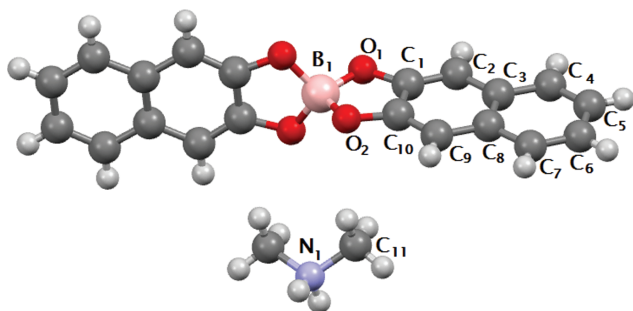


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Crystal structure of dimethylammonium bis(naphthalene-2,3-diolato)borate, $C_{22}H_{20}BNO_4$



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Abstract

$C_{22}H_{20}BNO_4$, monoclinic, $C2/c$ (no. 15), $a = 32.303(4)$ Å, $b = 8.2703(6)$ Å, $c = 7.3876(6)$ Å, $\beta = 92.889(8)^\circ$, $V = 1971.1(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0978$, $wR_{ref}(F^2) = 0.2063$, $T = 298$ K.

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Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

To a stirred DMF solution (10 mL) of 2,3-naphthalenediol (1650 mg, 10.30 mmol), $B(OH)_3$ (310.0 mg, 5.0 mmol) was carefully added at ambient temperature. The reaction mixture was stirred vigorously at 398 K for 130 min. resulting in formation of a pink coloured solid product. The solid material obtained was dissolved in DMSO (5 mL) and allowed to stand at room temperature for three months affording crystals. Yield: (1267 mg, 67%) (based on $B(OH)_3$); Elemental

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Table 1: Data collection and handling.

Crystal:	Prism, colourless
Size:	$0.36 \times 0.20 \times 0.06$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.09 mm^{-1}
Diffractometer, scan mode:	Xcalibur, φ and ω -scans
θ_{\max} , completeness:	27.8° , >91% (up to 25.2° , >98%)
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6269, 2126, 0.033
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1363
$N(\text{param})_{\text{refined}}$:	130
Programs:	CrysAlis ^{PRO} [1], SHELX [2]

analysis: (Found): C 70.16, H 5.39, N 3.69%. Calculated for $C_{22}H_{20}BNO_4$: C 70.80, H 5.40, N 3.75%.

Experimental details

The H atoms of structure were positioned geometrically (C–H = 0.93–0.96 Å; N–H = 0.89 Å) and refined using a riding model. Their U_{iso} values were set to $1.2U_{\text{eq}}$ of the parent atoms.

Comment

On the score of their excellent physical and chemical properties, borates attract attention in terms of industrial and academic since they can adopt a vast number of different crystal structures. The structures of borates are largely complicated, and exhibiting a great variety of potential applications notably in mineralogy and nonlinear optics (NLO) [3–5]. The coordination mode of boron in borates is either a BO_3 triangle or BO_4 tetrahedron that link together by the sharing of oxygen atoms, and the resulting anionic entities may in isolated chains, rings, or cages, or may condense further to form polymeric chains, sheets or three-dimensional networks [5]. The non-shared oxygen atoms will either bear a further negative charge (anhydrous borates) or will be protonated (hydrated borates). Hydrated borates are typically further hydrated by waters. Most borates synthesized and studied hitherto have been prepared under the templating effect of cations, such as a metal cations to form inorganic-organic hybrid borates [6].

Since its first reported preparation in 1878, arylspiropborates are of special importance consisting of two catecholato groups linked to a central boron atom [7]. These compounds offer a number of advantageous over other compounds such as being nontoxic, inexpensive and thermally, chemically and

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

Atom	x	y	z	U _{iso} [*] /U _{eq}
O1	0.02858(6)	0.9098(3)	0.1461(3)	0.0427(6)
O2	0.02738(7)	0.7117(3)	0.3700(3)	0.0471(7)
C1	0.06797(10)	0.8594(4)	0.1921(4)	0.0392(8)
N1	0.000000	0.2266(4)	0.250000	0.0534(11)
H1A ^a	0.004554	0.163085	0.155800	0.064*
H1B ^a	-0.004554	0.163086	0.344200	0.064*
C2	0.10387(10)	0.9096(4)	0.1256(5)	0.0514(9)
H2	0.103936	0.991314	0.039222	0.062*
C10	0.06710(10)	0.7381(4)	0.3243(4)	0.0421(8)
C9	0.10223(11)	0.6641(4)	0.3887(5)	0.0538(9)
H9	0.101198	0.583004	0.475492	0.065*
C8	0.14065(11)	0.7127(5)	0.3211(5)	0.0562(10)
C3	0.14155(11)	0.8361(5)	0.1890(5)	0.0561(10)
B1	0.000000	0.8107(6)	0.250000	0.0414(12)
C4	0.18036(12)	0.8822(6)	0.1251(7)	0.0803(13)
H4	0.181499	0.963630	0.038685	0.096*
C7	0.17842(13)	0.6403(6)	0.3828(7)	0.0813(14)
H7	0.178312	0.558870	0.469571	0.098*
C11	0.03717(12)	0.3231(5)	0.2921(5)	0.0673(12)
H11A	0.041439	0.396642	0.194271	0.101*
H11B	0.060729	0.252816	0.308111	0.101*
H11C	0.033753	0.383102	0.401560	0.101*
C5	0.21604(14)	0.8097(7)	0.1876(8)	0.0957(16)
H5	0.241240	0.841570	0.143513	0.115*
C6	0.21501(14)	0.6889(7)	0.3161(8)	0.0958(17)
H6	0.239594	0.639904	0.357864	0.115*

^aOccupancy: 0.5.

electrochemically stable and have found extensive usage in chemistry and industry. Other applications of these particular type of compounds involve employing as electrolytes in batteries [8] as catalysts, or co-catalysts, for the Diels-Alder reaction [9], methoxycarbonylation reactions [10] and in amide and ester condensation reactions [11]. As a continuation of our ongoing work on the synthesis and structure of metal or organoborate complexes [12–16], we have prepared the title compound.

The title compound was achieved in the presence of dimethylformamide acting a template. The asymmetric unit of the compound contains an [BO₄(C₁₀H₆)₂]⁻ anion, and [NH₂(CH₃)₂]⁺ cation. The [BO₄(C₁₀H₆)₂]⁻ anion consists of one set of a [BO₄] tetrahedron and two C₁₀H₆ planes. The boron atom is bonded to four oxygen atoms to form a tetrahedral environment (mean O–B–O bond angle of 109.51(7)°). Bond distances and angles are similar to those reported in related arylspiroborate compounds [16–18]. Dimethylformamide decomposes under experimental conditions forming the [NH₂(CH₃)₂]⁺ cation (*cf.* the figure).

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