The reaction of Ag[C 5(CN) 5] with anhydrous FeCl 2 in acetonitrile leads to colourless crystals of tetrakis(acetonitrile-κN)bis(pentacyanocyclopentadienido-κN)iron(II) acetonitrile 1.8-solvate, [Fe(C 10N 5) 2(CH 3CN) 4] 1.8CH 3CN or cis-[[C 5(CN) 5] 2(MeCN) 2Fe]-1.8MeCN. The compound crystallizes in the triclinic space group P 1 as monomers, which exhibit weak C—H⋯N and π⋯π interactions. The crystals contain ca 20% solvent-accessible voids, which are nearly completely filled by two MeCN molecules.

1. Introduction

The term ‘decacyanoferrocene’ appeared first in a publication about ‘diazotetracyanocyclopentadiene’ (Webster, 1966) and later in two US patents by the same author (Webster, 1970, 1974). It was used for the reaction product from silver pentacyanocyclopentadienide and FeCl 2 in acetonitrile, which led to ‘light-green crystals of decacyanoferrocene’, which were characterized, after drying at 112 °C under vacuum, by elemental analysis and IR and UV spectroscopy as ‘C 20N 10Fe·xH 2O’. No indication or proof was given for the formulation as a ‘ferrocene’. A couple of years later, a different research group repeated the experiment and described the primary product as ‘white crystals’ (Christopher & Venanzi, 1973). Drying of the crystals at room temperature in vacuo produced a white solid that still, according to its IR spectrum, contained acetonitrile. Further drying at 110 °C in vacuo produced a pale-yellow–green product, which analyzed as ‘C 20N 10Fe·xH 2O’ and was further characterized by IR spectroscopy and magnetic and conductivity measurements. In the absence of a crystal structure determination, these authors postulated a ‘polymeric structure in which the iron is in an approximately octahedral environment’, in which ‘each PP group bridges three iron atoms’. Within the last 15 years, the coordination chemistry of the pentacyanocyclopentadienide anion has been studied intensively by us and others (Sünkel & Reimann, 2013; Sünkel & Nimax, 2018; Nimax et al., 2018; Blockhaus & Sünkel, 2021; Bacska et al., 2011; Less et al., 2013). These studies showed that [C 5(CN) 5] + could behave either as a noncoordinating anion or use one to its five cyano groups for coordination, sometimes even in a bridging μ 2−κ′:κ′ fashion. We had also treated FeCl 2 with Ag[C 5(CN) 5] in methanol. Recrystallization from MeOH gave crystals of trans-[[C 5(CN) 5] 2Fe(H 2O) 4], in which both anions used only one cyano function each for coordination to iron in a mononuclear compound (Sünkel et al., 2019). Individual molecules were connected via hydrogen bridges into a three-dimensional...
network. Since all the above-mentioned reports described the formation of (either ‘light green’ or ‘white’) crystals as the primary product of the reaction in acetonitrile, we decided to repeat this reaction and to study the crystals.

2. Experimental

2.1. Synthesis and crystallization

The title compound, tetrakis(acetonitrile-κN)bis(penta-cyanocyclopentadienido-κN)iron(II) acetonitrile disolvate, (I) (Scheme 1), was prepared as described in the literature (Webster, 1966; Christopher & Venanzi, 1973). Recrystallization of the crude product by slow evaporation of an acetonitrile solution under an argon atmosphere gave colourless crystals suitable for X-ray diffraction analysis. Heating the crystals at 110 °C in vacuo for several hours left an amorphous powder. All attempts to obtain crystals of this product by dissolution in a noncoordinating solvent met with failure.

2.2. Refinement

The structure refinement showed, besides the molecular unit, two lattice acetonitrile (MeCN) molecules, which were both disordered. The disorder of one MeCN molecule could be resolved with the help of restraints into two positions in relative 80:20 occupancies. The disorder of the second molecule, however, could not be resolved. Due to some unfavourable close contacts with the ‘minor’ molecule, the site-occupancy factor (s.o.f.) of the second molecule was reduced to 0.8 anyway. After inclusion of these MeCN molecules, PLATON (Spek, 2020) analysis showed no more solvent-accessible voids. The results of the refinement using this model are shown in the second column of Table 1. As the PLATON analysis of the structure without the lattice acetonitrile molecules showed 20% solvent-accessible voids (for a ‘cavity plot’, see Fig. S1 of the supporting information), a refinement using the SQUEEZE routine (Spek, 2015) was tried. The results of this refinement are shown in the third column of Table 1. As can be seen, the SQUEEZE refinement led to slightly better R values. To obtain further insight into the importance of crystal voids in this structure, the ‘un-SQUEEZED’ CIF file was examined using the program CrystalExplorer (Version 21.5), using the subroutine ‘void’

![Scheme 1](image_url)
(Turner et al., 2011), both without and with the acetonitrile molecules. Fig. 1(a) shows the void plot obtained without the MeCN molecules, while Fig. 1(b) shows the same plot when the MeCN molecules were included (0.002 a.u. isosurfaces; for the results of the corresponding calculations using 0.0003 a.u. isosurfaces, see Fig. S2 in the supporting information). Table 2 summarizes the results of the void-space calculations using PLATON and CrystalExplorer.

As can be seen, the results obtained with PLATON (excluding the MeCN solvents) are intermediate between the CrystalExplorer results with the two different isosurfaces, which is rather unusual (Turner et al., 2011). After inclusion of the MeCN molecules, the PLATON results and the Crystal-Explorer results for a 0.0003 a.u. surface are nearly identical, and show that there are no permanent voids left after inclusion of the MeCN molecules. In view of this, together with the probable involvement of the lattice MeCN molecules in C—H···N hydrogen bonds, the SQUEEZEd structure was not examined further.

3. Results and discussion

The title compound crystallizes in the triclinic space group \( P\bar{1} \) with one molecule in the asymmetric unit. The Fe\(^{II} \) ion coordinates to two cis-oriented pentacyanocyclopentadienyl anions via one nitrile function each, and additionally to four acetonitrile molecules (Fig. 2).

The two cyclopentadienyl rings are coplanar [interplanar angle = 0.8 (2)\(^\circ\)]; the average distance of atoms C201–C205 from the best plane through C101–C105 is 0.044 ± 0.02 \( \AA \).

Table 2

|                  | PLATON VOID | PLATON SASA | CE (0.002 a.u.) | CE (0.0003 a.u.) |
|------------------|-------------|-------------|----------------|-----------------|
| Without MeCN     |             |             |                |                 |
| Void volume      | 346         | 473.4       | 191.0          |                 |
| Void surface     | 281         | 721.2       | 237.9          |                 |
| With 2MeCN       |             |             |                |                 |
| Void volume      | 0           | 211.6       | 0.3            |                 |
| Void surface     | 0           | 716.4       | 3.2            |                 |

Figure 1
Crystal void plots (0.002 a.u. isosurface) of the crystal structure (a) without and (b) including the MeCN lattice molecules.

Figure 2
Displacement ellipsoid plot (30% probability level) of (I). The lattice MeCN molecules are not shown.

Figure 3
Packing plot (Mercury; Macrae et al., 2020), viewed along the crystallographic a axis. The colour coding green/blue/yellow/red corresponds to the symmetry equivalents, as defined by Mercury. Red and blue lines show the hydrogen bonds according to Table 4.
The bond lengths from the Fe atom to the \([C_5(CN)5]\) N atoms are significantly (>10\(\sigma\)) longer [average 2.176 (3) Å] than to the acetonitrile N atoms [average 2.140 (4) Å], with the bond angles at the coordinating atoms N101 and N201 close to being linear (average 161.9°). Further important bond parameters can be found in Table 3.

Weak interactions with the contents of the voids contribute to the stability of the crystal lattice (Ghosh et al., 2019; Wang et al., 2020) and so a closer inspection of the packing plots seemed appropriate (Fig. 3).

A packing plot viewed down the crystallographic \(a\) axis shows ‘layers’ of cyclopentadienyl rings oriented parallel to the \(bc\) diagonal and orthogonal to the plane of projection. These layers contain also one of the lattice MeCN molecules (dark blue in Fig. 3). Individual molecules are connected via C—H\(\cdots\)N hydrogen bonds in the \(b\) and \(c\) directions using methyl groups C12 and C22 of the coordinated acetonitrile.

\[\text{Figure 4}\]
Packing plot (Mercury; Macrae et al., 2020), viewed perpendicular to the \(bc\) plane. The colour coding is as in Fig. 3.

\[\text{Figure 5}\]
\(\pi\)-Stacking of the cyclopentadienyl rings. [Symmetry codes: (i) \(x, y + 1, z - 1\); (ii) \(-x + 1, -y + 1, -z\); (iii) \(x, y, z - 1\); (iv) \(-x + 1, -y + 1, -z + 1\); (v) \(x, y, z\); (vi) \(-x + 1, -y, -z + 1\); (vii) \(x, y - 1, z\).]

The bond lengths from the Fe atom to the \([C_5(CN)5]\) N atoms are significantly (>10\(\sigma\)) longer [average 2.176 (3) Å] than to

\[\text{Figure 6}\]
(a) Hirshfeld surface of the asymmetric unit of (I) using normalized contact distances \(d_{\text{norm}}\) for colour coding. Red areas represent regions where the contact distances are significantly below the sum of the van der Waals radii. (b) Hirshfeld surface of one isolated metal complex, together with some close-by neighbours, indicating also the hydrogen bridges between them and the central fragment.
molecules (both in cis positions relative to the coordinated anions) as donors and the pentacyanocyclopentadienide atoms N103 and N204 (in the 3-position relative to the coordinated cyano N atom), as well as the lattice MeCN atoms N5 and N6B, as acceptors. In addition, there is also a hydrogen bond between the lattice MeCN group C52 and pentacyanocyclopentadienide atom N102 (Table 4).

A possibly more important intermolecular interaction becomes visible in Fig. 4.

The pentacyanocyclopentadienyl rings stack via \( \pi - \pi \) interactions (Carter-Fenk & Herbert, 2020; Thakuria et al., 2019), with the ring planes at a typical distance of ca 3.36 Å. A closer look (Fig. 5) shows that the stack is formed by alternating pairs of inversion-related C101–C105 (symmetry codes i/ii and v/vi) and C201–C205 (iii/iv) rings. The dotted ‘bonds’ in Fig. 5 join the ring centroids at distances of 3.575 (i/ii and v/vi), 3.580 (ii/iii, iv/v and vi/vii) and 3.597 Å (iii/iv), and angles of 141.3 and 142.8°. This corresponds to a ‘ring slippage’ of ca 1.15 Å.

In order to gain further insight into the interactions at work, a Hirshfeld analysis was undertaken with the help of the program CrystalExplorer (Spackman et al., 2021).

Fig. 6(a) shows the Hirshfeld surface of the asymmetric unit, with the \( d_{\text{norm}} \) surface property (range −0.65 to 1.30). The strong involvement of the lattice MeCN molecules in donor C–H···N (top right) and acceptor N···H–C (bottom left) interactions can be seen. Fig. 6(b) shows the Hirshfeld surface of an isolated complex fragment and its interactions with four further complex fragments and a few lattice MeCN molecules. In Fig. 7, the same surface showing the properties ‘curvedness’, ‘shape index’ and ‘electrostatic potential’ is displayed.

Both the ‘curvedness’ and the ‘shape index’ plots show the importance of planar \( \pi \)-stacking for both cyclopentadienyl rings (Spackman & Jayatilaka, 2009). Fig. 7(c) shows that the asymmetric unit contains both electropositive (blue) and electronegative (red) parts, together with small neutral (white) research papers.
areas. Fig. S3 (see supporting information) shows how in neighbouring molecules the positive and negative parts approach each other.

The so-called ‘fingerprints’ are a graphical representation of all the interactions of atoms ‘inside’ and ‘outside’ the Hirshfeld surface (Spackman & McKinnon, 2002). Fig. 8(a) shows such a plot when the two lattice MeCN molecules are left outside the Hirshfeld surface, while Fig. 8(b) represents such a plot when the complete asymmetric unit is inside the Hirshfeld surface. A plot showing the most important individual contributors is shown in Fig. S4 (see supporting information). The bright-green spots at ca (1.8/1.8) Å in Fig. 8 correspond to π–π stacking interactions; inspection of Fig. S4 shows that C⋯C interactions are responsible for ca 18% of all the intermolecular interactions, while C–H⋯π interactions make up less than 7%. C–H⋯N contacts make up nearly 50% of the weak interactions.

A last important point relates to the interaction energies in the crystal. Fig. S5 (see supporting information) shows that the interactions between the complex and the two unique MeCN solvent molecules are relatively weak, with the repulsive terms dominating. The interactions between the asymmetric unit and four close neighbours are displayed in Fig. S6. The energies range from −54 to −174 kJ mol\(^{-1}\). The strongest interaction occurs for the closest approach of two inversion-related molecules (magenta), with a clear dominance of the dispersion term. Another method for graphically representing these interactions is through the use of ‘energy frameworks’ (Turner et al., 2015), which are displayed in Fig. 9.

4. Conclusion

The primary reaction product from FeCl₂ and Ag[C₅(CN)₅] in acetonitrile is neither a ‘ferrocene’ nor a coordination polymer. The structure determination presented here shows a mononuclear octahedral coordination compound with two cis-oriented monodentate pentacyanocyclopentadienide anions and four acetonitrile ligands. The individual molecules interact in the lattice via weak C–H⋯N hydrogen bonds and displaced parallel cyclopentadienyl π-systems. In the absence of any crystals it is difficult to speculate about the structure of the compound ‘Fe[C₅(CN)₅]₂·xH₂O’ described over 50 years ago. However, one could imagine that after removal of all the acetonitrile molecules, the remaining fragments approach each other parallel to the bc plane and form ‘ribbons’ of Fe[C₅(CN)₅]₂ with the anions using two of their cyano groups, similar to the structure of Ca[C₅(CN)₅H]₂·4H₂O (Sünkel & Nimax, 2018). In contrast to the Ca compound, the Fe compound would have to be octahedrally coordinated with two additional bridging H₂O ligands (Fig. 10).

Acknowledgements

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Coordination chemistry of polynitriles. Part 9. Decacyanoferrocene revisited: crystal and molecular structure of cis-[[C₅(CN)₅]₂(MeCN)₄Fe]

Karlheinz Sünkel and Tobias Blockhaus

Computing details

Data collection: APEX2 (Bruker, 2011); cell refinement: APEX2 (Bruker, 2011); data reduction: SAINT (Bruker, 2011); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: SHELXL2018 (Sheldrick, 2015b).

Tetrakis(acetonitrile-κN)bis(pentacyanocyclopentadienido-κN)iron(II) acetonitrile disolvate

Crystal data

[Fe(C₁₀N₅)₂(C₂H₃N)₄]·1.8C₂H₃N

Mr = 674.29

Triclinic, P̅1

a = 11.9972 (7) Å
b = 12.8711 (7) Å

δ = 13.0907 (8) Å

α = 62.528 (2)°
β = 82.929 (2)°

γ = 77.210 (2)°

V = 1748.47 (18) Å³

Z = 2

\( F(000) = 696 \)

\( D_\text{x} = 1.296 \text{ Mg m}^{-3} \)

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 8142 reflections

θ = 2.7–26.5°

µ = 0.48 mm⁻¹

T = 109 K

Block, colourless

0.05 × 0.04 × 0.03 mm

Data collection

Bruker D8 Venture

diffraotmeter

Radiation source: rotating anode generator

Detector resolution: 7.391 pixels mm⁻¹

mix of ω and phi scans

Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

\( T_\text{min} = 0.616, T_\text{max} = 0.745 \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.064 \)

\( wR(F^2) = 0.163 \)

\( S = 1.02 \)

7081 reflections

464 parameters

3 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\( w = 1/[\sigma^2(F^2c) + (0.0525P)^2 + 4.4167P] \)

where \( P = (F_c^2 + 2F_s^2)/3 \)

\( (\Delta/\sigma)_{\text{max}} < 0.001 \)

\( \Deltaρ_{\text{max}} = 0.81 \text{ e Å}^{-3} \)

\( \Deltaρ_{\text{min}} = -0.63 \text{ e Å}^{-3} \)
**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)**

| Atomic symbol | x         | y         | z         | U_{iso}/U_{eq} | Occ. (<1) |
|---------------|-----------|-----------|-----------|----------------|-----------|
| Fe1           | 0.31525 (4) | 0.41288 (5) | 0.62909 (5) | 0.02179 (16)  | 0.02179 (16)  |
| C101          | 0.5159 (3)  | 0.1898 (3)  | 0.4444 (3)  | 0.0220 (8)    | 0.0220 (8)    |
| C102          | 0.4447 (3)  | 0.1551 (3)  | 0.3921 (3)  | 0.0227 (8)    | 0.0227 (8)    |
| C103          | 0.5156 (3)  | 0.0879 (3)  | 0.3416 (3)  | 0.0241 (8)    | 0.0241 (8)    |
| C104          | 0.6307 (3)  | 0.0814 (3)  | 0.3624 (3)  | 0.0240 (8)    | 0.0240 (8)    |
| C105          | 0.6311 (3)  | 0.1436 (3)  | 0.4257 (3)  | 0.0230 (8)    | 0.0230 (8)    |
| C106          | 0.4747 (3)  | 0.2595 (3)  | 0.5041 (3)  | 0.0208 (8)    | 0.0208 (8)    |
| C107          | 0.3223 (3)  | 0.1848 (3)  | 0.3910 (3)  | 0.0230 (8)    | 0.0230 (8)    |
| C108          | 0.4783 (3)  | 0.0347 (3)  | 0.2808 (3)  | 0.0277 (9)    | 0.0277 (9)    |
| C109          | 0.7278 (3)  | 0.0216 (3)  | 0.3229 (4)  | 0.0322 (9)    | 0.0322 (9)    |
| C110          | 0.7303 (3)  | 0.1586 (3)  | 0.4649 (3)  | 0.0273 (8)    | 0.0273 (8)    |
| N101          | 0.4360 (3)  | 0.3168 (3)  | 0.5504 (3)  | 0.0266 (7)    | 0.0266 (7)    |
| N102          | 0.2255 (3)  | 0.2088 (3)  | 0.3873 (3)  | 0.0368 (8)    | 0.0368 (8)    |
| N103          | 0.4496 (3)  | −0.0092 (3) | 0.2322 (3)  | 0.0413 (9)    | 0.0413 (9)    |
| N104          | 0.8048 (3)  | −0.0262 (3) | 0.2907 (4)  | 0.0484 (10)   | 0.0484 (10)   |
| N105          | 0.8099 (3)  | 0.1701 (3)  | 0.4953 (3)  | 0.0400 (9)    | 0.0400 (9)    |
| C201          | 0.5149 (3)  | 0.5561 (3)  | 0.8071 (3)  | 0.0221 (8)    | 0.0221 (8)    |
| C202          | 0.6298 (3)  | 0.5503 (3)  | 0.8270 (3)  | 0.0214 (7)    | 0.0214 (7)    |
| C203          | 0.6296 (3)  | 0.6124 (3)  | 0.8915 (3)  | 0.0241 (8)    | 0.0241 (8)    |
| C204          | 0.5152 (3)  | 0.6567 (3)  | 0.9116 (3)  | 0.0224 (8)    | 0.0224 (8)    |
| C205          | 0.4442 (3)  | 0.6224 (3)  | 0.8594 (3)  | 0.0229 (8)    | 0.0229 (8)    |
| C206          | 0.4744 (3)  | 0.5066 (3)  | 0.7450 (3)  | 0.0197 (7)    | 0.0197 (7)    |
| C207          | 0.7275 (3)  | 0.4903 (3)  | 0.7878 (3)  | 0.0284 (9)    | 0.0284 (9)    |
| C208          | 0.7274 (3)  | 0.6301 (4)  | 0.9295 (3)  | 0.0297 (9)    | 0.0297 (9)    |
| C209          | 0.4768 (3)  | 0.7244 (3)  | 0.9745 (3)  | 0.0256 (8)    | 0.0256 (8)    |
| C210          | 0.3214 (3)  | 0.6506 (3)  | 0.8589 (3)  | 0.0271 (8)    | 0.0271 (8)    |
| N201          | 0.4370 (2)  | 0.4697 (3)  | 0.6948 (3)  | 0.0249 (7)    | 0.0249 (7)    |
| N202          | 0.8045 (3)  | 0.4424 (3)  | 0.7558 (3)  | 0.0424 (9)    | 0.0424 (9)    |
| N203          | 0.8046 (3)  | 0.6454 (4)  | 0.9608 (3)  | 0.0432 (9)    | 0.0432 (9)    |
| N204          | 0.4457 (3)  | 0.7775 (3)  | 1.0254 (3)  | 0.0374 (8)    | 0.0374 (8)    |
| N205          | 0.2240 (3)  | 0.6733 (3)  | 0.8597 (3)  | 0.0396 (9)    | 0.0396 (9)    |
| C11           | 0.3267 (3)  | 0.1710 (3)  | 0.8712 (3)  | 0.0278 (8)    | 0.0278 (8)    |
| C12           | 0.3231 (4)  | 0.0659 (4)  | 0.9790 (4)  | 0.0449 (11)   | 0.0449 (11)   |
| H12A          | 0.244664    | 0.067321    | 1.010643    | 0.067*        | 0.067*        |
| H12B          | 0.373736    | 0.064058    | 1.033356    | 0.067*        | 0.067*        |
| H12C          | 0.348369    | −0.005159   | 0.966392    | 0.067*        | 0.067*        |
| N1            | 0.3295 (3)  | 0.2534 (3)  | 0.7868 (3)  | 0.0282 (7)    | 0.0282 (7)    |
| C21           | 0.3161 (3)  | 0.6547 (3)  | 0.3858 (3)  | 0.0237 (8)    | 0.0237 (8)    |
| C22           | 0.3187 (3)  | 0.7613 (3)  | 0.2786 (3)  | 0.0312 (9)    | 0.0312 (9)    |
|       | \(U_{11}'\)        | \(U_{22}'\)        | \(U_{33}'\)        | \(U_{12}'\)        | \(U_{13}'\)        | \(U_{23}'\)        |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fe1   | 0.0159 (3)      | 0.0225 (3)      | 0.0240 (3)      | -0.00369 (19)  | -0.00088 (19)  | -0.0078 (2)     |
| C101  | 0.0223 (18)     | 0.0172 (17)     | 0.0206 (19)     | -0.0047 (14)   | 0.0005 (14)    | -0.0034 (15)    |
| C102  | 0.0221 (18)     | 0.0194 (17)     | 0.0195 (18)     | -0.0068 (14)   | -0.0014 (14)   | -0.0013 (15)    |
| C103  | 0.028 (2)       | 0.0203 (18)     | 0.0173 (18)     | -0.0070 (15)   | -0.0005 (14)   | -0.0013 (15)    |
| C104  | 0.0233 (19)     | 0.0186 (18)     | 0.0220 (19)     | -0.0036 (14)   | 0.0009 (14)    | -0.0030 (15)    |
| C105  | 0.0185 (18)     | 0.0187 (18)     | 0.0240 (19)     | -0.0034 (14)   | -0.0006 (14)   | -0.0030 (15)    |
| C106  | 0.0160 (17)     | 0.0179 (18)     | 0.0221 (19)     | -0.0070 (14)   | -0.0029 (13)   | -0.0013 (16)    |
| C107  | 0.022 (2)       | 0.0211 (19)     | 0.0210 (19)     | -0.0062 (14)   | -0.0026 (14)   | -0.0038 (16)    |
| C108  | 0.031 (2)       | 0.022 (2)       | 0.022 (2)       | -0.0058 (16)   | -0.0009 (15)   | -0.0028 (17)    |
| C109  | 0.034 (2)       | 0.025 (2)       | 0.032 (2)       | -0.0040 (17)   | -0.0023 (17)   | -0.0085 (18)    |
### Geometric parameters (Å, °)

|                | Fe1—N1     | C1—N1     | C11—N1     | C12—N2     | C21—N2     | C22—N3     | C31—N4     | C32—N4     | C41—N5     | C42—N6     | C51A—N4    | C52A—N4    | C5A—N4    | C5B—N4    | C6A—N4    | C6B—N4    |
|----------------|-------------|-----------|-------------|------------|------------|------------|------------|------------|------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Fe1—N1        | 2.127 (3)   | C11—N1    | C1—N1       | C11—N1     | C12—N2     | C21—N2     | C22—N3     | C31—N4     | C32—N4     | C41—N5     | C42—N6    | C51A—N4   | C52A—N4   | C5A—N4   | C5B—N4   | C6A—N4   | C6B—N4   |
| Fe1—N2        | 2.141 (3)   | C11—C12   | C1—C12      | C11—C12    | C12—H12A   | C21—H12A   | C22—H12B   | C31—H12A   | C32—H12A   | C41—H12A   | C42—H12B | C51A—C11  | C52A—C11  | C5A—C11  | C5B—C11  | C6A—C11  | C6B—C11  |
| Fe1—N3        | 2.142 (3)   | C11—C12   | C1—C12      | C11—C12    | C12—H12A   | C21—H12A   | C22—H12B   | C31—H12A   | C32—H12A   | C41—H12A   | C42—H12B | C51A—C11  | C52A—C11  | C5A—C11  | C5B—C11  | C6A—C11  | C6B—C11  |
| Fe1—N4        | 2.147 (3)   | C11—C12   | C1—C12      | C11—C12    | C12—H12A   | C21—H12A   | C22—H12B   | C31—H12A   | C32—H12A   | C41—H12A   | C42—H12B | C51A—C11  | C52A—C11  | C5A—C11  | C5B—C11  | C6A—C11  | C6B—C11  |
| Fe1—N101      | 2.169 (3)   | C12—H12C  | C1—H12A     | C12—H12B   | C21—H12C   | C22—H12B   | C31—H12A   | C32—H12B   | C41—H12C   | C42—H12B   | C51A—C11  | C52A—C11  | C5A—C11  | C5B—C11  | C6A—C11  | C6B—C11  |
| Fe1—N201      | 2.185 (3)   | C21—N2    | C1—N1       | C11—N1     | C12—N2     | C21—N2     | C22—N3     | C31—N4     | C32—N4     | C41—N5     | C42—N6    | C51A—N4   | C52A—N4   | C5A—N4   | C5B—N4   | C6A—N4   | C6B—N4   |

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**supporting information**
| Bond                  | Length (Å) | Bond                  | Length (Å) | Bond                  | Length (Å) |
|----------------------|------------|----------------------|------------|----------------------|------------|
| C101—C102            | 1.412 (5)  | C21—C22              | 1.444 (5)  |
| C101—C105            | 1.418 (5)  | C22—H22A             | 0.9800     |
| C101—C106            | 1.420 (5)  | C22—H22B             | 0.9800     |
| C102—C103            | 1.404 (5)  | C22—H22C             | 0.9800     |
| C102—C107            | 1.433 (5)  | C31—N3               | 1.125 (5)  |
| C103—C104            | 1.416 (5)  | C31—C32              | 1.459 (6)  |
| C103—C108            | 1.423 (6)  | C32—H32A             | 0.9800     |
| C104—C105            | 1.395 (5)  | C32—H32B             | 0.9800     |
| C104—C109            | 1.427 (5)  | C32—H32C             | 0.9800     |
| C105—C110            | 1.435 (5)  | C41—N4               | 1.145 (5)  |
| C106—N101            | 1.148 (5)  | C41—C42              | 1.450 (6)  |
| C107—N102            | 1.135 (5)  | C42—H42A             | 0.9800     |
| C108—N103            | 1.148 (5)  | C42—H42B             | 0.9800     |
| C109—N104            | 1.141 (5)  | C42—H42C             | 0.9800     |
| C110—N105            | 1.142 (5)  | C51A—N5A             | 1.149 (9)  |
| C201—C205            | 1.411 (5)  | C51A—C52A            | 1.436 (10) |
| C201—C202            | 1.413 (5)  | C52A—H52A            | 0.9800     |
| C201—C206            | 1.420 (5)  | C52A—H52B            | 0.9800     |
| C202—C203            | 1.406 (5)  | C52A—H52C            | 0.9800     |
| C202—C207            | 1.431 (5)  | C61A—N6A             | 1.152 (9)  |
| C203—C204            | 1.407 (5)  | C61A—C62A            | 1.418 (10) |
| C203—C208            | 1.429 (5)  | C62A—H62A            | 0.9800     |
| C204—C205            | 1.406 (5)  | C62A—H62B            | 0.9800     |
| C204—C209            | 1.430 (5)  | C62A—H62C            | 0.9800     |
| C205—C210            | 1.437 (5)  | N6B—C61B             | 1.155 (18) |
| C206—N201            | 1.146 (4)  | C61B—C62B            | 1.430 (18) |
| C207—N202            | 1.141 (5)  | C62B—H62D            | 0.9800     |
| C208—N203            | 1.146 (5)  | C62B—H62E            | 0.9800     |
| C209—N204            | 1.138 (5)  | C62B—H62F            | 0.9800     |
| C210—N205            | 1.140 (5)  |                       |            |
| N1—Fe1—N2            | 175.79 (12)| N205—C210—C205       | 179.1 (4)  |
| N1—Fe1—N3            | 90.01 (12) | N206—N201—Fe1        | 161.2 (3)  |
| N2—Fe1—N3            | 92.83 (12) | N1—C11—C12           | 179.9 (6)  |
| N1—Fe1—N4            | 90.01 (12) | C11—C12—H12A         | 109.5      |
| N2—Fe1—N4            | 93.26 (12) | C11—C12—H12B         | 109.5      |
| N3—Fe1—N4            | 86.77 (12) | H12A—C12—H12B        | 109.5      |
| N1—Fe1—N101          | 88.79 (12) | C11—C12—H12C         | 109.5      |
| N2—Fe1—N101          | 88.66 (11) | H12A—C12—H12C        | 109.5      |
| N3—Fe1—N101          | 174.68 (12)| H12B—C12—H12C        | 109.5      |
| N4—Fe1—N101          | 88.04 (12) | C11—N1—Fe1           | 173.8 (3)  |
| N1—Fe1—N201          | 88.02 (12) | N2—C21—C22           | 179.6 (4)  |
| N2—Fe1—N201          | 89.04 (11) | C21—C22—H22A         | 109.5      |
| N3—Fe1—N201          | 86.53 (12) | C21—C22—H22B         | 109.5      |
| N4—Fe1—N201          | 173.02 (12)| H22A—C22—H22B        | 109.5      |
| N101—Fe1—N201        | 98.60 (11) | C21—C22—H22C         | 109.5      |
| C102—C101—C105       | 108.2 (3)  | H22A—C22—H22C        | 109.5      |
| C102—C101—C106       | 124.0 (3)  | H22B—C22—H22C        | 109.5      |
C105—C101—C106 127.9 (3) C21—N2—Fe1 178.6 (3)
C103—C102—C101 107.6 (3) N3—C31—C32 178.2 (6)
C103—C102—C107 127.0 (3) C31—C32—H32A 109.5
C101—C102—C107 125.4 (3) C31—C32—H32B 109.5
C102—C103—C104 108.2 (3) H32A—C32—H32B 109.5
C102—C103—C108 125.9 (3) C31—C32—H32C 109.5
C104—C103—C108 125.9 (3) H32B—C32—H32C 109.5
C105—C104—C103 108.3 (3) C31—N3—Fe1 166.2 (4)
C105—C104—C109 127.0 (3) C41—C42—H42A 109.5
C104—C105—C101 124.7 (4) N4—C41—C42 179.0 (5)
C104—C105—C107 107.8 (3) C41—C42—H42B 109.5
C101—C105—C107 126.2 (3) C41—C42—H42C 109.5
C101—C105—C110 126.0 (3) H42A—C42—H42B 109.5
N101—C106—C101 176.6 (4) C41—C42—H42C 109.5
N102—C107—C102 178.3 (4) H42A—C42—H42C 109.5
N103—C108—C103 179.1 (4) H42B—C42—H42C 109.5
N104—C109—C104 179.3 (5) C41—N4—Fe1 165.3 (3)
N105—C110—C105 179.2 (4) N5A—C51A—C52A 177.7 (8)
C106—N101—Fe1 162.4 (3) C51A—C52A—H52A 109.5
C205—C201—C202 107.9 (3) C51A—C52A—H52B 109.5
C205—C201—C206 124.6 (3) C51A—C52A—H52C 109.5
C202—C201—C206 127.5 (3) C61A—C62A—H62A 109.5
C203—C202—C201 107.9 (3) C61A—C62A—H62B 109.5
C203—C202—C207 127.1 (3) C61A—C62A—H62C 109.5
C201—C202—C207 125.0 (3) N6A—C61A—C62A 178.7 (9)
C202—C203—C204 108.0 (3) C61A—C62A—H62A 109.5
C202—C203—C208 126.7 (3) C61A—C62A—H62B 109.5
C204—C203—C208 125.2 (3) H62A—C62A—H62B 109.5
C205—C204—C203 108.3 (3) C61A—C62A—H62C 109.5
C205—C204—C209 125.4 (3) C61A—C62A—H62C 109.5
C203—C204—C209 126.3 (3) H62B—C62A—H62C 109.5
C204—C205—C201 107.8 (3) N6B—C61B—C62B 173 (6)
C204—C205—C210 126.0 (3) C61B—C62B—H62D 109.5
C201—C205—C210 126.2 (3) C61B—C62B—H62E 109.5
N201—C206—C201 177.0 (4) H62D—C62B—H62E 109.5
N202—C207—C202 179.2 (4) C61B—C62B—H62F 109.5
N203—C208—C203 178.8 (4) H62D—C62B—H62F 109.5
N204—C209—C204 179.3 (4) H62E—C62B—H62F 109.5

C105—C101—C102—C103 0.0 (4) C205—C201—C202—C203 0.2 (4)
C106—C101—C102—C103 179.8 (3) C206—C201—C202—C203 179.5 (3)
C105—C101—C102—C107 −179.5 (3) C205—C201—C202—C207 179.8 (3)
C106—C101—C102—C107 0.3 (6) C206—C201—C202—C207 −0.9 (6)
C101—C102—C103—C104 −0.2 (4) C201—C202—C203—C204 0.0 (4)
C107—C102—C103—C104 179.4 (3) C207—C202—C203—C204 −179.7 (3)
C101—C102—C103—C108 179.3 (3) C201—C202—C203—C208 −179.2 (3)
C107—C102—C103—C108 −1.1 (6) C207—C202—C203—C208 1.2 (6)
C102—C103—C104—C105 0.2 (4) C202—C203—C204—C205 −0.2 (4)
### Hydrogen-bond geometry (Å, °)

| D—H···A  | D—H  | H···A  | D···A  | D—H···A |
|----------|-------|--------|--------|---------|
| C12—H12A···N5Ai | 0.98  | 2.58   | 3.454 (7) | 149 |
| C12—H12B···N103i | 0.98  | 2.54   | 3.443 (6) | 154 |
| C12—H12C···N204ii | 0.98  | 2.56   | 3.469 (6) | 154 |
| C22—H22A···N5Ai | 0.98  | 2.39   | 3.308 (7) | 156 |
| C22—H22A···N6Bi | 0.98  | 2.61   | 3.41 (3)  | 138 |
| C22—H22B···N204iv | 0.98  | 2.52   | 3.407 (5) | 150 |
| C22—H22C···N103ii | 0.98  | 2.52   | 3.424 (6) | 154 |
| C52—H52B···N102 | 0.98  | 2.51   | 3.492 (8) | 176 |

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

### The geometry (Å, °) around the FeII ion

|             |       |            |            |       |
|-------------|-------|------------|------------|-------|
| Fe1—N101    | 2.170 (4) | N101—Fe1—N3 | 98.6 (1)   | 174.6 (1) |
| Fe1—N201    | 2.186 (3) | N101—Fe1—N3 | 173.0 (1)  | 174.6 (1) |
| Fe1—N1       | 2.127 (3) | N101—Fe1—N3 | 173.0 (1)  | 174.6 (1) |
| Fe1—N2       | 2.141 (3) | N101—Fe1—N3 | 173.0 (1)  | 174.6 (1) |
| Fe1—N3       | 2.143 (4) | N101—Fe1—N3 | 173.0 (1)  | 174.6 (1) |
| Fe1—N4       | 2.146 (3) | N101—Fe1—N3 | 173.0 (1)  | 174.6 (1) |

### Hydrogen-bond geometry (Å, °)

| D—H···A  | D—H  | H···A  | D···A  | D—H···A |
|----------|-------|--------|--------|---------|
| C12—H12A···N5Ai | 0.98  | 2.57   | 3.448  | 149 |
| C12—H12B···N103i | 0.98  | 2.54   | 3.440 (5) | 154 |
| C12—H12C···N204ii | 0.98  | 2.57   | 3.469 (5) | 153 |
| C22—H22A···N5iv | 0.98  | 2.38   | 3.302  | 156 |
| C22—H22A···N6Bi | 0.98  | 2.64   | 3.426  | 137 |
| C22—H22B···N204iv | 0.98  | 2.53   | 3.406 (5) | 149 |
| C22—H22C···N103iv | 0.98  | 2.52   | 3.421 (5) | 153 |
| C52—H52B···N102 | 0.98  | 2.51   | 3.489  | 177 |

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