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Crystal structure of 5*H*-dibenzo[*c,f*][1,5]oxabismocin-12 (7*H*)-yl acetate, C₁₆H₁₅O₃Bi

Table 1: Data collection and handling.

Crystal:	Rodlike, colorless
Size:	0.24 × 0.12 × 0.06 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	12.14 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	26.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13322, 2925, 0.041
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2697
$N(\text{param})_{\text{refined}}$:	182
Programs:	Bruker programs [1], SHELX [2, 3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.19495(2)	0.84302(5)	0.52398(4)	0.03465(13)
O1	0.2919(4)	0.8698(13)	0.4138(5)	0.0419(18)
O2	0.1217(4)	0.5831(17)	0.6013(4)	0.0406(16)
O3	0.1697(6)	0.8829(19)	0.6841(5)	0.067(2)
C1	0.3029(5)	0.6053(18)	0.5549(6)	0.030(2)
C2	0.3087(5)	0.412(2)	0.6147(6)	0.033(2)
H2	0.264774	0.365076	0.642290	0.040*
C3	0.3789(6)	0.291(2)	0.6330(5)	0.042(2)
H3	0.381799	0.158334	0.671582	0.050*
C4	0.4455(7)	0.3676(19)	0.5935(6)	0.046(3)
H4	0.493171	0.291307	0.606891	0.056*
C5	0.4407(5)	0.5556(19)	0.5348(8)	0.041(2)
H5	0.485423	0.602972	0.508533	0.049*
C6	0.3711(5)	0.6765(14)	0.5139(7)	0.035(3)
C7	0.3650(7)	0.8847(19)	0.4500(6)	0.043(2)
H7A	0.372842	1.074555	0.469253	0.052*
H7B	0.405524	0.846185	0.413675	0.052*
C8	0.1573(6)	0.5423(18)	0.4330(5)	0.032(2)
C9	0.0858(5)	0.409(2)	0.4351(5)	0.0344(19)
H9	0.053677	0.435516	0.476480	0.041*
C10	0.0612(6)	0.237(2)	0.3761(7)	0.046(2)
H10	0.013386	0.147559	0.378420	0.055*
C11	0.1078(7)	0.202(2)	0.3152(7)	0.052(3)
H11	0.091405	0.086759	0.276026	0.063*
C12	0.1779(7)	0.3331(19)	0.3104(6)	0.045(3)
H12	0.208435	0.310523	0.267721	0.054*
C13	0.2037(5)	0.5025(18)	0.3705(6)	0.035(2)
C14	0.2840(7)	0.626(2)	0.3652(7)	0.048(3)
H14A	0.321654	0.483382	0.379629	0.057*
H14B	0.294423	0.680323	0.313642	0.057*

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Abstract

C₁₆H₁₅O₃Bi, orthorhombic, *Pna*2₁ (no. 33), *a* = 17.277(3) Å, *b* = 4.7288(8) Å, *c* = 17.776(3) Å, *V* = 1452.3(4) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0292, *wR*(*F*²) = 0.0678, *T* = 296 K.

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The molecular 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.

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C15	0.1267(6)	0.685(2)	0.6685(6)	0.044(2)
C16	0.0783(8)	0.543(4)	0.7273(7)	0.073(4)
H16A	0.025539	0.603474	0.722529	0.110*
H16B	0.097354	0.592215	0.776352	0.110*
H16C	0.081107	0.341467	0.720865	0.110*

Source of material

The compound O(CH₂C₆H₄)₂BiCl is prepared by a literature known synthesis [4]. To a solution of O(CH₂C₆H₄)₂BiCl (0.265 g, 0.6 mmol) in 20 mL CH₂Cl₂, a suspension of CH₃CO₂Ag (0.110 g, 0.66 mmol) in 10 mL distilled water was added. The reaction mixture was stirred in the dark at room temperature for 24 h and then filtered. The organic phase was separated, washed with water and dried over anhydrous Na₂SO₄. After filtered, removal of the organic solvent under vacuum gave the title compound O(CH₂C₆H₄)₂BiO₂CCH₃. Crystals were obtained by crystallization from CH₂Cl₂/*n*-hexane. ¹H NMR (400 MHz, CDCl₃, TMS): δ = 8.16 (4H, d, *J* = 7.2 Hz), 7.54 (4H, t, *J* = 7.6 Hz), 7.41 (4H, d, *J* = 7.6 Hz), 7.27 (4H, t, *J* = 7.2 Hz), 5.21 (4H, d, *J* = 13.6 Hz), 4.80 (4H, d, *J* = 13.6 Hz), 2.31 (3H, s) ppm; ¹³C NMR (CDCl₃, 100 MHz, TMS): δ = 178.51, 145.15, 136.98, 131.34, 127.77, 127.25, 77.66, 22.79 ppm.

Experimental details

The methylene and aromatic H atoms were generated geometrically and refined using the riding model with *U*_{iso}(H) set to 1.2*U*_{eq}(C). The methyl H atoms were allowed, rotate with a fixed angle around the C—C bond to best fit the experimental electron density with *U*_{iso}(H) set to 1.5*U*_{eq}(C) and C—H = 0.96 Å.

Comment

Over recent years there has been an increasing interest in the chemistry of the hypervalent organobismuth compounds having intramolecular N, O, S→Bi coordination owing to their novel structure chemistry and use in areas such as organic synthesis, catalysis and medicine [4–13]. To the best of our knowledge, only one hypervalent organobismuth acetate with intramolecular N, O, S→Bi interactions, *i.e.* [2,6-(Me₂NCH₂)C₆H₃]Bi(O₂CCH₃)₂, has been reported so far [9].

The asymmetric unit of the title structure contains one complete molecule (*cf.* the figure). In the molecular structure of organobismuth acetate, O(CH₂C₆H₄)₂BiO₂CCH₃, the transannular interaction between the bismuth atom and the oxygen atom is observed, and the Bi1–O1 distance [2.581(8) Å] is longer than those of the organobismuth

halide, nitrate and cation with the 5,6,7,12-tetrahydrodibenz [c,f][1,5]oxabismocine framework, *i.e.* O(CH₂C₆H₄)₂BiCl (2.543(6) Å) [10], [O(CH₂C₆H₄)₂Bi]NO₃ (2.508(2) Å) [10], and [O(CH₂C₆H₄)₂Bi(OH₂)]⁺[SO₃CF₃][−] (2.417(7) Å) [4], indicating that the O→Bi coordination of the latter is slightly stronger than that of the former, and shorter than those of the organobismuth carbonate with same framework, *i.e.* [O(CH₂C₆H₄)₂Bi]₂CO₃ [2.587(4) and 2.618(3) Å] [12], suggesting that the O→Bi intramolecular interaction of the latter is slightly weaker than that of the former. The acetate group in the organobismuth acetate, O(CH₂C₆H₄)₂BiO₂CCH₃ acts as an asymmetric bidentate ligand [Bi(1)–O(2) 2.237(8) Å; Bi(1)–O(2) 2.8857(9) Å].

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References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
3. Sheldrick, G. M.: SHELXT – integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
4. Tan, N. Y.; Yin, S. F.; Li, Y. F.; Qiu, R. H.; Meng, Z. G.; Song, X. X.; Luo, S. L.; Au, C. T.; Wong, W. Y.: Synthesis and structure of an air-stable organobismuth triflate complex and its use as a high-efficiency catalyst for the ring opening of epoxides in aqueous media with aromatic amines. *J. Organomet. Chem.* **696** (2011) 1579–1583.
5. Toma, A.; Raț, C. I.; Silvestru, A.; Rüffer, T.; Lang, H.; Mehring, M.: Heterocyclic bismuth(III) compounds with transannular S→Bi interactions. An experimental and theoretical approach. *J. Organomet. Chem.* **806** (2016) 5–11.
6. Raț, C. I.; Silvestru, C.; Breunig, H. J.: Hypervalent organoantimony and -bismuth compounds with pendant arm ligands. *Coord. Chem. Rev.* **257** (2013) 818–879.
7. Tan, N. Y.; Chen, Y.; Yin, S. F.; Qiu, R. H.; Zhou, Y. B.; Au, C. T.: Synthesis and structures of hypervalent organoantimony and organobismuth chlorides containing asymmetric C,E,C-chelating (E = O, S) ligands. *Dalton Trans.* **42** (2013) 9476–9481.
8. Tan, N. Y.; Chen, Y.; Zhou, Y. B.; Au, C. T.; Yin, S. F.: Synthesis and structure of organobismuth chlorides and triflates containing (C,E)-chelating ligands (E=O, S) and their catalytic application in the allylation of aldehydes with tetraallyltin. *ChemPlusChem* **78** (2013) 1363–1369.
9. Fridrichová, A.; Svoboda, T.; Jambor, R.; Padělková, Z.; Růžicka, A.; Erben, M.; Jirásko, R.; Dostál, L.: Synthesis and structural study on organoantimony(III) and organobismuth(III) hydroxides containing an NCN pincer type ligand. *Organometallics* **28** (2009) 5522–5528.

10. Liu, Y. P.; Lei, J.; Tang, L. W.; Peng, Y.; Au, C. T.; Chen, Y.; Yin, S. F.: Studies on the cytotoxicity and anticancer performance of heterocyclic hypervalent organobismuth(III) compounds. *Eur. J. Med. Chem.* **139** (2017) 826–835.
11. Tan, N. Y.; Wu, S. S.; Yang, H. Q.; Lan, D. H.; Au, C. T.; Yi, B.: Crystal structure of 6-cyclohexyl-6,7-dihydrodibenzo[*c,f*][1,5]azabismocin-12 (5*H*)-yl nitrate, $C_{20}H_{23}O_3N_2Bi$. *Z. Kristallogr. NCS* **234** (2019) 509–511.
12. Tan, N. Y.; Dang, L. M.; Lan, D. H.; Wu, S. S.; Au, C. T.; Yi, B.: Crystal structure of bis{5*H*-dibenzo[*c,f*][1,5]oxabismocin-12(7*H*)-yl} carbonate, $C_{29}H_{24}O_5Bi_2$. *Z. Kristallogr. NCS* **233** (2018) 875–877.
13. Nema, M. G.; Breunig, H. J.; Soran, A.; Silvestru, C.: Diorganobismuth(III) compounds with the pendant arm 2-(Me_2NCH_2) C_6H_4 ligand – isothiocyanate, trifluoroacetate and nitrate. *J. Organomet. Chem.* **705** (2012) 23–29.