Synthesis and crystal structure of [(S\textsubscript{p})-(2-phenyl-ferrocenyl)methyl]trimethylammonium iodide dichloromethane monosolvate

Abdelhak Lachguar\textsuperscript{a,b}, Eric Deydier\textsuperscript{a,b}, Agnès Labande\textsuperscript{a}, Eric Manoury\textsuperscript{a}, Rinaldo Poli\textsuperscript{b} and Jean-Claude Daran\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}CNRS, LCC (Laboratoire de Chimie de Coordination), Université de Toulouse, UPS, INPT, 205 Route de Narbonne, F-31077 Toulouse Cedex 4, France, and \textsuperscript{b}IUT A Paul Sabatier, de Chimie, Avenue Georges Pompidou, CS 20258, F-81104, Castres Cedex, France. \textsuperscript{*}Correspondence e-mail: jean-claude.daran@lcc-toulouse.fr

As a follow-up to our research on the chemistry of disubstituted ferrocene derivatives, the synthesis and the structure of the title compound, [Fe(C\textsubscript{5}H\textsubscript{5})(C\textsubscript{15}H\textsubscript{19}N)]I-CH\textsubscript{2}Cl\textsubscript{2}, is described. The cation molecule is built up from a ferrocene disubstituted by a trimethylammonium methyl group and a phenyl ring. The asymmetric unit contains the iodide to equilibrate the charge and a disordered dichloromethane solvate. The disordered model results from a roughly statistical exchange (0.6/0.4) between one Cl and one H. The packing of the structure is stabilized by weak C—H/C1/C1/C1 (X) (X = I, Cl), C—H···π(Cp) and C—Cl···π(phenyl) interactions, building a three-dimensional network. The cation has planar chirality with S\textsubscript{p}(Fc) absolute configuration. The structure of the title compound is compared with related disubstituted (trimethylammonio)methyl ferrocenes.

1. Chemical context

Asymmetric catalysis by transition metals has received considerable attention over the last few decades and numerous chiral ligands and complexes allowing high activity and enantioselectivity have been reported (Jacobsen \textit{et al.}, 1999; Börner, 2008). For this purpose, catalysts need a chiral ligand presenting at least a chiral center, a chiral axis or a planar chirality. Amongst the various chiral ligands that have been synthesized, ferrocenyl phosphines have proven to be particularly efficient for numerous asymmetric reactions (Buergler \textit{et al.}, 2012; Gómez Arrayá\textsuperscript{s} \textit{et al.}, 2006; Toma \textit{et al.}, 2014).

Over the last few years, our team has developed the synthesis of various chiral ferrocenyl ligands for asymmetric catalysis (Audin \textit{et al.}, 2010; Labande \textit{et al.}, 2007; Bayda \textit{et al.}, 2014; Daran \textit{et al.}, 2010; Wei \textit{et al.}, 2012, 2014; Loxq \textit{et al.}, 2014). We mainly focused on a series of chiral bidentate PX ferrocenyl ligands (X = OR, SR, NHC) bearing planar chirality, which have been successfully used in different homogeneous asymmetric catalytic reactions: allylic substitution, methoxy-carbonylation, hydrogenation (Kozinets \textit{et al.}, 2012; Le Roux \textit{et al.}, 2007; Diab \textit{et al.}, 2008; Routaboul \textit{et al.}, 2005). All of these ligands present a planar chiral 1,2-disubstituted ferrocenyl group with coordination sites on both substituents. More recently, we wanted to extend the application of planar chiral 1,2-disubstituted ferrocenyl groups to the synthesis of ligands.
with only one substituent bearing a coordination site for fine tuning of existing ligands. To this aim, we needed an enantiomerically pure planar chiral building block bearing a good leaving group in order to introduce a planar chiral substituent on nucleophilic atoms. In this context, we report here the two-step synthesis of the title \([(S_p)-(2\text{-phenylferrocenyl})\text{methy}l]\text{trimethylammonium iodide salt.}\)

The latter is synthesized in two steps, the first consists in the enantioselective synthesis of \((S_p)-\text{A}\) following the procedure developed by S.-L. You and co-workers (Gao et al., 2013), the second step is a quaternization of the tertiary amine to the ammonium salt by reaction with an excess of iodo methane. (Ferrocenylmethyl) ammoniums have been used successfully as electrophiles because of the stabilization of carbocations in an \(\alpha\) position of ferrocene derivatives and because of the presence of a good leaving group: trimethylamine. Nucleophilic[EM2] substitution (Lin et al., 2020) on the methylene carbon atom in the \(\alpha\) position of the ferrocene moiety in compound \(\text{B}\), \([(S_p)-(2\text{-phenylferrocenyl})\text{methyl}\text{trimethylammonium iodide, should then be favoured and should provide an efficient access to a wide range of various enantiomerically pure ferrocene derivatives of type C including}\)

![Diagram](image1)

**Figure 1**
Synthesis of the title \((S_p)-\text{1-dimethylaminomethyl-2-phenylferrocenium iodide salt}\)

![Diagram](image2)

**Figure 2**
View of the asymmetric unit of the title compound with the atom-labelling scheme. Ellipsoids are drawn at the 30% probability level and the H atoms are represented as small circles of arbitrary radii. C—H⋯X (X = I, Cl) interactions are represented as dashed lines.
ligands, by reaction with various nucleophiles (amines, thiols, alcohols) (Fig. 1).

2. Structural commentary

The molecular structure is based on a ferrocene moiety in which one of the Cp rings is disubstituted in the 1,2 position by a tri-methylammonium-methyl and a phenyl substituent. The molecule has a positive charge, which is counterbalanced by an iodide (Fig. 2). Moreover, there is one disordered dichloromethane solvate molecule per asymmetric unit. The disordered model results from the exchange between one CI and one H in the ratio 0.6/0.4 (Fig. 3). This disorder might be induced by the occurrence of weak C—CI···I intramolecular and C—H···Cl intermolecular interactions. There are weak intramolecular C—H···I interactions within the asymmetric unit.

As a result of the presence of the two substituents on the Cp ring, the cation molecule has planar chirality and its absolute structure is $S_p$, which is confirmed by the refinement of the Flack parameter (Parsons et al., 2013). The phenyl ring is twisted with respect to the Cp ring by 48.74 (17)° and the C1–C11–N1 unit is roughly perpendicular to the Cp ring to which it is attached, making a dihedral angle of 89.7 (2)° (Fig. 4). Then the Cl2 atom of the chloroform solvate interacts with the C12—H12C methyl group, thus building a link between the strips, resulting in a layer parallel to the (T01) plane (Fig. 4). Moreover, there are two weak C—H···π interactions involving atom H13B of the C13 methyl group with the centroid of the Cp ring (C6–C10; C12) and atom C23 of the phenyl group with the centroid of the substituted Cp ring (C1–C5; C11). Finally, there is also a C—Cl···π interaction involving the Cl1 atom of the solvate [Cl3–C11···Cl3 (C21–C26), 1.757 (8), 3.4096 (2) and 4.7694 (3) Å, 132.13 (1)°]. All these interactions build up a three-dimensional network.

3. Supramolecular features

The crystal packing is governed by the occurrence of weak C—H···X (X = Cl, I), C—H···π and C—Cl···π interactions (Table 1). The iodine atom is engaged in many weak C—H···I interactions involving some of the H atoms of the methyl groups, one H atom of the methylene group and the non-disordered H atoms of the dichloromethane solvate. These interactions build up a ribbon developing parallel to the b axis (Fig. 4).

4. Database survey

A search in the Cambridge Structural Database (version 5.36; Groom et al., 2016) using a fragment containing a ferrocenyl substituted by a trimethylammoniummethyl and at least a C atom gave six hits that could be compared with the title compound. A comparison of C1–C11, C11–N1 distances and dihedral angles resulting in the formation of ribbons parallel to the b axis and C—H···Cl interactions linking the ribbons to form a layer parallel to the (T01) plane. The dichloromethane solvate builds the link between the layers.

Table 1

| D—H ···A | D—H  | H···A | D···A | D—H ···A |
|-----------|------|------|-------|---------|
| C11—H1A ···I | 0.99 | 3.17 | 3.988 (4) | 140 |
| C12—H1C ···I | 0.98 | 3.21 | 4.117 (5) | 154 |
| C12—H1B ···C12C | 0.98 | 3.51 | 3.787 (7) | 99 |
| C13—H1A ···I | 0.98 | 3.27 | 4.158 (5) | 151 |
| C14—H1A ···I | 0.98 | 3.14 | 4.057 (5) | 157 |
| C14—H1B ···I | 0.98 | 3.25 | 4.077 (5) | 143 |
| C30A—H30A ···I | 1.00 | 2.89 | 3.867 (7) | 169 |
| C30A—H30A ···I | 0.98 | 2.98 | 3.901 (6) | 158 |
| C23—H23 ···CT1 | 0.95 | 2.69 | 3.600 (7) | 160 |

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+2$; (ii) $-x, y+\frac{1}{2}, -z+1$; (iii) $-x+2, y-\frac{1}{2}, -z+2$; (iv) $-x+1, y+\frac{1}{2}, -z+1$.
N(CH₃)₃ group is always above the Cp ring to which it is attached. The dihedral angles between the Cp and the C–C–N plane range from 69.8 to 89.7° for the title compound.

5. Synthesis and crystallization

Synthesis of [(5,5)-1-dimethylaminomethyl-2-phenylferrocene ([(5,5)-A]: To a solution of phenylboronic acid (110 mg, 0.9 mmol) in DMA (8 mL) were added Boc–L–Val–OH (43.5 mg, 0.2 mmol), Pd(OAc)₂ (22.5 mg, 0.1 mmol), K₂CO₃ (138.21 mg, 1 mmol) and TEB (tetraethyl ammonium bromide; 80 mg, 0.25 mmol) and N,N-dimethylferrocenylmethyamine (243 mg, 1 mmol) successively. The mixture was stirred at 333 K under air (open flask). When the reaction was complete (TLC monitoring), the mixture was quenched with saturated aqueous NaHCO₃ and the organic phase was extracted three times with Et₂O and brine successively, dried (Na₂SO₄) and filtered.

1H NMR (400 MHz, CDCl₃) δ ppm 7.79–7.71 (m, 2H, CH Ph), 7.30–7.21 (m, 5H, CH subst Cp), 6.98 (d, J = 12.8 Hz, 1H, CH₂), 2.21 (s, 6H, CH₃), 1.53 (s, 3H, CH₂). 13C NMR (101 MHz, CDCl₃) δ ppm 138.91 (Cq subst Cp), 129.36 (CH Ph), 127.93 (CH Ph), 90.61 (CH subst Cp), 88.17 (Cq subst Cp), 82.24 (Cq subst Cp), 71.56 (CH subst Cp), 70.06 (CH subst Cp), 69.94 (CH subst Cp), 67.10 (CH subst Cp), 57.93 (CH₂), 45.08 (CH₃).

Synthesis of [(5,5)-(2-phenylferrocenyI)methyl]trimethylammonium iodide salt [(5,5)-B]: An excess of MeI (1 mL, 1.62 mmol) was added to a solution of A (250 mg, 0.78 mmol) in Et₂O (3 mL). The reaction mixture was stirred for 4 h at RT. An abundant yellow solid precipitated. The yellow solid was filtered, washed with Et₂O and dried to yield B as a yellow solid (332 mg, 92% yield), which was crystallized in dichloromethane.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms attached to C atoms were fixed geometrically and treated as riding with C–H = 0.95 Å (aromatic), 0.99 Å (methylene) and 1.0 Å (methine), respectively. The Uiso(H) values were constrained to 1.2Ueq(CH aromatic, methyl) and 0.98 Å (methyl) with Uiso(H) = 1.2Ueq(CH aromatic, methyl) or Uiso(H) = 1.5Ueq(CH₃).

The occurrence of three large residual densities around the C atom of the solvate with distances around 1.76 Å initially suggested the presence of a chloroform solvate molecule. However, if one of the Cl atoms (Cl1) could be refined...
correctly with full occupancy, the two others display large and elongated ellipsoids. Refining their occupancy factors using the restraints available in SHELXL gave a ratio of 0.6/0.4. So the disordered model is based on an exchange between one H and one Cl (Fig. 3). The model has been refined using the PART instruction to model two CH2Cl2 models. The non-disordered atoms C30, H30 and Cl1 were split with occupancy factor 0.5 and introduced in the two models (C30A, C30B, H30A, H30B, C1A, C1B). Their coordinates and thermal parameters were constrained to be identical using the EXYZ and EADP commands available in SHELXL. This disordered model is not perfect, as suggested by a large residual electron density in the vicinity of the atom H30B.

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Computing details

Data collection: APEX2 (Bruker, 2015); cell refinement: SAINT (Bruker, 2015); data reduction: SAINT (Bruker, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: ORTEPIII (Burnett & Johnson, 1996), ORTEP-3 for Windows (Farrugia, 2012) and Mercury (Macrae et al., 2020); software used to prepare material for publication: SHELXL2018 (Sheldrick, 2015b).

[(S\textsubscript{p})-(2-Phenylferrocenyl)methyl]trimethylammonium iodide dichloromethane monosolvate

Crystal data

[Fe(C\textsubscript{5}H\textsubscript{5})(C\textsubscript{15}H\textsubscript{19}N)]I·CH\textsubscript{2}Cl\textsubscript{2}

\( F(000) = 544 \)

\( D_x = 1.583 \text{ Mg m}^{-3} \)

Mo \( K\alpha \) radiation, \( \lambda = 0.71073 \text{ Å} \)

Cell parameters from 9989 reflections

\( \theta = 2.8-28.3^\circ \)

\( \mu = 2.24 \text{ mm}^{-1} \)

\( T = 110 \text{ K} \)

Stick, yellow

0.30 \times 0.10 \times 0.10 \text{ mm}

Data collection

Bruker APEXII CCD diffractometer

Radiation source: micro-focus sealed tube

Graphite monochromator

\( \varphi \) and \( \omega \) scans

Absorption correction: multi-scan

(SADABS, Krause \textit{et al.}, 2015)

\( T_{\text{min}} = 0.520, T_{\text{max}} = 0.746 \)

58547 measured reflections

6993 independent reflections

6822 reflections with \( I > 2\sigma(I) \)

\( R_{\text{int}} = 0.052 \)

\( \theta_{\text{max}} = 30.5^\circ, \theta_{\text{min}} = 2.1^\circ \)

\( h = -15 \rightarrow 15 \)

\( k = -14 \rightarrow 14 \)

\( l = -16 \rightarrow 16 \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.033 \)

\( wR(F^2) = 0.092 \)

\( S = 1.06 \)

6993 reflections

247 parameters

1 restraint

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
\[ w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.9038P] \]
\[ P = (F_o^2 + 2F_c^2)/3 \]
\[ (\Delta/\sigma)_{\text{max}} = 0.001 \]
\[ \Delta \rho_{\text{max}} = 1.50 \text{ e Å}^{-3} \]
\[ \Delta \rho_{\text{min}} = -0.68 \text{ e Å}^{-3} \]

**Absolute structure**: Flack \( x \) determined using 3144 quotients \([I^+]-[I^-])/([I^+]+[I^-])\) (Parsons et al., 2013)

**Absolute structure parameter**: 0.018 (6)

**Special details**

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

| Atom | x       | y       | z       | \(U_{iso}/U_{eq}\) | Occ. (<1) |
|------|---------|---------|---------|---------------------|-----------|
| Fe1  | 0.94060 (5) | 0.53142 (6) | 0.79508 (5) | 0.02716 (11) |           |
| I1   | 0.22433 (3)  | 0.13532 (3)  | 0.79999 (3)  | 0.04532 (10)  |           |
| N1   | 0.5997 (3)   | 0.3408 (3)   | 0.8610 (3)   | 0.0281 (6)    |           |
| C1   | 0.7697 (3)   | 0.4388 (3)   | 0.7817 (3)   | 0.0243 (6)    |           |
| C2   | 0.7375 (3)   | 0.5512 (4)   | 0.6967 (3)   | 0.0248 (6)    |           |
| C3   | 0.8016 (4)   | 0.5304 (5)   | 0.6083 (4)   | 0.0323 (7)    |           |
| H3   | 0.797426     | 0.587679     | 0.540618     | 0.039*        |           |
| C4   | 0.8728 (4)   | 0.4085 (5)   | 0.6395 (4)   | 0.0361 (8)    |           |
| H4   | 0.924513     | 0.371724     | 0.596435     | 0.043*        |           |
| C5   | 0.8532 (4)   | 0.3521 (4)   | 0.7450 (4)   | 0.0316 (7)    |           |
| H5   | 0.888964     | 0.270870     | 0.784766     | 0.038*        |           |
| C6   | 1.0323 (5)   | 0.6035 (7)   | 0.9762 (5)   | 0.0588 (18)   |           |
| H6   | 0.996901     | 0.602449     | 1.041048     | 0.071*        |           |
| C7   | 1.1125 (5)   | 0.5035 (6)   | 0.9540 (6)   | 0.0546 (14)   |           |
| H7   | 1.139685     | 0.424007     | 1.000841     | 0.065*        |           |
| C8   | 1.1439 (4)   | 0.5440 (6)   | 0.8501 (6)   | 0.0482 (11)   |           |
| H8   | 1.196503     | 0.496477     | 0.814202     | 0.058*        |           |
| C9   | 1.0835 (5)   | 0.6679 (6)   | 0.8081 (6)   | 0.0517 (13)   |           |
| H9   | 1.088663     | 0.717959     | 0.739283     | 0.062*        |           |
| C10  | 1.0143 (5)   | 0.7038 (6)   | 0.8864 (7)   | 0.0542 (14)   |           |
| H10  | 0.964387     | 0.782051     | 0.879465     | 0.065*        |           |
| C11  | 0.7314 (3)   | 0.4163 (4)   | 0.8937 (3)   | 0.0262 (6)    |           |
| H11A | 0.723121     | 0.502191     | 0.930581     | 0.031*        |           |
| H11B | 0.804794     | 0.367396     | 0.960681     | 0.031*        |           |
| C12  | 0.4841 (4)   | 0.4146 (5)   | 0.7671 (6)   | 0.0463 (11)   |           |
| H12A | 0.496041     | 0.423269     | 0.685738     | 0.069*        |           |
| H12B | 0.479920     | 0.501808     | 0.801502     | 0.069*        |           |
| H12C | 0.400292     | 0.367326     | 0.752068     | 0.069*        |           |
| C13  | 0.6057 (5)   | 0.2094 (4)   | 0.8064 (5)   | 0.0389 (9)    |           |
| H13A | 0.518810     | 0.165131     | 0.783295     | 0.058*        |           |
| H13B | 0.676498     | 0.156995     | 0.870448     | 0.058*        |           |
| H13C | 0.625814     | 0.219443     | 0.729424     | 0.058*        |           |
| C14  | 0.5803 (6)   | 0.3216 (6)   | 0.9844 (5)   | 0.0501 (13)   |           |
| H14A | 0.494379     | 0.277179     | 0.966431     | 0.075*        |           |
|        | U\(^{11}\)  | U\(^{22}\)  | U\(^{33}\)  | U\(^{12}\)  | U\(^{13}\)  | U\(^{23}\)  |
|--------|------------|------------|------------|------------|------------|------------|
| Fe1    | 0.0096 (2) | 0.0296 (2) | 0.0306 (2) | 0.0003 (18)| 0.0004 (18)| 0.0005 (18)|
| I1     | 0.0058 (17)| 0.0075 (16)| 0.0083 (16)| 0.0002 (12)| 0.0003 (12)| 0.0003 (12)|
| N1     | 0.0076 (14)| 0.0089 (14)| 0.0094 (14)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C1     | 0.0088 (16)| 0.0096 (16)| 0.0105 (16)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C2     | 0.0069 (15)| 0.0080 (15)| 0.0089 (15)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C3     | 0.0078 (16)| 0.0091 (16)| 0.0101 (16)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C4     | 0.0097 (17)| 0.0109 (17)| 0.0119 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C5     | 0.0079 (17)| 0.0093 (17)| 0.0109 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C6     | 0.0094 (17)| 0.0107 (17)| 0.0118 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C7     | 0.0087 (17)| 0.0100 (17)| 0.0111 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C8     | 0.0079 (17)| 0.0092 (17)| 0.0103 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C9     | 0.0088 (17)| 0.0101 (17)| 0.0112 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C10    | 0.0097 (17)| 0.0110 (17)| 0.0121 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C11    | 0.0106 (17)| 0.0119 (17)| 0.0130 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C12    | 0.0097 (17)| 0.0110 (17)| 0.0121 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C13    | 0.0087 (17)| 0.0100 (17)| 0.0111 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C14    | 0.0079 (17)| 0.0092 (17)| 0.0103 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C21    | 0.0094 (17)| 0.0107 (17)| 0.0118 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C22    | 0.0087 (17)| 0.0100 (17)| 0.0111 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C23    | 0.0079 (17)| 0.0092 (17)| 0.0103 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
| C24    | 0.0068 (17)| 0.0081 (17)| 0.0092 (17)| 0.0001 (11)| 0.0002 (11)| 0.0002 (11)|
### Geometric parameters (Å, °)

| Bond/ Angle | Distance/° | Distance/° | Distance/° | Distance/° | Distance/° | Distance/° | Distance/° | Distance/° | Distance/° |
|-------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Fe1—C1      | 2.025 (3)  | 2.037 (4)  | 2.037 (4)  | 2.038 (5)  | 2.041 (5)  | 2.043 (3)  | 2.048 (4)  | 2.055 (4)  | 1.488 (6)  |
| Fe1—C6      | 2.030 (5)  | 2.034 (5)  | 2.034 (5)  | 2.038 (5)  | 2.041 (5)  | 2.043 (3)  | 2.048 (4)  | 2.055 (4)  | 1.489 (5)  |
| Fe1—C7      | 2.034 (5)  | 2.037 (4)  | 2.037 (4)  | 2.038 (5)  | 2.041 (5)  | 2.043 (3)  | 2.048 (4)  | 2.055 (4)  | 1.500 (6)  |
| Fe1—C8      | 2.037 (4)  | 2.034 (5)  | 2.034 (5)  | 2.038 (5)  | 2.041 (5)  | 2.043 (3)  | 2.048 (4)  | 2.055 (4)  | 1.529 (5)  |
| Fe1—C9      | 2.030 (5)  | 2.034 (5)  | 2.034 (5)  | 2.038 (5)  | 2.041 (5)  | 2.043 (3)  | 2.048 (4)  | 2.055 (4)  | 1.500 (6)  |
| Fe1—C10     | 2.025 (3)  | 2.037 (4)  | 2.037 (4)  | 2.038 (5)  | 2.041 (5)  | 2.043 (3)  | 2.048 (4)  | 2.055 (4)  | 1.488 (6)  |
| C1—C5       | 1.433 (7)  | 1.435 (5)  | 1.449 (5)  | 1.495 (5)  | 1.449 (5)  | 1.449 (5)  | 1.495 (5)  | 1.449 (5)  | 1.495 (5)  |
| C1—C11      | 1.433 (7)  | 1.435 (5)  | 1.449 (5)  | 1.495 (5)  | 1.449 (5)  | 1.449 (5)  | 1.495 (5)  | 1.449 (5)  | 1.495 (5)  |
| C2—C3       | 1.435 (5)  | 1.435 (5)  | 1.435 (5)  | 1.435 (5)  | 1.435 (5)  | 1.435 (5)  | 1.435 (5)  | 1.435 (5)  | 1.435 (5)  |
| C3—H3       | 0.9500     | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  |
| C3—H4       | 0.9500     | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  |
| C3—H5       | 0.9500     | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  |
| C5—H5       | 0.9500     | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  | 1.412 (6)  |
| C6—C10      | 1.400 (10) | 1.400 (10) | 1.400 (10) | 1.400 (10) | 1.400 (10) | 1.400 (10) | 1.400 (10) | 1.400 (10) | 1.400 (10) |
| C7—C8       | 1.406 (9)  | 1.406 (9)  | 1.406 (9)  | 1.406 (9)  | 1.406 (9)  | 1.406 (9)  | 1.406 (9)  | 1.406 (9)  | 1.406 (9)  |
| C8—H8       | 0.9500     | 1.418 (9)  | 1.418 (9)  | 1.418 (9)  | 1.418 (9)  | 1.418 (9)  | 1.418 (9)  | 1.418 (9)  | 1.418 (9)  |
| C9—C10      | 1.411 (9)  | 1.411 (9)  | 1.411 (9)  | 1.411 (9)  | 1.411 (9)  | 1.411 (9)  | 1.411 (9)  | 1.411 (9)  | 1.411 (9)  |
| C1—Fe1—C6   | 108.39 (19)| 108.39 (19)| 108.39 (19)| 108.39 (19)| 108.39 (19)| 108.39 (19)| 108.39 (19)| 108.39 (19)| 108.39 (19)|
| C1—Fe1—C7   | 119.30 (19)| 119.30 (19)| 119.30 (19)| 119.30 (19)| 119.30 (19)| 119.30 (19)| 119.30 (19)| 119.30 (19)| 119.30 (19)|
| C6—Fe1—C7   | 41.0 (3)   | 41.0 (3)   | 41.0 (3)   | 41.0 (3)   | 41.0 (3)   | 41.0 (3)   | 41.0 (3)   | 41.0 (3)   | 41.0 (3)   |
| C1—Fe1—C8   | 153.2 (2)  | 153.2 (2)  | 153.2 (2)  | 153.2 (2)  | 153.2 (2)  | 153.2 (2)  | 153.2 (2)  | 153.2 (2)  | 153.2 (2)  |
| C7—C6—Fe1   | 69.7 (3)   | 69.7 (3)   | 69.7 (3)   | 69.7 (3)   | 69.7 (3)   | 69.7 (3)   | 69.7 (3)   | 69.7 (3)   | 69.7 (3)   |
| C10—C6—H6   | 125.7      | 125.7      | 125.7      | 125.7      | 125.7      | 125.7      | 125.7      | 125.7      | 125.7      |
| C7—C6—H6    | 125.7      | 125.7      | 125.7      | 125.7      | 125.7      | 125.7      | 125.7      | 125.7      | 125.7      |

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| Bond          | Angle (°) | Bond          | Angle (°) |
|---------------|-----------|---------------|-----------|
| C6—Fe1—C8    | 68.1 (2)  | C8—C7—C6     | 107.3 (5) |
| C7—Fe1—C8    | 40.4 (2)  | C8—C7—Fe1    | 69.9 (3)  |
| C1—Fe1—C5    | 41.37 (15)| C6—C7—Fe1    | 69.3 (3)  |
| C6—Fe1—C5    | 126.6 (2) | C8—C7—H7     | 126.4     |
| C7—Fe1—C5    | 106.4 (2) | C6—C7—H7     | 126.4     |
| C8—Fe1—C5    | 117.9 (2) | Fe1—C7—H7    | 126.0     |
| C1—Fe1—C10   | 127.2 (2) | C7—C8—C9     | 108.2 (5) |
| C6—Fe1—C10   | 40.3 (3)  | C7—C8—Fe1    | 69.7 (3)  |
| C7—Fe1—C10   | 68.5 (3)  | C9—C8—Fe1    | 69.8 (3)  |
| C8—Fe1—C10   | 68.3 (2)  | C7—C8—H8     | 125.9     |
| C5—Fe1—C10   | 164.6 (2) | C9—C8—H8     | 125.9     |
| C1—Fe1—C9    | 164.8 (2) | Fe1—C8—H8    | 126.2     |
| C6—Fe1—C9    | 67.8 (3)  | C10—C9—C8    | 108.0 (5) |
| C7—Fe1—C9    | 68.3 (2)  | C10—C9—Fe1   | 69.7 (3)  |
| C8—Fe1—C9    | 40.7 (2)  | C8—C9—Fe1    | 69.5 (3)  |
| C5—Fe1—C9    | 152.8 (2) | C10—C9—H9    | 126.0     |
| C10—Fe1—C9   | 40.5 (3)  | C8—C9—H9     | 126.0     |
| C1—Fe1—C2    | 41.75 (14)| Fe1—C9—H9    | 126.4     |
| C6—Fe1—C2    | 120.6 (2) | C6—C10—C9    | 107.8 (5) |
| C7—Fe1—C2    | 155.2 (2) | C6—C10—Fe1   | 69.6 (3)  |
| C8—Fe1—C2    | 163.3 (2) | C9—C10—Fe1   | 69.9 (3)  |
| C5—Fe1—C2    | 69.89 (15)| C6—C10—H10   | 126.1     |
| C10—Fe1—C2   | 108.24 (19)| C9—C10—H10   | 126.1     |
| C9—Fe1—C2    | 126.2 (2) | Fe1—C10—H10  | 126.1     |
| C1—Fe1—C4    | 68.89 (16)| C1—C11—N1    | 114.3 (3) |
| C6—Fe1—C4    | 163.1 (3) | C1—C11—H11A  | 108.7     |
| C7—Fe1—C4    | 124.6 (2) | N1—C11—H11A  | 108.7     |
| C8—Fe1—C4    | 106.3 (2) | C1—C11—H11B  | 108.7     |
| C5—Fe1—C4    | 40.44 (18)| N1—C11—H11B  | 108.7     |
| C10—Fe1—C4   | 154.4 (3) | H11A—C11—H11B| 107.6     |
| C9—Fe1—C4    | 119.1 (2) | N1—C12—H12A  | 109.5     |
| C2—Fe1—C4    | 69.31 (16)| N1—C12—H12B  | 109.5     |
| C1—Fe1—C3    | 69.09 (15)| H12A—C12—H12B| 109.5     |
| C6—Fe1—C3    | 155.3 (2) | N1—C12—H12C  | 109.5     |
| C7—Fe1—C3    | 162.3 (2) | H12A—C12—H12C| 109.5     |
| C8—Fe1—C3    | 125.5 (2) | H12B—C12—H12C| 109.5     |
| C5—Fe1—C3    | 68.75 (18)| N1—C13—H13A  | 109.5     |
| C10—Fe1—C3   | 120.5 (2) | N1—C13—H13B  | 109.5     |
| C9—Fe1—C3    | 107.8 (2) | H13A—C13—H13B| 109.5     |
| C2—Fe1—C3    | 40.99 (14)| N1—C13—H13C  | 109.5     |
| C4—Fe1—C3    | 40.88 (19)| H13A—C13—H13C| 109.5     |
| C12—N1—C13   | 108.7 (4) | H13B—C13—H13C| 109.5     |
| C12—N1—C14   | 110.2 (4) | N1—C14—H14A  | 109.5     |
| C13—N1—C14   | 108.1 (4) | N1—C14—H14B  | 109.5     |
| C12—N1—C11   | 110.9 (3) | H14A—C14—H14B| 109.5     |
| C13—N1—C11   | 111.6 (3) | N1—C14—H14C  | 109.5     |
| C14—N1—C11   | 107.2 (3) | H14A—C14—H14C| 109.5     |
| C5—C1—C2     | 108.2 (3) | H14B—C14—H14C| 109.5     |
C5—C1—C11 124.2 (3) C26—C21—C22 118.3 (4)
C2—C1—C11 127.5 (3) C26—C21—C2 123.4 (3)
C5—C1—Fe1 69.8 (2) C22—C21—C2 118.3 (4)
C2—C1—Fe1 69.78 (19) C21—C22—C23 119.8 (4)
C11—C1—Fe1 123.7 (2) C21—C22—H22 120.1
C3—C2—C1 106.7 (3) C23—C22—C2 121.6 (5)
C3—C2—C21 125.2 (3) C21—C22—C23 119.2
C1—C2—C11 127.9 (3) C22—C23—C24 120.1
C3—C2—Fe1 70.0 (2) C22—C23—H23 120.1
C1—C2—Fe1 68.47 (19) C23—C24—C25 121.6 (5)
C21—C2—Fe1 129.6 (3) C23—C24—H24 120.5
C4—C3—C2 108.4 (4) C24—C23—C25 120.5
C4—C3—C21 125.2 (3) C24—C23—H23 120.5
C1—C2—Fe1 68.47 (19) C26—C25—C24 120.3 (4)
C4—C3—Fe1 69.0 (2) C26—C25—H25 119.9
C2—C3—Fe1 125.8 C26—C25—H25 119.9
C2—C3—H3 125.8 C24—C25—H25 119.9
Fe1—C3—H3 121.1 (4)
C5—C4—C3 108.6 (4) C21—C26—C25 121.1 (4)
C5—C4—Fe1 69.4 (2) C21—C26—H26 119.5
C1—C5—Fe1 68.9 (2) C26—C25—H25 119.9
C4—C5—C1 108.1 (4) C26—C25—H25 119.9
C4—C5—Fe1 70.2 (2) C26—C25—H25 119.9
C1—C5—Fe1 68.9 (2) C26—C25—H25 119.9
C4—C5—H5 126.0 C26—C25—H25 119.9
C1—C5—H5 126.0 C26—C25—H25 119.9
Fe1—C5—H5 126.5 C26—C25—H25 119.9
C10—C6—C7 108.7 (5) C26—C25—H25 119.9
C10—C6—Fe1 70.2 (3) C26—C25—H25 119.9
N1—C11—C1—C2 92.4 (4) N1—C11—C1—C5 −91.2 (4)

Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H | H···A | D···A | D—H···A |
|-----------|------|-------|-------|---------|
| C11—H11A···I1 | 0.99 | 3.17  | 3.988 (4) | 140 |
| C12—H12C···I1 | 0.98 | 3.21  | 4.117 (5) | 154 |
| C12—H12B···I2C | 0.98 | 3.51  | 3.787 (7) | 99  |
| C13—H13A···I1 | 0.98 | 3.27  | 4.158 (5) | 151 |
| C14—H14A···I1 | 0.98 | 3.14  | 4.057 (5) | 157 |
| C14—H14B···I1 | 0.98 | 3.25  | 4.077 (5) | 143 |
| C30A···H30A···II | 1.00 | 2.89  | 3.867 (7) | 166 |
| C13—H13B···CT2 | 0.98 | 2.98  | 3.901 (6) | 158 |
| C23—H23···CT1 | 0.95 | 2.69  | 3.600 (7) | 160 |

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