Crystal structure of bis[3-(3,5-dichlorophenyl)-5-[6-(1H-pyrazol-1-yl)pyridin-2-yl]-4H,1,2,4-triazol-4-ido]iron(II) methanol disolvate

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Received 26 September 2022
Accepted 31 October 2022

The asymmetric unit of the title compound, [FeII(C16H9Cl2N6)2]·2CH3OH, consists of half of a charge-neutral complex molecule and a discrete methanol molecule. The planar anionic tridentate ligand 2-[5-(3,5-dichlorophenyl)-4H-1,2,4-triazol-3-ato]-6-(1H-pyrazol-1-yl)pyridine coordinates to the FeII ion through the N atoms of the pyrazole, pyridine and triazole groups, forming a coordination sphere of the central ion that deviates moderately from an octahedral geometry. The average Fe—N bond distance is 1.953 Å, indicating the low-spin state of the FeII ion. The cone-like-shaped molecules, nested into each other, are linked through double weak C—H(pz)/C1/C1/C1(ph) interactions into mono-periodic columns, which are further linked through weak C—H···N/C0 interactions into di-periodic layers. The layers interact through double weak C—H(ph)···Cl bonds with neighbouring molecules. Energy framework analysis at the B3LYP/6–31 G(d,p) theory level reproduces the strong interaction within the layers and the weaker interlayer interactions. Intermolecular contacts were quantified using Hirshfeld surface analysis and two-dimensional fingerprint plots, the relative contributions of the contacts to the crystal packing being H···H 26.1%, H···C/C/C···H 24.4%, H···Cl/Cl···H 18.9% and H···N/N···H 12.1%.

1. Chemical context

Meridional tridentate ligands, to which different bisazole-pyridines belong, are a common choice for the synthesis of FeII spin-crossover compounds able to switch between a high-spin state (t2g4e5g0, total spin S = 2) and the low-spin state (t2g6e8g0, total spin S = 0) due to temperature change, irradiation or external pressure (Goodwin, 2004; Halcrow et al., 2019). In the case of asymmetric ligands with one of the azole groups carrying a hydrogen on the nitrogen heteroatom, deprotonation can produce neutral [Fe(ligand)2] complexes that can be high-spin (Schäfer et al., 2013), low-spin (Shiga et al., 2019) or spin crossover (Seredyuk et al., 2014), depending on the constituent organic groups, solvent molecules and the way that the molecules interact in the lattice (Seredyuk et al., 2022).

Having an interest in FeII spin-crossover complexes formed by polydentate ligands (Bonhommeau et al., 2012; Valverde-Muñoz et al., 2020; Piñeiro-López et al., 2021), we report here on a structural characterization of a new complex [FeII{L2}]6 based on asymmetric deprotonable ligand L = 2-[5-(3,5-dichlorophenyl)-4H-1,2,4-triazol-3-yl]-6-(1H-pyrazol-1-yl)pyridine.
2. Structural commentary

The asymmetric unit comprises half of the molecule and a discrete MeOH molecule forming an O26—H26···N16 hydrogen bond with the triazole (trz) ring and a weak C5—H5···O26 bond with the pyridine (py) ring (Fig. 1). The FeII ion has a pseudo-octahedral coordination environment composed of the nitrogen donor atoms of the pyrazole (pz), py, and trz heterocycles with an averaged <Fe—N> distance of 1.953 Å (V[Fe3N4] = 9.610 Å³) that is typical for low-spin complexes with an N6 coordination environment (Gütlich & Goodwin, 2004). The pz, py, trz, and phenyl rings of the ligand protrude along the b-axis with a stacking periodicity equal to 10.4669 (6) Å (= cell parameter a) (Fig. 2a). As a result of their tapered shape, neighbouring complex molecules are embedded in each other and interact through hydrogen bonds in the range 2.826 (5)–3.779 (5) Å (Table 1), neighbouring columns are joined into corrugated di-periodic layers in the ac plane (Fig. 2b,c). The layers stack along the b-axis direction, forming weak C—H(ph)···Cl(ph+) interlayer interactions shorter than the sum of the van der Waals radii, two per each phenyl group (Fig. 2c). The voids between the layers are occupied by methanol molecules, which participate in the strong and weak hydrogen bonding mentioned above. A complete list of intermolecular interactions is given in Table 1.

4. Hirshfeld surface and 2D fingerprint plots

A Hirshfeld surface analysis was performed and the associated two-dimensional fingerprint plots were generated using Crystal Explorer (Spackman et al., 2021), with a standard resolution of the three-dimensional dnorm surfaces plotted over a fixed colour scale of −0.5982 (red) to 1.2057 (blue) a.u.

Table 1

| D—H ··· A | D—H | H ··· A | D···A | D—H ··· A |
|----------|-----|--------|-------|----------|
| C5—H5···O26 | 0.95 | 2.41 | 3.256 (6) | 149 |
| C7—H7···N25i | 0.95 | 2.48 | 3.406 (5) | 165 |
| C11—H11···O26ii | 0.95 | 2.23 | 3.144 (6) | 162 |
| C13—H13···N25i | 0.95 | 2.52 | 3.363 (6) | 148 |
| C20—H20···C21iii | 0.95 | 2.86 | 3.779 (5) | 162 |
| O26—H26···N16 | 0.88 (5) | 1.98 (5) | 2.826 (5) | 166 (5) |

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

The formed one-dimensional supramolecular columns protrude along the a-axis with a stacking periodicity equal to 4.4669 (6) Å (= cell parameter a) (Fig. 2a). As a result of weak intermolecular C—H(pz,py)···N/C(pz,trz)/OMeOH hydrogen bonds in the range 2.826 (5)–3.779 (5) Å (Table 1), neighbouring columns are joined into corrugated di-periodic layers in the ac plane (Fig. 2b,c). The layers stack along the b-axis direction, forming weak C—H(ph)···Cl(ph+) interlayer interactions shorter than the sum of the van der Waals radii, two per each phenyl group (Fig. 2c). The voids between the layers are occupied by methanol molecules, which participate in the strong and weak hydrogen bonding mentioned above. A complete list of intermolecular interactions is given in Table 1.

Figure 1

The molecular structure of half of the title compound with displacement ellipsoids drawn at the 50% probability level. The strong O—H···N and weak C—H···O/N/C/Cl hydrogen bonds are shown with the nearest neighbours. Symmetry codes: (i) −1+x, 1/2−y, 1/2+z; (ii) −1/2+x, 1/2−y, −1/2+z; (iii) −1/2+x, −1/2−y, −1/2+z; (iv) 2−x, 1−y, −z.

Figure 2

(a) A fragment of mono-periodic supramolecular column formed by stacking of molecules along the a axis; (b) supramolecular di-periodic layers formed by stacking of the supramolecular columns in the ac plane. For a better representation, each column has a different colour; (c) stacking of the di-periodic layers along the b axis. The methanol molecules are not shown for clarity.
The pale-red spots indicate short contacts and negative $d_{\text{norm}}$ values on the surface correspond to the interactions described above. The overall two-dimensional fingerprint plot is illustrated in Fig. 4. The Hirshfeld surfaces mapped over $d_{\text{norm}}$ are shown for the H···H, H···C/C···H, H···Cl/Cl···H, and H···N/N···H contacts, and the two-dimensional fingerprint plots, associated with their relative contributions to the Hirshfeld surface. At 26.1%, the largest contribution to the overall crystal packing is from H···H interactions, which are located mostly in the middle region of the fingerprint plot. H···C/C···H contacts contribute 24.4% and H···Cl/Cl···H 18.9%, resulting in a pair of characteristic wings. The H···N/N···H contacts, represented by a pair of sharp spikes in the fingerprint plot, make a 12.1% contribution to the Hirshfeld surface. The electrostatic potential energy calculated using the B3LYP/6-31G(d,p) basis set localizes the negative charge on the trz-ph moieties of the complex molecule, while the pz-py moieties are relatively positively charged (Fig. 3b). The polar nature of the molecule justifies the realized stacking in columns.

5. Energy framework analysis
The energy framework (Spackman et al., 2021) with total energy values ($E_{\text{tot}}$) calculated using the wavefunction at the B3LYP/6-31G(d,p) theory level are shown in Fig. 5a. The cylindrical radii are proportional to the relative strength of the corresponding energies. The major contribution to the intermolecular interactions comes from dispersion forces ($E_{\text{disp}}$), reflecting the dominant type of interactions in the network of the electroneutral molecules (see the table in Fig. 5). The energy framework topology reproduces the topology of intermolecular interactions within and between supramolecular layers, including the electron-density distribution within the molecule analyzed above using mapped Hirshfeld surfaces. The weak hydrogen bonding between the molecules

Figure 3
(a) A projection of $d_{\text{norm}}$ mapped on Hirshfeld surfaces, showing the intermolecular interactions within the molecule. Red/blue and white areas represent regions where contacts are shorter/larger than the sum and close to the sum of the van der Waals radii, respectively. (b) Electrostatic potential for the title compound derived from a B3LYP/6-31G(d,p) wavefunction mapped on the Hirshfeld surface in the range −0.1043 (red) to 0.1064 a.u. (blue).

Figure 4
(a) The overall two-dimensional fingerprint plot and those delineated into specified interactions. (b) Hirshfeld surface representations with the function $d_{\text{norm}}$ plotted onto the surface for the different interactions.
within the supramolecular columns and between the columns within the layers correspond to interaction energies of $-48.6$ and $-67.9$ kJ mol$^{-1}$, respectively (Fig. 5b). As for the interlayer interactions, the double supramolecular C—H$\cdots$C$_1$[symmetry code: (ii) $2-x$, 1$-y$, 1$-z$] bonding between neighbouring phenyl rings leads to an interaction energy of $-5.6$ kJ mol$^{-1}$, while the stacking of the moieties corresponds to an interaction energy of $-21.7$ kJ mol$^{-1}$ (Fig. 5c). The colour-coded interaction mappings within a radius of 3.8 Å of a central reference molecule for the title compound together with full details of the various contributions to the total energy ($E_{\text{ele}}$, $E_{\text{pol}}$, $E_{\text{dis}}$, $E_{\text{rep}}$) are shown in the table in Fig. 5.

### Table 2

Computed distortion indices (Å, °) for the title compound and similar complexes from the literature.

| CSD refcode     | Spin state | $<\text{Fe—N}>$ | $\Sigma$ | $\Theta$ | $E_{\text{sh}}$(O)]. |
|-----------------|------------|-----------------|----------|----------|----------------------|
| Title compound  | Low-spin   | 1.953           | 91.2     | 291.5    | 2.16                 |
| XODCEB$^a$      | Low-spin   | 1.950           | 87.4     | 276.6    | 1.92                 |
| IGERIX$^b$      | High-spin  | 2.179           | 149.7    | 553.2    | 6.06                 |
| IGERIX01$^b$    | Low-spin   | 1.986           | 105.6    | 350.6    | 2.85                 |
| LUTGEO$^c$      | Low-spin   | 1.933           | 85.0     | 309.6    | 2.10                 |

Notes: (a) Shiga et al. (2019); (b) Gentili et al. (2015); (c) Senthil Kumar et al. (2015).

6. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, last update February 2021; Groom et al., 2016) reveals similar neutral Fe$^{II}$ complexes with a deprotonable azole based on pyrazole-pyridine-benzimidazole, viz. XODCEB (Shiga et al., 2019) and pyrazole-pyridine-tetrazole, IGERIX and LUTGEO (Gentili et al., 2015; Senthil Kumar et al., 2015). The Fe—N distances for these complexes in the low-spin state are close to the value in the title compound, while in the high-spin state it is larger by $\sim 0.2$ Å. The trigonal distortion indices change correspondingly, and in the low-spin state they are systematically lower than in the high-spin state. Table 2 collates the structural parameters of the complexes and of the title compound.

7. Synthesis and crystallization

The synthesis of the title compound was performed using a layering technique in a standard test tube. The layering sequence was as follows: the bottom layer contains a solution of $[\text{Fe}((L^2)\text{BF}_4)]_2$ prepared by dissolving $L = [2-(3,5-$dichlorophenyl)-4-$H$\cdots$1,2,4-triazol-3-yl]6-$(1$H$\cdots$pyrazol-1-yl)pyridine (100 mg, 0.280 mmol) and Fe(BF$_4$)$_2$·6H$_2$O (47 mg, 0.140 mmol) in boiling acetone, to which chloroform (5 ml) was then added. The middle layer was a methanol–chloroform mixture (1:10, 10 ml), which was covered by a layer of methanol (10 ml), to which 100 ml of NEt$_3$ was added dropwise. The tube was sealed, and thin lustrous black plate-like single crystals appeared in 3–4 weeks (yield ca 60%).

Elemental analysis calculated for C$_{34}$H$_{26}$Cl$_4$FeN$_{12}$O$_2$: C, 49.06; H, 3.15; N, 20.19. Found: C, 49.24; H, 3.05; N, 20.10.

![Figure 5](image-url)

(a) The calculated energy frameworks, showing the total energy diagrams ($E_{\text{tot}}$). (b) decomposition of the energy framework into the part corresponding to the interactions within a supramolecular layer and (c) interlayer interactions. In the table the corresponding colour-coded energy values $E_{\text{tot}}$ are provided, including their $E_{\text{ele}}$, $E_{\text{pol}}$, $E_{\text{dis}}$ and $E_{\text{rep}}$ components. Tube size is set at 100 scale, the blue colour corresponds to the attractive interaction, yellow to the repulsive interaction.
8. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were placed in calculated positions using idealized geometries, with C—H = 0.98 Å for methyl groups and 0.95 Å for aromatic H atoms, and refined using a riding model with \( U_{\text{iso}}(\text{H}) = 1.2-1.5U_{\text{eq}}(\text{C}) \); the hydrogen atom H26 was refined freely.

Acknowledgements

Author contributions are as follows: Conceptualization, KZ and MS; methodology, KZ; formal analysis, IOF; synthesis, SOM; single-crystal measurements, SS; writing (original draft), MS; writing (review and editing of the manuscript), TYS, MS; visualization and calculations, VMA; funding acquisition, KZ, MS.

Funding information

Funding for this research was provided by a grant from the Ministry of Education and Science of Ukraine for perspective development of the scientific direction ‘Mathematical sciences and natural sciences’ at Taras Shevchenko National University of Kyiv and by the Ministry of Education and Science of Ukraine (grant Nos. 22BF037-03, 22BF037-04).

Table 3

| Parameter | Value |
|-----------|-------|
| Chemical formula | [Fe(C16H9Cl2N6)2]·2CH3O |
| Crystal system, space group | Orthorhombic, Pnma |
| Temperature (K) | 180 |
| a, b, c (Å) | 10.4669 (6), 26.5890 (16), 12.8313 (7) |
| V (Å³) | 3571.0 (4) |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 0.77 |
| Crystal size (mm) | 0.12 × 0.08 × 0.03 |
| No. of measured, independent and constrained reflections | 3571 |
| \( F^2 > 2\sigma(F^2) \), S | 0.068, 0.133, 1.02 |
| No. of parameters | 244 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| Δρ_{max}, Δρ_{min} (e Å⁻³) | 0.44, −0.50 |

Computer program: CrysAlis PRO (Rigaku OD, 2022), SHELXL2018/3 (Sheldrick, 2015) and OLEX2 (Dolomanov et al., 2009).

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Crystal structure of bis{3-(3,5-dichlorophenyl)-5-[6-(1H-pyrazol-1-yl)pyridin-2-yl]-4H-1,2,4-triazol-4-ido}iron(II) methanol disolvate

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Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2022); cell refinement: CrysAlis PRO (Rigaku OD, 2022); data reduction: CrysAlis PRO (Rigaku OD, 2022); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015); molecular graphics: Olex2 (Dolomanov et al., 2009); software used to prepare material for publication: Olex2 (Dolomanov et al., 2009).

Bis(3-(3,5-dichlorophenyl)-5-[6-(1H-pyrazol-1-yl)pyridin-2-yl]-4H-1,2,4-triazol-4-ido)iron(II) methanol disolvate

Crystal data

\[\text{[Fe(C}_{16}\text{H}_{9}\text{Cl}_{2}\text{N}_{6})_{2}]\cdot2\text{CH}_{4}\text{O}\]

\(M_r = 832.32\)

Orthorhombic, \(Pnna\)

\(a = 10.4669\ (6)\ \text{Å}\)

\(b = 26.5890\ (16)\ \text{Å}\)

\(c = 12.8313\ (7)\ \text{Å}\)

\(V = 3571.0\ (4)\ \text{Å}^3\)

\(Z = 4\)

\(F(000) = 1696\)

Data collection

Xcalibur, Eos diffractometer

\(\omega\) scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2022)

\(T_{\text{min}} = 0.772, T_{\text{max}} = 1.000\)

13877 measured reflections

3650 independent reflections

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2\sigma(F^2)] = 0.068\)

\(wR(F^2) = 0.133\)

\(S = 1.02\)

3650 reflections

244 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

\(\frac{\Delta \rho_{\text{max}}}{\rho_{\text{max}}} = 0.44\ \text{e} \ \text{Å}^{-3}\)

\(\Delta \rho_{\text{min}} = -0.50\ \text{e} \ \text{Å}^{-3}\)
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)

| Atom | x      | y      | z      | Uiso*/Ueq |
|------|--------|--------|--------|-----------|
| C3   | 0.5057 (4) | 0.32367 (15) | 0.3495 (3) | 0.0204 (10) |
| C4   | 0.4305 (4) | 0.30235 (16) | 0.4341 (3) | 0.0207 (10) |
| C5   | 0.4296 (4) | 0.31360 (16) | 0.5392 (3) | 0.0261 (11) |
| H5   | 0.486168 | 0.338141 | 0.566974 | 0.031*       |
| C6   | 0.3448 (4) | 0.28840 (16) | 0.6032 (3) | 0.0269 (11) |
| H6   | 0.343778 | 0.295610 | 0.675694 | 0.032*       |
| C7   | 0.2607 (4) | 0.25265 (16) | 0.5633 (3) | 0.0240 (10) |
| H7   | 0.201948 | 0.235235 | 0.606739 | 0.029*       |
| C8   | 0.2672 (4) | 0.24384 (15) | 0.4571 (3) | 0.0203 (10) |
| C11  | 0.1361 (4) | 0.17150 (16) | 0.2626 (3) | 0.0278 (11) |
| H11  | 0.134864 | 0.158847 | 0.193327 | 0.033*       |
| C12  | 0.0477 (4) | 0.15849 (17) | 0.3399 (4) | 0.0329 (12) |
| H12  | −0.022909 | 0.136283 | 0.332937 | 0.039*       |
| C13  | 0.0835 (4) | 0.18423 (16) | 0.4272 (3) | 0.0263 (11) |
| H13  | 0.042270 | 0.183520 | 0.493174 | 0.032*       |
| C15  | 0.6226 (4) | 0.36305 (15) | 0.2470 (3) | 0.0226 (10) |
| C17  | 0.7161 (4) | 0.39837 (15) | 0.2033 (3) | 0.0230 (10) |
| C18  | 0.7328 (5) | 0.40295 (16) | 0.0965 (3) | 0.0316 (12) |
| H18  | 0.680723 | 0.383994 | 0.050313 | 0.038*       |
| C19  | 0.8241 (5) | 0.43469 (18) | 0.0572 (4) | 0.0406 (14) |
| C20  | 0.8995 (5) | 0.46402 (18) | 0.1219 (4) | 0.0379 (13) |
| H20  | 0.960900 | 0.486591 | 0.093934 | 0.046*       |
| C21  | 0.8827 (4) | 0.45949 (16) | 0.2281 (4) | 0.0308 (12) |
| C22  | 0.7938 (4) | 0.42684 (16) | 0.2695 (3) | 0.0284 (11) |
| H22  | 0.785239 | 0.423707 | 0.342916 | 0.034*       |
| C23  | 0.84640 (18) | 0.43743 (7) | −0.07653 (11) | 0.0872 (7) |
| C24  | 0.97624 (13) | 0.49547 (5) | 0.31098 (11) | 0.0546 (4) |
| Fe1  | 0.35555 (8) | 0.250000 | 0.250000 | 0.0188 (2)    |
| N2   | 0.4852 (3) | 0.30368 (12) | 0.2542 (2) | 0.0181 (8)    |
| N9   | 0.3518 (3) | 0.26658 (12) | 0.3953 (2) | 0.0186 (8)    |
| N10  | 0.2211 (3) | 0.20353 (12) | 0.2984 (3) | 0.0205 (8)    |
| N14  | 0.1893 (3) | 0.21100 (12) | 0.4017 (3) | 0.0211 (9)    |
| N16  | 0.5911 (3) | 0.36088 (13) | 0.3493 (3) | 0.0222 (9)    |
| N25  | 0.5611 (3) | 0.32899 (13) | 0.1872 (2) | 0.0211 (9)    |
| C27  | 0.7592 (6) | 0.4265 (2) | 0.5709 (4) | 0.0617 (18)   |
| H27A | 0.843547 | 0.421309 | 0.539590 | 0.093*       |
| H27B | 0.768395 | 0.430711 | 0.646444 | 0.093*       |
| H27C | 0.719871 | 0.456689 | 0.541131 | 0.093*       |
| O26  | 0.6821 (4) | 0.38493 (13) | 0.5506 (3) | 0.0541 (12)   |
Atomic displacement parameters (Å²)

|          | \(U_11\)  | \(U_{22}\)  | \(U_{33}\)  | \(U_{12}\)  | \(U_{13}\)  | \(U_{23}\)  |
|----------|------------|------------|------------|------------|------------|------------|
| C3       | 0.024 (3)  | 0.021 (2)  | 0.016 (2)  | 0.001 (2)  | −0.001 (2) | −0.0012 (18) |
| C4       | 0.019 (3)  | 0.026 (2)  | 0.017 (2)  | −0.003 (2) | 0.002 (2)  | −0.001 (2)  |
| C5       | 0.026 (3)  | 0.035 (3)  | 0.018 (2)  | −0.005 (2) | −0.002 (2) | 0.000 (2)   |
| C6       | 0.033 (3)  | 0.034 (3)  | 0.014 (2)  | −0.002 (2) | 0.000 (2)  | −0.004 (2)  |
| C7       | 0.024 (3)  | 0.029 (3)  | 0.019 (2)  | −0.003 (2) | 0.004 (2)  | −0.002 (2)  |
| C8       | 0.022 (3)  | 0.016 (2)  | 0.023 (2)  | 0.002 (2)  | 0.001 (2)  | −0.0016 (19) |
| C11      | 0.031 (3)  | 0.026 (2)  | 0.027 (3)  | −0.008 (2) | −0.006 (2) | −0.001 (2)  |
| C12      | 0.026 (3)  | 0.036 (3)  | 0.037 (3)  | −0.015 (2) | −0.003 (2) | 0.001 (2)   |
| C13      | 0.019 (3)  | 0.030 (3)  | 0.030 (3)  | −0.008 (2) | 0.003 (2)  | 0.008 (2)   |
| C15      | 0.026 (3)  | 0.018 (2)  | 0.024 (2)  | 0.003 (2)  | −0.001 (2) | 0.006 (2)   |
| C17      | 0.018 (3)  | 0.021 (2)  | 0.030 (3)  | 0.002 (2)  | 0.000 (2)  | 0.000 (2)   |
| C18      | 0.035 (3)  | 0.034 (3)  | 0.026 (3)  | −0.013 (2) | 0.002 (2)  | 0.002 (2)   |
| C19      | 0.047 (4)  | 0.045 (3)  | 0.030 (3)  | −0.012 (3) | 0.010 (3)  | 0.009 (3)   |
| C20      | 0.029 (3)  | 0.038 (3)  | 0.046 (3)  | −0.013 (3) | 0.008 (3)  | 0.011 (3)   |
| C21      | 0.028 (3)  | 0.022 (2)  | 0.043 (3)  | −0.004 (2) | 0.001 (2)  | −0.005 (2)  |
| C22      | 0.027 (3)  | 0.027 (3)  | 0.031 (3)  | −0.002 (2) | 0.000 (2)  | 0.005 (2)   |
| Cl23     | 0.1066 (15)| 0.1186 (15)| 0.0365 (9) | −0.0712 (13) | 0.0153 (10) | 0.0100 (9) |
| Cl24     | 0.0470 (9) | 0.0536 (9) | 0.0631 (10)| −0.0229 (8) | −0.0128 (8) | −0.0011 (7) |
| Fe1      | 0.0207 (5) | 0.0225 (5) | 0.0132 (4) | 0.000       | 0.000       | −0.0013 (4) |
| N2       | 0.019 (2)  | 0.0223 (18)| 0.0134 (18)| 0.0009 (16) | 0.0027 (17) | 0.0002 (16) |
| N9       | 0.021 (2)  | 0.0197 (19)| 0.0154 (18)| 0.0006 (17) | 0.0019 (17) | 0.0007 (15) |
| N10      | 0.020 (2)  | 0.022 (2)  | 0.019 (2)  | 0.0008 (17) | 0.0005 (17) | −0.0017 (16)|
| N14      | 0.022 (2)  | 0.025 (2)  | 0.016 (2)  | −0.0007 (18)| 0.0035 (17) | 0.0010 (16) |
| N16      | 0.022 (2)  | 0.027 (2)  | 0.017 (2)  | −0.0023 (18)| 0.0021 (17) | 0.0025 (17) |
| N25      | 0.023 (2)  | 0.022 (2)  | 0.019 (2)  | 0.0022 (18)| 0.0059 (17) | 0.0041 (16) |
| C27      | 0.071 (5)  | 0.062 (4)  | 0.053 (4)  | −0.024 (4)  | −0.001 (3)  | −0.019 (3)  |
| O26      | 0.073 (3)  | 0.059 (3)  | 0.030 (2)  | −0.036 (2)  | −0.008 (2)  | 0.001 (2)   |

Geometric parameters (Å, °)

|          | C3—C4 1.456 (5) | C3—N2 1.351 (5) | C3—N16 1.333 (5) | C4—C5 1.382 (5) | C4—N9 1.353 (5) | C5—H5 0.9500 | C5—C6 1.383 (6) | C6—H6 0.9500 | C6—C7 1.393 (5) | C7—H7 0.9500 | C7—C8 1.385 (5) | C8—N9 1.334 (5) | C8—N14 1.391 (5) |
|----------|-----------------|-----------------|------------------|-----------------|-----------------|--------------|-----------------|--------------|-----------------|--------------|-----------------|-----------------|------------------|
| Bond          | Length (Å) | Bond          | Length (Å) | Bond          | Length (Å) |
|--------------|-----------|--------------|-----------|--------------|-----------|
| C11—H11      | 0.9500    | Fe1—N9       | 1.916 (3) |               |           |
| C11—C12      | 1.400 (6) | Fe1—N10 i    | 1.973 (3) |               |           |
| C11—N10      | 1.315 (5) | Fe1—N10      | 1.973 (3) |               |           |
| C12—H12      | 0.9500    | N2—N25       | 1.350 (4) |               |           |
| C12—C13      | 1.366 (6) | N10—N14      | 1.381 (4) |               |           |
| C13—H13      | 0.9500    | C27—H27A     | 0.9800    |               |           |
| C13—N14      | 1.357 (5) | C27—H27B     | 0.9800    |               |           |
| C15—C17      | 1.468 (6) | C27—H27C     | 0.9800    |               |           |
| C15—N16      | 1.355 (5) | C27—O26      | 1.393 (6) |               |           |
| C15—N25      | 1.350 (5) | O26—H26      | 0.88 (5)  |               |           |
| C17—C18      | 1.387 (5) | N2—C3—C4     | 115.8 (4) | C20—C21—C22  | 121.4 (4) |
|              |           | N16—C3—C4   | 130.8 (4) | C20—C21—Cl24 | 119.1 (4) |
|              |           | N16—C3—N2   | 113.4 (4) | C22—C21—Cl24 | 119.5 (4) |
|              |           | C5—C4—C3    | 130.3 (4) | C17—C22—H22  | 120.0     |
|              |           | N9—C4—C3    | 109.2 (3) | C21—C22—C17  | 119.9 (4) |
|              |           | N9—C4—C5    | 120.5 (4) | C21—C22—H22  | 120.0     |
|              |           | C4—C5—H5    | 120.7     | N2 i—Fe1—N2  | 92.94 (18) |
|              |           | C4—C5—C6    | 118.6 (4) | N2 i—Fe1—N10 | 92.64 (13) |
|              |           | C6—C5—H5    | 120.7     | N2 i—Fe1—N10 | 159.46 (13) |
|              |           | C6—C6—H6    | 119.4     | N2—Fe1—N10 i | 92.64 (13) |
|              |           | C5—C6—C7    | 121.3 (4) | N2—Fe1—N10   | 159.46 (13) |
|              |           | C7—C6—H6    | 119.4     | N9 i—Fe1—N2  | 79.69 (14) |
|              |           | C6—C7—H7    | 121.8     | N9 i—Fe1—N2  | 101.95 (13) |
|              |           | C8—C7—C6    | 116.5 (4) | N9—Fe1—N2    | 79.68 (14) |
|              |           | C8—C7—H7    | 121.8     | N9—Fe1—N2 i  | 101.95 (13) |
|              |           | C7—C8—N14   | 125.5 (4) | N9 i—Fe1—N9  | 177.7 (2)  |
|              |           | N9—C8—C7    | 122.8 (4) | N9 i—Fe1—N10 | 79.82 (14) |
|              |           | N9—C8—N14   | 111.7 (3) | N9 i—Fe1—N10 | 98.49 (14) |
|              |           | C12—C11—H11 | 124.5     | N9—Fe1—N10   | 79.82 (14) |
|              |           | N10—C11—H11 | 124.5     | N9—Fe1—N10 i | 98.49 (14) |
|              |           | N10—C11—C12 | 111.1 (4) | N10—Fe1—N10  | 89.01 (19) |
|              |           | C11—C12—H12 | 127.0     | C3—N2—Fe1    | 114.8 (3) |
|              |           | C13—C12—C11 | 106.0 (4) | N25—N2—C3    | 106.6 (3) |
|              |           | C13—C12—H12 | 127.0     | N25—N2—Fe1   | 138.5 (3) |
|              |           | C12—C13—H13 | 126.6     | C4—N9—Fe1    | 120.5 (3) |
|              |           | N14—C13—C12 | 106.8 (4) | C8—N9—C4     | 120.3 (3) |
|              |           | N14—C13—H13 | 126.6     | C8—N9—Fe1    | 119.2 (3) |
|              |           | N16—C15—C17 | 124.0 (4) | C11—N10—Fe1  | 141.1 (3) |
|              |           | N25—C15—C17 | 122.0 (4) | C11—N10—N14  | 105.4 (3) |
|              |           | N25—C15—N16 | 114.0 (4) | N14—N10—Fe1  | 112.6 (2) |
|              |           | C18—C17—C15 | 121.2 (4) | C13—N14—C8   | 133.2 (4) |
|              |           | C18—C17—C22 | 118.6 (4) | C13—N14—N10  | 110.7 (3) |
|              |           | C22—C17—C15 | 120.2 (4) | N10—N14—C8   | 116.1 (3) |
|              |           | C17—C18—H18 | 119.8     | C3—N16—C15   | 101.3 (3) |
|              |           | C19—C18—C17 | 120.4 (4) | N2—N25—C15   | 104.7 (3) |
|              |           | C19—C18—H18 | 119.8     | H27A—C27—H27B| 109.5     |
C18—C19—C20 121.5 (4) H27A—C27—H27C 109.5
C18—C19—Cl23 119.0 (4) H27B—C27—H27C 109.5
C20—C19—Cl23 119.6 (4) O26—C27—H27A 109.5
C19—C20—H20 121.0 O26—C27—H27B 109.5
C21—C20—C19 118.1 (4) O26—C27—H27C 109.5
C21—C20—H20 121.0 C27—O26—H26 114 (4)

C3—C4—C5—C6 178.0 (4) C18—C17—C22—C21 1.4 (7)
C3—C4—N9—C8 −175.6 (3) C18—C19—C20—C21 1.7 (8)
C3—C4—N9—Fe1 1.7 (5) C19—C20—C21—C22 0.0 (7)
C3—N2—N25—C15 −0.3 (4) Cl23—C19—C20—C21 179.7 (4)
C4—C3—N2—Fe1 0.6 (5) C20—C21—C22—C17 −1.5 (7)
C4—C3—N2—N25 178.7 (3) C22—C17—C18—C19 0.2 (7)
C4—C3—N16—C15 −178.2 (4) C17—C15—C17—C18 −177.5 (4)
C4—C5—C6—C7 −0.5 (7) C15—C17—C18—C19 1.4 (7)
C5—C4—N9—C8 3.9 (6) Fe1—N2—N25—C15 177.2 (3)
C5—C4—N9—Fe1 −178.7 (3) Fe1—N10—N14—C8 −8.8 (4)
C5—C6—C7—C8 0.2 (6) Fe1—N10—N14—C13 170.2 (3)
C6—C7—C8—N9 2.3 (6) N2—C3—C4—C5 179.1 (4)
C6—C7—C8—N14 −177.8 (4) N2—C3—C4—N9 −1.4 (5)
C7—C8—N9—C4 −4.4 (6) N2—C3—N16—C15 0.2 (4)
C7—C8—N9—Fe1 178.2 (3) N9—C4—C5—C6 −1.5 (6)
C7—C8—N14—C13 8.4 (7) N9—C4—C5—C6 −2.5 (8)
C7—C8—N14—N10 −173.0 (4) N9—C8—N14—C13 −171.8 (4)
C11—C12—C13—N14 −0.3 (5) N9—C8—N14—N10 6.9 (5)
C11—C12—C13—N14 179.7 (3) N10—C11—C12—C13 −172.0 (4)
C11—N10—N14—C8 −1.3 (4) N10—C11—C12—C13 −0.1 (5)
C12—C11—N14—C8 −166.3 (3) N10—C11—C12—C13 179.7 (3)
C12—C11—N14—N10 1.1 (5) N10—C11—C12—C13 −171.8 (4)
C12—C13—N14—C8 179.7 (4) N16—C15—C17—C18 −172.0 (4)
C12—C13—N14—N10 1.0 (5) N16—C15—C17—C18 10.3 (6)
C15—C17—C18—C19 −177.5 (4) N16—C15—C17—C18 −168.7 (4)
C15—C17—C22—C21 179.1 (4) N16—C15—C17—C18 8.9 (6)
C17—C15—N16—C3 −179.5 (4) N25—C15—C17—C18 0.5 (5)
C17—C15—N25—N2 179.6 (3) N25—C15—C17—C18 162 (6)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H  | H···A | D···A  | D—H···A |
|---------|------|-------|-------|--------|
| C5—H5···O26 | 0.95 | 2.41  | 3.256 (6) | 149 |
| C7—H7···N25i | 0.95 | 2.48  | 3.406 (5) | 165 |
| C11—H11···O26ii | 0.95 | 2.23  | 3.144 (6) | 162 |
| C13—H13···N25ii | 0.95 | 2.52  | 3.363 (6) | 148 |

Symmetry code: (i) x, −y+1/2, −z+1/2.

Hydrogen-bond geometry (Å, °)
### sup-6

|                      | d (Å) | r (Å)  | D (Å)     | θ (°)  |
|----------------------|-------|--------|-----------|--------|
| C20—H20···Cl23\(^{ii}\) | 0.95  | 2.86   | 3.779 (5) | 162    |
| O26—H26···N16        | 0.88 (5) | 1.96 (5) | 2.826 (5) | 166 (5) |

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