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A novel framework of N—H···Br hydrogen bonds forming Br(4,4′-bipyridinium)$_4$ supramolecular synthons: bis(4,4′-bipyridinium) tris[tetrabromidoferrate(III)] bromide

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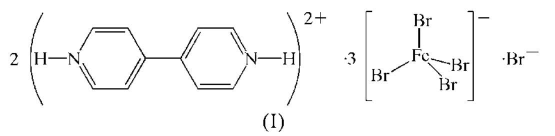
In the asymmetric unit of the title compound, $(C_{10}H_{10}N_2)_2[FeBr_4]_3Br$, the Fe atoms are in a distorted tetrahedral environment. The crystal structure contains a novel arrangement of Br(4,4′-bipyridinium)$_4$ supramolecular synthons assembled *via* short N—H···Br hydrogen bonds (H···Br = 2.55, 2.40, 2.38 and 2.55 Å), where four cations surround one nonbonded bromide ion in a tetrahedral arrangement. These synthons are further connected by hydrogen bonds using the remaining terminal NH hydrogens in each cation and the Br$^-$ ions to form an adamantoid-like network and thus produce a three-dimensional supramolecular architecture with the $[FeBr_4]^-$ ions located in the cavities. The structure shows no significant intermolecular Br···Br, Br···aryl or aryl–aryl interactions.

Comment

Research in the field of inorganic–organic hybrids is of great interest owing to their magnetic, electronic and optoelectric properties (Cui *et al.*, 2000; Lacroix *et al.*, 1994; Chakravarthy & Guloy, 1997). The interactions governing the crystal organization are expected to affect the packing and then the specific properties of such solids. For example, 4,4′-bipyridine (bpy) and similar ligands have been used through their two N atoms as neutral linkers to generate and stabilize many open one-, two- and three-dimensional coordination polymers to form supramolecular coordination assemblies (Díaz de Vivar *et al.*, 2007*a*,*b*; Dong *et al.*, 2007; Lu *et al.*, 2007; Xie *et al.*, 2007, *etc.*). We report here the crystal structure of the title complex, (I), where the protonated 4,4′-bipyridinium ligand, $(bpyH_2)^{2+}$, is not involved in coordination but does participate in extensive N—H···Br intermolecular interactions, affording a supramolecular assembly structure.

The asymmetric unit of the title compound, (I), contains two $(bpyH_2)^{2+}$ cations, three $[FeBr_4]^{2-}$ anions and one bromide ion (Fig. 1). The $[FeBr_4]^-$ anions exhibit a slightly distorted octahedral arrangement around the Fe atom, with Fe—Br bond lengths in the ranges 2.3210 (9)–2.3448 (9), 2.3350 (9)–2.3535 (9) and 2.3311 (9)–2.3443 (9) Å for atoms Fe1, Fe2 and Fe3, respectively, leading to mean values of 2.3369 (9), 2.3400 (9) and 2.3366 (9) Å (Table 1); the Br—Fe—Br angles, in turn, span the ranges 107.04 (3)–113.81 (4), 107.98 (4)–111.36 (3) and 105.60 (3)–112.80 (4)°, respectively. These values are in accordance with corresponding values in the literature (Benito-Garagorri *et al.*, 2006; Kruszynski & Wyrzykowski, 2006).



(I)

The bond distances and angles in the protonated cations do not differ from those reported in the neutral units (Diaz de Vivar *et al.*, 2007*a*,*b*; Dong *et al.*, 2007; Lu *et al.*, 2007). The rings in the two independent cations are planar, and are twisted around the central C—C bond by 37.32 (19) and 39.32 (17)°. This effect could be the result of packing stress associated with the formation of the Br(bpyH$_2$)$_4$ supramolecular synthon (see the description below).

Fig. 2 shows the intermolecular N—H···Br hydrogen bonds in (I). These interactions are significant, with short *D*···*A* distances (in the range 2.38–2.55 Å) and with *D*—H···*A* angles spanning the range 140–155° (Table 2).

The hydrogen bonds cause the formation of a supramolecular architecture, best described as built up by Br(bpyH$_2$)$_4$ supramolecular synthons (Fig. 2) assembled *via* short N—H···Br hydrogen bonds, where four cations surround one (central) nonbonded bromide ion in an approximately tetrahedral arrangement. These synthons are

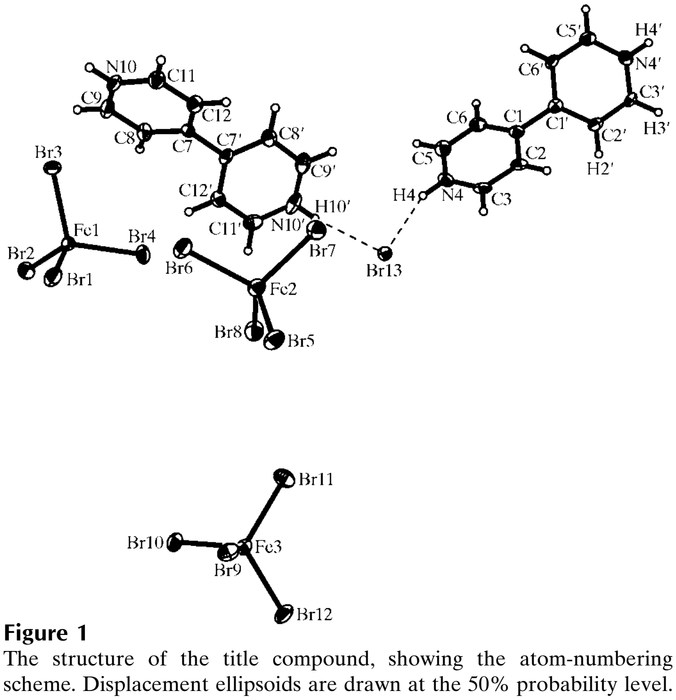


Figure 1
The structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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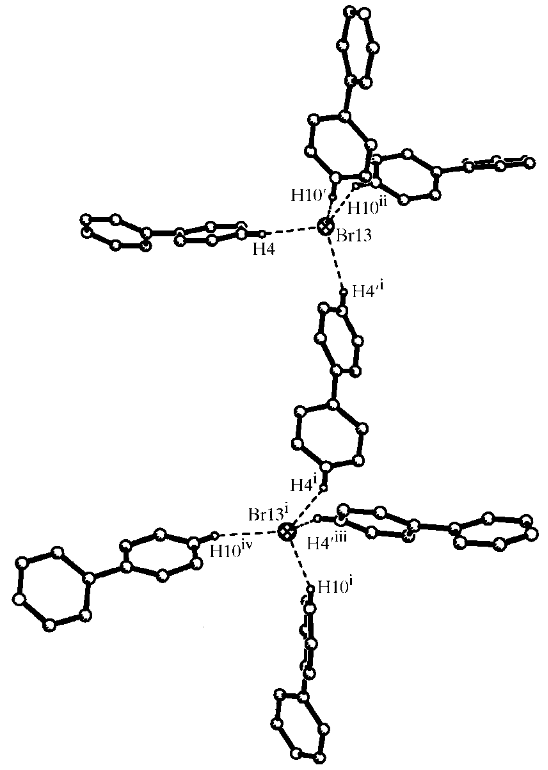

Figure 2
The Br(bpyH$_2$)$_4$ tetrahedral synthons in (I). The N—H···Br interactions are shown as dashed lines. [Symmetry codes: (i) $-\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (ii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, y, 1+z$; (iv) $-\frac{3}{2}+x, \frac{3}{2}-y, 1-z$.]

further connected by hydrogen bonds to the bromide ions by way of the remaining terminal NH hydrogens in each cation to form an adamantoid-like network that extends into a three-dimensional structure. The molecules of the discrete [FeBr$_4$]$^-$ anions occupy the cavities that result from the three-dimensional assembly of the Br(bpyH$_2$)$_4$ entities.

A number of structures containing both bpyH$_2$ and bromide groups have been reported, but few of them exhibit multiple bpyH$_2$···Br$^-$ interactions. In fact, in the more simple structures, such as 4,4′-bipyridin-1-ium bromide monohydrate (Iyere *et al.*, 2002, 2003) and 2,2′-bipyridinium(1+) bromide monohydrate (Bowen *et al.*, 2004), no N—H···Br interactions are present at all in the structures.

We could trace a few examples of complex hydrogen-bonding schemes of a similar sort to, but rather different from, that reported here, for example, 6-oxo-1,6-dihydro-3,4′-bipyridine-5-carbonitrile hydrogen bromide (Cody & Wojtczak, 1991), where the bromide ion connects, as in (I), four cations *via* hydrogen-bonding interactions, but only one of them is of the N—H···Br type, the remaining four being C—H···Br interactions. Another example is 4,4′-bipyridinediium dibromide (Ilyukhin & Petrosyants, 2006), where the N—H···Br hydrogen bonds are present as a bridging motif, leading to infinite ···bpyH$_2$···2Br$^-$···bpyH$_2$···2Br$^-$··· linear layers. The same motif is observed in the corresponding dichloride cation (Iyere *et al.*, 2003).

Finally, the structure of (I) shows no significant intermolecular Br···Br, Br···aryl or aryl–aryl interactions.

Experimental

For the preparation of (I), FeCl$_3$·6H$_2$O (0.811 g, 3 mmol) dissolved in absolute ethanol (15 ml) and liquid Br$_2$ (80%, 1 ml) were added dropwise to a (stirred) hot solution of 4,4′-bipyridyl (0.312 g, 2 mmol) dissolved in ethanol (15 ml) and HBr (60%, 3 ml). After heating for 2 h, the mixture was filtered and allowed to stand undisturbed at room temperature. The salt crystallized out over a period of 2 d as red block-shaped cubes. The crystals were filtered off, washed with ethanol and then diethyl ether, and dried under vacuum (yield 0.95 g, 62.4%).

Crystal data

(C$_{10}$H$_{10}$N$_2$)$_2$[FeBr$_4$]$_3$Br
M_r = 1522.65
Orthorhombic, $P2_12_12_1$
a = 11.5536 (6) Å
b = 18.4508 (9) Å
c = 18.9844 (10) Å
V = 4047.0 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 13.92 mm^{-1}
T = 84 (2) K
0.23 × 0.21 × 0.20 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{\min}$ = 0.056, $T_{\max}$ = 0.064
46358 measured reflections
9301 independent reflections
7964 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.055
S = 1.00
9301 reflections
361 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.60 e Å^{-3}
$\Delta\rho_{\min}$ = −0.43 e Å^{-3}
Absolute structure: Flack (1983), 5151 Friedel pairs
Flack parameter: 0.010 (8)

Table 1
Selected bond lengths (Å).

Fe1—Br1	2.3210 (9)	Fe2—Br8	2.3360 (9)
Fe1—Br4	2.3406 (9)	Fe2—Br6	2.3535 (9)
Fe1—Br3	2.3411 (8)	Fe3—Br11	2.3311 (9)
Fe1—Br2	2.3448 (9)	Fe3—Br12	2.3319 (9)
Fe2—Br5	2.3350 (9)	Fe3—Br9	2.3395 (9)
Fe2—Br7	2.3352 (9)	Fe3—Br10	2.3443 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
N4′—H4′···Br13^{i}	0.88	2.55	3.274 (4)	140
N4—H4···Br13	0.88	2.40	3.199 (4)	152
N10′—H10′···Br13	0.88	2.38	3.195 (4)	155
N10—H10···Br13^{ii}	0.88	2.55	3.290 (4)	142

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

H atoms were positioned geometrically (N—H = 0.88 Å and C—H = 0.95 Å) and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N).

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3043). Services for accessing these data are described at the back of the journal.

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