Crystal Structure of a Methanesulfonate Salt of 4-(*N*-Methyl)pyridinium Boronic Acid

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The structure of a methanesulfonate salt of 4-(*N*-methyl)pyridinium boronic acid, [4-(*N*-Me)PyB(OH)₂]⁺CH₃SO₃⁻·H₂O, was determined by X-ray crystallography, and was characterized as: $P\bar{1}$, $a = 5.6937(16)$, $b = 7.805(2)$, $c = 13.522(3)$ Å, $\alpha = 99.46(3)^\circ$, $\beta = 91.45(3)^\circ$, $\gamma = 108.014(17)^\circ$, $Z = 2$, $V = 561.8(2)$ Å³. In the crystals, the cation and the anion are linked by BOH...O(anion), BOH...O(water), and (water)OH...O(anion) hydrogen bonds to stabilize the 1:1:1-cation:anion:water salt unit.

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The development of highly water-soluble boronic acids is important for molecular design in chemical and biochemical aqueous systems, because the solubilities of common boronic acids in water are relatively low. An enhanced solubility of boronic acid, for example, reduces the amount of organic solvent needed to increase the solubility of an organoboron-based chemosensor, as has been seen in many studies.^{1,2} In this context, we recently reported the crystal structure of a methanesulfonate salt of 3-(*N*-methyl)pyridinium boronic acid, [3-(*N*-Me)PyB(OH)₂]⁺CH₃SO₃⁻,³ which can dissolve in water as much as 1 M.⁴ For the further development of highly water-soluble boronic acid counterparts, herein we report on the crystal structure of a methanesulfonate salt of 4-(*N*-methyl)pyridinium boronic acid, [4-(*N*-Me)PyB(OH)₂]⁺CH₃SO₃⁻·H₂O (Fig. 1), which can dissolve in water more than 0.5 M.

The present compound, [4-(*N*-Me)PyB(OH)₂]⁺CH₃SO₃⁻·H₂O, was obtained in a similar manner to that of [3-(*N*-Me)PyB(OH)₂]⁺CH₃SO₃⁻.^{3,4} Detailed procedure and NMR data are deposited as supplemental data.

The X-ray diffraction data at 100 K were collected on a Quantum Q315 CCD area detector with Si-monochromated synchrotron radiation at the BL38B1 beam line of SPring-8 (Hyogo, Japan). The structure was solved by direct methods,

and refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms bound to oxygen atoms were found in the difference Fourier map, while hydrogen atoms bound to carbon atoms were located at the theoretically calculated positions with

Table 1 Crystal and experimental data

Chemical formula: C ₇ H ₁₄ BNO ₆ S	
Formula weight = 251.06	
$T = 100$ K	
Crystal system: Triclinic	Space group: $P\bar{1}$
$a = 5.6937(16)$ Å	$\alpha = 99.46(3)^\circ$
$b = 7.805(2)$ Å	$\beta = 91.45(3)^\circ$
$c = 13.522(3)$ Å	$\gamma = 108.014(17)^\circ$
$V = 561.8(2)$ Å ³	$Z = 2$
$D_x = 1.484$ g/cm ³	
Radiation: synchrotron ($\lambda = 0.70000$ Å)	
$\mu = 0.300$ mm ⁻¹	$F(0\ 0\ 0) = 264$
Crystal size = $0.50 \times 0.50 \times 0.40$ mm ³	
No. of reflections collected = 2258	
No. of independent reflections = 2258 [$R(\text{int}) = 0.0000$]	
θ range for data collection: 1.51 to 28.64°	
Data/Restraints/Parameters = 2558/0/159	
Goodness-of-fit on $F^2 = 1.382$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0432$, $wR2 = 0.1553$	
R indices (all data): $R1 = 0.0445$, $wR2 = 0.1589$	
$(\Delta\rho)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 0.437$ eÅ ⁻³	$(\Delta\rho)_{\text{min}} = -0.456$ eÅ ⁻³
Measurement: HKL2000 (HKL Research)	
Program system: HKL2000 (HKL Research)	
Structure determination: direct method (SHELXS-97)	
Refinement: full matrix least-squares on F^2 (SHELXL-97)	
CCDC deposition number: 885172

Fig. 1 Chemical diagram of [4-(*N*-Me)PyB(OH)₂]⁺CH₃SO₃⁻·H₂O.

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Fig. 2 ORTEP view of a hydrogen-bonded 1:1:1-cation:anion:water unit of $[4-(N\text{-Me})\text{PyB}(\text{OH})_2]\text{CH}_3\text{SO}_3\cdot\text{H}_2\text{O}$, drawn with thermal ellipsoids at the 50% probability level. Hydrogen bonds are shown by fine dotted lines. Symmetry code: (i) $-x, -y, -z$.

the riding model. The crystal data and experimental parameters are given in Table 1.

A structure analysis revealed that the crystals are isolated as a hydrate salt, $[4-(N\text{-Me})\text{PyB}(\text{OH})_2]\text{CH}_3\text{SO}_3\cdot\text{H}_2\text{O}$. The crystal structure is shown in Fig. 2, and the selected bond lengths and angles are given in Table S1. All of the pyridine atoms, as well as boron and methyl-carbon atoms, are located on the same plane, because both sums of the angles around C(3) and N(1) atoms are 360° (Table S1). The averaged B–O bond length is 1.352 Å, which is very similar to that of $[3-(N\text{-Me})\text{PyB}(\text{OH})_2]\text{CH}_3\text{SO}_3$ (1.350 Å).³ On the other hand, the B–C bond length (1.593 Å) is longer than those of the reported trigonal boronic acids $\text{RB}(\text{OH})_2$, R = phenyl-, pyridyl-, or pyridinium-based substituent, whose B–C bond lengths are 1.556–1.579 Å).^{3,5,6}

Figure 2 indicates the formation of a cation:anion:water = 1:1:1 unit linked by three hydrogen bonds among cation, anion, and water molecules. Table 2 lists the structural parameters of the hydrogen bonds. Two hydrogen atoms of the boronic acid link to the CH_3SO_3^- oxygen ($\text{H}\cdots\text{O}$ length is 1.932 Å) and the H_2O oxygen atom (1.924 Å), respectively. In addition, one of the two hydrogen atoms of the water of crystallization links to one of the other oxygen atoms of CH_3SO_3^- ($\text{H}\cdots\text{O}$ length is 1.900 Å). These hydrogen-bond lengths are *ca.* 0.8 Å shorter than the sum of the standard van der Waals radii of O and H atoms (Table 2).⁷ Therefore, the strong hydrogen-bond network would stabilize the 1:1:1 cation:anion:water unit in the crystals.

Figure 3 shows the crystal packing diagram. The water hydrogen atom, which has no hydrogen bond in the 1:1:1 unit shown in Fig. 2, interacts with the oxygen of the other CH_3SO_3^- ion ($\text{H}\cdots\text{O}$ length is 1.994 Å), resulting in 1D array formation along with *a*-axis. It is of note that no π - π stacking interaction is found between the pyridine rings. Thus, the hydrogen bonds by the hydrate water molecule would be very important for the crystallization of $[4-(N\text{-Me})\text{PyB}(\text{OH})_2]\text{CH}_3\text{SO}_3\cdot\text{H}_2\text{O}$.

Similarly to the crystal structure of $[3-(N\text{-Me})\text{PyB}(\text{OH})_2]\text{CH}_3\text{SO}_3$,³ monomeric unit formation was found in the present compound. On the other hand, dimer unit formation has been reported for non-charged boronic acids.^{5,6} This difference suggests that the positive charge of the boronic acid cation prevents dimer unit formation due to its electrostatic repulsion.

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Table 3 Structural data of hydrogen-bonds

O–H $\cdots$ O	$d_{\text{H}\cdots\text{O}}/\text{\AA}$	$d_{\text{H}\cdots\text{O}}\text{-vdW}^*/\text{\AA}$	$d_{\text{O}\cdots\text{O}}/\text{\AA}$	$\angle_{\text{O}\cdots\text{H}\cdots\text{O}}^\circ$
O(1)–H(O1) $\cdots$ O(6) ⁱ	1.924	–0.796	2.685	157
O(2)–H(O2) $\cdots$ O(3) ⁱ	1.932	–0.788	2.709	159
O(6)–H(O3A) $\cdots$ O(5)	1.900	–0.820	2.780	173
O(6)–H(O3B) $\cdots$ O(3)	1.994	–0.726	2.819	173

Symmetry code: (i) $-x, -y, -z$.

*vdW: The sum of the van der Waals radii of O and H atoms (2.72 Å).⁷

Fig. 3 Crystal packing diagram of $[4-(N\text{-Me})\text{PyB}(\text{OH})_2]\text{CH}_3\text{SO}_3\cdot\text{H}_2\text{O}$. Hydrogen bonds are shown by fine dotted lines.

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