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Benzyl 5-ferrocenyl-3-(4-methylphenyl)-2-pyrazoline-1-dithiocarboxylate

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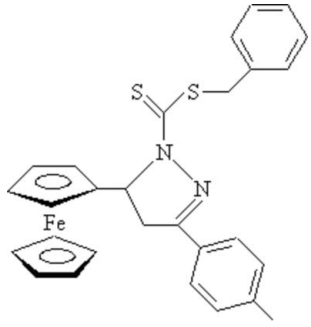
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.028; wR factor = 0.088; data-to-parameter ratio = 18.5.

In the title compound, $[Fe(C_5H_5)(C_{23}H_{21}N_2S_2)]$, the cyclopentadienyl rings of the ferrocenyl unit deviate slightly from the eclipsed form. In the pyrazoline ring, the N atom bonded to *S*-benzyl dithiocarbazate exhibits unconventional sp^2-hybrid character in order to form an extended conjugated system. The pyrazoline ring displays an envelope conformation. The molecules are linked into chains along the *b* axis *via* C—H···S intermolecular hydrogen bonds.

Related literature

For related literature, see: Fahrni *et al.* (2003); Huang & Katzenellenbogen (2000); Huang *et al.* (1998); Liu *et al.* (2007); Rivett *et al.* (1979); Shi *et al.* (2004); Sun *et al.* (2004); Wiley *et al.* (1958); Wilkinson *et al.* (1990).



Experimental

Crystal data

$[Fe(C_5H_5)(C_{23}H_{21}N_2S_2)]$
M_r = 510.50
Triclinic, $P\overline{1}$
a = 9.178 (1) Å
b = 10.468 (2) Å
c = 13.216 (2) Å
α = 99.37 (1)°
β = 101.55 (2)°
γ = 96.12 (1)°
V = 1214.6 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.81 mm^{-1}
T = 296 (2) K
0.33 × 0.31 × 0.28 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.776, T_{max} = 0.805
10742 measured reflections
5528 independent reflections
5035 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.088
S = 0.99
5528 reflections
299 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 2002).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2048).

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S1. Comment

Pyrazoline derivatives are an important class of conjugated fluorescent dyes emitting blue fluorescence and have been extensively applied in the industry due to the high fluorescence quantum yield (Wilkinson *et al.*, 1990; Rivett *et al.*, 1979). For example, pyrazolines have been widely used as optical brightening agents for textiles, paper and fabrics and as a hole-conveying medium in photoconductive materials (Sun *et al.*, 2004; Huang & Katzenellenbogen, 2000; Wiley *et al.*, 1958). We found that ferrocene derivatives have good properties of fluorescence and coordination chemistry with many metal ions (Huang *et al.*, 1998; Shi *et al.*, 2004). Continuing our research (Liu *et al.*, 2007) we report the synthesis and structure of the title compound, (I).

In the structure of (I), the substituted ring (*Cps*) and unsubstituted ring (*Cp*) of the ferrocenyl moiety are slightly deprived from eclipsed form, with the five pseudo-torsion angles in the range 10.5 (2) — 10.9 (3)°. The distances from central Fe(II) ion to Cps center [*Cg*(1)] and to Cp center [*Cg*(2)] are 1.651 (3) Å and 1.656 (2) Å, respectively. The angle *Cg*(1)–Fe–*Cg*(2) is 177.9 (3)° and the central Fe(II) ion is located almost in the middle of the two cyclopentadiene rings which are not parallel because their dihedral angle is 2.3 (4)° (Fig. 1).

In the pyrazolinyl ring, the C=N and C–N bond lengths are in agreement with those found in similar structures (Fahrni *et al.*, 2003). However, the N–N bond length is longer than those found in the above-cited structures. But the bond distance of C21–N1 is shorter than a C–N single bond and slight longer than a C=N double bond. It might contribute to unclassical sp^2-hybrid N1 atom which is evident from the sum of the three angles around the N1 atom being 360° (Table 1) and that atoms C21, N1, N2 and C13 are co-planar. Furthemore, atoms S2, C21, N1, N2, C13 along with adjacent phenyl ring result in a large cojugated system.

In its packing diagram, the molecules of (I) are linked into two invers chains *via* C— H···S intermolecular hydrogen-bonds with C···S distance 3.583 (3) Å and C26—H26···S2 angle 142°, along the *b* axis (Fig. 2, Table 2).

S2. Experimental

The title compound was synthesized by refluxing an absolute ethanol solution of 1-(4-methylphenyl)-3-ferrocenylprop-2-en-1-one (3.30 g, 10 mmol) and *S*-benzyldithiocarbazate (1.98 g, 10 mmol) for 24 h. After refrigeration (278 K) of the solution for 10 h, yellow pricipite separated out and recrystallized from a mixture of 1,2-dichloroethane and petroleum ether (5:1 volume ratio) (3.1 g, yield 61%). The yellow crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane solution at 278 K.

S3. Refinement

All H atoms were fixed geometrically at ideal positions and allowed to ride on the parent atoms with C—H distances 0.96, 0.97, 0.98 and 0.93 Å for CH_3, CH_2, CH and aromatic CH groups, respectively, and with U_{iso}(H) values of 1.2 and 1.5 times U_{eq}(C) for the nonmethyl and methyl groups, respectively.

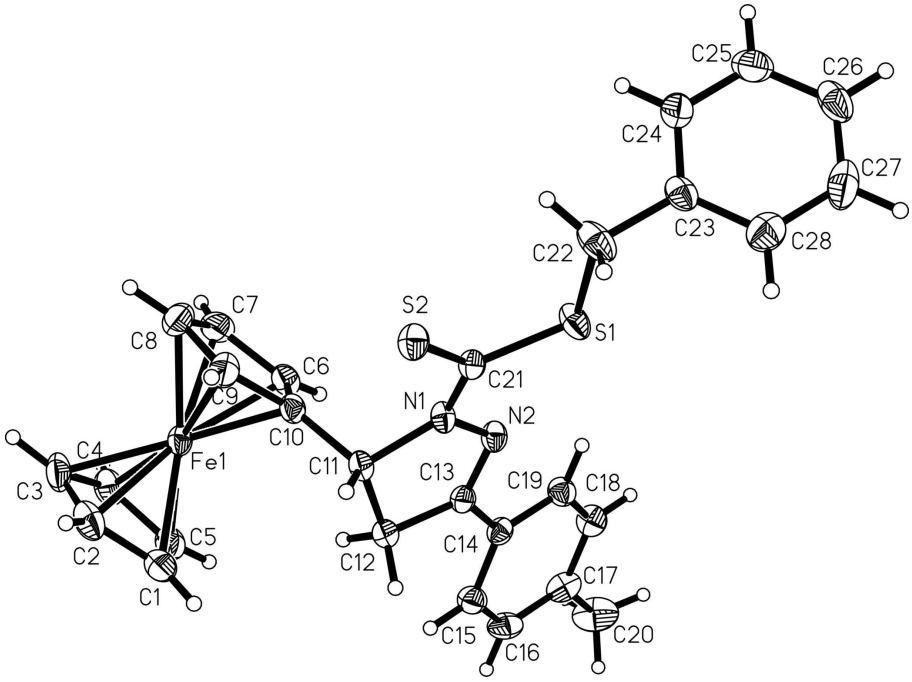

Figure 1

The molecular structure of (I); displacement ellipsoids are drawn at 50% probability level.

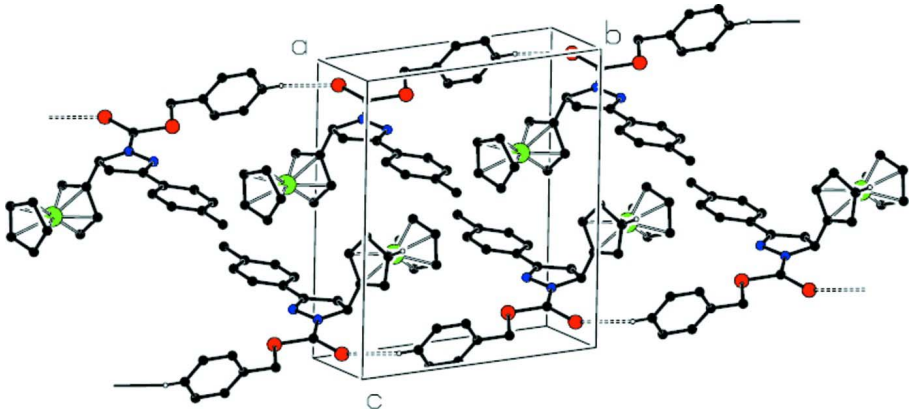

Figure 2

Packing diagram of (I), C—H···S inter-molecular hydrogen bonds shown as dashed lines. The H atoms not involved in hyydrogen bonding have been omitted.

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Crystal data

$[Fe(C_5H_5)(C_{23}H_{21}N_2S_2)]$
$M_r = 510.50$
Triclinic, $P\overline{1}$
Hall symbol: - P 1
$a = 9.178$ (1) Å
$b = 10.468$ (2) Å
$c = 13.216$ (2) Å
$\alpha = 99.37$ (1)°
$\beta = 101.55$ (2)°
$\gamma = 96.12$ (1)°
$V = 1214.6$ (3) Å^3
$Z = 2$
$F(000) = 532.0$
$D_x = 1.396$ Mg m^{-3}
Melting point: 345(2) K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7052 reflections
θ = 2.3–27.6°
μ = 0.81 mm^{-1}
T = 296 K
Block, yellow
0.33 × 0.31 × 0.28 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.776, T_{max} = 0.805
10742 measured reflections
5528 independent reflections
5035 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 27.7°, θ_{min} = 2.3°
h = −10→10
k = −12→12
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.088
S = 0.99
5528 reflections
299 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.4985P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Experimental. Analysis calculated for $C_{18}H_{16}N_4OS_2$: C 65.87, H 5.13, N 5.49%; found: C 65.82, H 5.11, N 5.51%. IR (KBr, cm^{-1}): ν(C=N), ν(S=C) and ν(N–N) 1559 (*m*), 1245 (*s*) and 1037 (w) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$,δ, p.p.m.): 7.23–7.76 (m, 9H, ArH), 6.04 (broad, 1H, CH), 4.50–4.47 (d, 1H, CH_2), 4.41–4.39 (d, 1H, CH_2), 4.15 (s, 5H, C_5H_5), 4.03 (s, 1H, C_5H_4), 4.12 (s, 1H, C_5H_4), 4.19 (s, 1H, C_5H_4), 4.71 (s, 1H, C_5H_4), 3.72 (s, 2H, $ArCH_2$), 2.41 (s, 3H, CH_3) p.p.m..
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_{iso}*/U_{eq}
Fe1	0.56551 (3)	−0.22018 (2)	0.364537 (18)	0.02183 (10)
S1	0.64012 (5)	0.30267 (4)	0.12369 (4)	0.02864 (13)
S2	0.72753 (5)	0.03133 (4)	0.06920 (3)	0.02501 (12)
N1	0.52328 (15)	0.09334 (13)	0.17619 (11)	0.0209 (3)
N2	0.43248 (16)	0.18040 (13)	0.21361 (11)	0.0219 (3)
C5	0.3598 (2)	−0.28594 (18)	0.38988 (16)	0.0310 (4)
H5	0.2866	−0.2347	0.4034	0.037*
C4	0.4760 (2)	−0.31695 (18)	0.46642 (16)	0.0322 (4)
H4	0.4920	−0.2897	0.5388	0.039*

C3	0.5633 (2)	−0.39647 (18)	0.41353 (16)	0.0342 (4)
H3	0.6465	−0.4305	0.4452	0.041*
C2	0.5017 (2)	−0.41532 (18)	0.30377 (16)	0.0351 (4)
H2	0.5376	−0.4637	0.2509	0.042*
C1	0.3750 (2)	−0.34678 (18)	0.28908 (16)	0.0324 (4)
H1	0.3133	−0.3427	0.2250	0.039*
C6	0.6003 (2)	−0.01980 (17)	0.39096 (14)	0.0262 (4)
H6	0.5385	0.0357	0.4175	0.031*
C7	0.7219 (2)	−0.06716 (19)	0.45157 (15)	0.0340 (4)
H7	0.7534	−0.0483	0.5245	0.041*
C8	0.7865 (2)	−0.1481 (2)	0.38121 (17)	0.0365 (5)
H8	0.8680	−0.1917	0.4001	0.044*
C9	0.7059 (2)	−0.15140 (18)	0.27690 (15)	0.0287 (4)
H9	0.7257	−0.1972	0.2158	0.034*
C10	0.58923 (19)	−0.07210 (16)	0.28218 (13)	0.0218 (3)
C11	0.47914 (18)	−0.04276 (16)	0.19133 (13)	0.0212 (3)
H11	0.4742	−0.1063	0.1271	0.025*
C12	0.32107 (19)	−0.03292 (16)	0.21151 (14)	0.0230 (4)
H12A	0.2439	−0.0746	0.1500	0.028*
H12B	0.3063	−0.0725	0.2708	0.028*
C13	0.31983 (18)	0.11285 (16)	0.23500 (12)	0.0211 (3)
C14	0.20317 (18)	0.17603 (17)	0.27623 (13)	0.0219 (3)
C15	0.0737 (2)	0.10168 (18)	0.28749 (14)	0.0271 (4)
H15	0.0607	0.0111	0.2677	0.033*
C16	−0.0357 (2)	0.16144 (19)	0.32793 (14)	0.0309 (4)
H16	−0.1212	0.1103	0.3349	0.037*
C17	−0.0196 (2)	0.2960 (2)	0.35799 (14)	0.0309 (4)
C18	0.1102 (2)	0.37050 (18)	0.34690 (14)	0.0296 (4)
H18	0.1230	0.4611	0.3671	0.036*
C19	0.2197 (2)	0.31208 (17)	0.30645 (14)	0.0260 (4)
H19	0.3048	0.3635	0.2993	0.031*
C20	−0.1389 (2)	0.3607 (3)	0.40227 (19)	0.0483 (6)
H20A	−0.2364	0.3153	0.3658	0.072*
H20B	−0.1313	0.4502	0.3934	0.072*
H20C	−0.1246	0.3576	0.4758	0.072*
C21	0.62648 (18)	0.13289 (16)	0.12474 (13)	0.0210 (3)
C22	0.7966 (2)	0.32849 (18)	0.06058 (17)	0.0356 (5)
H22A	0.8841	0.2976	0.0978	0.043*
H22B	0.7706	0.2810	−0.0115	0.043*
C23	0.8295 (2)	0.47341 (17)	0.06311 (14)	0.0263 (4)
C28	0.7407 (2)	0.5341 (2)	−0.00745 (16)	0.0370 (5)
H28	0.6566	0.4858	−0.0549	0.044*
C27	0.7770 (3)	0.6667 (2)	−0.00738 (18)	0.0442 (5)
H27	0.7181	0.7062	−0.0557	0.053*
C26	0.8997 (2)	0.73954 (19)	0.06398 (19)	0.0405 (5)
H26	0.9246	0.8279	0.0636	0.049*
C25	0.9849 (2)	0.6807 (2)	0.13578 (19)	0.0408 (5)
H25	1.0664	0.7300	0.1853	0.049*

C24	0.9504 (2)	0.54858 (19)	0.13486 (17)	0.0344 (4)
H24	1.0097	0.5098	0.1834	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.02452 (15)	0.02086 (15)	0.02275 (15)	0.00548 (10)	0.00666 (11)	0.00855 (10)
S1	0.0313 (2)	0.0201 (2)	0.0413 (3)	0.00543 (17)	0.0205 (2)	0.00872 (19)
S2	0.0281 (2)	0.0247 (2)	0.0256 (2)	0.00900 (17)	0.01053 (18)	0.00548 (17)
N1	0.0250 (7)	0.0185 (7)	0.0220 (7)	0.0066 (5)	0.0085 (6)	0.0057 (5)
N2	0.0242 (7)	0.0224 (7)	0.0221 (7)	0.0077 (6)	0.0085 (6)	0.0064 (6)
C5	0.0291 (9)	0.0274 (9)	0.0412 (11)	0.0029 (7)	0.0142 (8)	0.0125 (8)
C4	0.0403 (11)	0.0297 (10)	0.0319 (10)	0.0035 (8)	0.0138 (8)	0.0148 (8)
C3	0.0408 (11)	0.0239 (9)	0.0443 (12)	0.0099 (8)	0.0121 (9)	0.0180 (8)
C2	0.0442 (11)	0.0213 (9)	0.0415 (11)	0.0056 (8)	0.0147 (9)	0.0040 (8)
C1	0.0332 (10)	0.0254 (9)	0.0361 (11)	−0.0019 (8)	0.0038 (8)	0.0075 (8)
C6	0.0326 (9)	0.0209 (8)	0.0240 (9)	0.0000 (7)	0.0053 (7)	0.0049 (7)
C7	0.0351 (10)	0.0348 (10)	0.0268 (10)	−0.0067 (8)	−0.0032 (8)	0.0108 (8)
C8	0.0236 (9)	0.0423 (11)	0.0481 (12)	0.0062 (8)	0.0046 (8)	0.0248 (10)
C9	0.0270 (9)	0.0308 (10)	0.0356 (10)	0.0082 (7)	0.0144 (8)	0.0153 (8)
C10	0.0239 (8)	0.0201 (8)	0.0239 (9)	0.0021 (6)	0.0076 (7)	0.0092 (7)
C11	0.0268 (9)	0.0172 (8)	0.0205 (8)	0.0040 (6)	0.0059 (7)	0.0049 (6)
C12	0.0229 (8)	0.0213 (8)	0.0254 (9)	0.0027 (6)	0.0045 (7)	0.0071 (7)
C13	0.0228 (8)	0.0230 (8)	0.0175 (8)	0.0027 (7)	0.0024 (6)	0.0070 (6)
C14	0.0220 (8)	0.0265 (9)	0.0182 (8)	0.0054 (7)	0.0035 (6)	0.0069 (7)
C15	0.0267 (9)	0.0270 (9)	0.0270 (9)	0.0011 (7)	0.0051 (7)	0.0059 (7)
C16	0.0214 (9)	0.0424 (11)	0.0280 (9)	−0.0021 (8)	0.0073 (7)	0.0060 (8)
C17	0.0268 (9)	0.0444 (11)	0.0221 (9)	0.0080 (8)	0.0075 (7)	0.0032 (8)
C18	0.0331 (10)	0.0283 (9)	0.0277 (9)	0.0078 (8)	0.0082 (8)	0.0020 (7)
C19	0.0250 (9)	0.0260 (9)	0.0287 (9)	0.0034 (7)	0.0084 (7)	0.0074 (7)
C20	0.0334 (11)	0.0616 (15)	0.0477 (13)	0.0092 (10)	0.0175 (10)	−0.0079 (11)
C21	0.0222 (8)	0.0217 (8)	0.0190 (8)	0.0035 (6)	0.0030 (6)	0.0054 (6)
C22	0.0384 (11)	0.0265 (10)	0.0497 (12)	0.0037 (8)	0.0282 (9)	0.0076 (9)
C23	0.0271 (9)	0.0252 (9)	0.0320 (10)	0.0048 (7)	0.0171 (8)	0.0077 (7)
C28	0.0345 (10)	0.0428 (12)	0.0327 (11)	0.0070 (9)	0.0050 (8)	0.0066 (9)
C27	0.0503 (13)	0.0474 (13)	0.0487 (13)	0.0257 (11)	0.0184 (10)	0.0276 (10)
C26	0.0370 (11)	0.0266 (10)	0.0701 (15)	0.0109 (8)	0.0301 (11)	0.0178 (10)
C25	0.0266 (10)	0.0321 (11)	0.0620 (14)	0.0017 (8)	0.0098 (9)	0.0055 (10)
C24	0.0290 (10)	0.0342 (10)	0.0439 (11)	0.0074 (8)	0.0086 (8)	0.0159 (9)

Geometric parameters (Å, º)

Fe1—C8	2.0428 (19)	C10—C11	1.502 (2)
Fe1—C2	2.0452 (19)	C11—C12	1.538 (2)
Fe1—C1	2.0460 (19)	C11—H11	0.9800
Fe1—C9	2.0474 (18)	C12—C13	1.509 (2)
Fe1—C6	2.0488 (17)	C12—H12A	0.9700
Fe1—C7	2.0487 (19)	C12—H12B	0.9700

Fe1—C5	2.0493 (18)	C13—C14	1.466 (2)
Fe1—C10	2.0510 (16)	C14—C15	1.397 (2)
Fe1—C3	2.0521 (18)	C14—C19	1.398 (2)
Fe1—C4	2.0549 (18)	C15—C16	1.388 (3)
S1—C21	1.7708 (17)	C15—H15	0.9300
S1—C22	1.8167 (18)	C16—C17	1.383 (3)
S2—C21	1.6608 (17)	C16—H16	0.9300
N1—C21	1.340 (2)	C17—C18	1.399 (3)
N1—N2	1.3964 (19)	C17—C20	1.512 (3)
N1—C11	1.495 (2)	C18—C19	1.382 (3)
N2—C13	1.294 (2)	C18—H18	0.9300
C5—C1	1.420 (3)	C19—H19	0.9300
C5—C4	1.419 (3)	C20—H20A	0.9600
C5—H5	0.9300	C20—H20B	0.9600
C4—C3	1.414 (3)	C20—H20C	0.9600
C4—H4	0.9300	C22—C23	1.508 (2)
C3—C2	1.420 (3)	C22—H22A	0.9700
C3—H3	0.9300	C22—H22B	0.9700
C2—C1	1.428 (3)	C23—C24	1.378 (3)
C2—H2	0.9300	C23—C28	1.392 (3)
C1—H1	0.9300	C28—C27	1.392 (3)
C6—C7	1.422 (3)	C28—H28	0.9300
C6—C10	1.432 (2)	C27—C26	1.377 (3)
C6—H6	0.9300	C27—H27	0.9300
C7—C8	1.416 (3)	C26—C25	1.374 (3)
C7—H7	0.9300	C26—H26	0.9300
C8—C9	1.421 (3)	C25—C24	1.383 (3)
C8—H8	0.9300	C25—H25	0.9300
C9—C10	1.429 (2)	C24—H24	0.9300
C9—H9	0.9300		

C8—Fe1—C2	116.95 (9)	C6—C7—Fe1	69.69 (10)
C8—Fe1—C1	151.92 (9)	C8—C7—H7	126.1
C2—Fe1—C1	40.85 (8)	C6—C7—H7	126.1
C8—Fe1—C9	40.66 (8)	Fe1—C7—H7	126.3
C2—Fe1—C9	106.49 (8)	C7—C8—C9	108.51 (17)
C1—Fe1—C9	118.79 (8)	C7—C8—Fe1	69.98 (11)
C8—Fe1—C6	68.20 (8)	C9—C8—Fe1	69.85 (10)
C2—Fe1—C6	166.18 (8)	C7—C8—H8	125.7
C1—Fe1—C6	129.18 (7)	C9—C8—H8	125.7
C9—Fe1—C6	68.42 (7)	Fe1—C8—H8	126.0
C8—Fe1—C7	40.49 (9)	C8—C9—C10	108.07 (17)
C2—Fe1—C7	151.03 (8)	C8—C9—Fe1	69.49 (11)
C1—Fe1—C7	166.78 (8)	C10—C9—Fe1	69.73 (9)
C9—Fe1—C7	68.41 (8)	C8—C9—H9	126.0
C6—Fe1—C7	40.62 (8)	C10—C9—H9	126.0
C8—Fe1—C5	164.95 (8)	Fe1—C9—H9	126.4
C2—Fe1—C5	68.37 (8)	C9—C10—C6	107.23 (15)

C1—Fe1—C5	40.57 (8)	C9—C10—C11	127.04 (15)
C9—Fe1—C5	153.95 (8)	C6—C10—C11	125.67 (15)
C6—Fe1—C5	110.18 (7)	C9—C10—Fe1	69.46 (9)
C7—Fe1—C5	128.59 (8)	C6—C10—Fe1	69.47 (9)
C8—Fe1—C10	68.59 (7)	C11—C10—Fe1	128.36 (11)
C2—Fe1—C10	127.05 (8)	N1—C11—C10	109.61 (13)
C1—Fe1—C10	108.77 (7)	N1—C11—C12	100.44 (12)
C9—Fe1—C10	40.81 (7)	C10—C11—C12	114.22 (14)
C6—Fe1—C10	40.88 (7)	N1—C11—H11	110.7
C7—Fe1—C10	68.72 (7)	C10—C11—H11	110.7
C5—Fe1—C10	120.71 (7)	C12—C11—H11	110.7
C8—Fe1—C3	106.16 (8)	C13—C12—C11	102.75 (13)
C2—Fe1—C3	40.56 (8)	C13—C12—H12A	111.2
C1—Fe1—C3	68.31 (8)	C11—C12—H12A	111.2
C9—Fe1—C3	125.60 (8)	C13—C12—H12B	111.2
C6—Fe1—C3	152.81 (8)	C11—C12—H12B	111.2
C7—Fe1—C3	117.78 (8)	H12A—C12—H12B	109.1
C5—Fe1—C3	68.04 (8)	N2—C13—C14	121.50 (15)
C10—Fe1—C3	164.02 (8)	N2—C13—C12	113.60 (15)
C8—Fe1—C4	126.35 (8)	C14—C13—C12	124.88 (14)
C2—Fe1—C4	68.10 (8)	C15—C14—C19	118.43 (16)
C1—Fe1—C4	68.15 (8)	C15—C14—C13	120.79 (15)
C9—Fe1—C4	163.37 (8)	C19—C14—C13	120.77 (15)
C6—Fe1—C4	120.38 (8)	C16—C15—C14	120.77 (17)
C7—Fe1—C4	108.22 (8)	C16—C15—H15	119.6
C5—Fe1—C4	40.46 (8)	C14—C15—H15	119.6
C10—Fe1—C4	154.75 (7)	C17—C16—C15	120.92 (17)
C3—Fe1—C4	40.27 (8)	C17—C16—H16	119.5
C21—S1—C22	101.89 (8)	C15—C16—H16	119.5
C21—N1—N2	120.26 (13)	C16—C17—C18	118.34 (17)
C21—N1—C11	127.22 (14)	C16—C17—C20	120.75 (18)
N2—N1—C11	112.25 (12)	C18—C17—C20	120.91 (19)
C13—N2—N1	108.02 (13)	C19—C18—C17	121.25 (17)
C1—C5—C4	108.06 (17)	C19—C18—H18	119.4
C1—C5—Fe1	69.59 (11)	C17—C18—H18	119.4
C4—C5—Fe1	69.98 (11)	C18—C19—C14	120.30 (16)
C1—C5—H5	126.0	C18—C19—H19	119.9
C4—C5—H5	126.0	C14—C19—H19	119.9
Fe1—C5—H5	126.0	C17—C20—H20A	109.5
C3—C4—C5	108.19 (17)	C17—C20—H20B	109.5
C3—C4—Fe1	69.76 (10)	H20A—C20—H20B	109.5
C5—C4—Fe1	69.56 (10)	C17—C20—H20C	109.5
C3—C4—H4	125.9	H20A—C20—H20C	109.5
C5—C4—H4	125.9	H20B—C20—H20C	109.5
Fe1—C4—H4	126.4	N1—C21—S2	122.65 (13)
C4—C3—C2	108.20 (17)	N1—C21—S1	112.19 (12)
C4—C3—Fe1	69.97 (10)	S2—C21—S1	125.16 (10)
C2—C3—Fe1	69.46 (10)	C23—C22—S1	107.43 (12)

C4—C3—H3	125.9	C23—C22—H22A	110.2
C2—C3—H3	125.9	S1—C22—H22A	110.2
Fe1—C3—H3	126.2	C23—C22—H22B	110.2
C3—C2—C1	107.78 (18)	S1—C22—H22B	110.2
C3—C2—Fe1	69.98 (11)	H22A—C22—H22B	108.5
C1—C2—Fe1	69.60 (10)	C24—C23—C28	118.41 (17)
C3—C2—H2	126.1	C24—C23—C22	120.43 (17)
C1—C2—H2	126.1	C28—C23—C22	121.16 (18)
Fe1—C2—H2	125.9	C23—C28—C27	120.40 (19)
C5—C1—C2	107.77 (18)	C23—C28—H28	119.8
C5—C1—Fe1	69.84 (11)	C27—C28—H28	119.8
C2—C1—Fe1	69.54 (11)	C26—C27—C28	120.19 (19)
C5—C1—H1	126.1	C26—C27—H27	119.9
C2—C1—H1	126.1	C28—C27—H27	119.9
Fe1—C1—H1	126.1	C25—C26—C27	119.51 (18)
C7—C6—C10	108.33 (16)	C25—C26—H26	120.2
C7—C6—Fe1	69.69 (10)	C27—C26—H26	120.2
C10—C6—Fe1	69.64 (9)	C26—C25—C24	120.4 (2)
C7—C6—H6	125.8	C26—C25—H25	119.8
C10—C6—H6	125.8	C24—C25—H25	119.8
Fe1—C6—H6	126.4	C23—C24—C25	121.06 (19)
C8—C7—C6	107.85 (17)	C23—C24—H24	119.5
C8—C7—Fe1	69.53 (11)	C25—C24—H24	119.5

C21—N1—N2—C13	163.81 (15)	C1—Fe1—C7—C6	−43.9 (4)
C11—N1—N2—C13	−10.50 (18)	C9—Fe1—C7—C6	81.61 (12)
C8—Fe1—C5—C1	−151.8 (3)	C5—Fe1—C7—C6	−75.37 (13)
C2—Fe1—C5—C1	−38.01 (11)	C10—Fe1—C7—C6	37.61 (10)
C9—Fe1—C5—C1	45.3 (2)	C3—Fe1—C7—C6	−158.46 (11)
C6—Fe1—C5—C1	127.27 (11)	C4—Fe1—C7—C6	−115.72 (12)
C7—Fe1—C5—C1	169.42 (11)	C6—C7—C8—C9	0.0 (2)
C10—Fe1—C5—C1	83.21 (12)	Fe1—C7—C8—C9	59.42 (13)
C3—Fe1—C5—C1	−81.85 (12)	C6—C7—C8—Fe1	−59.37 (13)
C4—Fe1—C5—C1	−119.19 (16)	C2—Fe1—C8—C7	−156.34 (11)
C8—Fe1—C5—C4	−32.6 (3)	C1—Fe1—C8—C7	171.85 (15)
C2—Fe1—C5—C4	81.18 (12)	C9—Fe1—C8—C7	119.58 (16)
C1—Fe1—C5—C4	119.19 (16)	C6—Fe1—C8—C7	37.76 (11)
C9—Fe1—C5—C4	164.52 (16)	C5—Fe1—C8—C7	−49.0 (3)
C6—Fe1—C5—C4	−113.54 (12)	C10—Fe1—C8—C7	81.88 (12)
C7—Fe1—C5—C4	−71.39 (14)	C3—Fe1—C8—C7	−114.07 (12)
C10—Fe1—C5—C4	−157.60 (11)	C4—Fe1—C8—C7	−74.70 (14)
C3—Fe1—C5—C4	37.34 (12)	C2—Fe1—C8—C9	84.08 (13)
C1—C5—C4—C3	0.1 (2)	C1—Fe1—C8—C9	52.3 (2)
Fe1—C5—C4—C3	−59.26 (13)	C6—Fe1—C8—C9	−81.83 (12)
C1—C5—C4—Fe1	59.39 (12)	C7—Fe1—C8—C9	−119.58 (16)
C8—Fe1—C4—C3	−70.49 (15)	C5—Fe1—C8—C9	−168.6 (3)
C2—Fe1—C4—C3	37.61 (12)	C10—Fe1—C8—C9	−37.70 (11)
C1—Fe1—C4—C3	81.79 (13)	C3—Fe1—C8—C9	126.35 (12)

C9—Fe1—C4—C3	−36.3 (3)	C4—Fe1—C8—C9	165.72 (11)
C6—Fe1—C4—C3	−154.57 (12)	C7—C8—C9—C10	−0.2 (2)
C7—Fe1—C4—C3	−111.74 (13)	Fe1—C8—C9—C10	59.26 (12)
C5—Fe1—C4—C3	119.51 (17)	C7—C8—C9—Fe1	−59.50 (13)
C10—Fe1—C4—C3	169.66 (15)	C2—Fe1—C9—C8	−112.38 (13)
C8—Fe1—C4—C5	170.00 (12)	C1—Fe1—C9—C8	−154.87 (12)
C2—Fe1—C4—C5	−81.90 (13)	C6—Fe1—C9—C8	81.23 (13)
C1—Fe1—C4—C5	−37.72 (11)	C7—Fe1—C9—C8	37.40 (12)
C9—Fe1—C4—C5	−155.8 (2)	C5—Fe1—C9—C8	173.27 (16)
C6—Fe1—C4—C5	85.92 (13)	C10—Fe1—C9—C8	119.41 (16)
C7—Fe1—C4—C5	128.75 (12)	C3—Fe1—C9—C8	−72.06 (15)
C10—Fe1—C4—C5	50.2 (2)	C4—Fe1—C9—C8	−44.0 (3)
C3—Fe1—C4—C5	−119.51 (17)	C8—Fe1—C9—C10	−119.41 (16)
C5—C4—C3—C2	0.0 (2)	C2—Fe1—C9—C10	128.21 (11)
Fe1—C4—C3—C2	−59.13 (13)	C1—Fe1—C9—C10	85.72 (12)
C5—C4—C3—Fe1	59.14 (13)	C6—Fe1—C9—C10	−38.18 (10)
C8—Fe1—C3—C4	127.78 (12)	C7—Fe1—C9—C10	−82.01 (11)
C2—Fe1—C3—C4	−119.45 (17)	C5—Fe1—C9—C10	53.9 (2)
C1—Fe1—C3—C4	−81.37 (13)	C3—Fe1—C9—C10	168.53 (10)
C9—Fe1—C3—C4	167.97 (11)	C4—Fe1—C9—C10	−163.4 (2)
C6—Fe1—C3—C4	54.2 (2)	C8—C9—C10—C6	0.34 (19)
C7—Fe1—C3—C4	85.70 (13)	Fe1—C9—C10—C6	59.45 (11)
C5—Fe1—C3—C4	−37.51 (12)	C8—C9—C10—C11	177.69 (16)
C10—Fe1—C3—C4	−163.8 (2)	Fe1—C9—C10—C11	−123.19 (16)
C8—Fe1—C3—C2	−112.77 (13)	C8—C9—C10—Fe1	−59.12 (12)
C1—Fe1—C3—C2	38.08 (12)	C7—C6—C10—C9	−0.31 (19)
C9—Fe1—C3—C2	−72.58 (14)	Fe1—C6—C10—C9	−59.44 (11)
C6—Fe1—C3—C2	173.60 (15)	C7—C6—C10—C11	−177.71 (15)
C7—Fe1—C3—C2	−154.85 (12)	Fe1—C6—C10—C11	123.15 (16)
C5—Fe1—C3—C2	81.94 (13)	C7—C6—C10—Fe1	59.14 (12)
C10—Fe1—C3—C2	−44.4 (3)	C8—Fe1—C10—C9	37.56 (12)
C4—Fe1—C3—C2	119.45 (17)	C2—Fe1—C10—C9	−70.73 (14)
C4—C3—C2—C1	−0.1 (2)	C1—Fe1—C10—C9	−112.63 (12)
Fe1—C3—C2—C1	−59.58 (13)	C6—Fe1—C10—C9	118.56 (15)
C4—C3—C2—Fe1	59.45 (13)	C7—Fe1—C10—C9	81.19 (12)
C8—Fe1—C2—C3	83.47 (13)	C5—Fe1—C10—C9	−155.64 (11)
C1—Fe1—C2—C3	−118.83 (17)	C3—Fe1—C10—C9	−36.0 (3)
C9—Fe1—C2—C3	125.99 (12)	C4—Fe1—C10—C9	168.95 (16)
C6—Fe1—C2—C3	−167.7 (3)	C8—Fe1—C10—C6	−81.00 (12)
C7—Fe1—C2—C3	50.9 (2)	C2—Fe1—C10—C6	170.70 (11)
C5—Fe1—C2—C3	−81.07 (12)	C1—Fe1—C10—C6	128.81 (11)
C10—Fe1—C2—C3	166.04 (11)	C9—Fe1—C10—C6	−118.56 (15)
C4—Fe1—C2—C3	−37.35 (12)	C7—Fe1—C10—C6	−37.37 (11)
C8—Fe1—C2—C1	−157.71 (12)	C5—Fe1—C10—C6	85.80 (12)
C9—Fe1—C2—C1	−115.19 (12)	C3—Fe1—C10—C6	−154.5 (3)
C6—Fe1—C2—C1	−48.9 (4)	C4—Fe1—C10—C6	50.4 (2)
C7—Fe1—C2—C1	169.74 (15)	C8—Fe1—C10—C11	159.15 (17)
C5—Fe1—C2—C1	37.75 (12)	C2—Fe1—C10—C11	50.85 (18)

C10—Fe1—C2—C1	−75.14 (14)	C1—Fe1—C10—C11	8.96 (17)
C3—Fe1—C2—C1	118.83 (17)	C9—Fe1—C10—C11	121.59 (19)
C4—Fe1—C2—C1	81.48 (12)	C6—Fe1—C10—C11	−119.85 (19)
C4—C5—C1—C2	−0.2 (2)	C7—Fe1—C10—C11	−157.23 (17)
Fe1—C5—C1—C2	59.43 (13)	C5—Fe1—C10—C11	−34.05 (18)
C4—C5—C1—Fe1	−59.63 (13)	C3—Fe1—C10—C11	85.6 (3)
C3—C2—C1—C5	0.2 (2)	C4—Fe1—C10—C11	−69.5 (2)
Fe1—C2—C1—C5	−59.62 (12)	C21—N1—C11—C10	82.3 (2)
C3—C2—C1—Fe1	59.82 (13)	N2—N1—C11—C10	−103.92 (15)
C8—Fe1—C1—C5	164.87 (15)	C21—N1—C11—C12	−157.18 (16)
C2—Fe1—C1—C5	118.94 (16)	N2—N1—C11—C12	16.65 (16)
C9—Fe1—C1—C5	−159.12 (11)	C9—C10—C11—N1	−104.11 (18)
C6—Fe1—C1—C5	−74.48 (14)	C6—C10—C11—N1	72.8 (2)
C7—Fe1—C1—C5	−38.9 (4)	Fe1—C10—C11—N1	163.79 (12)
C10—Fe1—C1—C5	−115.62 (11)	C9—C10—C11—C12	144.09 (17)
C3—Fe1—C1—C5	81.13 (12)	C6—C10—C11—C12	−39.0 (2)
C4—Fe1—C1—C5	37.62 (11)	Fe1—C10—C11—C12	52.0 (2)
C8—Fe1—C1—C2	45.9 (2)	N1—C11—C12—C13	−15.48 (15)
C9—Fe1—C1—C2	81.94 (13)	C10—C11—C12—C13	101.72 (15)
C6—Fe1—C1—C2	166.58 (11)	N1—N2—C13—C14	179.95 (14)
C7—Fe1—C1—C2	−157.8 (3)	N1—N2—C13—C12	−1.10 (19)
C5—Fe1—C1—C2	−118.94 (16)	C11—C12—C13—N2	11.39 (18)
C10—Fe1—C1—C2	125.44 (12)	C11—C12—C13—C14	−169.70 (15)
C3—Fe1—C1—C2	−37.81 (12)	N2—C13—C14—C15	172.56 (16)
C4—Fe1—C1—C2	−81.33 (12)	C12—C13—C14—C15	−6.3 (2)
C8—Fe1—C6—C7	−37.65 (12)	N2—C13—C14—C19	−8.2 (2)
C2—Fe1—C6—C7	−152.3 (3)	C12—C13—C14—C19	172.93 (16)
C1—Fe1—C6—C7	168.21 (12)	C19—C14—C15—C16	−0.1 (3)
C9—Fe1—C6—C7	−81.56 (12)	C13—C14—C15—C16	179.08 (16)
C5—Fe1—C6—C7	126.32 (12)	C14—C15—C16—C17	0.1 (3)
C10—Fe1—C6—C7	−119.67 (16)	C15—C16—C17—C18	−0.2 (3)
C3—Fe1—C6—C7	45.3 (2)	C15—C16—C17—C20	−179.84 (18)
C4—Fe1—C6—C7	82.72 (13)	C16—C17—C18—C19	0.3 (3)
C8—Fe1—C6—C10	82.03 (11)	C20—C17—C18—C19	−179.98 (18)
C2—Fe1—C6—C10	−32.7 (4)	C17—C18—C19—C14	−0.4 (3)
C1—Fe1—C6—C10	−72.12 (13)	C15—C14—C19—C18	0.3 (3)
C9—Fe1—C6—C10	38.12 (10)	C13—C14—C19—C18	−178.90 (16)
C7—Fe1—C6—C10	119.67 (16)	N2—N1—C21—S2	−174.50 (11)
C5—Fe1—C6—C10	−114.01 (11)	C11—N1—C21—S2	−1.1 (2)
C3—Fe1—C6—C10	164.99 (15)	N2—N1—C21—S1	5.40 (19)
C4—Fe1—C6—C10	−157.61 (10)	C11—N1—C21—S1	178.78 (12)
C10—C6—C7—C8	0.2 (2)	C22—S1—C21—N1	175.13 (13)
Fe1—C6—C7—C8	59.27 (13)	C22—S1—C21—S2	−4.97 (14)
C10—C6—C7—Fe1	−59.11 (12)	C21—S1—C22—C23	−175.12 (14)
C2—Fe1—C7—C8	47.6 (2)	S1—C22—C23—C24	102.92 (18)
C1—Fe1—C7—C8	−163.0 (3)	S1—C22—C23—C28	−78.0 (2)
C9—Fe1—C7—C8	−37.54 (11)	C24—C23—C28—C27	2.2 (3)
C6—Fe1—C7—C8	−119.15 (16)	C22—C23—C28—C27	−176.87 (18)

C5—Fe1—C7—C8	165.48 (11)	C23—C28—C27—C26	−1.2 (3)
C10—Fe1—C7—C8	−81.54 (12)	C28—C27—C26—C25	−0.7 (3)
C3—Fe1—C7—C8	82.39 (13)	C27—C26—C25—C24	1.7 (3)
C4—Fe1—C7—C8	125.13 (12)	C28—C23—C24—C25	−1.2 (3)
C8—Fe1—C7—C6	119.15 (16)	C22—C23—C24—C25	177.82 (18)
C2—Fe1—C7—C6	166.76 (15)	C26—C25—C24—C23	−0.7 (3)