Tris(4,4′-bi-1,3-thiazole-$\kappa^2 N$,N')iron(II) tetrabromidoferrate(III) bromide

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In the $[\text{Fe}(4,4'\text{-bit})_3]^{2+}$ (4,4′-bit is 4,4′-bi-1,3-thiazole) cation of the title compound, $[\text{Fe}(\text{C}_6\text{H}_4\text{N}_2\text{S}_2)_3][\text{FeBr}_4]\text{Br}$, the Fe^{II} atom (3 symmetry) is six-coordinated in a distorted octahedral geometry by six N atoms from three 4,4′-bit ligands. In the $[\text{FeBr}_4]^-$ anion, the Fe^{III} atom (3 symmetry) is four-coordinated in a distorted tetrahedral geometry. In the crystal, intermolecular C—H···Br hydrogen bonds and Br···π interactions [Br···centroid distances = 3.562 (3) and 3.765 (2) Å] link the cations and anions, stabilizing the structure.

Related literature

For general background to metal complexes with 4,4′-bi-1,3-thiazole ligands, see: Baker & Goodwin (1985); Mahjoub & Morsali (2001, 2002a,b). For related structures, see: Al-Hashemi *et al.* (2009); Ali & Al-Far (2007); Amani *et al.* (2007a,b, 2009); Craig *et al.* (1988); Figgis *et al.* (1983); Jia *et al.* (2006); Khavasi *et al.* (2008); Kulkarni *et al.* (1998); Notash *et al.* (2008, 2009); Rahimi *et al.* (2009); Safari *et al.* (2009). For the synthesis of the ligand, see: Erlenmeyer & Ueberwasser (1939).
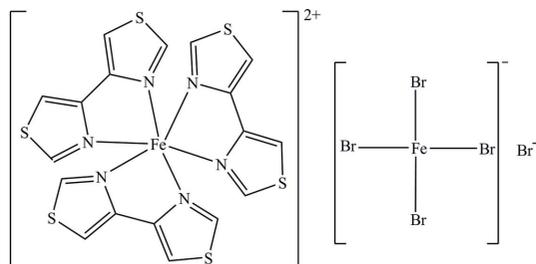
Experimental

Crystal data

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

$M_r = 1015.95$

Trigonal, $R3$

$a = 12.0638$ (7) Å

$c = 17.6907$ (13) Å

$V = 2229.7$ (2) Å³

$Z = 3$

Mo $K\alpha$ radiation

$\mu = 8.14$ mm^{-1}

$T = 100$ K

$0.45 \times 0.35 \times 0.30$ mm

Data collection

Bruker APEXII CCD diffractometer

Absorption correction: multi-scan (*SADABS*; Bruker, 2001)

$T_{\min} = 0.031$, $T_{\max} = 0.086$

8430 measured reflections

2508 independent reflections

2427 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.099$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.085$

$S = 1.01$

2508 reflections

112 parameters

1 restraint

H-atom parameters constrained

$\Delta\rho_{\max} = 0.93$ e Å^{-3}

$\Delta\rho_{\min} = -0.78$ e Å^{-3}

Absolute structure: Flack (1983), 1195 Friedel pairs

Flack parameter: 0.021 (9)

Table 1
Selected bond lengths (Å).

Fe1—N1	1.962 (3)	Fe2—Br1	2.3348 (5)
Fe1—N2	1.974 (3)	Fe2—Br2	2.3370 (12)

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···Br3	0.93	2.81	3.665 (5)	153
C5—H5A···Br3	0.93	2.97	3.798 (5)	149

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL*.

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supplementary materials

Tris(4,4'-bi-1,3-thiazole-$\kappa^2 N,N'$)iron(II) tetrabromidoferrate(III) bromide

A. Abedi, V. Amani and N. Safari

Comment

Erlenmeyer & Ueberwasser (1939) first reported the synthesis of 4,4'-bi-1,3-thiazole (4,4'-bit) and Craig *et al.* (1988) determined the structure of this compound. Although 4,4'-bit is a good bidentate ligand, a few of its metal complexes have been prepared, such as those of nickel and iron (Baker & Goodwin, 1985), lead (Mahjoub & Morsali, 2001, 2002*a*) and bismuth (Mahjoub & Morsali, 2002*b*). We recently introduced the coordination chemistry of 2,2'-dimethyl-4,4'-bi-1,3-thiazole with copper (Al-Hashemi *et al.*, 2009), zinc and mercury (Khavasi *et al.*, 2008; Safari *et al.*, 2009), cadmium (Notash *et al.*, 2009) and thallium (Notash *et al.*, 2008). We report here the synthesis and crystal structure of the title compound.

The asymmetric unit of the title compound (Fig. 1), contains one third of an $[Fe(4,4'-bit)_3]^{2+}$ cation, one third of an $[FeBr_4]^-$ anion and one third of a Br^- anion. In the $[Fe(4,4'-bit)_3]^{2+}$ cation, the Fe^{II} atom (3 symmetry) is six-coordinated in a distorted octahedral geometry by six N atoms from three 4,4'-bit ligands. The Fe—N bond lengths are 1.962 (3) and 1.974 (3) Å (Table 1). The average Fe—N bond distances in high-spin iron(II) and (III) complexes with phenanthroline and bipyridine are around 2.2 Å. However, for low-spin iron(II) and (III) complexes, the Fe—N distances less than 2.0 Å have been reported (Amani *et al.*, 2007*a*,b, 2009; Figgis *et al.*, 1983; Kulkarni *et al.*, 1998; Rahimi *et al.*, 2009). Therefore, in the $[Fe(4,4'-bit)_3]^{2+}$ cation, the Fe—N bond distances are unambiguous in accord with low-spin iron(II). The N—Fe—N bond angles are in the range of 82.00 (14) to 171.87 (14)°. The bond angles and distances are in good agreement to those of $[Fe(4,4'-bit)_3]^{2+}$ cations, which have been found in other structures (Baker & Goodwin, 1985). In the $[FeBr_4]^-$ anion, the Fe^{III} atom (3 symmetry) is four-coordinated in a distorted tetrahedral geometry by four Br atoms. The Fe—Br bond lengths are 2.3348 (5) and 2.3370 (12) Å. The Br—Fe—Br angles, in turn, span the ranges of 108.64 (3) to 110.29 (3)°, and the bond angles and distances are in good agreement to those of $[FeBr_4]^-$ anions, which have been found in other structures (Ali & Al-Far 2007; Jia *et al.*, 2006).

Fig. 2 shows significant intermolecular C—H···Br hydrogen bonds in the title compound (Table 2). The hydrogen bonds cause the formation of a supramolecular architecture, best described as built up by Br(thiazol)$_9$ supramolecular synthons (Fig. 2) assembled *via* C—H···Br hydrogen bonds, where nine thiazole groups surround one (central) uncoordinated bromide ion. These synthons are further connected into an adamantoid-like network that extends into a three-dimensional structure. The discrete $[FeBr_4]^-$ anions occupy the cavities that result from the three-dimensional assembly of the Br(thiazol)$_9$ entities. There also exist intermolecular Br···π interactions between the $[FeBr_4]^-$ anions and thiazole rings in the crystal structure (Fig. 3), with Br1···*Cg*1 = 3.562 (3) and Br1^i···*Cg*2 = 3.765 (2) Å [*Cg*1 and *Cg*2 are the centroids of C1, C2, C3, N2, S2 ring and C4, C5, C6, N1, S1 ring. Symmetry code: (i) 1-x+y, 2-x, z]. The hydrogen bonds and Br···π interactions link the cations and anions, which may be effective in the stabilization of the structure.

supplementary materials

Experimental

4,4'-bi-1,3-thiazole (0.11 g, 0.63 mmol) in CH_3OH (20 ml) was added to a solution of $FeBr_3$ (0.06 g, 0.21 mmol) in CH_3OH (10 ml) and the resulting red solution was stirred at 313 K for 1 h. The red colored precipitated product was recrystallized from CH_3CN/CH_3OH (v/v 2:1). After two weeks, dark-red prismatic crystals of the title compound were isolated (yield: 0.08 g, 75.0%; m.p. 464 K).

Refinement

All H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures
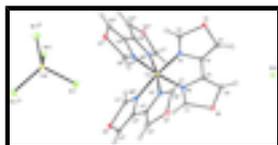
Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) 1-x+y, 2-x, z; (ii) 2-y, 1+x-y, z; (iii) 1-y, 1+x-y, z; (iv) -x+y, 1-x, z.]
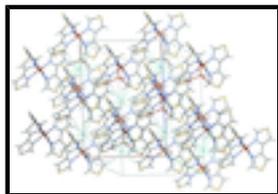
Fig. 2. Crystal packing diagram for the title compound. Hydrogen bonds are shown as dashed lines.
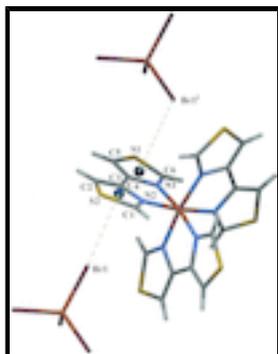
Fig. 3. Intermolecular Br···π interactions (dashed lines) in the title compound. [Symmetry code: (i) 1-x+y, 2-x, z.]

Tris(4,4'-bi-1,3-thiazole-κ^{2}N,N')iron(II) tetrabromidoferrate(III) bromide

Crystal data

$[Fe(C_6H_4N_2S_2)_3][FeBr_4]Br$	D_x = 2.270 Mg m^{-3}
M_r = 1015.95	Mo $K\alpha$ radiation, λ = 0.71073 Å
Trigonal, $R3$	Cell parameters from 1635 reflections
Hall symbol: R 3	θ = 3.0–28.0°
a = 12.0638 (7) Å	μ = 8.14 mm^{-1}
c = 17.6907 (13) Å	T = 100 K

$V = 2229.7\ (2)\ \text{Å}^3$

$Z = 3$

$F(000) = 1455$

Prism, dark-red

$0.45 \times 0.35 \times 0.30$ mm

Data collection

Bruker APEXII CCD diffractometer	2508 independent reflections
Radiation source: fine-focus sealed tube	2427 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.099$
φ and ω scans	$\theta_{max} = 28.9°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$h = -16 \rightarrow 16$
$T_{min} = 0.031$, $T_{max} = 0.086$	$k = -16 \rightarrow 16$
8430 measured reflections	$l = -24 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.036$	H-atom parameters constrained
$wR(F^2) = 0.085$	$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
2508 reflections	$\Delta\rho_{max} = 0.93$ e Å^{-3}
112 parameters	$\Delta\rho_{min} = -0.78$ e Å^{-3}
1 restraint	Absolute structure: Flack (1983), 1195 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.021 (9)

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

	x	y	z	$U_{iso}*/U_{eq}$
Br1	0.53314 (4)	0.70585 (5)	0.46767 (3)	0.02946 (13)
Br2	0.3333	0.6667	0.64196 (3)	0.01401 (14)
Br3	1.6667	1.3333	0.53208 (4)	0.01483 (14)
Fe1	1.0000	1.0000	0.48640 (5)	0.00941 (17)
Fe2	0.3333	0.6667	0.50986 (6)	0.01351 (18)
S1	1.25908 (10)	1.31480 (10)	0.64504 (6)	0.0182 (2)
S2	1.33303 (9)	1.07879 (10)	0.33584 (6)	0.01552 (19)
N1	1.1247 (3)	1.1426 (3)	0.54875 (19)	0.0120 (6)
N2	1.1543 (3)	1.0443 (3)	0.42603 (19)	0.0121 (6)
C1	1.1756 (4)	1.0038 (4)	0.3613 (2)	0.0141 (7)
H1A	1.1107	0.9401	0.3323	0.017*
C2	1.3758 (4)	1.1697 (4)	0.4169 (2)	0.0161 (7)
H2A	1.4589	1.2296	0.4310	0.019*
C3	1.2677 (4)	1.1394 (4)	0.4572 (2)	0.0132 (7)

C4	1.2524 (4)	1.1950 (4)	0.5268 (2)	0.0127 (7)
C5	1.3381 (4)	1.2906 (4)	0.5716 (3)	0.0185 (8)
H5A	1.4262	1.3361	0.5639	0.022*
C6	1.1159 (4)	1.1969 (4)	0.6109 (2)	0.0154 (7)
H6A	1.0383	1.1732	0.6345	0.019*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0213 (2)	0.0518 (3)	0.0176 (2)	0.0201 (2)	0.00229 (16)	−0.0064 (2)
Br2	0.01593 (18)	0.01593 (18)	0.0102 (3)	0.00796 (9)	0.000	0.000
Br3	0.01604 (19)	0.01604 (19)	0.0124 (3)	0.00802 (9)	0.000	0.000
Fe1	0.0096 (2)	0.0096 (2)	0.0090 (4)	0.00479 (11)	0.000	0.000
Fe2	0.0153 (3)	0.0153 (3)	0.0099 (4)	0.00764 (13)	0.000	0.000
S1	0.0184 (4)	0.0170 (4)	0.0170 (5)	0.0072 (4)	−0.0042 (4)	−0.0073 (4)
S2	0.0162 (4)	0.0198 (4)	0.0128 (4)	0.0107 (3)	0.0037 (3)	0.0013 (3)
N1	0.0113 (13)	0.0118 (14)	0.0122 (14)	0.0052 (12)	0.0016 (11)	0.0003 (11)
N2	0.0143 (14)	0.0143 (14)	0.0102 (13)	0.0090 (12)	0.0021 (12)	0.0016 (12)
C1	0.0135 (16)	0.0138 (16)	0.0157 (17)	0.0074 (14)	0.0000 (13)	−0.0008 (13)
C2	0.0161 (16)	0.0175 (17)	0.0139 (18)	0.0078 (14)	0.0027 (14)	0.0035 (14)
C3	0.0173 (17)	0.0131 (15)	0.0134 (16)	0.0106 (14)	0.0009 (13)	0.0036 (13)
C4	0.0156 (16)	0.0101 (15)	0.0126 (16)	0.0065 (13)	0.0010 (13)	0.0001 (12)
C5	0.0168 (17)	0.0198 (19)	0.0192 (19)	0.0092 (15)	−0.0020 (14)	−0.0002 (15)
C6	0.0135 (16)	0.0148 (17)	0.0151 (17)	0.0048 (13)	−0.0024 (14)	−0.0020 (13)

Geometric parameters (Å, °)

Fe1—N1	1.962 (3)	N2—C1	1.320 (5)
Fe1—N2	1.974 (3)	N2—C3	1.385 (5)
Fe2—Br1	2.3348 (5)	C1—H1A	0.9300
Fe2—Br2	2.3370 (12)	C2—C3	1.366 (6)
S1—C6	1.706 (4)	C2—H2A	0.9300
S1—C5	1.721 (4)	C3—C4	1.458 (5)
S2—C1	1.706 (4)	C4—C5	1.355 (6)
S2—C2	1.720 (4)	C5—H5A	0.9300
N1—C6	1.312 (5)	C6—H6A	0.9300
N1—C4	1.396 (5)		
N1—Fe1—N1^{i}	91.50 (14)	C6—N1—Fe1	133.8 (3)
N1—Fe1—N1^{ii}	91.50 (14)	C4—N1—Fe1	115.4 (3)
N1^{i}—Fe1—N1^{ii}	91.50 (14)	C1—N2—C3	111.0 (3)
N1—Fe1—N2^{i}	171.87 (13)	C1—N2—Fe1	134.5 (3)
N1^{i}—Fe1—N2^{i}	82.00 (14)	C3—N2—Fe1	114.6 (3)
N1^{ii}—Fe1—N2^{i}	93.53 (13)	N2—C1—S2	113.8 (3)
N1—Fe1—N2	82.00 (14)	N2—C1—H1A	123.1
N1^{i}—Fe1—N2	93.53 (13)	S2—C1—H1A	123.1
N1^{ii}—Fe1—N2	171.87 (13)	C3—C2—S2	108.8 (3)
N2^{i}—Fe1—N2	93.49 (14)	C3—C2—H2A	125.6

N1—Fe1—N2[ii]	93.53 (13)	S2—C2—H2A	125.6
N1[i]—Fe1—N2[ii]	171.87 (14)	C2—C3—N2	115.4 (3)
N1[ii]—Fe1—N2[ii]	82.00 (14)	C2—C3—C4	129.9 (4)
N2[i]—Fe1—N2[ii]	93.49 (14)	N2—C3—C4	114.7 (3)
N2—Fe1—N2[ii]	93.49 (14)	C5—C4—N1	115.0 (4)
Br1[iii]—Fe2—Br1[iv]	110.29 (3)	C5—C4—C3	131.9 (4)
Br1[iii]—Fe2—Br1	110.29 (3)	N1—C4—C3	113.0 (3)
Br1[iv]—Fe2—Br1	110.29 (3)	C4—C5—S1	109.5 (3)
Br1[iii]—Fe2—Br2	108.64 (3)	C4—C5—H5A	125.2
Br1[iv]—Fe2—Br2	108.64 (3)	S1—C5—H5A	125.2
Br1—Fe2—Br2	108.64 (3)	N1—C6—S1	114.3 (3)
C6—S1—C5	90.4 (2)	N1—C6—H6A	122.8
C1—S2—C2	91.01 (19)	S1—C6—H6A	122.8
C6—N1—C4	110.7 (3)		
N1[i]—Fe1—N1—C6	−86.9 (3)	S2—C2—C3—N2	1.7 (4)
N1[ii]—Fe1—N1—C6	4.6 (4)	S2—C2—C3—C4	−175.8 (3)
N2—Fe1—N1—C6	179.8 (4)	C1—N2—C3—C2	−1.2 (5)
N2[ii]—Fe1—N1—C6	86.7 (4)	Fe1—N2—C3—C2	178.8 (3)
N1[i]—Fe1—N1—C4	88.3 (3)	C1—N2—C3—C4	176.7 (3)
N1[ii]—Fe1—N1—C4	179.8 (3)	Fe1—N2—C3—C4	−3.3 (4)
N2—Fe1—N1—C4	−5.1 (3)	C6—N1—C4—C5	−1.7 (5)
N2[ii]—Fe1—N1—C4	−98.1 (3)	Fe1—N1—C4—C5	−178.0 (3)
N1—Fe1—N2—C1	−175.5 (4)	C6—N1—C4—C3	−179.1 (3)
N1[i]—Fe1—N2—C1	93.5 (4)	Fe1—N1—C4—C3	4.7 (4)
N2[i]—Fe1—N2—C1	11.3 (4)	C2—C3—C4—C5	−0.2 (7)
N2[ii]—Fe1—N2—C1	−82.4 (3)	N2—C3—C4—C5	−177.7 (4)
N1—Fe1—N2—C3	4.6 (3)	C2—C3—C4—N1	176.7 (4)
N1[i]—Fe1—N2—C3	−86.5 (3)	N2—C3—C4—N1	−0.8 (5)
N2[i]—Fe1—N2—C3	−168.6 (3)	N1—C4—C5—S1	1.4 (5)
N2[ii]—Fe1—N2—C3	97.6 (3)	C3—C4—C5—S1	178.2 (3)
C3—N2—C1—S2	0.0 (4)	C6—S1—C5—C4	−0.6 (3)
Fe1—N2—C1—S2	−180.0 (2)	C4—N1—C6—S1	1.2 (4)
C2—S2—C1—N2	0.8 (3)	Fe1—N1—C6—S1	176.5 (2)
C1—S2—C2—C3	−1.4 (3)	C5—S1—C6—N1	−0.3 (3)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2A···Br3	0.93	2.81	3.665 (5)	153
C5—H5A···Br3	0.93	2.97	3.798 (5)	149

Fig. 1

Fig. 2

Fig. 3