

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3,5-Diphenyl-1,2,4-dithiazolium tetra-bromidoferrate(III)

Ibukun O. Shotonwa and René T. Boéré*

Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge, Alberta, Canada T1K 3M4

Correspondence e-mail: boere@uleth.ca

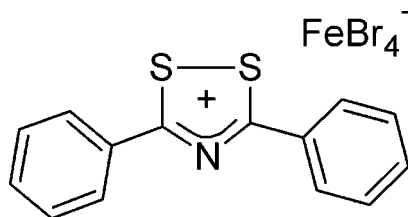
Received 30 December 2012; accepted 3 January 2013

 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.027; wR factor = 0.050; data-to-parameter ratio = 22.2.

The cation of the title salt, $(\text{C}_{14}\text{H}_{10}\text{NS}_2)[\text{FeBr}_4]$, contains a flat central NC_2S_2 ring (r.m.s. deviation = 0.005 Å), with two attached phenyl rings that are almost coplanar [the dihedral angles between the mean planes are 2.4 (1) and 7.7 (1)° for the two phenyl rings]. The $[\text{FeBr}_4]^-$ anion makes short $\text{Br} \cdots \text{S}$ contacts [$\text{Br} \cdots \text{S} = 3.4819$ (8), 3.6327 (9) and 3.5925 (9) Å] and also bridges by way of short contacts to ring H atoms of a second cation held parallel to the first by π -stacking, with a separation between the mean 1,2,4-dithiazolium rings of 3.409 Å. The closest contacts are between a phenyl ring centroid of one cation and the *ipso* C atom of the phenyl ring of another cation, for which the distance is 3.489 Å. The discrete dimers are linked laterally by further $\text{Br} \cdots \text{H}$ short contacts, resulting in double sheets located parallel to the b axis and to the bisector of a and c .

Related literature

For synthesis details, see: Corsaro *et al.* (1984); Liebscher & Hartmann (1977). For related structures, see: Clegg *et al.* (1996); Neels *et al.* (1986). For a description of the Cambridge Structural Database, see: Allen (2002). For bond lengths in tetrabromidoferrate complexes, see: Maithufi & Otto (2011); Bhattacharya & Sarkar (2010). For short-contact distances between stacked aryl rings, see: Martinez & Iverson (2012); McGaughey *et al.* (1998).



Experimental

Crystal data

$(\text{C}_{14}\text{H}_{10}\text{NS}_2)[\text{FeBr}_4]$
 $M_r = 631.84$
 Monoclinic, $P2_1/c$
 $a = 10.6492$ (5) Å
 $b = 11.4005$ (6) Å
 $c = 15.8046$ (8) Å
 $\beta = 96.482$ (1)°

$V = 1906.51$ (17) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 9.39$ mm⁻¹
 $T = 173$ K
 $0.22 \times 0.13 \times 0.07$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
 $T_{\min} = 0.556$, $T_{\max} = 0.746$
 27655 measured reflections
 4426 independent reflections
 3497 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.050$
 $S = 1.02$
 4426 reflections
 199 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.63$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.45$ e Å⁻³

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

The Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged for a Discovery Grant. The diffractometer was purchased with the help of NSERC and the University of Lethbridge.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QM2091).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Bhattacharya, D. & Sarkar, S. (2010). *Eur. J. Inorg. Chem.* pp. 3429–3435.
 Bruker (2008). *APEX2*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Clegg, W., Elsegood, M. R. J., Banister, A. J. & Hibbert, T. G. (1996). *Acta Cryst.* **C52**, 2148–2150.
 Corsaro, A., Compagnini, A., Perrini, G. & Purrello, G. (1984). *J. Chem. Soc. Perkin Trans. 1*, pp. 897–900.
 Liebscher, J. & Hartmann, H. (1977). *Liebigs Ann. Chem.* pp. 1005–1012.
 Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
 Maithufi, N. & Otto, S. (2011). *Acta Cryst.* **C67**, m279–m283.
 Martinez, C. R. & Iverson, B. L. (2012). *Chem. Sci.* **3**, 2191–2201.
 McGaughey, G. B., Gagné, M. & Rappé, A. M. (1998). *J. Biol. Chem.* **273**, 15458–15463.
 Neels, J., Ziemer, B., Meisel, M. & Leibnitz, P. (1986). *Z. Anorg. Allg. Chem.* **542**, 123–130.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2013). E69, m95 [doi:10.1107/S1600536813000275]

3,5-Diphenyl-1,2,4-dithiazolium tetrabromidoferrate(III)

Ibukun O. Shotonwa and René T. Boéré

S1. Comment

The structure of a cation–anion pair in (I) as found in the crystal lattice is shown in Fig. 1, wherein the short contacts from the anion Br atoms to the S atoms of the cation are highlighted. An extended diagram showing the dimerization of two rings through short inter-ring interactions and their lateral extensions into planes *via* short contacts between ring S and H atoms with the $[\text{FeBr}_4]^-$ anions is shown in Fig. 2. The separation between the approximately planar dimer components of 3.409 Å corresponds to typical minimum distances for off-center parallel stacking of electron-rich aromatic rings (Martinez & Iverson, 2012; McGaughey *et al.*, 1998).

Only two previous structures (II) and (III) are reported in the literature for 3,5-diaryl-1,2,4-dithiazolium ring compounds. For (II), the same 3,5-diphenyl-1,2,4-dithiazolium cation crystallizes with a large azathiophosphine cage anion, 1,3,5,7-tetrathio-10-aza-2,4,6,8,9-pentathia-1 λ^5 ,3 λ^5 ,5 λ^5 ,7 λ^5 -tetraphosphatricyclo(3.3.1.1^{3,7})decanide [Cambridge Structural Database (Allen, 2002) refcode FARXIF (Neels *et al.*, 1986)]. For (III), the anion is the more conventional AsF_6^- , but the substituents are 2-methylbenzene rings [refcode TEHRED (Clegg *et al.*, 1996)]. The S—S bond in (I) at 2.019 (1) Å is significantly longer than that in (III) at 2.004 (1) Å, but is within the e.s.d. range of that found in (II) at 2.008 (5) Å. A possible reason for the longer bond in (I) is the presence of stronger sulfur-halogen non-bonded contact interactions than occur for AsF_6^- . The packing arrangements in (II) and (III) do not involve cation ring dimerization as observed in (I).

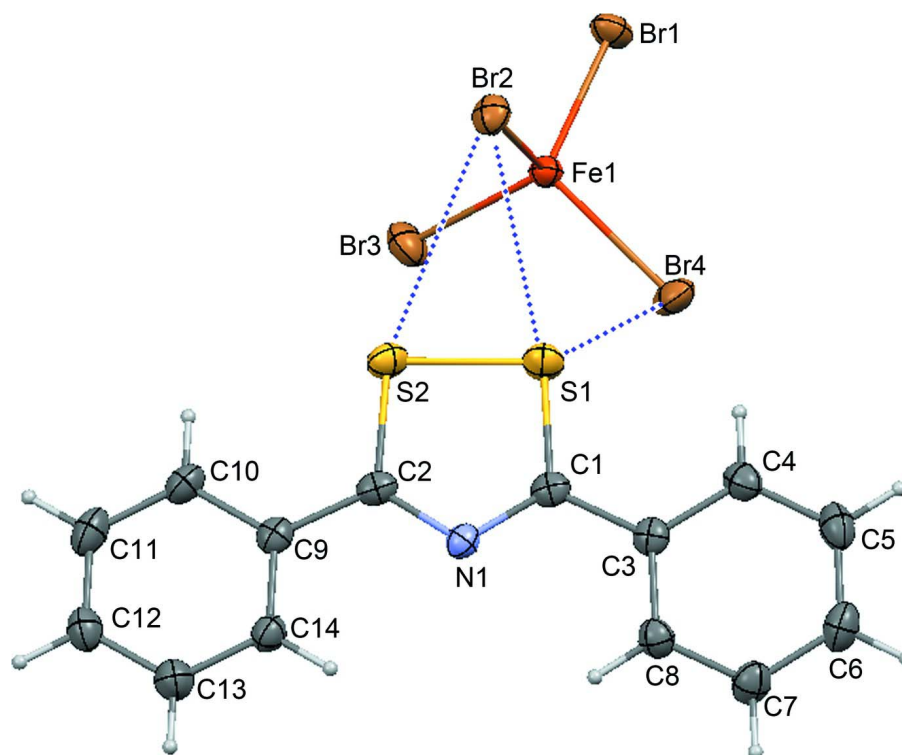
The bond distances in the $[\text{FeBr}_4]^-$ anion are entirely normal for high spin Fe^{III} (Fe—Br (av) = 2.332 (3) Å). For example, in a recent structure by Bhattacharya & Sarkar (2010) [refcode AKAZOC], Fe—Br (av) = 2.332 (7) Å. Distances in FeBr_4^{2-} (*i.e.* an Fe^{II} anion) are as much as 6% longer (Maithufi & Otto, 2011).

S2. Experimental

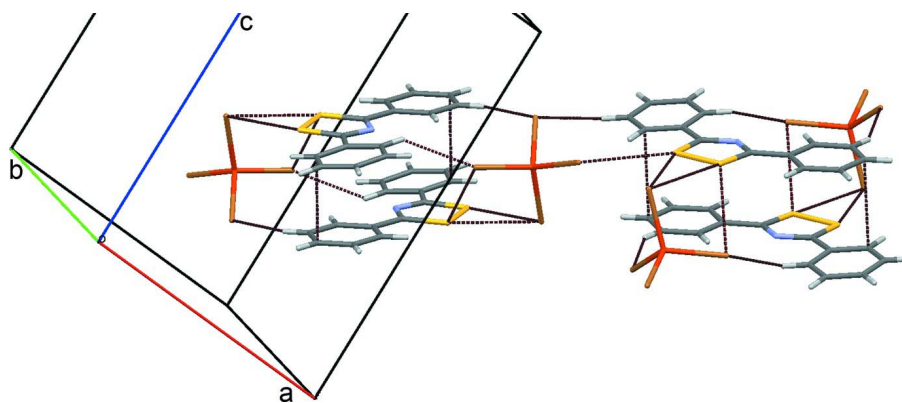
Crystals of (I) were obtained as a minor component during the synthesis of 3,5-diphenyl-1,2,4-dithiazolium perchlorate from *N,N*-dimorpholino-thiobenzamide bromine adduct and unsubstituted thiobenzamide in chloroform using the method of Corsaro *et al.* (1984). The intermediates are taken up in 6 N HClO_4 which is supposed to afford the perchlorate salt of the dithiazolium (Liebscher & Hartmann, 1977). The source of the iron is presumed to be rust that was digested by the perchloric acid, because the ferric aqua ion would be ripe for ligation by strongly nucleophilic bromide ions present as a byproduct from the previous step. Crystals of (I) form as well shaped red–orange prisms amongst the thin yellow plates of perchlorate salt, m.p. 169.3–171.1°C.

S3. Refinement

All H atoms were located on a difference map, but for purposes of refinement are treated as riding on their attached aromatic C atoms with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

**Figure 1**

A view of (I) plotted with displacement ellipsoids drawn at the 40% probability level. H atoms are shown as spheres of arbitrary radius. Dotted lines indicate the short cation–anion contacts $\text{Br2}\cdots\text{S1} = 3.4819$ (8), $\text{Br2}\cdots\text{S2} = 3.6327$ (9) and $\text{Br4}\cdots\text{S1} = 3.5925$ (9) Å.

**Figure 2**

Short off-center parallel stacking of electron-rich aromatic rings leads to sheets of double layers parallel to *b* and bisecting the *a* and *c* axes; $[\text{FeBr}_4]^-$ anions bridge between the upper and lower double-layer components.

3,5-Diphenyl-1,2,4-dithiazolium tetrabromidoferrate(III)

Crystal data

$(\text{C}_{14}\text{H}_{10}\text{NS}_2)[\text{FeBr}_4]$

$M_r = 631.84$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 10.6492$ (5) Å

$b = 11.4005$ (6) Å

$c = 15.8046 (8) \text{ \AA}$
 $\beta = 96.482 (1)^\circ$
 $V = 1906.51 (17) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 1196$
 Standard setting
 $D_x = 2.201 \text{ Mg m}^{-3}$
 Melting point: 442.5 K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 9924 reflections
 $\theta = 2.2\text{--}27.5^\circ$
 $\mu = 9.39 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
 Prism, red
 $0.22 \times 0.13 \times 0.07 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube, Bruker
 D8
 Graphite monochromator
 Detector resolution: 66.06 pixels mm^{-1}
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2008)

$T_{\min} = 0.556$, $T_{\max} = 0.746$
 27655 measured reflections
 4426 independent reflections
 3497 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 27.7^\circ$, $\theta_{\min} = 1.9^\circ$
 $h = -13 \rightarrow 13$
 $k = -14 \rightarrow 14$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.050$
 $S = 1.02$
 4426 reflections
 199 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: difference Fourier map
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0202P)^2 + 0.6153P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.63 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.45 \text{ e \AA}^{-3}$

Special details

Experimental. A crystal coated in Paratone (TM) oil was mounted on the end of a thin glass capillary and cooled in the gas stream of the diffractometer Kryoflex device.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br2	0.52392 (3)	0.78560 (3)	0.368206 (19)	0.03449 (8)
S2	0.66283 (7)	0.51567 (7)	0.45795 (5)	0.03375 (18)
S1	0.76220 (7)	0.65596 (7)	0.50609 (5)	0.03592 (18)
N1	0.8648 (2)	0.4568 (2)	0.56025 (14)	0.0258 (5)
C1	0.8760 (2)	0.5727 (2)	0.56450 (16)	0.0264 (6)
C2	0.7649 (3)	0.4159 (3)	0.51171 (16)	0.0273 (6)
C3	0.9797 (3)	0.6304 (2)	0.61626 (17)	0.0266 (6)

C4	0.9917 (3)	0.7527 (3)	0.61675 (19)	0.0342 (7)
H4	0.9323	0.7991	0.5821	0.041*
C5	1.0893 (3)	0.8059 (3)	0.6672 (2)	0.0412 (8)
H5	1.0965	0.8889	0.6681	0.049*
C6	1.1764 (3)	0.7384 (3)	0.71628 (19)	0.0399 (8)
H6	1.2439	0.7751	0.7509	0.048*
C7	1.1665 (3)	0.6175 (3)	0.71570 (18)	0.0371 (7)
H7	1.2274	0.5717	0.7497	0.045*
C8	1.0687 (3)	0.5628 (3)	0.66606 (17)	0.0315 (7)
H8	1.0621	0.4797	0.6658	0.038*
C9	0.7397 (3)	0.2903 (2)	0.50317 (17)	0.0276 (6)
C10	0.6429 (3)	0.2465 (3)	0.44497 (18)	0.0347 (7)
H10	0.5910	0.2985	0.4094	0.042*
C11	0.6230 (3)	0.1269 (3)	0.4395 (2)	0.0416 (8)
H11	0.5574	0.0966	0.3998	0.050*
C12	0.6980 (3)	0.0510 (3)	0.49137 (18)	0.0369 (7)
H12	0.6839	-0.0312	0.4871	0.044*
C13	0.7932 (3)	0.0946 (3)	0.5493 (2)	0.0379 (7)
H13	0.8441	0.0423	0.5853	0.045*
C14	0.8147 (3)	0.2137 (2)	0.55519 (18)	0.0311 (7)
H14	0.8808	0.2434	0.5948	0.037*
Fe1	0.67510 (4)	0.82072 (3)	0.27504 (2)	0.02488 (10)
Br1	0.61558 (3)	0.98672 (3)	0.194423 (18)	0.03480 (8)
Br3	0.68944 (3)	0.65879 (3)	0.18652 (2)	0.04436 (9)
Br4	0.87224 (3)	0.85136 (3)	0.35206 (2)	0.04081 (9)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br2	0.02809 (16)	0.03810 (18)	0.03845 (17)	-0.00452 (13)	0.00891 (13)	0.00027 (13)
S2	0.0321 (4)	0.0389 (4)	0.0287 (4)	0.0031 (3)	-0.0038 (3)	0.0027 (3)
S1	0.0400 (4)	0.0333 (4)	0.0329 (4)	0.0022 (3)	-0.0029 (3)	0.0078 (3)
N1	0.0239 (12)	0.0289 (13)	0.0247 (12)	-0.0012 (10)	0.0031 (10)	-0.0007 (10)
C1	0.0246 (15)	0.0331 (17)	0.0227 (14)	0.0011 (12)	0.0078 (12)	0.0033 (12)
C2	0.0241 (15)	0.0370 (17)	0.0214 (14)	0.0034 (12)	0.0046 (12)	0.0039 (12)
C3	0.0276 (15)	0.0306 (16)	0.0228 (14)	-0.0027 (12)	0.0089 (12)	0.0015 (12)
C4	0.0327 (17)	0.0301 (17)	0.0413 (18)	0.0011 (13)	0.0104 (14)	0.0039 (14)
C5	0.0426 (19)	0.0318 (18)	0.051 (2)	-0.0102 (15)	0.0146 (16)	-0.0056 (15)
C6	0.0397 (19)	0.046 (2)	0.0337 (17)	-0.0143 (15)	0.0019 (14)	-0.0044 (15)
C7	0.0392 (18)	0.0401 (19)	0.0307 (17)	-0.0056 (14)	-0.0019 (14)	0.0038 (14)
C8	0.0362 (17)	0.0290 (16)	0.0294 (16)	-0.0023 (13)	0.0044 (13)	0.0021 (13)
C9	0.0258 (15)	0.0332 (16)	0.0246 (14)	-0.0017 (12)	0.0065 (12)	-0.0014 (12)
C10	0.0273 (16)	0.045 (2)	0.0303 (16)	-0.0031 (14)	-0.0017 (13)	-0.0023 (14)
C11	0.0351 (18)	0.053 (2)	0.0358 (18)	-0.0111 (16)	0.0003 (14)	-0.0103 (16)
C12	0.0405 (19)	0.0312 (17)	0.0397 (18)	-0.0052 (14)	0.0078 (15)	-0.0068 (14)
C13	0.0378 (18)	0.0344 (18)	0.0409 (18)	-0.0014 (14)	0.0019 (14)	-0.0007 (14)
C14	0.0286 (16)	0.0334 (17)	0.0303 (15)	-0.0026 (13)	-0.0010 (12)	-0.0026 (13)
Fe1	0.0231 (2)	0.0242 (2)	0.0271 (2)	0.00182 (16)	0.00160 (16)	0.00272 (16)

Br1	0.04259 (18)	0.02889 (16)	0.03186 (16)	0.00849 (13)	-0.00040 (13)	0.00606 (12)
Br3	0.0519 (2)	0.02974 (18)	0.0529 (2)	0.00340 (15)	0.01216 (16)	-0.00932 (15)
Br4	0.02328 (15)	0.0481 (2)	0.0491 (2)	-0.00342 (14)	-0.00431 (13)	0.01204 (15)

Geometric parameters (Å, °)

Br2—Fe1	2.3357 (5)	C7—H7	0.9500
S2—C2	1.729 (3)	C8—H8	0.9500
S2—S1	2.0186 (11)	C9—C14	1.389 (4)
S1—C1	1.723 (3)	C9—C10	1.394 (4)
N1—C2	1.324 (3)	C10—C11	1.381 (4)
N1—C1	1.329 (3)	C10—H10	0.9500
C1—C3	1.455 (4)	C11—C12	1.382 (4)
C2—C9	1.460 (4)	C11—H11	0.9500
C3—C8	1.394 (4)	C12—C13	1.379 (4)
C3—C4	1.399 (4)	C12—H12	0.9500
C4—C5	1.377 (4)	C13—C14	1.379 (4)
C4—H4	0.9500	C13—H13	0.9500
C5—C6	1.375 (4)	C14—H14	0.9500
C5—H5	0.9500	Fe1—Br1	2.3291 (5)
C6—C7	1.382 (4)	Fe1—Br4	2.3311 (5)
C6—H6	0.9500	Fe1—Br3	2.3317 (5)
C7—C8	1.380 (4)		
C2—S2—S1	93.58 (10)	C3—C8—H8	120.2
C1—S1—S2	94.17 (10)	C14—C9—C10	119.9 (3)
C2—N1—C1	116.2 (2)	C14—C9—C2	118.3 (2)
N1—C1—C3	122.4 (2)	C10—C9—C2	121.8 (3)
N1—C1—S1	117.9 (2)	C11—C10—C9	119.4 (3)
C3—C1—S1	119.7 (2)	C11—C10—H10	120.3
N1—C2—C9	121.8 (2)	C9—C10—H10	120.3
N1—C2—S2	118.2 (2)	C10—C11—C12	120.5 (3)
C9—C2—S2	120.1 (2)	C10—C11—H11	119.8
C8—C3—C4	119.5 (3)	C12—C11—H11	119.8
C8—C3—C1	119.5 (3)	C13—C12—C11	120.0 (3)
C4—C3—C1	121.1 (3)	C13—C12—H12	120.0
C5—C4—C3	120.3 (3)	C11—C12—H12	120.0
C5—C4—H4	119.9	C14—C13—C12	120.3 (3)
C3—C4—H4	119.9	C14—C13—H13	119.9
C6—C5—C4	119.8 (3)	C12—C13—H13	119.9
C6—C5—H5	120.1	C13—C14—C9	119.9 (3)
C4—C5—H5	120.1	C13—C14—H14	120.0
C5—C6—C7	120.5 (3)	C9—C14—H14	120.0
C5—C6—H6	119.7	Br1—Fe1—Br4	109.714 (19)
C7—C6—H6	119.7	Br1—Fe1—Br3	110.324 (19)
C8—C7—C6	120.4 (3)	Br4—Fe1—Br3	108.411 (19)
C8—C7—H7	119.8	Br1—Fe1—Br2	108.648 (19)
C6—C7—H7	119.8	Br4—Fe1—Br2	109.921 (19)

C7—C8—C3	119.5 (3)	Br3—Fe1—Br2	109.817 (19)
C7—C8—H8	120.2		
