

Supramolecular aggregation in 4,4'-bipyridin-1,1'-ium dichloride, 4,4'-bipyridin-1,1'-ium dinitrate and 4,4'-bipyridin-1-ium bromide

Peter Abeta Iyere,^{a*} William Y Boadi,^a David Atwood^b and Sean Parkin^b

^aDepartment of Chemistry, Tennessee State University, 3500 John Merritt Blvd, Nashville, TN 37209, USA, and ^bDepartment of Chemistry, University of Kentucky, Lexington, Kentucky 40506, USA

Correspondence e-mail: piyere@tnstate.edu

4,4'-Bipyridin-1,1'-ium dichloride [$C_{10}H_{10}Cl_2N_2$ (I)] and 4,4'-bipyridin-1,1'-ium dinitrate [$C_{10}H_{10}N_4O_6$ (II)] have been prepared and the crystal structures determined at 90.0 (2) K. Molecules of (I) are linked by two chlorine-bridged, three-centered $N-H \cdots Cl$ hydrogen bonds into chains along the *b* axis. The chains are coupled by weak $C-H \cdots Cl$ interactions into a molecular ladder along the *c* direction. In (II) each nitrate is coordinated to four bipyridinium ions through the interplay of the $N-H \cdots O$ and $C-H \cdots O$ contacts, resulting in a three-dimensional zigzag sheet on the *ab* plane. The sheets stack along the *c* axis. In 4,4'-bipyridin-1-ium bromide monohydrate [$C_{10}H_9N_2^+ \cdot Br^- \cdot H_2O$ (III)] the bipyridinium ions are linked by three-center $N-H \cdots N'$ hydrogen bonds in a head-to-tail fashion to form chains along the *b* axis. The chains are linked by $C-H \cdots Br$ and $C-H \cdots OH_2$ into a three-dimensional framework.

Received 26 March 2003

Accepted 12 May 2003

1. Introduction

Supramolecular aggregation has been used in crystal synthesis by design to control the molecular components of a solid through the exploitation of monatomic (Pennington *et al.*, 1997; Iyere *et al.*, 1998) and polyatomic (Orpen *et al.*, 1999; Kelly *et al.*, 2002) synthons (Desiraju, 1995). Intermolecular interactions are used in crystal engineering to establish a consistent connection between molecules and supramolecular structures. Consequently, the interplay and directionality of hydrogen bonds and short contacts can be used as the basis for supramolecular construction using suitable building blocks. It has been reported that although $C-H \cdots O$ is not a van der Waals contact, it is strong enough to distort the geometry of the hydrogen bonds (Rowland & Taylor, 1996). Although the mode of interaction of the halogens is unclear when they form short non-bonded contacts in crystals, they are still used in systematic crystal engineering (Desiraju, 1995).

Current effort to merge supramolecules and polymers is based on the idea that the nanoscale structural design of the supramolecule and the organizing capability of supramolecular chemistry can be manipulated to produce a super-polymer with controllable and processable structures (Hannon *et al.*, 2002). In this regard some attempts have been made to create a supramolecular unit that could serve as a 'minor co-polymer in a copolymerization process' to build a polymer network that has numerous potential applications.

Many inorganic-organic hybrid materials have been synthesized by others (Hangman *et al.*, 1999; Ching-Hui *et al.*, 2001) and our group using the 4,4'-bipyridinium ion. None-

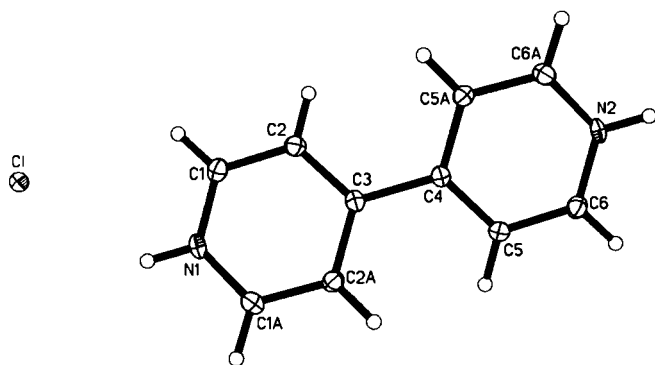


Figure 1
A molecule of (I) showing the thermal ellipsoids at 50% probability and the numbering scheme.

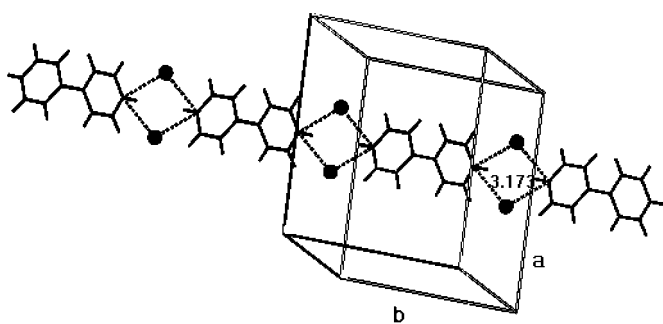


Figure 2
A single chain of (I) showing the asymmetric two-chlorine-bridged, three-centered N—H...Cl hydrogen bonds along the *b* axis.

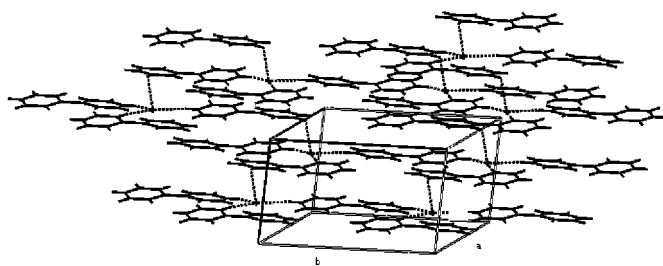


Figure 3
Packing diagram of (I) showing the distorted trigonal pyramidal contact environment of the chloride ions.

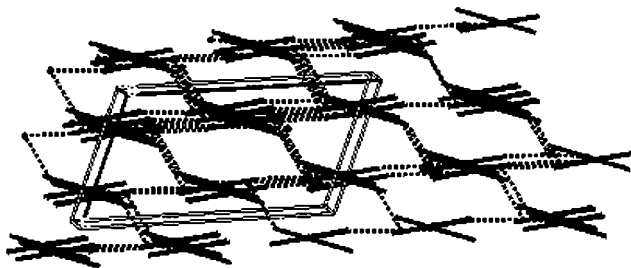
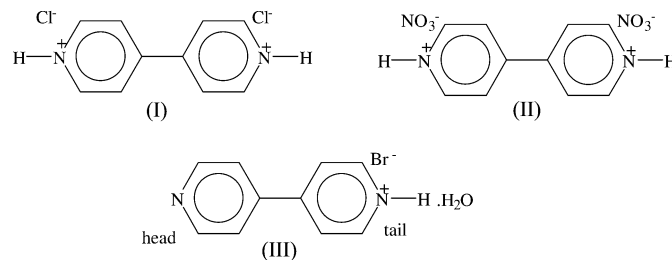


Figure 4
Packing diagram of (I) viewed along the *b* axis.

theless, not much has been done in the study of the simple halide salts of this versatile cation. In an exploration of the possibility of modifying the shape and planarity of the protonated 4,4' bipyridinium ion by halide ions and to extend our knowledge of their modes of supramolecular aggregation, we report the synthesis, crystal structure of (I) and short-contact analysis of (I) and (III). This is of particular interest because the herbicidal and other activities of paraquat and its analogues are influenced by the planarity of the bipyridinium rings. The synthesis, crystal structure and short-contact analysis of the dinitrate salt (II) are included for comparison.



2. Experimental

2.1. Synthesis

Compound (I) was prepared by adding drops (with stirring) of 69.8% hydrochloric acid (Fisher, ACS certified) to a mixture of 4.655 g (26 mmol) of 4,4'-bipyridyl (Aldrich) and 50 ml of purified water until a clear solution was formed. The solution was filtered to remove unreacted material and the filtrate yielded colorless irregular shards after slow evaporation for several days. Compound (II) was prepared in a similar fashion using 69.8% nitric acid (Fisher, ACS Plus). The nitrate solution yielded colorless blocks after slow evaporation for several days.

2.2. Data collection, structure solution and refinement

All H atoms were found in the difference Fourier maps. Those on the cation were refined using an appropriate riding model. Crystallographic data for (I) and (II) are displayed in Table 1, selected geometric parameters are given in Table 2 and short contacts less than the sum of the van der Waals radii of the respective elements are displayed in the figures and in Table 3.¹

3. Results and discussion

The low-temperature (173 K) structure of (I) was first reported to show the NH...Cl pattern in supramolecular metal-based structures (Dolling *et al.*, 2001). Essentially a two-chlorine-bridged three-centered N—H...Cl hydrogen bond was identified as the structure-directing motif in all of the

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA5002). Services for accessing these data are described at the back of the journal.

Table 1
Experimental table.

	Dichloride	Dinitrate
Crystal data		
Chemical formula	C ₁₀ H ₁₀ Cl ₂ N ₂	C ₁₀ H ₁₀ N ₄ O ₆
<i>M_r</i>	229.10	282.22
Cell setting, space group	Monoclinic, <i>C2/c</i>	Orthorhombic, <i>Fdd2</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.6630 (10), 12.0980 (10), 7.0330 (10)	27.4380 (16), 23.4310 (12), 3.5877 (2)
β (°)	112.6000 (10)	90.00
<i>V</i> (Å ³)	994.70 (18)	2306.5 (2)
<i>Z</i>	4	8
<i>D_x</i> (Mg m ⁻³)	1.530	1.625
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	1163	3415
θ range (°)	1.0–27.5	1.0–27.5
μ (mm ⁻¹)	0.61	0.14
Temperature (K)	90.0 (2)	90.0 (2)
Crystal form, color	Irregular shard, colorless	Block, colorless
Crystal size (mm)	0.50 × 0.25 × 0.13	0.35 × 0.22 × 0.22
Data collection		
Diffractometer	Nonius KappaCCD	Nonius KappaCCD
Data collection method	ω scans at fixed $\chi = 55^\circ$	ω scans at fixed $\chi = 55^\circ$
Absorption correction	Multi-scan (based on symmetry-related measurements)	SCALEPACK
<i>T_{min}</i>	0.750	0.954
<i>T_{max}</i>	0.925	0.971
No. of measured, independent and observed reflections	2173, 1135, 959	2901, 969, 910
Criterion for observed reflections	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R_{int}</i>	0.021	0.026
θ_{\max} (°)	27.4	25.0
Range of <i>h</i> , <i>k</i> , <i>l</i>	−16 ⇒ <i>h</i> ⇒ 16 −15 ⇒ <i>k</i> ⇒ 15 −9 ⇒ <i>l</i> ⇒ 9	−32 ⇒ <i>h</i> ⇒ 32 −24 ⇒ <i>k</i> ⇒ 27 −3 ⇒ <i>l</i> ⇒ 4
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.026, 0.065, 1.05	0.027, 0.068, 1.11
No. of reflections	1135	969
No. of parameters	66	92
H-atom treatment	Constrained	Constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 1.1028P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 1.7936P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	<0.0001	<0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.32, −0.24	0.17, −0.17
Extinction method	None	SHELXL
Extinction coefficient	–	0.0021 (4)
Absolute structure	–	Flack (1983)

Computer programs: COLLECT (Nonius, 1998), SCALEPACK, DENZO-SMN (Otwinowski & Minor, 1997), SHELXST7 (Sheldrick, 1990), SHELXL97 (Sheldrick, 1997), XP in Siemens SHELXTL (Sheldrick, 1994) and local procedures.

metal complexes reported. Our crystallographic parameters are in accordance with those obtained previously (Dolling *et al.*, 2001). The supramolecular aggregation of (I) is dominated by discrete bipyridinium cations and chloride anions (Fig. 1) that form chains stabilized by strong bifurcated two chlorine-bridged three-centered N–H···Cl hydrogen bonds in the crystallographic *b* direction (Fig. 2). The C–H···Cl contacts link the chains together to form sheets parallel to the *ab* plane. The sheets are linked together by additional C–H···Cl interactions to give a three-dimensional molecular ladder

along the *c* axis (Fig. 3). The packing diagram of (I) viewed along the *b* axis is shown in Fig. 4.

Compound (I) bears close structural resemblance to to triclinic (Iyere *et al.*, 1998), monoclinic (Weakley, 1987), orthorhombic (Barker *et al.*, 1990) and polymorphs of the bipyridinium dication (Tosik *et al.*, 1990). Although these complexes have N–H···X, C–H···O and N–H···O interactions, their packing diagrams are different. For example, in the diiodide salt (Iyere *et al.*, 1998) the contact environment of the iodide ion is distorted trigonal planar, while that of (I) is distorted tetrahedral or distorted trigonal pyramidal (Fig. 3) because of the interaction of a chloride ion with H1 at (*x*, *y*, *z*), H2 at (*x*, *y* + 1, *z*), H1A at ($\frac{1}{2} - x$, $\frac{1}{2} - y$, $-z$) and H2A at ($\frac{1}{2} - x$, $y + \frac{1}{2}$, $\frac{1}{2} - z$) (Table 3). Unlike in (I), the iodide and bipyridinium ions do not self-associate because of the absence of strong directional interactions. Consequently, the bipyridinium rings in the diiodide salt are planar, while the dichloride salt (I) exhibits a non-planar conformation with a dihedral angle of 26.4 (6) Å. The planarity and parallel stacking of the rings in the diiodide salt may allow for π–π stacking which is not possible in the dichloride, bromide and dinitrate salts (Chen *et al.*, 2000). The greater number of interactions in the chloride moiety is probably because of the greater electronegativity and the environment of the chloride ion.

The synthesis and crystal structure of (II) at room temperature was first reported in 1990 (Barker *et al.*, 1990). The study was centered on the use of Raman spectroscopy to show cation–anion interactions. We have prepared

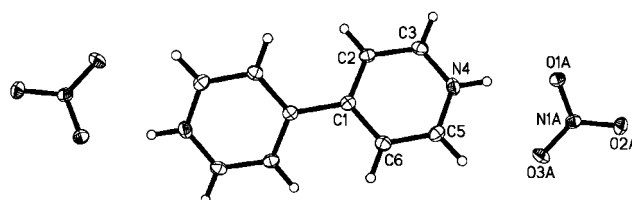


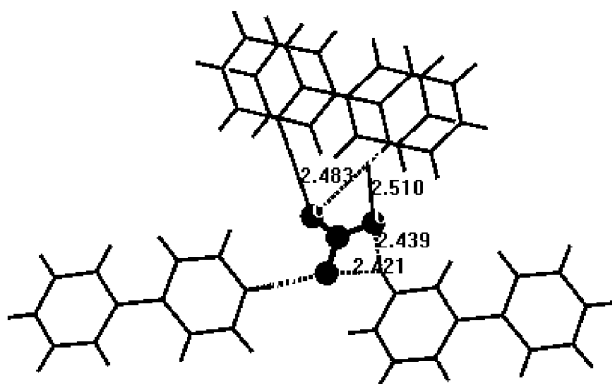
Figure 5
A molecule of (II) showing the thermal ellipsoids at 50% probability and the numbering scheme.

Table 2
Selected geometric parameters (Å, °).

Dichloride			
N1—C1	3.412 (18)	C3—C4	1.491 (3)
N2—C6	1.3391 (17)	C4—C5	1.3949 (18)
C1—C2	1.380 (2)	C5—C6	1.376 (2)
C2—C3	1.3991 (18)		
Dinitrate			
C1—C2	1.391 (2)	C5—C6	1.374 (2)
C1—C6	1.397 (2)	N1A—O2A	1.2459 (18)
C2—C3	1.380 (3)	N1A—O3A	1.2494 (19)
C3—N4	1.340 (2)	N1A—O1A	1.2727 (19)
N4—C5	1.341 (2)		
C2—C1—C6			
C2—C1—C6	119.34 (16)	C5—C6—C1	118.94 (16)
C3—C2—C1	119.42 (15)	O2A—N1A—O3A	121.71 (15)
N4—C3—C2	119.55 (16)	O2A—N1A—O1A	118.64 (14)
C3—N4—C5	122.56 (15)	O3A—N1A—O1A	119.65 (14)
N4—C5—C6	120.18 (15)		

the nitrate salt by a slightly different method and re-determined its structure at 90.0 (2) K. The structure (II) reported herein (Fig. 5) is somewhat more precise ($R = 0.027$). The pyridinium rings are twisted by $38.7(6)^\circ$ (reported 39.0°). Hydrogen bond lengths between the nitrate and the N—H of the pyridinium ring are N1---O1 = 2.668 and N1---O2 = 3.148 Å. These are different from those reported earlier (Barker *et al.*, 1990; N1---O1 = 2.67 Å for two of the O atoms on the nitrate moiety). The hydrogen-bond values in the present study are similar to the N---O in 4,4'-bipyridin-1-ium bromide monohydrate (Iyere *et al.*, 2002). However, the effect of the hydrogen bonds on the third N---O bond length of the nitrate ion is similar to that observed (Barker *et al.*, 1990).

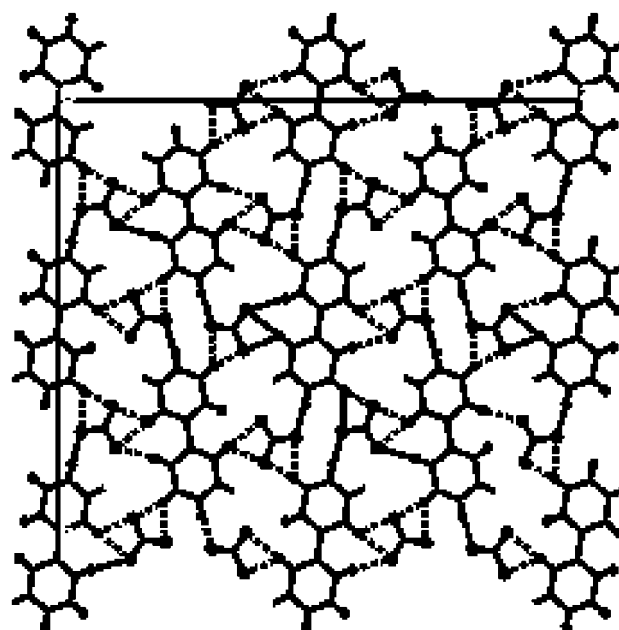
Supramolecular aggregation in the packing of the nitrate complex should be more complicated than those of the halide ion because of its size and the number of donor atoms. The crystal structure of (II) consists of discrete bipyridinium cations and nitrate anions. Each nitrate ion is hydrogen-bonded to one bipyridinium cation *via* one N4—H4---O1A contact and interacts with three other bipyridinium cations *via*

**Figure 6**
Partial packing diagram of (II) showing the contact environment of the nitrate ion.**Table 3**
Geometric parameters for N—H...Cl, C—H...Cl, N—H...O, C—H...O and N—H...N interactions in (I), (II) and (III) (Å, °).

$D-H \cdots A$	$D-H$ (Å)	$H \cdots A$ (Å)	$D \cdots A$ (Å)	$D-H \cdots A$ (°)
Compound (I), dichloride				
N2—H2...Cl ⁱ	0.88	2.51	3.173 (1)	132
N1—H1...Cl	0.88	2.52	3.173 (1)	132
C5—H5...Cl ⁱⁱ	0.95	2.65	3.587 (2)	170
C1—H1A...Cl ⁱⁱⁱ	0.95	2.74	3.414 (1)	129
C6—H6...Cl ^{iv}	0.95	2.76	3.302 (2)	117
C1—H1A...Cl	0.95	2.77	3.309 (2)	117
C2—H2A...Cl ^v	0.95	2.86	3.685 (2)	145
Compound (II), dinitrate				
N4—H4...O1A	0.88	1.81	2.686 (2)	173
N4—H4...N1A	0.88	2.57	3.337 (2)	146
C2—H2...O3A ^{vi}	0.95	2.48	3.409 (2)	165
C3—H3...O1A ^{vii}	0.95	2.42	3.139 (2)	132
C3—H3...O2A ^{viii}	0.95	2.44	3.310 (2)	152
C6—H6...O2A ^{viii}	0.95	2.51	3.130 (2)	123
C6—H6...O3A ^{viii}	0.95	2.49	3.435 (2)	172
Compound (III), bromide monohydrate				
N4—H4...N4 ^{ix}	0.88	1.80	2.680 (3)	173
O—H1W...Br1 ^x	0.88 (3)	2.43 (3)	3.301 (2)	171 (3)
O—H2W...Br1	0.76 (3)	2.68 (3)	3.435 (2)	173 (3)
C5'—H5'...Br1 ^{xi}	0.95	2.85	3.791 (3)	169

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

five C—H...O short contacts (Fig. 6). In addition, the nitrogen of the nitrate ion interacts with the hydrogen of the bipyridinium ion *via* an N4—H4...N1A contact (Table 3). When viewed down the c axis (as shown by Barker *et al.*, 1990), the two closest bipyridinium cations overlap giving the false impression that one nitrate ion is bonded to three cations (Fig. 7). Although the short-contact interactions are complex, there

**Figure 7**
Packing diagram of (II) viewed along the c axis

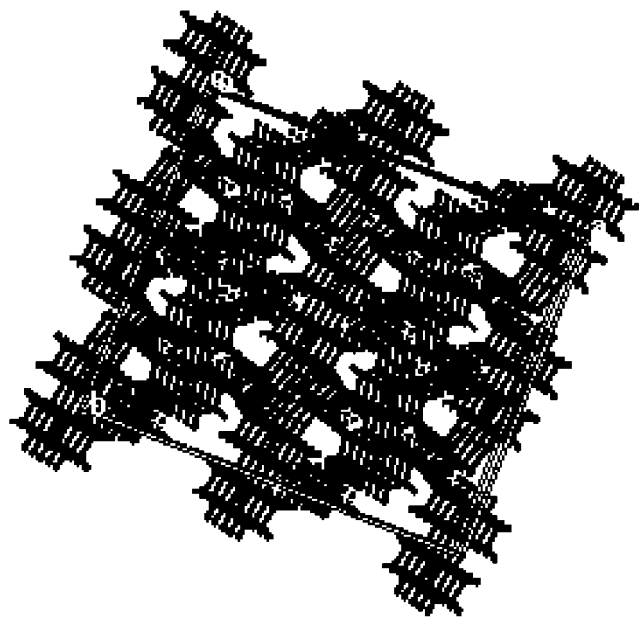


Figure 8
Packing diagram of (III) viewed along the *c* axis

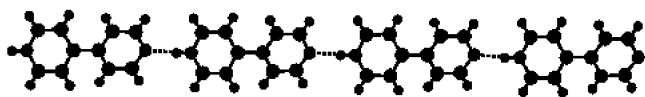


Figure 9
A single chain of (III) showing the asymmetric head-to-tail hydrogen bond along the *b* axis.

is some directionality in the overall packing of the ions. The cations and the anion form a sheet on the *ab* plane and stack along the *c* axis (Fig. 8).

We recently reported the synthesis and crystal structure of (III) without a detailed analysis of short contacts (Iyere *et al.*, 2002). In (III), the pyridinium ring is linked to the pyridine ring of another cation by a strong N4–H4···N4' hydrogen bond (Table 3) in a head-to-tail fashion to form a chain along the crystallographic *b* axis (Fig. 9). One water molecule is linked to two bromide ions by O–H1W···Br1 and O–H2W···Br1 (Table 3) hydrogen bonds which form a zigzag string along the *b* axis (Fig. 10). The chain and the water–bromide string are linked by C5–H5···O and C2'–H2'···O contacts to form a wavy sheet on the *bc* plane. The sheets stack along the *a* axis through another C5'–H5'···Br contact (Fig. 11). The packing mode of this molecule is greatly altered by the presence of a water molecule because of the propensity of the latter to form normal hydrogen bonds.

This work was supported in part by the National Science Foundation (ILI grant to Peter A. Iyere). We thank the staff and technicians in the Department of Chemistry at the University of Kentucky, Lexington, and Tennessee State University, Nashville, Tennessee, for their assistance.

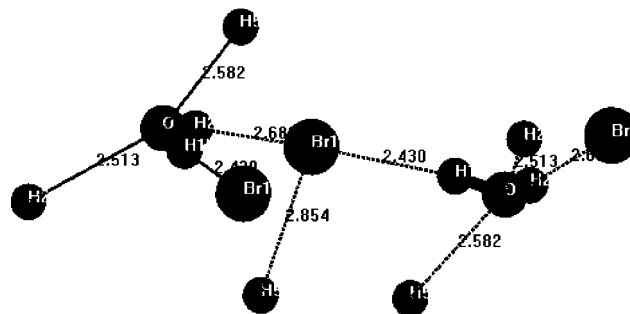


Figure 10
Partial packing diagram of (III) showing the contact environment of the bromide ion and the water molecule.

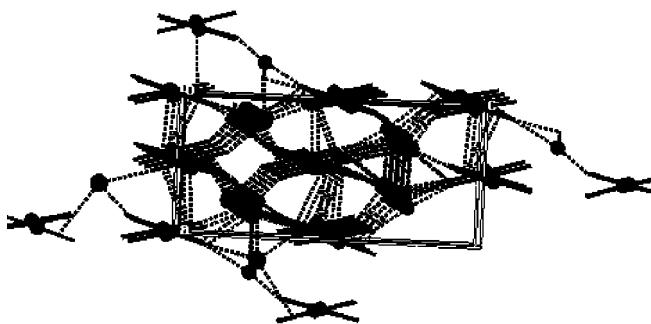


Figure 11
Packing diagram of (III) viewed along the *b* axis.

References

- Barker, D. J., Cooney, R. P., Buckleton, J. S., Clark, G. R. & Rickard, C. E. F. (1990). *J. Mol. Struct.* **239**, 249–255.
- Chen, H., Zhang, L., Cai, Z., Yang, G. & Chen, X. (2000). *J. Chem. Soc. Dalton Trans.* pp. 2463–2466.
- Ching-Hui, H., Li-Hsun, H. & Kwang-Hwa, L. (2001). *Inorg. Chem.* **40**, 2625–2627.
- Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311.
- Dolling, B., Orpen, G. A., Gillon, A. L., Starbuck, J. & Wang, X.-M. (2001). *Chem. Commun.* pp. 567–568.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hangman, P. J., Hangman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2640.
- Hannon, M. J., Arnaud, L., Jacqueline, H., Andrew, M. & David, M. H. (2002). *Chem. Commun.* DOI: 10.1039/b210019c.
- Iyere, P. A., Boadi, W. Y., Brooks, R. S., Atwood, D. & Parkin, S. (2002). *Acta Cryst.* **E58**, o825–o827.
- Iyere, P. A., Kayren, L. J., Cordes, A. W., Eagle, C. T., Nile, T. A., Schimek, G. L. & Pennington, W. T. (1998). *Cryst. Engng.* **1**, 159–167.
- Kelly, C. J., Wardell, J. L., Wardell, S. M. S. V., Low, J. N. & Glidewell, C. (2002). *Acta Cryst.* **B58**, 94–108.
- Nonius (1998). *KappaCCD Software*. Nonius BV, Delft, The Netherlands.
- Orpen, J., Gillon, A. L., Starbuck, J., Wang, X.-M., Rodriguez-Martin, Y. & Ruiz-Perez, C. (1999). *Chem. Commun.* p. 2287.
- Otwinowski, Z. & Minor, W. (1997). *Methods Emymol.* **276**, 307–326.
- Pennington, W. T., Hook, L. L., Hanks, T. W., Grabarczyk, M., Drake, W. G. & Bailey, R. D. (1997). *J. Chem. Soc. Perkin Trans. 2*, pp. 2773–2779.

Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

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

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Tosik, A., Bukowska-Strzyewska, M. & Mrozinski, J. (1990). *J. Coord. Chem.* **21**, 253.

Weakley, T. J. R. (1987). *Acta Cryst.* **C43**, 2144–2146.