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Crystal structure of bis{5*H*-dibenzo[*c,f*][1,5]oxabismocin-12(7*H*)-yl} carbonate, C₂₉H₂₄O₅Bi₂

Table 1: Data collection and handling.

Crystal:	Needle, colorless
Size:	0.20 × 0.05 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	13.79 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
$\theta_{\max}$, completeness:	27.6°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	26160, 5903, 0.047
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4612
$N(\text{param})_{\text{refined}}$:	325
Programs:	Bruker programs [1], SHELX [2, 3], OLEX2 [4]

<https://doi.org/10.1515/ncrs-2018-0067>

Received March 20, 2018; accepted July 11, 2018; available online July 20, 2018

Abstract

C₂₉H₂₄O₅Bi₂, orthorhombic, *Pbca* (no. 61), $a = 14.8835(6)$ Å, $b = 14.5551(6)$ Å, $c = 23.6000(9)$ Å, $V = 5112.5(4)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0293$, $wR(F^2) = 0.0579$, $T = 296(2)$ K.

CCDC no.: 1830566

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

The compound O(CH₂C₆H₄)₂BiCl is easily available by a literature known synthesis [5]. To a solution of O(CH₂C₆H₄)₂BiCl (0.221 g, 0.5 mmol) in 20 mL CH₂Cl₂, a solution of Na₂CO₃ (0.053 g, 0.5 mmol) in 10 mL distilled water was added. The mixture was stirred at room temperature for 48 h and then filtered. The organic layer was separated, washed with water and dried over anhydrous Na₂SO₄. After filtered,

removal of the solvent in vacuum gave the compound [O(CH₂C₆H₄)₂Bi]₂CO₃. Crystals suitable for X-ray diffraction analysis were obtained by crystallization of the compound [O(CH₂C₆H₄)₂Bi]₂CO₃ from CH₂Cl₂/*n*-hexane solution. ¹H NMR (400 MHz, CDCl₃, TMS): $\delta = 8.39$ (4H, d, $J = 7.6$ Hz), 7.53 (4H, t, $J = 7.2$ Hz), 7.41 (4H, d, $J = 7.6$ Hz), 7.24 (4H, t, $J = 7.2$ Hz), 5.22 (4H, d, $J = 13.6$ Hz), 4.81 (4H, d, $J = 13.6$ Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz, TMS): $\delta = 180.78$, 145.09, 137.05, 131.18, 127.62, 127.14, 77.93 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. $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$ for all H atoms.

Comment

The organobismuth compounds with intramolecular N, O, S→Bi interactions have received an increased interest in recent years because of their structure, chemistry and applications in areas such as organic synthesis, catalysis and medicine [5–11]. To our best knowledge, only the molecular structure of a few organobismuth carbonates having intramolecular N, O, S→Bi coordination, i.e. {[2-(Me₂NCH₂)C₆H₄]₂Bi]₂CO₃ [7], [2,6-(Me₂NCH₂)C₆H₃]₂BiCO₃ [8], [t-BuN(CH₂C₆H₄)₂Bi]₂CO₃ [9] and {[2-(Et₂NCH₂)C₆H₄]₂Bi]₂CO₃ [10] are reported. We herein report the crystal structure of a hypervalent organobismuth carbonate with secondary intramolecular O→Bi interactions.

The asymmetric unit contains one complete molecule (*cf.* the figure). In the molecular structure

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Bi1	0.06543(2)	0.38323(2)	0.19024(2)	0.03238(6)
Bi2	0.37560(2)	0.41277(2)	0.04612(2)	0.02673(6)
O1	−0.0294(3)	0.3363(3)	0.27755(15)	0.0462(10)
O2	0.5297(2)	0.3920(2)	−0.00571(14)	0.0312(8)
O3	0.1127(2)	0.3590(2)	0.10238(14)	0.0335(8)
O4	0.2438(3)	0.3970(3)	0.14066(16)	0.0471(10)
O5	0.2322(2)	0.3700(2)	0.04798(14)	0.0354(8)
C1	0.1049(3)	0.2407(3)	0.2164(2)	0.0311(11)
C2	0.1554(4)	0.1831(4)	0.1818(2)	0.0365(12)
H2	0.177113	0.204335	0.147246	0.044*
C3	0.1736(4)	0.0930(4)	0.1993(3)	0.0516(16)
H3	0.208004	0.054509	0.176617	0.062*
C4	0.1405(4)	0.0618(4)	0.2498(3)	0.0555(18)
H4	0.151279	0.001483	0.260864	0.067*
C5	0.0914(4)	0.1190(5)	0.2846(3)	0.0551(17)
H5	0.069246	0.096918	0.318788	0.066*
C6	0.0748(3)	0.2099(4)	0.2687(2)	0.0379(13)
C7	0.0279(4)	0.2759(5)	0.3076(2)	0.0534(16)
H7A	−0.007187	0.241588	0.335039	0.064*
H7B	0.072337	0.311436	0.328129	0.064*
C8	−0.0698(3)	0.3363(3)	0.1599(2)	0.0304(11)
C9	−0.0940(3)	0.3384(3)	0.1030(2)	0.0331(11)
H9	−0.054570	0.362955	0.076502	0.040*
C10	−0.1759(4)	0.3044(4)	0.0855(2)	0.0417(13)
H10	−0.191417	0.306717	0.047382	0.050*
C11	−0.2347(4)	0.2672(4)	0.1241(2)	0.0450(11)
H11	−0.289236	0.243086	0.111902	0.054*
C12	−0.2128(4)	0.2657(4)	0.1805(3)	0.0442(11)
H12	−0.252618	0.240243	0.206553	0.053*
C13	−0.1314(3)	0.3020(3)	0.1991(2)	0.0320(11)
C14	−0.1123(4)	0.2940(5)	0.2613(3)	0.0564(17)
H14A	−0.161054	0.322345	0.282275	0.068*
H14B	−0.110482	0.229505	0.271599	0.068*
C21	0.3572(3)	0.4292(3)	−0.0476(2)	0.0270(11)
C22	0.2797(4)	0.4695(3)	−0.0683(2)	0.0353(12)
H22	0.232265	0.482187	−0.043877	0.042*
C23	0.2724(4)	0.4909(4)	−0.1254(2)	0.0427(14)
H23	0.219715	0.517049	−0.139183	0.051*
C24	0.3428(4)	0.4738(4)	−0.1617(2)	0.0463(14)
H24	0.337476	0.487782	−0.200011	0.056*
C25	0.4217(4)	0.4357(4)	−0.1412(2)	0.0414(13)
H25	0.469902	0.425633	−0.165524	0.050*
C26	0.4287(3)	0.4126(3)	−0.0843(2)	0.0292(11)
C27	0.5127(3)	0.3656(3)	−0.0636(2)	0.0307(11)
H27A	0.505372	0.299497	−0.066005	0.037*
H27B	0.563259	0.383007	−0.087246	0.037*
C28	0.4202(3)	0.2653(3)	0.0511(2)	0.0312(11)
C29	0.3620(4)	0.1950(4)	0.0679(2)	0.0415(13)
H29	0.302209	0.208199	0.075943	0.050*
C30	0.3933(5)	0.1062(4)	0.0724(3)	0.0588(18)
H30	0.354547	0.059639	0.083874	0.071*
C31	0.4812(6)	0.0861(4)	0.0602(3)	0.064(2)
H31	0.501592	0.025936	0.063133	0.077*

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C32	0.5396(4)	0.1545(4)	0.0436(2)	0.0473(15)
H32	0.598775	0.140080	0.034597	0.057*
C33	0.5103(4)	0.2445(4)	0.0402(2)	0.0336(11)
C34	0.5747(3)	0.3209(4)	0.0253(2)	0.0392(13)
H34A	0.600084	0.346395	0.059767	0.047*
H34B	0.623578	0.296462	0.002679	0.047*
C40	0.1985(3)	0.3759(3)	0.0986(2)	0.0296(11)

of organobismuth carbonate [O(CH₂C₆H₄)₂Bi]₂CO₃, the planar CO₃ group attached to the two 5,6,7,12-tetrahydrodibenz[*c,f*][1,5]oxabismocine framework by the two covalent bismuth-oxygen bonds [Bi(1)–O(3) 2.217(3), Bi(2)–O(5) 2.223(3) Å], which are shorter than those [range of Bi–O bond lengths: 2.238(4)–2.444(8) Å] in {[2-(Me₂NCH₂)C₆H₄]₂Bi]₂CO₃ [7], [2,6-(Me₂NCH₂)C₆H₃]BiCO₃ [8], [t-BuN(CH₂C₆H₄)₂Bi]₂CO₃ [9] and {[2-(Et₂NCH₂)C₆H₄]₂Bi]₂CO₃ [10]. Furthermore, the Bi(1)–O(1) and Bi(2)–O(2) distances [2.587(4) and 2.618(3) Å] in the title compound are longer than that of the organobismuth cation, halide and nitrate with same framework, i.e. [O(CH₂C₆H₄)₂Bi(OH₂)]⁺[SO₃CF₃][−] (2.417(7) Å) [5], O(CH₂C₆H₄)₂BiCl (2.543(6) Å) [11] and [(CH₂C₆H₄)₂Bi]NO₃ (2.508(2) Å) [11], indicating that the O→Bi coordination of the latter is slightly stronger than that of the former.

Acknowledgements: The work was supported by the Scientific Research Fund of Hunan Province Education Department (Nos. 15A041 and 11C0331), and 2016 Talent Research Startup Fund of Hunan Institute of Engineering (No. 16RC001).

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