

Crystal structure of poly[bis(μ -2-bromopyrazine)-tetra- μ_2 -cyanido-dicopper(I)iron(II)]: a bimetallic metal-organic framework

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Received 10 November 2018

Accepted 22 November 2018

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; bromopyrazine; dicyanocuprate; iron(II); copper(I); bimetallic; metal-organic framework; MOF.

CCDC reference: 1880717

Supporting information: this article has supporting information at journals.iucr.org/e

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In the title metal-organic framework, $[\text{Fe}(\text{C}_4\text{H}_3\text{BrN}_2)_2\{\text{Cu}(\text{CN})_2\}_2]_n$, the Fe^{II} cation is located on an inversion center and has a slightly elongated octahedral coordination environment $[\text{FeN}_6]$, ligated by two pyrazine N atoms of symmetry-related bridging 2-bromopyrazine molecules in the axial positions and by four N atoms of pairs of symmetry-related cyanido groups in the equatorial positions. The Cu^{I} center has a fourfold coordination environment $[\text{CuC}_3\text{N}]$, with an almost perfect trigonal-pyramidal geometry, formed by three cyanido C atoms and an N atom of a bridging 2-bromopyrazine molecule. Copper(I) centers related by a twofold rotation axis are bridged by two carbon atoms from a pair of μ -CN groups, resulting in $\text{Cu}_2(\text{CN})_2$ units. Each $\text{Cu}_2(\text{CN})_2$ unit is linked to six Fe^{II} cations via a pair of linear CN units, the pair of μ -CN groups and two bridging 2-bromopyrazine ligands, resulting in the formation of a metal-organic framework, which is additionally stabilized by the short $\text{Cu}\cdots\text{Cu}$ contacts of 2.4450 (7) Å.

1. Chemical context

The rational design and synthesis of cyanide-based coordination materials is of key interest today. By using different approaches for their design and tunable structures, composition and porosity, various exciting properties of these compounds, such as catalytic, photoluminescent, magnetic, electrical and other can be achieved (Zhang *et al.*, 2015; Catala & Mallah, 2017). The cyanide anion is an important ligand in coordination chemistry as it can be used for stabilization of coordination materials formed by diverse transition metals. Cyanide-containing coordination materials of very different topologies have been proposed, although attention is frequently paid to heterometallic complexes.

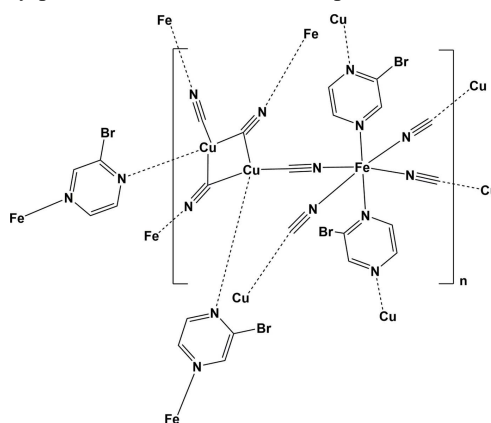
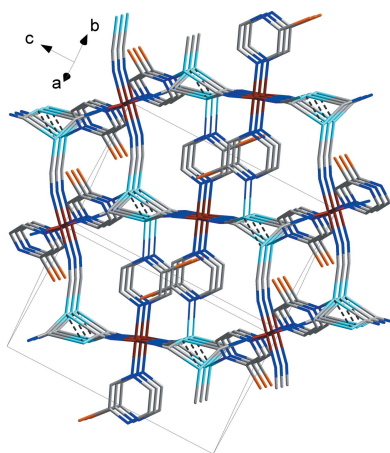


Table 1

Selected geometric parameters (Å, °).

Cu1—Cu1 ⁱ	2.4450 (7)	Cu1—C2 ^{iv}	2.181 (3)
Cu1—N4 ⁱⁱ	2.152 (2)	Fe1—N1	1.958 (2)
Cu1—C1	1.924 (3)	Fe1—N2	1.952 (2)
Cu1—C2 ⁱⁱⁱ	2.049 (3)	Fe1—N3	1.980 (2)
N4 ⁱⁱ —Cu1—C2 ^{iv}	99.77 (10)	N3—Fe1—N3 ^v	180
C2 ⁱⁱⁱ —Cu1—N4 ⁱⁱ	94.29 (10)	N2 ^v —Fe1—N3	87.27 (9)
C2 ⁱⁱⁱ —Cu1—C2 ^{iv}	104.00 (10)	N2—Fe1—N3	92.73 (9)
C1—Cu1—N4 ⁱⁱ	109.09 (10)	N2 ^v —Fe1—N1	92.19 (9)
C1—Cu1—C2 ^{iv}	116.07 (11)	N2—Fe1—N1	87.81 (9)
C1—Cu1—C2 ⁱⁱⁱ	128.08 (11)	N1—Fe1—N3	90.92 (9)
N1—Fe1—N1 ^v	180	N1 ^v —Fe1—N3	89.08 (9)
N2—Fe1—N2 ^v	180		

Symmetry codes: (i) $-x + 1, y, -z + \frac{3}{2}$; (ii) $x, y - 1, z$; (iii) $-x + 1, -y, -z + 1$; (iv) $x, -y, z + \frac{1}{2}$; (v) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$.

The first class of cyanide-based metallic complexes emerged in the 18th century with the discovery of Prussian blue. Later its analogues containing two types of metals were synthesized. The inclusion of different metals instead of iron resulted in the occurrence of various attractive physical properties of these materials, which allowed their use as molecular sieves, for nanoscale devices, for hydrogen storage, *etc.* (Newton *et al.*, 2011). Prussian blue analogues form networks with general formula $AM_A[M_B(\text{CN})_6]$ (A = alkali metal ion, M_A and M_B = transition metal ions) (Keggin & Miles, 1936). These complexes have a cubic structure in which the metallic centers are bridged in an $M_A\text{—C}\equiv\text{N—}M_B$ fashion, forming three-dimensional frameworks.

Another class of heterometallic cyanide coordination compounds that has attracted much attention is represented by f - d complexes composed of lanthanide(III) ions and d -block cyanometallates. This type of materials has been shown to have exceptional photoluminescent properties (Chorazy *et al.*, 2017). In addition, polynuclear octacyanides form a different family of cyanide-based heterometallic complexes.

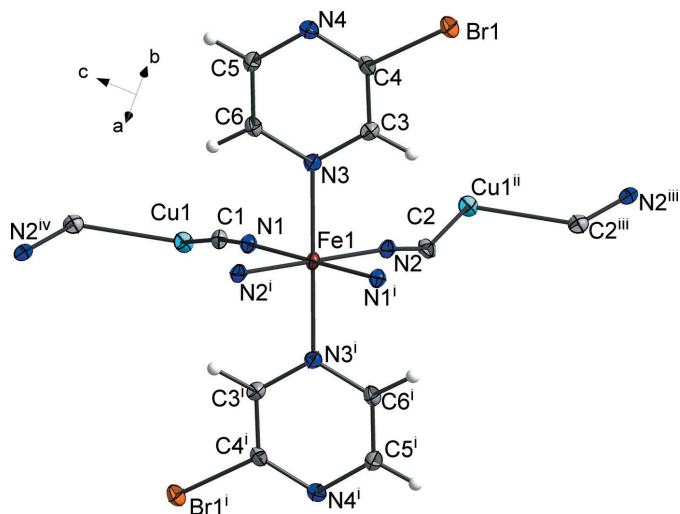


Figure 1

A fragment of the crystal structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at 50% probability level [symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x + 1, y, -z + \frac{1}{2}$; (iv) $x, -y, z + \frac{1}{2}$].

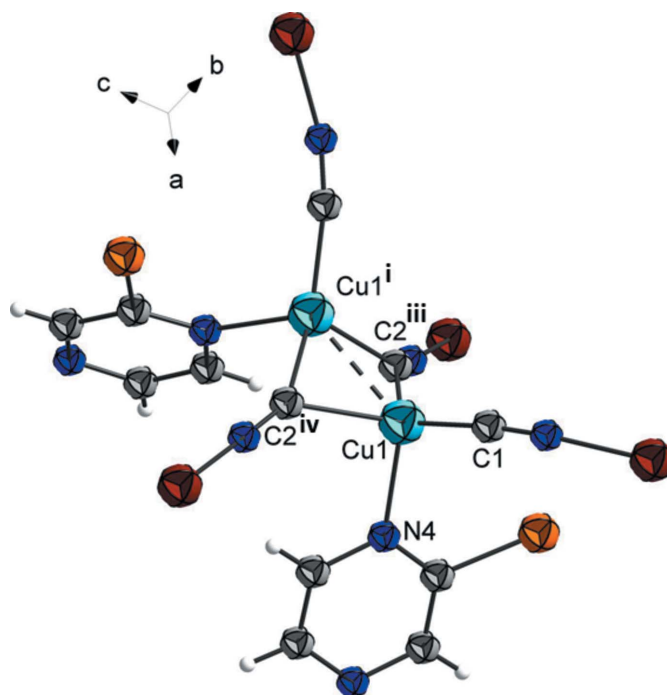


Figure 2

A view of the coordination environment of the Cu atoms in the title compound, with atom labelling [symmetry codes: (i) $-x + 1, -y, -z + 1$; (iii) $x, -y, z + \frac{1}{2}$; (iv) $x, -y, z + \frac{1}{2}$].

Compounds of this class can adopt very different geometries creating 0, 1, 2 or 3D assemblies. These materials are known for photomagnetism, molecular magnetism, and the ability to create chiral networks (Sieklucka *et al.*, 2011).

The Hofmann clathrate analogues of the general formula $[M_A(L)_x\{M_B(\text{CN})_y\}]$ constitute another prominent example of bimetallic cyanometallates (Hofmann & Küspert, 1897), which are famous for their switchable magnetic properties (Muñoz & Real, 2011). Here we describe the crystal structure of a new Hofmann clathrate analogue of general formula $[\text{Fe}(\text{Brpz})_2\{\text{Cu}(\text{CN})_2\}_2]_n$.

2. Structural commentary

A fragment of the structure of the title compound, illustrating the sixfold coordination environment of atom Fe1, is shown in Fig. 1. Selected geometrical parameters are given in Table 1. The Fe^{II} ion is located on an inversion centre and has a slightly elongated FeN₆ octahedral coordination environment. It is ligated by two N atoms of symmetry-related 2-bromopyrazine molecules in axial positions [Fe1—N3 = 1.980 (2) Å] and by four N atoms of symmetry related cyanido groups in the equatorial positions [Fe1—N1 = 1.958 (2) and Fe1—N2 = 1.952 (2) Å]. The Fe—N bond lengths clearly indicate that the Fe^{II} center is in the low-spin state at the temperature of the experiment, *i.e.* 296 K. The deviation from an ideal octahedron of the Fe^{II} center can be described by the octahedral distortion parameter $\Sigma|90 - \theta| = 23.36^\circ$, where θ is a *cis*-N—Fe—N angle. Notably, this sum is higher than that expected for a low-spin Fe^{II} ion. It is important to note, and should always

be taken into account, that the octahedral distortion value cannot always be used to judge the spin state of a metallic center, it is rather a characteristic of the order level in the structure, the measurement temperature, *etc.*

Atom Cu1 has a fourfold CuC_3N coordination environment (Fig. 2, Table 1) with a τ_4 descriptor of 0.82, close to that for a perfect trigonal-pyramidal geometry ($\tau_4 = 0.00$ for square-planar, 1.00 for tetrahedral and 0.85 for trigonal-pyramidal; Yang *et al.*, 2007). It is ligated by three C atoms of the cyanido groups and an N atom of a bridging 2-bromopyrazine molecule [$\text{Cu1}-\text{C1} = 1.924$ (3), $\text{Cu1}-\text{C2}^{\text{iv}} = 2.181$ (3), $\text{Cu1}-\text{C2}^{\text{iii}} = 2.049$ (3), $\text{Cu1}-\text{N4}^{\text{ii}} = 2.152$ (2) Å]. Notably, the coordination to atom Fe1 occurs only via the more sterically accessible atom N3 of the pyrazine ring, while atom Cu1 binds to atom N4 of the pyrazine ring.

3. Supramolecular features

The crystal packing of the title compound is shown in Fig. 3. The coordination framework is made up of bridging 2-bromopyrazine ligands and $\text{Cu}_2(\text{CN})_2$ moieties (Fig. 2). The latter are formed by a pair of copper atoms, centered about a twofold rotation axis, being bridged by two carbon atoms from a pair of μ -CN groups. Each $\text{Cu}_2(\text{CN})_2$ unit is linked to six Fe^{II} cations via a pair of linear CN units, the pair of μ -CN groups and two bridging 2-bromopyrazine ligands, resulting in the formation of a metal-organic framework (Fig. 3). The

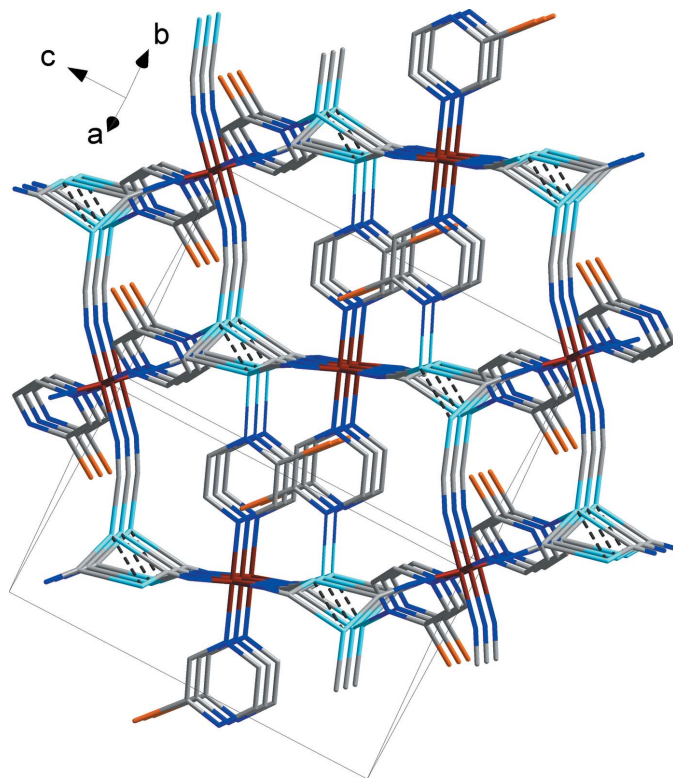


Figure 3

A view normal to plane (110) of the crystal structure of the title compound, showing the $\text{Cu}\cdots\text{Cu}$ contacts as dashed lines. H atoms have been omitted for clarity. Colour code: Fe dark red, Cu light blue, C grey, N blue, Br orange.

framework is additionally stabilized by the short $\text{Cu1}\cdots\text{Cu1}^{\text{i}}$ contact of 2.4550 (7) Å, which is significantly shorter than the sum of the corresponding van der Waals radii, *viz.* 2.8 Å. Additionally, within the framework there are weak $\text{Br}\cdots\pi$ contacts of 3.8298 (6) Å, that are of lone-pair $\cdots\pi$ origin.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.39, last update August 2018; Groom *et al.*, 2016) gave 15 hits for $\text{Fe}-\text{N}\equiv\text{C}-\text{Cu}$ bimetallic structures supported mainly by substituted pyridines and pyrimidines. These include a number of variable temperature measurements of certain compounds in order to study their spin-crossover behaviour; for example, the two-dimensional coordination polymer *catena*-[bis(μ^3 -cyano-*C,C,N*)(μ^2 -cyano-*C,N*)]tetrakis(3-cyanopyridyl)dicopper(I)iron(II)] (VEHHOG, VEHHOG01; Galet *et al.*, 2006), and the framework structures *catena*-[tetrakis(μ^2 -cyano-*C,N*)-bis(μ^2 -pyrimidine-*N,N'*)dicopper(I)iron(II)] (EHOQOH01, EHOQOH03; Agustí *et al.*, 2008) and *catena*-[octakis(μ^2 -cyano)octakis(3-chloropyridine)tetracopper(I)diiron(II)] (YUBRET, YUBRET03; Agustí *et al.*, 2009).

A search of the CSD for the bridging $\text{Cu}_2(\text{CN})_2$ unit gave 27 hits. The majority of these are monometallic copper(I) metal-organic frameworks (MOFs). The $\text{Cu}\cdots\text{Cu}$ distances vary from *ca.* 2.31 Å in the two-dimensional network structure *catena*-[bis(μ_3 -cyano)tetrakis(μ_2 -cyano)tris(*N,N,N',N'*-tetramethylethylenediamine)hexacopper(I)] (HIWHUQ; Stocker *et al.*, 1999) to *ca.* 2.72 Å in the MOF *catena*-[tris(μ -cyano)-tris(μ -cyano)diamminepentacopper] (OPODAA; Grifasi *et al.*, 2016). Two particular compounds resemble the title MOF, namely *catena*-[bis(μ_3 -cyano-*C,C,N*)(μ_2 -cyano-*C,N*)(μ_2 -2,3-dimethylpyrazine-*N,N'*)tricopper(I)] (FERWUV; Greve & Nather, 2004), which involves a bridging 2,3-dimethylpyrazine ligand, and *catena*-[(μ_3 -cyano)(μ_2 -4,4'-bipyridine)tris(μ_2 -cyano)hexamethyldicopper(I)ditin(IV)] (NUMRUI; Ibrahim *et al.*, 1998), which is a bimetallic MOF with a bridging 4,4'-bipyridine ligand. The respective $\text{Cu}\cdots\text{Cu}$ distances are *ca.* 2.49 and 2.62 Å, compared to 2.4550 (7) Å in the title MOF.

5. Synthesis and crystallization

Crystals of the title compound were obtained by slow diffusion within three layers in a 3 ml glass tube. The first layer was a solution of $\text{K}[\text{Cu}(\text{CN})_2]$ (7.8 mg, 0.05 mmol) in 1 ml of water; the second layer was a water/ethanol mixture (1:1, 1 ml); the third layer was a solution of $\text{Fe}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (9.1 mg, 0.025 mmol) and 2-bromopyrazine (8.0 mg, 0.05 mmol) in 0.5 ml of ethanol. After two weeks, brown crystals were formed in the middle layer. The crystals were kept under the mother solution prior to measurement.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the hydrogen atoms were

placed geometrically and refined as riding: C—H = 0.93 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Acknowledgements

We are grateful to the Ministry of Education and Science of Ukraine and H2020 Marie Skłodowska-Curie Actions for financial support.

Funding information

Funding for this research was provided by: Ministry of Education and Science of Ukraine (grant No. DZ/55-2018); H2020 Marie Skłodowska-Curie Actions (grant No. 734322).

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Table 2
Experimental details.

Crystal data	
Chemical formula	[Cu ₂ Fe(CN) ₄ (C ₄ H ₃ BrN ₂) ₂]
M_r	605.00
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	296
a, b, c (Å)	13.6143 (17), 9.3067 (11), 13.2101 (15)
β (°)	92.369 (4)
V (Å ³)	1672.3 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	8.17
Crystal size (mm)	0.2 × 0.1 × 0.05
Data collection	
Diffractometer	Bruker SMART
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2013)
$T_{\text{min}}, T_{\text{max}}$	0.487, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8711, 2023, 1799
R_{int}	0.029
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.661
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.026, 0.063, 1.04
No. of reflections	2023
No. of parameters	115
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.08, -0.76

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *DIAMOND* (Brandenburg, 1999).

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supporting information

Acta Cryst. (2018). E74, 1895-1898 [https://doi.org/10.1107/S2056989018016638]

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *S SAINT* (Bruker, 2013); data reduction: *S 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) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

poly[bis(μ -2-bromopyrazine)tetra- μ -cyanido-dicopper(I)iron(II)]

Crystal data

[Cu₂Fe(CN)₄(C₄H₃BrN₂)₂]

$M_r = 605.00$

Monoclinic, *C2/c*

$a = 13.6143$ (17) Å

$b = 9.3067$ (11) Å

$c = 13.2101$ (15) Å

$\beta = 92.369$ (4)°

$V = 1672.3$ (3) Å³

$Z = 4$

$F(000) = 1152$

$D_x = 2.403$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3458 reflections

$\theta = 2.7$ – 28.0 °

$\mu = 8.17$ mm⁻¹

$T = 296$ K

Plate, brown

$0.2 \times 0.1 \times 0.05$ mm

Data collection

Bruker SMART
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2013)

$T_{\min} = 0.487$, $T_{\max} = 0.746$

8711 measured reflections

2023 independent reflections

1799 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 28.0$ °, $\theta_{\min} = 2.7$ °

$h = -17 \rightarrow 17$

$k = -12 \rightarrow 12$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.063$

$S = 1.04$

2023 reflections

115 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 4.9236P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 1.08 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.76 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.58637 (3)	0.80466 (3)	0.43290 (2)	0.02782 (10)
Cu1	0.56339 (2)	-0.11583 (4)	0.68710 (2)	0.01446 (10)
Fe1	0.750000	0.250000	0.500000	0.00911 (12)
N2	0.64165 (17)	0.2082 (2)	0.40313 (17)	0.0125 (4)
N4	0.61897 (18)	0.6878 (3)	0.62526 (18)	0.0167 (5)
N3	0.68414 (17)	0.4233 (2)	0.55166 (16)	0.0131 (4)
N1	0.68406 (17)	0.1288 (2)	0.59751 (17)	0.0133 (4)
C6	0.6791 (2)	0.4482 (3)	0.6517 (2)	0.0179 (6)
H6	0.697279	0.376181	0.697551	0.022*
C2	0.5807 (2)	0.1643 (3)	0.3484 (2)	0.0144 (5)
C3	0.6541 (2)	0.5292 (3)	0.4890 (2)	0.0167 (5)
H3	0.654572	0.515097	0.419324	0.020*
C5	0.6474 (2)	0.5785 (3)	0.6873 (2)	0.0205 (6)
H5	0.645476	0.591957	0.756995	0.025*
C1	0.6393 (2)	0.0431 (3)	0.63961 (19)	0.0129 (5)
C4	0.6224 (2)	0.6594 (3)	0.5265 (2)	0.0164 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0441 (2)	0.02245 (17)	0.01682 (15)	0.01597 (14)	0.00049 (13)	0.00483 (11)
Cu1	0.01237 (17)	0.01466 (17)	0.01645 (17)	-0.00143 (13)	0.00172 (13)	0.00342 (13)
Fe1	0.0097 (3)	0.0095 (2)	0.0081 (2)	-0.00185 (19)	-0.00025 (19)	0.00029 (18)
N2	0.0139 (12)	0.0124 (10)	0.0114 (10)	0.0000 (9)	0.0031 (9)	0.0019 (8)
N4	0.0199 (13)	0.0148 (11)	0.0154 (11)	0.0042 (9)	0.0019 (10)	0.0007 (9)
N3	0.0124 (11)	0.0152 (11)	0.0118 (10)	-0.0003 (9)	0.0006 (9)	-0.0006 (9)
N1	0.0133 (11)	0.0142 (11)	0.0122 (10)	0.0002 (9)	-0.0011 (9)	-0.0018 (9)
C6	0.0245 (16)	0.0162 (13)	0.0130 (12)	0.0054 (11)	-0.0003 (11)	0.0026 (10)
C2	0.0162 (14)	0.0109 (11)	0.0158 (12)	0.0015 (10)	-0.0011 (10)	0.0019 (10)
C3	0.0193 (14)	0.0181 (13)	0.0126 (12)	0.0047 (11)	0.0005 (10)	-0.0022 (10)
C5	0.0302 (17)	0.0198 (14)	0.0115 (12)	0.0071 (12)	0.0019 (11)	0.0004 (11)
C1	0.0142 (13)	0.0144 (13)	0.0101 (11)	0.0008 (10)	-0.0001 (10)	0.0014 (9)
C4	0.0166 (14)	0.0173 (13)	0.0151 (13)	0.0054 (11)	-0.0003 (10)	0.0041 (10)

Geometric parameters (Å, °)

Br1—C4	1.884 (3)	N2—C2	1.153 (4)
Cu1—Cu1 ⁱ	2.4450 (7)	N4—C5	1.353 (4)
Cu1—N4 ⁱⁱ	2.152 (2)	N4—C4	1.334 (4)
Cu1—C1	1.924 (3)	N3—C6	1.347 (3)
Cu1—C2 ⁱⁱⁱ	2.049 (3)	N3—C3	1.340 (4)
Cu1—C2 ^{iv}	2.181 (3)	N1—C1	1.160 (4)
Fe1—N1	1.958 (2)	C6—H6	0.9300
Fe1—N2 ^v	1.952 (2)	C6—C5	1.376 (4)
Fe1—N2	1.952 (2)	C3—H3	0.9300
Fe1—N3	1.980 (2)	C3—C4	1.385 (4)
Fe1—N3 ^v	1.980 (2)	C5—H5	0.9300
Fe1—N1 ^v	1.958 (2)		
N4 ⁱⁱ —Cu1—Cu1 ⁱ	121.81 (7)	C2—N2—Fe1	170.7 (2)
N4 ⁱⁱ —Cu1—C2 ^{iv}	99.77 (10)	C5—N4—Cu1 ^{vi}	120.31 (19)
C2 ⁱⁱⁱ —Cu1—Cu1 ⁱ	57.25 (8)	C4—N4—Cu1 ^{vi}	124.53 (19)
C2 ^{iv} —Cu1—Cu1 ⁱ	52.20 (8)	C4—N4—C5	115.0 (2)
C2 ⁱⁱⁱ —Cu1—N4 ⁱⁱ	94.29 (10)	C6—N3—Fe1	121.39 (19)
C2 ⁱⁱⁱ —Cu1—C2 ^{iv}	104.00 (10)	C3—N3—Fe1	121.14 (18)
C1—Cu1—Cu1 ⁱ	128.71 (8)	C3—N3—C6	116.9 (2)
C1—Cu1—N4 ⁱⁱ	109.09 (10)	C1—N1—Fe1	167.4 (2)
C1—Cu1—C2 ^{iv}	116.07 (11)	N3—C6—H6	119.4
C1—Cu1—C2 ⁱⁱⁱ	128.08 (11)	N3—C6—C5	121.1 (3)
N1—Fe1—N1 ^v	180	C5—C6—H6	119.4
N2—Fe1—N2 ^v	180	Cu1 ⁱⁱⁱ —C2—Cu1 ^{vii}	70.56 (9)
N3—Fe1—N3 ^v	180	N2—C2—Cu1 ⁱⁱⁱ	151.5 (2)
N2 ^v —Fe1—N3	87.27 (9)	N2—C2—Cu1 ^{vii}	137.1 (2)
N2 ^v —Fe1—N3 ^v	92.73 (9)	N3—C3—H3	119.5
N2—Fe1—N3	92.73 (9)	N3—C3—C4	120.9 (3)
N2—Fe1—N3 ^v	87.27 (9)	C4—C3—H3	119.5
N2 ^v —Fe1—N1	92.19 (9)	N4—C5—C6	122.7 (3)
N2—Fe1—N1	87.81 (9)	N4—C5—H5	118.6
N2—Fe1—N1 ^v	92.19 (9)	C6—C5—H5	118.6
N2 ^v —Fe1—N1 ^v	87.81 (9)	N1—C1—Cu1	170.1 (2)
N1—Fe1—N3	90.92 (9)	N4—C4—Br1	118.8 (2)
N1 ^v —Fe1—N3 ^v	90.92 (9)	N4—C4—C3	123.2 (3)
N1 ^v —Fe1—N3	89.08 (9)	C3—C4—Br1	118.0 (2)
N1—Fe1—N3 ^v	89.08 (9)		
Cu1 ^{vi} —N4—C5—C6	176.8 (2)	N3—C3—C4—N4	−0.5 (5)
Cu1 ^{vi} —N4—C4—Br1	5.2 (3)	C6—N3—C3—C4	2.0 (4)
Cu1 ^{vi} —N4—C4—C3	−176.7 (2)	C3—N3—C6—C5	−2.0 (4)
Fe1—N3—C6—C5	169.6 (2)	C5—N4—C4—Br1	−179.1 (2)
Fe1—N3—C3—C4	−169.7 (2)	C5—N4—C4—C3	−1.0 (4)

N3—C6—C5—N4	0.6 (5)	C4—N4—C5—C6	1.0 (5)
N3—C3—C4—Br1	177.6 (2)		

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