

# Crystal structure of *fac*-bis[bis(pyridin-2-yl)methanamine]iron(II) 1,1,3,3-tetracyano-2-(dicyanomethylidene)propane-1,3-diide, [Fe(dipa)<sub>2</sub>](tcpd)

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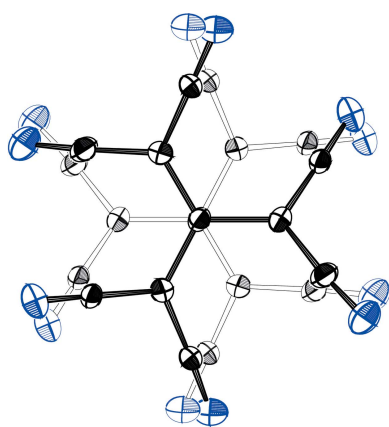
In the title compound, [Fe(C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>)<sub>2</sub>](C<sub>10</sub>N<sub>6</sub>), the Fe<sup>II</sup> cation is coordinated by two bis(pyridin-2-yl)methanamine (dipa) ligands and has crystallographic twofold symmetry. There are deviations from ideal octahedral geometry due to the steric requirements of the ligands. The polynitrile 1,1,3,3-tetracyano-2-(dicyanomethylidene)propane-1,3-diide (tcpd<sup>2-</sup>) dianion is disordered about an inversion center and is not coordinated to the Fe atom. The anion is not planar but has a propeller shape. In the crystal, weak N—H...N interactions between the amine H atoms of the dipa ligands and two nitrile groups of the anion form an alternating chain of cations and anions related by the *C*-centering of the unit cell.

## 1. Chemical context

Polynitrile anions have recently received considerable attention in the fields of coordination chemistry and molecular materials (Benmansour *et al.*, 2010). These organic anions are of interest for their ability to act towards metal centers with various coordination modes and for their high degree of electronic delocalization (Miyazaki *et al.*, 2003; Benmansour *et al.*, 2008; Yuste *et al.*, 2009; Atmani *et al.*, 2008; Karpov *et al.*, 2018). We are interested in using these anionic ligands in combination with other neutral bridging coligands to explore their structural features and properties relevant to the field of molecular materials exhibiting the spin-crossover (SCO) phenomenon (Setifi *et al.*, 2014; Dupouy *et al.*, 2009). In an attempt to prepare such an iron(II) complex using solvo-thermal synthesis, we obtained instead the title compound *fac*-bis[bis(pyridin-2-yl)methanamine]iron(II) 1,1,3,3-tetracyano-2-(dicyanomethylidene)propane-1,3-diide, [Fe(dipa)<sub>2</sub>](tcpd).

## 2. Structural commentary

The structure is built from Fe<sup>II</sup> cations coordinated by two bis(pyridin-2-yl)methanamine (C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>; dipa) ligands, and 1,1,3,3-tetracyano-2-(dicyanomethylidene)propane-1,3-diide (C<sub>10</sub>N<sub>6</sub><sup>2-</sup>; tcpd<sup>2-</sup>) anions. The Fe atom lies on a twofold axis, with its coordinated dipa ligands related by the twofold axis (Fig. 1). The anion lies on an inversion center and is disordered. Detailed geometry of the anion was extracted as

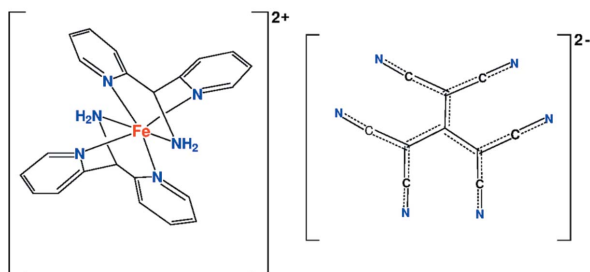


**Table 1**  
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H12···N25	0.88 (2)	2.12 (3)	2.950 (13)	156.9 (19)
N2—H13···N27 <sup>i</sup>	0.90 (2)	2.64 (2)	3.459 (8)	151.1 (17)
N2—H13···N28 <sup>i</sup>	0.90 (2)	2.61 (2)	3.138 (11)	118.2 (16)
C6—H6···N25 <sup>ii</sup>	1.00	2.47	3.129 (13)	123
C6—H6···N28 <sup>i</sup>	1.00	2.41	2.986 (13)	116

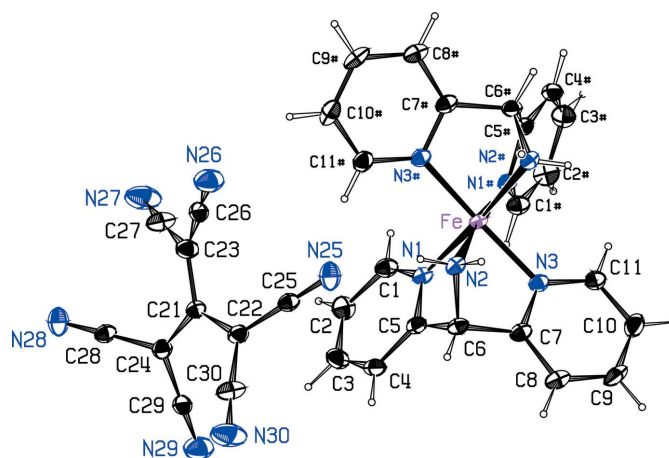
Symmetry codes: (i)  $x - \frac{1}{2}, y + \frac{1}{2}, z$ ; (ii)  $-x + 1, -y + 1, -z + 1$ .

described below. The dipa ligand coordinates the Fe atom through the central amino N atom and the two pyridinium N atoms in a *fac* arrangement. The dipa ligand assumes the butterfly conformation found previously (Setifi *et al.*, 2017), with an approximate mirror plane bisecting the ligand, and the pyridine rings are at an angle of 56.66 (6)° to each other. Fe—N distances to the pyridine N atoms average 1.959 (1) Å, slightly shorter than the Fe—N distance of 2.004 (2) Å to the amine group. The five-membered chelate ring angles at the Fe atom are 80.10 (6) and 81.55 (6)°, while the butterfly angle N1—Fe—N3 is 90.10 (6)°. The two independent *trans* angles at Fe in the octahedrally coordinated Fe atom are 172.75 (9) and 174.61 (6)°. Otherwise, bond lengths and angles within the ligand are as expected. The tcpd<sup>2-</sup> anion, which is disordered about a crystallographic inversion center, is propeller-shaped, with approximate C<sub>3</sub> symmetry, and a geometry similar to that described previously by Setifi *et al.* (2015). The C(CN)<sub>2</sub> planes are tilted by 31.1 (5), 24.7 (4), and 30.0 (5)° with respect to the C21—C24 central plane. The C—C distances average 1.414 (18) Å, indicative of the *sp*<sup>2</sup> hybridization of all the C atoms. The average C—N distance in the CN groups is 1.154 (11) Å.



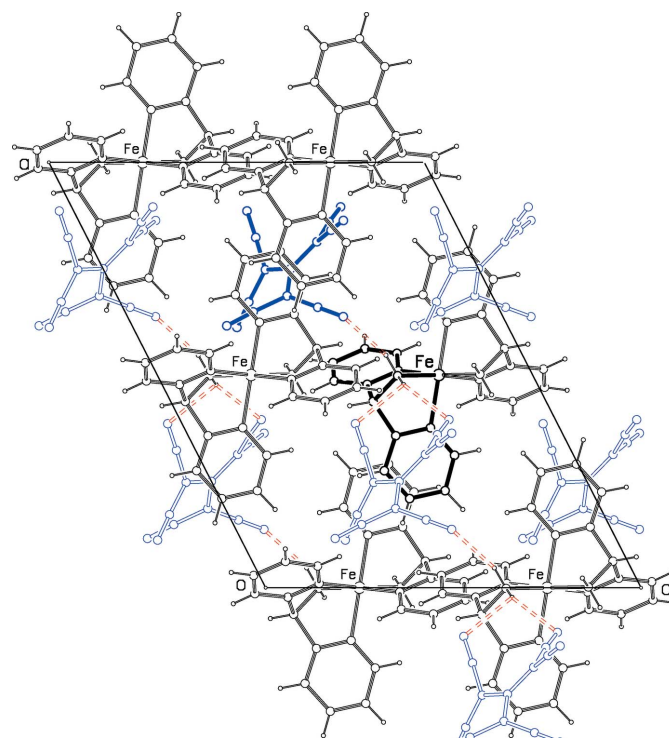
### 3. Supramolecular features

Fig. 2 shows the packing of the crystal structure. The cations stack along the *b*-axis direction in columns related by the glide planes and the *C*-centering. The N3/C7—C11 pyridine ring lies almost perpendicular to the *b* axis and partially overlaps the parallel ring related by the center of symmetry at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ . The planes of these pyridine rings are 3.442 (1) Å apart. The anion is disordered about a center of symmetry displaced by *b*/2 from the center of these pyridine rings. Fig. 2 shows the interactions between the amine H atoms and the CN groups. There is an N2—H12···N25 hydrogen bond, with N···N = 2.95 (1) Å and N—H···N = 157.1 (2)° (Table 1). The weaker



**Figure 1**  
The [Fe(dipa<sub>2</sub>)]<sup>2+</sup> cation and tcpd<sup>2-</sup> anion in the title compound. Atoms in the cation with the # suffix are related to the asymmetric unit by  $(1 - x, y, \frac{3}{2} - z)$ . Only one orientation of the disordered anion is shown. Displacement ellipsoids are drawn at the probability 50% level.

interactions N2—H13···N27( $x - \frac{1}{2}, y + \frac{1}{2}, z$ ) and N2—H13···N28( $x - \frac{1}{2}, y + \frac{1}{2}, z$ ) link the cations and anions into alternating chains along [1 $\bar{1}$ 0]. Possible interactions between CN groups and atom H6 are also listed in Table 1. Other short interactions are C6···N28( $x - \frac{1}{2}, \frac{1}{2} + y, z$ ) of 2.99 Å and C5···N28( $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$ ) of 3.11 Å.



**Figure 2**  
Projection of the structure down the *b* axis, with weak N—H···N interactions shown as dashed orange bonds. Only one disorder mate for the anion is shown. Cations have more solid bonds. The asymmetric unit is shown in bold.

#### 4. Database survey

A search for the  $\text{tcpd}^{2-}$  anion in the Cambridge Structural Database (CSD, Version of 2017; Groom *et al.*, 2016) produced 49 hits for structures with atomic coordinates available. We selected 20 of these hits for analysis, not using 23 variable-temperature studies and six with disordered  $\text{tcpd}^{2-}$  anions for which detailed parameters were not available. In nine of the 20 studies, the anion was present in an uncoordinated form, and in the rest, it was coordinated to a first-row transition metal. The bond lengths in the 20 structures analyzed were quite consistent, with sample deviations of 0.013 Å. The two types of C–C distances have the same average shortened distance of 1.417 (1) Å, and the  $\text{C}\equiv\text{N}$  bond lengths average 1.147 (1) Å, showing the same trends as in the present structure. In all cases, the anion as a whole was nonplanar, with each  $\text{C}(\text{CN})_2$  group twisted in the same direction relative to the central four-atom plane, with an average twist angle of 24.4 (7)°. Presumably, this minimizes repulsion between the N atoms, which carry a partial negative charge. The average twist angle is the same, regardless of whether the anion is coordinated. In an individual structure, the twist angles were invariably scattered, with the average minimum twist angle some 67% of the average maximum twist angle. The twist angles for  $\text{tcpd}^{2-}$  in the present structure average 28.6 (3)°, higher than the average twist angle in any of the nine free anions reviewed in the CSD.

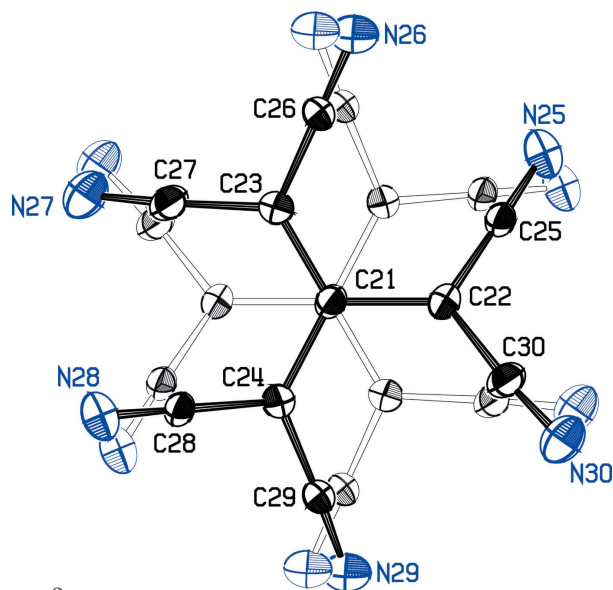
A search for the dipa ligand yielded nine hits, with one, two, or three dipa molecules coordinated to transition-metal atoms in all cases. There were only three instances of dipa coordinated to an Fe atom, including Setifi *et al.* (2017).

#### 5. Synthesis and crystallization

The title compound was synthesized solvothermally under autogenous pressure from a mixture of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (28 mg, 0.1 mmol), dipa (19 mg, 0.1 mmol) and  $\text{K}_2\text{tcpd}$  (28 mg, 0.1 mmol) in water–ethanol (4:1 *v/v*, 20 ml). This mixture was sealed in a Teflon-lined autoclave and held at 423 K for 3 d, and then cooled to room temperature at a rate of 10 K  $\text{h}^{-1}$  (yield 23%). Red blocks of the title compound suitable for single-crystal X-ray diffraction were selected directly from the synthesized product.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The  $\text{tcpd}^{2-}$  anion lies on an inversion center, which requires the anion to be disordered. The three C atoms bonded to the central C21 atom are easily resolved from their centrosymmetric equivalents, but the six CN groups are close enough to a centric array that the disorder mates are not resolved in a difference map. Indeed, a preliminary refinement that constrained the cyanide C and N atoms to centrically related positions converged successfully. This treatment led to unreasonable  $\text{C}-\text{C}\equiv\text{N}$  bond angles, however, and hindered a detailed analysis of the anion



**Figure 3**  
The  $\text{tcpd}^{2-}$  anion structure superimposed on its disorder mate related by  $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$ . Atom C21 lies on the center of symmetry at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ .

geometry. Scrutiny of a model indicated that while the cyanide C atoms might be very close to their centric counterparts, the cyanide N atoms ought to lie far enough apart to refine separately. Accordingly, the positions for the N atoms were calculated manually, assuming linear  $\text{C}-\text{C}\equiv\text{N}$  bonding and typical C–C and  $\text{C}\equiv\text{N}$  distances. The complete anion could then be refined by tightly restricting differences from three-fold symmetry in chemically equivalent C–C distances and C–C–C angles, and refining the C and N atoms first isotropically and then anisotropically. At this point, cyanide C atoms had moved an average of 0.4 Å from their centric images, and cyanide N atoms were at an average distance of 0.5 Å from their images (Fig. 3). The restraints could now be removed for the final refinements, except that displacement parameters for nitrile groups 25–27 were constrained to be the same as those for nitrile groups 28–30, and a restraint on the anisotropy of C atoms 25–30 was added *via* an ISOR instruction. In a separate refinement, the coordinates of the cyanide C atoms were arbitrarily moved small amounts before the restrained refinements, but the same final structure was obtained. C-bound H atoms were constrained to idealized positions, with C–H distances of 1.00 Å for the CH group and 0.95 Å for aromatic H atoms, and with *U* values set at 1.2 times the  $U_{\text{iso}}$  value of their bonded atoms. The positions of the amino H atoms were refined independently, although their final positions are very close to what would have been predicted. Their *U* values were set at 1.5 times the  $U_{\text{iso}}$  value for N2. We also explored refinements in the space group *Cc*, which would not force disorder on the anion model, nor impose twofold symmetry on the cation. Although the noncentric model refined smoothly, it was abandoned because some of the displacement ellipsoids were unreasonable and convergence occurred at  $R_1 = 0.043$  and  $wR = 0.109$ , values higher than in our final centric model, even though many more variables were refined in the noncentric model.

### Acknowledgements

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Table 2

Experimental details.

Crystal data	
Chemical formula	[Fe(C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> ) <sub>2</sub> ](C <sub>10</sub> N <sub>6</sub> )
<i>M<sub>r</sub></i>	630.46
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	162
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.5394 (7), 13.5094 (7), 13.7913 (6)
$\beta$ (°)	117.006 (3)
<i>V</i> (Å <sup>3</sup> )	2911.5 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.56
Crystal size (mm)	0.39 × 0.20 × 0.02
Data collection	
Diffractionmeter	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.667, 0.746
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	11328, 3227, 2623
<i>R</i> <sub>int</sub>	0.035
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.642
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.036, 0.085, 1.04
No. of reflections	3227
No. of parameters	243
No. of restraints	18
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.31, -0.42

Computer programs: *APEX2* and *SAINTE* (Bruker, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2017* (Sheldrick, 2015), *ORTEP III* (Burnett & Johnson, 1996) and *publCIF* (Westrip, 2010).

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## supporting information

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### Computing details

Data collection: *APEX2* (Bruker, 2015); cell refinement: *SAINTE* (Bruker, 2015); data reduction: *SAINTE* (Bruker, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015); molecular graphics: *ORTEP3* (Burnett & Johnson, 1996); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

### *fac*-Bis[bis(pyridin-2-yl)methanamine]iron(II) 1,1,3,3-tetracyano-2-(dicyanomethylene)propane-1,3-diide, [Fe(dipa)<sub>2</sub>](tcpd)

#### Crystal data

[Fe(C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>)<sub>2</sub>](C<sub>10</sub>N<sub>6</sub>)  
*M<sub>r</sub>* = 630.46  
 Monoclinic, *C2/c*  
*a* = 17.5394 (7) Å  
*b* = 13.5094 (7) Å  
*c* = 13.7913 (6) Å  
 $\beta$  = 117.006 (3)°  
*V* = 2911.5 (2) Å<sup>3</sup>  
*Z* = 4

*F*(000) = 1296  
*D<sub>x</sub>* = 1.438 Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 3760 reflections  
 $\theta$  = 2.2–27.1°  
 $\mu$  = 0.56 mm<sup>-1</sup>  
*T* = 162 K  
 Plate, red  
 0.39 × 0.20 × 0.02 mm

#### Data collection

Bruker APEXII CCD  
 diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2015)  
*T<sub>min</sub>* = 0.667, *T<sub>max</sub>* = 0.746  
 11328 measured reflections

3227 independent reflections  
 2623 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.035  
 $\theta_{\max}$  = 27.1°,  $\theta_{\min}$  = 2.0°  
*h* = -22→22  
*k* = -17→17  
*l* = -17→17

#### Refinement

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036  
*wR*(*F*<sup>2</sup>) = 0.085  
*S* = 1.03  
 3227 reflections  
 243 parameters  
 18 restraints

Primary atom site location: structure-invariant  
 direct methods  
 Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 2.4992P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Fe	0.500000	0.33107 (3)	0.750000	0.01516 (11)	
N1	0.51003 (9)	0.23776 (11)	0.64840 (12)	0.0171 (3)	
N2	0.49834 (10)	0.42852 (12)	0.63946 (12)	0.0182 (3)	
H12	0.5465 (14)	0.4381 (15)	0.6361 (17)	0.027*	
H13	0.4774 (13)	0.4883 (16)	0.6433 (16)	0.027*	
N3	0.37599 (9)	0.34028 (11)	0.65615 (12)	0.0178 (3)	
C1	0.55086 (12)	0.15040 (13)	0.66787 (15)	0.0220 (4)	
H1	0.573114	0.122972	0.738919	0.026*	
C2	0.56168 (13)	0.09904 (15)	0.58871 (16)	0.0271 (4)	
H2	0.591205	0.037572	0.605156	0.032*	
C3	0.52888 (13)	0.13836 (15)	0.48477 (16)	0.0269 (4)	
H3	0.535829	0.104295	0.429038	0.032*	
C4	0.48589 (11)	0.22779 (14)	0.46310 (15)	0.0223 (4)	
H4	0.462349	0.255803	0.392230	0.027*	
C5	0.47789 (11)	0.27554 (13)	0.54654 (14)	0.0185 (4)	
C6	0.43762 (11)	0.37540 (13)	0.53883 (14)	0.0190 (4)	
H6	0.427589	0.411685	0.470869	0.023*	
C7	0.35729 (11)	0.36624 (13)	0.55295 (15)	0.0194 (4)	
C8	0.27498 (12)	0.38700 (14)	0.47501 (16)	0.0246 (4)	
H8	0.263606	0.403702	0.402782	0.030*	
C9	0.20953 (12)	0.38291 (15)	0.50458 (17)	0.0287 (5)	
H9	0.152425	0.397943	0.453107	0.034*	
C10	0.22812 (12)	0.35672 (15)	0.60976 (17)	0.0288 (5)	
H10	0.183929	0.353757	0.631450	0.035*	
C11	0.31139 (11)	0.33492 (14)	0.68303 (15)	0.0225 (4)	
H11	0.323508	0.315486	0.754795	0.027*	
C21	0.750000	0.250000	0.500000	0.0192 (5)	
C22	0.6860 (2)	0.3267 (3)	0.4533 (3)	0.0222 (8)	0.5
C23	0.8132 (2)	0.2577 (3)	0.6062 (3)	0.0238 (8)	0.5
C24	0.7474 (2)	0.1695 (3)	0.4309 (3)	0.0208 (7)	0.5
C25	0.6592 (6)	0.3810 (9)	0.5196 (6)	0.0197 (11)	0.5
C26	0.8404 (9)	0.3491 (10)	0.6596 (15)	0.0225 (16)	0.5
C27	0.8597 (9)	0.1729 (6)	0.6652 (11)	0.0289 (14)	0.5
C28	0.8232 (6)	0.1203 (9)	0.4490 (6)	0.0197 (11)	0.5
C29	0.6717 (9)	0.1319 (10)	0.3432 (15)	0.0225 (16)	0.5
C30	0.6485 (9)	0.3540 (6)	0.3413 (12)	0.0289 (14)	0.5
N25	0.6372 (6)	0.4221 (10)	0.5748 (6)	0.0298 (14)	0.5
N26	0.8632 (6)	0.4253 (8)	0.7055 (10)	0.0391 (14)	0.5

N27	0.8951 (7)	0.1069 (8)	0.7166 (6)	0.0490 (14)	0.5
N28	0.8855 (6)	0.0826 (10)	0.4618 (6)	0.0298 (14)	0.5
N29	0.6118 (6)	0.0972 (8)	0.2768 (10)	0.0391 (14)	0.5
N30	0.6157 (7)	0.3822 (8)	0.2521 (6)	0.0490 (14)	0.5

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Fe	0.01275 (17)	0.01604 (19)	0.01247 (18)	0.000	0.00205 (14)	0.000
N1	0.0157 (7)	0.0164 (8)	0.0154 (7)	−0.0002 (6)	0.0038 (6)	0.0006 (6)
N2	0.0149 (7)	0.0163 (8)	0.0201 (8)	0.0001 (6)	0.0051 (6)	0.0007 (6)
N3	0.0170 (7)	0.0163 (8)	0.0173 (7)	−0.0017 (6)	0.0052 (6)	−0.0021 (6)
C1	0.0228 (9)	0.0191 (10)	0.0199 (10)	0.0015 (7)	0.0059 (8)	0.0015 (7)
C2	0.0305 (10)	0.0196 (10)	0.0291 (11)	0.0035 (8)	0.0117 (9)	−0.0027 (8)
C3	0.0300 (10)	0.0281 (11)	0.0233 (10)	−0.0040 (9)	0.0126 (9)	−0.0089 (8)
C4	0.0215 (9)	0.0268 (10)	0.0150 (9)	−0.0046 (8)	0.0051 (8)	−0.0006 (8)
C5	0.0150 (8)	0.0206 (10)	0.0166 (9)	−0.0029 (7)	0.0044 (7)	0.0009 (7)
C6	0.0178 (9)	0.0196 (9)	0.0148 (9)	0.0005 (7)	0.0034 (7)	0.0033 (7)
C7	0.0182 (8)	0.0149 (9)	0.0197 (9)	−0.0008 (7)	0.0040 (7)	−0.0009 (7)
C8	0.0203 (9)	0.0222 (10)	0.0215 (10)	−0.0004 (8)	0.0008 (8)	0.0004 (8)
C9	0.0136 (9)	0.0295 (11)	0.0303 (11)	0.0001 (8)	−0.0013 (8)	−0.0044 (9)
C10	0.0172 (9)	0.0325 (12)	0.0349 (12)	−0.0035 (8)	0.0102 (9)	−0.0087 (9)
C11	0.0194 (9)	0.0246 (10)	0.0215 (9)	−0.0048 (8)	0.0076 (8)	−0.0056 (8)
C21	0.0173 (12)	0.0220 (14)	0.0160 (13)	0.0025 (10)	0.0057 (10)	0.0021 (10)
C22	0.0199 (17)	0.0241 (19)	0.0181 (18)	0.0045 (16)	0.0048 (15)	0.0017 (16)
C23	0.0263 (19)	0.021 (2)	0.0196 (19)	0.0034 (16)	0.0066 (16)	−0.0027 (15)
C24	0.0195 (17)	0.0201 (18)	0.0204 (18)	0.0023 (15)	0.0069 (15)	−0.0019 (15)
C25	0.019 (3)	0.0175 (10)	0.018 (3)	0.002 (2)	0.005 (3)	0.002 (3)
C26	0.022 (3)	0.024 (4)	0.0198 (12)	0.006 (3)	0.008 (2)	−0.003 (3)
C27	0.029 (2)	0.023 (4)	0.0211 (16)	−0.001 (3)	−0.0001 (15)	0.000 (3)
C28	0.019 (3)	0.0175 (10)	0.018 (3)	0.002 (2)	0.005 (3)	0.002 (3)
C29	0.022 (3)	0.024 (4)	0.0198 (12)	0.006 (3)	0.008 (2)	−0.003 (3)
C30	0.029 (2)	0.023 (4)	0.0211 (16)	−0.001 (3)	−0.0001 (15)	0.000 (3)
N25	0.031 (4)	0.0234 (15)	0.041 (5)	0.004 (3)	0.021 (3)	0.002 (4)
N26	0.040 (5)	0.035 (5)	0.032 (4)	−0.001 (3)	0.008 (4)	−0.010 (3)
N27	0.063 (3)	0.045 (2)	0.024 (4)	0.0162 (19)	0.007 (3)	0.009 (3)
N28	0.031 (4)	0.0234 (15)	0.041 (5)	0.004 (3)	0.021 (3)	0.002 (4)
N29	0.040 (5)	0.035 (5)	0.032 (4)	−0.001 (3)	0.008 (4)	−0.010 (3)
N30	0.063 (3)	0.045 (2)	0.024 (4)	0.0162 (19)	0.007 (3)	0.009 (3)

*Geometric parameters (Å, °)*

Fe—N1 <sup>i</sup>	1.9512 (15)	C7—C8	1.382 (2)
Fe—N1	1.9512 (15)	C8—C9	1.383 (3)
Fe—N3 <sup>i</sup>	1.9659 (14)	C8—H8	0.9500
Fe—N3	1.9659 (14)	C9—C10	1.381 (3)
Fe—N2 <sup>i</sup>	2.0042 (16)	C9—H9	0.9500
Fe—N2	2.0043 (16)	C10—C11	1.379 (3)

N1—C1	1.343 (2)	C10—H10	0.9500
N1—C5	1.354 (2)	C11—H11	0.9500
N2—C6	1.494 (2)	C21—C23	1.383 (4)
N2—H12	0.88 (2)	C21—C24	1.433 (4)
N2—H13	0.90 (2)	C21—C22	1.447 (4)
N3—C11	1.345 (2)	C22—C25	1.408 (12)
N3—C7	1.354 (2)	C22—C30	1.425 (15)
C1—C2	1.377 (3)	C23—C26	1.406 (14)
C1—H1	0.9500	C23—C27	1.427 (11)
C2—C3	1.385 (3)	C24—C28	1.403 (11)
C2—H2	0.9500	C24—C29	1.424 (15)
C3—C4	1.383 (3)	C25—N25	1.143 (18)
C3—H3	0.9500	C26—N26	1.18 (2)
C4—C5	1.381 (3)	C27—N27	1.133 (15)
C4—H4	0.9500	C28—N28	1.145 (18)
C5—C6	1.504 (3)	C29—N29	1.13 (2)
C6—C7	1.512 (2)	C30—N30	1.161 (16)
C6—H6	1.0000		
N1 <sup>i</sup> —Fe—N1	99.51 (9)	C4—C5—C6	125.61 (16)
N1 <sup>i</sup> —Fe—N3 <sup>i</sup>	90.09 (6)	N2—C6—C5	104.56 (14)
N1—Fe—N3 <sup>i</sup>	94.59 (6)	N2—C6—C7	103.44 (14)
N1 <sup>i</sup> —Fe—N3	94.59 (6)	C5—C6—C7	110.64 (15)
N1—Fe—N3	90.09 (6)	N2—C6—H6	112.5
N3 <sup>i</sup> —Fe—N3	172.75 (9)	C5—C6—H6	112.5
N1 <sup>i</sup> —Fe—N2 <sup>i</sup>	81.55 (6)	C7—C6—H6	112.5
N1—Fe—N2 <sup>i</sup>	174.61 (6)	N3—C7—C8	122.63 (17)
N3 <sup>i</sup> —Fe—N2 <sup>i</sup>	80.10 (6)	N3—C7—C6	111.19 (15)
N3—Fe—N2 <sup>i</sup>	95.10 (6)	C8—C7—C6	126.07 (17)
N1 <sup>i</sup> —Fe—N2	174.61 (6)	C7—C8—C9	118.46 (18)
N1—Fe—N2	81.55 (6)	C7—C8—H8	120.8
N3 <sup>i</sup> —Fe—N2	95.10 (6)	C9—C8—H8	120.8
N3—Fe—N2	80.10 (6)	C10—C9—C8	119.23 (17)
N2 <sup>i</sup> —Fe—N2	97.89 (9)	C10—C9—H9	120.4
C1—N1—C5	118.15 (16)	C8—C9—H9	120.4
C1—N1—Fe	129.65 (13)	C11—C10—C9	119.42 (18)
C5—N1—Fe	111.76 (12)	C11—C10—H10	120.3
C6—N2—Fe	98.58 (11)	C9—C10—H10	120.3
C6—N2—H12	108.6 (14)	N3—C11—C10	122.08 (18)
Fe—N2—H12	117.1 (14)	N3—C11—H11	119.0
C6—N2—H13	110.4 (13)	C10—C11—H11	119.0
Fe—N2—H13	114.2 (13)	C23—C21—C24	122.0 (2)
H12—N2—H13	107.5 (19)	C23—C21—C22	120.3 (2)
C11—N3—C7	118.15 (15)	C24—C21—C22	117.6 (2)
C11—N3—Fe	129.34 (13)	C25—C22—C30	116.3 (7)
C7—N3—Fe	112.09 (11)	C25—C22—C21	120.3 (4)
N1—C1—C2	122.49 (17)	C30—C22—C21	123.4 (6)
N1—C1—H1	118.8	C21—C23—C26	122.6 (7)



C2—C1—H1	118.8	C21—C23—C27	121.3 (5)
C1—C2—C3	119.01 (18)	C26—C23—C27	115.9 (8)
C1—C2—H2	120.5	C28—C24—C29	115.2 (7)
C3—C2—H2	120.5	C28—C24—C21	120.0 (4)
C4—C3—C2	119.21 (18)	C29—C24—C21	124.8 (6)
C4—C3—H3	120.4	N25—C25—C22	177.7 (12)
C2—C3—H3	120.4	N26—C26—C23	179.2 (19)
C5—C4—C3	118.67 (17)	N27—C27—C23	176.0 (16)
C5—C4—H4	120.7	N28—C28—C24	177.7 (12)
C3—C4—H4	120.7	N29—C29—C24	176.1 (17)
N1—C5—C4	122.46 (17)	N30—C30—C22	175.0 (12)
N1—C5—C6	111.87 (15)		
C5—N1—C1—C2	0.6 (3)	C5—C6—C7—N3	68.77 (19)
Fe—N1—C1—C2	-171.08 (14)	N2—C6—C7—C8	133.42 (18)
N1—C1—C2—C3	-0.4 (3)	C5—C6—C7—C8	-115.1 (2)
C1—C2—C3—C4	-0.3 (3)	N3—C7—C8—C9	1.3 (3)
C2—C3—C4—C5	0.7 (3)	C6—C7—C8—C9	-174.40 (18)
C1—N1—C5—C4	-0.2 (3)	C7—C8—C9—C10	-1.1 (3)
Fe—N1—C5—C4	172.93 (14)	C8—C9—C10—C11	-0.2 (3)
C1—N1—C5—C6	-177.48 (15)	C7—N3—C11—C10	-1.2 (3)
Fe—N1—C5—C6	-4.33 (17)	Fe—N3—C11—C10	170.60 (14)
C3—C4—C5—N1	-0.4 (3)	C9—C10—C11—N3	1.4 (3)
C3—C4—C5—C6	176.44 (16)	C23—C21—C22—C25	-31.1 (7)
Fe—N2—C6—C5	-56.76 (13)	C24—C21—C22—C25	151.7 (6)
Fe—N2—C6—C7	59.12 (13)	C23—C21—C22—C30	147.0 (6)
N1—C5—C6—N2	42.55 (18)	C24—C21—C22—C30	-30.2 (7)
C4—C5—C6—N2	-134.61 (18)	C24—C21—C23—C26	151.9 (9)
N1—C5—C6—C7	-68.22 (19)	C22—C21—C23—C26	-25.2 (10)
C4—C5—C6—C7	114.62 (19)	C24—C21—C23—C27	-22.8 (9)
C11—N3—C7—C8	-0.1 (3)	C22—C21—C23—C27	160.1 (8)
Fe—N3—C7—C8	-173.35 (14)	C23—C21—C24—C28	-26.7 (6)
C11—N3—C7—C6	176.15 (15)	C22—C21—C24—C28	150.5 (6)
Fe—N3—C7—C6	2.94 (18)	C23—C21—C24—C29	152.0 (10)
N2—C6—C7—N3	-42.71 (18)	C22—C21—C24—C29	-30.9 (10)

Symmetry code: (i)  $-x+1, y, -z+3/2$ .

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H12 $\cdots$ N25	0.88 (2)	2.12 (3)	2.950 (13)	156.9 (19)
N2—H13 $\cdots$ N27 <sup>ii</sup>	0.90 (2)	2.64 (2)	3.459 (8)	151.1 (17)
N2—H13 $\cdots$ N28 <sup>ii</sup>	0.90 (2)	2.61 (2)	3.138 (11)	118.2 (16)
C6—H6 $\cdots$ N25 <sup>iii</sup>	1.00	2.47	3.129 (13)	123
C6—H6 $\cdots$ N28 <sup>ii</sup>	1.00	2.41	2.986 (13)	116

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