Crystal structure of tetrakis(*N,N*-dimethylacetamide-*O*)borane tris(dibromiodide), $\{B[CH_3CON(CH_3)_2]_4\}(Br_2I)_3$

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Abstract

$C_{16}H_{36}BBr_6I_3N_4O_4$, tetragonal, $P4_2/mbc$ (No. 135), $a = 13.032(1)$ Å, $c = 21.119(1)$ Å, $V = 3586.6$ Å³, $Z = 4$, $\rho_m = 2.24(2)$ g·cm⁻³, $R_{gt}(F) = 0.048$, $wR_{ref}(F^2) = 0.152$, $T = 180$ K.

Source of material

The title compound is prepared as following : to an ice cooled solution of 127 g (0.5 mol) of iodine in excess of dimethylacetamide (348 g, 4 mol), 150 mL of a 1M dichloromethane solution of borontribromide (0.15 mol) are slowly added. Temperature is maintained besides 283 K for 30 minutes, 200 mL of anhydrous acetic acid are then added and the boronic solution is left for crystallization at room temperature. After 24 hours, the crystalline material is filtered off, washed with ethanol and diethylether giving 192 g of $[B(DMA)_4](Br_2I)_3$ as purple needles (yield: 80%).

Discussion

Organoboronic compounds are well known; besides organoboranes like 9-BBN and others used in the hydroboration reaction [1], organoboronic reagents including an oxygen-boron interaction are of special interest. Catecholboronate or the more regioselective pinacolboronate have been used in Suzuki-like enantioselective synthesis [2]. Chiral boron complexes have been developed in the Lewis acid catalysed hetero Diels-Alder reaction [3] or the Brønsted acid Lewis acid hetero Diels-Alder reaction [4]. The crystallographic structures of bis(catecholato)borate [5] and tetrakis(*N,N*-dimethylformamide-*O*)borane bis(tribromide) bromide [6] have recently been established as tetrahedral geometry. Introduction of an iodine atom into organic molecules is frequently an important step in organic synthesis since the halogen can easily be replaced by another group in a transition metal catalysed condensation. A variety of iodinating reagents have been introduced; the most commercially available products are phosphorus triiodide, *N*-iodosuccinimide or 4-bis(pyridine) iodonium tetrafluoroborate [7].

In the title compound, the cationic tetrahedral complex $B(DMA)_4$ possess the Lewis acid character of $B(III)$ and the counter anion dibromiodide (IBr_2^-) brings an iodination activity. The crystal structure is built up from discrete $[B(DMA)_4]^+$ cations and three dibromiodide $[IBr_2]^-$ anions. The boron atom is surrounded by the DMA molecules in a nearly regular tetrahedral arrangement with O—B—O angles of 108.0(2)° and 112.5(4)°. The B—O bond length [1.476(5) Å] is within the range of those found in the tetrakis(*N,N*-dimethylformamide-*O*)borane bis(tribromide) bromide $\{BCH_3)_2NCHO_4\}(Br_3)_2Br$ [1.44(1) Å – 1.48(1) Å] [6]. The DMA molecules are essentially planar; the maximum deviation out of the mean plane PL-1 (O1—C1—C2—N3—C4—C5) is 0.024(6) Å for N3. The torsion angle $\angle B-O1-C1-N3 = 176.2(5)^\circ$ and the distance of the B atom from PL-1 [0.064(8) Å] show that the boron is approximately coplanar with each DMA molecule and in the lone-pair direction of each carbonyl group (trans to the N atom). The O—C bond [1.295(9) Å] and C—N bond of the amide group [1.302(9) Å] are longer than those found in non-coordinating DMA [on average: $d(O-C) = 1.23(2)$ Å and $d(C-N) = 1.25(3)$ Å] [8]. Since each central iodine atom of the three $[IBr_2]^-$ ions is located at inversion centre, the geometry of these three atomic systems is linear. The I—Br bond lengths situated in the range of 2.709(1) Å to 2.819(1) Å are significantly longer than those found in the bis(1,4,7-trithiacyclononane)palladium(II) bis(dibromiodide) complex [2.683(1) Å – 2.698(1) Å] in [9]. The crystal packing is characterized by the presence of layers perpendicular

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to *c* axis, consisting of dibromiodide ions (Br2–I2–Br2ii and Br3–I3–Br3iii with ii: 1–*x*, 1–*y*, 1–*z* and iii: –*x*, 1–*y*, 1–*z*) with a height of *c*/2 (10.56 Å). [B(DMA)₄]³⁺ cations are placed in sandwich in equal distance between these layers; the dibromiodide Br1–I1–Br1i (i: 1–*x*, 2–*y*, *z*) are coplanar with the bore atoms forming intermediate layers. The crystalline cohesion is ensured by many van der Waals contacts, the shortest being 3.543(9) Å.

Table 1. Data collection and handling.

Crystal:	purple parallelepiped, size 0.20 × 0.25 × 0.30 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	93.25 cm ^{−1}
Diffractometer, scan mode:	Stoe IPDS, φ
$2\theta_{\max}$:	49.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	23991, 1547
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1366
$N(\text{param})_{\text{refined}}$:	82
Programs:	SIR92 [10], SHELXL-97 [11], WinGX [12], CAMERON [13], SADABS [14]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(41)	16 <i>k</i>	0.2676	0.7241	0.4257	0.09(1)
H(42)	16 <i>k</i>	0.2929	0.6105	0.4443	0.09
H(43)	16 <i>k</i>	0.2104	0.6334	0.3921	0.09
H(21)	16 <i>k</i>	0.3614	0.4169	0.3184	0.09
H(22)	16 <i>k</i>	0.2593	0.4729	0.3370	0.09
H(23)	16 <i>k</i>	0.3427	0.4507	0.3887	0.09
H(51)	16 <i>k</i>	0.3702	0.8039	0.3724	0.09
H(52)	16 <i>k</i>	0.3844	0.7680	0.3021	0.09
H(53)	16 <i>k</i>	0.4720	0.7493	0.3517	0.09

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
B	4 <i>b</i>	1/2	1/2	1/4	0.027(6)	<i>U</i> ₁₁	0.02(1)	0	0	0
O(1)	16 <i>k</i>	0.4504(4)	0.5800(3)	0.2888(2)	0.040(2)	0.030(2)	0.030(3)	0.000(2)	0.005(2)	−0.001(2)
C(1)	16 <i>k</i>	0.3802(5)	0.5688(5)	0.3317(3)	0.038(3)	0.034(3)	0.029(4)	0.002(3)	−0.001(3)	−0.004(3)
N(3)	16 <i>k</i>	0.3540(5)	0.6522(4)	0.3615(3)	0.048(4)	0.036(3)	0.032(3)	0.003(3)	0.004(3)	−0.002(2)
C(4)	16 <i>k</i>	0.2744(6)	0.6553(6)	0.4100(4)	0.050(4)	0.048(4)	0.042(5)	0.007(3)	0.011(3)	−0.002(3)
C(2)	16 <i>k</i>	0.3316(6)	0.4685(6)	0.3451(4)	0.045(4)	0.047(4)	0.034(5)	−0.006(3)	0.004(3)	−0.001(3)
C(5)	16 <i>k</i>	0.39903(5)	0.75195(5)	0.3456(4)	0.071(5)	0.035(4)	0.042(5)	−0.006(4)	0.011(4)	−0.003(3)
I(1)	4 <i>d</i>	1/2	0	1/4	0.0578(6)	<i>U</i> ₁₁	0.0471(9)	−0.0217(5)	0	0
I(2)	4 <i>a</i>	1/2	1/2	1/2	0.0337(6)	0.0405(6)	0.0424(8)	0.0037(3)	0	0
I(3)	4 <i>c</i>	0	1/2	1/2	0.0439(6)	0.0319(5)	0.0422(8)	−0.0019(3)	0	0
Br(1)	8 <i>g</i>	0.34905(5)	1/2– <i>x</i>	1/4	0.0506(5)	<i>U</i> ₁₁	0.0476(8)	−0.0111(5)	0.0087(3)	<i>U</i> ₁₃
Br(2)	8 <i>h</i>	0.45229(5)	0.28899(5)	1/2	0.0282(5)	0.0263(5)	0.0552(7)	0.0012(3)	0	0
Br(3)	8 <i>h</i>	−0.18882(5)	0.58687(5)	1/2	0.0384(6)	0.0354(6)	0.0436(7)	−0.0020(4)	0	0

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