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

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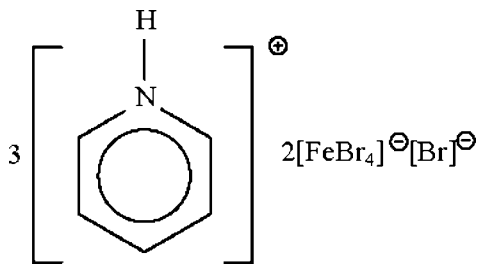
Received 25 February 2009; accepted 26 February 2009

Key indicators: single-crystal X-ray study;  $T = 123$  K; mean  $\sigma(\text{C}-\text{C}) = 0.016$  Å;  
 $R$  factor = 0.043;  $wR$  factor = 0.106; data-to-parameter ratio = 24.6.

The asymmetric unit of the title double salt,  $(\text{C}_5\text{H}_6\text{N})_3\text{[FeBr}_4\text{]}_2\text{Br}$ , consists of three pyridinium cations, two tetrahedral bromidoferrate(III) anions and a bromide anion. The three cations each form one  $\text{N}-\text{H}\cdots\text{Br}$  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

$(\text{C}_5\text{H}_6\text{N})_3\text{[FeBr}_4\text{]}_2\text{Br}$   
 $M_r = 1071.21$

Monoclinic,  $P2_1$   
 $a = 7.5602$  (1) Å

$b = 14.0125$  (2) Å  
 $c = 13.5609$  (2) Å  
 $\beta = 95.172$  (1)°  
 $V = 1430.76$  (3) Å<sup>3</sup>  
 $Z = 2$

Mo  $K\alpha$  radiation  
 $\mu = 13.59$  mm<sup>-1</sup>  
 $T = 123$  K  
 $0.30 \times 0.25 \times 0.20$  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  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.038$

### 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  
 $\Delta\rho_{\text{max}} = 1.29$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.71$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983),  
3046 Friedel pairs  
Flack parameter: 0.10 (2)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{Br9}$	0.88	2.35	3.202 (9)	163
$\text{N2}-\text{H2}\cdots\text{Br9}$	0.88	2.59	3.292 (8)	137
$\text{N3}-\text{H3}\cdots\text{Br9}$	0.88	2.52	3.279 (7)	146

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE*; 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).

## References

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**supplementary materials**

*Acta Cryst.* (2009). E65, m402 [ doi:10.1107/S1600536809007090 ]

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

S. W. Ng

### Comment

(type here to add)

### 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.

### Refinement

The refinement initially 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  $U(\text{H})$  set to  $1.2U(\text{C},\text{N})$ .

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

### Figures

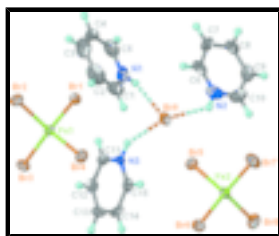


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of  $[\text{C}_5\text{H}_6\text{N}]_3[\text{FeBr}_4]_2[\text{Br}]$ .

### tripyridinium bis[tetrabromidoferrate(III)] bromide

#### Crystal data

$(\text{C}_5\text{H}_6\text{N})_3[\text{FeBr}_4]_2\text{Br}$

$M_r = 1071.21$

$F_{000} = 992$

$D_x = 2.487 \text{ Mg m}^{-3}$

# supplementary materials

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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<sup>3</sup>

$Z = 2$

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 8983 reflections

$\theta = 2.7$ – $28.3$ °

$\mu = 13.59$  mm<sup>-1</sup>

$T = 123$  K

Irregular block, brown

$0.30 \times 0.25 \times 0.20$  mm

## Data collection

Bruker SMART APEX  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 123$  K

$\omega$  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  $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 27.5$ °

$\theta_{\min} = 1.5$ °

$h = -9 \rightarrow 9$

$k = -18 \rightarrow 18$

$l = -17 \rightarrow 17$

## 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<sup>-3</sup>

$\Delta\rho_{\min} = -1.71$  e Å<sup>-3</sup>

Extinction correction: none

Absolute structure: Flack (1983), 3046 Friedel pairs

Flack parameter: 0.10 (2)

## Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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)

## supplementary materials

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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, °)*

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, °)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...Br9	0.88	2.35	3.202 (9)	163

## supplementary materials

N2—H2...Br9	0.88	2.59	3.292 (8)	137
N3—H3...Br9	0.88	2.52	3.279 (7)	146

Fig. 1

