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2,2′-Bipyridinium(1+) bromide monohydrate

Richard J. Bowen, Manuel A. Fernandes, Patricia W. Gitari and Marcus Layh*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, PO Wits 2050, South Africa
Correspondence e-mail: marcus@aurum.chem.wits.ac.za

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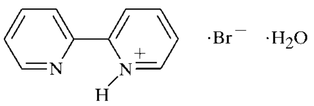
In the crystal structure of 2,2′-bipyridinium(1+) bromide monohydrate, $C_{10}H_9N_2^+\cdot Br^-\cdot H_2O$, the cation has a *cisoid* conformation with an intramolecular N—H···N hydrogen bond. The cation also forms an N—H···O hydrogen bond to an adjacent water molecule, which in turn forms O—H···Br⁻ hydrogen bonds to adjacent Br⁻ anions. In this way, a chain is formed extending along the *b* axis. Additional interactions (C—H···Br⁻ and π–π) serve to stabilize the structure further.

Comment

A number of structure determinations of monoprotonated 2,2′-bipyridine with various counter-anions have been reported in recent years [Cambridge Structural Database (Version 5.24, update 3 of July 2003; Allen, 2002) refcodes ZUTDAT (Bakshi *et al.*, 1996), NOXXED01 (Kraus & Breu, 2002), YIPYEB01 (Fialho De Assis *et al.*, 1996) and TEKLOK (Mrvoš-Sermek *et al.*, 1996)]. The geometry of the bipyridinium(1+) cation has been discussed in considerable detail by Bakshi *et al.* (1996). Against this background, the structure of the title 2,2′-bipyridinium(1+) bromide salt, (I), is presented here.



(I)

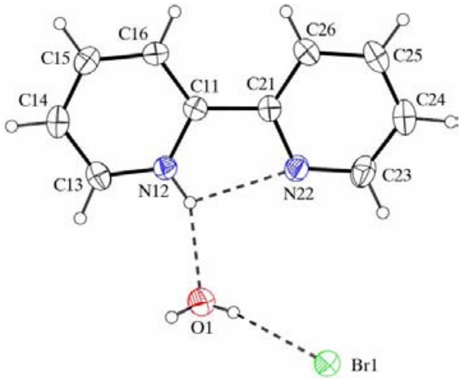


Figure 1
A view of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Intra- and intermolecular hydrogen bonds are shown as dashed lines.

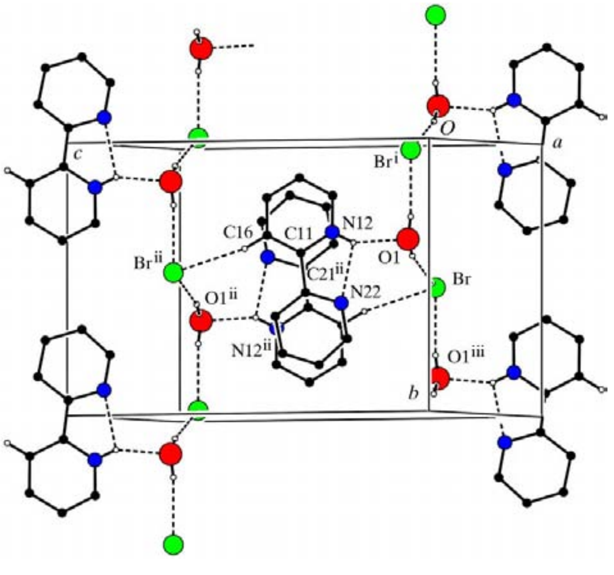


Figure 2
A view of the chain of cations, anions and water molecules running along the *b* axis in (I). Symmetry codes (i) and (ii) are as in Table 1, while (iii) is $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

In (I), the cation (Fig. 1) has a *cisoid* conformation that is comparable with previously reported bipyridinium(1+) salts and is in contrast with the *transoid* conformation found in unprotonated bipyridines [Almenningen *et al.*, 1989; Chisholm *et al.*, 1981 (CSD refcode BIPYRL03); Sengül *et al.*, 1998 (NOFZUD); Osakada *et al.*, 1991 (TAJBOV)], bipyridine adducts [Zakaria *et al.*, 2002 (AFAZAI); Bowes *et al.*, 2003 (HUSVIA)] or bipyridinium(2+) cations [Ma *et al.*, 2000 (XEGKOJ); Linden *et al.*, 1999 (FEQYIJ); Arulsamy *et al.*, 1999 (MAHNUE)]. The dihedral angle between the planes of the aromatic rings in (I) is 3.4 (2)°, which is on the smaller side of values in the observed range of 1.3–19.0° reported by Bakshi *et al.* (1996). The C—N—C angle for the protonated N12 atom [123.6 (3)°] is about 6° larger than that at the unprotonated N22 atom [117.0 (3)°]. This effect has previously been attributed to the strong electron-withdrawing effect of the H atom (Bakshi *et al.*, 1996). The distance between atoms N12 and N22 [2.626 (4) Å] is considerably shorter than that between atoms C16 and C26 [3.020 (5) Å]. The angle subtended by the cross-ring lines C14···C11 and C21···C24 is 170.55 (4)°. Similar intramolecular distances have been found in other bipyridinium(1+) cations (Bakshi *et al.*, 1996) and are

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a consequence of the intramolecular N12—H12···N22 hydrogen bond (Table 1).

The cation in (I) forms an intermolecular hydrogen bond to an adjacent water molecule (Table 1 and Fig. 1), which is further hydrogen bonded to two adjacent Br$^-$ anions, so forming a chain which extends along the *b* axis (Figs. 1 and 2). The O···Br separations (Table 1) compare well with the mean value of 3.339 (7) Å reported by Steiner (1998). These chains of hydrogen-bonded moieties are the basic building blocks of the crystal structure and are further held together by two additional types of inter-moiety interactions. Also present are significant C—H···Br interactions (Table 1, and Figs. 1 and 2), which serve to link the ribbon chains. In addition, there are significant π–π interactions between inversion-related bipyridinium cations at (x, y, z) and ($1-x$, $1-y$, $1-z$) [also denoted (ii)], as shown in Fig. 2. In this way, a layer of molecules is formed running parallel to the (101) plane. The centroid–centroid separation for ring C11–C16 at (x, y, z) and ring C21–C26 at ($1-x, 1-y, 1-z$) is 3.699 (3) Å, and the perpendicular distance between the centroid of the C11–C16 ring and the plane of the C21–C26 ring at ($1-x, 1-y, 1-z$) is 3.038 (3) Å. The shortest interatomic separation is N12···C25$^{\text{ii}}$ of 3.305 (5) Å.

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12—H12···N22	0.86	2.24	2.626 (4)	107
N12—H12···O1	0.86	2.00	2.779 (4)	150
O1—H1*A*···Br1	0.80	2.56	3.349 (3)	171
O1—H1*B*···Br1$^{\text{i}}$	0.80	2.52	3.306 (3)	167
C16—H16···Br1$^{\text{ii}}$	0.93	2.84	3.723 (4)	160

Symmetry codes: (i) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $1-x, 1-y, 1-z$.

Experimental

2,2′-Bipyridinium bromide monohydrate was obtained serendipitously as a by-product from the recrystallization of butyltris(2-pyridyl)phosphonium bromide from hot acetone after adding hexane and cooling to 253 K.

Crystal data

$C_{10}H_9N_2^+\cdot Br^-\cdot H_2O$
$M_r = 255.12$
Monoclinic, $P2_1/n$
$a = 7.954$ (6) Å
$b = 9.681$ (7) Å
$c = 14.037$ (10) Å
$\beta = 96.449$ (12)°
$V = 1074.2$ (13) Å^3
$Z = 4$
$D_x = 1.578$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 867 reflections
$\theta = 3.3$–27.8°
$\mu = 3.80$ mm^{-1}
$T = 293$ (2) K
Rectangular, light brown
0.44 × 0.14 × 0.13 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.275$, $T_{\max} = 0.613$
6413 measured reflections
2334 independent reflections
1651 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.038$
$\theta_{\max} = 27.0°$
$h = -10 \rightarrow 7$
$k = -10 \rightarrow 12$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.102$
$S = 1.03$
2334 reflections
128 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.4109P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.58$ e Å^{-3}
$\Delta\rho_{\min} = -0.85$ e Å^{-3}

All H atoms were first located from difference maps, then positioned geometrically (C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.80 Å) and allowed to ride on their respective parent atoms [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N,O})$]. Water H atoms H1*A* and H1*B* were constrained to ride on their parent O atom using an AFIX3 instruction.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*, *PLATON* (Spek, 2003) and *ORTEP*-3 (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1717). Services for accessing these data are described at the back of the journal.

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