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Low-temperature rerefinement of non-merohedrally twinned tripyridinium bis[tetrabromidoferrate(III)] bromide

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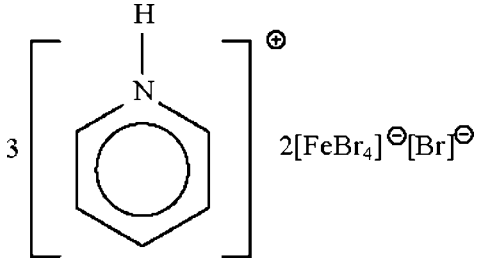
Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.016 Å; R factor = 0.043; wR factor = 0.106; data-to-parameter ratio = 24.6.

The asymmetric unit of the title double salt, $(C_5H_6N)_3[FeBr_4]_2Br$, consists of three pyridinium cations, two tetrahedral bromidoferrate(III) anions and a bromide anion. The three cations each form one N—H···Br hydrogen bond to the bromide anion. The crystal under investigation was a non-merohedral twin, with a portion of 22% for the minor twin component.

Related literature

The authors of the original room-temperature study noted twinning but the refinement program then could not take this into consideration; see: Lowe *et al.* (1994).



Experimental

Crystal data

$(C_5H_6N)_3[FeBr_4]_2Br$
M_r = 1071.21
Monoclinic, $P2_1$
a = 7.5602 (1) Å
b = 14.0125 (2) Å
c = 13.5609 (2) Å
β = 95.172 (1)°
V = 1430.76 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 13.59 mm^{-1}
T = 123 K
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.098, T_{max} = 0.154
13428 measured reflections
6460 independent reflections
6006 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.106
S = 1.07
6460 reflections
263 parameters
109 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.29 e Å^{-3}
$\Delta\rho_{min}$ = −1.71 e Å^{-3}
Absolute structure: Flack (1983), 3046 Friedel pairs
Flack parameter: 0.10 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Br9	0.88	2.35	3.202 (9)	163
N2—H2···Br9	0.88	2.59	3.292 (8)	137
N3—H3···Br9	0.88	2.52	3.279 (7)	146

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2009).

The author thanks the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2380).

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supporting information

Acta Cryst. (2009). E**65**, m402 [doi:10.1107/S1600536809007090]

Low-temperature rerefinement of nonmerohedrally twinned tripyridinium bis-[tetrabromidoferrate(III)] bromide

Seik Weng Ng

S1. Experimental

The crystals were provided by Dr. Nasser Safari of Shahid Beheshti University. Pyridine (2.2 ml, 25 mmol) was added to a solution of ferric bromide (1.25 g, 4.23 mmol) dissolved in a mixture of 1.2 *M* hydrobromic acid and 2.4 *M* acetic acid (20 ml). The red solution was set aside for two weeks, after which crystals separated out.

S2. Refinement

The refinement initally converged to an R_1 value of 0.088, but there were large peaks/deep holes. The crystal is in fact a nonmerohedral twin. The law, as given by *PLATON* (Spek, 2003), is (-1 0 0, 0 - 1 0, 0.323 0 1). The refinement, with an approximate twin component of 22%, halved the R_1 index. The twinning affected the anisotropic temperature factors of the carbon and nitrogen atoms; these were restrained to be nearly isotropic.

Carbon- and nitrogen-bound H-atoms were placed in calculated positions (C–H 0.95, N–H 0.88 Å) and were included in the refinement in the riding model approximation, with *U*(H) set to 1.2*U*(C,*N*).

The final difference Fourier map had large peaks/holes in the vicinity of the bromide atoms.

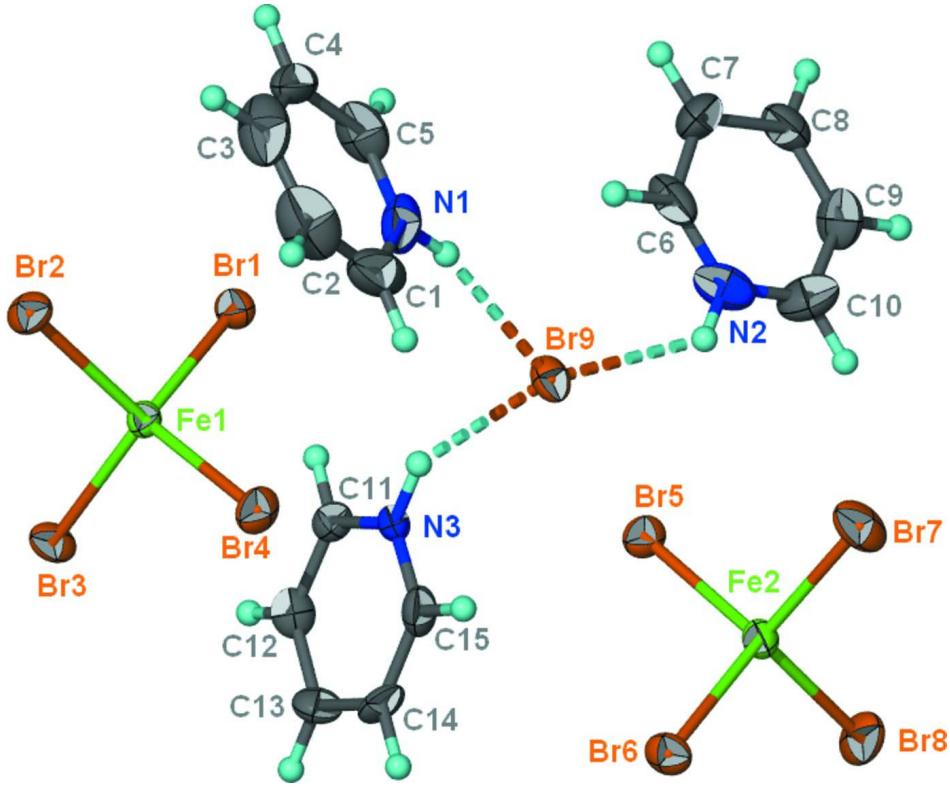

Figure 1

Thermal ellipsoid plot (Barbour, 2001) of $[C_5H_6N]_3[FeBr_4]_2[Br]$.

tripyridinium bis[tetrabromidoferrate(III)] bromide

Crystal data

$(C_5H_6N)_3[FeBr_4]_2Br$
$M_r = 1071.21$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 7.5602$ (1) Å
$b = 14.0125$ (2) Å
$c = 13.5609$ (2) Å
$\beta = 95.172$ (1)°
$V = 1430.76$ (3) Å^3
$Z = 2$
$F(000) = 992$
$D_x = 2.487$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8983 reflections
$\theta = 2.7$–$28.3°$
$\mu = 13.59$ mm^{-1}
$T = 123$ K
Irregular block, brown
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.098$, $T_{max} = 0.154$
13428 measured reflections
6460 independent reflections
6006 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.5°$
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 18$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.106$
$S = 1.07$
6460 reflections
263 parameters
109 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 4.7139P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.29$ e Å^{-3}
$\Delta\rho_{min} = -1.71$ e Å^{-3}
Absolute structure: Flack (1983), 3046 Friedel pairs
Absolute structure parameter: 0.10 (2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.27784 (12)	0.49992 (6)	0.74070 (6)	0.02428 (19)
Br2	0.27108 (13)	0.35971 (6)	0.50468 (7)	0.0250 (2)
Br3	0.02833 (11)	0.60181 (6)	0.50814 (7)	0.02457 (19)
Br4	0.52742 (11)	0.59765 (7)	0.52624 (7)	0.0268 (2)
Br5	0.52708 (11)	0.89250 (6)	0.95876 (7)	0.02335 (19)
Br6	0.75284 (12)	1.00789 (7)	0.74713 (6)	0.02522 (19)
Br7	1.02585 (12)	0.91096 (8)	0.97548 (8)	0.0356 (3)
Br8	0.74006 (15)	1.13935 (7)	0.98802 (7)	0.0350 (2)
Br9	0.74762 (11)	0.65558 (7)	0.83903 (6)	0.02359 (19)
Fe1	0.27879 (15)	0.51483 (9)	0.56879 (9)	0.0177 (2)
Fe2	0.76356 (16)	0.98860 (9)	0.91855 (9)	0.0197 (3)
N1	0.7426 (11)	0.4395 (6)	0.7619 (7)	0.038 (2)
H1	0.7427	0.4931	0.7959	0.045*
N2	0.7876 (12)	0.7029 (7)	1.0778 (6)	0.0343 (19)
H2	0.7993	0.7233	1.0173	0.041*
N3	0.3634 (10)	0.7457 (5)	0.7543 (5)	0.0203 (15)
H3	0.4324	0.7032	0.7863	0.024*
C1	0.8048 (15)	0.4412 (10)	0.6741 (9)	0.047 (3)
H1A	0.8457	0.4988	0.6470	0.056*
C2	0.8080 (17)	0.3569 (11)	0.6239 (9)	0.054 (3)
H2A	0.8582	0.3549	0.5622	0.065*
C3	0.7408 (16)	0.2758 (9)	0.6606 (10)	0.048 (3)
H3A	0.7363	0.2182	0.6234	0.058*
C4	0.6797 (14)	0.2790 (8)	0.7523 (9)	0.038 (2)
H4	0.6371	0.2226	0.7810	0.046*
C5	0.6802 (15)	0.3618 (9)	0.8016 (7)	0.038 (2)
H5	0.6357	0.3647	0.8649	0.046*
C6	0.7428 (14)	0.6150 (8)	1.0919 (7)	0.035 (2)
H6	0.7246	0.5738	1.0363	0.042*
C7	0.7210 (16)	0.5797 (8)	1.1832 (9)	0.041 (3)
H7	0.6873	0.5151	1.1919	0.049*
C8	0.7500 (12)	0.6418 (8)	1.2642 (7)	0.032 (2)

H8	0.7361	0.6199	1.3294	0.039*
C9	0.7984 (14)	0.7340 (8)	1.2482 (7)	0.035 (2)
H9	0.8192	0.7771	1.3021	0.042*
C10	0.8163 (16)	0.7633 (7)	1.1548 (8)	0.039 (2)
H10	0.8497	0.8274	1.1433	0.047*
C11	0.1903 (12)	0.7447 (6)	0.7669 (6)	0.0208 (17)
H11	0.1435	0.6989	0.8092	0.025*
C12	0.0815 (12)	0.8104 (7)	0.7182 (6)	0.0260 (18)
H12	−0.0420	0.8102	0.7262	0.031*
C13	0.1503 (13)	0.8766 (6)	0.6576 (7)	0.0256 (19)
H13	0.0757	0.9231	0.6241	0.031*
C14	0.3330 (13)	0.8744 (6)	0.6459 (7)	0.0260 (19)
H14	0.3831	0.9190	0.6035	0.031*
C15	0.4375 (12)	0.8082 (7)	0.6956 (7)	0.0269 (19)
H15	0.5614	0.8062	0.6888	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0313 (4)	0.0211 (4)	0.0195 (4)	−0.0010 (4)	−0.0025 (3)	−0.0005 (3)
Br2	0.0325 (5)	0.0188 (4)	0.0241 (4)	−0.0009 (4)	0.0039 (4)	−0.0032 (3)
Br3	0.0164 (4)	0.0285 (5)	0.0285 (4)	0.0046 (4)	0.0009 (3)	0.0077 (4)
Br4	0.0168 (4)	0.0268 (5)	0.0369 (5)	−0.0041 (4)	0.0030 (3)	0.0016 (4)
Br5	0.0181 (4)	0.0236 (4)	0.0286 (4)	−0.0015 (3)	0.0038 (3)	0.0022 (3)
Br6	0.0311 (4)	0.0272 (4)	0.0175 (4)	0.0014 (4)	0.0031 (3)	0.0012 (4)
Br7	0.0186 (4)	0.0520 (7)	0.0356 (5)	0.0033 (4)	−0.0007 (4)	0.0137 (5)
Br8	0.0507 (6)	0.0292 (6)	0.0246 (5)	−0.0099 (5)	0.0008 (4)	−0.0090 (4)
Br9	0.0204 (4)	0.0272 (5)	0.0225 (4)	0.0047 (4)	−0.0019 (3)	−0.0033 (3)
Fe1	0.0153 (5)	0.0167 (6)	0.0206 (6)	0.0002 (5)	−0.0005 (4)	−0.0003 (5)
Fe2	0.0186 (5)	0.0230 (6)	0.0173 (6)	−0.0020 (5)	0.0003 (4)	0.0008 (5)
N1	0.025 (4)	0.030 (4)	0.056 (5)	0.003 (3)	−0.013 (4)	−0.012 (4)
N2	0.038 (4)	0.043 (5)	0.023 (4)	0.011 (4)	0.010 (3)	0.009 (3)
N3	0.020 (3)	0.019 (3)	0.021 (3)	−0.002 (3)	−0.006 (3)	0.002 (3)
C1	0.030 (5)	0.055 (6)	0.055 (6)	−0.009 (5)	−0.004 (4)	0.028 (5)
C2	0.042 (6)	0.083 (8)	0.038 (5)	0.003 (6)	0.009 (5)	0.000 (6)
C3	0.040 (5)	0.047 (6)	0.056 (6)	0.008 (5)	−0.005 (5)	−0.021 (5)
C4	0.028 (5)	0.028 (5)	0.055 (6)	−0.007 (4)	−0.013 (4)	0.016 (4)
C5	0.036 (5)	0.058 (6)	0.021 (4)	0.001 (5)	0.005 (4)	−0.002 (4)
C6	0.043 (5)	0.035 (5)	0.024 (4)	0.013 (4)	−0.011 (4)	−0.005 (4)
C7	0.044 (5)	0.026 (5)	0.051 (6)	−0.013 (4)	−0.009 (5)	0.005 (4)
C8	0.028 (4)	0.045 (5)	0.024 (4)	0.000 (4)	−0.001 (3)	0.010 (4)
C9	0.037 (5)	0.039 (5)	0.029 (5)	−0.002 (4)	0.004 (4)	−0.013 (4)
C10	0.049 (5)	0.022 (4)	0.048 (5)	0.002 (4)	0.010 (5)	0.001 (4)
C11	0.023 (4)	0.019 (4)	0.021 (4)	−0.002 (3)	0.004 (3)	−0.001 (3)
C12	0.023 (4)	0.031 (4)	0.025 (4)	0.001 (4)	0.004 (3)	−0.004 (3)
C13	0.027 (4)	0.020 (4)	0.029 (4)	0.008 (4)	0.001 (3)	0.005 (3)
C14	0.028 (4)	0.020 (4)	0.031 (4)	−0.010 (3)	0.008 (4)	0.005 (3)
C15	0.021 (4)	0.032 (4)	0.028 (4)	−0.007 (4)	−0.003 (3)	−0.003 (4)

Geometric parameters (Å, º)

Br1—Fe1	2.341 (2)	C3—H3A	0.9500
Br2—Fe1	2.340 (2)	C4—C5	1.340 (16)
Br3—Fe1	2.338 (1)	C4—H4	0.9500
Br4—Fe1	2.326 (1)	C5—H5	0.9500
Br5—Fe2	2.342 (1)	C6—C7	1.357 (15)
Br6—Fe2	2.335 (1)	C6—H6	0.9500
Br7—Fe2	2.331 (2)	C7—C8	1.404 (15)
Br8—Fe2	2.326 (2)	C7—H7	0.9500
N1—C1	1.319 (15)	C8—C9	1.366 (15)
N1—C5	1.320 (15)	C8—H8	0.9500
N1—H1	0.8800	C9—C10	1.349 (15)
N2—C6	1.296 (14)	C9—H9	0.9500
N2—C10	1.347 (14)	C10—H10	0.9500
N2—H2	0.8800	C11—C12	1.364 (13)
N3—C11	1.335 (11)	C11—H11	0.9500
N3—C15	1.340 (12)	C12—C13	1.372 (13)
N3—H3	0.8800	C12—H12	0.9500
C1—C2	1.36 (2)	C13—C14	1.405 (13)
C1—H1A	0.9500	C13—H13	0.9500
C2—C3	1.357 (19)	C14—C15	1.358 (13)
C2—H2A	0.9500	C14—H14	0.9500
C3—C4	1.366 (17)	C15—H15	0.9500
Br4—Fe1—Br3	107.44 (6)	N1—C5—C4	119.7 (9)
Br4—Fe1—Br2	111.41 (6)	N1—C5—H5	120.2
Br3—Fe1—Br2	111.18 (6)	C4—C5—H5	120.2
Br4—Fe1—Br1	111.51 (6)	N2—C6—C7	122.4 (10)
Br3—Fe1—Br1	108.77 (6)	N2—C6—H6	118.8
Br2—Fe1—Br1	106.55 (6)	C7—C6—H6	118.8
Br8—Fe2—Br7	112.54 (6)	C6—C7—C8	117.7 (10)
Br8—Fe2—Br6	107.52 (6)	C6—C7—H7	121.1
Br7—Fe2—Br6	109.63 (6)	C8—C7—H7	121.1
Br8—Fe2—Br5	109.89 (6)	C9—C8—C7	119.1 (9)
Br7—Fe2—Br5	107.40 (6)	C9—C8—H8	120.4
Br6—Fe2—Br5	109.86 (6)	C7—C8—H8	120.4
C1—N1—C5	123.5 (10)	C10—C9—C8	119.2 (10)
C1—N1—H1	118.2	C10—C9—H9	120.4
C5—N1—H1	118.2	C8—C9—H9	120.4
C6—N2—C10	120.6 (9)	N2—C10—C9	121.0 (10)
C6—N2—H2	119.7	N2—C10—H10	119.5
C10—N2—H2	119.7	C9—C10—H10	119.5
C11—N3—C15	123.4 (8)	N3—C11—C12	119.1 (8)
C11—N3—H3	118.3	N3—C11—H11	120.4
C15—N3—H3	118.3	C12—C11—H11	120.4
N1—C1—C2	117.3 (11)	C11—C12—C13	120.1 (8)
N1—C1—H1A	121.4	C11—C12—H12	120.0

C2—C1—H1A	121.4	C13—C12—H12	120.0
C3—C2—C1	121.2 (11)	C12—C13—C14	118.9 (8)
C3—C2—H2A	119.4	C12—C13—H13	120.6
C1—C2—H2A	119.4	C14—C13—H13	120.6
C2—C3—C4	118.3 (11)	C15—C14—C13	119.5 (8)
C2—C3—H3A	120.8	C15—C14—H14	120.3
C4—C3—H3A	120.8	C13—C14—H14	120.3
C5—C4—C3	119.8 (10)	N3—C15—C14	119.1 (8)
C5—C4—H4	120.1	N3—C15—H15	120.5
C3—C4—H4	120.1	C14—C15—H15	120.5
C5—N1—C1—C2	−1.8 (17)	C7—C8—C9—C10	0.3 (17)
N1—C1—C2—C3	3.5 (19)	C6—N2—C10—C9	−0.3 (17)
C1—C2—C3—C4	−4.1 (19)	C8—C9—C10—N2	−0.2 (17)
C2—C3—C4—C5	2.9 (18)	C15—N3—C11—C12	−0.2 (13)
C1—N1—C5—C4	0.6 (17)	N3—C11—C12—C13	−0.3 (13)
C3—C4—C5—N1	−1.2 (17)	C11—C12—C13—C14	0.9 (14)
C10—N2—C6—C7	0.7 (16)	C12—C13—C14—C15	−1.0 (14)
N2—C6—C7—C8	−0.5 (17)	C11—N3—C15—C14	0.1 (13)
C6—C7—C8—C9	0.0 (16)	C13—C14—C15—N3	0.5 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br9	0.88	2.35	3.202 (9)	163
N2—H2···Br9	0.88	2.59	3.292 (8)	137
N3—H3···Br9	0.88	2.52	3.279 (7)	146