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Crystal structure of 12-chloro-5,6,7,12-tetrahydrodibenzo[*c,f*][1,5]oxastibocine, C₁₄H₁₂ClOSb

Table 1: Data collection and handling.

Crystal:	Prismatic, colorless
Size:	0.165 × 0.113 × 0.045 mm
Wavelength:	Mo K α radiation ($\lambda = 0.71073$ Å)
μ :	2.315 mm ^{−1}
Diffractometer, scan mode:	SMART, ϕ and ω -scans
2 $\theta_{\max}$, completeness:	25.5°, 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6765, 4729, 0.0328
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3750
$N(\text{param})_{\text{refined}}$:	308
Programs:	Bruker programs [1], SADABS [2], ShelX [3], Diamond [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Sb1	−0.00143(6)	0.28609(5)	0.04207(4)	0.0370(2)
Sb2	0.49536(6)	0.20953(5)	0.43228(4)	0.0392(2)
Cl1	0.2035(4)	0.2650(3)	−0.0746(3)	0.0889(10)
Cl2	0.7003(4)	0.1638(3)	0.5399(2)	0.0751(8)
O1	−0.1087(8)	0.3360(7)	0.2035(6)	0.0646(19)
O2	0.3977(9)	0.2968(8)	0.2857(6)	0.076(2)
C1	0.0568(14)	0.1722(11)	0.1628(11)	0.076(3)
C2	0.1189(16)	0.0745(14)	0.1360(13)	0.093(4)
H2	0.1457	0.0629	0.0702	0.112
C3	0.1381(17)	−0.0049(16)	0.2147(14)	0.109(5)
H3	0.1759	−0.0716	0.1988	0.131
C4	0.1040(19)	0.0112(17)	0.3124(15)	0.120(5)
H4	0.1217	−0.0398	0.3632	0.144
C5	0.0405(14)	0.1098(13)	0.3322(12)	0.095(4)
H5	0.0100	0.1202	0.3973	0.115
C6	0.0220(13)	0.1897(12)	0.2609(10)	0.070(3)
C7	−0.0418(14)	0.2965(13)	0.2893(9)	0.076(4)
H7A	−0.1171	0.2669	0.3409	0.092
H7B	0.0382	0.3692	0.3167	0.092
C8	−0.0818(12)	0.4702(10)	0.2013(9)	0.060(3)
H8A	−0.0994	0.5013	0.2671	0.073
H8B	−0.1501	0.4896	0.1535	0.073
C9	0.0786(12)	0.5352(10)	0.1711(8)	0.060(3)
C10	0.1646(16)	0.6527(12)	0.2178(10)	0.085(4)
H10	0.1233	0.6877	0.2698	0.102
C11	0.3085(14)	0.7149(11)	0.1867(11)	0.081(4)
H11	0.3637	0.7936	0.2150	0.097
C12	0.3723(13)	0.6551(11)	0.1086(10)	0.077(4)
H12	0.4690	0.6972	0.0861	0.092
C13	0.2929(11)	0.5372(10)	0.0668(9)	0.063(3)
H13	0.3363	0.4978	0.0188	0.075
C14	0.1438(12)	0.4780(10)	0.0991(8)	0.059(3)

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Abstract

C₁₄H₁₂ClOSb, triclinic, $P\bar{1}$ (no. 2), $a = 9.3453(14)$ Å, $b = 10.9826(16)$ Å, $c = 13.303(2)$ Å, $\alpha = 90.823(3)^\circ$, $\beta = 90.394(3)^\circ$, $\gamma = 108.307(2)^\circ$, $V = 1296.0(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0587$, $wR(F^2) = 0.1767$, $T = 293(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Bis(2-bromobenzyl) ether (3.65 g, 10.0 mmol) was dissolved in dried ethyl ether (100 mL), and 8.8 mL (22 mmol, 2.5 M in hexane) of *n*-butyllithium was added dropwise to the solution at -30 °C. The obtained mixture was stirred at -30 °C for 0.5 h, and subsequently stirred at room temperature for 3 h, then a solution of SbCl₃ (2.39 g, 10.5 mmol) in dried

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C15	0.5707(12)	0.1309(11)	0.2959(9)	0.062(3)
C16	0.6296(14)	0.0297(12)	0.3006(9)	0.075(3)
H16	0.6425	−0.0027	0.3631	0.090
C17	0.6689(14)	−0.0235(13)	0.2164(10)	0.083(4)
H17	0.7150	−0.0870	0.2206	0.099
C18	0.6376(16)	0.0208(15)	0.1230(13)	0.101(5)
H18	0.6630	−0.0141	0.0643	0.121
C19	0.5710(16)	0.1132(15)	0.1169(10)	0.097(4)
H19	0.5465	0.1372	0.0539	0.117
C20	0.5376(13)	0.1745(12)	0.2037(8)	0.068(3)
C21	0.4792(13)	0.2866(13)	0.1952(9)	0.074(3)
H21A	0.5625	0.3647	0.1867	0.088
H21B	0.4128	0.2747	0.1370	0.088
C22	0.4120(14)	0.4272(13)	0.3121(11)	0.084(4)
H22A	0.3336	0.4295	0.3588	0.101
H22B	0.4012	0.4735	0.2525	0.101
C23	0.5676(13)	0.4902(12)	0.3608(9)	0.069(3)
C24	0.6434(16)	0.6210(12)	0.3462(11)	0.092(4)
H24	0.5994	0.6691	0.3068	0.110
C25	0.7833(17)	0.6785(14)	0.3904(12)	0.099(4)
H25	0.8341	0.7648	0.3798	0.119
C26	0.8500(16)	0.6044(14)	0.4530(10)	0.088(4)
H26	0.9422	0.6429	0.4851	0.105
C27	0.7742(14)	0.4735(12)	0.4647(9)	0.076(3)
H27	0.8179	0.4247	0.5037	0.091
C28	0.6314(14)	0.4140(12)	0.4179(8)	0.069(3)

ethyl ether (50 mL) was added at -78°C . The resulting mixture was gradually warmed to room temperature and then stirred for 6 h at room temperature. After removal of solvent under vacuum and toluene extraction, the undissolved material was filtered out, and the organic layer washed with brine and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2 /hexane to give the title compound as colorless crystals. ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 4.79 (2H, d, J = 13.6 Hz), 5.20 (2H, d, J = 13.6 Hz), 7.14 (2H, d, J = 7.6 Hz), 7.30 (2H, t, J = 7.6 Hz), 7.41 (2H, t, J = 7.2 Hz), 8.16 (2H, d, J = 7.2 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz, TMS): δ = 75.33, 124.44, 128.83, 129.28, 134.32, 139.63, 141.21 ppm.

Experimental details

All H atoms were generated geometrically and refined using the riding model, with C–H = 0.93 Å for aryl and 0.97 Å for methylene H atoms, respectively. $U_{iso}(\text{H})$ set to $1.2U_{eq}(\text{C})$ for all H atoms.

Comment

Hypervalent organoantimony compounds with intramolecular N, O, S $\rightarrow$ Sb coordinations have received much attention due to their novel structure chemistry and use in the fields of

organic synthesis, catalysis and medicine [5, 6]. Most of these compounds have C, E or E, C, E and C, E, C-chelating aryl ligands (E = N, O, S) such as 2-(Me_2NCH_2) C_6H_4 [7], 2,6-(Me_2NCH_2) C_6H_3 [8], 2,6-(ROCH_2) C_6H_3 (R = Me, t-Bu) [9], $\text{PhN}(\text{CH}_2\text{C}_6\text{H}_4)_2$ [10] and $\text{E}(\text{CH}_2\text{C}_6\text{H}_4)_2$ (E = O, S) [11], which are usually used to enhance the stability of the organoantimony compounds. Among these compounds, those with intramolecular N $\rightarrow$ Sb coordinations are intensively investigated, while those with O, S $\rightarrow$ Sb intramolecular interactions are somewhat rarely reported [5, 6].

In the title structure there are two independent molecules in the asymmetric unit. The geometrical parameters of the two independent molecules are very similar. Consequently, we describe only the one shown in the figure in detail. The geometry around the central Sb atom can be described as a distorted *pseudo*-trigonal bipyramid, where both the C(1) and C(14) atoms occupy the equatorial positions along with a lone electron pair of antimony, while the O(1) and Cl(1) atoms exist at the apical positions. The Sb(1)–C(1) and Sb(1)–C(14) distances are 2.216(12) and 2.237(11) Å, respectively. The C(1)–Sb(1)–C(14) angle is $96.5(4)^\circ$ while the O(1)–Sb(1)–Cl(1) angle is $156.06(18)^\circ$ (rather than 180°). The Sb(1)–O(1) bond lengths (2.502(8) Å) is shorter than that [range of Sb–O bond lengths: 2.523(2)–2.691(13) Å] in organoantimony dichlorides [2,6-(ROCH_2) C_6H_3]SbCl₂ (R = Me, t-Bu) [9], which suggests a stronger Sb–O interaction than had been found in the latter, and slightly longer than that (2.425(2) Å) in the analogous organoantimony chloride ($\text{C}_6\text{H}_4\text{CH}_2\text{OCH}_2\text{C}_{10}\text{H}_6$)SbCl [11], indicating that the O $\rightarrow$ Sb coordination of the latter is slightly stronger than that of the former.

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