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Benzene Solvates of Tris(4-Fluorophenyl)antimony Diaryloxides $(4\text{-}FC_6H_4)_3Sb(OAr)_2 \cdot 1/2PhH$ (Ar = C_6H_4Cl-4, C_6H_4Br-4, $C_6H_3Br_2$-2,4). Synthesis and Structure

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Abstract—The solvates of tris(4-fluorophenyl)antimony diaryloxides with benzene, $(4\text{-}FC_6H_4)_3Sb(OAr)_2 \cdot 1/2PhH$ (Ar = C_6H_4Cl-4 (**I**), C_6H_4Br-4 (**II**), and $C_6H_3Br_2$-2,4 (**III**)), were prepared by the reaction of tris(4-fluorophenyl)antimony with 4-chlorophenol, 4-bromophenol, and 2,4-dibromophenol in diethyl ether in the presence of *tert*-butyl hydroperoxide followed by recrystallization from a benzene–heptane mixture (2 : 1). The antimony atoms in **I**, **II**, and **III** form a distorted trigonal-bipyramidal coordination with oxygen atoms in axial positions (CIF files CCDC nos. 1047500 (**I**), 1048172 (**II**), 1048212 (**III**)). The OSbO angles are 177.23(8)° (**I**), 177.34(12)° (**II**), and 179.47(16)° (**III**). The Sb–O and Sb–C bond lengths are 2.0519(16), 2.0508(18), and 2.105(2)–2.121(2) Å (**I**); 2.045(3), 2.055(3), and 2.105(4)–2.126(4) Å (**II**); and 2.066(3), 2.058(3), and 2.100(6)–2.107(5) Å (**III**). The structural organization in crystals **I**–**III** is formed by weak intermolecular C–H···F hydrogen bonds (H···F 2.52 Å (**I**), 2.52 Å (**II**), and 2.61 and 2.51Å (**III**)).

Keywords: solvate, benzene, diaryloxide, tris(4-fluorophenyl)antimony, synthesis

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INTRODUCTION

Some organic compounds of pentavalent antimony are known to be biologically active [1–3]; in particular, tris(4-fluorophenyl)antimony dicarboxylates exhibited antitumor properties [4, 5]. Derivatives with 4-fluorophenyl groups at antimony atoms are little studied. Presumably, tris(4-fluorophenyl)antimony aryloxides, differing from dicarboxylates by only the type of oxygen-containing ligand, can also possess practically valuable properties. Here we synthesized benzene solvates of tris(4-fluorophenyl)antimony diaryloxides $(4\text{-}FC_6H_4)_3Sb(OAr)_2 \cdot 1/2PhH$ (Ar = C_6H_4Cl-4 (**I**), C_6H_4Br-4 (**II**), and $C_6H_3Br_2$-2,4 (**III**)) and studied their structural features by X-ray diffraction.

EXPERIMENTAL

Synthesis of solvate I. A 70% aqueous solution of *tert*-butyl hydroperoxide (0.048 g, 0.37 mmol) was added to a solution of tris(4-fluorophenyl)antimony (0.150 g, 0.37 mmol) and 4-chlorophenol (0.095 g, 0.74 mmol) in diethyl ether (30 mL), and the mixture was kept for 24 h at 20°C. After solvent evaporation, the solid residue was recrystallized from a benzene–heptane solvent mixture (2 : 1). The yield of compound **I** was 0.241 g (88%); mp = 156°C.

For $C_{33}H_{23}O_2F_3Cl_2Sb$		
anal. calcd., %:	C, 56.49;	H, 3.28.
Found, %:	C, 56.38;	H, 3.34.

Compounds **II** and **III** were synthesized by a similar procedure.

Solvate **II**: yield 86%, mp = 147°C.

For $C_{33}H_{23}O_2F_3Br_2Sb$		
anal. calcd., %:	C, 50.13;	H, 2.91.
Found, %:	C, 49.83;	H, 3.01.

Solvate **III**: yield 91%, mp = 176°C.

For $C_{33}H_{21}F_3Br_4O_2Sb$		
anal. calcd., %:	C, 41.77;	H, 2.22.
Found, %:	C, 41.56;	H, 2.36.

The X-ray diffraction study of the crystals of compounds **I**–**III** was carried out on a D8 Quest Bruker four-circle automated diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator) at

Table 1. Crystallographic data and X-ray experiment and structure refinement details for **I**–**III**

Parameter	Value		
	I	**II**	**III**
M	701.16	790.08	947.89
System	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	8.9462(10)	8.9480(4)	9.4119(3)
b, Å	17.178(2)	17.5127(7)	11.8179(4)
c, Å	19.736(2)	19.8352(10)	15.5556(6)
α, deg	90.00	90.00	107.689(2)
β, deg	97.222(4)	97.825(2)	94.439(2)
γ, deg	90.00	90.00	95.030(2)
V, Å^3	3008.9(6)	3079.3(2)	1632.18(10)
Z	4	4	2
ρ_{calc}, g/cm^3	1.548	1.704	1.929
μ, mm^{-1}	1.142	3.538	5.788
F(000)	1396.0	1540.0	906.0
Crystal size, mm	0.51 × 0.45 × 0.38	0.57 × 0.23 × 0.2	0.45 × 0.28 × 0.15
θ Range, deg	6.26–68.8	7.0–50.76	5.9–52.82
Ranges of reflection indices	$-14 \leqslant h \leqslant 14$, $-27 \leqslant k \leqslant 27$, $-31 \leqslant l \leqslant 31$	$-10 \leqslant h \leqslant 10$, $-21 \leqslant k \leqslant 21$, $-23 \leqslant l \leqslant 23$	$-11 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 14$, $-19 \leqslant l \leqslant 19$
Number of measured reflections	137158	20104	36862
Number of unique reflections	12636	5607	6681
R_{int}	0.0408	0.0326	0.0594
Number of refined parameters	370	370	388
GOOF	1.071	1.030	1.039
R-factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0483$, $wR_2 = 0.1021$	$R_1 = 0.0364$, $wR_2 = 0.0799$	$R_1 = 0.0475$, $wR_2 = 0.0988$
R-factors (all data)	$R_1 = 0.0719$, $wR_2 = 0.1152$	$R_1 = 0.0548$, $wR_2 = 0.0875$	$R_1 = 0.0706$, $wR_2 = 0.1088$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.41/–0.68	1.15/–0.94	1.80/–1.32

296(2) K. Data collection and editing and refinement of unit cell parameters as well as application of absorption corrections were performed using the SMART and SAINT-Plus software [6]. All structure solution and refinement calculations were conducted using the SHELXL/PC [7] and OLEX2 [8] software. The structures of compounds **I**–**III** were solved by the direct method and refined by the least-squares method in the anisotropic approximation for nonhydrogen atoms. The key crystallographic data and structure refinement details are summarized in Table 1 and selected bond lengths and angles are given in Table 2.

Full tables of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (nos. 1047500 (**I**), 1048172 (**II**), and 1048212 (**III**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

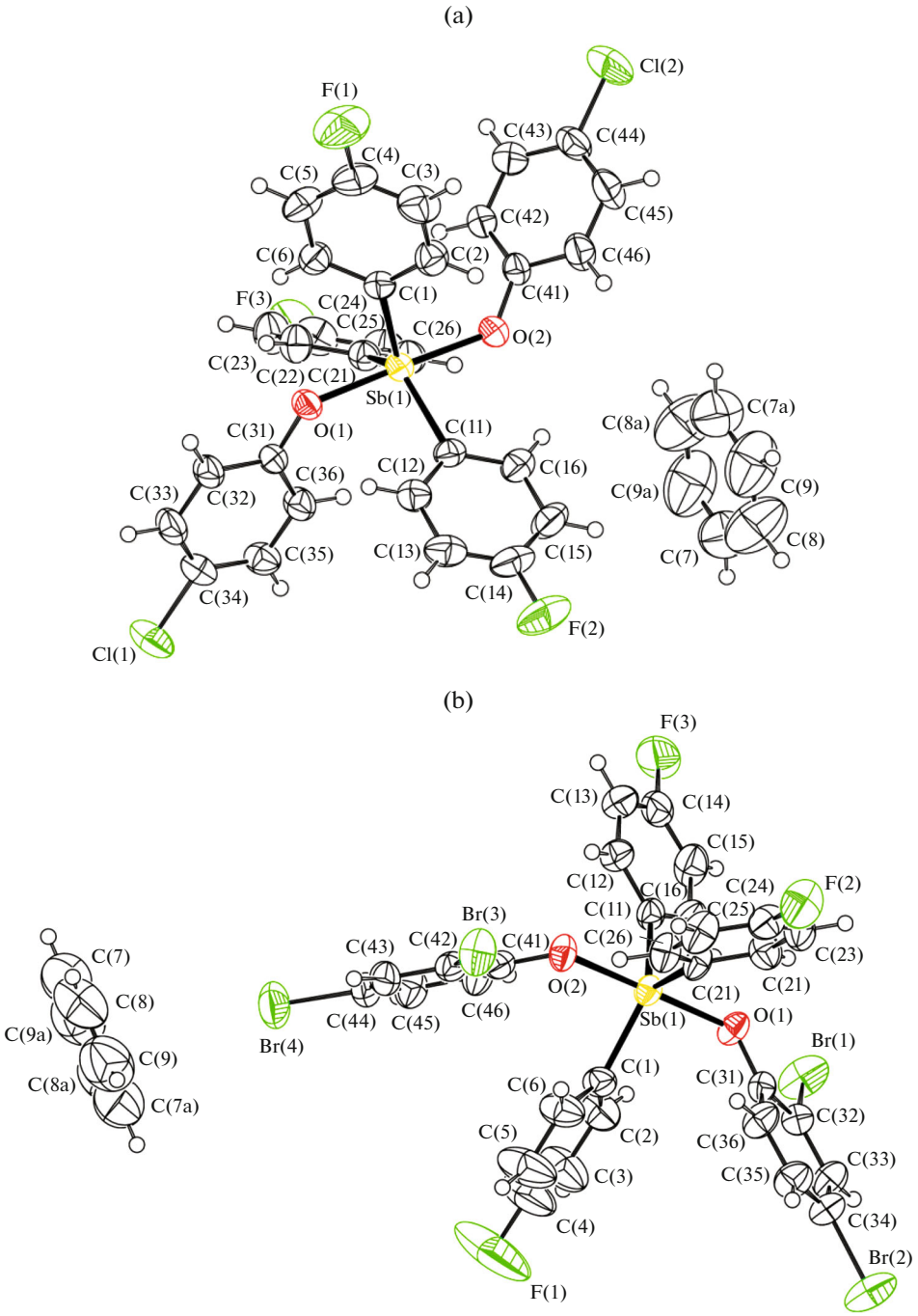
RESULTS AND DISCUSSION

Tris(4-fluorophenyl)antimony diaryloxides were synthesized by the oxidative addition of phenol to tris(4-fluorophenyl)antimony in the presence of *tert*-butyl hydroperoxide:

$$(4\text{-}FC_6H_4)_3Sb + 2HOAr + \textit{tert}\text{-}BuOOH$$
$$\rightarrow (4\text{-}FC_6H_4)_3Sb(OAr)_2 + \textit{tert}\text{-}BuOH + H_2O$$
$$Ar = C_6H_4Cl\text{-}4,\ C_6H_4Br\text{-}4,\ C_6H_3Br_2\text{-}2,4.$$

Table 2. Selected bond lengths and bond angles in structures **I**–**III**

Bond *d*, Å		Angle ω, deg	
		I	
Sb(1)–O(1)	2.0519(16)	O(1)Sb(1)C(1)	86.58(8)
Sb(1)–C(1)	2.105(2)	O(1)Sb(1)C(11)	91.32(9)
Sb(1)–O(2)	2.0508(18)	O(1)Sb(1)C(21)	90.65(8)
Sb(1)–C(11)	2.121(2)	C(1)Sb(1)C(11)	117.86(9)
Sb1–C(21)	2.114(2)	C(1)Sb(1)C(21)	115.71(9)
Cl(2)–C(44)	1.735(3)	O(2)Sb(1)O(1)	177.23(8)
Cl(1)–C(34)	1.743(3)	O(2)Sb(1)C(1)	93.06(9)
F(1)–C(4)	1.351(3)	O(2)Sb(1)C(11)	86.42(9)
F(2)–C1(4)	1.360(4)	O(2)Sb(1)C(21)	91.98(9)
F(3)–C(24)	1.355(4)	C(21)Sb(1)C(11)	126.41(9)
O(1)–C(31)	1.351(3)	C(31)O(1)Sb(1)	128.63(14)
O(2)–C(41)	1.342(3)	C(41)O(2)Sb(1)	131.70(16)
		II	
Sb(1)–O(1)	2.045(3)	O(1)Sb(1)O(2)	177.34(12)
Sb(1)–O(2)	2.055(3)	O(1)Sb(1)C(1)	93.03(14)
Sb(1)–C(1)	2.105(4)	O(1)Sb(1)C(11)	86.56(15)
Sb(1)–C(11)	2.126(4)	O(1)Sb(1)C(21)	91.83(15)
Sb(1)–C(21)	2.124(4)	O(2)Sb(1)C(1)	86.70(14)
Br(1)–C(34)	1.897(4)	O(2)Sb(1)C(11)	91.23(15)
Br(2)–C(44)	1.903(4)	O(2)Sb(1)C(21)	90.68(14)
F(1)–C(4)	1.347(6)	C(1)Sb(1)C(11)	118.16(16)
F(2)–C(14)	1.362(6)	C(1)Sb(1)C(21)	115.41(16)
F(3)–C(24)	1.353(5)	C(21)Sb(1)C(11)	126.42(16)
O(1)–C(31)	1.344(5)	C(31)O(1)Sb(1)	131.4(3)
O(2)–C(41)	1.355(5)	C(41)O(2)Sb(1)	128.2(3)
		III	
Sb(1)–O(1)	2.066(3)	O(1)Sb(1)C(1)	90.14(19)
Sb(1)–O(2)	2.058(3)	O(1)Sb(1)C(11)	87.65(17)
Sb(1)–C(1)	2.100(6)	O(1)Sb(1)C(21)	93.35(17)
Sb(1)–C(11)	2.105(5)	O(2)Sb(1)O(1)	179.47(16)
Sb(1)–C(21)	2.107(5)	O(2)Sb(1)C(1)	89.41(19)
Br(1)–C(32)	1.891(5)	O(2)Sb(1)C(11)	92.36(18)
Br(2)–C(34)	1.902(6)	O(2)Sb(1)C(21)	87.14(17)
Br(3)–C(42)	1.894(5)	C(1)Sb(1)C(11)	123.3(2)
Br(4)–C(44)	1.902(6)	C(1)Sb(1)C(21)	124.4(2)
O(1)–C(31)	1.334(6)	C(11)Sb(1)C(21)	112.3(2)
F(2)–C(24)	1.349(6)	C(31)O(1)Sb(1)	127.8(3)
O(2)–C(41)	1.337(6)	C(41)O(2)Sb(1)	128.6(3)
F(1)–C(4)	1.365(9)	O(1)C(31)C(32)	120.1(4)
F(3)–C(14)	1.358(7)	O(1)C(31)C(36)	124.4(5)



Structures of compounds (a) **I** and (b) **III**.

Single crystals suitable for X-ray diffraction study were prepared by recrystallizing the compounds from a benzene–heptane mixture.

The IR spectra of the benzene solvates **I**–**III** exhibit absorption bands at 450–460 cm^{-1} corresponding to vibrations of the Sb–C(Ph) bonds of the SbC_3 groups [9] and modes for C–O vibrations (1276–1295 cm^{-1}).

According to X-ray diffraction data, in the molecules of **I**–**III**, the antimony atoms have a distorted trigonal-bipyramidal coordination with oxygens of the phenoxide ligands in the axial positions (figure). The crystals of **I** and **II** are isostructural. In the molecules of **I** and **II**, the conformations of the aryl rings relative to the equatorial C_3 plane are nearly identical and differ only slightly from the conformation in molecule **III**. The angles between the C_3 plane and aryl

ring planes are 50.39° [C(1)–C(6)], 58.47° [C(21)–C(26)], and 75.18° [C(11)–C(16)] in **I**; 50.22° [C(1)–C(6)], 58.69° [C(21)–C(26)], and 77.14° [C(11)–C(16)] in **II**; and 38.65° [C(1)–C(6)], 65.18° [C(21)–C(26)], and 68.87° [C(11)–C(16)] in **III**. The aryloxy group planes are arranged at 86.00°, 64.61° (**I**); 85.71°, 64.16° (**II**), and 62.64°, 65.61° (**III**) angles relative to the equatorial plane.

The sums of the equatorial angles are 360° (within the experimental error); the sizes of particular CSbC angles differ from the theoretical value by not more than 8°. The SbC_3 fragments are nearly planar, the antimony atom deviating from the C_3 plane by 0.014 Å in each of the three structures.

The average Sb–C bond lengths are 2.113(5) Å in **I**, 2.118(7) Å in **II**, and 2.104(5) Å in **III**. In all structures, equatorial bonds are longer than the axial ones, which are comparable with the sum of the antimony and oxygen covalent radii (2.07 Å [10]). In the triphenylantimony diaryloxides [11, 12], the Sb–C and Sb–O bond lengths are close to those in **I**–**III**.

The structural organization of the crystals of **I**, **II**, and **III** is formed by weak F···H–C (F···H 2.51–2.61), Cl···H–C (Cl···H 2.87), and Br···H–C (Br···H 3.00 Å) hydrogen bonds. No close contacts between the tris(4-fluorophenyl)antimony diaryloxide and benzene molecules were found in the crystals.

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