Crystal structure of a low-spin poly[di-μ₃-cyanido-di-μ₂-cyanido-bis(μ₂-2-ethylpyrazine)dicopper(I)-iron(II)]

Sofiia V. Partsevska,[a]* Dina D. Naumova,[a] Igor P. Matushko,[a] Olesia I. Kucheriv[a,b] and Il'ya A. Gural'skiy[a,b]

[a]Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska St 64, Kyiv 01601, Ukraine, and [b]UkrOrgSyntez Ltd, Chervonotkatska St 67, Kyiv 02094, Ukraine. *Correspondence e-mail: sofiia.partsevska@univ.kiev.ua

In the title metal–organic framework, $[Fe(C_6H_8N_2)_2\{Cu(CN)_2\}_2]_n$, the low-spin Fe^{II} ion lies at an inversion centre and displays an elongated octahedral $[FeN_6]$ coordination environment. The axial positions are occupied by two symmetry-related bridging 2-ethylpyrazine ligands, while the equatorial positions are occupied by four N atoms of two pairs of symmetry-related cyanide groups. The Cu^I centre is coordinated by three cyanide carbon atoms and one N atom of a bridging 2-ethylpyrazine molecule, which form a tetrahedral coordination environment. Two neighbouring Cu atoms have a short $Cu\cdots Cu$ contact [2.4662 (7) Å] and their coordination tetrahedra are connected through a common edge between two C atoms of cyanide groups. Each $Cu_2(CN)_2$ unit, formed by two neighbouring Cu atoms bridged by two carbons from a pair of μ-CN groups, is connected to six Fe^{II} centres via two bridging 2-ethylpyrazine molecules and four cyanide groups, resulting in the formation of a polymeric three-dimensional metal–organic coordination framework.

1. Chemical context

The phenomenon of spin crossover (SCO) occurs in some metal complexes where the spin state of a compound changes as a result of the influence of external stimuli (temperature, pressure, light irradiation, magnetic field etc.) (Gütlich & Goodwin, 2004). Analogues of Hofmann clathrates (Hofmann & Höchtlen, 1903) are the most diverse SCO compounds with switchable properties because of their specific structural features. They are bimetallic two- or three-dimensional coordination frameworks formed by Fe^{II} ions coordinated by cyanometallic anions $[M(CN)_x]^{y-}$ and N-donor heterocyclic ligands (Ohkoshi et al., 2014; Muñoz & Real, 2011). Such frameworks have been prepared in forms of single crystals, thin films (Bell et al., 1994) and nanoparticles (Volatron et al., 2008), thus presenting a group of materials characterized by the presence of sharp and hysteretic SCO. A large variety of Hofmann-like polymeric SCO complexes originates from a set of available cyanometallates (formed by Ni, Pt, Pd, Ag, Au, Cu and Nb) and organic ligands, which potentially could promote the spin state change of Fe atoms (Muñoz & Real, 2011). Pyridine (Kitazawa et al., 1996), aminopyridine (Liu et al., 2015), pyrazine (Niel et al., 2001), azopyridine (Agustí et al., 2008), pyrimidine (Niel et al., 2003) and some others have been reported as coligands in these frameworks. Among the above-mentioned azines, the simplest μ_2-bridging system is pyrazine, which provides 1,4-binding and the formation of
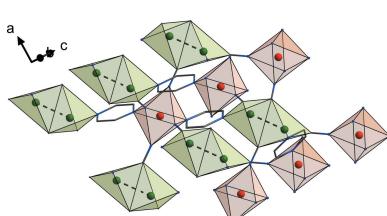
compact frameworks (Southon *et al.*, 2009). Taking into account that the modification of pyrazine can influence not only the structure of a complex but also the spin state of Fe, and being inspired by a previously published structure with 2-bromopyrazine as a coligand and bridging cyanocuprates (Kucheriv *et al.*, 2018), here we describe the crystal structure of a new Hofmann clathrate analogue of general formula [Fe(Etpz)$_2${Cu(CN)$_2$}$_2$]$_n$ (where Etpz is 2-ethylpyrazine).

Figure 1
A fragment of the crystal structure of the title compound with atom labelling. Displacement ellipsoids are drawn at the 90% probability level [symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $x, -y, -\frac{1}{2} + z$; (iii) $x, 1 - y, -\frac{1}{2} + z$; (iv) $1 - x, -y, 1 - z$; (v) $1 - x, y, \frac{1}{2} - z$; (vi) $1 - x, 1 - y, 1 - z$]. The Cu···Cu short contact is shown as a dashed line.

2. Structural commentary

A fragment of the structure of the title compound is shown in Fig. 1. The Fe^{II} ion is coordinated *via* N atoms by two pairs of symmetry-related cyanido groups in the equatorial positions [Fe1—N1 = 1.966 (2) and Fe1—N2 = 1.953 (2) Å]. The axial positions are occupied by the N atoms of two symmetry-related 2-ethylpyrazine molecules [Fe1—N3 = 1.981 (2) Å]. The low-spin state of the Fe^{II} centre at the temperature of experiment (T = 173 K) is confirmed by the Fe—N bond lengths (*i.e.* < 2.0 Å). Each Cu^{I} ion (Cu1^{ii} and Cu1^{iv}) is coordinated by one bridging 2-ethylpyrazine molecule *via* the N atom and by the C atoms of three cyanido groups [Cu1^{ii}—N4^{iii}, Cu1^{iv}—N4^{vi} = 2.122 (2), Cu1^{ii}—C1^{ii}, Cu1^{iv}—C1^{iv} = 1.933 (3), Cu1^{ii}—C2, Cu1^{iv}—C2^{v} = 2.078 (3), Cu1^{ii}—C2^{v}, Cu1^{iv}—C2 = 2.151 (3) Å; symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $x, -y, -\frac{1}{2} + z$; (iii) $x, 1 - y, -\frac{1}{2} + z$; (iv) $1 - x, -y, 1 - z$; (v) $1 - x, y, \frac{1}{2} - z$; (vi) $1 - x, 1 - y, 1 - z$]. The separation between two neighboring Cu atoms is 2.4662 (7) Å, which is significantly shorter than the sum of the corresponding van der Waals radii (2.8 Å; Bondi, 1964), could indicate the presence of metallophilic interactions, namely cuprophilic (Hermann *et al.*, 2001). The Cu atom binds to atom N4 of the 2-ethyl-pyrazine, which is close to the ethyl substituent, while the coordination of the Fe^{II} ion occurs through the more sterically accessible N3 atom of the pyrazine ring.

The coordination polyhedra of Fe and Cu atoms of the title compound and their relative positions are shown in Fig. 2. Six

N atoms form a slightly elongated octahedral coordination environment of the Fe^{II} ion. The deviation from an ideal octahedron of the Fe1 centre can be described by the octahedral distortion parameter $\Sigma|90 - \theta| = 20.59°$, where θ is a *cis*-N—Fe—N angle. The fourfold CuC$_3$N coordination environment of the Cu^{I} centre adopts a tetrahedral geometry. Two tetrahedra of neighboring Cu centres are connected through a common edge between two C atoms of cyanido groups. This common edge is perpendicular to the Cu···Cu contact. Each Fe octahedron is surrounded by six double Cu–Cu edge-connected tetrahedra and is bound with them by four cyanido groups and two bridging pyrazine rings. At the same time, dicopper two edge-connected tetrahedra are linked to four Fe^{II} ion octahedrons *via* cyanido bridges and to two Fe octahedra *via* pyrazine rings.
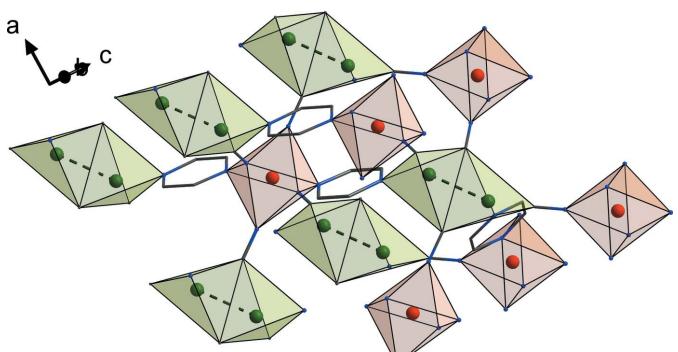
Figure 2
Coordination polyhedra of the Fe and Cu atoms in the title compound. Cu···Cu contacts are shown as dashed lines. Colour code: Fe red, Cu green, C grey, N blue.
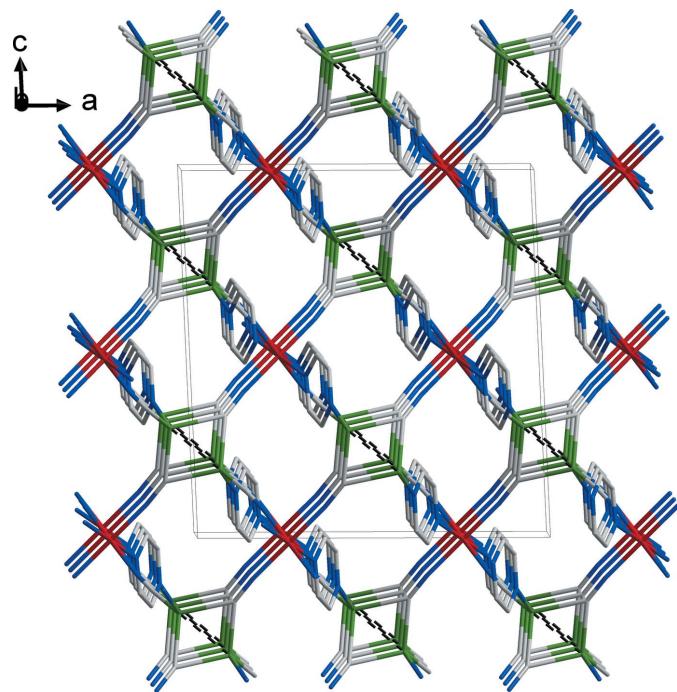
Figure 3
A view normal to the *ac* plane of the crystal structure of the title compound showing the Cu···Cu contacts as dashed lines. Ethyl substituents of 2-ethylpyrazine rings and H atoms have been omitted for clarity. Colour code: Fe dark red, Cu green, C grey, N blue.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Cu_2Fe(CN)_4](C_6H_8N_2)_2$
M_r	503.30
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	173
a, b, c (Å)	13.1997 (17), 9.2923 (11), 13.8010 (17)
β (°)	92.399 (2)
V (Å^3)	1691.3 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.36
Crystal size (mm)	$0.17 \times 0.14 \times 0.06$
Data collection	
Diffractometer	Bruker SMART
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.614, 0.746
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	5344, 2022, 1594
R_{int}	0.065
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.657
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.030, 0.065, 0.93
No. of reflections	2022
No. of parameters	124
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.71, −0.48

Computer programs: *SAINT* and *APEX* (Bruker, 2013), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

3. Supramolecular features

Fig. 3 illustrates the crystal packing of the title compound. The unit cell contains four units of the title compound with empirical formula $C_{16}H_{16}Cu_2FeN_8$. The latter consists of bridging 2-ethylpyrazine ligands and $Cu_2(CN)_2$ pairs, in which two Cu atoms, centred about a twofold rotation axis, are interconnected by two μ-CN groups through C atoms. The resulting polymeric three-dimensional metal–organic coordination framework is additionally stabilized by supramolecular Cu···Cu contacts in each $Cu_2(CN)_2$ unit.

4. Database survey

A search through the Cambridge Structural Database (CSD, version 5.40, last update May 2019; Groom *et al.*, 2016) gave 36 hits for the $Cu_2(CN)_2$ unit, the majority of which are copper monometallic metal–organic frameworks (MOFs). Several bimetallic MOFs are slightly similar to the title compound, namely *catena*-[bis(μ_3-chloro)bis(μ_3-cyano)tetrakis(μ_2-cyano)bis(*N*-methylethane-1,2-diamine)dicadmium(II)dicopper(I)copper(II)] (TIDJIB; Kuchár & Černák, 2013) and *catena*-[bis(μ_3-cyano)tetrakis(μ_2-cyano)tetrakis(dimethylformamidetetracopper(I)zinc(II)] (UBUROY; Cui *et al.*, 2001), the structure of which was described as a 3D network with two types of bridging cyanides. The Cu···Cu distances are 2.5431 (11) and 2.5734 (13) Å, respectively, compared to 2.4662 (7) Å in the title MOF.

A search through the CSD for the Fe ion ligated by four N≡C–Cu and two azines gave 15 hits, which are all bimetallic MOFs with pyrimidine, cyanopyridine and fluoro-, chloro-, bromo- and iodopyridine as ligands.

A search through the CSD for 2-ethylpyrazine gave 20 hits, in most of which 2-ethylpyrazine molecule binds to Cu, Ag, Mn or Rh ions. In the majority of compounds containing copper, the 2-ethylpyrazine serves as a bridging ligand between two Cu atoms in MOFs. An example closely related to the title structure is *catena*-[(μ_3-cyano)tris(μ_2-cyano)bis-(μ_2-2-ethylpyrazine)tetracopper(I)] (SUYDEV; Chesnut *et al.*, 2001), in which neighbouring Cu^I ions are connected by (i) bridging 2-ethylpyrazine molecules and (ii) bridging cyano groups, thus forming one-dimensional $\{Cu(CN)\}_n$ chains and double-stranded $\{Cu(CN)\}_n$ ribbons, linked into a network by bridging ethylpyrazine ligands.

5. Synthesis and crystallization

Crystals of the title compound were obtained by a slow diffusion within three layers in a 3 ml glass tube. The first layer was a solution of $K[Cu(CN)_2]$ (9.3 mg, 0.06 mmol) in 1 ml of H_2O; the second layer was an H_2O/EtOH mixture (1:1, 1 ml); the third layer was a solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (10.9 mg, 0.03 mmol) and 2-ethylpyrazine (6.5 mg, 0.06 mmol) in 0.5 ml of EtOH. After two weeks, brown crystals were formed in the middle layer. The crystals were kept under the mother solution prior to measurement.

research communications

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All hydrogen atoms were placed geometrically and refined as riding: C—H = 0.95 Å with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic hydrogens, C—H = 0.99 Å with $U_{iso}(H) = 1.2U_{eq}(C)$ for CH_2 groups and C—H = 0.98 Å with $U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 groups.

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Crystal structure of a low-spin poly[di-μ_3-cyanido-di-μ_2-cyanido-bis(μ_2-2-ethyl-pyrazine)dicopper(I)iron(II)]

Sofiia V. Partsevska, Dina D. Naumova, Igor P. Matushko, Olesia I. Kucheriv and Il'ya A. Gural'skiy

Computing details

Data collection: *SAINT* (Bruker, 2013); cell refinement: *APEX* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

poly[di-μ_3-cyanido-di-μ_2-cyanido-bis(μ_2-2-ethylpyrazine)dicopper(I)iron(II)]

Crystal data
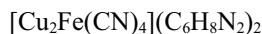
$[Cu_2Fe(CN)_4](C_6H_8N_2)_2$	$F(000) = 1008$
$M_r = 503.30$	$D_x = 1.977$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 13.1997\,(17)$ Å	Cell parameters from 1806 reflections
$b = 9.2923\,(11)$ Å	$\theta = 2.7–27.8°$
$c = 13.8010\,(17)$ Å	$\mu = 3.36$ mm^{-1}
$\beta = 92.399\,(2)°$	$T = 173$ K
$V = 1691.3\,(4)$ Å^3	Plate, brown
$Z = 4$	$0.17 \times 0.14 \times 0.06$ mm

Data collection

Bruker SMART diffractometer	2022 independent reflections
ω scan	1594 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2013)	$R_{int} = 0.065$
	$\theta_{max} = 27.9°$, $\theta_{min} = 2.7°$
$T_{min} = 0.614$, $T_{max} = 0.746$	$h = -17 \rightarrow 17$
5344 measured reflections	$k = -11 \rightarrow 12$
	$l = -17 \rightarrow 18$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.030$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.065$	
$S = 0.93$	H-atom parameters constrained
2022 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0096P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
124 parameters	
0 restraints	$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.71$ e Å^{-3} $\Delta\rho_{min} = -0.47$ 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)

	x	*y*	*z*	U_{iso}*/U_{eq}
Fe1	0.750000	0.250000	0.500000	0.00838 (13)
N3	0.67750 (17)	0.4182 (2)	0.55164 (15)	0.0112 (5)
C6	0.6721 (2)	0.4390 (3)	0.64784 (18)	0.0130 (6)
H6	0.690965	0.363327	0.691266	0.016*
Cu1	0.56898 (3)	−0.12263 (4)	0.69244 (2)	0.01200 (10)
C5	0.6397 (2)	0.5687 (3)	0.68428 (19)	0.0149 (6)
H5	0.636763	0.579116	0.752586	0.018*
N4	0.61203 (18)	0.6806 (2)	0.62788 (16)	0.0123 (5)
C4	0.6133 (2)	0.6591 (3)	0.53050 (18)	0.0116 (6)
C3	0.6452 (2)	0.5271 (3)	0.49461 (18)	0.0126 (6)
H3	0.644046	0.513708	0.426328	0.015*
C7	0.5820 (3)	0.7817 (3)	0.46507 (19)	0.0193 (7)
H7A	0.621459	0.868000	0.485232	0.023*
H7B	0.509562	0.802998	0.474233	0.023*
C8	0.5965 (3)	0.7554 (3)	0.35783 (19)	0.0205 (7)
H8A	0.574269	0.840394	0.320653	0.031*
H8B	0.668292	0.736985	0.347349	0.031*
H8C	0.556167	0.671850	0.336328	0.031*
N2	0.64347 (17)	0.2077 (2)	0.40162 (15)	0.0104 (5)
C2	0.5888 (2)	0.1671 (3)	0.33956 (19)	0.0123 (6)
N1	0.68194 (18)	0.1220 (2)	0.59018 (15)	0.0121 (5)
C1	0.6394 (2)	0.0361 (3)	0.63471 (18)	0.0130 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0087 (3)	0.0087 (3)	0.0077 (3)	−0.0002 (2)	−0.00018 (19)	0.0000 (2)
N3	0.0117 (12)	0.0109 (12)	0.0109 (11)	0.0007 (9)	0.0009 (9)	0.0007 (9)
C6	0.0172 (14)	0.0111 (13)	0.0106 (13)	0.0016 (12)	0.0010 (11)	0.0027 (11)
Cu1	0.01269 (17)	0.01261 (18)	0.01078 (17)	−0.00052 (14)	0.00136 (12)	0.00098 (14)
C5	0.0177 (14)	0.0178 (14)	0.0093 (13)	0.0025 (13)	0.0016 (11)	0.0004 (12)
N4	0.0130 (12)	0.0123 (12)	0.0117 (11)	0.0021 (10)	0.0022 (9)	−0.0024 (10)
C4	0.0107 (13)	0.0145 (14)	0.0098 (12)	0.0021 (11)	−0.0001 (10)	0.0002 (11)
C3	0.0138 (13)	0.0154 (15)	0.0087 (13)	−0.0003 (12)	0.0004 (10)	−0.0001 (11)
C7	0.0274 (17)	0.0183 (15)	0.0123 (14)	0.0081 (14)	0.0019 (12)	0.0020 (12)
C8	0.0327 (18)	0.0182 (15)	0.0107 (14)	0.0073 (14)	0.0009 (12)	0.0008 (12)
N2	0.0108 (11)	0.0102 (11)	0.0105 (11)	0.0006 (9)	0.0045 (9)	0.0028 (9)
C2	0.0142 (14)	0.0093 (13)	0.0132 (13)	−0.0001 (11)	−0.0016 (11)	−0.0012 (11)

| N1 | 0.0108 (11) | 0.0130 (12) | 0.0122 (11) | 0.0011 (10) | −0.0020 (9) | −0.0039 (10) |
| C1 | 0.0118 (13) | 0.0163 (15) | 0.0110 (13) | 0.0022 (12) | 0.0013 (10) | −0.0025 (11) |

Geometric parameters (Å, º)

Fe1—N3	1.981 (2)	C5—H5	0.9500
Fe1—N3^i	1.981 (2)	C5—N4	1.340 (3)
Fe1—N2	1.953 (2)	N4—C4	1.360 (3)
Fe1—N2^i	1.953 (2)	C4—C3	1.394 (4)
Fe1—N1^i	1.966 (2)	C4—C7	1.501 (4)
Fe1—N1	1.966 (2)	C3—H3	0.9500
N3—C6	1.346 (3)	C7—H7A	0.9900
N3—C3	1.341 (3)	C7—H7B	0.9900
C6—H6	0.9500	C7—C8	1.520 (4)
C6—C5	1.381 (4)	C8—H8A	0.9800
Cu1—Cu1^{ii}	2.4662 (7)	C8—H8B	0.9800
Cu1—N4^{iii}	2.122 (2)	C8—H8C	0.9800
Cu1—C2^{iv}	2.151 (3)	N2—C2	1.160 (3)
Cu1—C2^v	2.078 (3)	N1—C1	1.166 (3)
Cu1—C1	1.933 (3)		
N3^i—Fe1—N3	180.0	C6—C5—H5	118.4
N2—Fe1—N3^i	86.31 (9)	N4—C5—C6	123.1 (2)
N2^i—Fe1—N3^i	93.69 (9)	N4—C5—H5	118.4
N2—Fe1—N3	93.69 (9)	C5—N4—Cu1^{vi}	119.72 (18)
N2^i—Fe1—N3	86.31 (9)	C5—N4—C4	116.5 (2)
N2—Fe1—N2^i	180.0	C4—N4—Cu1^{vi}	123.81 (18)
N2—Fe1—N1^i	90.94 (9)	N4—C4—C3	119.8 (2)
N2—Fe1—N1	89.06 (9)	N4—C4—C7	118.0 (2)
N2^i—Fe1—N1	90.94 (9)	C3—C4—C7	122.2 (2)
N2^i—Fe1—N1^i	89.06 (9)	N3—C3—C4	123.3 (2)
N1^i—Fe1—N3	89.48 (9)	N3—C3—H3	118.4
N1^i—Fe1—N3^i	90.51 (9)	C4—C3—H3	118.4
N1—Fe1—N3	90.52 (9)	C4—C7—H7A	108.5
N1—Fe1—N3^i	89.48 (9)	C4—C7—H7B	108.5
N1^i—Fe1—N1	180.0	C4—C7—C8	114.9 (2)
C6—N3—Fe1	120.93 (19)	H7A—C7—H7B	107.5
C3—N3—Fe1	122.06 (18)	C8—C7—H7A	108.5
C3—N3—C6	116.2 (2)	C8—C7—H7B	108.5
N3—C6—H6	119.5	C7—C8—H8A	109.5
N3—C6—C5	120.9 (3)	C7—C8—H8B	109.5
C5—C6—H6	119.5	C7—C8—H8C	109.5
N4^{iii}—Cu1—Cu1^{ii}	119.23 (6)	H8A—C8—H8B	109.5
N4^{iii}—Cu1—C2^{iv}	91.28 (10)	H8A—C8—H8C	109.5
C2^v—Cu1—Cu1^{ii}	55.71 (8)	H8B—C8—H8C	109.5
C2^{iv}—Cu1—Cu1^{ii}	52.95 (7)	C2—N2—Fe1	170.6 (2)
C2^v—Cu1—N4^{iii}	102.36 (10)	Cu1^{vii}—C2—Cu1^{iv}	71.33 (8)
C2^v—Cu1—C2^{iv}	104.11 (10)	N2—C2—Cu1^{vii}	146.7 (2)

C1—Cu1—Cu1[ii]	130.26 (8)	N2—C2—Cu1[iv]	141.4 (2)
C1—Cu1—N4[iii]	110.04 (10)	C1—N1—Fe1	172.3 (2)
C1—Cu1—C2[iv]	122.70 (11)	N1—C1—Cu1	172.0 (2)
C1—Cu1—C2[v]	120.75 (11)		
Fe1—N3—C6—C5	167.2 (2)	C5—N4—C4—C3	−1.9 (4)
Fe1—N3—C3—C4	−166.3 (2)	C5—N4—C4—C7	179.5 (3)
N3—C6—C5—N4	−0.1 (5)	N4—C4—C3—N3	−1.4 (4)
C6—N3—C3—C4	3.8 (4)	N4—C4—C7—C8	173.5 (3)
C6—C5—N4—Cu1[vi]	−177.6 (2)	C3—N3—C6—C5	−3.1 (4)
C6—C5—N4—C4	2.7 (4)	C3—C4—C7—C8	−5.0 (4)
Cu1[vi]—N4—C4—C3	178.3 (2)	C7—C4—C3—N3	177.1 (3)
Cu1[vi]—N4—C4—C7	−0.2 (4)		

Symmetry codes: (i) −*x*+3/2, −*y*+1/2, −*z*+1; (ii) −*x*+1, *y*, −*z*+3/2; (iii) *x*, *y*−1, *z*; (iv) −*x*+1, −*y*, −*z*+1; (v) *x*, −*y*, *z*+1/2; (vi) *x*, *y*+1, *z*; (vii) *x*, −*y*, *z*−1/2.