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Synthesis and Structure of Bismuth-Containing Complexes $[(Ph_4BiO)_2\{2,5\text{-}(CH_3)_2C_6H_3S(O)\}]_2^+[Ph_2Bi_2I_6]^{2-}$, $[(Ph_4Bi]^+[PhBi(C_5H_5N)I_3]^-$, $[Ph_4Sb]_4^+[Bi_4I_{16}]^{4-} \cdot 2(CH_3)_2C{=}O$, and $[Ph_4Sb]_3^+[Bi_5I_{18}]^{3-}$

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Abstract—The reactions of tetraphenylbismuthonium and -stibonium salts Ph_4EX (E = Bi, Sb; X = I, $OSO_2(C_6H_3(CH_3)_2\text{-}2,5)$, $OSO_2C_6H_3(OH\text{-}4)(COOH\text{-}3)$) with bismuth triiodide in acetone afford complexes $[Ph_4Bi]^+[PhBi(C_5H_5N)I_3]^-$, $[(Ph_4BiO)_2S(O)\{2,5\text{-}(CH_3)_2C_6H_3S(O)\}]_2^+[Ph_2Bi_2I_6]^{2-}$, $[Ph_4Sb]_4^+[Bi_4I_{16}]^{4-} \cdot 2(CH_3)_2C{=}O$, and $[Ph_4Sb]_3^+[Bi_5I_{18}]^{3-}$, whose structural units, according to the X-ray diffraction data, are tetraphenylbismuthonium (-stibonium) cations and mono-, di-, tetra-, and pentanuclear anions, respectively.

INTRODUCTION

The reactions of tetraphenylantimony halides with phenylbismuth bis(arenesulfonates) are known to afford complexes containing tetraphenylstibonium cations and cyclic bismuth-containing anions [1, 2]. To continue our studies in this direction, we studied the reactions of tetraphenylbismuthonium (-stibonium) salts with bismuth triiodide and determined crystal structures of four products of these reactions.

EXPERIMENTAL

Synthesis of $[(Ph_4BiO)_2\{2,5\text{-}(CH_3)_2C_6H_3S(O)\}]_2^+[Ph_2Bi_2I_6]^{2-}$ (I). A solution of bismuth triiodide (0.39 g) in acetone (20 ml) was added to a solution of tetraphenylbismuth 2,5-dimethylbenzenesulfonate (0.50 g) in acetone (20 ml), and the reaction mixture was stored for 12 h. Red-orange crystals that formed were filtered and dried. The yield of complex **I** was 67% (0.60 g), T_m = 116°C (140°C decomp.).

Synthesis of $[Ph_4Bi]^+[PhBi(C_5H_5N)I_3]^-$ (II). Pyridine (10 ml) was added to a mixture of tetraphenylbismuth 3-carboxy-4-oxybenzenesulfonate (0.30 g) and bismuth triiodide (0.19 g) in acetone (10 ml), and the reaction mixture was stirred for 12 h. The reaction mixture was concentrated to a volume of 5 ml and cooled to –18°C. Yellow crystals that formed were filtered and dried. Complex **II** was obtained in 67% yield (0.27 g), T_{decomp} > 200°C.

Synthesis of $[Ph_4Sb]_4^+[Bi_4I_{16}]^{4-} \cdot 2(CH_3)_2C{=}O$ (III). A solution of tetraphenylantimony iodide (0.50 g) in acetone (20 ml) was added to a solution of bismuth triiodide (0.53 g) in acetone (50 ml), and the reaction mixture was stored for 12 h. After the solvent was evaporated, red-cherry crystals of compound **III** were obtained in 90% yield (0.95 g), T_m = 128°C.

Synthesis of $[Ph_4Sb]_3^+[Bi_5I_{18}]^{3-}$ (IV). A solution of tetraphenylantimony 2,5-dimethylbenzenesulfonate (0.50 g) in acetone (20 ml) was added to a solution of bismuth triiodide (0.80 g) in acetone (80 ml), and the reaction mixture was stored for 12 h. Large red-cherry crystals of compound **IV** were obtained in 44% yield (0.55 g) on slow evaporation of the solvent, T_m = 156°C (decomp.).

X-ray diffraction analyses of crystals of compounds **I**–**IV** were carried out on a SMART 1000 CCD diffractometer (graphite monochromator, MoK_α radiation, λ = 0.71073 Å). The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The positions of H atoms were calculated geometrically and included into the "riding" model refinement.

The data were collected and processed and the unit cell parameters were refined using the SMART and

Table 1. Crystallographic data and results of refinement for structures **I–IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Molecular formula	$C_{62}H_{54}Bi_3I_3O_3S$	$C_{35}H_{30}Bi_2I_3N$	$C_{51}H_{46}Bi_2I_8OSb_2$	$C_{72}H_{60}Bi_5I_{18}Sb_3$
M	1886.75	1263.26	2351.54	4619.55
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
T, K	295(2)	293(2)	243(2)	243(2)
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$Pnma$
Unit cell parameters:				
a, Å	10.436(1)	10.038(2)	16.440(2)	42.339(2)
b, Å	19.068(3)	10.699(2)	16.144(2)	18.336(8)
c, Å	30.489(4)	17.734(3)	14.067(3)	13.136(5)
α, deg		99.656(3)		
β, deg	92.639(3)	101.045(3)	101.889(2)	
γ, deg		95.168(3)		
V, Å^3	6060.7(1)	1828.0(5)	6251(1)	10198.0(7)
Z	4	2	4	4
ρ(calcd), g/cm^3	2.068	2.295	2.499	3.009
μ_{Mo}, mm^{-1}	10.294	12.169	10.452	14.860
F(000)	3496	1144	4208	8056
Shape (crystal size, mm)	Plate (0.07 × 0.20 × 0.29)	Prism (0.07 × 0.14 × 0.21)	Prism (0.35 × 0.32 × 0.30)	Prism (0.20 × 0.25 × 0.30)
θ, deg	2.68–23.29	1.95–23.28	2.88–27.50	1.47–28.00
Intervals of reflection indices	$-8 \le h \le 11$	$-11 \le h \le 11$	$-20 \le h \le 21$	$-55 \le h \le 44$
	$-21 \le k \le 21$	$-11 \le k \le 11$	$-20 \le k \le 12$	$-24 \le k \le 21$
	$-33 \le l \le 33$	$-19 \le l \le 19$	$-31 \le l \le 29$	$-17 \le l \le 17$
All reflections	27071	15634	39744	63138
Independent reflections	8712 (R_{int} = 0.0661)	5259 (R_{int} = 0.0479)	14332 (R_{int} = 0.0512)	12349 (R_{int} = 0.0606)
Reflections with $I > 2\sigma(I)$	5198	4010	10261	8948
Number of refined parameters	651	371	580	485
GOOF	0.799	1.015	1.027	1.056
R-factors against $F^2 > 2\sigma(F^2)$	R_1 = 0.0344, wR_2 = 0.0553	R_1 = 0.0314, wR_2 = 0.0680	R_1 = 0.0366, wR_2 = 0.0771	R_1 = 0.0367, wR_2 = 0.0720
R factors against all reflections	R_1 = 0.0747, wR_2 = 0.0606	R_1 = 0.0529, wR_2 = 0.0764	R_1 = 0.0674, wR_2 = 0.0877	R_1 = 0.0618, wR_2 = 0.0805
Molar absorption coefficient	Ignored	0.00018(4)	0.000077(8)	0.000104(3)
Residual electron density (min/max), e/Å^3	–0.816/0.745	–0.935/0.886	–1.427/1.519	–1.236/1.256

Table 2. Coordinates of non-hydrogen atoms ($\times 10^4$) and their equivalent isotropic temperature factors U_{equiv} ($\times 10^3$) in structures **I–IV**

Atom	*x*	*y*	*z*	U_{equiv}, Å^2	Atom	*x*	*y*	*z*	U_{equiv}, Å^2
		I					**I**		
Bi(1)	10008.6(4)	3969.5(1)	1313.18(9)	58.0(1)	C(53)	6280(9)	7973(4)	1184(2)	76(3)
Bi(2)	9235.6(3)	7434.6(1)	2222.97(8)	44.52(8)	C(54)	6675(10)	8592(4)	1024(2)	95(4)
Bi(3)	1244.5(3)	9495.4(1)	622.76(8)	43.67(8)	C(55)	7824(10)	8867(4)	1201(2)	87(3)
I(1)	–835.0(6)	10739.7(2)	438.9(1)	51.4(2)	C(56)	8506(8)	8534(3)	1533(2)	67(3)
I(2)	1485.4(6)	9756.7(2)	1582.7(1)	69.9(2)	C(61)	11099(7)	6987(3)	2115(2)	40(2)
I(3)	2813.6(1)	8196.1(2)	711(2)	71.1(2)	C(62)	11876(9)	7218(4)	1800(2)	75(3)
S	7861(2)	5833.6(8)	1373.5(5)	44.6(6)	C(63)	13101(8)	6967(4)	1771(2)	74(3)
O(1)	8295(5)	5121(2)	1295(1)	57(2)	C(64)	13579(9)	6507(4)	2049(2)	82(3)
O(2)	8811(5)	6250(2)	1613(1)	47(1)	C(65)	12843(10)	6256(4)	2364(3)	116(4)
O(3)	6624(6)	5860(2)	1565(1)	65(2)	C(66)	11598(9)	6498(4)	2402(2)	81(3)
C(1)	7600(8)	6218(3)	850(2)	46(2)	C(71)	8165(7)	6812(3)	2702(2)	45(2)
C(2)	8468(8)	6741(3)	730(2)	51(2)	C(72)	7279(8)	6324(3)	2585(2)	70(3)
C(3)	8334(9)	7098(3)	328(2)	66(3)	C(73)	6688(9)	5964(4)	2899(2)	81(3)
C(4)	7254(11)	6899(4)	59(2)	101(4)	C(74)	6988(9)	6099(4)	3333(2)	80(3)
C(5)	6502(11)	6387(4)	176(2)	106(4)	C(75)	7783(10)	6594(4)	3448(2)	91(4)
C(6)	6577(9)	6018(3)	569(2)	69(3)	C(76)	8431(9)	6972(4)	3142(2)	72(3)
C(7)	5616(10)	5458(4)	679(3)	111(4)	C(81)	9751(8)	8387(3)	2593(2)	45(2)
C(8)	9209(10)	7669(3)	224(2)	107(4)	C(82)	11025(9)	8544(3)	2696(2)	69(3)
C(11)	10985(8)	4771(3)	926(2)	66(3)	C(83)	11312(9)	9175(4)	2902(3)	97(3)
C(12)	11160(9)	4602(4)	503(3)	90(3)	C(84)	10407(10)	9610(4)	3027(2)	89(4)
C(13)	11659(11)	5082(4)	232(3)	111(4)	C(85)	9148(10)	9447(4)	2922(3)	95(4)
C(14)	11991(12)	5715(5)	366(3)	131(4)	C(86)	8827(10)	8842(3)	2709(3)	90(3)
C(15)	11797(10)	5900(4)	789(3)	112(4)	C(91)	2966(8)	10166(3)	514(2)	55(2)
C(16)	11287(10)	5407(4)	1070(3)	93(3)	C(92)	4100(8)	10031(3)	741(2)	66(3)
C(21)	9912(8)	4107(3)	2023(2)	57(2)	C(93)	5123(9)	10429(4)	666(3)	86(3)
C(22)	9672(9)	4740(4)	2203(2)	82(3)	C(94)	5090(9)	10969(4)	374(2)	78(3)
C(23)	9656(11)	4775(4)	2663(2)	114(4)	C(95)	3941(9)	11129(4)	161(2)	78(3)
C(24)	9877(11)	4235(5)	2920(3)	113(4)	C(96)	2948(8)	10714(3)	240(2)	61(3)
C(25)	10119(11)	3595(5)	2741(3)	136(5)			**II**		
C(26)	10154(9)	3540(4)	2281(3)	88(3)	Bi(1)	8686.8(2)	6627.6(2)	2858.1(1)	46.42(7)
C(31)	8291(8)	3531(3)	971(2)	52(2)	Bi(2)	8390.8(2)	8803.8(2)	8348.1(2)	50.98(7)
C(32)	7079(9)	3726(3)	1068(2)	76(3)	I(1)	10928.6(4)	5216.9(4)	2380.0(3)	66.1(1)
C(33)	6057(9)	3422(4)	844(3)	97(3)	I(2)	10626.1(5)	8748.2(4)	3980.9(3)	73.5(2)
C(34)	6208(9)	2917(4)	531(3)	84(3)	I(3)	6321.0(4)	4745.3(4)	1662.1(3)	63.3(1)
C(35)	7383(10)	2744(4)	443(3)	91(4)	N	6707(5)	7815(5)	3376(3)	59(2)
C(36)	8464(10)	3024(4)	666(2)	88(3)	C(1)	6866(7)	9077(6)	3662(5)	74(2)
C(41)	11241(8)	3036(3)	1293(2)	63(3)	C(2)	5847(7)	9671(7)	3918(5)	83(3)
C(42)	10737(10)	2377(4)	1369(3)	115(4)	C(3)	4643(7)	8988(8)	3903(4)	83(3)
C(43)	11515(11)	1805(4)	1350(3)	125(5)	C(4)	4450(7)	7669(7)	3627(4)	72(2)
C(44)	12760(11)	1837(4)	1279(3)	109(4)	C(5)	5500(6)	7155(7)	3376(4)	65(2)
C(45)	13233(9)	2470(4)	1209(2)	92(3)	C(11)	8460(6)	5441(6)	3778(4)	49(2)
C(46)	12518(9)	3094(4)	1203(2)	69(3)	C(12)	8341(6)	5985(6)	4516(4)	59(2)
C(51)	8116(8)	7917(3)	1680(2)	48(2)	C(13)	8211(7)	5256(7)	5076(5)	76(2)
C(52)	6985(7)	7620(3)	1523(2)	52(2)	C(14)	8199(6)	3987(7)	4908(4)	74(2)

Table 2. (Contd.)

Atom	x	y	z	U_{equiv}, Å^2	Atom	x	y	z	U_{equiv}, Å^2
		II					**III**		
C(15)	8333(7)	3425(6)	4174(5)	82(3)	C(5)	3749(4)	2236(4)	2396(3)	63(2)
C(16)	8456(7)	4156(6)	3608(4)	65(2)	C(6)	4035(3)	2984(3)	2221(2)	47(2)
C(21)	10514(6)	9402(5)	8284(4)	48(2)	C(11)	3929(3)	4509(3)	590(2)	37(1)
C(22)	11286(6)	8469(6)	8058(5)	71(2)	C(12)	3742(4)	3796(4)	281(2)	68(2)
C(23)	12641(7)	8820(6)	8035(5)	77(2)	C(13)	3654(4)	3802(5)	–300(2)	86(2)
C(24)	13183(6)	10104(6)	8223(4)	61(2)	C(14)	3746(4)	4510(5)	–574(2)	76(2)
C(25)	12390(6)	10997(6)	8467(4)	57(2)	C(15)	3927(4)	5237(4)	–276(2)	65(2)
C(26)	11064(6)	10664(6)	8480(4)	55(2)	C(16)	4032(3)	5243(3)	314(2)	53(2)
C(31)	7424(6)	10495(6)	8783(3)	48(2)	C(21)	5399(3)	4255(3)	1724(2)	33(1)
C(32)	7206(6)	11404(6)	8323(4)	60(2)	C(22)	5688(3)	3486(4)	1579(2)	50(2)
C(33)	6579(7)	12427(6)	8596(4)	71(2)	C(23)	6537(3)	3337(4)	1713(3)	59(2)
C(34)	6204(7)	12543(6)	9304(4)	69(2)	C(24)	7080(3)	3918(4)	1975(3)	61(2)
C(35)	6430(7)	11611(7)	9748(5)	74(2)	C(25)	6794(3)	4666(4)	2112(2)	49(2)
C(36)	7080(6)	10581(6)	9488(4)	58(2)	C(26)	5948(3)	4847(3)	1995(2)	37(1)
C(41)	8452(6)	7583(5)	9228(3)	45(2)	C(31)	3852(3)	5601(3)	1814(2)	28(1)
C(42)	9701(6)	7377(5)	9637(4)	54(2)	C(32)	4180(3)	5784(3)	2375(2)	36(1)
C(43)	9743(7)	6601(6)	10188(4)	66(2)	C(33)	4046(3)	6566(3)	2593(2)	44(2)
C(44)	8574(7)	6016(6)	10310(4)	59(2)	C(34)	3576(3)	7141(3)	2250(2)	47(2)
C(45)	7302(7)	6246(6)	9904(4)	63(2)	C(35)	3235(3)	6956(3)	1692(2)	50(2)
C(46)	7247(6)	7021(6)	9360(4)	56(2)	C(36)	3371(3)	6189(3)	1466(2)	37(1)
C(51)	7144(6)	7911(5)	7173(3)	49(2)	C(41)	5660(3)	8858(3)	1650(2)	37(1)
C(52)	6067(6)	7020(6)	7125(4)	59(2)	C(42)	5273(4)	8134(4)	1740(3)	68(2)
C(53)	5240(7)	6567(7)	6403(5)	79(2)	C(43)	5651(4)	7378(4)	1700(3)	74(2)
C(54)	5531(8)	6964(7)	5756(5)	82(3)	C(44)	6438(4)	7355(4)	1592(2)	63(2)
C(55)	6639(8)	7850(7)	5825(4)	76(2)	C(45)	6793(4)	8050(4)	1481(3)	78(2)
C(56)	7474(7)	8338(6)	6556(4)	67(2)	C(46)	6412(4)	8832(4)	1516(3)	71(2)
		III			C(51)	5077(3)	10792(4)	1102(2)	52(2)
Bi(1)	5799.3(1)	4096.9(1)	4536.6(1)	25.53(4)	C(52)	5845(4)	11075(4)	1005(3)	90(3)
Bi(2)	6061.0(1)	6975.4(1)	4340.6(1)	31.58(5)	C(53)	5843(5)	11575(5)	537(4)	112(3)
Sb(1)	4104.5(2)	4461.2(2)	1473.2(1)	28.0(1)	C(54)	5112(5)	11780(5)	179(4)	103(3)
Sb(2)	5082.6(2)	9975.2(2)	1775.8(2)	38.8(1)	C(55)	4399(5)	11515(5)	291(3)	104(3)
I(1)	6979.0(2)	2765.0(2)	4889.6(2)	52.7(1)	C(56)	4351(4)	11033(4)	750(3)	74(2)
I(2)	5903.5(2)	4035.8(2)	3352.1(1)	45.6(1)	C(61)	5732(3)	10457(3)	2547(2)	44(2)
I(3)	7243.7(2)	5380.8(2)	4797.9(2)	41.5(1)	C(62)	5960(3)	9921(4)	3001(2)	51(2)
I(4)	4353.7(2)	2889.6(2)	4361.2(1)	42.1(1)	C(63)	6344(4)	10232(5)	3532(3)	80(2)
I(5)	6554.9(3)	6741.3(3)	3253.1(2)	58.9(1)	C(64)	6478(5)	11040(5)	3599(3)	100(3)
I(6)	7393.5(2)	8132.7(2)	4792.8(2)	60.3(1)	C(65)	6229(5)	11588(5)	3169(4)	108(3)
I(7)	4843.3(3)	8261.5(2)	3876.6(2)	60.6(1)	C(66)	5864(4)	11294(4)	2619(4)	85(3)
I(8)	4496.3(2)	5640.3(2)	4154.8(1)	26.8(1)	C(71)	3879(3)	9684(3)	1876(2)	35(1)
O	2227(2)	4736(2)	1057(2)	62(1)	C(72)	3707(3)	9699(3)	2409(2)	44(2)
C(1)	3597(3)	3369(3)	1741(2)	28(1)	C(73)	2913(4)	9511(4)	2474(2)	55(2)
C(2)	2891(3)	3006(3)	1434(2)	38(1)	C(74)	2298(3)	9305(3)	2001(3)	54(2)
C(3)	2612(3)	2264(4)	1596(3)	55(2)	C(75)	2487(3)	9272(4)	1478(2)	52(2)
C(4)	3043(4)	1879(4)	2079(3)	63(2)	C(76)	3274(3)	9470(3)	1408(2)	47(2)

Table 2. (Contd.)

Atom	*x*	*y*	*z*	U_{equiv}, Å^2	Atom	*x*	*y*	*z*	U_{equiv}, Å^2
		III					**IV**		
C(77)	1597(4)	4962(3)	751(3)	52(2)	C(24)	991(2)	2500	3201(6)	48(2)
C(78)	1389(5)	4685(4)	161(3)	86(3)	C(31)	78(2)	6582(4)	4749(4)	41(2)
C(79)	1006(5)	5519(4)	968(3)	86(3)	C(32)	–185(2)	6432(4)	5350(5)	60(2)
		IV			C(33)	–379(2)	5852(5)	5118(6)	74(3)
Bi(1)	0	5000	0	29.54(6)	C(34)	–312(2)	5430(4)	4277(6)	67(2)
Bi(2)	890.61(5)	5016.8(1)	1009.5(2)	30.64(5)	C(35)	–56(2)	5575(4)	3686(5)	59(2)
Bi(3)	1816.57(5)	4958.3(1)	2001.2(2)	37.10(5)	C(36)	143(2)	6141(4)	3929(5)	51(2)
Sb(1)	1285.0(1)	2500	6768.7(4)	32.5(1)	C(41)	761(2)	7500	4141(6)	36(2)
Sb(2)	357.3(1)	7500	5073.2(4)	35.2(1)	C(42)	729(2)	7500	3105(6)	40(2)
Sb(3)	3023.3(1)	2500	1892.6(4)	34.6(1)	C(43)	1006(2)	7500	2509(6)	39(2)
I(1)	364.54(9)	6272.8(2)	976.4(3)	34.02(8)	C(44)	1297(2)	7500	2940(8)	59(3)
I(2)	601.31(9)	4680.4(2)	–1259.4(2)	34.28(9)	C(45)	1329(2)	7500	3966(9)	68(3)
I(3)	290.11(9)	3979.2(2)	1621.1(3)	39.74(9)	C(46)	1058(2)	7500	4613(6)	59(3)
I(4)	1062.36(9)	5324.0(2)	3143.6(3)	39.00(9)	C(51)	478(2)	7500	6603(5)	34(2)
I(5)	1314.29(9)	3734.3(2)	889.3(3)	38.15(9)	C(52)	526(2)	6850(4)	7126(4)	53(2)
I(6)	1376.7(1)	6034.5(2)	256.3(3)	44.7(1)	C(53)	616(2)	6861(4)	8136(5)	56(2)
I(7)	2297.2(1)	4623.0(3)	552.3(3)	49.5(1)	C(54)	670(2)	7500	8633(6)	45(2)
I(8)	2109.5(1)	6212.9(3)	2904.3(3)	59.3(1)	C(61)	2612(2)	2500	1047(6)	42(2)
I(9)	2004.7(2)	3950.8(3)	3543.8(4)	72.5(2)	C(62)	2323(2)	2500	1572(7)	46(2)
C(1)	889(2)	2500	7712(6)	32(2)	C(63)	2041(2)	2500	1017(7)	48(2)
C(2)	585(2)	2500	7310(7)	42(2)	C(64)	2041(2)	2500	1(8)	52(3)
C(3)	324(2)	2500	7940(7)	48(2)	C(65)	2326(3)	2500	–552(7)	54(3)
C(4)	368(2)	2500	8996(7)	41(2)	C(66)	2613(2)	2500	–31(6)	45(2)
C(5)	668(2)	2500	9396(6)	41(2)	C(71)	3295(1)	3435(3)	1564(4)	36(1)
C(6)	923(2)	2500	8760(6)	37(2)	C(72)	3213(2)	3880(4)	764(5)	47(2)
C(11)	1568(1)	3418(3)	7077(4)	36(1)	C(73)	3409(2)	4475(4)	537(5)	60(2)
C(12)	1503(2)	3858(4)	7907(4)	48(2)	C(74)	3668(2)	4619(4)	1097(6)	64(2)
C(13)	1716(2)	4400(4)	8140(5)	59(2)	C(75)	3744(2)	4179(5)	1905(6)	70(2)
C(14)	1981(2)	4510(4)	7565(6)	60(2)	C(76)	3560(2)	3582(4)	2156(5)	62(2)
C(15)	2038(2)	4082(4)	6750(6)	64(2)	C(81)	2905(2)	2500	3428(6)	37(2)
C(16)	1833(2)	3531(4)	6486(5)	52(2)	C(82)	2862(2)	3156(4)	3944(4)	46(2)
C(21)	1156(2)	2500	5218(6)	34(2)	C(83)	2766(2)	3153(4)	4943(5)	55(2)
C(22)	1118(2)	3148(4)	4717(5)	64(2)	C(84)	2723(3)	2500	5444(6)	57(3)
C(23)	1031(3)	3134(4)	3705(5)	84(3)					

Table 3. Bond lengths and bond angles in structures **I–IV**

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
		I				**III**	
Bi(2)–C(61)	2.163(7)	C(61)Bi(2)C(51)	120.2(2)	Sb(1)–C(1)	2.107(5)	I(6)Bi(2)I(5)	95.24(1)
Bi(2)–C(51)	2.185(6)	C(61)Bi(2)C(81)	101.8(3)	Sb(1)–C(21)	2.116(5)	I(6)Bi(2)I(7)	95.15(2)
Bi(2)–C(81)	2.192(6)	C(51)Bi(2)C(81)	98.7(2)	Sb(1)–O	3.075(4)	I(5)Bi(2)I(7)	92.54(1)
Bi(2)–C(71)	2.223(6)	C(61)Bi(2)C(71)	111.9(2)	Sb(2)–C(51)	2.089(6)	I(6)Bi(2)I(3)	97.71(1)
Bi(2)–O(2)	2.947(4)	C(51)Bi(2)C(71)	117.1(3)	Sb(2)–C(41)	2.088(5)	I(5)Bi(2)I(3)	86.80(1)
Bi(3)–C(91)	2.241(8)	C(81)Bi(2)C(71)	102.8(2)	Sb(2)–C(61)	2.092(5)	I(7)Bi(2)I(3)	173.14(1)
Bi(3)–I(2)	2.9682(6)	C(61)Bi(2)O(2)	73.2(2)	Sb(2)–C(71)	2.096(5)	I(6)Bi(2)I(8)	165.93(1)
Bi(3)–I(3)	2.9733(7)	C(51)Bi(2)O(2)	77.5(2)	I(4)–Bi(2)'	3.3395(5)	I(5)Bi(2)I(8)	98.41(1)
Bi(3)–I(1)	3.2467(7)	C(81)Bi(2)O(2)	170.5(2)	I(8)–Bi(1)'	3.3116(5)	I(7)Bi(2)I(8)	87.66(1)
Bi(3)–I(1)'	3.2762(6)	C(71)Bi(2)O(2)	86.5(2)	O–C(77)	1.196(6)	I(3)Bi(2)I(8)	85.68(1)
Bi(1)–C(21)	2.187(6)	C(91)Bi(3)I(2)	91.0(1)	C(1)–C(2)	1.373(6)	I(6)Bi(2)I(4)'	83.77(1)
Bi(1)–C(31)	2.198(7)	C(91)Bi(3)I(3)	92.6(1)	C(1)–C(6)	1.378(6)	I(5)Bi(2)I(4)'	174.29(1)
Bi(1)–C(41)	2.199(7)	I(2)Bi(3)I(3)	92.16(2)	C(2)–C(3)	1.368(7)	I(7)Bi(2)I(4)'	93.15(1)
Bi(1)–C(11)	2.209(7)	C(91)Bi(3)I(1)	95.2(2)	C(3)–C(4)	1.378(8)	I(3)Bi(2)I(4)'	87.61(1)
Bi(1)–O(1)	2.831(4)	I(2)Bi(3)I(1)	94.19(1)	C(4)–C(5)	1.379(8)	I(8)Bi(2)I(4)'	82.32(1)
S–O(2)	1.442(4)	I(3)Bi(3)I(1)	169.79(2)	C(5)–C(6)	1.391(8)	Bi(1)I(3)Bi(2)	94.59(1)
S–O(3)	1.443(6)	C(91)Bi(3)I(1)'	90.0(1)	C(34)–C(35)	1.376(7)	Bi(1)I(4)Bi(2)'	97.64(1)
S–O(1)	1.455(4)	I(2)Bi(3)I(1)'	176.83(2)	C(35)–C(36)	1.391(7)	Bi(1)I(8)Bi(1)'	92.64(1)
S–C(1)	1.767(6)	I(3)Bi(3)I(1)'	90.76(1)	C(41)–C(46)	1.341(8)	Bi(1)I(8)Bi(2)	90.70(1)
C(1)–C(6)	1.39(1)	I(1)Bi(3)I(1)'	82.74(1)	C(41)–C(42)	1.369(8)	Bi(1)"I(8)Bi(2)	92.88(1)
		II				**IV**	
Bi(1)–C(11)	2.261(6)	C(11)Bi(1)N	83.9(2)	Bi(1)–I(1)	3.0780(4)	I(1)Bi(1)I(3)	88.44(1)
Bi(1)–N	2.678(5)	C(11)Bi(1)I(1)	92.2(2)	Bi(1)–I(3)	3.0898(4)	I(1)Bi(1)I(2)	87.35(1)
Bi(1)–I(1)	2.9957(6)	NBi(1)I(1)	176.0(1)	Bi(1)–I(2)	3.0923(4)	I(3)Bi(1)I(2)	85.79(1)
Bi(1)–I(2)	3.0175(6)	C(11)Bi(1)I(2)	94.4(1)	Bi(2)–I(6)	2.9492(5)	I(6)Bi(2)I(4)	91.49(1)
Bi(1)–I(3)	3.1575(6)	NBi(1)I(2)	85.3(1)	Bi(2)–I(4)	2.9505(4)	I(6)Bi(2)I(5)	93.54(1)
Bi(2)–C(41)	2.193(6)	I(1)Bi(1)I(2)	94.08(2)	Bi(2)–I(5)	2.9618(4)	I(4)Bi(2)I(5)	93.04(1)
Bi(2)–C(21)	2.199(6)	C(11)Bi(1)I(3)	89.4(1)	Bi(2)–I(1)	3.2042(4)	I(6)Bi(2)I(1)	91.48(1)
Bi(2)–C(51)	2.222(6)	NBi(1)I(3)	86.6(1)	Bi(2)–I(3)	3.2755(5)	I(4)Bi(2)I(1)	92.69(1)
Bi(2)–C(31)	2.224(6)	I(1)Bi(1)I(3)	94.34(2)	Bi(2)–I(2)	3.2808(4)	I(5)Bi(2)I(1)	172.28(1)
N–C(1)	1.344(8)	I(2)Bi(1)I(3)	170.61(2)	Bi(3)–I(7)	2.8534(5)	I(6)Bi(2)I(3)	172.53(1)
N–C(5)	1.346(8)	C(41)Bi(2)C(21)	107.7(2)	Bi(3)–I(9)	2.8554(6)	I(4)Bi(2)I(3)	93.96(1)
C(1)–C(2)	1.36(1)	C(41)Bi(2)C(51)	114.6(2)	Bi(3)–I(8)	2.8700(5)	I(5)Bi(2)I(3)	91.26(1)
C(2)–C(3)	1.35(1)	C(21)Bi(2)C(51)	111.1(2)	Bi(3)–I(5)	3.4194(4)	I(1)Bi(2)I(3)	83.18(1)
C(3)–C(4)	1.40(1)	C(41)Bi(2)C(31)	106.3(2)	Bi(3)–I(6)	3.5518(5)	I(6)Bi(2)I(2)	94.29(1)
C(4)–C(5)	1.347(9)	C(21)Bi(2)C(31)	110.0(2)	Bi(3)–I(4)	3.5915(5)	I(4)Bi(2)I(2)	172.34(1)
C(11)–C(16)	1.356(8)	C(51)Bi(2)C(31)	107.0(2)	Sb(1)–C(1)	2.087(7)	I(5)Bi(2)I(2)	91.63(1)
C(11)–C(12)	1.373(9)	C(1)NC(5)	116.7(6)	Sb(1)–C(11)	2.105(6)	I(1)Bi(2)I(2)	82.14(1)
C(12)–C(13)	1.38(1)	C(1)NBi(1)	122.6(4)	Sb(1)–C(21)	2.109(7)	I(3)Bi(2)I(2)	79.85(1)
C(13)–C(14)	1.34(1)	C(5)NBi(1)	120.7(4)	Sb(2)–C(51)	2.073(7)	I(7)Bi(3)I(9)	97.76(2)
C(14)–C(15)	1.38(1)	NC(1)C(2)	121.9(6)	Sb(2)–C(31)	2.101(6)	I(7)Bi(3)I(8)	98.06(2)
		III		Sb(2)–C(41)	2.104(8)	I(9)Bi(3)I(8)	96.01(2)
Bi(1)–I(2)	2.8926(5)	I(2)Bi(1)I(1)	95.25(1)	Sb(3)–C(61)	2.065(9)	I(7)Bi(3)I(5)	90.99(1)
Bi(1)–I(1)	2.9030(4)	I(2)Bi(1)I(4)	92.57(1)	Sb(3)–C(81)	2.078(8)	I(9)Bi(3)I(5)	92.98(2)
Bi(1)–I(4)	3.0349(4)	I(1)Bi(1)I(4)	91.25(1)	Sb(3)–C(71)	2.109(6)	I(8)Bi(3)I(5)	166.25(2)
Bi(1)–I(3)	3.1169(4)	I(2)Bi(1)I(3)	91.38(1)			I(7)Bi(3)I(6)	93.62(1)
Bi(1)–I(8)	3.2908(4)	I(1)Bi(1)I(3)	89.90(1)			I(9)Bi(3)I(6)	164.50(2)
Bi(1)–I(8)'	3.3116(5)	I(4)Bi(1)I(3)	175.77(1)			I(8)Bi(3)I(6)	92.75(1)
Bi(2)–I(6)	2.9139(4)	I(2)Bi(1)I(8)	85.29(1)			I(5)Bi(3)I(6)	76.29(1)
Bi(2)–I(5)	2.9201(5)	I(1)Bi(1)I(8)	178.54(1)			I(7)Bi(3)I(4)	162.38(1)
Bi(2)–I(7)	2.9400(5)	I(4)Bi(1)I(8)	90.08(1)			I(9)Bi(3)I(4)	94.14(2)
Bi(2)–I(3)	3.2768(5)	I(2)Bi(1)I(8)'	172.65(1)			I(8)Bi(3)I(4)	93.54(2)
Bi(2)–I(8)	3.3150(4)	I(1)Bi(1)I(8)'	92.10(1)			I(5)Bi(3)I(4)	75.41(1)
Bi(2)–I(4)'	3.3395(5)	I(4)Bi(1)I(8)'	87.16(1)			I(6)Bi(3)I(4)	72.53(1)
Sb(1)–C(11)	2.087(4)	I(3)Bi(1)I(8)'	88.73(1)			Bi(1)I(2)Bi(2)	77.63(1)
Sb(1)–C(31)	2.091(4)	I(8)Bi(1)I(8)'	87.36(1)			Bi(2)I(4)Bi(3)	77.67(1)

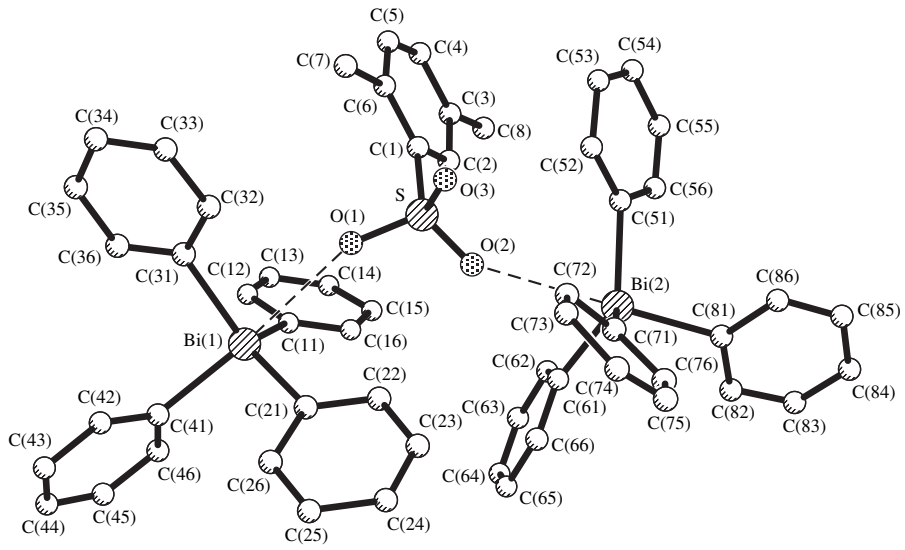

Fig. 1. Structure of the $[(Ph_4BiO)_2\{2,5\text{-}(CH_3)_2C_6H_3S(O)\}]_2^+$ cation in compound **I**.

SAINT-*Plus* programs [3]. All calculations on determination and refinement of the structures were performed using the SHELXTL/PC programs [4].

The crystallographic data and results of refinement of structures **I**–**IV** are presented in Table 1. The coordinates and temperature factors of atoms are given in Table 2. The bond lengths and bond angles are presented in Table 3.

RESULTS AND DISCUSSION

The reaction of tetraphenylbismuth 2,5-dimethylbenzenesulfonate with BiI_3 in acetone is accompanied by the formation of red-orange crystals of complex **I**, whose singly charged cations consist of two Ph_4Bi fragments connected by the bridging 2,5-dimethylbenzenesulfonate group (Fig. 1)

$$Ph_4Bi\{OSO_2(C_6H_3(CH_3)_2\text{-}2,5)\} + BiI_3 \longrightarrow [(Ph_4BiO)_2\{2,5\text{-}(CH_3)_2C_6H_3S(O)\}]_2^+[Ph_2Bi_2I_6]^{2-}. \quad (\mathbf{I})$$

The bismuth atoms in cation **I** have a trigonal bipyramidal coordination with the oxygen atoms of the arenesulfonate group in axial positions. The Bi(1)–O(1) and Bi(2)–O(2) bond lengths (2.831(4) and 2.947(4) Å, respectively) exceed significantly the sum of the covalent radii of the Bi and O atoms (2.31 Å) [5], and the Bi–C distances in the Ph_4Bi fragments vary within 2.163(7)–2.223(6) Å.

In the centrosymmetric, doubly charged binuclear anion $[Ph_2Bi_2I_6]^{2-}$, the bismuth atoms are connected by two bridging iodine atoms (the BiIBi and IBiI angles are 97.26(1)° and 82.74(1)°, 90.76(1)°, 92.16(2)°, 94.19(1)°) (Fig. 2). The bismuth atoms have a tetragonal pyramidal coordination. Four iodine atoms lie in the equatorial plane, and the carbon atom of the phenyl ligand is localized in the axial plane. With account of the stereochemical activity of a lone electron pair (the so-called phantom ligand), the $PhBiI_4$ coordination unit can be described as a distorted octahedron. The iodine and bismuth atoms lie in the same plane; the phenyl rings in anion **I** are perpendicular to this plane and arranged at its different sides. Unlike the Bi_2I_6 fragment in **I**, a similar fragment in the $[Ph_2Bi_2I_6]^{2-}[NEt_4]_2^+$ complex [6] is nonplanar (the inflection angle along the μ-I–μ-I line is 74.7°), and the Ph substituents are arranged on one side of the fragment.

The terminal Bi–I bonds (2.9682(6) and 2.9733(7) Å) in **I** are much shorter than the bridging bonds (3.2467(7) and 3.2762(6) Å) and close in lengths to the corresponding terminal (2.944–2.971 Å) and bridging (3.257–3.328 Å) bonds in $[Ph_2Bi_2I_6]^{2-}[NEt_4]_2^+$. The Bi–C(Ph) distances in both complexes are comparable.

When the 2,5-dimethylbenzenesulfonate ligand in the starting tetraphenylbismuth arenesulfonate is replaced by the 3-carboxy-4-oxybenzenesulfonate ligand, no reaction occurs between the starting reagents. However, when pyridine is added to the reaction mixture, yellow crystals with a temperature of decomposition higher than 200°C are isolated from the reaction mixture. According to the X-ray diffraction data, complex **II** consists of tetraphenylbismuthonium

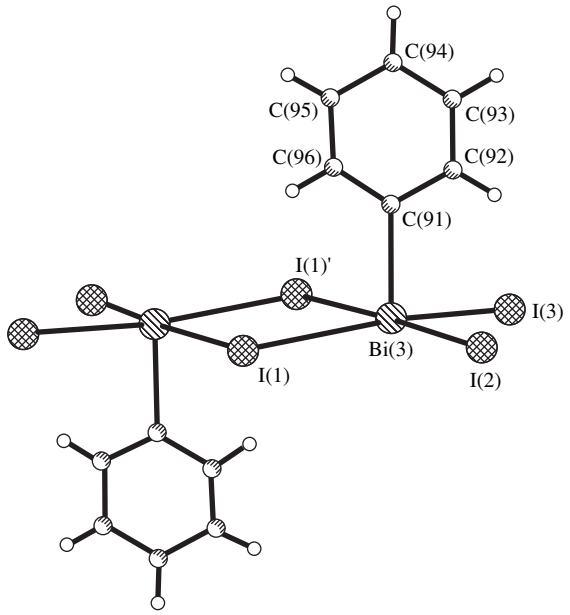

Fig. 2. Structure of the $[Ph_2Bi_2I_6]^{2-}$ anion in compound **I**.

cations and singly charged $[PhBiI_3(C_5H_5N)]^-$ anions (Fig. 3).

$$Ph_4Bi\{OSO_2C_6H_3(OH\text{-}4)(COOH\text{-}3)\} + BiI_3 \xrightarrow{C_5H_5N} [Ph_4Bi]^+[PhBi(C_5H_5N)I_3]^-.$$

(**II**)

The Bi atom in cation **II** has somewhat distorted tetrahedral coordination (the CBiC angles are 106.3(2)°–114.6(2)°). The Bi–C distances in the Ph_4Bi fragments vary in an interval 2.193(6)–2.224(6) Å. In the anion, the bismuth atom has an octahedral coordination: three iodine atoms are coplanar with the nitrogen atoms of the pyridine ligand and bismuth. The sixth vertex in the octahedral anion is occupied by a lone electron pair.

The reaction of tetraphenylantimony with bismuth triiodide was found to afford a complex of the different type: $[Ph_4Sb]_4^+[Bi_4I_{16}]^{4-} \cdot 2(CH_3)_2C{=}O$ (**III**), forming red-cherry crystals

$$4Ph_4SbI + 4BiI_3 \xrightarrow{(CH_3)_2C=O} [Ph_4Sb]_4^+[Bi_4I_{16}]^{4-} \cdot (CH_3)_2C{=}O.$$

(**III**)

It follows from the X-ray diffraction data that in complex **III**, two independent Ph_4Sb^+ cations have somewhat different geometries (Fig. 4). In one of them, the Sb(2) atom has a distorted tetrahedral coordination (the Sb–C bond lengths lie in the 2.089(6)–2.096(5) Å interval, and the CSbC bond angles are 106.9(2)°–112.2(2)°). The coordination sphere of another $[Ph_4Sb]^+$ cation contains an acetone molecule (the Sb(1)···O distance is 3.075(4) Å), which results in contribution of the trigonal bipyramidal component to the tetrahedral structure. Some change in the length of one of the Sb(1)–C bonds (pseudoaxial bond, 2.116(5) Å), compared to the other three bonds (pseudoequatorial bonds, 2.087(4)–2.107(5) Å), and a noticeable distor-

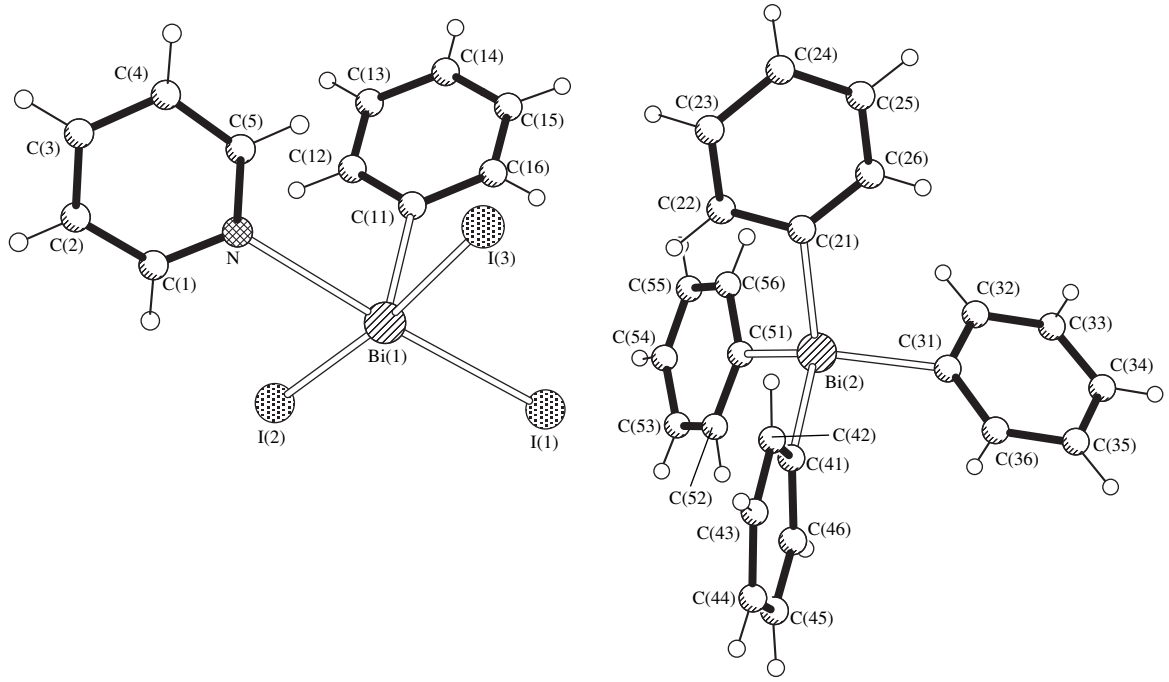

Fig. 3. Structure of complex **II**.

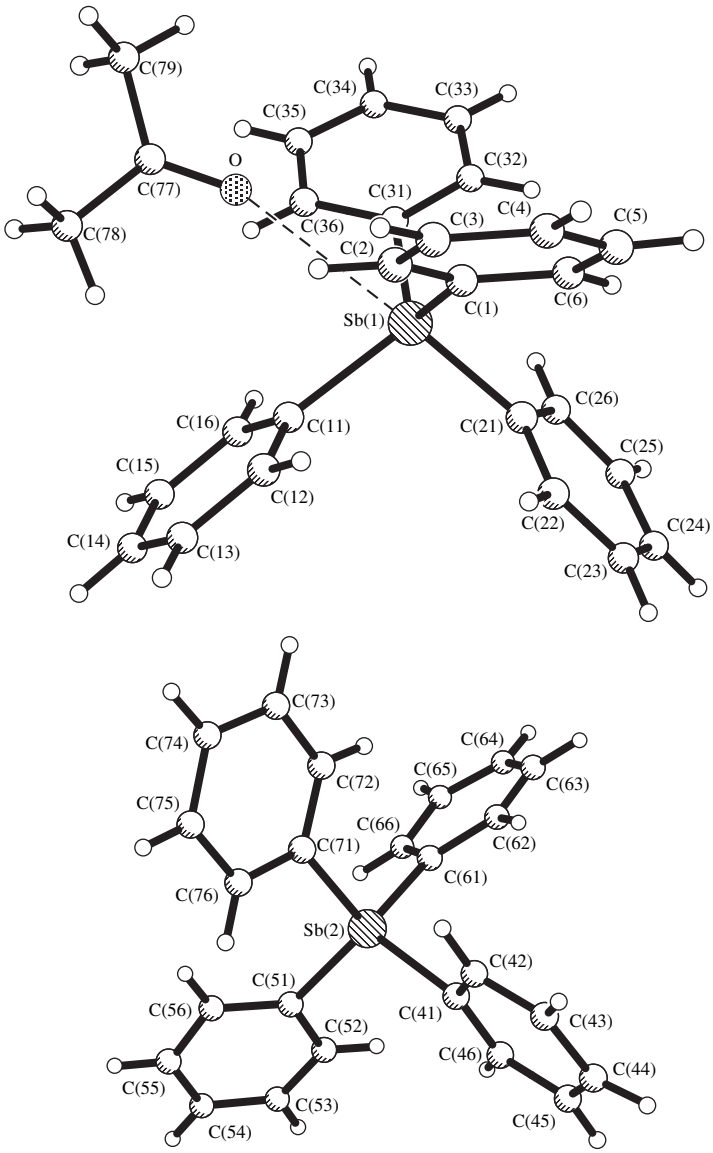

Fig. 4. Structures of the $[Ph_4Sb]^+$ cations in compound **III**.

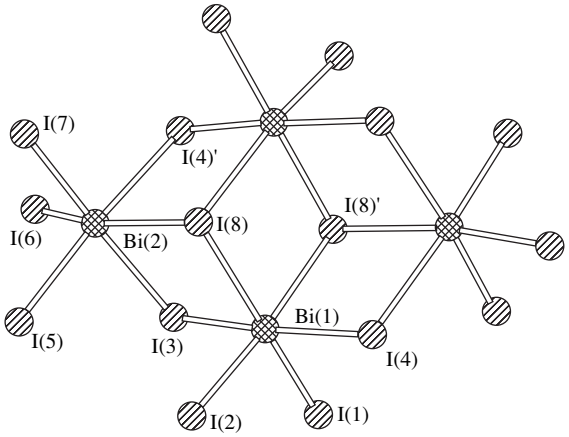

Fig. 5. Structure of the $[Bi_4I_{16}]^{4-}$ anion in compound **III**.

tion of the CSb(1)C bond angles from the value ideal for a tetrahedron (102.7(2)°–119.6(2)°) are observed. The pseudoaxial CSb(1)O angle is equal to 177.5(2)°, and the sum of angles in the pseudoequatorial plane is 342.5(2)°.

The tetranuclear centrosymmetric $[Bi_4I_{16}]^{4-}$ anion consists of two pairs of BiI_6 octahedra sharing common edges (Fig. 5). In one pair, the environment of the Bi(2) atom contains three terminal and three bridging iodine atoms (the Bi(2)–I distances are 2.9139(4)–2.9400(5) and 3.2768(5)–3.3395(2) Å, respectively). In another pair, the Bi(1) atom has two and four iodine atoms, respectively (2.8926(5), 2.9030(4), and 3.0349(4)–3.3116(5) Å). In the $[Bi_4I_{16}]^{4-}$ anion, the Bi···Bi distances (4.700, 4.775, 4.802 Å) are close to the doubled van der Waals radius of the bismuth atom, unlike simi-

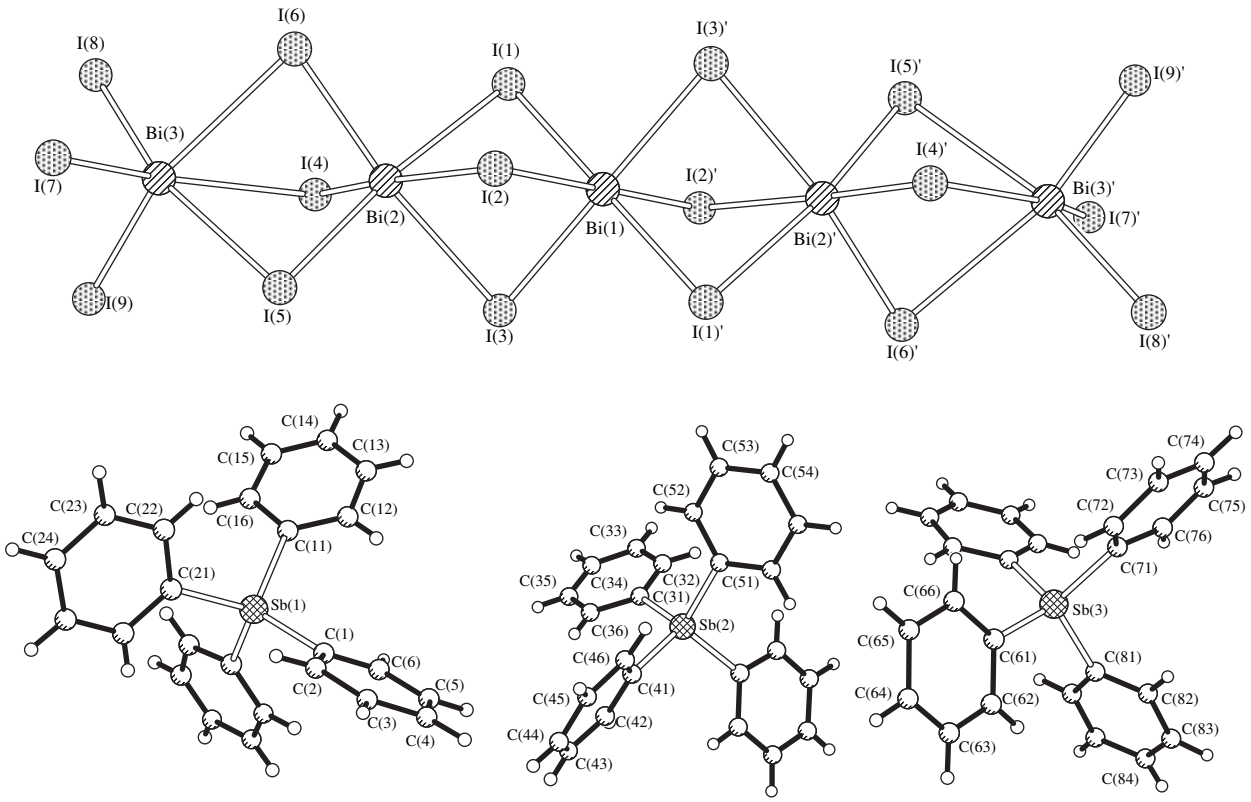

Fig. 6. Structures of the $[Bi_5I_{18}]^{3-}$ anion and $[Ph_4Sb]^+$ cations in compound **IV**.

lar $[Bi_4Br_{16}]^{4-}$ anions in which the Bi···Bi distances are much shorter (4.093(1), 4.610(1) Å) [2].

Under similar conditions, the reactions of tetraphenylstibium 2,5-dimethylbenzenesulfonate and tetraphenylstibium sulfosalicylate with bismuth triiodide occur in somewhat different way. In these cases, crystals of complex **IV** were isolated from the reaction mixture. The crystals of **IV** consist of tetraphenylstibonium cations and $[Bi_5I_{18}]^{3-}$ anions (Fig. 6)

$$3Ph_4SbOSO_2Ar + 6BiI_3 \longrightarrow [Ph_4Sb]_3^+[Bi_5I_{18}]^{3-},$$

(**IV**)

$$Ar = 2,5\text{-}(CH_3)_2C_6H_3, C_6H_3(OH\text{-}4)(COOH\text{-}3).$$

Three independent $[Ph_4Sb]^+$ cations have distorted tetrahedral structures (the CSbC angles are 106.2°–111.5°). In the centrosymmetric pentanuclear $[Bi_5I_{18}]^{3-}$ anion, the octahedrally coordinated Bi atoms are combined in pairs by triple iodine bridges. The terminal Bi(3) atom is linked with the adjacent Bi(2) atom by Bi(3)–I(4–6) bonds, which are weaker than Bi(2)–I(4–6) (3.4194(4)–3.5915(5) and 2.9492(5)–2.9618(4) Å, respectively). The terminal Bi(3)–I(2,7,9) bonds (2.8534(5)–2.8700(5) Å) are the shortest in the $[Bi_5I_{18}]^{3-}$ anion of structure **IV**.

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