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4,4′-Bipyridin-1-ium bromide monohydrate

Peter A. Iyere,[a]* William Y. Boadi,[a] Roxanne S. Brooks,[a] David Atwood[b] and Sean Parkin[b]

[a]Department of Chemistry, Tennessee State University, Nashville, Tennessee 37209, USA, and [b]Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, USA

Correspondence e-mail: piyere@tnstate.edu

Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.004 Å
R factor = 0.025
wR factor = 0.052
Data-to-parameter ratio = 16.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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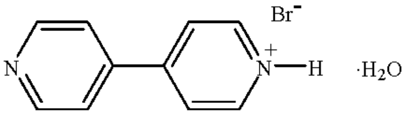
The title compound, $C_{10}H_9N_2^+ \cdot Br^- \cdot H_2O$, crystallizes in the orthorhombic crystal system. The structure consists of separate bipyridinium cations stacked along the *a* axis. The pyridine and pyridinium rings deviate from coplanarity by 29.6 (4)° about the C—C bridging bond. The Br^- 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.



(I)

The two rings are twisted by 29.6 (4)° about the C1—C1′ bond (Fig. 2). This is typical for non-planar 4,4′-bipyridinium cations, where torsion angles normally range between 17 (1) and 38.4 (9)° (Subbotin & Aslanov, 1986; Baker *et al.*, 1990; Fedin *et al.*, 1992; Alcock *et al.*, 1993; Lipka, 1983). The cations stack perpendicular to the short *a* axis (Fig. 3). The Br^- ions and water molecules are situated between the stacks. Atom N4 is hydrogen bonded to atom N4′ of a neighbouring (x, y+1, z) cation. This is different from the structure reported for its closest analogue, 4,4′-bipyridine-3,3′-dicarboxylic acid dihydrate, a zwitterionic molecule (Bond *et al.*, 2001), which exhibits an extensive network of hydrogen bonds.

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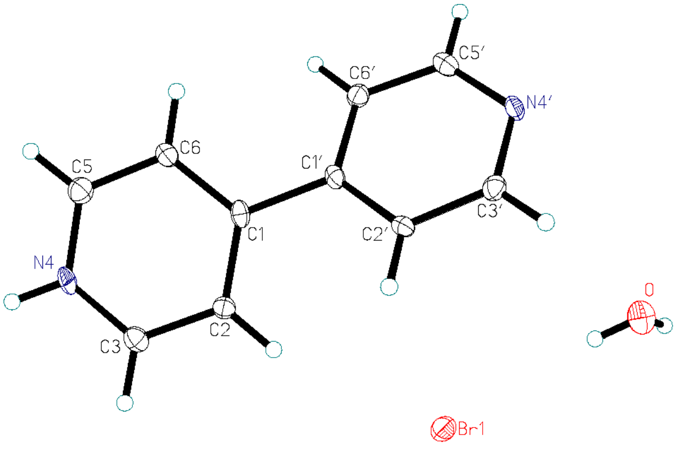

Figure 1
Displacement ellipsoid plot, at the 50% probability level, for (I).

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

$C_{10}H_9N_2^+\cdot Br^-\cdot H_2O$
$M_r = 255.12$
Orthorhombic, $P2_12_12_1$
$a = 7.0273$ (14) Å
$b = 9.6840$ (19) Å
$c = 15.240$ (3) Å
$V = 1037.1$ (4) Å^3
$Z = 4$
$D_x = 1.634$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3777 reflections
$\theta = 1.0$–27.5°
$\mu = 3.93$ 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 $\chi = 55°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.395$, $T_{max} = 0.455$
6291 measured reflections
2315 independent reflections
2141 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 8$
$k = -12 \rightarrow 8$
$l = -19 \rightarrow 18$

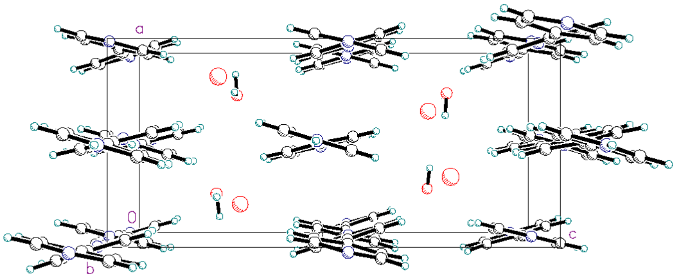

Figure 2
Packing diagram for (I), viewed along the *b* axis

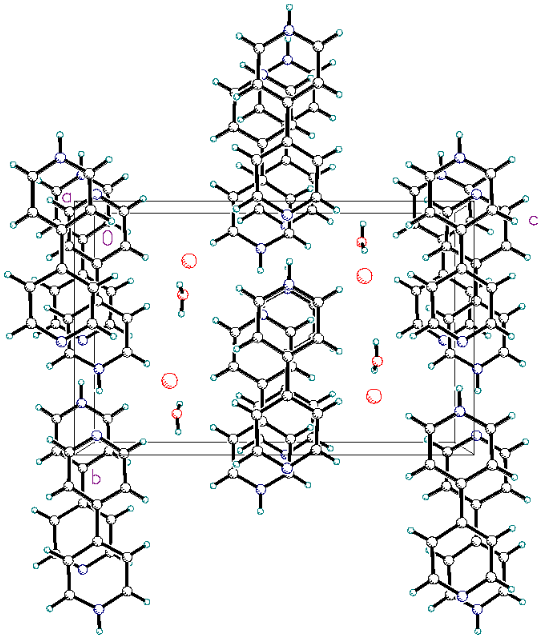

Figure 3
Packing diagram of (I), viewed along the *a* axis

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.052$
$S = 1.07$
2315 reflections
137 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 0.1011P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ 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, °).

C1—C2	1.393 (4)	N4—C5	1.340 (3)
C1—C6	1.395 (4)	C5—C6	1.383 (3)
C1—C1′	1.494 (3)	O—H1W	0.88 (3)
C2—C3	1.380 (3)	O—H2W	0.76 (3)
C3—N4	1.338 (3)		
C2—C1—C6	118.7 (2)	N4—C3—C2	120.2 (3)
C2—C1—C1′	120.9 (2)	C3—N4—C5	121.9 (2)
C6—C1—C1′	120.3 (2)	N4—C5—C6	120.3 (3)
C3—C2—C1	119.6 (3)	C5—C6—C1	119.2 (3)
C6—C1—C1′—C6′	−29.6 (4)	C2—C1—C1′—C2′	−29.6 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···N4′^{i}	0.88	1.81	2.681 (3)	173
O—H1*W*···Br1^{ii}	0.88 (3)	2.43 (3)	3.301 (2)	172 (3)
O—H2*W*···Br1	0.76 (3)	2.68 (3)	3.426 (2)	174 (3)

Symmetry codes: (i) $x, 1+y, z$; (ii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

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: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

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References

Alcock, N. W., Samotus, A. & Szklarzewicz, J. (1993). *J. Chem. Soc. Dalton Trans.* pp. 885–887.

Baker, D. J., Buckleton, J. S., Clark, G. R., Cooney, R. P. & Rickard, C. E. F. (1990). *J. Mol. Struct.* pp. 239–242.

Bond, A. D., Feeder, N., Redman, J. E. & Sanders, J. K. M. (2001). *Acta Cryst.* E**57**, o869–o871.

Chakravarthy, V. & Guloy, A. M. (1997). *Chem. Commun.* pp. 697–699.

Cooney, R. P., Baker, D. J., Buckleton, J. S., Clark, G. R. & Rickard, C. E. F. (1990). *J. Mol. Struct.* **239**, 249–255.

Fedin, V. P., Sokolov, M. N., Virovets, A. V., Podberezskaya, N.V. & Fedorov, V. Ye. (1992). *Polyhedron*, **11**, 853–857.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Iyere, P. A., Kayren L. J., Cordes, A. W., Eagle, C. T., Nile, T. A., Schimek, G. L. & Pennington, W. T. (1998). *Cryst. Eng.* **1**(2), 159–167.

Lipka, A. Z. (1983). *Z. Naturforsch. Teil B*, **38**, 1615–1619.

Mestvedt, B. (1960). *Acta Cryst.* **13**, 1043.

Nonius (1998). *KappaCCD Software*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1994). *SHELXTL*. University of Göttingen, Germany.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Subbotin, M. Yu. & Aslanov, L. A. (1986). *Zh. Neorg. Khim.* **31**, 901–904.

Zapf, P. J., Haushalter, R. C. & Zubieta, J. (1997). *Chem. Commun.* pp. 321–323.