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3-Ammonio-2,6-dibromopyridine bromide hemihydrate

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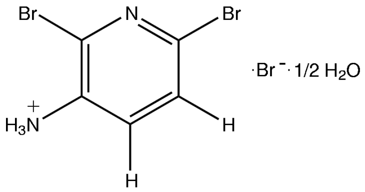
Key indicators
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.032
wR factor = 0.079
Data-to-parameter ratio = 21.6

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

In the title compound, $C_5H_5Br_2N_2^+\cdot Br^-\cdot 0.5H_2O$, 3-amino-2,6-dibromopyridine is protonated on the amine N atom and this cation is planar, excluding the H atoms attached to N. The organic cation, bromide anion and interstitial water molecule are held together by hydrogen bonding, bromine–bromine interactions and by a special type of electrostatic interaction between aryl bromine and the centroids of two pyridine rings, forming a bridge-like non-covalent bond.

Comment

Supramolecular chemistry, broadly the chemistry of multicomponent molecular assemblies in which the component structural units are typically held together by a variety of weaker non-covalent interactions, has developed rapidly over recent years (Lindoy & Atkinson, 2000). Non-covalent bonds, such as electrostatic interactions (Price & Stone, 1987), hydrogen bonding (Jeffrey, 2003), van der Waals interactions, halogen–halogen interactions (Bent, 1968), π–π stacking (Hunter & Sanders, 1990), anion–π interactions (Tarakeshwar *et al.*, 2004), halogen–π stacking (Berg & Seddon, 2003), and CH_3–π facial hydrogen bonding (Desiraju, 1995), form the main toolbox in modern supramolecular chemistry. We can use this toolbox to describe the crystallization process as a self-assembly process. Each one of these forces has its importance in describing the complete theory of how building blocks take their final geometric positions to form a model of packing that is different from or similar to another with the same synthons.



(I)

As a part of our studies of weak non-covalent bonds in the crystal systems of pyridine and its derivatives, with and without metal halides (Willett *et al.*, 2003; Haddad *et al.*, 2003), we have prepared and characterized the title compound, (I), in order to compare it with the previously reported compound 2,6-diaminopyridinium bromide monohydrate (Haddad & Al-Far, 2003), in which protonation of 2,6-diaminopyridinium takes place on the pyridine N atom, as has regularly been found in our studies of similar compounds. In (I), protonation takes place on the amine N atom rather than on the pyridine N atom. It seems that the presence of two aryl Br atoms *ortho*

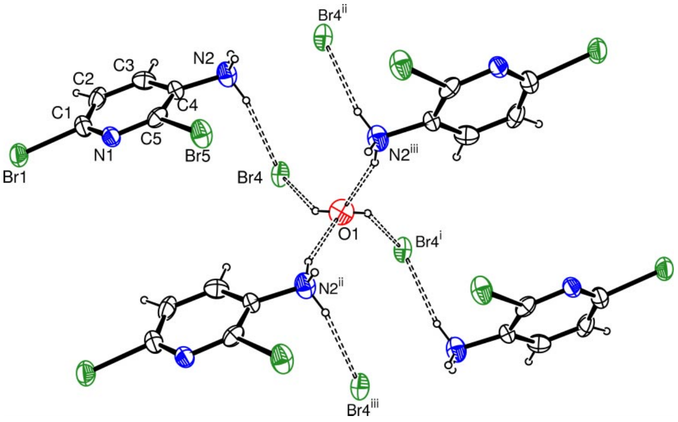


Figure 1
ORTEP-3 (Farrugia, 1997) view of the tetramer arrangement around the water molecule, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, 1 - y, z$; (ii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $\frac{1}{2} + x, 1 - y, z - \frac{1}{2}$.]

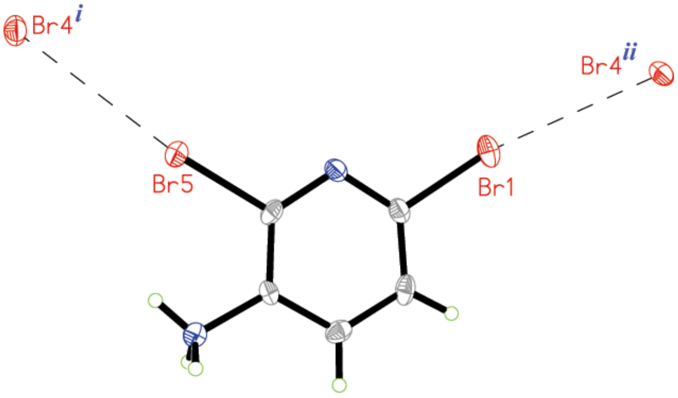


Figure 2
Representative Br$\cdots$Br interactions. [Symmetry codes: (i) $x, y, -z + 1$; (ii) $x - \frac{1}{4}, \frac{1}{4} - y, z - \frac{1}{4}$.]

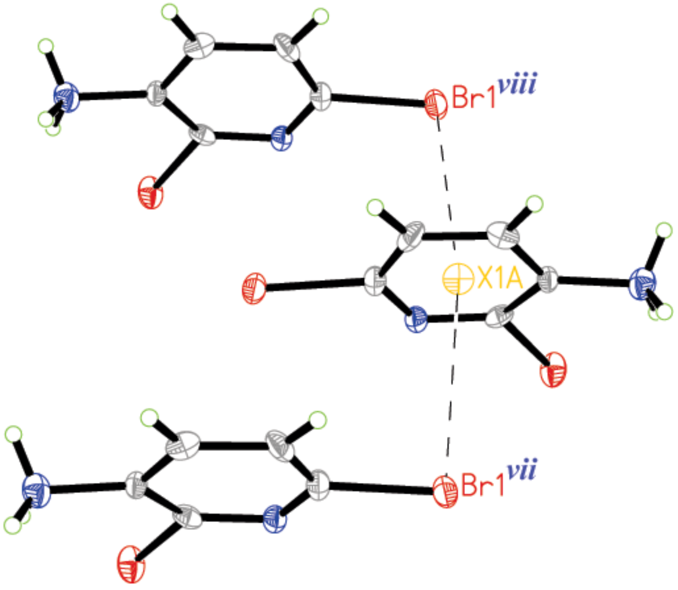


Figure 3
Bridges formed by centroids and bromide ions. [Symmetry codes: (vii) $x + \frac{1}{4}, -y + \frac{1}{4}, z + \frac{1}{4}$; (viii) $-x + \frac{1}{4}, -y + \frac{1}{4}, -z + \frac{1}{4}$.]

and *para* to the –NH_2 group renders the amine N atom more basic, and more susceptible to protonation, than the pyridine N atom. The title compound was obtained on three different occasions and the structure was determined three times employing different diffractometers at different temperatures (room temperature and 213 K), but the same result was obtained.

The organic cation, bromide anion and interstitial water molecule are held together by hydrogen bonding, bromine–bromine interactions, and a special type of electrostatic interaction between aryl atom Br1 and the centroids, *X*, of two pyridine rings.

The O atom of the water molecule behaves both as an acceptor and as a donor in hydrogen-bonding interactions. Indeed, the water molecule is linked to NH_3 and the bromide anion through N—H$\cdots$O and O—H$\cdots$Br$^-$ hydrogen bonds. Moreover, the occurrence of N—H$\cdots$Br$^-$ interactions results in a tetramer arrangement around the water molecule (Fig. 1 and Table 1). There are also weak C—H$\cdots$N interactions between one of the CH groups of the pyridine ring and the N atom of a symmetry-related pyridine ring (Table 1).

Br$\cdots$Br contacts between ionic and aryl bromides exist, with Br5$\cdots$Br4$(x, y, z - 1)$ and Br1$\cdots$Br4$(x - \frac{1}{4}, \frac{1}{4} - y, z - \frac{1}{4})$ distances of 3.3622 (12) and 3.4384 (12) Å, respectively (Fig. 2). Br–π interactions occur between the aryl bromide and a symmetry-related pyridine ring, with Br–centroid contacts Br1$\cdots$*X*1*A*$(x + \frac{1}{4}, -y + \frac{1}{4}, z + \frac{1}{4})$ = 3.428 Å and Br1$\cdots$*X*1*A*$(-x + \frac{1}{4}, y + \frac{3}{4}, z + \frac{3}{4})$ = 3.449 Å, with a bridging angle, *X*1*A*$\cdots$Br1$\cdots$*X*1*A*, of 165.4° (Fig. 3). The planar cations lie approximately in the (602) and $(60\overline{2})$ planes of the unit cell.

Experimental

Crystals were obtained from a 95% ethanol solution containing metal chloride (0.5 mmol), such as $FeCl_3$ or $HgCl_2$, and 3-aminopyridine (0.5 mmol), to which HBr (3 ml, 48%) and Br_2 (3 ml) were added. Colorless large flat crystals of hexagonal morphology developed, mixed with other crystals with a brown color in the case of $FeCl_3$ or with a different morphology in the case of $HgCl_2$. A fragment cut from a large crystal was used for the structure determination.

Crystal data

$C_5H_5Br_2N_2^+\cdot Br^-\cdot 0.5H_2O$
$M_r = 341.82$
Orthorhombic, *Fdd*2
$a = 12.123$ (5) Å
$b = 48.809$ (17) Å
$c = 6.262$ (2) Å
$V = 3705$ (2) Å^3
$Z = 16$
$D_x = 2.451$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2190 reflections
$\theta = 0.8$–27.9°
$\mu = 13.01$ mm^{-1}
$T = 293$ (2) K
Chunk, colorless
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-8 CCD Mercury diffractometer
ω scans
Absorption correction: numerical (*WinGX*; Farrugia, 1999)
$T_{min} = 0.074$, $T_{max} = 0.093$
11 841 measured reflections

2189 independent reflections
1569 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$
$\theta_{max} = 27.9°$
$h = -15 \rightarrow 15$
$k = -64 \rightarrow 64$
$l = -7 \rightarrow 8$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.079$
$S = 0.84$
2189 reflections
100 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0104P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.045$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.91$ e Å^{-3}
Absolute structure: Flack (1983), 996 Friedel pairs
Flack parameter = 0.04 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1′···Br4	0.86 (6)	2.48 (5)	3.224 (5)	144 (7)
N2—H2A···Br4	0.89	2.42	3.282 (6)	163
N2—H2B···O1^{i}	0.89	1.94	2.783 (7)	158
N2—H2C···Br4^{ii}	0.89	2.69	3.376 (6)	134
N2—H2C···Br4^{iii}	0.89	3.01	3.606 (6)	126
C2—H2···N1^{iv}	0.93	2.87	3.795 (9)	176

Symmetry codes: (i) $x-\frac{1}{2}, y, \frac{1}{2}+z$; (ii) $1-x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, y, z-\frac{1}{2}$; (iv) $x-\frac{1}{4}, \frac{1}{4}-y, \frac{3}{4}+z$.

The H atoms of the water molecule were restrained to chemically reasonable values [O—H = 0.85 (6) Å]. Other H atoms were positioned geometrically and refined with a riding model, with the $U_{\rm iso}$(H) values constrained to be 1.2$U_{\rm eq}$ of the carrier atom. The largest residual electron-density peak is 0.98 Å from atom Br4.

Data collection: *CrystalClear* (Pflugrath, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *XP* in *SHELXTL* (Bruker, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Data were collected at the X-ray Diffraction Facility, Al-Balqa Applied University, Salt, Jordan. Thanks also go to Brendan Twamely of The University Research Office, University of Idaho at Moscow, Idaho, USA.

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