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COORDINATION COMPOUNDS

6,6,6-Trifluoro-3-hexanone-5,5-diolatotriphenylantimony: Synthesis and Structure

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Abstract—6,6,6-Trifluoro-3-hexanone-5,5-diolatotriphenylantimony, $Ph_3SbO_2C(CF_3)CH_2C(O)CMe_3$, was synthesized by reacting triphenylantimony with 6,6,6-trifluoro-2,2-dimethylhexanedione-3,5 in the presence of hydrogen peroxide in diethyl ether. According to X-ray diffraction, the antimony atom in the complex has a distorted octahedral coordination. Sb–C distances are within 2.123(4)–2.131(4) Å. Sb–O(1,2,3) bond lengths are 2.052(2), 2.047(3) and 2.669(2) Å, respectively.

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The synthesis and structure of diolato triarylantimony complexes where diolate ligands are fluoro derivatives of butanedione-1,3 and pentanedione-2,4 are described in [1–4]. In this work, we synthesized 6,6,6-trifluoro-3-hexanone-5,5-diolatotriphenylantimony $Ph_3SbO_2C(CF_3)CH_2C(O)CMe_3$ (**I**) from triphenylantimony and 6,6,6-trifluorohexanedione-3,5 in the presence of hydrogen peroxide and studied its structure.

EXPERIMENTAL

Synthesis of complex I. To a solution of 0.09 g (0.26 mmol) triphenylantimony in 10 mL of diethyl ether at 20°C, added were 0.07 g (0.26 mmol) 6,6,6-trifluorohexanedione-3,5 in 10 mL of diethyl ether and 0.03 mL (0.26 mmol) of 31% aqueous hydrogen peroxide. After 24 h, the solvent was removed and the residue was recrystallized from heptane. Water-colored crystals were obtained (0.10 g; 59%) with $T_m = 113°C$. IR spectrum (ν, cm^{-1}): 1685 vs, 1440 m, 1150 vs, 1070 vs, 1000 m.

For $C_{32}H_{24}O_3F_3Sb$, anal. calcd., %: C, 60.47; H, 3.78.

Found, %: C, 60.05; H, 3.98.

IR spectrum was recorded as a KBr pellet on an FSM 1201 Fourier-transform spectrometer.

Single-crystal X-ray diffraction experiment for complex **I** was carried out on a Bruker SMART-1000 CCD diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator).

The structure was solved by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms (SHELX-97) [8]. The hydrogen atoms were calculated geometrically and included into the refinement in the riding model.

SMART and SAINT Plus software [5] was used in data collection and editing and the refinement of unit cell parameters. The SHELXTL/PC program package [6] was used in all calculations in the structure solution and refinement.

Selected crystallographic parameters and the results of structure refinement for complex **I** are listed in Table 1, atomic coordinates and thermal parameters are in Table 2, and selected bond lengths and bond angles in Table 3.

RESULTS AND DISCUSSION

6,6,6-Trifluorohexanedione-3,5 reacts with triphenylantimony in the presence of *tert*-butyl hydroperoxide in toluene to yield a diolate complex in 85% yield [1]. We found that this reaction also occurs in the presence of hydrogen peroxide; in this case, however, the yield of complex **I** is lower (59%).

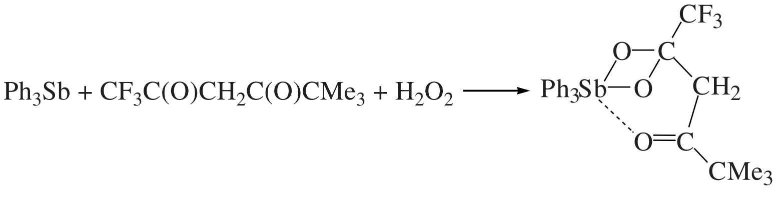


Table 1. Crystal data and the parameters of X-ray diffraction experiment and structure refinement for complex **I**

Parameter	Quantity
FW	565.22
T, K	298(2)
Crystal system	Trigonal
Space group	$P\bar{1}$
a, Å	9.964(3)
b, Å	10.521(3)
c, Å	12.691(4)
α, deg	83.055(4)
β, deg	74.233(4)
γ, deg	77.070(4)
V, Å^3	1245.3(6)
Z	2
ρ_{calcd}, g/cm^3	1.507
μ, mm^{-1}	1.154
F(000)	568
Crystal habit (size, mm)	Prism (0.38 × 0.24 × 0.21)
θ range, deg	3.69–28.44
Index ranges	$-13 \le h \le 13, -14 \le k \le 14,$ $-17 \le l \le 16$
Measured reflections	15037
Unique reflections	6022 ($R_{int} = 0.0535$)
Reflections with $I > 2\sigma(I)$	4670
Refinement variables	347
GOOF	1.069
R for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0576$, $wR_2 = 0.1394$
R for all reflections	$R_1 = 0.0814$, $wR_2 = 0.1576$
Residual electron density (min/max), e/Å^3	–1.320/2.300

Table 2. Atomic coordinates (×10^4) and their isotropic equivalent thermal parameters (×10^3) in the structure of complex **I**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Sb	2062.9(2)	2964.3(2)	2298.0(2)	32.35(6)
F(1)	4067(3)	4862(3)	4429(3)	84.9(9)
F(2)	2290(3)	4231(3)	5593(2)	73.4(9)
F(3)	3878(3)	2865(3)	4577(2)	76.1(9)
O(1)	1369(2)	3512(2)	3884(2)	35.8(6)
O(2)	3235(2)	4131(2)	2677(2)	38.5(6)
O(3)	629(3)	5430(2)	2253(2)	41.8(6)
C(1)	3144(4)	4073(4)	4576(3)	52(1)
C(2)	2284(3)	4389(4)	3708(3)	38.8(8)
C(3)	1513(4)	5809(4)	3733(3)	40.4(8)
C(4)	804(4)	6218(3)	2808(3)	38.2(8)
C(5)	304(4)	7696(4)	2552(3)	44.8(9)
C(6)	1565(6)	8177(5)	1791(5)	85(2)
C(7)	–896(6)	7880(6)	1966(6)	109(2)
C(8)	–222(8)	8467(5)	3574(5)	98(2)
C(21)	35(3)	2565(3)	2368(3)	34.8(8)
C(22)	–1131(4)	2920(4)	3234(3)	48(1)
C(23)	–2419(5)	2640(5)	3274(4)	64(1)
C(24)	–2600(4)	2018(5)	2437(4)	65(1)
C(25)	–1453(5)	1661(4)	1572(4)	66(1)
C(26)	–122(4)	1924(4)	1529(3)	46.8(9)
C(31)	2824(4)	3534(3)	611(3)	34.4(8)
C(32)	1886(4)	4036(4)	–38(3)	44(1)
C(33)	2391(5)	4503(4)	–1112(3)	55(1)
C(34)	3818(5)	4479(4)	–1533(3)	56(1)
C(35)	4753(5)	3987(4)	–893(3)	52(1)
C(36)	4260(4)	3505(4)	179(3)	43.5(9)
C(41)	3314(4)	1091(4)	2551(3)	41.4(9)
C(42)	3151(7)	509(5)	3599(4)	80(2)
C(43)	3979(7)	–692(5)	3791(5)	91(2)
C(44)	4939(6)	–1334(5)	2937(5)	77(2)
C(45)	5080(5)	–797(4)	1896(4)	64(1)
C(46)	4287(5)	428(4)	1682(3)	51(1)

The IR spectrum of complex **I** contains a strong absorption band (1685 cm^{-1}) in the region of the stretching vibrations of carbonyl groups, as the IR spectra of known diolate complexes [1–4].

According to X-ray diffraction, an antimony atom in crystals of complex **I** is bonded with three phenyl groups and with the diketonate ligand via two oxygen atoms (figure). The Sb...O(3) distance (2.669(2) Å) is far smaller than the sum of the van der Waals radii of Sb and O atoms (3.70 Å [7]). This points to the donor–acceptor interaction of the carbonyl oxygen atom O(3) with the central atom, whose coordination number increases to six. A distorted octahedron, which can fit the coordination polyhedron around the antimony atom in complex **I**, has the O(3) carbonyl oxygen atom and the C(41) phenyl atom in axial positions (the angle O(3)SbC(41) is 170.5(1)°) and the O(1) and O(2) diolate atoms and the C(21)and C(31) phenyl atoms in equatorial positions (the angle sum in the equatorial plane is 348.7(1)°). The C(21)C(31)O(1)O(2) fragment is planar. The antimony atom is displaced from this plane toward the C(41) atom. The C(41)SbC(21), C(41)SbC(31), C(41)SbO(1), and C(41)SbO(2) bond angles are, respectively, 103.7(1), 105.6(1), 99.5(1), and 100.4(1)°; that is, they exceed 90°, which is characteristic of a regular octahedron. A similar distorted octahedral coordination of an antimony(V) atom, with close angles, was observed for 5,5,5-trifluoro-2-pentanone-4,4-diolatotriphenylantimony $Ph_3SbO_2C(CF_3)CH_2C(O)Me$ (**II**) [1], 5,5,5-trifluoro-2-pentatanone-4,4-diolato-tris(*p*-chlorophenyl)antimony (p-$ClC_6H_4)_3SbO_2C(CF_3)CH_2C(O)Me$ (**III**) [2], and 4,4,4-trifluoro-1-phenyl-1-butanone-3,3-diolato-tris(*p*-tolyl)antimony (p-$MeC_6H_4)_3SbO_2C(CF_3)CH_2C(O)Ph$ (**IV**) [3, 4].

The Sb–C(Ph) bond lengths in complex **I** (2.123(4), 2.129(3), and 2.131(4) Å; Table 3) are close to the respective bond lengths: Sb–C(Ph) (2.117–2.137 Å) in complex Sb–C(p-ClC_6H_4) (2.107–2.142 Å) in complex **III**, and Sb–C(p-MeC_6H_4) (2.113–2.137 Å) in complex **IV**. Distances from the antimony atom to diolate oxygen atoms (Sb–O(1,2), 2.052(2) and 2.047(3) Å) are equalized, as in complex **III** (2.032 and 2.036 Å) and complex *IV* (2.042 and 2.051 Å). In complex **II**, these bonds are noticeably differentiated (2.029 and 2.058 Å). In all compounds, Sb–O bond lengths do not exceed the sum of the covalent radii of Sb and O atoms (2.07 Å [7]). The C(2)–O(1) and C(2)–O(2) distances in complex **I** are also close to each other (1.396(4) and 1.408(4) Å) and are smaller than the average O–C(sp^3) bond length, which is 1.426 Å [8]. The respective bond lengths in complexes **II**, **III**, and **IV** are 1.397, 1.405; 1.403, 1.432; and 1.398, 1.405 Å.

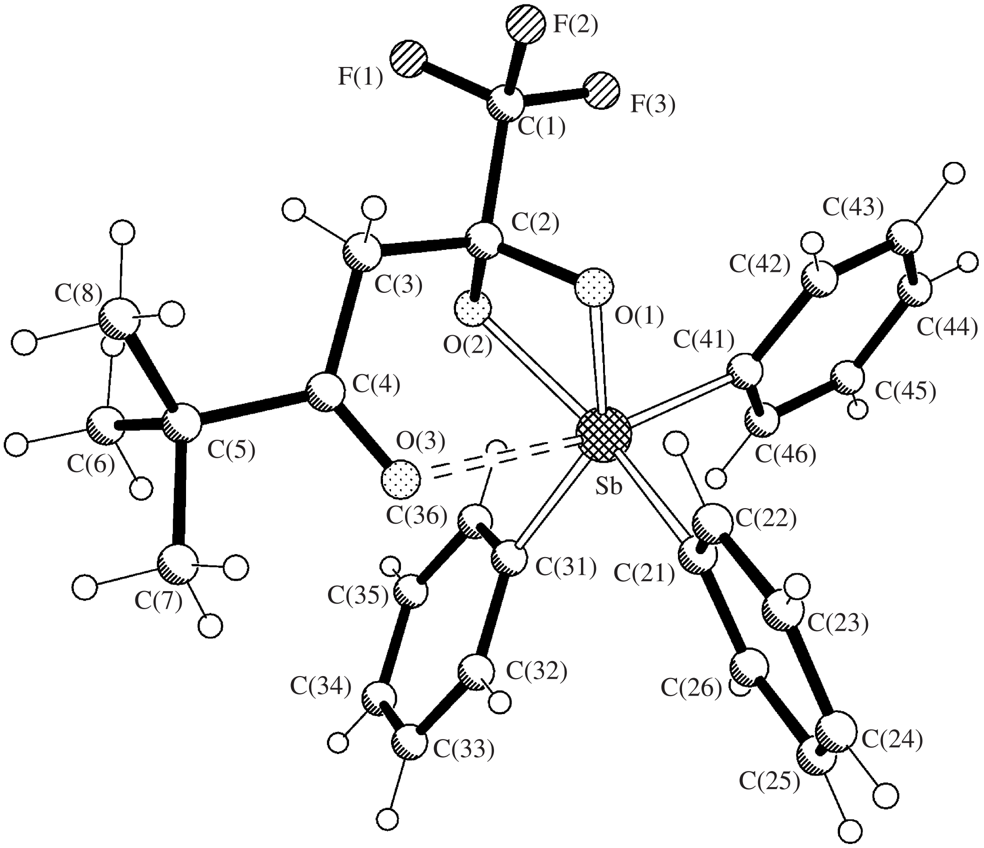
In the diketonate group of complex **I**, distances C(1)–C(2) (1.534(5) Å), C(2)–C(3) (1.519(5) Å), and C(3)–C(4) (1.502(5) Å) are close to the average lengths of C(sp^3)–C(sp^3) and C(sp^3)–C(sp^2) bonds in organic compounds (1.530 and 1.511 Å, respectively) [8]. However, the C(4)–C(5) distance in complex *I* (1.546(5) Å) far exceeds the average value (1.511 Å).

Table 3. Selected bond lengths and bond angles in the structure of complex **I**

Bond	*d*, Å	Angle	ω, deg
Sb–O(2)	2.047(3)	O(2)SbO(1)	65.98(9)
Sb–O(1)	2.052(2)	O(2)SbC(41)	100.4(1)
Sb–C(41)	2.123(4)	O(1)SbC(41)	99.5(1)
Sb–C(31)	2.129(3)	O(2)SbC(31)	88.8(1)
Sb–C(21)	2.131(4)	O(1)SbC(31)	147.2(1)
Sb–C(2)	2.551(4)	C(41)SbC(31)	105.6(1)
Sb–O(3)	2.669(2)	O(2)SbC(21)	149.1(1)
F(1)–C(1)	1.335(5)	O(1)SbC(21)	91.1(1)
F(2)–C(1)	1.345(4)	C(41)SbC(21)	103.7(1)
F(3)–C(1)	1.317(5)	C(31)SbC(21)	102.8(1)
O(1)–C(2)	1.396(4)	O(2)SbO(3)	71.75(9)
O(2)–C(2)	1.408(4)		
O(3)–C(4)	1.219(5)		
C(1)–C(2)	1.534(5)		
C(2)–C(3)	1.519(5)		
C(3)–C(4)	1.502(5)		

The C(4)–O(3) bond length (1.219(5) Å) in the carbonyl group of complex **I**, as the relevant distances in complexes **II** (1.230 Å), **III** (1.214 Å), and **IV** (1.228 Å), is close to the length of C=O double bonds in ketones (1.210 Å [8]). Thus, the involvement of the carbonyl oxygen atom in the intermolecular interaction with the central atom does not considerably affect the bond length in the carbonyl group. The observed Sb···O=C distances in complexes **I**, **II**, **III**, and **IV** are 2.669, 2.705, 2.534, and 2.568 Å, respectively; therefore, we can state the absence of the expected correlation between the strength of the intermolecular contact and the C=O bond length.

A certain role in generating the intermolecular contact Sb···O=C is played by electronic factors, in particular, the nature of substituents at the antimony atom and the donor properties of the extra coordinated fragment. The shortest Sb···O=C distance (2.534 Å) in complex **III** can be assigned to enhancement of the acceptor properties of the antimony atom as a result of the negative inductive effect of chlorine atoms in aryl groups. The strengthening of this contact in complex **I** relative



Molecular structure of 6,6,6-trifluoro-3-hexanone-5,5-diolatotriphenylantimony.

to complex *II* likely arises from the positive inductive effect of the *tert*-butyl radical and the associated enhancement of the donor properties of the carbonyl oxygen atom.

Molecules of complex **I** in crystals are associated into centrosymmetric dimers via weak hydrogen bonds between the O(1) and H(3A)C(3) atoms of neighboring molecules. The O···H distance (2.61 Å) is slightly smaller than the sum of the van der Waals radii of O and H atoms (2.70 Å [7]), but far larger than the typical length of strong hydrogen bonds O···H–C (less than 2.1 Å). Angle O(1)···H(3A)–C(3) in complex *I* (171°) is close to 180°. Notably, similar pseudodimers exist in crystals of complex **II**, whereas complexes **III** and **IV** in crystals are monomeric.

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