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The crystal structure of *n*-propylammonium bis(2,3-dimethylbutane-2,3-diolato)borate-boric acid (1/1), $[\text{C}_3\text{H}_{10}\text{N}][\text{C}_{12}\text{H}_{24}\text{BO}_4] \cdot \text{B}(\text{OH})_3$

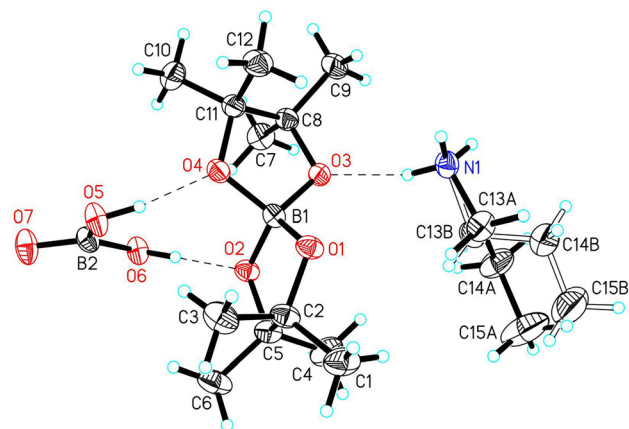


Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.48 × 0.45 × 0.40 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffractometer, scan mode:	STOE IPDS 2, rotation method
θ_{max} , completeness:	27.1°, 99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	26,188, 4629, 0.039
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4497
$N(\text{param})_{\text{refined}}$:	288
Programs:	X-RED/X-Area [1], SHELX [2, 3], ORTEP-3 [4]

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Abstract

$[\text{C}_3\text{H}_{10}\text{N}][\text{C}_{12}\text{H}_{24}\text{BO}_4] \cdot \text{B}(\text{OH})_3$, orthorhombic, *Fdd2* (no. 43), $a = 30.3986(6)$ Å, $b = 40.4094(13)$ Å, $c = 7.0603(2)$ Å, $V = 8672.8(4)$ Å³, $Z = 16$, $R_{\text{gt}}(F) = 0.0324$, $wR_{\text{ref}}(F^2) = 0.0828$, $T = 153$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

All experiments were carried out under a dry argon atmosphere using standard Schlenk technique [5].

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In a representative experiment 2.223 g pinacolborane (0.0174 mol, TCI – Tokyo Chemical Industry) were placed in a 50 mL round bottom flask. About 10 mL 1,2-dimethoxyethane (Acros Organics, distilled from CaH_2) were added. The resulting solution was stirred at room temperature and cooled in an ice bath (ice/ NaCl) to -20°C . *O*-Triethylsilyl-*N*-*n*-propylcarbamate (0.855 g, 0.0039 mol, synthesized according to [6]) was slowly added into this solution within 5 min while a gas evolution was visible. The dropping funnel was flushed with about 5 mL of 1,2-dimethoxyethane. The clear solution was stirred at room temperature for a week. Then, the solution was heated under reflux for about 1 h. Afterwards, the solution was stirred at room temperature until a white precipitate was formed. After standing an additional night at room temperature, the viscosity of the solution had increased. Crystals suitable for single crystal X-ray diffraction were obtained from this suspension after standing 6 months at room temperature. Colourless prisms, m.p. 130°C .

2 Comment

Pinacolborane is utilized for a variety of transformations like iron-catalysed alkene hydroboration, catalytic enantioselective hydroboration of ketones and imines, and other types of hydroborations [7–9]. Herein we describe the crystal structure of an ionic borate complex formed out of pinacolborane and a silylcarbamate. The crystal structure was obtained as side product during our work about the hydrogenation of carbamates of aluminium and silicon [10–13].

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
B1	0.68493 (6)	0.39062 (5)	0.4898 (3)	0.0224 (4)
O1	0.66234 (4)	0.41465 (3)	0.6114 (2)	0.0267 (3)
O2	0.72643 (4)	0.40745 (3)	0.43799 (19)	0.0240 (3)
C1	0.66995 (7)	0.47085 (5)	0.7228 (4)	0.0398 (5)
H1A	0.653757	0.478198	0.610441	0.060*
H1B	0.691437	0.487798	0.758898	0.060*
H1C	0.649311	0.467293	0.827501	0.060*
C2	0.69384 (6)	0.43859 (5)	0.6788 (3)	0.0283 (4)
C3	0.71512 (8)	0.42566 (6)	0.8593 (3)	0.0383 (5)
H3A	0.692233	0.420462	0.952431	0.058*
H3B	0.734842	0.442574	0.911155	0.058*
H3C	0.732006	0.405614	0.830649	0.058*
C4	0.71070 (9)	0.46363 (5)	0.3528 (3)	0.0403 (5)
H4A	0.730342	0.461735	0.243282	0.061*
H4B	0.710741	0.486518	0.398640	0.061*
H4C	0.680782	0.457369	0.315535	0.061*
C5	0.72660 (6)	0.44073 (5)	0.5096 (3)	0.0272 (4)
C6	0.77344 (7)	0.45010 (6)	0.5647 (4)	0.0405 (5)
H6A	0.784932	0.433878	0.655194	0.061*
H6B	0.773463	0.472116	0.622913	0.061*
H6C	0.792040	0.450339	0.451319	0.061*
O3	0.65527 (4)	0.38154 (3)	0.33421 (18)	0.0252 (3)
O4	0.69718 (4)	0.35858 (3)	0.57469 (19)	0.0244 (3)
C7	0.69660 (7)	0.34397 (5)	0.1413 (3)	0.0337 (4)
H7A	0.688444	0.356892	0.029193	0.051*
H7B	0.700152	0.320677	0.105837	0.051*
H7C	0.724360	0.352385	0.192900	0.051*
C8	0.66052 (6)	0.34703 (5)	0.2908 (3)	0.0256 (4)
C9	0.61739 (7)	0.33396 (5)	0.2093 (4)	0.0366 (5)
H9A	0.593626	0.337578	0.300812	0.055*
H9B	0.620220	0.310233	0.183459	0.055*
H9C	0.610622	0.345693	0.091371	0.055*
C10	0.70329 (7)	0.30175 (5)	0.4757 (4)	0.0357 (5)
H10A	0.730239	0.307483	0.406921	0.054*
H10B	0.687942	0.283906	0.408860	0.054*
H10C	0.710842	0.294409	0.603907	0.054*
C11	0.67350 (6)	0.33203 (4)	0.4871 (3)	0.0250 (4)
C12	0.63385 (7)	0.32407 (5)	0.6111 (3)	0.0342 (4)
H12A	0.643792	0.318998	0.739913	0.051*
H12B	0.618253	0.304903	0.558863	0.051*
H12C	0.614013	0.343173	0.614239	0.051*
B2	0.80650 (7)	0.35419 (5)	0.5795 (3)	0.0262 (4)
O5	0.77645 (4)	0.35143 (4)	0.7230 (2)	0.0308 (3)
H5O	0.7483 (11)	0.3563 (8)	0.683 (5)	0.060 (9)*
O6	0.79634 (4)	0.36891 (4)	0.40959 (19)	0.0273 (3)
H6O	0.7721 (12)	0.3822 (8)	0.419 (5)	0.071 (10)*
O7	0.84689 (5)	0.34168 (4)	0.6151 (2)	0.0357 (3)
H7O	0.8649 (10)	0.3436 (8)	0.524 (5)	0.057 (9)*
N1	0.57369 (6)	0.40936 (4)	0.3146 (2)	0.0281 (3)
H1D	0.5572 (8)	0.4029 (6)	0.211 (4)	0.044 (7)*
H1E	0.5609 (10)	0.4004 (8)	0.424 (4)	0.062 (9)*
H1F	0.6024 (8)	0.4014 (8)	0.300 (5)	0.061 (9)*
C13A ^a	0.57046 (14)	0.44498 (9)	0.3624 (6)	0.0322 (8)
H13A ^a	0.590060	0.450179	0.470368	0.039*
H13B ^a	0.539904	0.450520	0.399172	0.039*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C14A ^a	0.58394 (14)	0.46510 (8)	0.1895 (5)	0.0436 (10)
H14A ^a	0.613155	0.457566	0.144900	0.052*
H14B ^a	0.562506	0.461345	0.086097	0.052*
C15A ^a	0.5859 (3)	0.50146 (10)	0.2347 (9)	0.0752 (19)
H15A ^a	0.556772	0.509103	0.274946	0.113*
H15B ^a	0.595073	0.513752	0.121730	0.113*
H15C ^a	0.607149	0.505213	0.336870	0.113*
C13B ^b	0.5834 (3)	0.44626 (17)	0.2849 (14)	0.0324 (18)
H13C ^b	0.600660	0.454693	0.393698	0.039*
H13D ^b	0.601471	0.449049	0.169233	0.039*
C14B ^b	0.5425 (2)	0.46587 (17)	0.2660 (12)	0.045 (2)
H14C ^b	0.525586	0.464445	0.385632	0.054*
H14D ^b	0.524170	0.456250	0.163936	0.054*
C15B ^b	0.5514 (4)	0.5014 (2)	0.2219 (19)	0.068 (3)
H15D ^b	0.568414	0.511319	0.325299	0.103*
H15E ^b	0.523469	0.513261	0.207801	0.103*
H15F ^b	0.568188	0.502960	0.103741	0.103*

^aOccupancy: 0.663 (6), ^bOccupancy: 0.337 (6).

The asymmetric unit contains one molecule boric acid, $\text{B}(\text{OH})_3$, a bispinacolylborate anion, $[\text{Bpin}_2]^-$, and an *n*-propylammonium cation, $\text{CH}_3\text{--CH}_2\text{--NH}_3^+$. These are linked to each other by hydrogen bonds as shown in the figure. The boron atom B2 in boric acid is planar coordinated by the three oxygen atoms O5, O6, O7 (sum of O–B–O angles is 360°). The hydrogen atoms at O5 and O6 are orientated towards the neighbouring oxygen atoms O4 and O2, forming hydrogen bonds to the $[\text{Bpin}_2]^-$ anion. The boron atom B1 is distorted tetrahedrally coordinated by the four oxygen atoms of the pinacolyl groups. The angles O1–B1–O2 and O3–B1–O4 are smaller with values of $103.8(1)^\circ$ and $103.9(1)^\circ$, respectively. This can be explained with the coordination of the pinacolyl units, which form five membered rings with the boron atom. These small inner-cyclic angles are compensated by larger angles between both pinacolyl units which spread up to a value of $117.5(2)^\circ$ for O1–B1–O4. The B–O bond lengths are similar as in comparable compounds [14–16]. The $[\text{Bpin}_2]^-$ anion is linked to the *n*-propylammonium cation via a hydrogen bond N1–H1F...O3. Further hydrogen bonds from the *n*-propylammonium cation to symmetry equivalent oxygen atoms from neighbouring boronic acid molecules form an infinite network of molecules parallel to the crystallographic *a* axis.

There are three related crystal structures in the literature. These contain boric acid, $\text{B}(\text{OH})_3$, the bispinacolylborate anion, $[\text{Bpin}_2]^-$, and different ammonium ions to compensate the negative charge of the $[\text{Bpin}_2]^-$ unit. These cations are tetra-*n*-butylammonium [14], dibenzylammonium [15], and 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]

azepin-1-ium (protonated DBU) [16]. The combination of boric acid with $[\text{Bpin}_2]^-$ and alkylammonium ions results in complicated patterns of intermolecular interactions in these crystal structures; similar as in the structure which is presented here. As can be seen from the available structural analyses, the combination of these three structural elements allows the formation of unique networks of hydrogen bonds.

3 Experimental details

The carbon-bound H atoms were geometrically placed ($\text{C}-\text{H} = 0.98\text{--}0.99 \text{ \AA}$) and refined as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. The disordered *n*-propyl group was refined with a split atom model. Site occupation factors for parts A and B were refined to 0.66/0.34, respectively. Restraints were applied to keep the bond lengths of the disordered propyl group to sensible values.

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