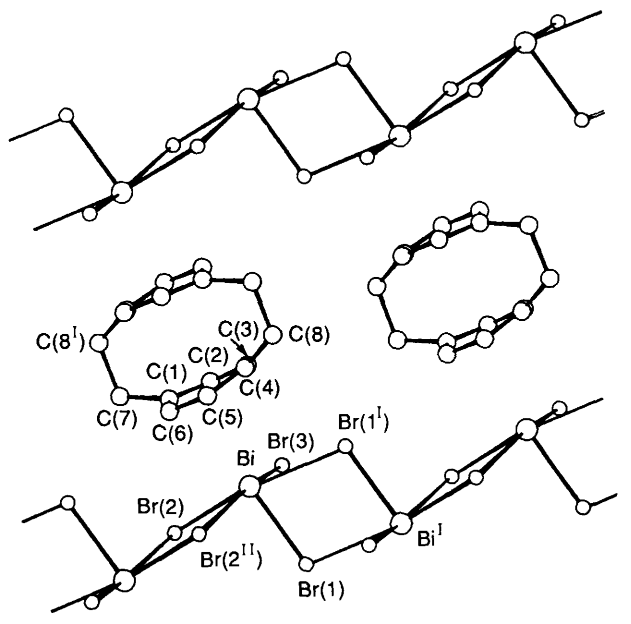

Fig. 1 Perspective view of the structure

Table 1 Experimental data for the crystallographic analysis

Formula	$C_{16}H_{16}Bi_2Br_6$
M	1105.7
Crystal symmetry	Monoclinic
Space group	$P2_1/c$
a/Å	7.896(3)
b/Å	14.198(6)
c/Å	10.803(8)
β/°	101.27(5)
U/Å^3	1188(1)
Z	2
D_c/g cm^{-3}	3.09
D_m/g cm^{-3}	3.12
Reflections for lattice parameters: number	25
Reflections for lattice parameters: θ range/°	9.3–16.0
F(000)	976
T/K	294
Crystal size (mm)	0.36 × 0.46 × 0.58
λ(Mo-Kα)/Å	0.710 69
μ/cm^{-1}	247.1
Scan speed/° min^{-1}	1.27–3.30
Scan width/°	1.28 + 0.35 tanθ
θ range/°	3–24
h,*k*,*l* ranges	−10 to 10, 0–20, 0–18
Standard reflection	−1 6 2
Maximum intensity variations (%)	3.2
Scan mode	ω–2θ
No. of reflections	
measured	2054
used in the refinement	1222
No. of refined parameters	69
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0457
$R' = [\Sigma w(\Delta F^2)/\Sigma w F^2_o]^{\frac{1}{2}}$	0.0476
k,g in $w = k/[\sigma^2(F_o) + gF_o^2]$	0.3518, 4.364 × 10^{-3}
Maximum, minimum height in final Δ*F* map/e Å^{-3}	1.9, −1.95

Table 2 Atomic fractional coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Bi	2279.5(10)	628.1(6)	4120.3(7)
Br(1)	4282(3)	533(2)	6421(2)
Br(2)	−439(3)	1338(2)	4919(2)
Br(3)	3447(4)	2290(2)	3744(3)
C(1)	2129(26)	−470(15)	1054(19)
C(2)	765(30)	−902(16)	1568(22)
C(3)	−603(25)	−310(14)	1763(19)
C(4)	−607(27)	665(16)	1456(20)
C(5)	889(30)	1097(16)	1230(21)
C(6)	2206(27)	503(15)	1006(20)
C(7)	3130(32)	−1077(18)	354(23)
C(8)	−2387(37)	1194(22)	1128(27)

Table 3 Selected interatomic distances (Å) and angles (°) with e.s.d.s in parentheses

Br–Br(1)	2.676(3)	Br–Br(1^{I})	3.325(3)
Bi–Br(2)	2.663(3)	Bi–Br(2^{II})	3.402(2)
Bi–Br(3)	2.595(3)		
Bi ··· C(1)	3.64(2)	Bi ··· C(4)	3.30(2)
Bi ··· C(2)	3.53(2)	Bi ··· C(5)	3.17(2)
Bi ··· C(3)	3.34(2)	Bi ··· C(6)	3.36(6)
C(1)–C(2)	1.44(3)	C(3)–C(4)	1.42(3)
C(1)–C(6)	1.38(3)	C(4)–C(5)	1.39(3)
C(1)–C(7)	1.47(3)	C(4)–C(8)	1.57(3)
C(2)–C(3)	1.42(3)	C(5)–C(6)	1.40(3)
C(7)–C(8^{II})	1.60(3)		
Br(1)–Bi–Br(2)	94.9(1)	Br(3)–Bi–Br(1^{I})	95.5(1)
Br(1)–Bi–Br(3)	91.6(1)	Br(1^{I})–Bi–Br(2^{II})	71.1(1)
Br(2)–Bi–Br(3)	92.3(1)	Br(1)–Bi–Br(2^{II})	69.5(1)
Br(1)–Bi–Br(1^{I})	77.5(1)	Br(2)–Bi–Br(2^{II})	71.1(1)
Br(2)–Bi–Br(1^{I})	162.2(1)	Br(3)–Bi–Br(2^{II})	153.0(1)
C(1)–C(2)–C(3)	117(2)	C(2)–C(1)–C(7)	118(2)
C(2)–C(3)–C(4)	121(2)	C(6)–C(1)–C(7)	122(2)
C(3)–C(4)–C(8)	118(2)	C(4)–C(5)–C(6)	117(2)
C(3)–C(4)–C(5)	120(2)	C(1)–C(6)–C(5)	124(2)
C(5)–C(4)–C(8)	120(2)	C(1)–C(7)–C(8^{III})	116(2)
C(2)–C(1)–C(6)	119(2)	C(4)–C(8)–C(7^{III})	108(2)

Symmetry equivalents: I 1 − *x*, −*y*, 1 − *z*; II −*x*, −*y*, 1 − *z*; III −*x*, −*y*, −*z*.

the π system of the ligand to the metal. Comparison of the IR spectra of the free donor and those of the complex in the 500–1700 cm^{-1} region reveals that the bands at 721, 895 and 930 cm^{-1} associated with the distorted benzene rings in the [2.2]paracyclophane system[19a,b] are also present for the complex. The intensity maximum at 1593 cm^{-1} of the free ligand (1600 cm^{-1} for the complex), due to ring stretching,[19c] increases upon c.t. complex formation. The far infrared spectrum of the complex shows in the range 150–220 cm^{-1} three strong bands at 166, 185 and 208 cm^{-1} tentatively assigned to ν(Bi–Br) stretching related to the differences in Bi–Br bond lengths. The complex in the solid state exhibits the electrical properties of a semiconductor at room temperature with a conductivity of σ = 1.05 × 10^{-7} Ω^{-1} cm^{-1}.

As shown in Fig. 1, the structure is built up by polymeric linear chains of $BiBr_3$ units in which Br(1) and Br(2) each form two centrosymmetric bridges connecting two adjacent and different symmetry-translated metals: Bi ··· Bi^{I} 4.697(2) Å (I 1 − *x*, −*y*, 1 − *z*), Bi ··· Bi^{II} 4.736(2) Å (II −*x*, −*y*, 1 − *z*). The bismuth is closely bonded to three bromines with Bi–Br 2.595(3), 2.663(3) and 2.676(3) Å (Table 3) and loosely to Br(1^{I}) and Br(2^{II}) of adjacent polyhedra at 3.325(3) and 3.402(2) Å respectively; the sixth site of a very distorted octahedron is occupied by a benzene ring of the hydrocarbon. The result is a two-dimensional structure of linear inorganic chains connected by centrosymmetric [2.2]paracyclophane molecules; these layers are held together by van der Waals contacts. The Bi–Br bond distances compare well with the values found in the $BiBr_3$-fluoranthene complex [2.570(8)–2.764(4) Å] and 2-methylpyridinium tetrabromobismuthate[20] [2.63(2) and 2.65(3) Å]; in the latter case the shorter Bi–Br(1) distance corresponds to the unshared bromine atom. The longer bonds involving bridges have similar values to those of 3.335(7), 3.369(6) and 3.494(7) Å found in the above fluoranthene complex, and the same can be said for the interbond angles [91.6(1)–94.9(1)°]. The two Bi_2Br_2 planes of the bridges form a dihedral angle of 67.27(9)°.

The bismuth–arene distances [3.17(2)–3.64(2) Å], spread over a wide range, are typical for these compounds, *e.g.* $BiCl_3$·pyrene [3.25(4)–3.62(3) Å] and $2BiBr_3$·fluoranthene·0.5*p*-xylene[12] [3.23(4)–3.66(5) Å], showing differentiated interactions between the metal and the π system of the ring. The positional parameters of the organic molecule are affected by large errors due to the presence of the heavy atoms so that the bond angles and distances are of very low accuracy, but these values agree with those found *e.g.* in (η^5-cyclopentadienyl)(η^6-[2.2]paracyclophane)iron(II) tetrafluoroborate[21] and in [2.2]paracyclophane[22] itself, in particular the strain in the methylene bridges is revealed by the longer $C(sp^3)$–$C(sp^3)$ bonds [1.57(3), 1.60(3) Å] and by the moderate puckering of the ring.

The [2.2]paracyclophane seems to show good complexing properties, in fact the present complex is much more stable to air and to moisture when compared to similar complexes with the usual arenes. This suggests that the formation and stabilization of this complex are unaffected by the deformation of the rings and reflect mainly π-electronic transannular effects.

Acknowledgements

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