



# Crystal structure of bis[4-(1*H*-pyrrol-1-yl)phenyl]ferrocene-1,1'-dicarboxylate: a potential chemotherapeutic drug

Wanda I. Pérez,<sup>a</sup> Arnold L. Rheingold<sup>b</sup> and Enrique Meléndez<sup>a\*</sup>Received 2 April 2015  
Accepted 15 April 2015<sup>a</sup>University of Puerto Rico, Department of Chemistry, PO Box 9019, Mayaguez, Puerto Rico 00681, USA, and <sup>b</sup>University of California-San Diego, Department of Chemistry, Urey Hall 5128, 9500 Gilman Drive, La Jolla, CA 92093-0358, USA.  
\*Correspondence e-mail: enrique.melendez@upr.edu

Edited by R. F. Baggio, Comisión Nacional de Energía Atómica, Argentina

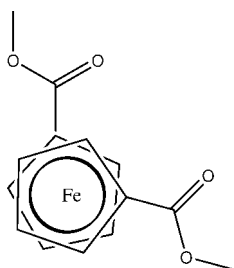
**Keywords:** crystal structure; disubstituted ferrocene; antiproliferative; chemotherapeutic drug; MCF-7; pyrrole**CCDC reference:** 1054149**Supporting information:** this article has supporting information at journals.iucr.org/e

The title iron(II) complex, [Fe(C<sub>16</sub>H<sub>12</sub>NO<sub>2</sub>)<sub>2</sub>], crystallizes in the orthorhombic space group *Pbca* with the Fe<sup>2+</sup> cation positioned on an inversion center. The cyclopentadienyl (Cp) rings adopt an *anti* conformation in contrast with other substituted ferrocenes in which the Cp rings appear in a nearly eclipsed conformation. The Cp and the aromatic rings are positioned out of the plane, with a twist angle of 70.20 (12)°, and the C(Cp)—C(CO) bond length is shorter than a typical C—C single bond, which suggests a partial double-bond character and delocalization with the Cp π system. The structure of the complex is compared to other functionalized ferrocenes synthesized in our laboratory.

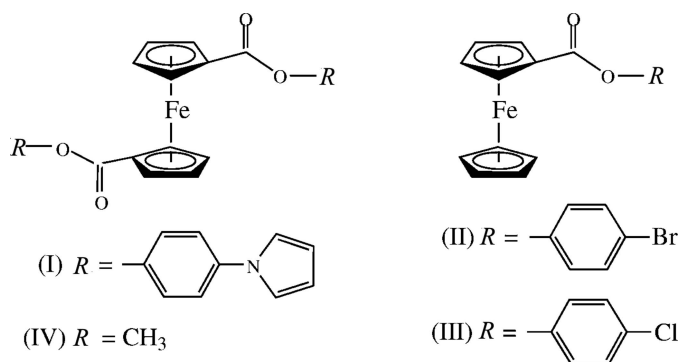
## 1. Chemical context

The gold standard of treatment for breast cancer has traditionally been cisplatin, a metal-based agent. Its administration, alone or in combination with other drugs, is also highly effective against various other types of cancers, including ovarian, head and neck, bladder, testicular and lung cancers (Galanski *et al.*, 2005; Sandler *et al.*, 2011). However, its clinical use suffers from major drawbacks, such as severe toxic side effects including neurotoxicity, hepatotoxicity, and nephrotoxicity (Pabla & Dong, 2008), as well as a drug-resistance phenomenon which leads to unsuccessful treatment (Dempke *et al.*, 2000). Consequently, other metal-based drugs have been investigated, among them ferrocenes (Köpf-Maier *et al.*, 1984). Ferrocene has the versatility of easy functionalization providing a fertile field for structural modification and to study structure–activity relationship (SAR).

Our group has been working in this field for many years, leading to exciting and biologically active ferrocenes. A wide variety of pendant (functional) groups have been attached or linked to the Cp ring to tailor the anti-proliferative properties of ferrocene, many of them with great success (Braga & Silva, 2013; Gasser *et al.*, 2011; Jaouen & Metzler-Nolte, 2010; Fouda *et al.*, 2007; Jaouen, 2006; van Staveren & Metzler-Nolte, 2004; Nguyen *et al.*, 2009; Top *et al.*, 2003; Vessières *et al.*, 2005, 2006; Meléndez, 2012; Vera *et al.*, 2011, 2014). Lately, a new range of organic chemotherapeutic compounds have been studied using pyrrole derivatives. These pyrrole derivatives have revealed good anti-proliferative activity and an increase in membrane permeability, allowing the compounds to reach the nucleus (Ghorab *et al.*, 2014; Abou El Ella *et al.*, 2008; Chatzopoulou *et al.*, 2014; Mohamed *et al.*, 2013; Hassan *et al.*, 2009; Esteves *et al.*, 2010; Clark *et al.*, 2007; Merighi *et al.*, 2003). Therefore, we functionalized ferrocene with a pyrrole, 4-(1*H*-



pyrrol-1-yl)phenol, obtaining three new ferrocenes: 1,1'-4-(1*H*-pyrrol-1-yl)phenyl ferrocenedicarboxylate, 1,4-(1*H*-pyrrol-1-yl)phenyl, 1'-carboxyl ferrocenedicarboxylate (Fc-(CO<sub>2</sub>-Ph-4-Py)CO<sub>2</sub>H) and 4-(1*H*-pyrrol-1-yl)phenyl ferroceneacetylacetyl (Fc-CH<sub>2</sub>CO<sub>2</sub>-Ph-4-Py). We investigated their biological activities on breast cancer cell line (MCF-7) and among these ferrocenes, 1,1'-4-(1*H*-pyrrol-1-yl)phenyl ferrocenedicarboxylate (I) was shown to be most active in this series (Pérez *et al.*, 2015). Nevertheless, the solid-state structure of (I) has been elusive (Pérez *et al.*, 2015). The importance of this complex is the incorporation of pyrrole groups, which are derivatives of biologically active compounds, as well as pyrrole being an electrochemically active group precursor of polymeric material. In addition, ferrocene anticancer activity has been associated with its redox behavior and the capability to produce reactive oxygen species (ROS) (Acevedo *et al.*, 2012; Kovjazin *et al.*, 2003; Tabbi *et al.*, 2002; Osella *et al.*, 2005). Thus, the attachment of an electrochemically active group on ferrocene could potentiate the production of ROS and enhance its anticancer activity.



Given that the solid-state structure of this complex is not available, we determined the crystal structure of bis[4-(1*H*-pyrrol-1-yl)phenyl] ferrocene-1,1'-dicarboxylate, (I). Additionally, we compared the obtained crystal structure with other functionalized ferrocenes synthesized in our laboratory *viz.*: 4-bromophenyl (II) and 4-chlorophenyl ferrocenedicarboxylate (III) (Vera *et al.*, 2014), and 1,1'-methyl ferrocenedicarboxylate (IV) (Gao *et al.*, 2009).

## 2. Structural commentary

The asymmetric unit contains one half-molecule since Fe<sup>2+</sup> lies on an inversion center, Fig. 1. This symmetry is implied by the NMR data where only one set of signals were found for H2/H5 and H3/H4 of the Cp rings, as well as the H2/H6 and H3/H5 of the phenyl and H2/H5 and H3/H4 of the pyrrole groups. Consequently, the Cp rings adopt a perfect *anti* conformation. The average Fe—C(Cp) bond length is 2.044 (10) Å, which is very similar to that reported for ferrocene (Dunitz *et al.*, 1956) and other structures previously reported by our lab (Vera *et al.*, 2014; Gao *et al.*, 2009). The Fe—C bond length of the substituted carbon [Fe—C1 2.032 (2) Å] is shorter than the remaining Fe—C bond lengths due to the inductive effect of

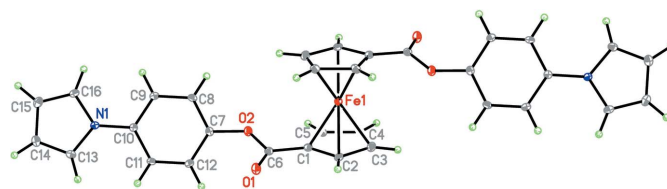


Figure 1

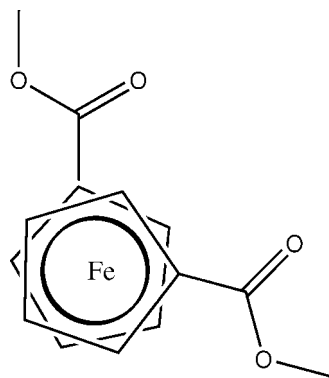
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. Unlabelled atoms are related to labelled ones by the symmetry operation  $-x, -y, -z$ .

the carboxylate on the Cp ring. The twist angles between the Cp ring and the carboxylate and the Cp ring and the aromatic ring are 14.4 (3)° (above the Cp plane) and 70.20 (12)°, respectively.

To put it in perspective, we compare (I) with previously synthesized ferrocenes in our group containing only one Cp functionalized and a phenyl group attached to the carboxylate, but with Br and Cl instead of pyrrole in the 4-position, (II) and (III) (CCDC 949002 and 949003, Vera *et al.*, 2014). First, in the 4-bromophenyl and 4-chlorophenyl derivatives, the Cp rings are positioned in a nearly eclipsed conformation and parallel with stagger angles < 3° and Cp tilt angles of 0.48–1.25°. In contrast, (I) has a perfect *anti* conformation. The carbonyl carbon of (I) has a distorted trigonal-planar geometry, analogous to the 4-chlorophenyl and 4-bromophenyl ferrocenedicarboxylates. The twist angles between the Cp ring and the carboxylate for 4-bromo and 4-chlorophenyl ferrocenedicarboxylates (6.75–10.15°) are smaller than that of the subject complex, 14.4 (3)°. Additionally, as mentioned previously, the carbonyl oxygen of (I) lies above the Cp plane whereas for the bromo and chloro derivatives, the carbonyl oxygens lie below the Cp plane. The twist angle between the Cp and the aromatic ring is 70.20 (12)° in (I), while in (II) and (III) the two rings are positioned at higher angles, approaching a perpendicular position.

The average Fe—C(Cp\*) bond lengths of the substituted Cp rings in the 4-bromo and 4-chlorophenyl derivatives are identical, within experimental error, as in (I) [2.044 (13) Å]. As mentioned before, the Fe—C bond length where the pendant group is attached is substantially shorter than the remaining Fe—C(Cp) distances. The same bonding pattern is also observed for the 4-bromo and 4-chlorophenyl ferrocenedicarboxylates. The C(Cp)—C(CO) bond length in (I), C1—C6, is shorter than a typical C—C single bond, [1.473 (3) versus 1.54 Å (single bond); Pauling, 1960]. This suggests partial double-bond character and delocalization with the Cp  $\pi$  system in analogous manner to that for the 4-bromo and 4-chloro derivatives.

In the structure of the disubstituted ferrocene Fe(C<sub>5</sub>H<sub>4</sub>-CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, (IV) (Gao *et al.*, 2009), the average Fe—C(Cp) bond lengths are 2.048 (11)/2.049 (14) Å, similar to the title complex but the Cp rings adopt almost an eclipsed conformation with a stagger angle of 2.37° (Fig. 2). In addition, the functional groups are not positioned perfectly *anti* to each other. The Fe—C(Cp)—C(CO) bond in (IV) [1.477 (4) Å] is notably shorter than a typical C—C single bond (1.54 Å), in a



**Figure 2**  
A Newman projection of  $\text{Fe}(\text{C}_5\text{H}_4\text{CO}_2\text{CH}_3)_2$ .

similar manner to the title complex, suggesting delocalization with the Cp  $\pi$  system.

Finally, (I) contains two  $\pi$  ring systems, 4-(1*H*-pyrrol-1-yl)phenyl, which in principle could be involved in intramolecular  $\pi$ - $\pi$  or C-H... $\pi$  stacking similar to other 1,1'-disubstituted ferrocenes with an extended  $\pi$  ring system (Okabe *et al.*, 2009; Togni *et al.*, 1994; Gelin & Thummel, 1992). However, such  $\pi$ - $\pi$  or C-H... $\pi$  stacking is not observed in (I) since the Cp rings adopt an *anti* conformation.

### 3. Synthesis and crystallization

The synthesis of (I) was accomplished by treating 1,1'-ferrocenedicarboxylic acid with oxalyl chloride according to our recently published procedure (Pérez *et al.*, 2015).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) ( $\delta$  p.p.m.): 7.37 (2H, *d*, ph;  $^3J = 8.8$  Hz), 7.25 (2H, *d*, py;  $^3J = 2.8$  Hz), 7.03 (2H, *dd*, ph;  $^3J = 1.3$  Hz), 6.34 (2H, *dd*, py;  $^3J = 1.6$  Hz), 5.08 (2H, overlapping doublets, AA', Cp), 4.64 (2H, overlapping doublets, BB', Cp).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) ( $\delta$  p.p.m.): 169.0 (C=O), 148.3, 138.6, 122.9, 121.5, 119.5, 110.5, 73.4, 72.4, 72.0. Analysis calculated for  $\text{C}_{32}\text{H}_{24}\text{O}_4\text{FeN}_2$ : C, 69.05; H, 4.40; found: C, 68.62; H, 4.46.

Crystallization of (I) was performed inside an NMR tube containing  $\text{CD}_2\text{Cl}_2$  for a period of two weeks, obtaining block-shaped orange crystals suitable for X-ray diffraction.

### 4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned in idealized locations ( $\text{C}_{(6)}-\text{H} = 0.95$ ,  $\text{C}_{(5)}-\text{H} = 1.00$  Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

### Acknowledgements

EM is thankful for the financial support of NIH-RISE 2 Best program (NIH-R25GM088023) for the research assistantship of WIP (graduate student).

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**Table 1**

Experimental details.

|  |  |
|--|--|
| Crystal data   |  |
| Chemical formula   | $[\text{Fe}(\text{C}_{16}\text{H}_{12}\text{NO}_2)_2]$ |
| $M_r$  | 556.38   |
| Crystal system, space group  | Orthorhombic, <i>Pbca</i>                              |
| Temperature (K)  | 100  |
| $a, b, c$ (Å)  | 10.6386 (15), 7.3948 (10),<br>30.554 (4)               |
| $V$ (Å <sup>3</sup> )  | 2403.7 (6)   |
| $Z$  | 4  |
| Radiation type   | Mo $K\alpha$   |
| $\mu$ (mm <sup>-1</sup> )  | 0.67   |
| Crystal size (mm)  | 0.28 × 0.26 × 0.23                                     |
| Data collection  |  |
| Diffractometer   | Bruker APEXII CCD                                      |
| Absorption correction  | Multi-scan ( <i>SADABS</i> ; Bruker, 2010)             |
| $T_{\text{min}}, T_{\text{max}}$   | 0.833, 0.877   |
| No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections | 12444, 2999, 2247                                      |
| $R_{\text{int}}$   | 0.077  |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )                    | 0.669  |
| Refinement   |  |
| $R[F^2 > 2\sigma(F^2)], wR(F^2), S$  | 0.044, 0.117, 1.02                                     |
| No. of reflections   | 2999   |
| No. of parameters  | 178  |
| H-atom treatment   | H-atom parameters constrained                          |
| $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )    | 0.34, -0.62  |

Computer programs: *APEX2* and *SAINT* (Bruker, 2010), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2013* (Sheldrick, 2015).

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## supporting information

*Acta Cryst.* (2015). E71, 536-539 [doi:10.1107/S2056989015007446]

## Crystal structure of bis[4-(1*H*-pyrrol-1-yl)phenyl] ferrocene-1,1'-dicarboxylate: a potential chemotherapeutic drug

Wanda I. Pérez, Arnold L. Rheingold and Enrique Meléndez

### Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINTE* (Bruker, 2010); data reduction: *SAINTE* (Bruker, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

### Bis[4-(1*H*-pyrrol-1-yl)phenyl] ferrocene-1,1'-dicarboxylate

#### Crystal data

[Fe(C<sub>16</sub>H<sub>12</sub>NO<sub>2</sub>)<sub>2</sub>]

*M<sub>r</sub>* = 556.38

Orthorhombic, *Pbca*

*a* = 10.6386 (15) Å

*b* = 7.3948 (10) Å

*c* = 30.554 (4) Å

*V* = 2403.7 (6) Å<sup>3</sup>

*Z* = 4

*F*(000) = 1152

*D<sub>x</sub>* = 1.537 Mg m<sup>-3</sup>

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 2807 reflections

θ = 2.7–28.1°

μ = 0.67 mm<sup>-1</sup>

*T* = 100 K

Block, orange

0.28 × 0.26 × 0.23 mm

#### Data collection

Bruker APEXII CCD  
diffractometer

φ and ω scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2010)

*T<sub>min</sub>* = 0.833, *T<sub>max</sub>* = 0.877

12444 measured reflections

2999 independent reflections

2247 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.077

θ<sub>max</sub> = 28.4°, θ<sub>min</sub> = 2.7°

*h* = -13→14

*k* = -9→9

*l* = -37→40

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.044

*wR*(*F*<sup>2</sup>) = 0.117

*S* = 1.01

2999 reflections

178 parameters

0 restraints

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.047*P*)<sup>2</sup> + 0.928*P*]  
where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.34 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.62 e Å<sup>-3</sup>

*Special details*

**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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

|      | <i>x</i>     | <i>y</i>   | <i>z</i>    | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|------------|-------------|----------------------------------|
| Fe1  | 0.5000       | 0.5000     | 0.5000      | 0.01323 (14)                     |
| O1   | 0.23108 (15) | 0.4748 (2) | 0.41347 (5) | 0.0213 (4)                       |
| O2   | 0.41465 (13) | 0.3430 (2) | 0.39352 (4) | 0.0173 (3)                       |
| N1   | 0.37269 (16) | 0.3889 (2) | 0.21120 (5) | 0.0133 (4)                       |
| C1   | 0.3680 (2)   | 0.3523 (3) | 0.46783 (7) | 0.0149 (4)                       |
| C2   | 0.3145 (2)   | 0.4294 (3) | 0.50667 (6) | 0.0169 (4)                       |
| H2A  | 0.2415       | 0.5142     | 0.5081      | 0.020*                           |
| C3   | 0.3857 (2)   | 0.3643 (3) | 0.54286 (7) | 0.0216 (5)                       |
| H3A  | 0.3716       | 0.3970     | 0.5742      | 0.026*                           |
| C4   | 0.4812 (2)   | 0.2469 (3) | 0.52692 (7) | 0.0191 (5)                       |
| H4A  | 0.5454       | 0.1827     | 0.5451      | 0.023*                           |
| C5   | 0.4712 (2)   | 0.2403 (3) | 0.48035 (7) | 0.0166 (4)                       |
| H5A  | 0.5262       | 0.1693     | 0.4601      | 0.020*                           |
| C6   | 0.3264 (2)   | 0.3975 (3) | 0.42318 (6) | 0.0144 (4)                       |
| C7   | 0.3923 (2)   | 0.3684 (3) | 0.34853 (6) | 0.0145 (4)                       |
| C8   | 0.48316 (19) | 0.4601 (3) | 0.32540 (7) | 0.0155 (4)                       |
| H8A  | 0.5502       | 0.5182     | 0.3404      | 0.019*                           |
| C9   | 0.47630 (19) | 0.4673 (3) | 0.27993 (7) | 0.0151 (4)                       |
| H9A  | 0.5398       | 0.5288     | 0.2639      | 0.018*                           |
| C10  | 0.37736 (19) | 0.3853 (2) | 0.25769 (6) | 0.0121 (4)                       |
| C11  | 0.28353 (19) | 0.2994 (3) | 0.28206 (7) | 0.0149 (4)                       |
| H11A | 0.2137       | 0.2469     | 0.2674      | 0.018*                           |
| C12  | 0.29095 (19) | 0.2899 (3) | 0.32731 (6) | 0.0154 (4)                       |
| H12A | 0.2272       | 0.2302     | 0.3436      | 0.018*                           |
| C13  | 0.2795 (2)   | 0.3154 (3) | 0.18518 (7) | 0.0174 (4)                       |
| H13A | 0.2077       | 0.2518     | 0.1954      | 0.021*                           |
| C14  | 0.3076 (2)   | 0.3494 (3) | 0.14240 (7) | 0.0195 (5)                       |
| H14A | 0.2587       | 0.3153     | 0.1177      | 0.023*                           |
| C15  | 0.4232 (2)   | 0.4449 (3) | 0.14143 (7) | 0.0213 (5)                       |
| H15A | 0.4661       | 0.4862     | 0.1161      | 0.026*                           |
| C16  | 0.4613 (2)   | 0.4663 (3) | 0.18374 (7) | 0.0184 (4)                       |
| H16A | 0.5364       | 0.5248     | 0.1929      | 0.022*                           |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$      | $U^{13}$      | $U^{23}$     |
|-----|------------|------------|------------|---------------|---------------|--------------|
| Fe1 | 0.0159 (2) | 0.0111 (2) | 0.0127 (2) | -0.00228 (16) | -0.00142 (16) | 0.00108 (15) |
| O1  | 0.0196 (9) | 0.0274 (8) | 0.0169 (8) | 0.0076 (7)    | -0.0004 (6)   | -0.0006 (6)  |
| O2  | 0.0162 (8) | 0.0220 (8) | 0.0137 (7) | 0.0029 (6)    | -0.0003 (6)   | -0.0013 (6)  |

|     |             |             |             |              |             |             |
|-----|-------------|-------------|-------------|--------------|-------------|-------------|
| N1  | 0.0123 (8)  | 0.0123 (8)  | 0.0154 (8)  | -0.0003 (7)  | 0.0015 (7)  | -0.0003 (6) |
| C1  | 0.0164 (10) | 0.0125 (9)  | 0.0160 (10) | -0.0039 (8)  | 0.0003 (8)  | -0.0003 (7) |
| C2  | 0.0161 (10) | 0.0168 (10) | 0.0179 (10) | -0.0040 (9)  | 0.0031 (8)  | 0.0006 (8)  |
| C3  | 0.0292 (12) | 0.0190 (11) | 0.0165 (11) | -0.0081 (10) | 0.0015 (9)  | 0.0016 (8)  |
| C4  | 0.0232 (12) | 0.0139 (10) | 0.0201 (11) | -0.0055 (9)  | -0.0051 (9) | 0.0046 (8)  |
| C5  | 0.0197 (11) | 0.0105 (9)  | 0.0197 (11) | -0.0009 (9)  | -0.0040 (9) | 0.0007 (8)  |
| C6  | 0.0149 (10) | 0.0121 (9)  | 0.0162 (10) | -0.0015 (8)  | 0.0004 (8)  | -0.0014 (7) |
| C7  | 0.0157 (10) | 0.0137 (9)  | 0.0142 (10) | 0.0024 (8)   | -0.0008 (8) | -0.0014 (7) |
| C8  | 0.0135 (10) | 0.0150 (10) | 0.0180 (10) | -0.0025 (8)  | -0.0008 (8) | -0.0027 (8) |
| C9  | 0.0127 (10) | 0.0135 (9)  | 0.0192 (10) | -0.0006 (8)  | 0.0023 (8)  | 0.0003 (8)  |
| C10 | 0.0127 (10) | 0.0085 (9)  | 0.0151 (10) | 0.0031 (8)   | 0.0003 (8)  | -0.0006 (7) |
| C11 | 0.0118 (10) | 0.0136 (9)  | 0.0193 (10) | -0.0027 (8)  | -0.0012 (8) | 0.0004 (8)  |
| C12 | 0.0150 (10) | 0.0138 (9)  | 0.0173 (10) | -0.0010 (8)  | 0.0023 (8)  | 0.0018 (8)  |
| C13 | 0.0139 (10) | 0.0163 (10) | 0.0219 (11) | -0.0002 (9)  | -0.0005 (8) | -0.0016 (8) |
| C14 | 0.0211 (11) | 0.0196 (11) | 0.0177 (10) | 0.0066 (9)   | -0.0016 (9) | -0.0022 (8) |
| C15 | 0.0250 (13) | 0.0211 (11) | 0.0179 (11) | 0.0031 (10)  | 0.0048 (9)  | 0.0015 (9)  |
| C16 | 0.0161 (10) | 0.0176 (10) | 0.0217 (11) | -0.0032 (9)  | 0.0035 (9)  | 0.0024 (8)  |

*Geometric parameters (Å, °)*

|                                      |            |            |            |
|--------------------------------------|------------|------------|------------|
| Fe1—C1                               | 2.032 (2)  | C3—H3A     | 1.0000     |
| Fe1—C1 <sup>i</sup>                  | 2.033 (2)  | C4—C5      | 1.428 (3)  |
| Fe1—C5                               | 2.035 (2)  | C4—H4A     | 1.0000     |
| Fe1—C5 <sup>i</sup>                  | 2.035 (2)  | C5—H5A     | 1.0000     |
| Fe1—C3 <sup>i</sup>                  | 2.050 (2)  | C7—C8      | 1.376 (3)  |
| Fe1—C3                               | 2.050 (2)  | C7—C12     | 1.386 (3)  |
| Fe1—C2                               | 2.051 (2)  | C8—C9      | 1.392 (3)  |
| Fe1—C2 <sup>i</sup>                  | 2.051 (2)  | C8—H8A     | 0.9500     |
| Fe1—C4 <sup>i</sup>                  | 2.055 (2)  | C9—C10     | 1.392 (3)  |
| Fe1—C4                               | 2.055 (2)  | C9—H9A     | 0.9500     |
| O1—C6                                | 1.201 (3)  | C10—C11    | 1.398 (3)  |
| O2—C6                                | 1.366 (2)  | C11—C12    | 1.387 (3)  |
| O2—C7                                | 1.407 (2)  | C11—H11A   | 0.9500     |
| N1—C13                               | 1.382 (3)  | C12—H12A   | 0.9500     |
| N1—C16                               | 1.386 (3)  | C13—C14    | 1.364 (3)  |
| N1—C10                               | 1.422 (3)  | C13—H13A   | 0.9500     |
| C1—C5                                | 1.427 (3)  | C14—C15    | 1.418 (3)  |
| C1—C2                                | 1.434 (3)  | C14—H14A   | 0.9500     |
| C1—C6                                | 1.473 (3)  | C15—C16    | 1.364 (3)  |
| C2—C3                                | 1.424 (3)  | C15—H15A   | 0.9500     |
| C2—H2A                               | 1.0000     | C16—H16A   | 0.9500     |
| C3—C4                                | 1.423 (3)  |            |            |
| C1—Fe1—C1 <sup>i</sup>               | 180.0      | C3—C2—Fe1  | 69.63 (13) |
| C1—Fe1—C5                            | 41.09 (8)  | C1—C2—Fe1  | 68.75 (12) |
| C1 <sup>i</sup> —Fe1—C5              | 138.91 (8) | C3—C2—H2A  | 126.3      |
| C1—Fe1—C5 <sup>i</sup>               | 138.91 (8) | C1—C2—H2A  | 126.3      |
| C1 <sup>i</sup> —Fe1—C5 <sup>i</sup> | 41.09 (8)  | Fe1—C2—H2A | 126.3      |

|                                      |             |              |             |
|--------------------------------------|-------------|--------------|-------------|
| C5—Fe1—C5 <sup>i</sup>               | 180.0       | C4—C3—C2     | 108.66 (19) |
| C1—Fe1—C3 <sup>i</sup>               | 111.35 (8)  | C4—C3—Fe1    | 69.90 (12)  |
| C1 <sup>i</sup> —Fe1—C3 <sup>i</sup> | 68.66 (8)   | C2—C3—Fe1    | 69.74 (12)  |
| C5—Fe1—C3 <sup>i</sup>               | 111.27 (9)  | C4—C3—H3A    | 125.7       |
| C5 <sup>i</sup> —Fe1—C3 <sup>i</sup> | 68.73 (9)   | C2—C3—H3A    | 125.7       |
| C1—Fe1—C3                            | 68.65 (8)   | Fe1—C3—H3A   | 125.7       |
| C1 <sup>i</sup> —Fe1—C3              | 111.34 (8)  | C3—C4—C5     | 107.97 (18) |
| C5—Fe1—C3                            | 68.73 (9)   | C3—C4—Fe1    | 69.54 (12)  |
| C5 <sup>i</sup> —Fe1—C3              | 111.27 (9)  | C5—C4—Fe1    | 68.84 (11)  |
| C3 <sup>i</sup> —Fe1—C3              | 180.0       | C3—C4—H4A    | 126.0       |
| C1—Fe1—C2                            | 41.11 (8)   | C5—C4—H4A    | 126.0       |
| C1 <sup>i</sup> —Fe1—C2              | 138.89 (8)  | Fe1—C4—H4A   | 126.0       |
| C5—Fe1—C2                            | 69.15 (9)   | C1—C5—C4     | 107.75 (18) |
| C5 <sup>i</sup> —Fe1—C2              | 110.85 (9)  | C1—C5—Fe1    | 69.36 (11)  |
| C3 <sup>i</sup> —Fe1—C2              | 139.37 (9)  | C4—C5—Fe1    | 70.30 (11)  |
| C3—Fe1—C2                            | 40.63 (9)   | C1—C5—H5A    | 126.1       |
| C1—Fe1—C2 <sup>i</sup>               | 138.89 (8)  | C4—C5—H5A    | 126.1       |
| C1 <sup>i</sup> —Fe1—C2 <sup>i</sup> | 41.11 (8)   | Fe1—C5—H5A   | 126.1       |
| C5—Fe1—C2 <sup>i</sup>               | 110.85 (9)  | O1—C6—O2     | 123.84 (18) |
| C5 <sup>i</sup> —Fe1—C2 <sup>i</sup> | 69.15 (9)   | O1—C6—C1     | 126.17 (19) |
| C3 <sup>i</sup> —Fe1—C2 <sup>i</sup> | 40.63 (9)   | O2—C6—C1     | 109.97 (18) |
| C3—Fe1—C2 <sup>i</sup>               | 139.37 (9)  | C8—C7—C12    | 120.85 (19) |
| C2—Fe1—C2 <sup>i</sup>               | 180.0       | C8—C7—O2     | 116.66 (18) |
| C1—Fe1—C4 <sup>i</sup>               | 111.29 (8)  | C12—C7—O2    | 122.16 (18) |
| C1 <sup>i</sup> —Fe1—C4 <sup>i</sup> | 68.71 (8)   | C7—C8—C9     | 119.63 (19) |
| C5—Fe1—C4 <sup>i</sup>               | 139.13 (9)  | C7—C8—H8A    | 120.2       |
| C5 <sup>i</sup> —Fe1—C4 <sup>i</sup> | 40.87 (9)   | C9—C8—H8A    | 120.2       |
| C3 <sup>i</sup> —Fe1—C4 <sup>i</sup> | 40.56 (9)   | C10—C9—C8    | 120.67 (19) |
| C3—Fe1—C4 <sup>i</sup>               | 139.44 (9)  | C10—C9—H9A   | 119.7       |
| C2—Fe1—C4 <sup>i</sup>               | 111.44 (9)  | C8—C9—H9A    | 119.7       |
| C2 <sup>i</sup> —Fe1—C4 <sup>i</sup> | 68.56 (9)   | C9—C10—C11   | 118.55 (18) |
| C1—Fe1—C4                            | 68.71 (8)   | C9—C10—N1    | 120.40 (18) |
| C1 <sup>i</sup> —Fe1—C4              | 111.29 (8)  | C11—C10—N1   | 121.05 (17) |
| C5—Fe1—C4                            | 40.87 (9)   | C12—C11—C10  | 120.90 (19) |
| C5 <sup>i</sup> —Fe1—C4              | 139.13 (9)  | C12—C11—H11A | 119.5       |
| C3 <sup>i</sup> —Fe1—C4              | 139.44 (9)  | C10—C11—H11A | 119.5       |
| C3—Fe1—C4                            | 40.56 (9)   | C7—C12—C11   | 119.31 (19) |
| C2—Fe1—C4                            | 68.56 (9)   | C7—C12—H12A  | 120.3       |
| C2 <sup>i</sup> —Fe1—C4              | 111.44 (9)  | C11—C12—H12A | 120.3       |
| C4 <sup>i</sup> —Fe1—C4              | 180.00 (11) | C14—C13—N1   | 108.78 (19) |
| C6—O2—C7                             | 119.52 (16) | C14—C13—H13A | 125.6       |
| C13—N1—C16                           | 107.58 (17) | N1—C13—H13A  | 125.6       |
| C13—N1—C10                           | 126.34 (17) | C13—C14—C15  | 107.54 (19) |
| C16—N1—C10                           | 126.08 (18) | C13—C14—H14A | 126.2       |
| C5—C1—C2                             | 108.28 (18) | C15—C14—H14A | 126.2       |
| C5—C1—C6                             | 127.65 (19) | C16—C15—C14  | 107.2 (2)   |
| C2—C1—C6                             | 123.89 (19) | C16—C15—H15A | 126.4       |
| C5—C1—Fe1                            | 69.56 (12)  | C14—C15—H15A | 126.4       |



|           |             |              |           |
|-----------|-------------|--------------|-----------|
| C2—C1—Fe1 | 70.14 (12)  | C15—C16—N1   | 108.9 (2) |
| C6—C1—Fe1 | 122.25 (14) | C15—C16—H16A | 125.6     |
| C3—C2—C1  | 107.3 (2)   | N1—C16—H16A  | 125.6     |

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Symmetry code: (i)  $-x+1, -y+1, -z+1$ .