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= COORDINATION COMPOUNDS =

Tetraphenylantimony Aroxides Ph_4SbOAr (Ar = $C_6H_4C_6H_7$, $C_6H_2(Br_2-2,6)(tert-Bu-4)$, $C_6H_3(NO_2)_2-2,4$, $C_6H_2(Br_2-2,6)(NO_2-4)$): Synthesis and Structure

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Abstract—Tetraphenylantimony aroxides Ph₄SbOAr, where $Ar = C_6H_4C_6H_7$ (I), $C_6H_2(Br_2-2,6)(tert-Bu-4)$ (II), $C_6H_2(Br_2-2,6)(NO_2-4)$ (III), and $C_6H_3(NO_2)_2-2,4$ (IV), have been synthesized by the reaction of pentaphenylantimony with 4-cyclohexadienylphenol, 2,6-dibromo-4-*tert*-butylphenol, 2,6-dibromo-4-nitrophenol, and 2,4-dinitrophenol. The antimony atoms in molecules of complexes I–IV have a differently distorted trigonal bipyramidal coordination to the oxygen atoms of aroxy groups in axial positions. The OSbC angles are 177.63(13)° (I), 174.29(7)° (II), 177.8(6)° (III), and 174.01(7)° (IV). The Sb–O bond length is 2.117(3) Å (I), 2.2613(15) Å (II), 2.409(11) Å (III), and 2.4296(15) Å (IV).

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The analysis of published data on the structure of tetraphenylantimony aroxides, whose aroxy group contains substituents with different electronic effects, shows that their nature governs both the bond angles at the antimony atom and the Sb–O bond length [1-6].

In continuation of studying the effect produced by the nature of phenol on the structure of tetraphenylantimony aroxides, we have synthesized and structurally characterized four new aroxides Ph₄SbOAr, where $Ar = C_6H_4C_6H_7$ (I), $C_6H_2(Br_2-2,6)(tert-Bu-4)$ (II), $C_6H_2(Br_2-2,6)(NO_2-4)$ (III), and $C_6H_3(NO_2)_2-$ 2,4 (IV).

EXPERIMENTAL

Synthesis of tetraphenylantimony 4-cyclohexadienylphenoxide (I). A mixture of pentaphenylantimony (0.250 g, 0.50 mmol) and 4-cyclohexadienylphenol (0.085 g, 0.50 mmol) in toluene (2 mL) was heated for 1 h at 100°C in a sealed ampoule. After cooling, the formed colorless crystals were filtered out and dried. Complex I (0.279 g, 93%) with $T_{melt} = 218$ °C was obtained.

IR spectrum (v, cm⁻¹): 3065, 3047, 3013, 2988, 2919, 2847, 2361, 1601, 1502, 1477, 1434, 1280, 1257, 1172, 1062, 997, 847, 825, 726, 692, 594, 455. For $C_{36}H_{31}OSb$, anal. calcd. (%): C, 71.91; H, 5.16. Found (%): C, 71.82; H, 5.20.

The other tetraphenylantimony aroxides **II–IV** were synthesized in a similar way.

Tetraphenylantimony 2,6-dibromo-4*-tert***-butylphenoxide (II)** is colorless crystals with a yield of 75% and $T_{\text{decomp}} = 198^{\circ}$ C. IR spectrum (v, cm⁻¹): 3048, 2958, 2864, 1578, 1478, 1435, 1383, 1292, 1246, 1182, 1065, 1021, 997, 865, 830, 733, 693, 578, 521, 472, 449. For C₃₄H₃₁Br₂OSb, anal. calcd. (%): C, 55.39; H, 4.21. Found (%): C, 55.25; H, 4.35.

Tetraphenylantimony 2,6-dibromo-4-nitrophenoxide (III) is colorless crystals with a yield of 95% and $T_{\text{decomp}} = 230^{\circ}$ C. IR spectrum (v, cm⁻¹): 3068, 1560, 1547, 1480, 1460, 1435, 1325, 1308, 1187, 1160, 996, 907, 899, 843, 828, 750, 729, 690, 658, 514, 455. For $C_{30}H_{22}Br_2NO_3Sb$, anal. calcd. (%): C, 49.62; H, 3.03. Found (%): C, 49.43; H, 3.12.

Tetraphenylantimony 2,4-dinitrophenoxide (IV) is yellow crystals with a yield of 86% and $T_{melt} = 198^{\circ}C$. IR spectrum (v, cm⁻¹): 3102, 3055, 1591, 1518, 1473, 1434, 1314, 1135, 1059, 997, 907, 835, 736, 718, 689, 635, 454. For $C_{30}H_{23}N_2O_5Sb$, anal. calcd. (%): C, 58.75; H, 3.75. Found (%): C, 58.64; H, 3.84. **IR spectra** of complexes **I**–**IV** were recorded on a Bruker Tensor 27 IR spectrometer as KBr pellets.

Single-crystal X-ray diffraction analysis of complexes I–IV was performed on a Bruker D8 QUEST diffractometer at 296(2) K (Mo K_{α} radiation, $\lambda =$ 0.71073 Å, graphite monochromator). The collection and edition of data, the refinement of unit cell parameters, and the application of absorption corrections were performed by the SMART and SAINT-*Plus* software [7]. All calculations in the solution and refine-

Parameter	Value				
	Ι	II	III	IV	
Formula weight	601.36	737.16	726.06	613.25	
Symmetry system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	
Space group	$P2_{1}/c$	$P2_{1}/n$	$P2_{1}/c$	Pbca	
<i>a</i> , Å	13.5466(5)	11.4559(4)	11.6869(9)	15.2941(11)	
<i>b</i> , Å	18.1514(5)	11.8871(4)	14.8454(12)	17.6270(14)	
<i>c</i> , Å	12.2064(5)	22.5093(7)	16.0131(12)	19.6112(16)	
β, deg	99.609(2)	100.6670(10)	93.006(2)	90.00	
$V, Å^3$	2959.32(18)	3012.29(17)	2774.4(4)	5287.0(7)	
Ζ	4	4	4	8	
$\rho_{calc}, g/cm^3$	1.350	1.625	1.738	1.541	
μ , mm ⁻¹	0.958	3.594	3.907	1.087	
<i>F</i> (000)	1224.0	1456.0	1416.0	2464.0	
Crystal size, mm	$0.48 \times 0.2 \times 0.16$	$0.44 \times 0.27 \times 0.12$	$0.35 \times 0.21 \times 0.18$	$0.81\times0.27\times0.17$	
2θ range of data collection, deg	6.1-49.54	6.02-52.82	6.02-38.7	5.72-52.76	
Reflection index ranges	$-15 \le h \le 15,$	$-14 \le h \le 14,$	$-10 \le h \le 10,$	$-19 \le h \le 19,$	
	$-21 \le k \le 21,$	$-14 \le k \le 14,$	$-13 \le k \le 13,$	$-22 \le k \le 22,$	
M	$-14 \le l \le 14$	$-28 \le l \le 2/$	$-14 \le l \le 13$	$-24 \le l \le 24$	
Measured reflections	13557	82835	103 288	3/954/	
Independent reflections $P_{\rm eff}(t) = \frac{1}{2} \frac{1}{$	4995	6168	53/5	2346	
Reflections with $I \ge 2\sigma(I)$	4111	5314	4619	2161	
<i>K</i> _{int}	0.0238	0.0326	0.0462	0.0466	
Refinement variables	343	346	334	343	
GOOF	1.061	1.047	1.315	1.107	
<i>R</i> -factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0373,$	$R_1 = 0.0229,$	$R_1 = 0.0590,$	$R_1 = 0.0236,$	
	$wR_2 = 0.0912$	$wR_2 = 0.0504$	$wR_2 = 0.1508$	$wR_2 = 0.0547$	
<i>R</i> -factors for all reflections	$R_1 = 0.0490,$	$R_1 = 0.0311,$	$R_1 = 0.0633,$	$R_1 = 0.0315,$	
	$wR_2 = 0.0978$	$wR_2 = 0.0539$	$wR_2 = 0.1531$	$wR_2 = 0.0604$	
Residual electron density	0.51/-0.45	0.71/-0.62	1.49/-0.88	0.51/-0.25	
(max/min), e/Å ³					

 Table 1. Crystallographic data, parameters of X-ray diffraction experiment, and refinement details for the structures of complexes I–IV

ment of structures were performed by the software SHELXL/PC [8] and OLEX2 [9]. The structures were solved by direct methods and refined by the least-squares technique in the anisotropic approximation for non-hydrogen atoms. Selected crystallographic data and refinement results for the structures of complexes **I**–**IV** are given in Table 1, and selected bind lengths and bond angles are presented in Table 2.

Complete tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Structure Database (nos. 1415722 for I, 1043638 for II, 1043901 for III, and 1043507 for IV, deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Tetraphenylantimony aroxides **I**–**IV** were synthesized via dephenylation of pentaphenylantimony by a corresponding phenol with nearly quantitative yields:

Complexes **I**–**IV** were crystallized immediately during the cooling of a reaction mixture.

According to X-ray diffraction data, the antimony atom in molecules of complexes I-IV has a differently distorted trigonal bipyramidal coordination to the oxygen atom of an aroxyl group in axial position (Figs. 1–4).

The axial OSbC angles in complexes I, II, III, and IV are $177.63(13)^{\circ}$, $174.29(7)^{\circ}$, $177.8(6)^{\circ}$, and $174.01(7)^{\circ}$, respectively, and the sums of angles in the equatorial CSbC plane is $358.47(16)^{\circ}$ (I), $357.61(9)^{\circ}$ (II), $354.4(7)^{\circ}$ (III), and $352.99(8)^{\circ}$ (IV). The antimony atoms in complexes I, II, III, and IV are, respectively, 0.152, 0.188, 0.289, and 0.326 Å out of equatorial plane C_3 towards the axial carbon atom, and this is accompanied by the deviation of the angles between axial and equatorial bonds from the theoretical value of 90° . The OSbC_{eq} angles variate within $83.13(13)^{\circ}-87.85(14)^{\circ}$ Å (I), $83.38(7)^{\circ}-87.81(8)^{\circ}$ Å (II), $80.1(5)^{\circ}-83.9(5)^{\circ}$ Å (III), and $76.67(7)^{\circ}-84.33(7)^{\circ}$ Å (IV), and the C_{ax}SbC_{eq} angles are $92.40(15)^{\circ}-95.33(15)^{\circ}$ Å (I), $93.60(8)^{\circ}-97.79(9)^{\circ}$ Å (II), $97.8(6)^{\circ}-98.1(7)^{\circ}$ Å (III), and $97.42(8)^{\circ}-99.65(8)^{\circ}$ (IV).

The average Sb– C_{eq} bond lengths are 2.123(4) Å (I), 2.116(2) Å (II), 2.101(18) Å (III), and 2.118(2) Å (IV). Axial Sb $-C_{ax}$ bonds are longer than equatorial ones (2.195(4), 2.173(2), 2.144(17), and 2.148(2) Å in I, II, III, and IV, respectively), and the ratios of Sb- C_{ax} bond lengths to average $Sb-C_{eq}$ bond lengths are 1.034, 1.027, 1.020, and 1.014. The Sb-O distances in complexes I, II, III, and IV are 2.117(3), 2.2613(15), 2.409(11), and 2.4296(15) Å, and the mentioned distance in complex I is shorter than $Sb-C_{ax}$. Hence, the series of tetraphenylantimony aroxides I-IV exhibits a trend to distortion in the trigonal bipyramidal coordination of the central atom towards a tetrahedron. This is indicated by an increase in the deviation of the antimony atom from the equatorial plane in this series, a decrease in the sum of equatorial angles, the trend of the ratio $Sb-C_{ax}/(Sb-C_{eq})_{av}$ to unity, and the monotonical elongation of Sb–O bonds.

Such a transformation in the coordination polyhedron of the antimony atom can be explained by the redistribution of electron density in the aroxy group depending on the nature of substituents in it. The substituents with a negative inductive effect (bromine and, especially, a nitro group) stabilize the phenolate anion, increasing the contribution of the ionic component to the Sb–O bond, which may be considered as a coordination one in this case. On the contrary, the presence of carbon radicals with a positive inductive effect in the aroxy group does not produce any appreciable shift of electron density from the oxygen atom. In this case, the Sb–O bond has a covalent character (e.g., the length of this bond in complex I is comparable with the sum of the antimony and oxygen covalent radii of 2.07 Å [10]). It is noteworthy that an increase in the Sb–O distance in complexes I–IV is accompanied by a decrease in the O-C bond length (1.337(5),

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Table 2.	Selected	bond	lengths	(d)	and	bond	angles	(ω)	in
the struc	tures of c	omple	xes I-I	V			-		

Bond	<i>d</i> , Å	Angle ω, deg					
I							
Sb(1)-O(1)	2.117(3)	O(1)Sb(1)C(31)	177.63(13)				
Sb(1)-C(11)	2.126(4)	C(1)Sb(1)C(11)	116.70(16)				
Sb(1)-C(1)	2.125(4)	C(21)Sb(1)C(11)	124.91(16)				
Sb(1)-C(21)	2.116(4)	C(21)Sb(1)C(1) 116.86(
Sb(1)-C(31)	2.195(4)	O(1)Sb(1)C(1) 83.16(13					
O(1)-C(41)	1.337(5)	C(1)Sb(1)C(31)	94.64(15)				
		C(41)O(1)Sb(1)	131.7(3)				
		II	ļ.				
Sb(1)-O(1)	2.2613(15)	O(1) Sb(1)C(31)	174.29(7)				
Sb(1)-C(1)	2.114(2)	C(1)Sb(1)C(11)	119.13(9)				
Sb(1)-C(11)	2.118(2)	C(1)Sb(1)C(21)	128.67(9)				
Sb(1)-C(21)	2.116(2)	C(21)Sb(1)C(11)	109.81(9)				
Sb(1)-C(31)	2.173(2)	O(1)Sb(1)C(1)	83.94(7)				
O(1)-C(41)	1.320(3)	C(1)Sb(1)C(31)	94.25(9)				
		C(41)O(1)Sb(1)	126.57(14)				
		III	,				
Sb(1)-O(1)	2.409(11)	O(1)Sb(1)C(31)	177.8(6)				
Sb(1)-C(1)	2.107(17)	C(11)Sb(1)C(1)	121.8(7)				
Sb(1)-C(11)	2.094(18)	C(11)Sb(1)C(21)	113.3(7)				
Sb(1)-C(31)	2.144(17)	C(21)Sb(1)C(1)	119.3(7)				
Sb(1)-C(21)	2.102(18)	C(11)Sb(1)C(31)	97.8(7)				
O(1)-C(41)	1.305(18)	O(1)Sb(1)C(11) 83.9(5					
		C(41)O(1)Sb(1)	133.9(9)				
IV							
Sb(1)-O(1)	2.4296(15)	O(1)Sb(1)C(1)	174.01(7)				
Sb(1)–C(1)	2.148(2)	C(21)Sb(1)C(11)	119.63(8)				
Sb(1)-C(21)	2.106(2)	C(21)Sb(1)C(31)	118.40(8)				
Sb(1)-C(11)	2.124(2)	C(31)Sb(1)C(11)	114.96(8)				
Sb(1)-C(31)	2.123(2)	O(1) Sb(1)C(11)	84.33(7)				
O(1)–C(41)	1.278(3)	C(11)Sb(1)C(1)	99.65(8)				
		C(41)O(1)Sb(1)	131.61(14)				



Fig. 1. Structure of complex I.



Fig. 2. Structure of complex II.







Fig. 4. Structure of complex IV.

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Compley		Bond length, Å	Sum of angles	Deference		
Complex	Sb-O	O-C _{Ar}	Sb-C _{ax}	$C_{eq}SbC_{eq}$, deg	Kelerence	
$Ph_4SbOC_6H_3(NO_2)_2-2,4$ (IV)	2.4296(15)	1.278(3)	2.148(2)	352.99(8)	This work	
$Ph_4SbOC_6H_2(Br_2-2,6)(NO_2-4)$ (III)	2.409(11)	1.305(18)	2.144(17)	354.4(7)	This work	
$Ph_4SbOC_6H_2Br_3-2,4,6$	2.269(2)	1.315(4)	2.161(4)	356.86(8)	[1]	
$Ph_4SbOC_6H_2(Br_2-2,6)(t-Bu-4)$ (II)	2.2613(15)	1.320(3)	2.173(2)	357.61(9)	This work	
$Ph_4SbOC_6H_4(NO_2-4)$	2.224(2)	1.314(2)	2.165(2)	357.07(9)	[2]	
$Ph_4SbOC_6H_4(NO_2-2)$	2.221(4)	1.317(6)	2.181(5)	357.6(2)	[3]	
$Ph_4SbOC_6H_4(t-Bu-2)$	2.143(4)	1.363(8)	2.180(7)	358.5(3)	[4]	
$Ph_4SbOC_6H_3(Me_2-2,6)$	2.132(6)	1.41(2)	2.176(8)	359.1(5)	[5]	
$Ph_4SbOC_6H_3(Me-2)(i-Pr-5)$	2.128(3)	1.333(5)	2.187(4)	359.2(9)	[5]	
$Ph_4SbOC_6H_3(t-Bu_2-3,5)$	2.121(4)	1.342(6)	2.194(6)	358.4(2)	[6]	
$Ph_4SbOC_6H_4C_6H_7-4$ (I)	2.117(3)	1.337(5)	2.195(4)	358.47(16)	This work	

Table 3. Selected parameters of the molecular structure of aroxy tetraphenylantimony compounds

1.320(3), 1.305(18), and 1.278(3) Å in complexes I, II, III, and IV, respectively).

The revealed regularities are confirmed in the series of the earlier structurally characterized tetraphenylantimony aroxides containing bromine, a nitro group, and alkyl radicals in phenol residues (Table 3).

Hence, the distortion of the trigonal bipyramidal configuration of molecules aroxy tetraaryl antimony compounds and the elongation of the Sb–O bond are due to the aroxy group having electron-drawing properties, which become stronger with an increase in the number of electron-drawing substituents in the aromatic ring.

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