

## 4,4'-Bipyridin-1-ium bromide monohydrate

Peter A. Iyere,<sup>a\*</sup> William Y. Boadi,<sup>a</sup> Roxanne S. Brooks,<sup>a</sup> David Atwood<sup>b</sup> and Sean Parkin<sup>b</sup><sup>a</sup>Department of Chemistry, Tennessee State University, Nashville, Tennessee 37209, USA, and <sup>b</sup>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  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
R factor = 0.025  
wR factor = 0.052  
Data-to-parameter ratio = 16.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\text{C}_{10}\text{H}_9\text{N}_2^+\cdot\text{Br}^-\cdot\text{H}_2\text{O}$ , 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  $29.6 (4)^\circ$  about the C—C bridging bond. The  $\text{Br}^-$  ions and the water molecules are situated between the stacks.

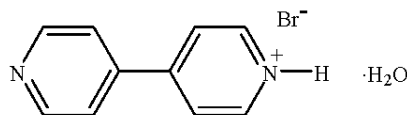
Received 12 June 2002

Accepted 3 July 2002

Online 12 July 2002

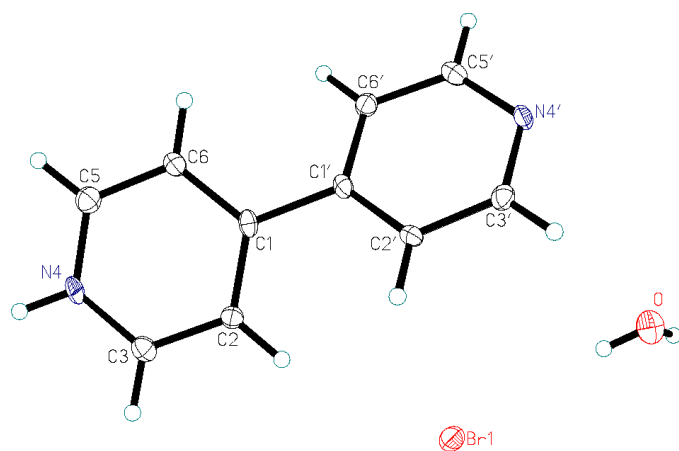
## Comment

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  $29.6 (4)^\circ$  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  $38.4 (9)^\circ$  (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  $\text{Br}^-$  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.



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

## Experimental

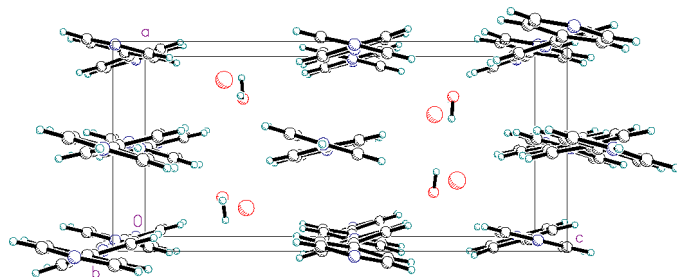
The title compound was prepared by adding drops (with stirring) of 48% hydrobromic acid (Fisher, ACS certified) to a mixture of 4.657 g (26 mmol) of 4,4'-bipyridyl (Aldrich) and 100 ml of purified water until a clear solution was formed. The solution was filtered to remove unreacted materials and the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

### Crystal data

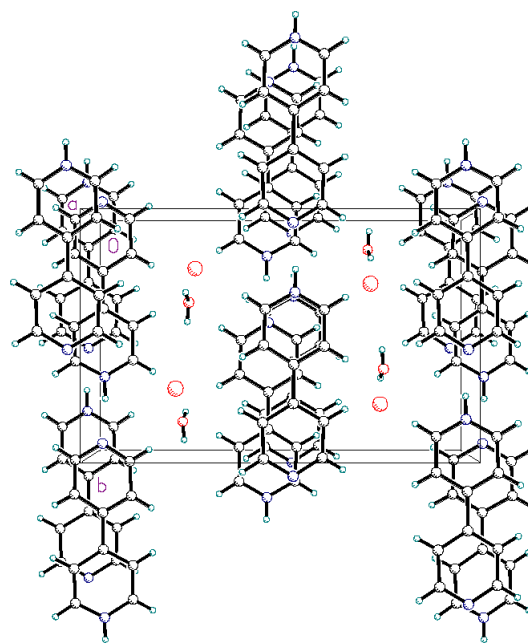
$C_{10}H_9N_2^+ \cdot Br^- \cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 255.12$	Cell parameters from 3777 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 1.0\text{--}27.5^\circ$
$a = 7.0273$ (14) Å	$\mu = 3.93$ mm $^{-1}$
$b = 9.6840$ (19) Å	$T = 90.0$ (2) K
$c = 15.240$ (3) Å	Skewed hexagonal column, colourless
$V = 1037.1$ (4) Å $^3$	$0.25 \times 0.22 \times 0.20$ mm
$Z = 4$	
$D_x = 1.634$ Mg m $^{-3}$	

### Data collection

Nonius KappaCCD diffractometer	2141 reflections with $I > 2\sigma(I)$
$\omega$ scans at fixed $\chi = 55^\circ$	$R_{int} = 0.030$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{max} = 27.5^\circ$
$T_{min} = 0.395$ , $T_{max} = 0.455$	$h = -9 \rightarrow 8$
6291 measured reflections	$k = -12 \rightarrow 8$
2315 independent reflections	$l = -19 \rightarrow 18$



**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 $F^2$	$w = 1/[\sigma^2(F_o^2) + 0.1011P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.052$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.37$ e Å $^{-3}$
2315 reflections	$\Delta\rho_{min} = -0.36$ e Å $^{-3}$
137 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	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, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N4—H4 $\cdots$ N4 <sup>(i)</sup>	0.88	1.81	2.681 (3)	173
O—H1W $\cdots$ Br1 <sup>(ii)</sup>	0.88 (3)	2.43 (3)	3.301 (2)	172 (3)
O—H2W $\cdots$ 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: *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*.

This project was supported in part by a National Science Foundation grant (ILI) to PAI. The contributions of staff and technicians are deeply appreciated.

## 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.* **E57**, 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.* **A39**, 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.* **A46**, 467–473.
- Sheldrick, G. M. (1994). *SHELXTL*. University of Göttingen, Germany.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. 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.