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Isopropyl *N*-[1'-(methoxycarbonyl)ferrocenyl]carbamate–ethyl *N*-[1'-(methoxycarbonyl)ferrocenyl]carbamate (0.6/0.4)

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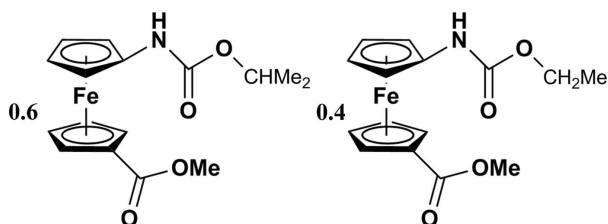
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 Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in main residue; R factor = 0.040; wR factor = 0.100; data-to-parameter ratio = 13.1.

Herein we report the crystal structure and synthesis of two cocrystallized complexes, $[\text{Fe}(\text{C}_7\text{H}_7\text{O}_2)(\text{C}_9\text{H}_{12}\text{NO}_2)]_{0.6}$ – $[\text{Fe}(\text{C}_7\text{H}_7\text{O}_2)(\text{C}_8\text{H}_{10}\text{NO}_2)]_{0.4}$. The molecules crystallize as layers in the bc plane with van der Waals interactions allowing the alkyl chains to interact and the ferrocene units to form a herringbone pattern up the c axis. Every second layer is linked via $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding. The two complexes were modelled as disordered in a ratio of 0.60:0.40.

Related literature

For background information, see: Barišić *et al.* (2002, 2006); Pavlović *et al.* (2003).



Experimental

Crystal data

$[\text{Fe}(\text{C}_7\text{H}_7\text{O}_2)(\text{C}_9\text{H}_{12}\text{NO}_2)]_{0.6}$
 $[\text{Fe}(\text{C}_7\text{H}_7\text{O}_2)(\text{C}_8\text{H}_{10}\text{NO}_2)]_{0.4}$
 $M_r = 339.56$
 Monoclinic, $P2_1/c$
 $a = 9.7494$ (19) Å
 $b = 15.624$ (3) Å
 $c = 9.860$ (2) Å
 $\beta = 100.82$ (3)°
 $V = 1475.2$ (5) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.04$ mm⁻¹
 $T = 150$ K
 $0.40 \times 0.22 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
 $T_{\min} = 0.740$, $T_{\max} = 0.906$
 14609 measured reflections
 3377 independent reflections
 2817 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.100$
 $S = 1.05$
 3377 reflections
 257 parameters
 391 restraints
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.44$ e Å⁻³
 $\Delta\rho_{\min} = -0.46$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N15A}-\text{H15A}\cdots\text{O7}^i$ | 0.88 | 1.93 | 2.793 (14) | 168 |
| $\text{N15B}-\text{H15B}\cdots\text{O7}^i$ | 0.88 | 2.21 | 2.962 (19) | 143 |

 Symmetry code: (i) $-x + 2, -y + 2, -z + 1$.

Data collection: COLLECT (Nonius, 2001); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL/PC (Sheldrick, 2008); software used to prepare material for publication: SHELXTL/PC.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KJ2117).

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supplementary materials

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Isopropyl *N*-[1'-(methoxycarbonyl)ferrocenyl]carbamate-ethyl
(methoxycarbonyl)ferrocenyl]carbamate (0.6/0.4)

N-[1'-

A. Lataifeh, H.-B. Kraatz and M. C. Jennings

Comment

Methoxy-2'-(tertbutyloxycarbonylamino)ferrocene-1-carboxylate [$\{\text{MeOC(O)Cp}\}\text{Fe}\{\text{CpN(H)C(O)OCMe}_3\}$] (where Cp = $\eta^5\text{-C}_5\text{H}_4$) has been used as a synthon in the preparation of ferrocene amino acid (Fca) peptide conjugates. This unnatural amino acid provides a convenient route to C- or N-terminal labelling of α -amino acids and peptides in both solution and solid phase (Barišić *et al.* 2006). The C-terminal conjugation of the natural amino acid and peptides to Fca requires the removal of the *tert*-butyloxy (t-Boc) group under acidic conditions. The resultant product $\{\text{MeOC(O)Cp}\}\text{Fe}\{\text{CpNH}_2\}$ is highly unstable, and usually coupled *in situ* to the active ester derivative of amino acids. In our attempts to trap and crystallize this species, the title compounds (1) and (2) were produced, which might give an insight into the decomposition pathways of the t-Boc group in acidic medium. It is believed that crystallization occurred during partial decomposition and two intermediates in the stepwise decomposition were isolated crystallographically.

There were two molecules co-crystallized in the asymmetric unit. The two molecules were crystallographically identical except for the side chain; one was -N(H)C(O)OCHMe_2 (60%) and the other was $\text{-N(H)C(O)OCH}_2\text{Me}$ (40%). The molecules revealed close contacts between the hydrogen atom attached to the nitrogen and the carbonyl atoms of the adjacent molecule. Essentially, dimers are formed *via* hydrogen bonding (Table 1).

Experimental

The ferrocene compound $\{\text{MeOC(O)Cp}\}\text{Fe}\{\text{CpN(H)C(O)OCMe}_3\}$ was prepared by standard procedures reported by Rapić and coworkers (Barišić *et al.*, 2002; Pavlović *et al.*, 2003). The synthesis of the ferrocene derivative $\{\text{MeOC(O)Cp}\}\text{Fe}\{\text{CpNH}_2\}$ requires the removal of the t-Boc group using trifluoroacetic acid (TFA) under argon. After several minutes, the reaction progress was quenched with a base (triethyl amine). Orange plates of the mixed crystal of the title compounds [$\{\text{MeOC(O)Cp}\}\text{Fe}\{\text{CpN(H)C(O)OCHMe}_2\}$] and [$\{\text{MeOC(O)Cp}\}\text{Fe}\{\text{CpN(H)C(O)OCH}_2\text{Me}\}$] were grown from a concentrated methylene chloride solution by slow diffusion of hexane.

Refinement

All H atoms were positioned geometrically and constrained as riding atoms with C—H = 1.00 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methyne H atoms and C—H = 0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene H atoms and C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and N—H = 0.88 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for amine H atoms. Soft proximity (SIMU) and rigid-bond restraints (DELU) were applied to the anisotropic displacement parameters.

Figures

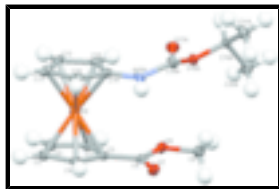


Fig. 1. The molecular structure of the title compound with 30% probability displacement ellipsoids and the atom labelling scheme.

Isopropyl *N*-[1'-(methoxycarbonyl)ferrocenyl]carbamate–ethyl *N*-[1'-(methoxycarbonyl)ferrocenyl]carbamate (0.6/0.4)

Crystal data

| | |
|--|---|
| $[\text{Fe}(\text{C}_7\text{H}_7\text{O}_2)(\text{C}_9\text{H}_{12}\text{NO}_2)]_{0.6}[\text{Fe}(\text{C}_7\text{H}_7\text{O}_2)(\text{C}_8\text{H}_{10}\text{NO}_2)]_{0.4}$ | $M_{\text{r}} = 707$ |
| $M_{\text{r}} = 339.56$ | $D_{\text{x}} = 1.529 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| Hall symbol: $-P\ 2_1/c$ | $\lambda = 0.71073 \text{ \AA}$ |
| $a = 9.7494 (19) \text{ \AA}$ | Cell parameters from 13419 reflections |
| $b = 15.624 (3) \text{ \AA}$ | $\theta = 2.0\text{--}27.5^\circ$ |
| $c = 9.860 (2) \text{ \AA}$ | $\mu = 1.04 \text{ mm}^{-1}$ |
| $\beta = 100.82 (3)^\circ$ | $T = 150 \text{ K}$ |
| $V = 1475.2 (5) \text{ \AA}^3$ | Plate, orange |
| $Z = 4$ | $0.40 \times 0.22 \times 0.10 \text{ mm}$ |

Data collection

| | |
|---|--|
| Nonius KappaCCD diffractometer | 3377 independent reflections |
| Radiation source: fine-focus sealed tube | 2817 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.063$ |
| $T = 150 \text{ K}$ | $\theta_{\text{max}} = 27.5^\circ$ |
| φ scans, and ω scans with κ offsets | $\theta_{\text{min}} = 2.6^\circ$ |
| Absorption correction: multi-scan from symmetry-related measurements (SORTAV; Blessing, 1995) | $h = -12 \rightarrow 12$ |
| $T_{\text{min}} = 0.740$, $T_{\text{max}} = 0.906$ | $k = -20 \rightarrow 20$ |
| 14609 measured reflections | $l = -12 \rightarrow 12$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.040$ | H-atom parameters constrained |
| $wR(F^2) = 0.100$ | $w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 1.0113P]$ |
| | where $P = (F_o^2 + 2F_c^2)/3$ |

$S = 1.05$ $(\Delta/\sigma)_{\max} = 0.002$
 3377 reflections $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
 257 parameters $\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$
 391 restraints Extinction correction: none
 Primary atom site location: structure-invariant direct methods

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.

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)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|--------------|---------------|--------------|----------------------------------|-----------|
| Fe | 0.78558 (3) | 1.126971 (18) | 0.20906 (3) | 0.02654 (11) | |
| C1 | 0.6804 (2) | 1.19504 (13) | 0.3330 (2) | 0.0321 (4) | |
| H1A | 0.5807 | 1.1867 | 0.3418 | 0.039* | |
| C2 | 0.7297 (3) | 1.25123 (14) | 0.2403 (2) | 0.0367 (5) | |
| H2A | 0.6705 | 1.2887 | 0.1706 | 0.044* | |
| C3 | 0.8778 (3) | 1.24367 (14) | 0.2608 (2) | 0.0372 (5) | |
| H3A | 0.9403 | 1.2750 | 0.2080 | 0.045* | |
| C4 | 0.9215 (2) | 1.18269 (14) | 0.3677 (2) | 0.0323 (4) | |
| H4A | 1.0197 | 1.1642 | 0.4040 | 0.039* | |
| C5 | 0.7997 (2) | 1.15270 (13) | 0.4133 (2) | 0.0281 (4) | |
| C6 | 0.7987 (2) | 1.08701 (13) | 0.5188 (2) | 0.0279 (4) | |
| O7 | 0.90170 (15) | 1.05702 (10) | 0.59097 (17) | 0.0360 (4) | |
| O8 | 0.66914 (15) | 1.06384 (10) | 0.53090 (16) | 0.0329 (3) | |
| C9 | 0.6609 (3) | 1.00237 (16) | 0.6387 (3) | 0.0401 (5) | |
| H9A | 0.7121 | 0.9504 | 0.6229 | 0.060* | |
| H9B | 0.5629 | 0.9880 | 0.6377 | 0.060* | |
| H9C | 0.7022 | 1.0270 | 0.7285 | 0.060* | |
| C10 | 0.8967 (2) | 1.03436 (15) | 0.1286 (2) | 0.0364 (5) | |
| H10A | 0.9987 | 1.0223 | 0.1575 | 0.044* | |
| C11 | 0.8348 (3) | 1.09292 (16) | 0.0240 (2) | 0.0390 (5) | |
| H11A | 0.8860 | 1.1292 | -0.0336 | 0.047* | |
| C12 | 0.6877 (2) | 1.09098 (15) | 0.0158 (2) | 0.0366 (5) | |
| H12A | 0.6178 | 1.1258 | -0.0484 | 0.044* | |
| C13 | 0.6566 (2) | 1.03129 (14) | 0.1156 (2) | 0.0326 (5) | |
| H13A | 0.5618 | 1.0167 | 0.1336 | 0.039* | |
| C14 | 0.7866 (2) | 0.99586 (13) | 0.1840 (2) | 0.0308 (4) | |

supplementary materials

| | | | | | |
|------|-------------|--------------|-------------|-------------|------|
| N15A | 0.8170 (15) | 0.9348 (8) | 0.2832 (15) | 0.0298 (18) | 0.60 |
| H15A | 0.9036 | 0.9299 | 0.3281 | 0.036* | 0.60 |
| C16A | 0.7063 (14) | 0.8747 (8) | 0.3191 (11) | 0.034 (2) | 0.60 |
| O17A | 0.5884 (19) | 0.8780 (12) | 0.2670 (11) | 0.039 (2) | 0.60 |
| O18A | 0.7847 (3) | 0.80918 (19) | 0.3703 (3) | 0.0288 (6) | 0.60 |
| C19A | 0.6961 (4) | 0.7395 (3) | 0.4008 (5) | 0.0297 (8) | 0.60 |
| H19A | 0.6203 | 0.7287 | 0.3191 | 0.036* | 0.60 |
| C20A | 0.6332 (6) | 0.7639 (4) | 0.5229 (6) | 0.0466 (13) | 0.60 |
| H20A | 0.7078 | 0.7762 | 0.6019 | 0.070* | 0.60 |
| H20B | 0.5759 | 0.7166 | 0.5462 | 0.070* | 0.60 |
| H20C | 0.5747 | 0.8149 | 0.5005 | 0.070* | 0.60 |
| C21A | 0.7913 (5) | 0.6619 (3) | 0.4267 (7) | 0.0431 (12) | 0.60 |
| H21A | 0.8368 | 0.6530 | 0.3473 | 0.065* | 0.60 |
| H21B | 0.7360 | 0.6113 | 0.4398 | 0.065* | 0.60 |
| H21C | 0.8624 | 0.6715 | 0.5098 | 0.065* | 0.60 |
| N15B | 0.797 (2) | 0.9282 (13) | 0.289 (2) | 0.032 (3) | 0.40 |
| H15B | 0.8683 | 0.9303 | 0.3582 | 0.038* | 0.40 |
| C16B | 0.7224 (19) | 0.8744 (13) | 0.2867 (15) | 0.024 (2) | 0.40 |
| O17B | 0.595 (3) | 0.8684 (18) | 0.2333 (18) | 0.039 (3) | 0.40 |
| O18B | 0.7611 (6) | 0.8251 (3) | 0.4349 (6) | 0.0426 (12) | 0.40 |
| C19B | 0.6752 (9) | 0.7564 (6) | 0.4736 (12) | 0.052 (2) | 0.40 |
| H19B | 0.5754 | 0.7688 | 0.4374 | 0.062* | 0.40 |
| H19C | 0.6887 | 0.7526 | 0.5755 | 0.062* | 0.40 |
| C20B | 0.7132 (13) | 0.6753 (6) | 0.4178 (12) | 0.078 (3) | 0.40 |
| H20D | 0.6956 | 0.6784 | 0.3167 | 0.117* | 0.40 |
| H20E | 0.6570 | 0.6292 | 0.4469 | 0.117* | 0.40 |
| H20F | 0.8124 | 0.6638 | 0.4522 | 0.117* | 0.40 |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|--------------|--------------|--------------|--------------|---------------|---------------|
| Fe | 0.02407 (16) | 0.03112 (17) | 0.02215 (17) | 0.00247 (11) | -0.00153 (11) | -0.00056 (11) |
| C1 | 0.0310 (10) | 0.0354 (11) | 0.0288 (11) | 0.0068 (8) | 0.0026 (9) | -0.0032 (8) |
| C2 | 0.0463 (13) | 0.0294 (10) | 0.0315 (12) | 0.0075 (9) | -0.0005 (10) | -0.0002 (9) |
| C3 | 0.0430 (12) | 0.0326 (11) | 0.0338 (12) | -0.0065 (9) | 0.0012 (10) | 0.0016 (9) |
| C4 | 0.0280 (10) | 0.0373 (11) | 0.0286 (11) | -0.0048 (8) | -0.0024 (8) | -0.0038 (9) |
| C5 | 0.0295 (10) | 0.0305 (9) | 0.0222 (10) | 0.0007 (8) | -0.0008 (8) | -0.0044 (8) |
| C6 | 0.0258 (10) | 0.0331 (10) | 0.0229 (10) | 0.0007 (8) | -0.0004 (8) | -0.0056 (8) |
| O7 | 0.0279 (8) | 0.0424 (9) | 0.0335 (9) | 0.0016 (6) | -0.0052 (6) | 0.0066 (7) |
| O8 | 0.0255 (7) | 0.0429 (8) | 0.0287 (8) | -0.0008 (6) | 0.0008 (6) | 0.0046 (6) |
| C9 | 0.0379 (12) | 0.0491 (13) | 0.0325 (12) | -0.0051 (10) | 0.0045 (10) | 0.0053 (10) |
| C10 | 0.0332 (11) | 0.0426 (12) | 0.0324 (12) | 0.0082 (9) | 0.0042 (9) | -0.0071 (9) |
| C11 | 0.0418 (13) | 0.0499 (13) | 0.0255 (11) | 0.0050 (10) | 0.0066 (9) | -0.0041 (9) |
| C12 | 0.0390 (12) | 0.0428 (12) | 0.0228 (10) | 0.0048 (9) | -0.0074 (9) | -0.0022 (9) |
| C13 | 0.0283 (10) | 0.0349 (11) | 0.0298 (11) | 0.0012 (8) | -0.0072 (8) | -0.0048 (9) |
| C14 | 0.0284 (10) | 0.0302 (10) | 0.0291 (11) | 0.0031 (8) | -0.0068 (9) | -0.0061 (8) |
| N15A | 0.022 (4) | 0.027 (2) | 0.036 (3) | -0.010 (2) | -0.005 (3) | -0.003 (2) |
| C16A | 0.033 (4) | 0.027 (2) | 0.040 (6) | -0.004 (2) | -0.004 (3) | 0.003 (3) |

| | | | | | | |
|------|-------------|-------------|-------------|--------------|--------------|-------------|
| O17A | 0.027 (2) | 0.045 (4) | 0.040 (5) | -0.002 (2) | -0.011 (4) | 0.000 (4) |
| O18A | 0.0233 (13) | 0.0283 (14) | 0.0325 (17) | -0.0025 (10) | -0.0009 (13) | 0.0076 (13) |
| C19A | 0.032 (2) | 0.028 (2) | 0.027 (2) | -0.0064 (14) | 0.0018 (17) | 0.0043 (16) |
| C20A | 0.044 (3) | 0.056 (3) | 0.044 (3) | -0.010 (2) | 0.021 (2) | 0.000 (2) |
| C21A | 0.040 (2) | 0.031 (2) | 0.055 (3) | 0.0009 (19) | 0.000 (2) | 0.0122 (19) |
| N15B | 0.013 (5) | 0.030 (5) | 0.047 (5) | 0.004 (3) | -0.012 (3) | 0.008 (4) |
| C16B | 0.017 (4) | 0.037 (4) | 0.017 (5) | 0.002 (3) | 0.001 (3) | 0.006 (3) |
| O17B | 0.031 (4) | 0.048 (6) | 0.032 (7) | -0.006 (3) | -0.008 (5) | -0.002 (5) |
| O18B | 0.038 (3) | 0.038 (3) | 0.045 (3) | -0.007 (2) | -0.009 (2) | 0.014 (2) |
| C19B | 0.045 (5) | 0.054 (5) | 0.057 (7) | -0.010 (4) | 0.012 (4) | 0.023 (4) |
| C20B | 0.115 (9) | 0.047 (5) | 0.069 (6) | -0.020 (6) | 0.011 (7) | 0.004 (4) |

Geometric parameters (Å, °)

| | | | |
|-----------|-------------|-----------|-------------|
| Fe—C5 | 2.033 (2) | C12—C13 | 1.429 (3) |
| Fe—C1 | 2.037 (2) | C12—H12A | 1.0000 |
| Fe—C11 | 2.042 (2) | C13—C14 | 1.431 (3) |
| Fe—C12 | 2.043 (2) | C13—H13A | 1.0000 |
| Fe—C4 | 2.045 (2) | C14—N15A | 1.358 (13) |
| Fe—C10 | 2.054 (2) | C14—N15B | 1.467 (18) |
| Fe—C3 | 2.055 (2) | N15A—C16A | 1.522 (17) |
| Fe—C2 | 2.055 (2) | N15A—H15A | 0.8800 |
| Fe—C13 | 2.057 (2) | C16A—O17A | 1.17 (2) |
| Fe—C14 | 2.064 (2) | C16A—O18A | 1.320 (14) |
| C1—C2 | 1.415 (3) | O18A—C19A | 1.455 (5) |
| C1—C5 | 1.439 (3) | C19A—C20A | 1.500 (6) |
| C1—H1A | 1.0000 | C19A—C21A | 1.518 (6) |
| C2—C3 | 1.425 (3) | C19A—H19A | 1.0000 |
| C2—H2A | 1.0000 | C20A—H20A | 0.9800 |
| C3—C4 | 1.425 (3) | C20A—H20B | 0.9800 |
| C3—H3A | 1.0000 | C20A—H20C | 0.9800 |
| C4—C5 | 1.426 (3) | C21A—H21A | 0.9800 |
| C4—H4A | 1.0000 | C21A—H21B | 0.9800 |
| C5—C6 | 1.463 (3) | C21A—H21C | 0.9800 |
| C6—O7 | 1.211 (2) | N15B—C16B | 1.11 (3) |
| C6—O8 | 1.340 (2) | N15B—H15B | 0.8800 |
| O8—C9 | 1.446 (3) | C16B—O17B | 1.26 (3) |
| C9—H9A | 0.9800 | C16B—O18B | 1.632 (16) |
| C9—H9B | 0.9800 | O18B—C19B | 1.455 (9) |
| C9—H9C | 0.9800 | C19B—C20B | 1.457 (15) |
| C10—C11 | 1.425 (3) | C19B—H19B | 0.9900 |
| C10—C14 | 1.425 (3) | C19B—H19C | 0.9900 |
| C10—H10A | 1.0000 | C20B—H20D | 0.9800 |
| C11—C12 | 1.421 (3) | C20B—H20E | 0.9800 |
| C11—H11A | 1.0000 | C20B—H20F | 0.9800 |
| C5—Fe—C1 | 41.42 (8) | O7—C6—O8 | 122.3 (2) |
| C5—Fe—C11 | 162.38 (9) | O7—C6—C5 | 125.03 (19) |
| C1—Fe—C11 | 154.35 (9) | O8—C6—C5 | 112.62 (17) |
| C5—Fe—C12 | 155.67 (10) | C6—O8—C9 | 115.33 (17) |

supplementary materials

| | | | |
|------------|-------------|----------------|------------|
| C1—Fe—C12 | 120.25 (9) | O8—C9—H9A | 109.5 |
| C11—Fe—C12 | 40.72 (10) | O8—C9—H9B | 109.5 |
| C5—Fe—C4 | 40.93 (9) | H9A—C9—H9B | 109.5 |
| C1—Fe—C4 | 69.25 (9) | O8—C9—H9C | 109.5 |
| C11—Fe—C4 | 124.55 (10) | H9A—C9—H9C | 109.5 |
| C12—Fe—C4 | 162.28 (10) | H9B—C9—H9C | 109.5 |
| C5—Fe—C10 | 125.42 (9) | C11—C10—C14 | 107.5 (2) |
| C1—Fe—C10 | 163.99 (9) | C11—C10—Fe | 69.20 (13) |
| C11—Fe—C10 | 40.71 (9) | C14—C10—Fe | 70.10 (12) |
| C12—Fe—C10 | 68.51 (9) | C11—C10—H10A | 126.2 |
| C4—Fe—C10 | 106.41 (9) | C14—C10—H10A | 126.2 |
| C5—Fe—C3 | 68.50 (9) | Fe—C10—H10A | 126.2 |
| C1—Fe—C3 | 68.52 (10) | C12—C11—C10 | 108.2 (2) |
| C11—Fe—C3 | 106.72 (10) | C12—C11—Fe | 69.68 (13) |
| C12—Fe—C3 | 125.58 (10) | C10—C11—Fe | 70.09 (13) |
| C4—Fe—C3 | 40.69 (9) | C12—C11—H11A | 125.9 |
| C10—Fe—C3 | 118.89 (10) | C10—C11—H11A | 125.9 |
| C5—Fe—C2 | 68.59 (9) | Fe—C11—H11A | 125.9 |
| C1—Fe—C2 | 40.46 (9) | C11—C12—C13 | 108.5 (2) |
| C11—Fe—C2 | 119.57 (10) | C11—C12—Fe | 69.60 (13) |
| C12—Fe—C2 | 108.02 (9) | C13—C12—Fe | 70.12 (12) |
| C4—Fe—C2 | 68.59 (9) | C11—C12—H12A | 125.8 |
| C10—Fe—C2 | 153.80 (10) | C13—C12—H12A | 125.8 |
| C3—Fe—C2 | 40.57 (9) | Fe—C12—H12A | 125.8 |
| C5—Fe—C13 | 120.63 (9) | C12—C13—C14 | 107.0 (2) |
| C1—Fe—C13 | 108.29 (9) | C12—C13—Fe | 69.08 (12) |
| C11—Fe—C13 | 68.71 (10) | C14—C13—Fe | 69.93 (12) |
| C12—Fe—C13 | 40.80 (9) | C12—C13—H13A | 126.5 |
| C4—Fe—C13 | 154.95 (9) | C14—C13—H13A | 126.5 |
| C10—Fe—C13 | 68.74 (9) | Fe—C13—H13A | 126.5 |
| C3—Fe—C13 | 163.45 (9) | N15A—C14—C10 | 119.6 (6) |
| C2—Fe—C13 | 126.64 (9) | N15A—C14—C13 | 131.7 (6) |
| C5—Fe—C14 | 108.30 (9) | C10—C14—C13 | 108.7 (2) |
| C1—Fe—C14 | 127.19 (9) | C10—C14—N15B | 128.0 (8) |
| C11—Fe—C14 | 68.11 (10) | C13—C14—N15B | 123.3 (8) |
| C12—Fe—C14 | 68.11 (9) | N15A—C14—Fe | 128.0 (6) |
| C4—Fe—C14 | 119.81 (9) | C10—C14—Fe | 69.39 (12) |
| C10—Fe—C14 | 40.51 (9) | C13—C14—Fe | 69.43 (12) |
| C3—Fe—C14 | 154.02 (9) | N15B—C14—Fe | 129.3 (10) |
| C2—Fe—C14 | 164.38 (9) | C14—N15A—C16A | 122.2 (11) |
| C13—Fe—C14 | 40.65 (8) | C14—N15A—H15A | 118.9 |
| C2—C1—C5 | 107.62 (19) | C16A—N15A—H15A | 118.9 |
| C2—C1—Fe | 70.47 (13) | O17A—C16A—O18A | 130.7 (14) |
| C5—C1—Fe | 69.14 (12) | O17A—C16A—N15A | 123.6 (14) |
| C2—C1—H1A | 126.2 | O18A—C16A—N15A | 100.6 (10) |
| C5—C1—H1A | 126.2 | C16A—O18A—C19A | 109.7 (6) |
| Fe—C1—H1A | 126.2 | O18A—C19A—C20A | 108.9 (4) |
| C1—C2—C3 | 108.39 (19) | O18A—C19A—C21A | 105.3 (4) |
| C1—C2—Fe | 69.07 (12) | C20A—C19A—C21A | 113.4 (4) |

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|--------------|--------------|-----------------|--------------|
| C3—C2—Fe | 69.68 (12) | O18A—C19A—H19A | 109.7 |
| C1—C2—H2A | 125.8 | C20A—C19A—H19A | 109.7 |
| C3—C2—H2A | 125.8 | C21A—C19A—H19A | 109.7 |
| Fe—C2—H2A | 125.8 | C16B—N15B—C14 | 125.1 (19) |
| C2—C3—C4 | 108.3 (2) | C16B—N15B—H15B | 117.5 |
| C2—C3—Fe | 69.74 (12) | C14—N15B—H15B | 117.5 |
| C4—C3—Fe | 69.29 (12) | N15B—C16B—O17B | 131 (2) |
| C2—C3—H3A | 125.8 | N15B—C16B—O18B | 107.6 (17) |
| C4—C3—H3A | 125.8 | O17B—C16B—O18B | 112.6 (15) |
| Fe—C3—H3A | 125.8 | C19B—O18B—C16B | 122.3 (9) |
| C3—C4—C5 | 107.58 (19) | O18B—C19B—C20B | 110.0 (9) |
| C3—C4—Fe | 70.02 (13) | O18B—C19B—H19B | 109.7 |
| C5—C4—Fe | 69.08 (12) | C20B—C19B—H19B | 109.7 |
| C3—C4—H4A | 126.2 | O18B—C19B—H19C | 109.7 |
| C5—C4—H4A | 126.2 | C20B—C19B—H19C | 109.7 |
| Fe—C4—H4A | 126.2 | H19B—C19B—H19C | 108.2 |
| C4—C5—C1 | 108.09 (19) | C19B—C20B—H20D | 109.5 |
| C4—C5—C6 | 124.89 (19) | C19B—C20B—H20E | 109.5 |
| C1—C5—C6 | 126.95 (19) | H20D—C20B—H20E | 109.5 |
| C4—C5—Fe | 69.99 (12) | C19B—C20B—H20F | 109.5 |
| C1—C5—Fe | 69.44 (12) | H20D—C20B—H20F | 109.5 |
| C6—C5—Fe | 123.90 (14) | H20E—C20B—H20F | 109.5 |
| C5—Fe—C1—C2 | 118.61 (18) | C4—Fe—C10—C14 | 116.94 (13) |
| C11—Fe—C1—C2 | -46.8 (3) | C3—Fe—C10—C14 | 159.18 (12) |
| C12—Fe—C1—C2 | -82.43 (16) | C2—Fe—C10—C14 | -168.33 (18) |
| C4—Fe—C1—C2 | 80.95 (14) | C13—Fe—C10—C14 | -37.06 (13) |
| C10—Fe—C1—C2 | 157.9 (3) | C14—C10—C11—C12 | 0.4 (3) |
| C3—Fe—C1—C2 | 37.20 (13) | Fe—C10—C11—C12 | -59.44 (16) |
| C13—Fe—C1—C2 | -125.52 (14) | C14—C10—C11—Fe | 59.87 (15) |
| C14—Fe—C1—C2 | -166.73 (13) | C5—Fe—C11—C12 | 163.0 (3) |
| C11—Fe—C1—C5 | -165.4 (2) | C1—Fe—C11—C12 | -50.5 (3) |
| C12—Fe—C1—C5 | 158.97 (13) | C4—Fe—C11—C12 | -166.63 (13) |
| C4—Fe—C1—C5 | -37.65 (12) | C10—Fe—C11—C12 | 119.3 (2) |
| C10—Fe—C1—C5 | 39.3 (4) | C3—Fe—C11—C12 | -125.60 (15) |
| C3—Fe—C1—C5 | -81.41 (14) | C2—Fe—C11—C12 | -83.45 (16) |
| C2—Fe—C1—C5 | -118.61 (18) | C13—Fe—C11—C12 | 37.56 (13) |
| C13—Fe—C1—C5 | 115.87 (13) | C14—Fe—C11—C12 | 81.42 (15) |
| C14—Fe—C1—C5 | 74.67 (15) | C5—Fe—C11—C10 | 43.7 (4) |
| C5—C1—C2—C3 | 0.7 (2) | C1—Fe—C11—C10 | -169.82 (19) |
| Fe—C1—C2—C3 | -58.74 (16) | C12—Fe—C11—C10 | -119.3 (2) |
| C5—C1—C2—Fe | 59.40 (14) | C4—Fe—C11—C10 | 74.08 (17) |
| C5—Fe—C2—C1 | -38.60 (13) | C3—Fe—C11—C10 | 115.10 (15) |
| C11—Fe—C2—C1 | 158.74 (13) | C2—Fe—C11—C10 | 157.25 (14) |
| C12—Fe—C2—C1 | 115.77 (14) | C13—Fe—C11—C10 | -81.73 (15) |
| C4—Fe—C2—C1 | -82.72 (14) | C14—Fe—C11—C10 | -37.87 (14) |
| C10—Fe—C2—C1 | -166.43 (19) | C10—C11—C12—C13 | 0.2 (3) |
| C3—Fe—C2—C1 | -120.12 (19) | Fe—C11—C12—C13 | -59.54 (16) |
| C13—Fe—C2—C1 | 74.38 (16) | C10—C11—C12—Fe | 59.71 (16) |
| C14—Fe—C2—C1 | 42.8 (4) | C5—Fe—C12—C11 | -167.56 (19) |

supplementary materials

| | | | |
|--------------|--------------|------------------|--------------|
| C5—Fe—C2—C3 | 81.52 (14) | C1—Fe—C12—C11 | 157.25 (14) |
| C1—Fe—C2—C3 | 120.12 (19) | C4—Fe—C12—C11 | 38.7 (4) |
| C11—Fe—C2—C3 | -81.14 (16) | C10—Fe—C12—C11 | -37.68 (14) |
| C12—Fe—C2—C3 | -124.11 (14) | C3—Fe—C12—C11 | 73.22 (17) |
| C4—Fe—C2—C3 | 37.40 (14) | C2—Fe—C12—C11 | 114.68 (15) |
| C10—Fe—C2—C3 | -46.3 (3) | C13—Fe—C12—C11 | -119.62 (19) |
| C13—Fe—C2—C3 | -165.50 (14) | C14—Fe—C12—C11 | -81.43 (15) |
| C14—Fe—C2—C3 | 162.9 (3) | C5—Fe—C12—C13 | -47.9 (3) |
| C1—C2—C3—C4 | -0.4 (3) | C1—Fe—C12—C13 | -83.13 (15) |
| Fe—C2—C3—C4 | -58.72 (15) | C11—Fe—C12—C13 | 119.62 (19) |
| C1—C2—C3—Fe | 58.36 (15) | C4—Fe—C12—C13 | 158.4 (3) |
| C5—Fe—C3—C2 | -81.77 (15) | C10—Fe—C12—C13 | 81.94 (14) |
| C1—Fe—C3—C2 | -37.10 (14) | C3—Fe—C12—C13 | -167.16 (13) |
| C11—Fe—C3—C2 | 116.20 (15) | C2—Fe—C12—C13 | -125.70 (14) |
| C12—Fe—C3—C2 | 75.49 (17) | C14—Fe—C12—C13 | 38.19 (13) |
| C4—Fe—C3—C2 | -119.8 (2) | C11—C12—C13—C14 | -0.7 (2) |
| C10—Fe—C3—C2 | 158.62 (14) | Fe—C12—C13—C14 | -59.91 (15) |
| C13—Fe—C3—C2 | 44.9 (4) | C11—C12—C13—Fe | 59.22 (16) |
| C14—Fe—C3—C2 | -169.58 (19) | C5—Fe—C13—C12 | 159.17 (13) |
| C5—Fe—C3—C4 | 38.06 (13) | C1—Fe—C13—C12 | 115.40 (14) |
| C1—Fe—C3—C4 | 82.74 (14) | C11—Fe—C13—C12 | -37.49 (14) |
| C11—Fe—C3—C4 | -123.97 (14) | C4—Fe—C13—C12 | -164.6 (2) |
| C12—Fe—C3—C4 | -164.67 (13) | C10—Fe—C13—C12 | -81.33 (15) |
| C10—Fe—C3—C4 | -81.55 (16) | C3—Fe—C13—C12 | 39.4 (4) |
| C2—Fe—C3—C4 | 119.8 (2) | C2—Fe—C13—C12 | 74.24 (17) |
| C13—Fe—C3—C4 | 164.7 (3) | C14—Fe—C13—C12 | -118.27 (19) |
| C14—Fe—C3—C4 | -49.7 (3) | C5—Fe—C13—C14 | -82.56 (15) |
| C2—C3—C4—C5 | -0.1 (2) | C1—Fe—C13—C14 | -126.33 (14) |
| Fe—C3—C4—C5 | -59.08 (14) | C11—Fe—C13—C14 | 80.78 (15) |
| C2—C3—C4—Fe | 59.00 (15) | C12—Fe—C13—C14 | 118.27 (19) |
| C5—Fe—C4—C3 | -118.89 (19) | C4—Fe—C13—C14 | -46.4 (3) |
| C1—Fe—C4—C3 | -80.80 (15) | C10—Fe—C13—C14 | 36.94 (14) |
| C11—Fe—C4—C3 | 74.64 (17) | C3—Fe—C13—C14 | 157.6 (3) |
| C12—Fe—C4—C3 | 44.9 (3) | C2—Fe—C13—C14 | -167.49 (13) |
| C10—Fe—C4—C3 | 115.47 (15) | C11—C10—C14—N15A | 177.8 (7) |
| C2—Fe—C4—C3 | -37.30 (14) | Fe—C10—C14—N15A | -122.9 (7) |
| C13—Fe—C4—C3 | -169.8 (2) | C11—C10—C14—C13 | -0.9 (2) |
| C14—Fe—C4—C3 | 157.33 (14) | Fe—C10—C14—C13 | 58.44 (15) |
| C1—Fe—C4—C5 | 38.09 (12) | C11—C10—C14—N15B | 176.4 (12) |
| C11—Fe—C4—C5 | -166.47 (13) | Fe—C10—C14—N15B | -124.3 (13) |
| C12—Fe—C4—C5 | 163.8 (3) | C11—C10—C14—Fe | -59.30 (15) |
| C10—Fe—C4—C5 | -125.64 (13) | C12—C13—C14—N15A | -177.5 (9) |
| C3—Fe—C4—C5 | 118.89 (19) | Fe—C13—C14—N15A | 123.2 (9) |
| C2—Fe—C4—C5 | 81.58 (14) | C12—C13—C14—C10 | 0.9 (2) |
| C13—Fe—C4—C5 | -50.9 (3) | Fe—C13—C14—C10 | -58.42 (15) |
| C14—Fe—C4—C5 | -83.78 (14) | C12—C13—C14—N15B | -176.4 (12) |
| C3—C4—C5—C1 | 0.5 (2) | Fe—C13—C14—N15B | 124.2 (12) |
| Fe—C4—C5—C1 | -59.19 (14) | C12—C13—C14—Fe | 59.37 (15) |
| C3—C4—C5—C6 | 177.69 (19) | C5—Fe—C14—N15A | -11.5 (8) |

| | | | |
|----------------|--------------|---------------------|--------------|
| Fe—C4—C5—C6 | 118.0 (2) | C1—Fe—C14—N15A | -53.7 (8) |
| C3—C4—C5—Fe | 59.68 (15) | C11—Fe—C14—N15A | 150.1 (8) |
| C2—C1—C5—C4 | -0.7 (2) | C12—Fe—C14—N15A | -165.8 (8) |
| Fe—C1—C5—C4 | 59.53 (15) | C4—Fe—C14—N15A | 31.8 (8) |
| C2—C1—C5—C6 | -177.8 (2) | C10—Fe—C14—N15A | 112.1 (8) |
| Fe—C1—C5—C6 | -117.6 (2) | C3—Fe—C14—N15A | 66.8 (8) |
| C2—C1—C5—Fe | -60.24 (15) | C2—Fe—C14—N15A | -87.3 (8) |
| C1—Fe—C5—C4 | -119.31 (18) | C13—Fe—C14—N15A | -127.5 (8) |
| C11—Fe—C5—C4 | 39.5 (4) | C5—Fe—C14—C10 | -123.56 (14) |
| C12—Fe—C5—C4 | -168.1 (2) | C1—Fe—C14—C10 | -165.78 (13) |
| C10—Fe—C5—C4 | 73.07 (16) | C11—Fe—C14—C10 | 38.06 (14) |
| C3—Fe—C5—C4 | -37.84 (13) | C12—Fe—C14—C10 | 82.10 (15) |
| C2—Fe—C5—C4 | -81.59 (14) | C4—Fe—C14—C10 | -80.25 (15) |
| C13—Fe—C5—C4 | 157.56 (12) | C3—Fe—C14—C10 | -45.3 (3) |
| C14—Fe—C5—C4 | 114.70 (13) | C2—Fe—C14—C10 | 160.6 (3) |
| C11—Fe—C5—C1 | 158.8 (3) | C13—Fe—C14—C10 | 120.42 (19) |
| C12—Fe—C5—C1 | -48.8 (3) | C5—Fe—C14—C13 | 116.01 (14) |
| C4—Fe—C5—C1 | 119.31 (18) | C1—Fe—C14—C13 | 73.79 (16) |
| C10—Fe—C5—C1 | -167.61 (13) | C11—Fe—C14—C13 | -82.37 (15) |
| C3—Fe—C5—C1 | 81.47 (14) | C12—Fe—C14—C13 | -38.33 (14) |
| C2—Fe—C5—C1 | 37.73 (13) | C4—Fe—C14—C13 | 159.33 (13) |
| C13—Fe—C5—C1 | -83.12 (14) | C10—Fe—C14—C13 | -120.42 (19) |
| C14—Fe—C5—C1 | -125.99 (13) | C3—Fe—C14—C13 | -165.7 (2) |
| C1—Fe—C5—C6 | 121.4 (2) | C2—Fe—C14—C13 | 40.2 (4) |
| C11—Fe—C5—C6 | -79.7 (4) | C5—Fe—C14—N15B | -0.8 (10) |
| C12—Fe—C5—C6 | 72.6 (3) | C1—Fe—C14—N15B | -43.0 (10) |
| C4—Fe—C5—C6 | -119.3 (2) | C11—Fe—C14—N15B | 160.8 (10) |
| C10—Fe—C5—C6 | -46.2 (2) | C12—Fe—C14—N15B | -155.1 (10) |
| C3—Fe—C5—C6 | -157.1 (2) | C4—Fe—C14—N15B | 42.5 (10) |
| C2—Fe—C5—C6 | 159.2 (2) | C10—Fe—C14—N15B | 122.8 (10) |
| C13—Fe—C5—C6 | 38.3 (2) | C3—Fe—C14—N15B | 77.5 (10) |
| C14—Fe—C5—C6 | -4.56 (19) | C2—Fe—C14—N15B | -76.6 (11) |
| C4—C5—C6—O7 | 8.7 (3) | C13—Fe—C14—N15B | -116.8 (10) |
| C1—C5—C6—O7 | -174.7 (2) | C10—C14—N15A—C16A | -163.1 (9) |
| Fe—C5—C6—O7 | 96.7 (2) | C13—C14—N15A—C16A | 15.1 (18) |
| C4—C5—C6—O8 | -172.83 (19) | N15B—C14—N15A—C16A | 9(10) |
| C1—C5—C6—O8 | 3.8 (3) | Fe—C14—N15A—C16A | 110.8 (11) |
| Fe—C5—C6—O8 | -84.8 (2) | C14—N15A—C16A—O17A | -2(2) |
| O7—C6—O8—C9 | 1.7 (3) | C14—N15A—C16A—O18A | 155.1 (11) |
| C5—C6—O8—C9 | -176.83 (18) | O17A—C16A—O18A—C19A | -20.4 (14) |
| C5—Fe—C10—C11 | -165.14 (14) | N15A—C16A—O18A—C19A | -174.9 (7) |
| C1—Fe—C10—C11 | 163.9 (3) | C16A—O18A—C19A—C20A | -70.8 (7) |
| C12—Fe—C10—C11 | 37.69 (15) | C16A—O18A—C19A—C21A | 167.3 (6) |
| C4—Fe—C10—C11 | -124.34 (15) | N15A—C14—N15B—C16B | -149 (13) |
| C3—Fe—C10—C11 | -82.10 (16) | C10—C14—N15B—C16B | -140.6 (19) |
| C2—Fe—C10—C11 | -49.6 (3) | C13—C14—N15B—C16B | 36 (3) |
| C13—Fe—C10—C11 | 81.65 (15) | Fe—C14—N15B—C16B | 126 (2) |
| C14—Fe—C10—C11 | 118.7 (2) | C14—N15B—C16B—O17B | -27 (4) |
| C5—Fe—C10—C14 | 76.14 (15) | C14—N15B—C16B—O18B | -170.7 (18) |

supplementary materials

| | | | |
|----------------|-------------|---------------------|------------|
| C1—Fe—C10—C14 | 45.2 (4) | N15B—C16B—O18B—C19B | 173.6 (16) |
| C11—Fe—C10—C14 | -118.7 (2) | O17B—C16B—O18B—C19B | 22 (2) |
| C12—Fe—C10—C14 | -81.02 (14) | C16B—O18B—C19B—C20B | 84.4 (11) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N15A—H15A \cdots O7 ⁱ | 0.88 | 1.93 | 2.793 (14) | 168 |
| N15B—H15B \cdots O7 ⁱ | 0.88 | 2.21 | 2.962 (19) | 143 |

Symmetry codes: (i) $-x+2, -y+2, -z+1$.

Fig. 1

