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Dimethylpyrazinium tetrabromidoferrate(II): Br···aryl···Br and Br···Br intermolecular interactions

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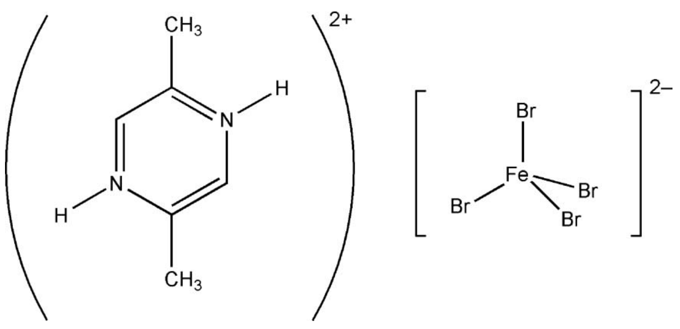
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.014 Å; R factor = 0.043; wR factor = 0.113; data-to-parameter ratio = 18.4.

In the title compound, $(C_6H_{10}N_2)[FeBr_4]$, the asymmetric unit contains one half-cation and one half-anion, where the Fe atom has a distorted tetrahedral environment. The Fe atom and two Br atoms lie on a mirror plane; the cation is centrosymmetric. In the crystal structure, the cations and anions are packed into alternate stacking with no significant intermolecular Br···Br and/or aryl···aryl interactions within each stack. The anion···anion stacks interact *via* Br···Br interactions [Br···Br = 3.8773 (15) Å] to form one-dimensional arrays. The Br···aryl interactions are arranged in a ···Br···aryl···Br···aryl··· infinite motif [Br···centroid distance of 3.928 (1) Å]. All of them link the anions and cations into two-dimensional layers.

Related literature

For general background, see: Cui *et al.* (2000); Lacroix *et al.* (1994); Chakravarthy & Guloy (1997); Huang & Wang (2007); Al-Far & Ali (2007). For related literature, see: Benito-Garagorri *et al.* (2006); Kruszynski & Wyrzykowski (2006); Hao & Liu (2007); Churakov *et al.* (2006); Yang *et al.* (2004).



Experimental

Crystal data

$(C_6H_{10}N_2)[FeBr_4]$
M_r = 485.61
Monoclinic, $P2_1/m$
a = 6.6591 (13) Å
b = 14.352 (3) Å
c = 6.8583 (14) Å
β = 90.92 (3)°
V = 655.4 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 13.31 mm^{-1}
T = 294 (2) K
0.20 × 0.15 × 0.10 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: numerical (Shape Tracing Software; Rigaku, 2000)
T_{min} = 0.103, T_{max} = 0.262
5269 measured reflections
1213 independent reflections
856 reflections with $I > 2\sigma(I)$
R_{int} = 0.084

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.113
S = 0.97
1213 reflections
66 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.92 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—Br1	2.3182 (17)	Fe1—Br3	2.3348 (11)
Fe1—Br2	2.3343 (17)		
Br1—Fe1—Br2	109.74 (7)	Br2—Fe1—Br3	109.51 (4)
Br1—Fe1—Br3	108.72 (4)	Br3^i—Fe1—Br3	110.63 (7)

Symmetry code: (i) $x, -y + \frac{3}{2}, z$.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2247).

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supplementary materials

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Dimethylpyrazinium tetrabromidoferrate(II): Br...aryl...Br and Br...Br intermolecular interactions

R. Al-Far and **B. F. Ali**

Comment

The research in the field of inorganic-organic hybrids is of great interest due to their magnetic, electronic and optoelectric properties (Cui *et al.*, 2000; Lacroix *et al.*, 1994; Chakravarthy & Guloy, 1997). The packing interactions that govern the crystal organization is expected to affect the packing and then the specific properties of such solids. For example, pyrazine (pyz) and similar ligands have been used through their two nitrogen atoms as neutral linkers to generate and stabilize many open 1-, 2- and 3-D coordination polymers and forming supramolecular coordination assemblies (Hao & Liu, 2007; Huang & Wang, 2007). We herein report the crystal structure of the title complex, (I), wherein, the protonated dimethylpyrazinium ligand $[\mathrm{pyzH_2}]^{2+}$ is not involved in coordination, but in extensive infinite aryl···Br···aryl···Br intermolecular interactions, affording a 2-D network structure by the aid of Br···Br interactions.

The asymmetric unit of the title compound, (I), contains one half $[\mathrm{pyzH_2}]^{2+}$ cation and $[\mathrm{FeBr_3}]^{1-}$ unit of the anion, where the Fe atom has a distorted tetrahedral environment (Fig. 1, Table 1). The Fe—Br bonds and Br—Fe—Br angles are in the range of 2.3182 (17)–2.3348 (11) Å [mean value is 2.3305 (14) Å] and 108.72 (4)–110.63 (7) °, respectively, in which they are in accordance with the corresponding values (Benito-Garagorri *et al.*, 2006; Kruszynski & Wyrzykowski, 2006). The bond lengths and angles in the brominated cation are also in accordance with the corresponding ones (Hao & Liu, 2007; Churakov *et al.*, 2006; Yang *et al.*, 2004).

The molecules of discrete anions, packed into stacks, are separated by stacks of cations. The anion stacks along the *c* axis are parallel to the cation stacks with Fe···Fe distance of 6.8583 (14) Å, with no significant interactions between anions and cations within a stack. Inter anion-stacks are linked only through one Br···Br interaction parallel to *b* axis [Br3···Br3A = 3.8773 (15) Å (symmetry code A: $2-x$, $1-y$, $1-z$)]. The anions and cations are not involved in any of Br···H interactions, but only through Br···aryl interactions, that are represented in the ···Br···aryl···Br···aryl··· infinite motif (Al-Far & Ali, 2007), in which the bromide ions of the anion lie between the two cationic species with centroid···Br···centroid (symmetry code: $2-x$, $1/2+y$, $1-z$) repeat distance of 3.928 (1) Å. Beside these interactions along with inter anion-stacks, the Br···Br interactions also link the anions and cations together into 2-D layers approximately normal to the *a* axis (Fig 2).

Experimental

For the preparation of (I), $\mathrm{FeCl_2}$ (127 mg, 1 mmol) dissolved in absolute ethanol (10 ml) and liquid $\mathrm{Br_2}$ (20%, 1 ml), was added dropwise to a stirred hot ethanolic solution of dimethylpyrazine (77%, 1 ml) dissolved in ethanol (10 ml) and HBr (60%, 2 ml). After heating for 3 h, the mixture was filtered off and allowed to stand undisturbed at room temperature. The salt crystallized out over 3 d as black blocks. Crystals were filtered off, washed with ethanol then diethylether, and dried under vacuum (yield; 300 mg, 61.8%).

Refinement

H atoms were positioned geometrically, with N—H = 0.86 Å (for NH) and C—H = 0.93 and 0.96 Å for aromatic and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C,N)$, where x = 1.5 for methyl H, and x = 1.2 for all other H atoms.

Figures

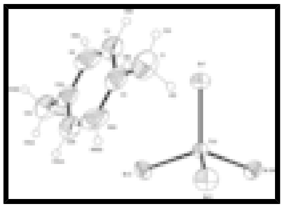

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level (symmetry code A: x, $3/2 - y$, z).

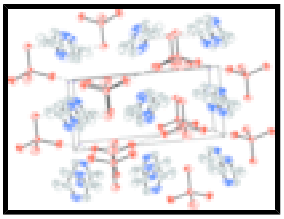

Fig. 2. A packing diagram for (I). The Br···Br and Br···aryl interactions are shown as dashed lines.

Dimethylpyrazinium tetrabromidoferrate(II)

Crystal data

$(C_6H_{10}N_2)[FeBr_4]$	$F_{000} = 452$
$M_r = 485.61$	$D_x = 2.461$ Mg m^{-3}
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yb	Cell parameters from 1974 reflections
$a = 6.6591$ (13) Å	$\theta = 3.0$–27.9°
$b = 14.352$ (3) Å	$\mu = 13.31$ mm^{-1}
$c = 6.8583$ (14) Å	$T = 294$ (2) K
$\beta = 90.92$ (3)°	Block, black
$V = 655.4$ (2) Å^3	0.20 × 0.15 × 0.10 mm
$Z = 2$	

Data collection

Rigaku Mercury CCD diffractometer	1213 independent reflections
Radiation source: fine-focus sealed tube	856 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.084$
Detector resolution: 14.6306 pixels mm^{-1}	$\theta_{max} = 25.2$°
$T = 294(2)$ K	$\theta_{min} = 3.0$°
dtintegrate.ref scans	$h = -6 \rightarrow 7$

Absorption correction: numerical (Shape Tracing Software; REFERENCE?)	$k = -15 \rightarrow 17$
$T_{\min} = 0.103$, $T_{\max} = 0.262$	$l = -8 \rightarrow 8$
5269 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\max} = 0.043$
$S = 0.97$	$\Delta\rho_{\max} = 0.66$ e Å^{-3}
1213 reflections	$\Delta\rho_{\min} = -0.91$ e Å^{-3}
66 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.032 (3)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Fe1	0.81018 (19)	0.7500	0.77976 (18)	0.0431 (4)
Br2	0.92375 (18)	0.7500	1.10355 (15)	0.0725 (4)
Br1	0.46205 (15)	0.7500	0.76938 (16)	0.0627 (4)
Br3	0.92512 (11)	0.61623 (5)	0.62320 (11)	0.0649 (4)
C3	0.3172 (15)	0.5452 (7)	1.0157 (16)	0.084 (3)
H3A	0.1937	0.5752	1.0225	0.100*
N4	0.3605 (14)	0.4879 (7)	0.8654 (18)	0.123 (4)
H4A	0.2698	0.4790	0.7766	0.148*
C2	0.4576 (15)	0.5570 (7)	1.1530 (15)	0.085 (3)
C1	0.4033 (16)	0.6165 (7)	1.3151 (13)	0.095 (3)
H1A	0.2912	0.5898	1.3814	0.143*
H1B	0.3673	0.6772	1.2669	0.143*

H1C	0.5154	0.6219	1.4042	0.143*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0450 (8)	0.0465 (8)	0.0377 (7)	0.000	−0.0013 (6)	0.000
Br2	0.0831 (9)	0.0942 (10)	0.0398 (6)	0.000	−0.0103 (6)	0.000
Br1	0.0458 (6)	0.0744 (8)	0.0681 (8)	0.000	0.0037 (5)	0.000
Br3	0.0702 (6)	0.0626 (6)	0.0617 (6)	0.0158 (4)	−0.0042 (4)	−0.0125 (4)
C3	0.077 (7)	0.080 (6)	0.092 (7)	−0.006 (5)	−0.027 (6)	0.015 (6)
N4	0.082 (6)	0.125 (8)	0.160 (10)	−0.036 (6)	−0.062 (6)	0.057 (7)
C2	0.083 (7)	0.081 (7)	0.090 (7)	−0.028 (5)	−0.026 (6)	0.037 (5)
C1	0.110 (8)	0.096 (8)	0.080 (7)	−0.024 (6)	−0.010 (6)	−0.011 (6)

Geometric parameters (Å, °)

Fe1—Br1	2.3182 (17)	N4—C2^{ii}	1.380 (13)
Fe1—Br2	2.3343 (17)	N4—H4A	0.8600
Fe1—Br3^{i}	2.3348 (11)	C2—N4^{ii}	1.380 (13)
Fe1—Br3	2.3348 (11)	C2—C1	1.452 (13)
C3—C2	1.328 (12)	C1—H1A	0.9600
C3—N4	1.353 (13)	C1—H1B	0.9600
C3—H3A	0.9300	C1—H1C	0.9600
Br1—Fe1—Br2	109.74 (7)	C2^{ii}—N4—H4A	118.3
Br1—Fe1—Br3^{i}	108.72 (4)	C3—C2—N4^{ii}	119.0 (10)
Br2—Fe1—Br3^{i}	109.51 (4)	C3—C2—C1	115.9 (11)
Br1—Fe1—Br3	108.72 (4)	N4^{ii}—C2—C1	125.1 (10)
Br2—Fe1—Br3	109.51 (4)	C2—C1—H1A	109.5
Br3^{i}—Fe1—Br3	110.63 (7)	C2—C1—H1B	109.5
C2—C3—N4	117.5 (10)	H1A—C1—H1B	109.5
C2—C3—H3A	121.2	C2—C1—H1C	109.5
N4—C3—H3A	121.2	H1A—C1—H1C	109.5
C3—N4—C2^{ii}	123.5 (9)	H1B—C1—H1C	109.5
C3—N4—H4A	118.3		
C2—C3—N4—C2^{ii}	−1.0 (16)	N4—C3—C2—C1	−178.0 (9)
N4—C3—C2—N4^{ii}	1.0 (16)		

Symmetry codes: (i) *x*, −*y*+3/2, *z*; (ii) −*x*+1, −*y*+1, −*z*+2.

Fig. 1

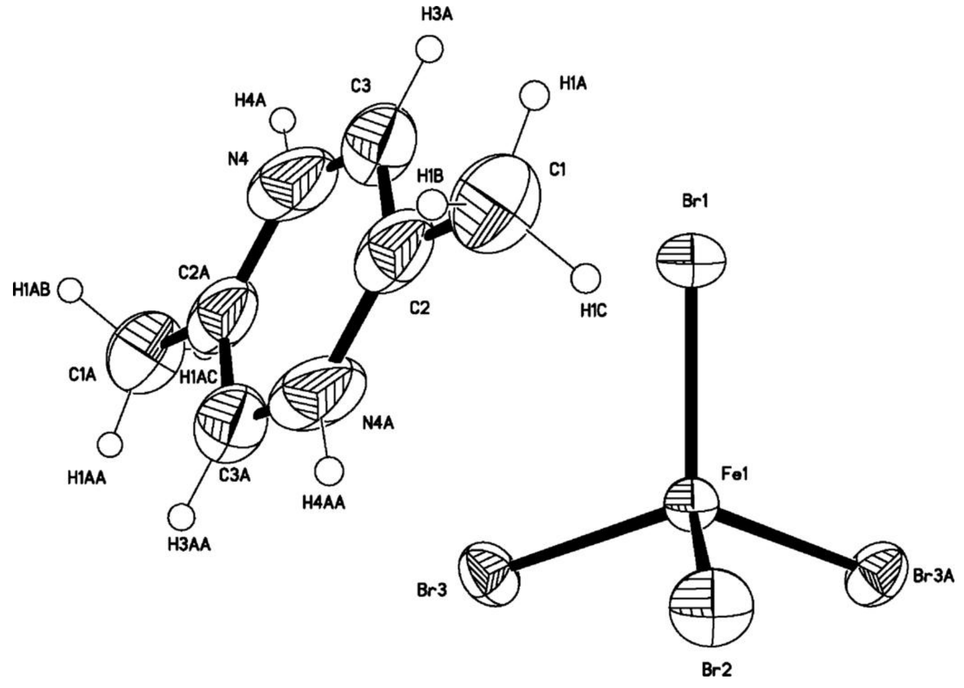
H3A
H1A
H4A
C3
N4
H1B
C1
Br1
C2A
H1AB
C2
H1C
C1A
H1AC
N4A
H1AA
C3A
H4AA
Fe1
H3AA
Br3
Br3A
Br2

Fig. 2