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Synthesis and Crystal Structure Determination of a Dimeric Complex of Dimethylammoniumbis(*p-tert*-butylcatecholato) borate

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The structure of a dimeric complex, namely dimethylammoniumbis{(*p-tert*-butylcatecholato) borate}, was determined by X-ray crystallography. The compound crystallized in a triclinic system, and was characterized to be in the space group *P*-1, with cell parameters a = 11.929(7)Å, *b* = 16.833(6)Å, *c* = 11.259(11)Å, α = 93.75(5)°, β = 91.00(7)°, γ = 100.37(4)°, *Z* = 4, and *V* = 2218(3)Å^3. The crystal packing is conducted by intermolecular/intramolecular N–H···O hydrogen bonds. The B atom adopts a distorted tetrahedral geometry with four O atoms of *p-tert*-butylcatechol ligands.

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For decades, there has been growing interest in borates mainly due to the fact that B atoms are capable of forming both the BO_3 triangles or the BO_4 tetrahedra. Through polymerization these B–O groups can result in constructing one dimensional (1D) chains, 2D layers, and 3D networks.[1] The wide range of applications of borates virtually stems from the structure-property relationship that render possible their huge structural varieties and the functionality of the BO units.[2] Such structure diversities make the structure chemistry of borates extraordinary. Thus far, a series of borate materials have been reported for a number of utilizations, including, birefringence, piezoelectric, pyroelectric, and nonlinear optics.[3-6] Boron compounds formed by a non-metallic support unit can be displayed in a binary fashion composed of an anionic borate structural unit and a cationic interstitial complex.[7] The role of non-metal cations differs from metal cations, since they generally do not coordinate to oxygen in the same way, and may act instead as hydrogen bond donors to the structural unit. Continuation persistently our progressing work on borates,[8-11] the process of the self-assembly of organic and inorganic moieties has been performed under DMF solution conditions, and yielded original borate with organic amine, namely dimethyl ammonium bis(*p-tert*-butylcatecholato) borate.

The aforesaid compound (Fig. 1) was prepared by employing a DMF solution (10 mL) of 4-*tert*-butylcatechole (4.65 mmol), onto which was afterwards added solid boric acid (2.15 mmol) with strong stirring. The reaction mixture was allowed to be stirred at 120°C for 3 h, resulting in the formation of a colorless material. The crude product was crystallized from a water/acetone mixture. Crystals of the title compound were obtained by slow evaporation.

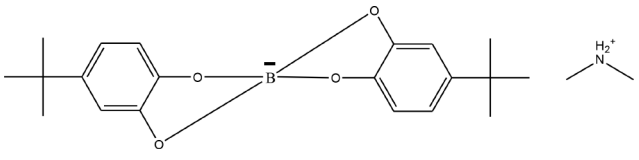


Fig. 1 Chemical diagram of the title compound.

X-ray crystallography was performed at 223.15 K on a RIGAKU AFC73 diffractometer employing graphite-monochromated fine focussed sealed-tube Mo-$K\alpha$ radiation. Crystal data and details related to the data collection are given in Table 1. The structure was solved by an intrinsic phasing

Table 1 Crystal data and experimental data of compound **1**

Chemical formula: $C_{22}H_{32}BNO_4$	
Formula weight = 385.29	
T = 223.2 K	
Crystal system: triclinic	Space group: *P*-1
a = 11.929(7)Å	α = 93.75(5)0
b = 16.833(6)Å	β = 91.00(7)°
c = 11.259(11)Å	γ = 100.37(4)°
V = 2218.3 Å^3	Z = 4
D_x = 1.154 g/cm^3	
Radiation Mo $K\alpha$ (λ = 0.71069 Å)	
μ(Mo $K\alpha$) = 0.077 mm^{-1}	F(0 0 0) = 832
Crystal size = 0.10 × 0.08 × 0.45	
No. of reflections collected = 5452	
No. of independent reflections = 5115	
θ range for data collection: 2.548 to 22.493	
Data/Restraints/Parameters = 5115/0/521	
Goodness-of-fit on F^2 = 0.999	
R indices [$I > 2\sigma(I)$]: $R1$ = 0.0770, $wR2$ = 0.1824	
R indices (all data): $R1$ = 0.3117, $wR2$ = 0.2738	
$(\Delta\rho)_{max}$ = 0.111 eÅ^{-3}	$(\Delta\rho)_{min}$ = –0.01 eÅ^{-3}
Measurement: RIGAKU AFC73	
Programs system: Olex2[12]	
Structure determination: olex2.solve[13], olex2.refine[13]	
CCDC deposition number: 1975259	

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Table 2 Selected geometric parameters, bond lengths and angles (Å, °)

Bond	Bond length/Å	Bond	Bond angle/°
O1-B1	1.477(14)	O2-B1-O1	105.7(10)
O2-B1	1.472(15)	O2-B1-O4	113.3(10)
O3-B1	1.486(13)	O1-B1-O4	111.6(11)
O4-B1	1.476(14)	O1-B1-O3	110.1(10)
O5-B2	1.483(15)	O2-B1-O3	111.5(11)
O6-B2	1.473(14)	O4-B1-O3	104.7(9)
O7-B2	1.495(13)	O6-B2-O5	105.9(10)
O8-B2	1.473(14)	O6-B2-O7	111.4(10)
O1-C1	1.386(12)	O6-B2-O8	112.0(10)
O2-C10	1.363(11)	O7-B2-O8	104.4(10)
O3-C11	1.404(10)	O7-B2-O5	110.8(10)
O4-C20	1.392(10)	O8-B2-O5	112.5(10)
O5-C23	1.399(11)	B1-O1-C1	106.4(9)
O6-C32	1.357(12)	B1-O2-C10	104.5(9)
O7-C33	1.382(11)	B1-O3-C11	107.7(8)
O8-C42	1.383(11)	B1-O4-C10	107.8(9)
C4-C5	1.538(13)	B2-O5-C23	104.5(9)
C14-C15	1.495(13)	B2-O6-C32	105.5(10)
C26-C27	1.529(14)	B2-O7-C33	106.7(8)
C35-C36	1.546(14)	B2-O8-C42	108.3(8)
N1-C21	1.408(11)	O1-C1-C2	130.4(12)
N1-C22	1.474(12)	O2-C10-C9	124.9(12)
N2-C43	1.446(13)	O2-C10-C1	113.9(10)
N2-C44	1.458(13)	C12-C11-O3	132.6(11)
		C19-C20-O4	128.0(11)
		C11-C20-O4	110.2(10)
		O5-C23-C24	127.2(2)
		O6-C32-C31	127.1(11)
		C32-C23-O5	110.5(11)
		C34-C33-O7	126.7(10)
		C41-C42-O8	130.9(11)
		C42-C33-O7	111.1(10)

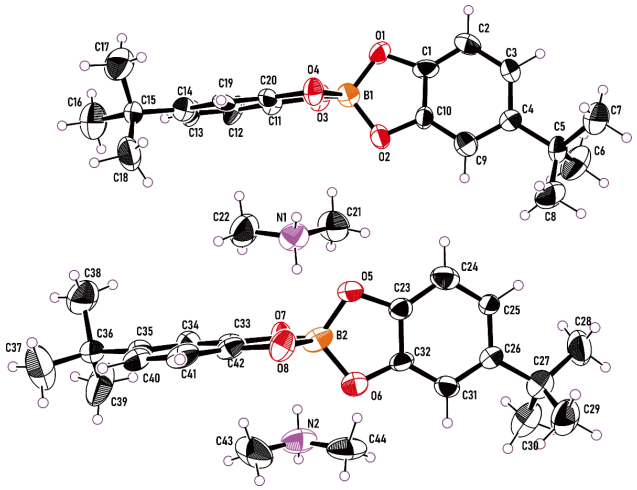


Fig. 2 ORTEP structure of compound **1** with ellipsoids shown at the 50% probability level.

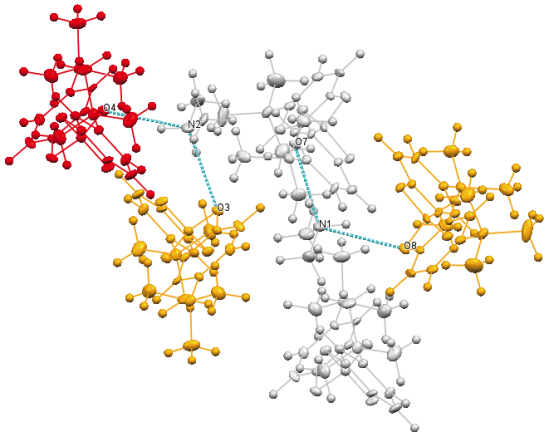


Fig. 3 Molecular structure of the title compound, showing the intermolecular/intramolecular hydrogen bonds.

method and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were inserted at their calculated positions, and fixed there. All calculations were carried out on a Window 7 Core i7 computer using olex2.solve[12] and olex2.refine.[13] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre (Deposit numbers CCDC-1975259). Copies of the data can be obtained free of charge *via* http://www.ccdc.com.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK: Fax, +44 1223 336033: email, deposit@ccdc.cam.ac.uk). The crystal data and selected bond lengths and angles are summarized in Tables 1 and 2, respectively.

An ORTEP perspective view of the compound is shown in Fig. 2. The compound consists of protonated dimethyl ammonium cation and complex anion units, which built up from one BO_4 tetrahedron and two *p-tert*-butylcatecholate groups. The fundamental building block of the compound is $[BO_4(C_{10}H_{12})_2]^-$ anions built up from a BO_4 tetrahedron bounded to two 4-*tert*-butylcatecholate groups through four oxygen atoms. The protonated dimethylammonium cations located between isolated units reinforce them connectivity *via* electrostatic and hydrogen bonding interactions as well as balance the charge of each layer. There are two independent molecules in the unit cell and two dimethylammonium cations serve as a bridge to link two borate molecules through intermolecular/intramolecular hydrogen bonds. N-H···O hydrogen bonds connect the $[BO_4(C_{10}H_{12})_2]^-$ units, which perform a certain function on stabilizing the structure (Fig. 3). $[BO_4(C_{10}H_{12})_2]^-$ units connected *via* electrostatic and hydrogen bonding extend to three directions forming a three-dimensional structure. The angle between $C_6H_3O_2$ plane B(1)-O(1)-O(2)-C(1)-C(2)-C(3)-C(4)-C(9)-C(10) (mean deviation of fitted atoms from the plane(1) is 0.0509 Å), B(1)-O(3)-O(4)-C(11)-C(12)-C(13)-C(14)-C(19)-C(20) (mean deviation of fitted atoms from the plane(2) is 0.0389 Å), B(2)-O(5)-O(6)-C(23)-C(24)-C(25)-C(26)-C(31)-C(32) (mean deviation of fitted atoms from the plane(3) is 0.0467 Å) and B(2)-O(7)-O(8)-C(33)-C(34)-C(35)-C(40)-C(41)-C(42) (mean deviation of fitted atoms from the plane is 0.0239 Å), respectively. The angle between plane(1) and plane(2) is 89.809°, plane(2) and plane(3) is 86.117°and lastly, plane(3) and plane(4) is 89.928°. There are some N-H···O hydrogen bonding interactions observed in the crystal structure, and these N-H···O hydrogen bonds play an important role in contributing to the stability of the compound. The three oxygen atoms of each unit cell (O(3), O(4) for one, O(8) for the other), which are coordinated with B(1) and B(2) atoms and the nitrogen atoms (N(1) and N(2)) of the dimethylammonium form the intermolecular hydrogen bonds N(2)-H(2A)···O(3), N(2)-H(2B)···O(4)

Table 3 Inter and Intra molecular hydrogen bonds geometry (Å, °)

D-H···A	d(D-H)/Å	d(H···A)/Å	D-H···A/⁰	d(D···A)/Å	Type
N1-H1A-O8(i)	0.9	2.127	151.5	2.949	Inter
N1-H1B-O7	0.9	2.035	160.32	2.899	Intra
N2-H2A-O3(ii)	0.9	2.108	157	2.957	Inter
N2-H2B-O4(iii)	0.9	2.045	158.85	2.903	Inter

(i): –*x*+1.0, –*y*, –*z*; (ii): –*x*+1.0, –*y*, –*z*+1.0; (iii): *x*+1.0, *y*, *z*.

and N(1)-H(1A)···O(8). As well as intermolecular hydrogen bonds, there are intramolecular hydrogen bonds observed between the oxygen atom (O(7)) coordinating B(2) atom and N(1) atom contribute to the formation of an N(1)-H(1B)···O(7) hydrogen bond (Table 3). The B-O distances range from 1.472(15) to 1.495(13)Å, and the mean distance for the B-O bonds is 1.479 Å, with the O-B-O angles ranging from 104.4(10) to 113.3(10)° (Table 2). The bond distances and angles are similar to those reported previously in related borate compounds.[14-25] The C-O distances range from 1.357(12) to 1.404(10)Å, with the O-C-C angles ranging from 110.2(10) to 132.6(11)°.

Acknowledgements

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