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Notes

(Perylene)$_3$[Bi$_4$Br$_{12}$]: A New Arene π-Complex Containing the [Bi$_4$Br$_{12}$] Unit

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Introduction

Aromatic hydrocarbons form well-defined π-donor−acceptor complexes with various organic and inorganic π-electron acceptors.[2] They can be ionic or not, depending on the degree of charge transfer in the ground state. Perylene, for example, forms molecular metals with [M(mnt)$_2$]$^{n-}$ anions, where M = Pt, Pd, Au, Cu and mnt = maleonitriledithiolato, being present in these solids as the radical cation.[3] Since the donor ability of polycyclic arenes is relatively weak, they usually form neutral charge transfer (CT) complexes, mainly with d-block elements. Few examples are know for main group elements. We have been studying the interaction between VB main group metal halides with several π-donor polycyclic hydrocarbons for long time, and we have been able to isolate neutral CT complexes. It has been found by us[4] and by other groups[5] that bismuth(III) halides coordinate arenes with various stoichiometries and in unusual structural motifs. With the aim of extending the chemistry of bismuth−π-arene donor−acceptor systems, we have studied the reaction of perylene and pyrene molecules, either by themselves or as a mixture, with BiBr$_3$. Perylene contains five benzenoid rings and pyrene four. So each donor molecule in principle can coordinate more than one metal atom.

Experimental Section

All reagents were commercial grade. BiBr$_3$ was recrystallized from toluene and dried over P$_4$O$_{10}$. Perylene (Aldrich Chemical) was used as received. The solvents were dried with Na metal and distilled prior to use.

Preparation of (Perylene)$_3$[Bi$_4$Br$_{12}$]. The compound was obtained by mixing a *p*-xylene 1:1 solution of perylene and pyrene and a solution of BiBr$_3$ in a metal bromide:hydrocarbon molar ratio of 4:1 at about 70 °C. Black prismatic crystals were isolated on slow cooling after a few days. In the absence of pyrene, the title compound was not obtained.[6]

Table 1. Crystal Data for (Perylene)$_3$[Bi$_4$Br$_{12}$]

formula	C$_{30}$H$_{18}$Bi$_2$Br$_6$	V	1470(2) Å^3
M	1275.8	Z	2
space group	$P\bar{1}$	λ(Mo Kα)	0.7107 Å
a	10.250(11) Å	ρ_{obsd}	2.80 g cm^{-3}
b	10.605(10) Å	ρ_{calcd}	2.88 g cm^{-3}
c	14.418(10) Å	temp	294 K
α	101.44(7)°	μ	200.2 cm^{-1}
β	91.33(7)°	R^a	0.0495
γ	106.23(9)°	$R_w{}^b$	0.0512

^{a} $R = \sum|\Delta F|/|F_o|$. ^{b} $R_w = [\sum w(\Delta F^2)/\sum wF_o{}^2]^{1/2}$.

Anal. Calcd for C$_{60}$H$_{36}$Bi$_4$Br$_{12}$: C, 28.24; H, 1.42; Bi, 32.76; Br, 37.58. Found: C, 27.9; H, 1.30; Bi, 32.70; Br, 37.45.

Physical Measurements. Elemental analyses were performed by the Analytical Laboratory of the Department of Chemistry of Modena University. The weight loss from a batch of (perylene)$_3$[Bi$_4$Br$_{12}$] was measured on a Stanton-Redcroft STA-781 thermoanalyzer. Room-temperature diffuse reflectance spectra were recorded on KBr-diluted samples by using a Cary 5 spectrophotometer. IR spectra were recorded on a FT-IR Bruker 113V spectrophotometer using KBr pellets (4000−400 cm^{-1}) and polythene pellets (500−50 cm^{-1}). X-band EPR spectra were recorded at room temperature by using a Varian E9 spectrometer.

Crystallography. The crystal was sealed under dry atmosphere in a glass capillary, mounted on a three-circle automated diffractometer, and examined by X-ray diffraction. The resulting crystallographic data are summarized in Table 1. After the usual data reduction, the structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures with anisotropic thermal parameters only for Bi and Br atoms, hydrogens were not located, and a correction for absorption was also applied.[7]

Table 2 reports the final coordinates for non-hydrogen atoms. The scattering factors were taken from ref 8. All the calculations were performed on a Gould 6040 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR of Parma using SHELX76,[9] ORTEP,[10] and PARST[11] programs.

Results and Discussion

Mixing a 1:1 perylene−pyrene solution and anhydrous BiBr$_3$ in *p*-xylene in a ligand to metal molar ratio of 1:4 has led to the formation of a black crystalline complex of formula (perylene)$_3$[Bi$_4$Br$_{12}$]. The weight loss from a sample of the title compound at 252 °C was 8.4%, close to that expected for one perylene molecule per formula unit. The crystal structure of (perylene)$_3$[Bi$_4$Br$_{12}$] contains a discrete tetrameric [Bi$_4$Br$_{12}$] centrosymmetric unit (see Figure 1), in which the metal atoms are connected by asymmetrically bridging bromine atoms: Br(1) is tribridging, connecting Bi(1), Bi(2), and Bi(1$^{\text{i}}$) (i = $-x$, $-y$, $1 - z$); Br(2) bridges Bi(1) and Bi(2$^{\text{i}}$), Br(4) bridges Bi(1) and Bi(2), and Br(3), Br(5), and Br(6) form terminal Bi−Br

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Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (A^2 × 10^4) for Non-Hydrogen Atoms with Esd's in Parentheses

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]
Bi(1)	−498(2)	−2157(2)	4034(1)	255(8)
Bi(2)	473(2)	1335(2)	2524(1)	331(9)
Br(1)	1604(5)	101(5)	4288(4)	331(20)
Br(2)	641(5)	−2880(5)	5439(4)	359(21)
Br(3)	615(6)	−3354(6)	2679(4)	616(28)
Br(4)	−1729(5)	−642(5)	2708(4)	472(23)
Br(5)	−950(7)	2395(6)	1564(4)	587(28)
Br(6)	1141(7)	−146(7)	1077(5)	730(31)
C(1)	−5559(42)	−1823(40)	4233(29)	464(106)
C(2)	−5564(70)	−1983(67)	3270(47)	490(200)
C(3)	−4934(44)	−2841(43)	2786(30)	366(100)
C(4)	−4183(51)	−3409(49)	3349(35)	179(135)
C(5)	−4126(33)	−3272(32)	4260(23)	61(77)
C(6)	−4939(54)	−2514(52)	4793(38)	268(136)
C(7)	−3318(69)	−3742(68)	4798(47)	136(202)
C(8)	−2744(61)	−4820(59)	4341(42)	405(169)
C(9)	−2645(56)	−4922(54)	3308(39)	506(149)
C(10)	−3369(57)	−4253(54)	2809(38)	536(147)
C(11)	−3377(44)	−3736(42)	5823(31)	158(107)
C(12)	−2714(45)	−4341(43)	6343(31)	648(110)
C(13)	−2582(41)	−4123(38)	7344(28)	288(97)
C(14)	−3361(71)	−3310(69)	7860(48)	662(202)
C(15)	−4070(52)	−2659(49)	7334(36)	152(130)
C(16)	−4033(56)	−2857(52)	6306(38)	112(144)
C(17)	−4818(49)	−2324(48)	5805(34)	131(127)
C(18)	−5563(45)	−1424(43)	6331(32)	375(110)
C(19)	−5483(54)	−1260(53)	7338(37)	504(155)
C(20)	−4760(54)	−1888(51)	7816(37)	476(142)
C(21)	6171(51)	−2091(49)	319(35)	1062(131)
C(22)	5502(81)	−1325(73)	523(51)	1564(217)
C(23)	4194(83)	−1854(76)	485(52)	984(229)
C(24)	3339(70)	−3189(66)	316(45)	990(189)
C(25)	4277(80)	−4032(87)	183(54)	745(240)
C(26)	5742(53)	−3484(49)	221(35)	650(134)
C(27)	3681(58)	−5366(59)	51(38)	1018(147)
C(28)	2377(56)	−5788(52)	−52(37)	844(147)
C(29)	1326(55)	−4977(56)	128(37)	1232(144)
C(30)	1835(59)	−3751(56)	322(37)	1185(144)

[a] Equivalent isotropic *U* defined as one-third trace of the diagonalized matrix.

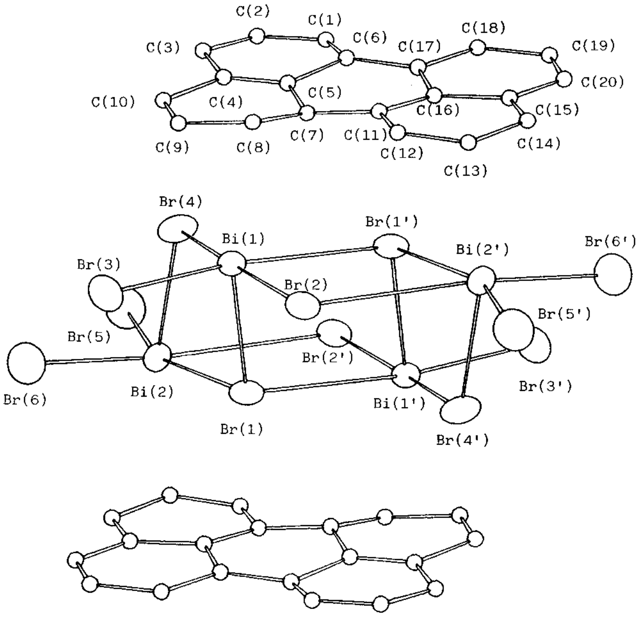

Figure 1. View of the bismuth environment with hydrogen atoms omitted for clarity (50% probability thermal ellipsoids).

bonds. The coordination of the bismuth is very distorted octahedral, with three bromine atoms strictly bonded, *i.e.* Br(1), Br(2), and Br(3) to Bi(1), and Br(4), Br(5), and Br(6) bonded to Bi(2) (2.580(7)−2.691(6) Å), and two additional bridging bromine atoms belonging to adjacent polyhedra (range 3.174(7)−3.450(6) Å) (Table 3). The sixth site is occupied by the benzene ring belonging the perylene 1 molecule. The distances of Bi(1) and Bi(2) from the carbon atoms of the corresponding perylene rings are different (Table 3). Comparison of the individual Bi···C distances shows that the π-bonding is closer to an η^2 mode than to an η^6 one.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) in the Coordination Polyhedra[a]

Bi(1)−Br(1)	2.691(6)	Bi(2)−Br(4)	2.676(6)
Bi(1)−Br(2)	2.657(7)	Bi(2)−Br(5)	2.597(8)
Bi(1)−Br(3)	2.580(7)	Bi(2)−Br(6)	2.580(7)
Bi(1)−Br(4)	3.174(7)	Bi(2)−Br(1)	3.400(7)
Bi(1)−Br(1$^{\mathrm{i}}$)	3.363(6)	Bi(2)−Br(2$^{\mathrm{i}}$)	3.450(6)
Bi(1)···C(4)	3.68(5)	Bi(1)···C(10)	3.36(5)
Bi(1)···C(5)	3.62(3)	Bi(2)···C(12i)	3.43(3)
Bi(1)···C(7)	3.25(7)	Bi(2)···C(13i)	3.10(3)
Bi(1)···C(8)	3.22(6)	Bi(2)···C(14i)	3.24(7)
Bi(1)···C(9)	3.10(5)	Bi(2)···C(15i)	3.54(5)
Br(1)−Bi(1)−Br(2)	89.3(2)	Br(4)−Bi(2)−Br(5)	92.3(2)
Br(1)−Bi(1)−Br(3)	91.5(2)	Br(4)−Bi(2)−Br(6)	92.5(2)
Br(1)−Bi(1)−Br(4)	81.9(2)	Br(5)−Bi(2)−Br(6)	96.4(2)
Br(1)−Bi(1)−Br(1$^{\mathrm{i}}$)	79.2(1)	Br(4)−Bi(2)−Br(1)	77.9(1)
Br(2)−Bi(1)−Br(1$^{\mathrm{i}}$)	87.2(1)	Br(4)−Bi(2)−Br(2$^{\mathrm{i}}$)	80.1(1)
Br(2)−Bi(1)−Br(3)	96.6(2)	Br(5)−Bi(2)−Br(1)	161.7(1)
Br(2)−Bi(1)−Br(4)	166.5(2)	Br(5)−Bi(2)−Br(2$^{\mathrm{i}}$)	87.9(1)
Br(3)−Bi(1)−Br(4)	94.0(2)	Br(6)−Bi(2)−Br(2$^{\mathrm{i}}$)	171.6(1)
Br(3)−Bi(1)−Br(1$^{\mathrm{i}}$)	170.0(2)	Br(6)−Bi(2)−Br(1)	99.4(1)
Br(4)−Bi(1)−Br(1$^{\mathrm{i}}$)	81.0(1)	Br(1)−Bi(2)−Br(2$^{\mathrm{i}}$)	75.3(1)

[a] i = $-x$, $-y$, $1 - z$.

Bi−Br bond distances are in agreement with those of the few reported structurally characterized complexes[4] and range between 2.580(7) and 2.691(6) Å: longer bonds are those opposite to the metal−arene bonds. The shortest metal−metal distances inside the unit are as follows: Bi(1)···Bi(2), 4.548(5) Å; Bi(1)···Bi(1$^{\mathrm{i}}$), 4.683(5) Å; Bi(1)···Bi(2$^{\mathrm{i}}$), 4.863(4) Å. Other nearest *inter*cluster Bi···Bi distances are much longer. Two independent perylene molecules are present in the unit cell (see Figure 2): Perylene 1 (labeled C(1) to C(20)) interacts with the two metal atoms by means of the C(4), C(10) and C(11), C(16) rings and generates contacts by itself with shortest distances of C(2)···C(18$^{\mathrm{ii}}$) = 3.40(8) Å (ii = $-x - 1$, $-y$, $1 - z$) and C(8)···C(17$^{\mathrm{iii}}$) = 3.31(7) Å (iii = $-x - 1$, $-y - 1$, $1 - z$). The overlapping of the molecules is considerable only with the molecule at iii, while is very restricted with that at ii, so that no columnar structures are produced. The perylene 2 molecule, located on a symmetry center, does not interact with any metal and is arranged in such a way that the angle with perylene 1 is 91.2(9)°. This molecule shows no short contacts, in agreement with the observed large thermal motion, and is little involved with the perylene 1 molecule (C(14)···C(26)$^{\mathrm{iv}}$ = 3.58(8) Å (iv = $x - 1$, y, $1 + z$) and C(14)···C(27)$^{\mathrm{v}}$ = 3.55(9) Å (v = $-x$, $-1 - y$, $1 - z$)) and with the bromine atoms (Br···C(30)$^{\mathrm{vi}}$ = 3.53(6) Å (vi = $-x$, $-y$, $-z$)). Furthermore it is the first to be lost on heating. The neutral tetranuclear [Bi_4Br_{12}] units are held together by the dimeric perylene 1 molecules. Similar extended contacts are present in the structures of (fluoranthene)bismuth bromide[4b] and of (pyrene)bismuth chloride.[4c] So, in these structures noncovalent $\pi\cdots\pi$ interactions between the arene molecules and between bismuth and the π-systems are mainly responsible for the packing inside the unit cell and for the stability of the compounds. The purity and homogeneity of the samples used for physical measurements were checked by the X-ray powder diffraction patterns, which were indexed according to the space group found in the single-crystal studies. A very weak and narrow EPR signal was

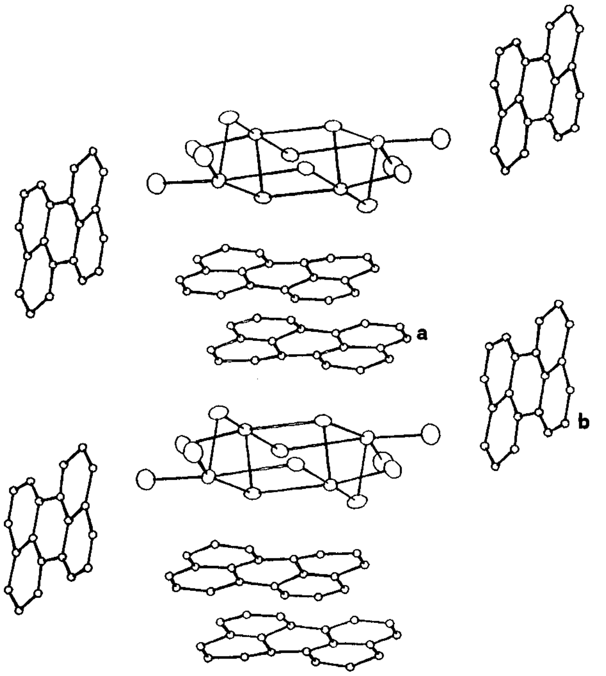

Figure 2. Crystal structure of (perylene)$_3$[Bi$_4$Br$_{12}$]. Perylene 1 is labeled as **a**, and perylene 2, as **b**. (Thermal ellipsoids are drawn at the 50% probability level.)

observed at room temperature, indicating diamagnetic behavior. The electronic absorption spectrum of this compound features no absorption bands below 20 000 cm^{-1}. The first strong peak appears at 21 900 cm^{-1}, and the other four appear at 25 000, 25 300, 32 000, and 37 000 cm^{-1}, respectively. The peak at 21 900 cm^{-1} can be assigned to a CT transition from the π-system of the benzene ring of the perylene to the sp^{3}d metal orbital.[12] The band at about 25 000 cm^{-1} has been previously observed for the **a** form of neutral perylene. It is ascribed to a transition to an excited state, where the promoted electron is transferred to the nearest perylene molecule, and it is commonly called a *charge-transfer exciton*.[13] The IR spectra of both the free perylene molecule and the compound, recorded in the range 3100−500 cm^{-1}, do not differ except for an increase of intensity of the band at 1600 cm^{-1} (ring stretching vibration) and a decrease of intensity observed in the band at 540 cm^{-1} (deformation ring) upon CT complex formation. Below 500 cm^{-1}, the spectrum of the complex shows the band at 185 cm^{-1}, which corresponds to ligand vibration, while the other strong bands at 164 and 206 cm^{-1} and a shoulder at 195 cm^{-1} are attributed to the Bi−Br stretching vibrations. The multiplicity of the bands in this spectral region is due to the different Bi−Br distances present in the molecular structure of the tetramer.

To conclude, this work shows that is possible to obtain relatively stable charge-transfer compounds by combining perylene and bismuth halides. The crystal structure of the title compound reveals the packing, and the one-dimensional motif is determined by two different noncovalent interactions: (a) bismuth−arene contacts and (b) $\pi-\pi$ interactions between perylene molecules.

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Supporting Information Available: Tables of crystallographic data, anisotropic and isotropic thermal parameters, remaining bond distances and angles, and contacts less than 3.6 Å (5 pages). Ordering information is given on any current masthead page.

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