Synthesis and structures of the six-coordinate donor-acceptor complexes $R_3(C_6H_4O_2)Sb...L$ (R = Ph, L = $OSMe_2$ or ONC_5H_5; R = Me, L = ONC_5H_5 or NC_5H_5) and $R_3(C_2H_4O_2)Sb...L$ (R = Ph, L = ONC_5H_5; R = Cl or C_6F_5, L = $OPPh_3$)

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One-pot oxidation of R_3Sb (R = Ph, Me, Cl, or C_6F_5) with *tert*-butyl hydroperoxide in the presence of 1,2-diols and monodentate donor compounds was studied. The structures of the resulting neutral organic donor-acceptor Sb^V complexes, $Ph_3(C_6H_4O_2)Sb...OSMe_2$, $Ph_3(C_6H_4O_2)Sb...ONC_5H_5$, $Me_3(C_6H_4O_2)Sb...ONC_5H_5$, $Me_3(C_6H_4O_2)Sb...NC_5H_5$, $Ph_3(C_2H_4O_2)Sb...ONC_5H_5$, and $Cl(C_6F_5)_2(C_2H_4O_2)Sb...OPPh_3$, were established by X-ray diffraction analysis. In these complexes, the coordination environment about the Sb atoms is a distorted octahedron. The Sb—O(N) distances and the Sb—O—E angles (E = S, N, or P) vary over wide ranges.

Key words: one-pot oxidation reactions, six-coordinate Sb^V complexes, synthesis, X-ray diffraction analysis, molecular and crystal structure.

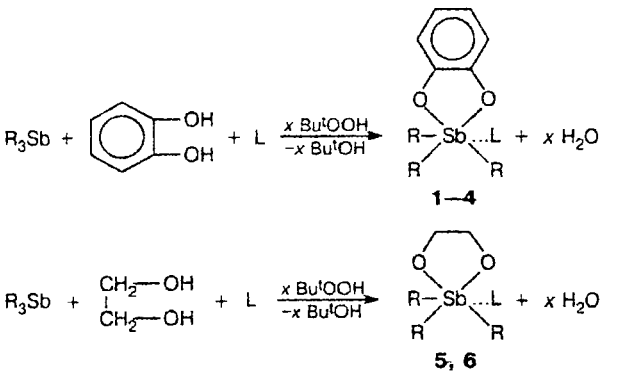
The radical activity series (A. N. Nesmeyanov, G. A. Razuvaev, and M. S. Karash), which characterize the stability of organometallic compounds of main-group metals (Hg, Pb, Sn, Sb, Bi, *etc.*) with respect to exchange reactions under the action of metal halides or H-acids, have been known as early as the 1930s. These investigations formed the basis of the chemistry of compounds of main-group metals with the simplest structures, corresponding to the formal valences of metal atoms. Later on, the chemistry of main-group metals, in particular, of antimony, took two paths, *viz.*, the synthesis of high-coordinate compounds[1–9] and the synthesis of low-coordinate compounds.[10]

The majority of six-coordinate donor-acceptor Sb^V compounds are halide complexes of the $Hal_5Sb...L$ type (L is a donor molecule).[1–9] Much less is known about the structures and properties of $R_5Sb...L$ complexes (R is an organic ligand).[11,12] The present work is devoted to studies of the characteristic features of coordination of monodentate donor molecules (L = $OSMe_2$, ONC_5H_5, NC_5H_5, and $OPPh_3$) to Sb atoms in organometallic compounds of the $R_3R'Sb^V$ type (R and R′ are monodentate and bidentate organic ligands, respectively) and to elucidation of the factors that affect the geometry of the donor-acceptor Sb...L bonds.

Results and Discussion

The six-coordinate $R_3R'Sb^V...L$ complexes were prepared by oxidation of R_3Sb (R = Ph, Me, Cl, or C_6F_5) with *tert*-butyl hydroperoxide in the presence of 1,2-diols and monodentate donor compounds according to Scheme 1. Presently, these reactions are widely used in the synthesis of various bismuth- and antimony-containing organic compounds.[13–15]

Scheme 1



Complex	R [R_3]	L	*x*
1	Ph	$OSMe_2$	1
2	Ph	ONC_5H_5	1
3	Me	ONC_5H_5	1
4	Me	NC_5H_5	1
5	Ph	ONC_5H_5	1
6	$[Cl(C_6F_5)_2]$	$OPPh_3$	2

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X-ray diffraction analysis of the complexes $Ph_3(C_6H_4O_2)Sb...OSMe_2$ (**1**), $Ph_3(C_6H_4O_2)Sb...ONC_5H_5$ (**2**), $Me_3(C_6H_4O_2)Sb...ONC_5H_5$ (**3**), $Me_3(C_6H_4O_2)Sb...NC_5H_5$ (**4**), $Ph_3(C_2H_4O_2)Sb...ONC_5H_5$ (**5**), and $Cl(C_6F_5)_2(C_2H_4O_2)Sb...OPPh_3$ (**6**) demonstrated that the coordination environment about the Sb atoms

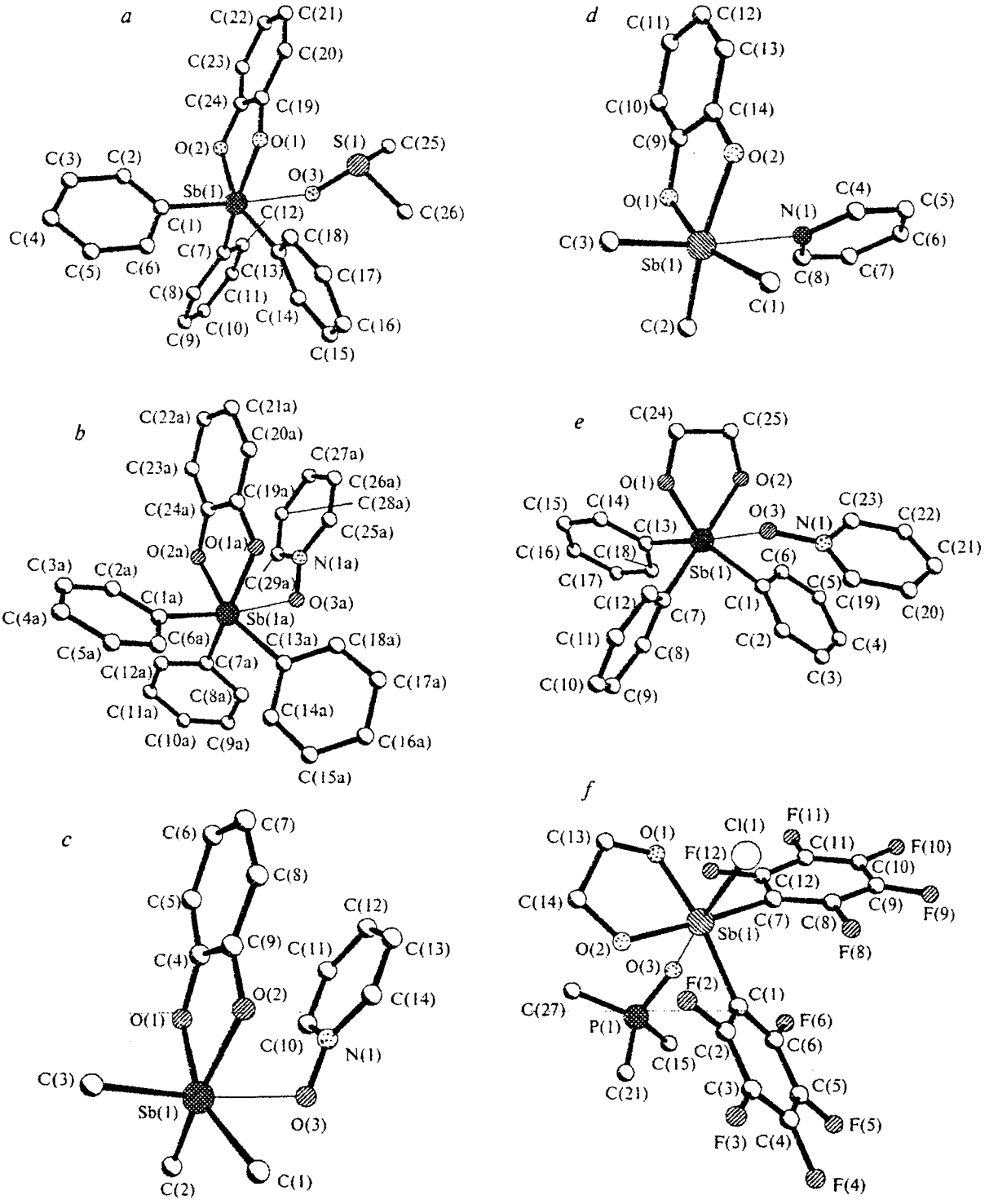

Fig. 1. Molecular structures of complexes **1** (*a*), **2** (*b*), **3** (*c*), **4** (*d*), **5** (*e*), and **6** (*f*). For complex **2** (*b*), the structure of one independent molecule is shown; for complex **6** (*f*), the Ph rings in Ph_3PO are omitted.

is a distorted octahedron (Fig. 1, *a*—*e*). The chelate ring ($C_6H_4O_2$ or $C_2H_4O_2$) and two R groups (Ph, Me, or C_6F_5) lie in the equatorial plane. The third R group (Ph, Me, or Cl) and the L donor molecules are in the axial positions. The axial C(Ph or Me)—Sb—O(N) and Cl—Sb—O angles in complexes **1**—**6** vary in the range of 171.7(2)—177.4(2)°. The sums of the O—Sb—O, O—Sb—C, and C—Sb—C angles in the equatorial plane vary in the range of 355.2—359.8°. The Sb atoms deviate from the equatorial plane of the OOCC fragments in the direction opposite to the additionally coordinated L molecules by 0.27—0.30 Å in complexes **1**—**5** and by 0.10 Å in complex **6**.

The Sb—C bond lengths in complexes **1**—**6** vary in the range of 2.112(5)—2.184(9) Å (Tables 1—6), the Sb—C(C_6F_5) distances in complex **6** (2.153(9) and 2.184(9) Å) being somewhat larger than the analogous Sb—C(Ph) distances in the structures of **1**, **2**, and **5** (2.132(7)—2.161(4) Å). The Sb—C(Me) bonds in complex **4** (2.112(5)—2.125(5) Å) are slightly shorter than the corresponding bonds in complex **3** (2.138(10)—2.148(10) Å), which is, apparently, due to more substantial steric repulsions between the substituents in the latter compound. On the whole, the Sb—C bond lengths in complexes **1**—**6** are comparable with the lengths of the analogous bonds in other antimony compounds (2.115(4)—2.188(5) Å).[16] The Sb—Cl distance in com-

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **1**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Sb(1)—O(1)	2.048(2)	O(1)—Sb(1)—O(2)	79.7(1)	O(2)—Sb(1)—C(7)	87.9(1)
Sb(1)—O(2)	2.049(2)	O(1)—Sb(1)—O(3)	82.8(1)	O(3)—Sb(1)—C(13)	82.5(1)
Sb(1)—O(3)	2.336(2)	O(2)—Sb(1)—O(3)	80.8(1)	C(1)—Sb(1)—C(13)	100.3(1)
Sb(1)—C(1)	2.139(3)	O(1)—Sb(1)—C(1)	95.1(1)	C(7)—Sb(1)—C(13)	100.9(1)
Sb(1)—C(7)	2.133(3)	O(2)—Sb(1)—C(1)	96.0(1)	O(3)—S(1)—C(25)	102.0(2)
Sb(1)—C(13)	2.140(3)	O(3)—Sb(1)—C(1)	176.4(1)	O(3)—S(1)—C(26)	106.4(2)
S(1)—O(3)	1.532(2)	O(1)—Sb(1)—C(7)	163.1(1)	C(25)—S(1)—C(26)	95.7(2)
S(1)—C(25)	1.814(5)	O(3)—Sb(1)—C(7)	84.1(1)	Sb(1)—O(1)—C(19)	112.4(2)
S(1)—C(26)	1.776(4)	C(1)—Sb(1)—C(7)	97.5(1)	Sb(1)—O(2)—C(24)	112.4(2)
O(1)—C(19)	1.352(3)	O(1)—Sb(1)—C(13)	87.7(1)	Sb(1)—O(3)—S(1)	122.6(1)
O(2)—C(24)	1.360(4)	O(2)—Sb(1)—C(13)	160.3(1)		

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **2** (for two independent molecules A and B)

Bond	*d*/Å		Angle	ω/deg		Angle	ω/deg	
	A	B		A	B		A	B
Sb(1)—O(1)	2.074(4)	2.060(4)	O(1)—Sb(1)—O(2)	79.7(2)	80.0(2)	O(1)—Sb(1)—C(13)	89.3(2)	86.6(2)
Sb(1)—O(2)	2.055(4)	2.062(4)	O(1)—Sb(1)—O(3)	81.6(2)	83.0(2)	O(2)—Sb(1)—C(13)	161.1(2)	161.9(2)
Sb(1)—O(3)	2.266(5)	2.275(5)	O(2)—Sb(1)—O(3)	83.5(2)	83.9(2)	O(3)—Sb(1)—C(13)	79.7(2)	82.5(2)
Sb(1)—C(1)	2.150(7)	2.153(7)	O(1)—Sb(1)—C(1)	90.1(2)	94.9(2)	C(1)—Sb(1)—C(13)	101.3(2)	98.9(2)
Sb(1)—C(7)	2.141(6)	2.132(7)	O(2)—Sb(1)—C(1)	94.1(2)	94.2(2)	C(7)—Sb(1)—C(13)	100.0(2)	101.1(2)
Sb(1)—C(13)	2.154(7)	2.152(6)	O(3)—Sb(1)—C(1)	171.7(2)	177.4(2)	Sb(1)—O(1)—C(19)	112.1(3)	112.1(4)
O(1)—C(19)	1.375(8)	1.363(6)	O(1)—Sb(1)—C(7)	162.1(2)	160.7(2)	Sb(1)—O(2)—C(24)	113.4(4)	112.6(3)
O(2)—C(24)	1.349(7)	1.364(7)	O(2)—Sb(1)—C(7)	87.0(2)	88.4(2)	Sb(1)—O(3)—N(1)	119.1(4)	122.3(3)
O(3)—N(1)	1.340(6)	1.330(6)	O(3)—Sb(1)—C(7)	84.9(2)	80.5(2)	O(3)—N(1)—C(25)	118.6(5)	119.4(5)
			C(1)—Sb(1)—C(7)	102.9(2)	101.3(3)	O(3)—N(1)—C(29)	119.9(4)	119.0(6)

Table 3. Selected bond lengths (*d*) and bond angles (ω) in complex **3**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Sb(1)—O(1)	2.062(5)	O(1)—Sb(1)—O(2)	79.3(2)	C(1)—Sb(1)—C(2)	101.3(4)
Sb(1)—O(2)	2.058(5)	O(1)—Sb(1)—O(3)	81.8(2)	O(1)—Sb(1)—C(3)	93.7(3)
Sb(1)—O(3)	2.345(6)	O(2)—Sb(1)—O(3)	81.9(2)	O(2)—Sb(1)—C(3)	92.7(4)
Sb(1)—C(1)	2.148(10)	O(1)—Sb(1)—C(1)	159.0(4)	O(3)—Sb(1)—C(3)	173.5(3)
Sb(1)—C(2)	2.142(10)	O(2)—Sb(1)—C(1)	87.2(3)	C(1)—Sb(1)—C(3)	102.9(5)
Sb(1)—C(3)	2.138(10)	O(3)—Sb(1)—C(1)	80.5(4)	C(2)—Sb(1)—C(3)	100.2(5)
O(1)—C(4)	1.356(8)	O(1)—Sb(1)—C(2)	88.0(3)	C(2)—Sb(1)—C(3)	100.2(5)
O(2)—C(9)	1.356(8)	O(2)—Sb(1)—C(2)	162.4(4)	Sb(1)—O(1)—C(4)	112.9(4)
O(3)—N(1)	1.341(7)	O(3)—Sb(1)—C(2)	84.3(4)	Sb(1)—O(2)—C(9)	113.6(4)
		Sb(1)—O(3)—N(1)	119.0(4)	O(3)—N(1)—C(10)	120.7(6)

Table 4. Selected bond lengths (d) and bond angles (ω) in complex **4**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Sb(1)—O(1)	2.061(3)	O(1)—Sb(1)—O(2)	79.0(1)	N(1)—Sb(1)—C(2)	83.5(1)
Sb(1)—O(2)	2.059(3)	O(1)—Sb(1)—N(1)	79.4(1)	C(1)—Sb(1)—C(2)	101.0(2)
Sb(1)—N(1)	2.595(3)	O(2)—Sb(1)—N(1)	77.9(1)	O(1)—Sb(1)—C(3)	94.7(2)
Sb(1)—C(1)	2.125(5)	O(1)—Sb(1)—C(1)	161.2(2)	O(2)—Sb(1)—C(3)	96.7(2)
Sb(1)—C(2)	2.125(4)	O(2)—Sb(1)—C(1)	87.8(2)	N(1)—Sb(1)—C(3)	172.6(2)
Sb(1)—C(3)	2.112(5)	N(1)—Sb(1)—C(1)	84.8(2)	C(1)—Sb(1)—C(3)	100.1(2)
O(1)—C(9)	1.347(5)	O(1)—Sb(1)—C(2)	87.4(1)	C(2)—Sb(1)—C(3)	100.8(2)
O(2)—C(14)	1.347(5)	O(2)—Sb(1)—C(2)	158.6(1)		
N(1)—C(4)	1.326(5)				
N(1)—C(8)	1.338(5)				

Table 5. Selected bond lengths (d) and bond angles (ω) in complex **5**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Sb(1)—O(1)	2.001(3)	O(1)—Sb(1)—O(2)	81.8(1)	O(1)—Sb(1)—C(13)	96.9(1)
Sb(1)—O(2)	2.040(3)	O(1)—Sb(1)—O(3)	78.1(1)	O(2)—Sb(1)—C(13)	96.3(1)
Sb(1)—O(3)	2.377(3)	O(2)—Sb(1)—O(3)	83.7(1)	O(3)—Sb(1)—C(13)	174.9(1)
Sb(1)—C(1)	2.161(4)	O(1)—Sb(1)—C(1)	159.7(1)	C(1)—Sb(1)—C(13)	101.4(1)
Sb(1)—C(7)	2.146(4)	O(2)—Sb(1)—C(1)	87.4(1)	C(7)—Sb(1)—C(13)	95.0(1)
Sb(1)—C(13)	2.142(4)	O(3)—Sb(1)—C(1)	83.7(1)	Sb(1)—O(1)—C(24)	112.3(2)
O(1)—C(24)	1.419(6)	O(1)—Sb(1)—C(7)	87.4(1)	Sb(1)—O(2)—C(25)	112.1(2)
O(2)—C(25)	1.412(4)	O(2)—Sb(1)—C(7)	165.3(1)	Sb(1)—O(3)—N(1)	125.4(2)
O(3)—N(1)	1.332(4)	O(3)—Sb(1)—C(7)	84.3(1)	O(3)—N(1)—C(19)	119.0(3)
N(1)—C(19)	1.345(5)	C(1)—Sb(1)—C(7)	99.7(1)	O(3)—N(1)—C(23)	120.1(3)
N(1)—C(23)	1.354(5)				

Table 6. Selected bond lengths (d) and bond angles (ω) in complex **6**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Sb(1)—Cl(1)	2.532(2)	Cl(1)—Sb(1)—O(1)	90.6(2)	O(2)—Sb(1)—C(1)	88.7(3)
Sb(1)—O(1)	1.974(8)	Cl(1)—Sb(1)—O(2)	96.6(2)	O(3)—Sb(1)—C(1)	86.9(3)
Sb(1)—O(2)	1.962(7)	O(1)—Sb(1)—O(2)	82.7(3)	Cl(1)—Sb(1)—C(7)	90.9(3)
Sb(1)—O(3)	2.125(6)	Cl(1)—Sb(1)—O(3)	175.2(2)	O(1)—Sb(1)—C(7)	89.7(3)
Sb(1)—C(1)	2.184(9)	O(1)—Sb(1)—O(3)	89.7(3)	O(2)—Sb(1)—C(7)	169.4(3)
Sb(1)—C(7)	2.153(9)	O(2)—Sb(1)—O(3)	88.2(3)	O(3)—Sb(1)—C(7)	84.4(3)
P(1)—O(3)	1.515(7)	Cl(1)—Sb(1)—C(1)	93.5(2)	C(1)—Sb(1)—C(7)	98.3(4)
O(1)—C(13)	1.372(15)	O(1)—Sb(1)—C(1)	170.9(3)	Sb(1)—O(3)—P(1)	143.2(4)
O(2)—C(14)	1.381(16)				

plex **6** (2.532(2) Å) is substantially larger than the Sb—Cl distances in donor-acceptor complexes of antimony pentachloride (2.29—2.39 Å).[1—9]

The Sb—O($C_6H_4O_2$) bonds in complexes **1**—**4** (2.048(2)—2.074(4) Å) are longer than the Sb—O($C_2H_4O_2$) bonds in complexes **5** and **6** (2.002(3) and 2.039(3) Å in **5** and 1.962(7) and 1.974(8) Å in **6**). The corresponding bonds in molecule **1** (2.048(2) and 2.049(2) Å) are somewhat shorter than those in **2** (2.074(4) and 2.055(4) Å; 2.060(4) and 2.062(4) Å in two independent molecules), **3** (2.062(5) and 2.058(5) Å), and **4** (2.061(3) and 2.059(3) Å). Noteworthy is the substantial difference in the Sb—O distances in the chelate ring of the first independent molecule of complex **2** (2.074(4) and 2.055(4) Å) as well in complex **5** (2.002(3) and 2.039(3) Å).

The C—O distances in the five-membered metallacycles in complexes **1**—**4** and **6** have close values and vary in the range of 1.347(5)—1.381(16) Å. The C—O bond lengths in complex **5** (1.413(4) and 1.430(6) Å) are larger than the analogous bonds in complexes **1**—**4** and **6**. Note that the C—O bonds (1.349(7) and 1.375(8) Å), like the Sb—O bonds, in the first independent molecule of complex **2** are nonequalized.

The Sb—C and Sb—O distances in the acceptor $Ph_3(C_6H_4O_2)Sb$ molecules of complexes **1** and **2** are close to the corresponding distances observed in the previously studied complexes $Ph_3(C_6H_4O_2)Sb...OH_2$

(2.137—2.143 Å; and 2.048 and 2.049 Å, respectively)[11] and $Ph_3(C_6H_4O_2)Sb...OPPh_3$ (2.139(6)—2.153(6) Å; and 2.046(4) and 2.049(4) Å, respectively).[12] On the whole, the Sb—C and Sb—O distances in complexes **1**—**6** are comparable with the analogous distances in the $Ph_3(C_6H_4O_2)Sb$ molecule (2.099—2.114 Å for Sb—C and 2.060 and 2.010 Å for Sb—O).[11] Therefore, the geometric parameters of the acceptor $R_3R'Sb$ molecules in complexes **1**—**6** are only slightly affected by the coordination of the donor L molecules.

The coordination of DMSO and pyridine oxide to the Sb atoms of the acceptor $R_3R'Sb$ molecules (**1**—**3** and **5**) leads to a slight elongation of the S—O and N—O bonds. The O(3)—S(1) distance in complex **1** (1.532(2) Å) and the O(3)—N(1) distances in complexes **2**, **3**, and **5** (1.340(6) (1.330(6)), 1.341(7), and 1.332(4) Å, respectively) are substantially larger than the corresponding distances in the molecules of noncoordinated DMSO (1.497 Å)[17] and pyridine oxide (1.304 Å).[17] The S(1)—C(25) and S(1)—C(26) distances in complex **1** (1.814(5) and 1.776(4) Å) are also somewhat different from the corresponding distances in the noncoordinated DMSO molecule (1.809 Å).[17] The N—C and C—C distances in the pyridine oxide residues in complexes **2**, **3**, and **5** vary in the ranges of 1.335(9)—1.355(7) Å (N—C) and 1.352(6)—1.390(7) Å (C—C).

The coordination of the pyridine and triphenylphosphine oxide molecules in complexes **4** and **6** is not accompanied by a substantial distortion of their geometry. The C—C (1.364(7)—1.379(9) Å) and C—N (1.326(5) and 1.338(5) Å) distances in complex **4** virtually coincide with the analogous distances in the free pyridine molecule (1.379 and 1.337 Å, respectively).[17] The P—O distance in complex **6** (1.515(7) Å) nearly coincides with the corresponding distances in the noncoordinated $C_3P{=}O$ fragments (1.489 Å)[17] and with the P—O distance in the $Ph_3(C_6H_4O_2)Sb...OPPh_3$ complex (1.494(4) Å).[12]

The O(3) atoms of the pyridine oxide groups (in **2**, **3**, and **5**) lie in the plane of the pyridine ring. The average deviations of the O(3) atoms from this plane are 0.006 (0.005), 0.023, and 0.044 Å in complexes **2**, **3**, and **5**, respectively. The angles between the planes of the central CCSbOO fragments and the pyridine molecules are 31.3° (35.2°), 28.3°, and 52.8° in complexes **2**, **3**, and **5**, respectively. In complex **4**, the angle between the planes of the central CCSbOO fragment and the coordinated pyridine molecule is 89.4°.

The Sb(1)—O(3)—S(1) angles in complex **1** (122.6(1)°) and the Sb(1)—O(3)—N(1) angles in complexes **2**, **3**, and **5** (119.1(4)° (122.3(3)°), 119.0(4)°, and 125.4(2)°, respectively) are substantially smaller than the Sb(1)—O(3)—P(1) angle (143.2(4)°) in complex **6** (see Tables 1—6). Note that in the $Ph_3(C_6H_4O_2)Sb...OPPh_3$ complex studied by us previously,[12] the corresponding Sb(1)—O(1)—P(1) angle is 153.0(3)°. The substantial increase in the Sb(1)—O(3)—P(1) angle in complex **6** compared to the analogous angles in complexes **1**—**3** and **5** may be associated either with the transfer of the electron density from two lone electron pairs of the O atom of the Ph_3PO molecule or with nonbonded repulsions between the donor and acceptor molecules of complex **6**. Analysis of the geometric parameters of the latter compound demonstrates that the mutual arrangement of the Ph rings (C(21)—C(26) in the donor molecule and C(1)—C(6) in the acceptor molecule) prevents a further decrease in the Sb(1)—O(3)—P(1) angle (the shortest distance between these rings, *viz.*, C(1)...C(21), is 3.425 Å, *i.e.*, it is comparable with the average value for intermolecular C...C contacts (3.42 Å)[18]). The O(3)—P(1)—C(21) angle (112.6(4)°) is somewhat larger than the O(3)—P(1)—C(15) and O(3)—P(1)—C(27) angles (107.1(4)° and 110.1(4)°, respectively). An analogous situation was also observed in the $Ph_3(C_6H_4O_2)Sb...OPPh_3$ complex.[12]

Hence, the large values of the Sb—O—P angles in complex **6** and in $Ph_3(C_6H_4O_2)Sb...OPPh_3$ are due to nonbonded interactions in the coordination sphere about the Sb atoms. However, it should be noted that the Sb—O—P angle in the $Cl_5Sb...OPMe_3$ complex (141.3°)[1] is also substantially larger than the corresponding angles in complexes **1**—**3** and **5**, although nonbonded interactions in the former (similar to those in **6**) are not observed.

The Sb...O(N) distances in complexes **1**—**6** vary over a wide range (2.125(6)—2.595(3) Å), the lower limit being comparable with the sums of the covalent radius of the Sb atom and the radii of the O and N atoms (2.16 and 2.17 Å, respectively).[19] The Sb...O distances in the $Cl_5Sb...OR$ compounds[1—9] vary in the range of 1.996—2.361 Å, *i.e.*, this range is somewhat shifted to smaller values. However, the Sb...O bond lengths in most of these compounds (1.996—2.151 Å)[1—5] are no larger than the sum of the covalent radii of the Sb and O atoms (2.16 Å).

The size of the sixth coordination site in complexes **1**—**6** is determined by the values of the O—Sb—O and C—Sb—C dihedral angles (the O and C atoms are located in the equatorial planes of the complexes). At large dihedral angles, a larger area of the coordination sphere about the Sb atom is accessible to coordination. The values of the above-mentioned dihedral angles in complexes **1**—**6** vary within a narrow range (155.9—158.6° for **1**—**5** and 171.4° for **6**) and are virtually independent of the Sb...O(N) distances. Note that the coordination of the Sb atom in the noncoordinated $Ph_3(C_6H_4O_2)Sb$ molecule can be considered as a strongly distorted tetragonal pyramid.[11] The dihedral angle in the base of this pyramid is 140.8°, which is somewhat smaller than the corresponding angles in complexes **1**—**6**. This suggests that it is at this site that the donor L molecules add to the acceptor $Ph_3(C_6H_4O_2)Sb$ molecules.

A comparison of the Sb...O distances in complexes **2**, **3**, and **5** containing the same donor molecules allows one to follow the effect of the substituents in the

acceptor molecules of these complexes on the lengths of the donor-acceptor bonds. The larger Sb...O distance in complex **3** (2.345(6) Å) compared to those in complex **2** (2.266(5) and 2.275(5) Å) is consistent with the higher electron-donating ability of Me groups compared to that of Ph substituents. The Sb...O distances, in turn, in complex **2** (2.266(5) and 2.275(5) Å) are smaller than the corresponding distance in **5** (2.337(3) Å) due to the stronger electron-withdrawing properties of the *o*-OC_6H_4O— group in complex **2** compared to those of the —OCH_2CH_2O— group in complex **5**. In complex **6**, the presence of the strong electron-withdrawing substituents (Cl and C_6F_5) in the acceptor molecule leads to the substantial decrease in the Sb...O distance (2.125(6) Å) compared to the analogous distance in $Ph_3(C_6H_4O_2)Sb...OPPh_3$ (2.338(4) Å).[12]

In the crystalline state, only complexes **1** and **6** occur as isolated molecules. In the other structures, the molecules are linked in infinite chains (**2** and **4**) or two-dimensional networks (**3** and **5**) *via* weak C—H...O interactions. The lengths of the intermolecular O...H contacts in complexes **2**—**5** vary in the range of 2.39(3)—2.57(5) Å. Apparently, it is these intermolecular O...H interactions in the crystal structure of **2** that lead to the difference between the Sb(1)—O(1) and Sb(1)—O(2) distances (2.074(4) and 2.055(4) Å) as well as to the difference between the O(1)—C and O(2)—C distances (1.349(7) and 1.375(8) Å) in one independent molecule compared to the corresponding distances in the second independent molecule. This is evidenced by the difference in the lengths of the intermolecular contacts for two independent molecules of complex **2**. The O(1ac)...H(28b) and O(1ab)...H(28a) intermolecular distances in the first independent molecule of complex **2** (2.39(5) Å) are shorter than the corresponding distances in the second independent molecule of this complex (2.54(5) Å) (Fig. 2).

Hence, donor-acceptor complexes **1**—**6** are formed as a result of addition of the donor L molecules on the side of the base of the distorted tetragonal pyramid, which is the coordination polyhedron about the Sb atoms of the acceptor molecules $R_3R'Sb^V$, the octahedral complexes $R_3R'Sb^V...L$ being formed. Analysis of the geometric parameters of complexes **1**—**6** demonstrates that the lengths of the donor-acceptor Sb...L bonds are affected primarily by the electronic factors (the donor and acceptor properties of the substituents at the Sb atoms). To the contrary, the Sb—O—E angle is determined to a larger extent by the steric factors.

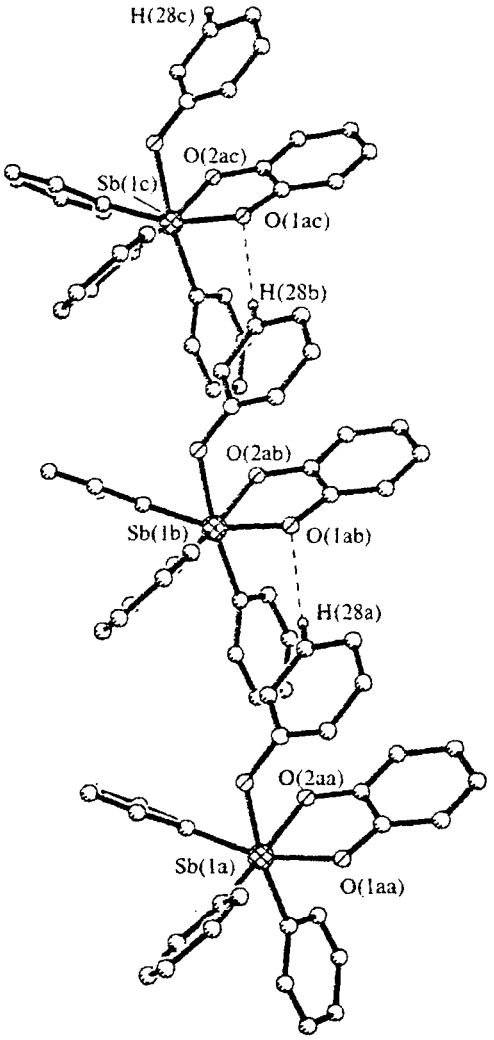

Fig. 2. Crystal structure of complex **2** (one independent molecule is shown).

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer (200.13 and 50.32 MHz, respectively). The IR spectra were measured on a Specord 75 IR spectrometer as Nujol mulls.

Adduct of triphenyl(pyrocatecholato-*O,O*)antimony(v) with dimethyl sulfoxide (1). A solution of *tert*-butyl hydroperoxide (0.31 g, 3.4 mmol) in benzene (10 mL) was slowly added with stirring to a mixture of triphenylantimony (1.34 g, 3.4 mmol), pyrocatechol (0.42 g, 3.4 mmol), and DMSO (0.26 g, 3.4 mmol) in benzene (20 mL). After completion of the reaction, volatile products were recondensed under reduced pressure. The solid residue was recrystallized from a 1 : 1 benzene—hexane mixture. Compound **1** was isolated in a yield of 1.24 g (68%), m.p. 113 °C. Found (%): C, 57.59; H, 4.91; Sb, 22.25. $C_{26}H_{25}O_3SSb$. Calculated (%): C, 57.88; H, 4.64; Sb, 22.63. IR, ν/cm^{-1}: 440 (Sb—Ph); 600 (Sb—O); 1235 (C—O); 980 (S=O). ^1H NMR (DMSO-d_6), δ: 2.50 (s, 6 H, CH_3); 6.50—6.80 (m, 4 H, C_6H_4); 7.30—7.70 (m, 15 H, C_6H_5).

Adduct of triphenyl(pyrocatecholato-*O,O*)antimony(v) with pyridine oxide (2) was synthesized analogously from triphenylantimony (1.00 g, 2.8 mmol), pyrocatechol (0.31 g, 2.8 mmol), pyridine oxide (0.22 g, 2.8 mmol), and *tert*-butyl hydroperoxide (0.25 g, 2.8 mmol). Compound **2** was isolated in a yield of 1.13 g (75%), m.p. 58 °C (dioxane—benzene—hexane, 1 : 4 : 5). Found (%): C, 62.55; H, 4.59; Sb, 22.25. $C_{29}H_{24}NO_3Sb$. Calculated (%): C, 62.59; H, 4.32; Sb, 21.94. IR, ν/cm^{-1}: 440 (Sb—Ph); 605 (Sb—O); 1250 (C—O, N—O). ^1H NMR ($CDCl_3$), δ: 6.50—6.90 (m, 4 H, C_6H_4); 7.30—8.20 (m, 20 H,

C_6H_5, NC_5H_5). ^{13}C NMR ($CDCl_3$), δ: 112.5, 117.4, 131.1, 131.6, 144.1, 148.1 (C_6H_4); 124.2, 135.2, 139.1 (NC_5H_5); 127.3, 127.9, 128.6, 134.1 (C_6H_5).

Adduct of triphenyl(ethylene glycolato-*O,O*)antimony(v) with pyridine oxide (5) was synthesized analogously from triphenylantimony (0.81 g, 2.0 mmol), ethylene glycol (0.14 g,

Table 7. Atomic coordinates (×10⁴) and equivalent isotropic temperature factors (U_{eq}) for complex **1**

Atom	*x*	*y*	*z*	U_{eq}/Å²
Sb(1)	7840(1)	416(1)	648(1)	21(1)
S(1)	8099(1)	−3064(1)	556(1)	35(1)
O(1)	7580(1)	−763(2)	1581(1)	29(1)
O(2)	8872(1)	442(2)	1461(1)	28(1)
O(3)	8346(1)	−1659(2)	278(1)	29(1)
C(1)	7420(2)	2300(3)	1062(2)	27(1)
C(2)	7875(2)	3068(3)	1680(2)	34(1)
C(3)	7631(2)	4331(4)	1919(2)	43(1)
C(4)	6921(2)	4857(4)	1531(3)	45(1)
C(5)	6464(2)	4100(4)	928(3)	44(1)
C(6)	6708(2)	2823(3)	681(2)	36(1)
C(7)	8410(2)	1287(3)	−249(2)	24(1)
C(8)	8080(2)	2434(3)	−699(2)	30(1)
C(9)	8444(2)	3072(3)	−1258(2)	36(1)
C(10)	9141(2)	2577(3)	−1386(2)	36(1)
C(11)	9466(2)	1432(4)	−957(2)	42(1)
C(12)	9097(2)	798(3)	−392(2)	34(1)
C(13)	6816(2)	−353(3)	−123(2)	26(1)
C(14)	6783(2)	−451(3)	−971(2)	35(1)
C(15)	6118(2)	−956(4)	−1485(2)	43(1)
C(16)	5503(2)	−1359(3)	−1164(3)	48(1)
C(17)	5537(2)	−1286(4)	−323(3)	45(1)
C(18)	6189(2)	−778(4)	198(2)	37(1)
C(19)	8210(2)	−1128(3)	2141(2)	26(1)
C(20)	8201(2)	−2112(3)	2752(2)	37(1)
C(21)	8879(3)	−2454(4)	3290(2)	49(1)
C(22)	9566(2)	−1831(4)	3224(2)	48(1)
C(23)	9576(2)	−839(4)	2610(2)	37(1)
C(24)	8903(2)	−498(3)	2077(2)	28(1)
C(25)	8939(3)	−4113(5)	540(5)	96(3)
C(26)	7516(2)	−3833(4)	−325(2)	47(1)
C(1S)	4035(3)	238(4)	−2949(3)	57(2)
C(2S)	4620(3)	38(5)	−3373(3)	61(2)
C(3S)	4787(2)	−1276(4)	−3589(3)	49(1)
C(4S)	4381(2)	−2377(4)	−3385(2)	50(1)
C(5S)	3808(2)	−2173(4)	−2957(2)	52(1)
C(6S)	3625(2)	−861(5)	−2744(3)	52(1)

Table 8. Atomic coordinates (×10⁴) and equivalent isotropic temperature factors (U_{eq}) for complex **2**

Atom	*x*	*y*	*z*	U_{eq}/Å²
Sb(1A)	3639(1)	−2539(1)	−4637(1)	23(1)
O(1A)	3771(5)	−3544(2)	−5633(2)	27(1)
O(2A)	1644(5)	−2471(2)	−5389(2)	27(1)
O(3A)	1832(5)	−3512(3)	−4478(3)	30(1)
N(1A)	460(6)	−3873(3)	−5017(3)	27(1)
C(1A)	5355(7)	−1750(4)	−4949(3)	26(2)
C(2A)	4807(8)	−1318(4)	−5420(4)	33(2)
C(3A)	5900(9)	−880(5)	−5680(4)	43(2)
C(4A)	7598(8)	−868(4)	−5496(4)	40(2)
C(5A)	8168(8)	−1299(4)	−5042(4)	39(2)
C(6A)	7082(8)	−1713(4)	−4772(4)	31(2)
C(7A)	2699(7)	−1662(4)	−3721(4)	28(2)
C(8A)	2466(9)	−1828(4)	−3058(4)	45(2)
C(9A)	1828(10)	1252(5)	−2467(4)	52(2)
C(10A)	1431(9)	−531(4)	−2532(4)	43(2)
C(11A)	1680(9)	−358(4)	−3179(4)	46(2)
C(12A)	2329(8)	−932(4)	3764(4)	35(2)
C(13A)	5295(7)	−3018(4)	−3962(3)	25(2)
C(14A)	6403(8)	−2462(4)	−3318(4)	37(2)
C(15A)	7493(8)	−2752(5)	−2863(4)	45(2)
C(16A)	7477(8)	−3605(5)	−3063(4)	40(2)
C(17A)	6377(7)	−4160(4)	−3704(4)	29(2)
C(18A)	5312(7)	−3862(4)	−4147(4)	29(2)
C(19A)	2615(7)	−3600(4)	−6260(3)	29(2)
C(20A)	2496(8)	−4197(4)	−7003(4)	30(2)
C(21A)	1208(8)	−4254(4)	−7595(4)	38(2)
C(22A)	68(8)	−3717(5)	−7447(4)	42(2)
C(23A)	196(8)	−3094(4)	−6709(4)	36(2)
C(24A)	1472(7)	−3044(4)	−6117(3)	27(2)
C(25A)	458(8)	−4630(4)	−5576(4)	31(2)
C(26A)	−920(8)	−5027(4)	−6121(4)	36(2)
C(27A)	−2326(8)	−4649(4)	−6113(4)	41(2)
C(28A)	−2296(7)	−3873(5)	−5535(4)	38(2)
C(29A)	−898(8)	−3494(4)	−4980(4)	33(2)
Sb(1B)	698(1)	−2375(1)	197(1)	23(1)
O(1B)	204(5)	−2118(2)	1304(2)	27(1)
O(2B)	2672(5)	−1450(3)	831(2)	29(1)
O(3B)	2329(5)	−3229(3)	523(3)	36(1)
N(1B)	3598(6)	−2941(3)	1117(3)	27(1)
C(1B)	−816(7)	−1528(4)	−58(4)	30(2)
C(2B)	−1900(8)	−1175(4)	424(4)	32(2)
C(3B)	−2845(9)	−606(4)	268(4)	44(2)
C(4B)	−2684(9)	−386(4)	−363(4)	44(2)
C(5B)	−1592(8)	−722(4)	−835(4)	40(2)
C(6B)	−676(8)	−1286(4)	−677(4)	34(2)
C(7B)	1982(8)	−2692(4)	−760(4)	31(2)
C(8B)	1604(8)	−3511(4)	−1314(4)	37(2)
C(9B)	2473(9)	−3774(4)	−1926(4)	43(2)
C(10B)	3719(9)	−3209(5)	−1989(4)	47(2)
C(11B)	4103(8)	−2421(5)	−1450(4)	43(2)
C(12B)	3254(8)	−2153(4)	−839(4)	37(2)
C(13B)	−1164(7)	−3464(4)	−162(4)	28(2)
C(14B)	−1178(8)	−4051(4)	179(4)	34(2)
C(15B)	−2420(9)	−4728(4)	−69(4)	43(2)
C(16B)	−3679(8)	−4839(4)	−678(4)	43(2)
C(17B)	−3718(8)	−4263(4)	−1030(4)	47(2)
C(18B)	−2473(8)	−3568(4)	−770(4)	35(2)
C(19B)	1240(7)	−1439(4)	1842(3)	27(2)
C(20B)	1087(8)	−1127(4)	2627(4)	33(2)
C(21B)	2213(9)	−436(4)	3147(4)	41(2)
C(22B)	3456(8)	−77(4)	2894(4)	42(2)
C(23B)	3653(8)	−401(4)	2115(4)	35(2)
C(24B)	2544(7)	−1080(4)	1595(3)	25(2)
C(25B)	3332(8)	−2833(4)	1834(4)	36(2)
C(26B)	4653(9)	−2559(5)	2456(4)	44(2)
C(27B)	6220(9)	−2404(5)	2328(5)	52(2)
C(28B)	6451(8)	−2522(5)	1585(5)	48(2)
C(29B)	5136(8)	−2799(4)	976(4)	39(2)

Table 9. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (U_{eq}) for complex **3**

Atom	x	y	z	U_{eq}/Å^2	Atom	x	y	z	U_{eq}/Å^2
Sb(1)	1596(1)	4898(1)	−1268(1)	50(1)	C(6)	−634(9)	4708(10)	2202(5)	74(3)
O(1)	721(5)	3838(4)	−203(4)	48(1)	C(7)	−480(9)	5951(10)	2163(5)	68(3)
O(2)	1006(5)	6218(5)	−281(4)	58(2)	C(8)	63(8)	6490(7)	1350(5)	61(2)
O(3)	−489(5)	5097(6)	−1838(4)	72(2)	C(9)	503(7)	5761(6)	569(4)	44(2)
N(1)	−1440(5)	5025(5)	−1180(4)	47(1)	C(10)	−1953(8)	3950(7)	−947(6)	60(2)
C(1)	1858(12)	6338(10)	−2333(7)	86(4)	C(11)	−2915(8)	3860(8)	−266(8)	70(3)
C(2)	1637(12)	3324(10)	−2212(6)	81(3)	C(12)	−3343(7)	4888(10)	181(8)	77(3)
C(3)	3415(9)	4757(12)	−583(9)	89(4)	C(13)	−2836(10)	5992(10)	−59(8)	76(3)
C(4)	340(6)	4490(6)	601(5)	42(2)	C(14)	−1886(7)	6048(7)	−735(7)	60(2)
C(5)	−241(7)	3971(8)	1425(5)	59(2)					

Table 10. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (U_{eq}) for complex **4**

Atom	x	y	z	U_{eq}/Å^2	Atom	x	y	z	U_{eq}/Å^2
Sb(1)	−100(1)	−2561(1)	−820(1)	41(1)	C(22)	1107(5)	−1605(4)	−3481(2)	58(2)
P(1)	−1721(1)	−2318(1)	−3372(1)	42(1)	C(23)	2234(5)	−876(5)	−3407(3)	72(2)
P(2)	−4109(1)	−7338(1)	−3378(1)	44(1)	C(24)	1960(6)	156(5)	−3114(3)	78(2)
O(1)	1365(3)	−3673(2)	−425(1)	47(1)	C(25)	575(6)	471(5)	−2903(3)	77(2)
O(2)	1257(3)	−1376(2)	−507(2)	49(1)	C(26)	−574(5)	−260(4)	−2970(3)	63(2)
O(3)	−1168(3)	−3538(3)	−3402(2)	59(1)	C(27)	−3145(4)	−2161(4)	−2735(2)	44(1)
O(4)	−4629(3)	−8554(3)	−3410(2)	62(1)	C(28)	−3282(5)	−3051(5)	−2254(2)	61(2)
N(1)	−1074(3)	−2510(3)	368(2)	45(1)	C(29)	−4325(7)	−2955(8)	−1742(3)	91(3)
C(1)	−1585(5)	−1152(4)	−945(2)	60(2)	C(30)	−5218(6)	−1990(8)	−1701(3)	98(3)
C(2)	−1493(5)	−4022(3)	−789(2)	51(1)	C(31)	−5101(6)	−1107(6)	−2183(3)	81(2)
C(3)	962(6)	−2610(5)	−1748(2)	68(2)	C(32)	−4080(4)	−1193(4)	−2703(2)	57(2)
C(4)	−1252(5)	−1499(3)	642(2)	53(1)	C(33)	−2948(4)	−6822(4)	−4071(2)	48(1)
C(5)	−1857(6)	−1379(5)	1249(3)	69(2)	C(34)	−3272(6)	5898(5)	−4463(3)	71(2)
C(6)	−2328(6)	−2375(6)	1603(3)	79(2)	C(35)	−2352(8)	−5581(6)	−5000(3)	93(3)
C(7)	−2139(6)	−3440(5)	1332(3)	71(2)	C(36)	−1116(8)	−6197(7)	−5153(3)	90(3)
C(8)	−1519(5)	−3471(4)	720(2)	54(1)	C(37)	−747(8)	−7113(7)	−4758(3)	98(3)
C(9)	2469(4)	−3113(3)	−220(2)	41(1)	C(38)	−1644(7)	−7428(6)	−4230(3)	85(2)
C(10)	3637(4)	−3686(4)	16(2)	54(1)	C(39)	−5603(4)	−6298(4)	−3279(2)	47(1)
C(11)	4722(5)	−3032(4)	219(3)	63(2)	C(40)	−5470(5)	−5222(4)	−3031(3)	68(2)
C(12)	4658(5)	−1837(5)	183(3)	67(2)	C(41)	−6672(5)	−4462(4)	−2692(2)	78(2)
C(13)	3493(5)	−1257(4)	−60(2)	55(1)	C(42)	−7982(5)	−4795(4)	−3135(2)	79(2)
C(14)	2401(4)	−1879(3)	−258(2)	41(1)	C(43)	−8100(5)	−5846(6)	−3381(3)	74(2)
C(15)	−2495(4)	−1791(4)	−4077(2)	48(1)	C(44)	−6921(5)	−6617(5)	−3458(2)	59(2)
C(16)	−3555(8)	−2448(6)	−4278(3)	95(3)	C(45)	−3069(4)	−7190(3)	−2720(2)	44(1)
C(17)	−4183(9)	−2087(7)	−4825(3)	107(3)	C(46)	−2071(4)	−6315(4)	−2706(2)	54(1)
C(18)	−3700(7)	−1114(6)	−5173(3)	88(3)	C(47)	−1361(5)	−6229(5)	−2173(3)	67(2)
C(19)	−2653(9)	−487(7)	−4979(3)	99(3)	C(48)	−1620(6)	−7013(6)	−1666(3)	77(2)
C(20)	−2042(7)	−807(5)	−4434(3)	76(2)	C(49)	−2594(6)	−7906(5)	−1683(3)	77(2)
C(21)	−315(4)	−1304(4)	−3262(2)	46(1)	C(50)	−3320(5)	−7998(4)	−2211(2)	61(2)

2.0 mmol), pyridine oxide (0.22 g, 2.0 mmol), and *tert*-butyl hydroperoxide (0.36 g, 4.0 mmol). Compound **5** was isolated in a yield of 0.63 g (62%), m.p. 126 °C (benzene—hexane—dioxane, 3 : 6 : 1). Found (%): C, 59.25; H, 4.84; Sb, 24.11. $C_{25}H_{24}NO_3Sb$. Calculated (%): C, 59.08; H, 4.73; Sb, 23.98. IR, ν/cm^{-1}: 590, 630 (Sb—O); 1220—1250 (N—O, C—O).

Adduct of di(pentafluorophenyl)chloro(ethylene glycolato-*O,O*)antimony(v) with triphenylphosphine oxide (6) was synthesized analogously from $(C_6F_5)_2SbCl$ (0.49 g, 1.0 mmol), triphenylphosphine (0.26 g, 1.0 mmol), ethylene glycol (0.06 g, 1.0 mmol), and *tert*-butyl hydroperoxide (0.18 g, 2.0 mmol). Compound **6** was isolated in a yield of 0.37 g (40%), m.p. 131 °C (benzene—hexane, 2 : 3). Found (%): C, 49.84; H, 3.43; Sb, 13.71. $C_{38}H_{29}ClF_{10}O_3PSb$. Calculated (%): C, 50.04; H, 3.18; Sb, 13.36. IR, ν/cm^{-1}: 550 (P—Ph); 570, 630 (Sb—O); 1080 (C—O); 970, 1090 (C—F); 1150 (P=O).

Adduct of trimethyl(pyrocatecholato-*O,O*)antimony(v) with pyridine oxide (3). A solution of pyridine oxide (0.63 g, 6.0 mmol) and pyrocatechol (0.73 g, 6.0 mmol) in anhydrous benzene (30 mL) was placed into a tube with two side arms. The second tube, containing a solution of *tert*-butyl hydroperoxide (0.54 g, 6.0 mmol) in anhydrous benzene (10 mL), was joined to the first tube. The tubes were degassed and trimethylantimony (1.11 g, 6.0 mmol) was frozen into the first tube. A solution of *tert*-butyl hydroperoxide was slowly added with stirring to the mixture of the reagents in the first tube. After 2 h, volatile products were removed and the solid residue was purified by recrystallization from a 3 : 6 : 1 benzene—hexane—dioxane mixture. Compound **3** was isolated in a yield of 1.65 g (74%), m.p. 110 °C. Found (%): C, 45.49; H, 4.62; Sb, 32.71. $C_{14}H_{18}NO_3Sb$. Calculated (%): C, 45.44; H, 4.87; Sb, 32.93. IR, ν/cm^{-1}: 590, 630 (Sb—O); 1220—1250 (N—O, C—O).

Table 11. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (U_{eq}) for complex **5**

Atom	x	y	z	$U_{eq}/Å^2$	Atom	x	y	z	$U_{eq}/Å^2$
Sb(1)	3022(1)	1728(1)	812(1)	17(1)	C(11)	3864(3)	4242(4)	−1081(2)	31(1)
O(1)	4539(2)	1349(3)	695(1)	27(1)	C(12)	3877(3)	3645(4)	−407(2)	28(1)
O(2)	3374(2)	943(3)	1792(1)	23(1)	C(13)	2472(3)	−339(4)	385(2)	22(1)
O(3)	3782(2)	3959(3)	1255(1)	32(1)	C(14)	3184(3)	−1211(4)	35(2)	29(1)
N(1)	3358(2)	4860(3)	1718(2)	24(1)	C(15)	2873(4)	−2491(5)	−306(2)	38(2)
C(1)	1614(3)	2631(4)	1227(2)	21(1)	C(16)	1851(4)	−2933(5)	−309(2)	43(2)
C(2)	1248(3)	4001(4)	998(2)	22(1)	C(17)	1124(4)	−2082(5)	32(2)	41(2)
C(3)	385(3)	4633(5)	1297(2)	31(1)	C(18)	1435(3)	−789(4)	377(2)	31(1)
C(4)	−132(3)	3887(5)	1817(2)	32(1)	C(19)	3271(3)	6316(4)	1569(2)	33(1)
C(5)	223(3)	2504(5)	2038(2)	30(1)	C(20)	2880(3)	7272(6)	2041(2)	36(1)
C(6)	1086(3)	1871(4)	1743(2)	24(1)	C(21)	2553(3)	6759(4)	2676(2)	34(1)
C(7)	3018(3)	2861(4)	−175(2)	21(1)	C(22)	2625(3)	5257(4)	2817(2)	28(1)
C(8)	2162(3)	2679(4)	−633(2)	22(1)	C(23)	3044(3)	4314(4)	2336(2)	25(1)
C(9)	2150(3)	3269(4)	−1299(2)	30(1)	C(24)	4981(3)	462(8)	1242(2)	60(2)
C(10)	3004(3)	4042(4)	−1519(2)	31(1)	C(25)	4454(3)	726(6)	1908(2)	42(1)

Table 12. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (U_{eq}) for complex **6**

Atom	x	y	z	$U_{eq}/Å^2$	Atom	x	y	z	$U_{eq}/Å^2$
Sb(1)	−3270(1)	2013(1)	−661(1)	39(1)	C(12)	−1535(7)	1828(10)	549(6)	63(2)
P(1)	−2354(2)	4290(2)	−1185(1)	41(1)	C(13)	−4344(8)	3080(12)	53(6)	79(2)
Cl(1)	−4163(1)	383(1)	−497(1)	33(1)	C(14)	−4638(8)	3496(12)	−676(6)	75(2)
O(1)	−3494(5)	2672(7)	180(3)	61(2)	C(15)	−1198(7)	4480(8)	−1141(5)	55(2)
O(2)	−4294(5)	2894(6)	−1129(3)	57(2)	C(16)	−940(10)	5305(11)	−1541(8)	87(3)
O(3)	−2424(4)	3313(5)	−752(3)	44(2)	C(17)	−24(10)	5467(13)	−1485(9)	99(3)
F(2)	−4712(4)	1335(6)	−2149(3)	70(2)	C(18)	571(9)	4824(15)	−1093(12)	120(3)
F(3)	−4543(6)	738(7)	−3369(3)	95(2)	C(19)	340(9)	4022(14)	−708(9)	100(3)
F(4)	−2889(7)	520(7)	−3611(4)	102(2)	C(20)	−575(8)	3827(9)	−746(7)	68(2)
F(5)	−1397(6)	969(8)	−2587(4)	93(2)	C(21)	−2934(7)	4132(7)	−2069(4)	51(2)
F(6)	−1574(4)	1624(6)	−1352(3)	68(2)	C(22)	−3851(7)	4321(9)	−2276(5)	58(2)
F(8)	−2217(7)	−260(5)	−695(5)	98(2)	C(23)	−4334(9)	4110(9)	−2936(6)	78(2)
F(9)	−788(9)	−1166(8)	126(8)	152(3)	C(24)	−3908(11)	3748(9)	−3440(5)	89(3)
F(10)	128(8)	−142(12)	1277(8)	176(3)	C(25)	−2986(10)	3586(11)	−3234(6)	80(3)
F(11)	−319(7)	1871(10)	1574(7)	148(3)	C(26)	−2506(8)	3785(9)	−2565(5)	63(2)
F(12)	−1712(4)	2820(6)	713(3)	71(2)	C(27)	−2764(6)	5423(7)	−838(4)	45(2)
C(1)	−3140(7)	1497(7)	−1680(4)	47(2)	C(28)	−2784(8)	5436(7)	−121(5)	56(2)
C(2)	−3881(7)	1260(8)	−2222(5)	54(2)	C(29)	−3039(8)	6332(10)	146(6)	67(2)
C(3)	−3789(8)	943(8)	−2863(5)	60(2)	C(30)	−3247(9)	7263(9)	−227(6)	68(2)
C(4)	−3000(10)	818(8)	−2981(6)	68(2)	C(31)	−3251(12)	7245(10)	−966(8)	92(3)
C(5)	−2233(8)	1077(9)	−2469(5)	61(2)	C(32)	−3004(10)	6370(8)	−1211(5)	74(2)
C(6)	−2322(7)	1397(7)	−1819(5)	50(2)	C(1S)	−1833(20)	7937(21)	1820(16)	171(3)
C(7)	−2063(6)	1307(7)	−38(5)	50(2)	C(2S)	−1691(17)	7256(20)	2210(12)	174(3)
C(8)	−1787(8)	292(8)	−133(6)	63(2)	C(3S)	−2605(17)	6855(17)	2340(12)	146(3)
C(9)	−1058(10)	−221(10)	279(9)	87(3)	C(4S)	−3333(13)	7372(17)	2067(10)	115(3)
C(10)	−558(12)	338(13)	874(10)	105(3)	C(5S)	−3307(17)	8167(20)	1670(12)	140(3)
C(11)	−810(9)	1325(12)	998(7)	87(3)	C(6S)	−2491(20)	8479(19)	1525(13)	157(3)

Adduct of trimethyl(pyrocatecholato-*O,O*)antimony(v) with pyridine (4) was synthesized analogously from trimethylantimony (0.83 g, 5.0 mmol), triphenylphosphine (1.30 g, 5.0 mmol), pyrocatechol (0.98 g, 5.0 mmol), and *tert*-butyl hydroperoxide (0.9 g, 10 mmol). The resulting compound was recrystallized from a 4 : 8 : 1 : 1 benzene—hexane—dioxane—pyridine mixture. Compound **4** was isolated in a yield of 1.62 g (51%), m.p. 80 °C. Found (%): C, 65.49; H, 5.11; Sb, 13.84. $C_{50}H_{48}NO_4P_2Sb$. Calculated (%): C, 65.95; H, 5.28; Sb, 13.38.

X-ray diffraction studies were carried out on a four-circle Siemens P3/CP diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scanning technique). The structures of complexes **1**—**6** were solved by direct methods and refined by the least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. For complex **3** (the noncentrosymmeric space group), the inverted structure was also refined. The *R* factors for the inverted structure of **3** (0.057 and 0.072) were somewhat larger than those for the noninverted structure (0.054 and 0.067, respectively). The crystals of complexes **1**, **4**, and **6** contain C_6H_6 (**1** and **6**) and Ph_3PO molecules (**4**; two independent molecules per asymmetric unit) of solvation. The positions of the H atoms in complexes **1**, **2**, and **5** (except for H(24a), H(24b) and H(25a), H(25b)) were located from difference electron density syntheses and refined isotropically. The

Table 13. Crystallographic data and details of X-ray diffraction studies for complexes **1**—**6**

Parameter	**1**	**2**	**3**	**4**	**5**	**6**
Molecular formula	$C_{26}H_{25}O_3SSb \cdot C_6H_6$	$2C_{29}H_{24}O_3NSb$	$C_{14}H_{18}O_3NSb$	$C_{14}H_{18}O_2NSb \cdot 2Ph_3PO$	$C_{25}H_{24}O_3NSb$	$C_{32}H_{19}ClF_{10}O_3Sb \cdot C_6H_6$
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	17.808(5)	8.258(3)	10.578(3)	9.284(2)	12.858(9)	15.458(8)
b/Å	9.701(3)	17.320(8)	10.962(3)	11.431(2)	9.003(4)	12.528(3)
c/Å	16.550(6)	18.652(9)	13.426(3)	21.352(4)	19.132(8)	19.888(6)
α/deg		110.67(1)		86.56(3)		
β/deg	101.53(2)	97.78(1)		83.32(3)	92.01(5)	104.60(3)
γ/deg		95.62(1)		88.89(3)		
V/Å^3	2801(1)	2442(2)	1557(1)	2246(1)	2213(2)	3727(2)
d_{calc}/g cm^{-3}	1.464	1.513	1.579	1.346	1.525	1.618
Z	4	4	4	2	4	4
μ/cm^{-1}	10.90	11.64	17.84	7.29	12.72	9.42
θ/2θ scanning range/deg	2.0—54.0	2.0—46.0	2.0—58.0	5.0—52.0	2.0—48.0	2.0—60.0
Number of measured reflections	6380	6951	3064	8433	3272	7438
Number of reflections with $I > 3\sigma(I)$	4846	4893 ($I > 2\sigma(I)$)	2131	6320	2637	4822
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.002F^2$	$w^{-1} = \sigma^2(F) + 0.0005F^2$	$w^{-1} = \sigma^2(F) + 0.002F^2$	$w^{-1} = \sigma^2(F) + 0.002F^2$	$w^{-1} = \sigma^2(F) + 0.001F^2$	$w^{-1} = \sigma^2(F) + 0.015F^2$
R	0.036	0.039	0.054	0.049	0.030	0.091
R_w	0.047	0.044	0.067	0.066	0.037	0.122

H atoms in complexes **3**, **4**, and **6** were placed in geometrically calculated positions and refined isotropically using the riding model. The H atoms of the methyl groups in complexes **3** and **4**, the H atoms of the benzene molecule of solvation in complex **6**, and the H(24a), H(24b), H(25a), and H(25b) atoms in complex **5** were refined with fixed thermal parameters U_{iso} equal to 0.08 Å^2. The remaining H atoms in complexes **3**, **4**, and **6** were refined with variable U_{iso}.

All crystallographic calculations were performed on a PC computer using the SHELXTL PLUS program package.[20] The selected bond lengths and bond angles in complexes **1**—**6** are given in Tables 1—6, respectively. The atomic coordinates and equivalent isotropic factors are listed in Tables 7—12. The selected crystallographic characteristics and details of X-ray diffraction studies are given in Table 13.

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