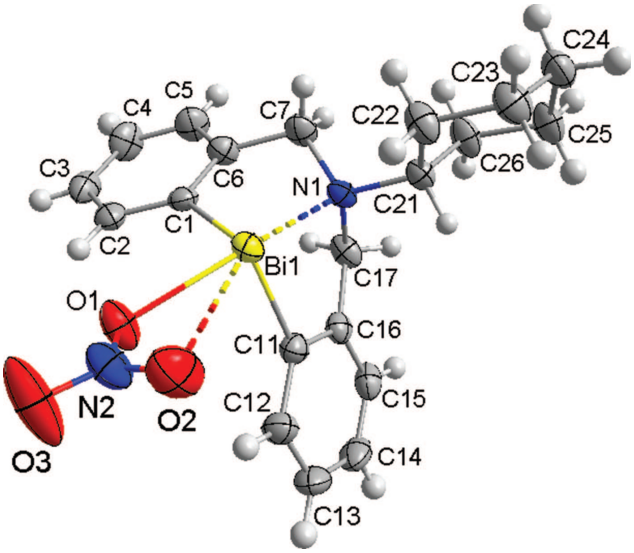
Nianyuan Tan*, Shuisheng Wu, Yang Huiqiong, Donghui Lan, Chak-Tong Au and Bing Yi*

Crystal structure of 6-cyclohexyl-6,7-dihydrodibenzo[*c*,*f*][1,5]azabismocin-12(5*H*)-yl nitrate, $C_{20}H_{23}O_3N_2Bi$



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Abstract

$C_{20}H_{23}O_3N_2Bi$, monoclinic, $P2_1/n$ (no. 14), $a = 10.6897(5)$ Å, $b = 10.5590(5)$ Å, $c = 17.4099(9)$ Å, $\beta = 105.491(2)°$, $V = 1893.71(16)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0253$, $wR(F^2) = 0.0576$, $T = 296(2)$ K.

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The asymmetric unit of the title 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.

***Corresponding authors: Nianyuan Tan and Bing Yi,** Hunan Provincial Key Laboratory of Environmental Catalysis and Waste Regeneration, Hunan Institute of Engineering, Xiangtan 411104, China, e-mail: nytan@sina.com (N. Tan); bingyi2005@126.com (B. Yi)

Shuisheng Wu, Donghui Lan and Chak-Tong Au: Hunan Provincial Key Laboratory of Environmental Catalysis and Waste Regeneration, Hunan Institute of Engineering, Xiangtan 411104, China

Yang Huiqiong: College of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.05 × 0.04 × 0.03 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	9.33 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.5°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14351, 4174, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3516
$N(param)_{refined}$:	235
Programs:	Bruker programs [1], SHELX programs [2, 3], Olex2 [2]

Source of material

The compound $C_6H_{11}N(CH_2C_6H_4)_2BiCl$ is prepared by the literature known synthesis [5]. To a solution of $C_6H_{11}N(CH_2C_6H_4)_2BiCl$ (0.274 g, 0.5 mmol) in 20 mL CH_2Cl_2, a solution of $AgNO_3$ (0.085 g, 0.5 mmol) in 10 mL distilled water was added. The mixture was stirred in the dark at room temperature for 12 h and then filtered. The organic phase was separated from aqueous phase and dried over anhydrous Na_2SO_4. After removal of the solvent in vacuum, the compound $C_6H_{11}N(CH_2C_6H_4)_2BiNO_3$ was obtained. Crystals suitable for X-ray diffraction analysis were obtained by crystallization from CH_2Cl_2/*n*-hexane solution. **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): $\delta = 8.19$ (2H, s), 7.54 (4H, dd, $J = 14.8$, 7.6 Hz), 7.33 (2H, t, $J = 7.6$ Hz), 4.53 (2H, d, $J = 15.2$ Hz), 4.32 (2H, d, $J = 15.2$ Hz), 2.97 (1H, t, $J = 11.2$ Hz), 2.07 (2H, d, $J = 11.6$ Hz), 1.90 (2H, d, $J = 12.8$ Hz), 1.69 (1H, d, $J = 12.8$ Hz), 1.44−1.26 (4H, m), 1.17–1.08 (1H, m) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz, TMS): $\delta = 150.65$, 137.80, 131.10, 128.39, 128.15, 65.75, 62.40, 31.20, 25.62, 25.36 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}(H) set to 1.2U_{eq}(C) for all H atoms.

Comment

The interest in the chemistry of hypervalent organobismuth compounds with intramolecular N, O, S → Bi interactions

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Bi1	0.99740(2)	0.27546(2)	0.04107(2)	0.02798(6)
N1	0.7606(3)	0.2827(3)	0.0321(2)	0.0278(7)
N2	1.2999(4)	0.2434(4)	0.0921(3)	0.0468(10)
O1	1.2198(3)	0.3143(4)	0.1148(2)	0.0489(8)
O2	1.2588(4)	0.1543(4)	0.0483(3)	0.0654(11)
O3	1.4140(4)	0.2673(6)	0.1160(3)	0.104(2)
C1	0.9601(4)	0.4611(4)	0.0942(2)	0.0284(8)
C2	1.0537(4)	0.5374(4)	0.1441(2)	0.0341(9)
H2	1.140489	0.513098	0.157202	0.041*
C3	1.0187(5)	0.6488(4)	0.1742(3)	0.0408(11)
H3	1.080823	0.697209	0.209703	0.049*
C4	0.8908(5)	0.6878(5)	0.1515(3)	0.0471(12)
H4	0.867252	0.764362	0.170084	0.057*
C5	0.7980(5)	0.6137(4)	0.1012(3)	0.0433(11)
H5	0.711924	0.640368	0.086460	0.052*
C6	0.8313(4)	0.5003(4)	0.0726(2)	0.0331(9)
C7	0.7285(4)	0.4196(4)	0.0175(3)	0.0366(10)
H7A	0.644519	0.437010	0.026526	0.044*
H7B	0.723842	0.440334	−0.037520	0.044*
C11	0.9738(4)	0.1542(4)	0.1411(2)	0.0304(9)
C12	1.0714(4)	0.0771(4)	0.1870(3)	0.0401(10)
H12	1.153524	0.077946	0.178304	0.048*
C13	1.0471(5)	−0.0001(5)	0.2447(3)	0.0466(11)
H13	1.112556	−0.051772	0.274777	0.056*
C14	0.9258(5)	−0.0011(5)	0.2582(3)	0.0464(12)
H14	0.909919	−0.052417	0.297985	0.056*
C15	0.8275(4)	0.0740(4)	0.2129(3)	0.0401(10)
H15	0.745323	0.071621	0.221378	0.048*
C16	0.8517(4)	0.1535(4)	0.1541(2)	0.0294(8)
C17	0.7498(4)	0.2458(4)	0.1123(3)	0.0341(10)
H17A	0.664900	0.208630	0.106965	0.041*
H17B	0.755940	0.321317	0.144792	0.041*
C21	0.6808(4)	0.1959(4)	−0.0309(2)	0.0293(9)
H21	0.701868	0.108994	−0.012014	0.035*
C22	0.7152(4)	0.2078(5)	−0.1097(3)	0.0414(11)
H22A	0.807185	0.191697	−0.101281	0.050*
H22B	0.697792	0.293666	−0.129509	0.050*
C23	0.6381(4)	0.1156(5)	−0.1716(3)	0.0435(11)
H23A	0.657075	0.131380	−0.222210	0.052*
H23B	0.665158	0.029779	−0.155355	0.052*
C24	0.4933(4)	0.1273(5)	−0.1824(3)	0.0454(11)
H24A	0.463730	0.208979	−0.205780	0.054*
H24B	0.448588	0.062045	−0.218711	0.054*
C25	0.4604(4)	0.1142(5)	−0.1037(3)	0.0435(11)
H25A	0.482539	0.029721	−0.082579	0.052*
H25B	0.367883	0.126333	−0.111571	0.052*
C26	0.5350(4)	0.2120(5)	−0.0442(3)	0.0416(11)
H26A	0.509770	0.296561	−0.064311	0.050*
H26B	0.513188	0.202497	0.006064	0.050*

has increased in recent years owing to their fascinating chemistry, structure and uses in organic synthesis, catalysis and medicine [5–13]. As part of our work on hypervalent organobismuth compounds with intramolecular N, O, S → Bi interactions, we report herein the crystal structure of a hypervalent organobismuth nitrate with intramolecular N → Bi coordinations.

In the molecular structure of organobismuth nitrate (*cf.* the figure), $C_6H_{11}N(CH_2C_6H_4)_2BiNO_3$, the N → Bi coordination is observed, and the Bi(1)—N(1) distance [2.495(3) Å] is shorter than those of the organobismuth chloride and triphenylgermylpropionate with same framework, *e.g.* $C_6H_{11}N(CH_2C_6H_4)_2BiCl$ (2.517(4) Å) [5] and $C_6H_{11}N(CH_2C_6H_4)_2BiOC(O)CH_2CH_2GePh_3$ (2.563(3) Å) [5], while this distance is longer than those of the organobismuth perfluorooctanesulfonate and tetrafluoroborate with same framework, *i.e.* $C_6H_{11}N(CH_2C_6H_4)_2BiOSO_2C_8F_{17}$ (2.397(5) Å) [6] and $C_6H_{11}N(CH_2C_6H_4)_2BiBF_4$ (2.394(8) Å) [7]. The geometry around the central Bi atom can be described as a distorted pseudo-trigonal bipyramid. The N(1) and O(1) atoms occupy at the apical positions, and both the C(1) and C(11) atoms at the equatorial positions along with a lone electron pair of bismuth. The nitrate group in the title compound can be considered as acting as an asymmetric bidentate ligand (*cf.* the figure). One O atom of nitrate group is covalently bound to the bismuth [Bi(1)—O(1) 2.416(3) Å], while the other O atom is weakly coordinated to the bismuth [Bi(1)—O(2) 3.0451(4) Å vs. r_{vdW} (Bi,O) 3.80 Å] [14]. Similar Bi—O distances were found for nitrate ligands in the related [2,6-$(Me_2NCH_2)_2C_6H_3$]$Bi(NO_3)_2$ [8], [2-$(Me_2NCH_2)C_6H_4]_2BiNO_3$ [9], $C_6H_5CH_2N(CH_2C_6H_4)_2BiNO_3$ [10], $O(CH_2C_6H_4)_2BiNO_3$ [12], $S(CH_2C_6H_4)_2BiNO_3$ [13]. Taking in account these contacts and the increased coordination number of the bismuth, the title compound might be described as 12-Bi-5 hypervalent species [15–17].

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