Crystal structure of tetrakis(*N*,*N*-dimethylformamide-*O*)borane bis(tribromide) bromide, $\{B[(CH_3)_2NCHO]_4\}(Br_3)_2Br$

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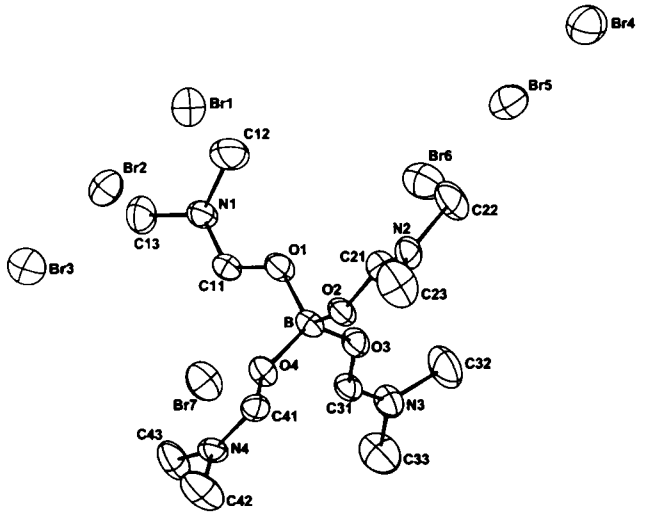

Abstract

$C_{12}H_{28}BBr_7N_4O_4$, triclinic, $P\bar{1}$ (No. 2), $a = 8.464(1)$ Å, $b = 9.542(1)$ Å, $c = 18.466(2)$ Å, $\alpha = 99.94(1)°$, $\beta = 99.42(1)°$, $\gamma = 104.42(1)°$, $V = 1388.9$ Å^3, $Z = 2$, $\rho_m = 2.08(2)$ g·cm^{-3}, $R_{gt}(F) = 0.061$, $wR_{ref}(F^2) = 0.191$, $T = 293$ K.

Source of material

The title compound **I** is prepared as following: to an ice cooled solution of 48 g (0.3 mol) of bromine in 200 mL of dimethylformamide, 130 mL of one mol·L^{-1} CH_2Cl_2 solution of BBr_3 are slowly added (caution with gas evolution and warming) the brown solution becomes slowly orange. Some hours later at room temperature orange needles of the complex **I** appear in the reaction medium. A day later the crystalline product is filtered off, washed with diethylether and propan-1-ol.

Recrystallization from propan-1-ol / hexane 1/1 gives a 77 % yield of **I** as orange-yellow needles (mp = 403 K). The complex is stable at room temperature but hygroscopic. Single crystals were obtained from CH_2Cl_2. The suitable crystal used for structure determination was sealed in Lindemann-glass capillary to avoid a gradually deterioration in air.

Discussion

Bromination of organic substrates is a real challenge in organic chemistry due to elemental bromine reactivity excess. For these reasons, we have tried to found a more specific soft acting brominating reactant starting from the fact that keto compound can be specifically activated by soft Lewis acid like B(III) giving a regiospecific controlled reaction. Moreover, we postulated that Lewis acid activity of B(III) could be modulated by ligand coordination. Dimethylformamide was chosen as a good ligand in accordance with our previous work describing $Al(DMF)_6(Br_3)_3$, a regiospecific soft bromating reagent [1]. Organoboronic complexes are well-known molecules. Chiral β aminoalcohol derived boron complexes are used in asymmetric Diels-Alder reaction as Lewis Acid catalyst [2]. Binaphtol interaction with boron gives a Brönsted acid assisted chiral Lewis acid catalyst used in enantioselective chemistry.

π-π Donor-acceptor interactions give an anionic character to the boron nucleus, as found in $[B(OPh)_4]^-$, H^+ [3]. But to our knowledge, the title compound $\{B[(CH_3)_2NCHO]_4\}(Br_3)_2Br$ is the first crystalline organoboronic complex with reverse donor-acceptor electronic interactions. Boron amide interactions imply that **I** is a cationic entity, neutrality being given by the Br_3^- and Br^- anions. ^{11}B -NMR gives a signal at 2.89 ppm for **I** in accordance with similar result (δ: 3.00 ppm) obtained for $[B(OPh)_4]^-$, H^+ suggesting that **I** is a tetrahedral entity [3]. The crystal structure is built up from discrete $[B(DMF)_4]^{3+}$ cations, two $[Br_3]^-$ and one Br^- anions. The boron atom is surrounded by the DMF molecules in a nearly regular tetrahedral arrangement with O–B–O angles in the range of 107.9(6)° to 111.1(7)°. The B—O bond distances [1.442(10) Å – 1.480(10) Å] fall within the range expected for tetrahedral boron complexes with O-atom donors in the literature ([4] and refs. therein). The DMF molecules are essentially planar. The B–O–C angles [119.1(6)° – 127.1(6)°] and the B–O–C–N angles [177.9(7)° – 179.6(7)°] show that the boron is approximatively coplanar with each amide plane and in the lone-pair direction of each carbonyl group (*trans* to the N atom). A slight deviation of these angles from the idealized values (120° and 180°) may be an indication of small steric effects due to the crowded coordination structure [5]. In the formamide radical, the O—C bonds [1.288(9) Å – 1.311(11) Å] are longer and C—N bonds [1.277(10) Å – 1.285(10) Å] shorter than those found in non-coordinating DMF [average d(O—C) = 1.24(1) Å and d(C—N) = 1.31(1) Å] [6]. The bond lengths of the two $[Br_3]^-$ ions are 2.651(2) Å and 2.483(2) Å for one and 2.609(2) Å and 2.504(2) Å for the other. The degree of asymmetry of the anion is intermediate between that of the symmetric $[Br_3]^-$ found in $[(CH_3)_3NH^+]_2[Br]^-[Br_3]^-$ [2.53 Å and 2.54 Å] and the asymmetric $[Br_3]^-$ in $CsBr_3$ [2.444(6) Å and 2.698(6) Å] [7,8]. The crystal packing is characterized by the presence of layers parallel to (100) plane, consisting of $[B(DMF)_4]^{3+}$ cations with an interval

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of *a*. $[Br_3]^-$ and Br^- anions are placed in sandwich between these layers giving a neutral character to the crystal. The crystalline cohesion is ensured by many van der Waals contacts, the shortest being 3.371(6) Å.

This compound shows an interesting structure by the fact that B^{3+} is coordinated by four neutral molecules (DMF). To our knowledge, it is the first example of a stable B(III) cationic complex.

Table 1. Data collection and handling.

Crystal:	orange-yellow parallelepiped, size 0.25 × 0.27 × 0.28 mm
Wavelength:	Cu K_α radiation (1.54180 Å)
μ:	123.33 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	116°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3943, 3809
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2921
$N(param)_{refined}$:	255
Programs:	SIR92 [9], SHELXL-97 [10], WinGX [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(11)	2*i*	0.6636	–0.2169	0.1474	0.19(2)
H(121)	2*i*	0.8712	0.2090	0.1846	0.19(2)
H(122)	2*i*	0.8448	0.1488	0.2569	0.19(2)
H(123)	2*i*	0.6915	0.1617	0.2007	0.19(2)
H(131)	2*i*	0.9244	0.0659	0.0971	0.19(2)
H(132)	2*i*	0.7795	–0.0775	0.0555	0.19(2)
H(133)	2*i*	0.9328	–0.0890	0.1122	0.19(2)
H(21)	2*i*	0.4873	–0.0265	0.3496	0.19(2)
H(221)	2*i*	0.1929	0.1166	0.4162	0.19(2)
H(222)	2*i*	0.3630	0.1817	0.3942	0.19(2)
H(223)	2*i*	0.3547	0.0813	0.4531	0.19(2)
H(231)	2*i*	0.0178	–0.0528	0.3360	0.19(2)
H(232)	2*i*	0.0575	–0.2052	0.3168	0.19(2)
H(233)	2*i*	0.0690	–0.1007	0.2598	0.19(2)
H(31)	2*i*	0.6116	–0.4589	0.2568	0.19(2)
H(321)	2*i*	0.7949	–0.3846	0.4720	0.19(2)
H(322)	2*i*	0.6296	–0.3412	0.4496	0.19(2)
H(323)	2*i*	0.7991	–0.2436	0.4388	0.19(2)
H(331)	2*i*	0.8186	–0.5746	0.3981	0.19(2)
H(332)	2*i*	0.8360	–0.5585	0.3165	0.19(2)
H(333)	2*i*	0.6666	–0.6511	0.3299	0.19(2)
H(41)	2*i*	0.1820	–0.4145	0.1694	0.19(2)
H(421)	2*i*	0.0745	–0.7112	0.0140	0.19(2)
H(422)	2*i*	0.0077	–0.5742	0.0365	0.19(2)
H(423)	2*i*	0.0162	–0.6837	0.0903	0.19(2)
H(431)	2*i*	0.3233	–0.6707	0.0187	0.19(2)
H(432)	2*i*	0.4463	–0.6142	0.0978	0.19(2)
H(433)	2*i*	0.4348	–0.5054	0.0438	0.19(2)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	2*i*	1.3145(2)	0.2175(1)	0.21992(6)	0.0915(8)	0.0722(8)	0.0570(7)	0.0199(6)	0.0197(6)	0.0149(6)
Br(2)	2*i*	1.3307(1)	0.0040(1)	0.11470(5)	0.0507(6)	0.0649(7)	0.0580(6)	0.0152(5)	0.0089(4)	0.0245(5)
Br(3)	2*i*	1.3567(1)	–0.2022(1)	0.01752(6)	0.0625(6)	0.0647(8)	0.0697(7)	0.0187(5)	0.0086(5)	0.0114(6)
Br(4)	2*i*	0.7570(2)	0.5233(2)	0.64015(8)	0.0949(9)	0.0744(9)	0.096(1)	0.0212(7)	0.0415(7)	0.0215(7)
Br(5)	2*i*	0.7768(1)	0.3194(1)	0.54164(6)	0.0671(7)	0.0610(8)	0.0729(8)	0.0126(5)	0.0103(5)	0.0255(6)
Br(6)	2*i*	0.8094(2)	0.1084(1)	0.43606(7)	0.0834(8)	0.0613(8)	0.0788(8)	0.0171(6)	0.0004(6)	0.0044(6)
Br(7)	2*i*	0.8378(1)	–0.4217(1)	0.15763(6)	0.0514(6)	0.0707(8)	0.0648(7)	0.0231(5)	0.0148(4)	0.0016(5)
B(1)	2*i*	0.483(1)	–0.241(1)	0.2481(5)	0.043(4)	0.032(5)	0.037(5)	0.002(4)	0.008(4)	–0.005(4)
O(1)	2*i*	0.5969(7)	–0.1118(6)	0.2307(3)	0.051(3)	0.036(3)	0.042(3)	0.008(3)	0.013(3)	–0.001(2)
N(1)	2*i*	0.7727(8)	–0.0082(8)	0.1635(4)	0.045(4)	0.038(4)	0.052(4)	0.009(3)	0.012(3)	0.004(3)
C(11)	2*i*	0.6763(9)	–0.1236(9)	0.1769(4)	0.044(4)	0.035(5)	0.036(4)	0.005(4)	0.004(3)	0.002(4)
C(12)	2*i*	0.797(2)	0.140(1)	0.2049(7)	0.092(8)	0.039(6)	0.085(8)	–0.003(5)	0.038(6)	0.005(5)
C(13)	2*i*	0.860(1)	–0.029(1)	0.1017(6)	0.079(7)	0.065(7)	0.059(6)	0.005(5)	0.036(5)	0.010(5)
O(2)	2*i*	0.3457(7)	–0.1946(6)	0.2710(3)	0.050(3)	0.035(3)	0.037(3)	0.010(3)	0.009(2)	–0.003(3)
N(2)	2*i*	0.2587(9)	–0.0329(8)	0.3475(4)	0.066(4)	0.043(4)	0.045(4)	0.024(4)	0.025(3)	0.011(3)
C(21)	2*i*	0.377(1)	–0.078(1)	0.3260(5)	0.059(5)	0.048(6)	0.042(5)	0.016(4)	0.012(4)	0.010(4)
C(22)	2*i*	0.295(2)	0.098(1)	0.4079(6)	0.109(9)	0.073(8)	0.058(6)	0.036(7)	0.030(6)	–0.003(6)
C(23)	2*i*	0.087(1)	–0.104(1)	0.3121(7)	0.054(6)	0.093(9)	0.085(8)	0.025(6)	0.015(5)	–0.003(7)
O(3)	2*i*	0.5760(7)	–0.2828(6)	0.3109(3)	0.059(3)	0.044(4)	0.037(3)	0.022(3)	0.010(2)	0.006(3)
N(3)	2*i*	0.7054(8)	–0.4330(8)	0.3612(4)	0.050(4)	0.047(4)	0.042(4)	0.021(3)	0.006(3)	0.008(3)
C(31)	2*i*	0.6292(9)	–0.3986(9)	0.3043(4)	0.045(4)	0.034(5)	0.042(4)	0.013(4)	0.013(4)	0.002(4)
C(32)	2*i*	0.735(2)	–0.343(1)	0.4368(5)	0.110(9)	0.084(9)	0.037(5)	0.039(7)	–0.006(5)	–0.003(5)
C(33)	2*i*	0.761(2)	–0.566(1)	0.3505(6)	0.092(8)	0.073(8)	0.071(7)	0.043(7)	–0.006(6)	0.015(6)
O(4)	2*i*	0.4245(6)	–0.3635(6)	0.1820(3)	0.040(3)	0.040(3)	0.038(3)	0.006(2)	0.007(2)	–0.003(2)
N(4)	2*i*	0.2418(8)	–0.5457(7)	0.0936(4)	0.041(3)	0.032(4)	0.043(4)	0.003(3)	0.008(3)	0.002(3)
C(41)	2*i*	0.2698(9)	–0.4384(9)	0.1507(4)	0.040(4)	0.036(5)	0.038(4)	0.006(3)	0.008(3)	0.005(4)
C(42)	2*i*	0.070(1)	–0.637(1)	0.0552(6)	0.035(4)	0.056(6)	0.086(7)	–0.006(4)	0.009(4)	–0.015(5)
C(43)	2*i*	0.373(1)	–0.588(1)	0.0607(5)	0.052(5)	0.055(6)	0.054(5)	0.005(4)	0.022(4)	–0.010(5)

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