The title compound, C_{10}H_{9}N_{2}^{+}\cdot Br^{-}\cdot H_{2}O, crystallizes in the orthorhombic crystal system. The structure consists of separate bipyridinium cations stacked along the a axis. The pyridine and pyridinium rings deviate from coplanarity by 29.6 (4)° about the C—C bridging bond. The Br^{-} ions and the water molecules are situated between the stacks.

Comment

The study of inorganic–organic hybrid materials is motivated by their potential for creating materials in which the properties of the inorganic and organic components can be controlled (Iyere et al., 1998). For instance, diprotonated 4,4’-bipyridinium cations have been used in the stabilization of molybdenum oxide layers (Zapf et al., 1997) and the isolation of a new anionic lead iodide chain structure (Chakravarthy & Guloy, 1997). Although the literature is replete with the crystal structures of the 4,4’-bipyridinium dication with a variety of anions and alkyl substituents (Cooney et al., 1990), structural details for the protonated cation with halide anions are scarce. The structure of the diprotonated 4,4’-bipyridinium dibromide (Mestvedt, 1960), dinitrate (Cooney et al., 1990) and diiodide salts (Iyere et al., 1998) have been reported. To the best of our knowledge of monoprotonated bipyridinium compounds, only the crystal structure of 4,4’-bipyridine-3,3’-dicarboxylic acid dihydrate (Bond et al., 2001), a zwitterionic molecule, viz. 3’-carboxy-4,4’-bipyridin-4-ium-3-carboxylate dihydrate, has been reported. Here we present the first structural details of the bromide salt, (I), of a monoprotonated 4,4’-bipyridinium cation.
Experimental

The title compound was prepared by adding drops (with stirring) of 48% hydrobromic acid (Fisher, ACS certified) to a mixture of 4.657 g (26 mmol) of 4,4'-bipyridyl (Aldrich) and 100 ml of purified water until a clear solution was formed. The solution was filtered to remove unreacted materials and the filtrate yielded colourless skewed hexagonal columns after slow evaporation for several days.

Crystal data

C₁₀H₉N₂⁺·Br⁻·H₂O
d = 255.12
Orthorhombic, P2₁2₁2₁
a = 7.0273 (14) Å
b = 9.6840 (19) Å
C = 15.240 (3) Å
V = 1037.1 (4) Å³
Z = 4
Dx = 1.634 Mg m⁻³

Mo Kα radiation
Cell parameters from 3777 reflections
θ = 1.0–27.5°
µ = 3.93 mm⁻¹
T = 90.0 (2) K
Skewed hexagonal column, colourless

0.25 × 0.22 × 0.20 mm

Data collection
Nonius KappaCCD diffractometer
ω scans at fixed ω = 55°
Absorption correction: multi-scan (SADABS, Sheldrick, 1996)
Tmin = 0.395, Tmax = 0.455
6291 measured reflections
2315 independent reflections
2141 reflections with I > 2σ(I)
Rint = 0.030
θmax = 27.5°
h = −9 → 8
k = −12 → 8
l = −19 → 18

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.025
wR(F²) = 0.052
S = 1.07
2315 reflections
137 parameters

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(F²) + 0.101P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)max = 0.001
Δρmax = 0.37 e Å⁻³
Δρmin = −0.36 e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.0058 (6)
Absolute structure: Flack (1983), 924 Friedel pairs
Flack parameter = 0.025 (11)

Table 1

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th></th>
<th>D–H</th>
<th>A</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1—C2</td>
<td>1.393 (4)</td>
<td>N4—C5</td>
<td>1.340 (3)</td>
</tr>
<tr>
<td>C1—C6</td>
<td>1.395 (4)</td>
<td>C5—C6</td>
<td>1.383 (3)</td>
</tr>
<tr>
<td>C1—C1'</td>
<td>1.494 (3)</td>
<td>O—H1W</td>
<td>0.88 (3)</td>
</tr>
<tr>
<td>C2—C3</td>
<td>1.380 (3)</td>
<td>O—H2W</td>
<td>0.76 (3)</td>
</tr>
<tr>
<td>C3—N4</td>
<td>1.338 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2—C1—C6</td>
<td>118.7 (2)</td>
<td>N4—C3—C2</td>
<td>120.2 (3)</td>
</tr>
<tr>
<td>C2—C1—C1'</td>
<td>120.9 (2)</td>
<td>C3—N4—C5</td>
<td>121.9 (2)</td>
</tr>
<tr>
<td>C6—C1—C1'</td>
<td>120.3 (2)</td>
<td>N4—C5—C6</td>
<td>120.3 (3)</td>
</tr>
<tr>
<td>C3—C2—C1</td>
<td>119.6 (3)</td>
<td>C5—C6—C1</td>
<td>119.2 (3)</td>
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<tr>
<td>C6—C1—C1'—C6'</td>
<td>−29.6 (4)</td>
<td>C2—C1—C1'—C2'</td>
<td>−29.6 (4)</td>
</tr>
</tbody>
</table>

Table 2

Hydrogen-bonding geometry (Å, °).

<table>
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<th>D–H</th>
<th>A</th>
<th>Δ</th>
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</thead>
<tbody>
<tr>
<td>N4—H4—N4'</td>
<td>0.88</td>
<td>1.81</td>
<td>2.681 (3)</td>
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<tr>
<td>O—H1W—Br1'</td>
<td>0.88 (3)</td>
<td>2.43 (3)</td>
<td>3.301 (2)</td>
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<tr>
<td>O—H2W—Br1</td>
<td>0.76 (3)</td>
<td>2.68 (3)</td>
<td>3.426 (2)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x, 1 + y, z; (ii) −x, y − 1/2, −z.

All H atoms were found in difference Fourier maps. Those on the cation were refined using an appropriate riding model, whereas the
water H atoms were freely refined with isotropic displacement parameters.

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO-SMN (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL (Sheldrick, 1994); software used to prepare material for publication: SHELXL97.

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References