



Crystal structure and Hirshfeld analysis of *trans*-bis(5-fluoroindoline-2,3-dione 3-oximato- κ^2O^2,N^3)-*trans*-bis(pyridine- κN)copper(II)

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Received 10 February 2018
Accepted 27 February 2018

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Edited by C. Rizzoli, Università degli Studi di Parma, Italy

Keywords: crystal structure; 5-fluoroisatin 3-oxime copper complex; Hirshfeld surface analysis.

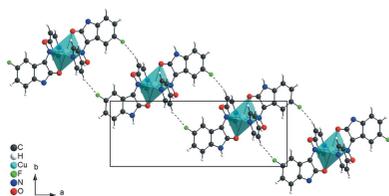
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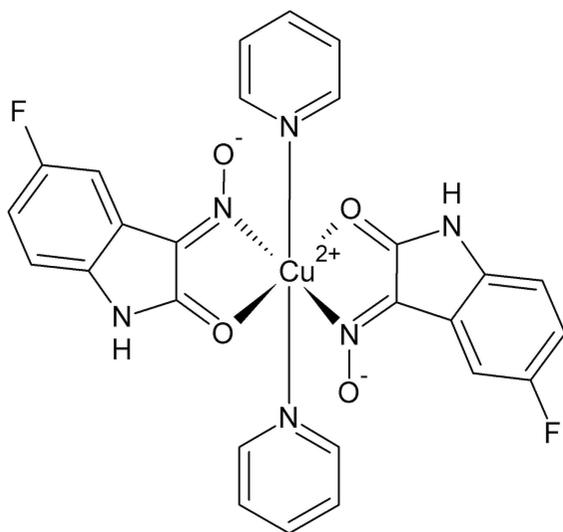
The reaction in methanol of Cu^{II} acetate monohydrate with 5-fluoroisatin 3-oxime deprotonated with KOH in a 1:2 molar ratio and recrystallization from pyridine yielded the title compound, [Cu(C₈H₄FN₂O₂)₂(C₅H₅N)₂]. In the centrosymmetric complex, the anionic form of the isatin oxime acts as a κ^2N,O donor, building five-membered metallarings. The Cu^{II} cation is sixfold coordinated in a slightly distorted octahedral environment by two *trans*, equatorial, anionic isatin derivatives and two *trans* pyridine ligands in axial positions. The complexes are linked by hydrogen bonding into a three-dimensional network, which is also stabilized by π - π stacking interactions [centroid-to-centroid distance = 3.7352 (9) Å] and C-H \cdots π contacts. The Hirshfeld surface analysis indicates that the major contributions for the crystal packing are H \cdots H (31.80%), H \cdots C (24.30%), H \cdots O (15.20%) and H \cdots F (10.80%). This work is the second report in the literature of a crystal structure of a coordination compound with isatin 3-oxime ligands (coordination chemistry).

1. Chemical context

By the first half of the 19th century, the first reports on the chemistry of the isatin fragment were published independently in Germany and France (Erdmann, 1841*a,b*; Laurent, 1841). One very nice review concerning the organic synthesis of the isatin derivatives was published 74 years ago (Sumpter, 1944) and the topic remains up-to-date. From the early years, the chemistry of isatin-based molecules emerged from the synthetic approach to a large class of organic compounds with applications in biochemistry and pharmacology. For two recent examples, see: 1-[(2-methylbenzimidazol-1-yl) methyl]-2-oxo-indolin-3-ylidene]amino]thiourea, a derivative with *in silico* and *in vitro* inhibition of Chikungunya virus replication (Mishra *et al.*, 2016) and 5-chloroisatin-4-methylthiosemicarbazone, another derivative which appears as an intermediate in the synthesis of an HIV-1 RT inhibitor (Meleddu *et al.*, 2017). The abbreviation HIV-1 RT stands for human immunodeficiency virus type 1 reverse transcriptase. Along the same line of research of the present work, the crystal structure, the Hirshfeld surface analysis and the lock-and-key supramolecular analysis through *in silico* evaluation with the vascular endothelial growth factor receptor-2 (VEGFR-2) of the isatin derivative ligand of the title complex were recently carried out. The (3*Z*)-5-fluoro-3-(hydroxyimino)-indolin-2-one molecule showed a structure-activity relationship with the



selected biological target through hydrogen bonding (Martins *et al.*, 2017). Although the chemistry of isatins is already well reported in several scientific disciplines, crystal structures of complexes with isatin 3-oxime derivatives are surprisingly few in number. Thus, the crystal structure determination of isatin-based molecules has become our major research interest and herein, the synthesis, crystal structure and Hirshfeld surface analysis of a 5-fluoroisatin 3-oxime complex with copper(II) is reported.



2. Structural commentary

The asymmetric unit of the title coordination compound consists of one Cu^{II} cation, which lies on an inversion center, and two ligands in general positions, the anionic form of 5-fluoroisatin 3-oxime and one pyridine molecule. The Cu^{II} atoms are sixfold coordinated in a slightly distorted octahedral

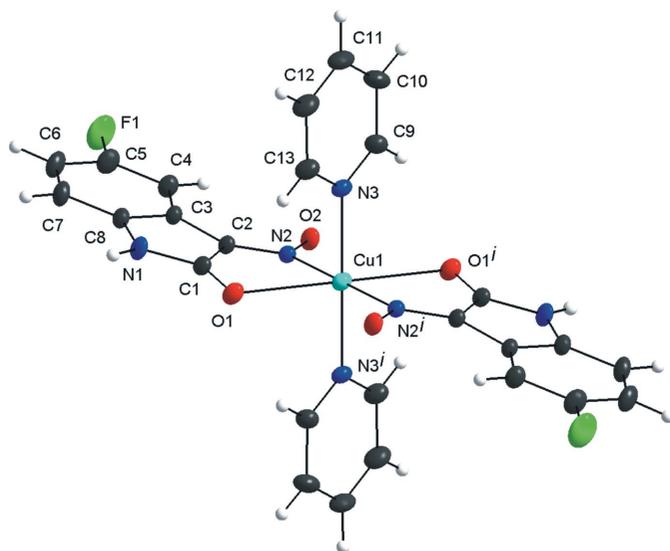


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 40% probability level. [Symmetry code: (i) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$.]

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

Cg1 is the centroid of the N3/C9–C13 ring

<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>
C9–H5...O1 ⁱ	0.95	2.54	3.1424 (18)	121
C12–H8...F1 ⁱⁱ	0.95	2.49	3.287 (2)	142
C13–H9...O1	0.95	2.54	3.1077 (19)	119
N1–H4...O2 ⁱⁱⁱ	0.88	2.00	2.7529 (14)	143
C6–H2...Cg1 ^{iv}	0.95	2.79	3.7076 (17)	162

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

environment by two five-membered chelate 5-fluoroisatin-3-oximate ligands, acting as κ^2N,O -donors in equatorial positions, and by two pyridine ligands in axial positions (Fig. 1). The isatin 3-oxime derivative is nearly planar with an r.m.s. deviation from the mean plane of the non-H atoms of 0.0145 Å and a maximum deviation of 0.0344 (9) Å for the N2 atom. The dihedral angle between the pyridine ring and the mean plane through the indoline ring system is 73.82 (3)°. For the five-membered ring, the r.m.s. from the mean plane through the Cu1/C1/C2/N2/O1 fragment is 0.074 Å and the maximum deviation from that plane is 0.0945 (7) Å for the N2 atom. The N2–Cu1–N3 and O1–Cu1–N3 angles are 88.75 (4) and 89.01 (4)°, respectively. Four intramolecular C–H...O hydrogen bonds are observed for the title compound, forming rings with *S*(5) graph-set motif. As an interesting feature of the structure, a hydrogen-bonded macrocyclic coordination environment can be assumed based on the *S*(5) rings (Fig. 2, Table 1).

3. Supramolecular features and Hirshfeld analysis

In the crystal, the molecules of the centrosymmetric title compound are connected into a three-dimensional hydrogen-

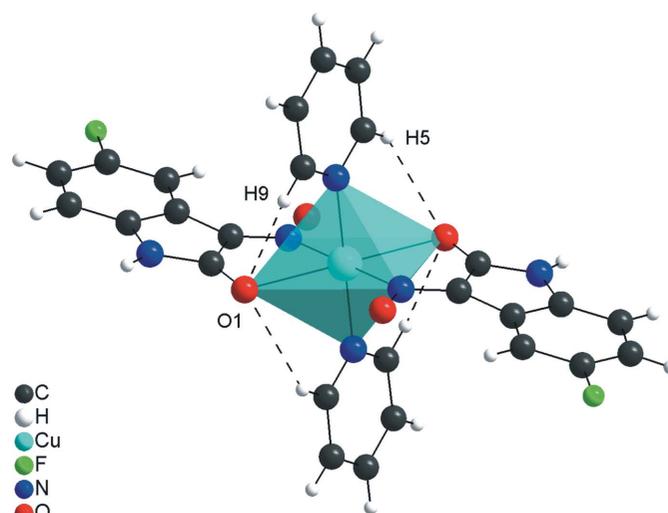


Figure 2
The intramolecular C–H...O hydrogen interactions of the title compound (dashed lines) forming a ring of *S*(5) graph-set motif.

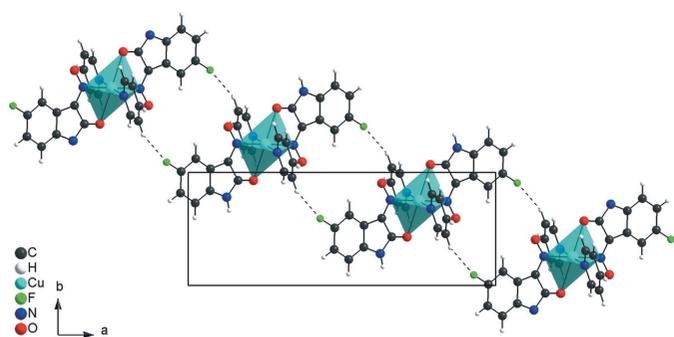


Figure 3
Partial crystal packing of the title compound, viewed down the c axis, showing the $C-H\cdots F$ interactions (dashed lines) forming rings of $R_2^2(22)$ graph-set motif connecting the molecules into a chain along the $[110]$ direction.

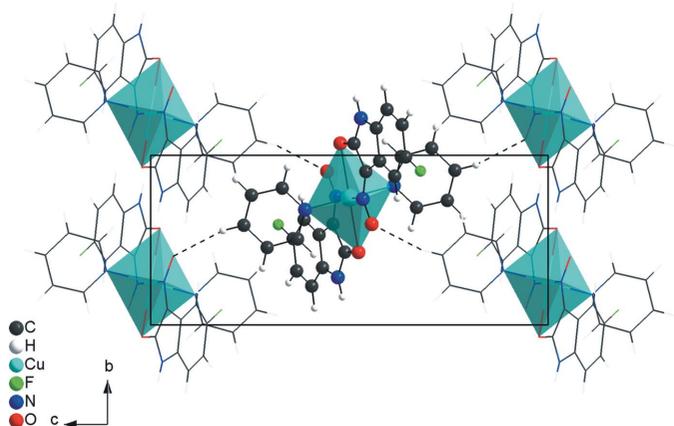


Figure 4
Partial crystal packing of the title compound, viewed down the a axis, showing the $C-H\cdots O$ interactions (dashed lines) organized in a $C(8)$ graph-set motif along the $[001]$ direction.

bonded network (Table 1). The complexes are linked by centrosymmetric pairs of $C-H\cdots F$ interactions into dimers with graph-set motif $R_2^2(22)$. The dimers are the subunits of the periodic arrangement along the $[110]$ direction (Fig. 3).

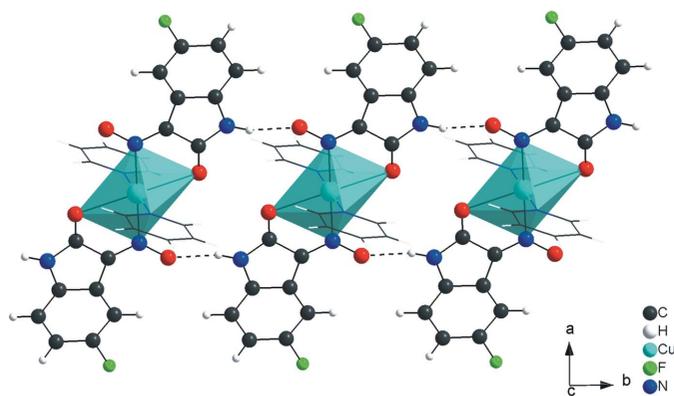


Figure 5
Partial crystal packing of the title compound, viewed along the c axis, showing the $C-H\cdots O$ interactions (dashed lines) forming rings of $R_2^2(14)$ graph-set motif connecting the molecules into a chain along the $[010]$ direction.

The molecular units are also connected by $C-H\cdots O$ interactions into a one-dimensional hydrogen-bonded polymer along the $[001]$ direction (Fig. 4) and finally, the complexes are linked by $N-H\cdots O$ interactions into centrosymmetric dimers with graph-set motif $R_2^2(14)$. Like the dimers of the first structural element, with $C-H\cdots F$ interactions connecting the molecules, the latter element is also based on dimers as subunits of the polymeric motif, connected through $N-H\cdots O$ interactions but in this case along the $[010]$ direction (Fig. 5). In addition, $\pi-\pi$ stacking interactions [centroid-to-centroid distance: $3.7352(9)$ Å] and $C-H\cdots\pi$ contacts (Table 1) stabilize the crystal structure.

The Hirshfeld surface analysis (Hirshfeld, 1977) of the crystal structure suggests that the contributions of the $H\cdots H$, $H\cdots C$ and $H\cdots O$ intermolecular interactions to the crystal

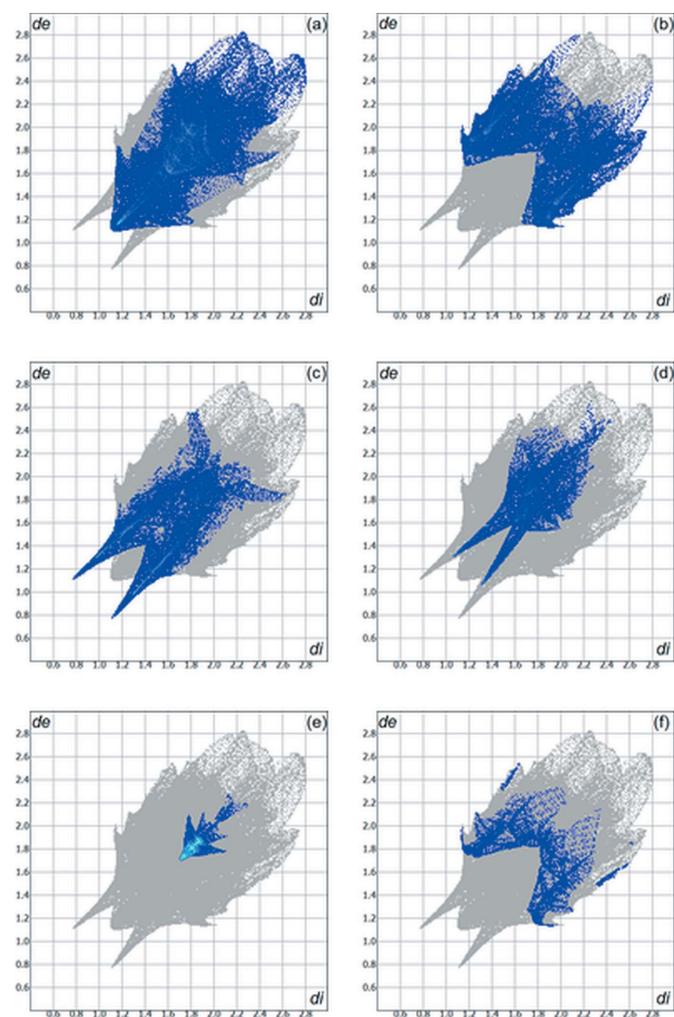


Figure 6
Hirshfeld surface two-dimensional fingerprint plot for the title compound showing (a) $H\cdots H$, (b) $H\cdots C$, (c) $O\cdots H$ and (d) $H\cdots F$, (e) $C\cdots C$ and (f) $H\cdots N$ contacts in detail (cyan dots). The contribution of the interactions to the crystal packing amounts to 31.80, 24.30, 15.20, 10.80, 06.20 and 04.30%, respectively. The d_e (y axis) and d_i (x axis) values are the closest external and internal distances (values in Å) from given points on the Hirshfeld surface contacts.

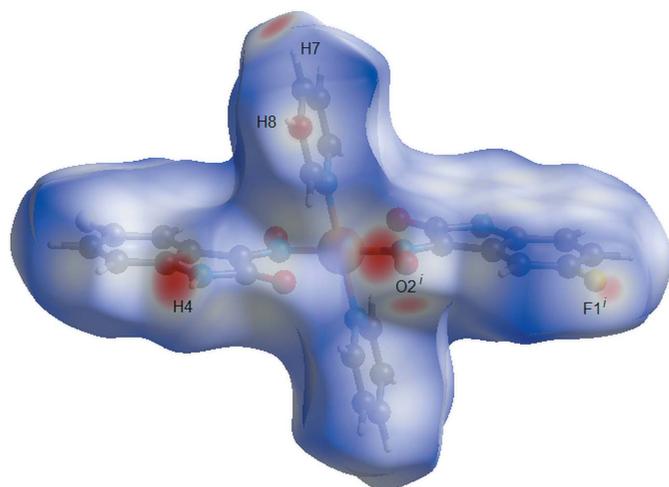


Figure 7
Graphical representation of the Hirshfeld surface (d_{norm}) for the title compound. The surface is drawn with transparency and simplified for clarity. The surface regions with strongest intermolecular interactions are drawn in magenta and the respective atoms are labelled. [Symmetry code: (i) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 1$]

packing amount to 31.80, 24.30 and 15.20%, respectively. Other important intermolecular contacts for the cohesion of the structure are (values given in %): $\text{H} \cdots \text{F} = 10.80$, $\text{C} \cdots \text{C} = 6.20$, and $\text{H} \cdots \text{N} = 4.30$. The contributions to the crystal cohesion are shown as two-dimensional Hirshfeld surface fingerprint plots with cyan dots (Wolff *et al.*, 2012). The d_e (y axis) and d_i (x axis) values are the closest external and internal distances (values in Å) from given points on the Hirshfeld surface contacts (Fig. 6). The graphical representation of the Hirshfeld surface for the title compound with transparency and labelled atoms (Fig. 7) indicates, in magenta, the locations of the strongest intermolecular contacts, e.g. the H4, H7, H8, O2 and F1 atoms.

4. Database survey

A search of *SciFinder* (SciFinder, 2018) revealed a single report in the literature about the crystal structure of

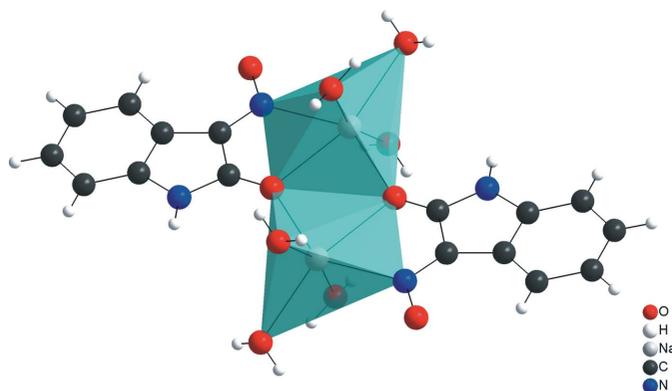


Figure 8
Partial view of the structure of catena-poly[[[aqua-sodium]-di- μ -aqua-[aqua-sodium]-bis(μ -2-oxoindoline-2,3-dione 3-oximato)] tetrakis(oxoindoline-2,3-dione 3-oxime)].

Table 2
Experimental details.

Crystal data	
Chemical formula	[Cu(C ₈ H ₄ FN ₂ O ₂) ₂ (C ₅ H ₅ N) ₂]
M_r	580.00
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	200
a, b, c (Å)	19.9709 (14), 7.2155 (5), 17.1989 (12)
β (°)	98.579 (2)
V (Å ³)	2450.6 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.95
Crystal size (mm)	0.40 × 0.24 × 0.20
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.674, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18806, 4481, 3966
R_{int}	0.017
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.760
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.033, 0.086, 1.12
No. of reflections	4481
No. of parameters	178
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.40, -0.34

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2016* (Sheldrick, 2015b), *WinGX* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006), *CrystalExplorer* (Wolff *et al.*, 2012), *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

coordination compounds with isatin 3-oxime derivatives, *i.e.* the one-dimensional coordination polymer, catena-poly-[[[aqua-sodium]-di- μ -aqua-[aqua-sodium]-bis(μ -2-oxoindoline-2,3-dione 3-oximato)] tetrakis(oxoindoline-2,3-dione 3-oxime)] (Barreto Martins *et al.*, 2011). For that complex, the Na cations shows an octahedral coordination environment builded by the anionic form of the isatin 3-oxime and water molecules (Fig. 8).

5. Synthesis and crystallization

All the starting materials were commercially available and were used without further purification. The synthesis of the ligand followed the procedure reported previously (Martins *et al.*, 2017). 5-Fluoroisatin 3-oxime was dissolved in methanol (4 mmol, 50 mL) and deprotonated with one pellet of KOH with stirring maintained for 60 min. Simultaneously, a green solution of copper acetate monohydrate in methanol (2 mmol, 50 mL) was prepared under continuous stirring. A dark-coloured mixture of both solutions was maintained with stirring at room temperature for 8 h. A crude dark-red material was obtained by evaporation of the solvent. Purple crystals of the complex, suitable for X-ray analysis, were obtained by recrystallization of the solid from a pyridine/methanol (1:10 v/v) solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were located in a difference-Fourier map, but were positioned with idealized geometry and refined isotropically using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$, and with C–H = 0.95 and N–H = 0.88 Å.

Acknowledgements

ABO is a former DAAD scholarship holder and *alumnus* of the University of Bonn, Germany, and thanks both of the institutions for long-term support, in particular Professor Johannes Beck and Dr Jörg Daniels.

Funding information

APLM thanks the CAPES foundation for a scholarship.

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supporting information

Acta Cryst. (2018). E74, 428–432 [https://doi.org/10.1107/S2056989018003365]

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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *WinGX* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *CrystalExplorer* (Wolff *et al.*, 2012); software used to prepare material for publication: *pubCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

trans-Bis(5-fluoroindoline-2,3-dione 3-oximato- κ^2O^2,N^3)-*trans*-bis(pyridine- κN)copper(II)

Crystal data

[Cu(C₈H₄FN₂O₂)₂(C₅H₅N)₂]

$M_r = 580.00$

Monoclinic, *C2/c*

$a = 19.9709$ (14) Å

$b = 7.2155$ (5) Å

$c = 17.1989$ (12) Å

$\beta = 98.579$ (2)°

$V = 2450.6$ (3) Å³

$Z = 4$

$F(000) = 1180$

$D_x = 1.572$ Mg m⁻³

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

Cell parameters from 9537 reflections

$\theta = 2.4$ – 32.7 °

$\mu = 0.95$ mm⁻¹

$T = 200$ K

Prismatic, purple

$0.40 \times 0.24 \times 0.20$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed X-ray tube,
Bruker APEX2 CCD

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.674$, $T_{\max} = 0.746$

18806 measured reflections

4481 independent reflections

3966 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 32.7$ °, $\theta_{\min} = 2.1$ °

$h = -30$ → 30

$k = -10$ → 7

$l = -26$ → 26

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.086$

$S = 1.12$

4481 reflections

178 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
 $w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 2.817P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.66193 (6)	0.43044 (17)	0.51144 (7)	0.0202 (2)
C2	0.62981 (6)	0.59529 (16)	0.54136 (7)	0.0179 (2)
C3	0.57200 (6)	0.53285 (17)	0.57616 (7)	0.0190 (2)
C4	0.52421 (7)	0.6220 (2)	0.61397 (8)	0.0252 (2)
H1	0.524139	0.752687	0.620565	0.030*
C5	0.47665 (7)	0.5092 (2)	0.64150 (10)	0.0308 (3)
C6	0.47458 (7)	0.3189 (2)	0.63286 (10)	0.0330 (3)
H2	0.440637	0.248844	0.652851	0.040*
C7	0.52236 (8)	0.2300 (2)	0.59479 (10)	0.0292 (3)
H3	0.521610	0.099354	0.587721	0.035*
C8	0.57102 (6)	0.33887 (17)	0.56761 (8)	0.0213 (2)
C9	0.79324 (7)	0.8070 (2)	0.66905 (8)	0.0271 (3)
H5	0.778142	0.929489	0.656022	0.033*
C10	0.81834 (9)	0.7655 (3)	0.74669 (9)	0.0361 (3)
H6	0.820299	0.858192	0.786181	0.043*
C11	0.84039 (8)	0.5880 (3)	0.76578 (9)	0.0374 (4)
H7	0.857425	0.556392	0.818653	0.045*
C12	0.83737 (9)	0.4571 (3)	0.70703 (10)	0.0359 (3)
H8	0.852688	0.334216	0.718775	0.043*
C13	0.81167 (8)	0.5072 (2)	0.63051 (9)	0.0285 (3)
H9	0.809607	0.416673	0.590100	0.034*
Cu1	0.750000	0.750000	0.500000	0.01704 (6)
F1	0.42924 (6)	0.59199 (17)	0.67886 (8)	0.0505 (3)
N1	0.62487 (6)	0.28139 (15)	0.52904 (8)	0.0242 (2)
H4	0.633443	0.165583	0.517849	0.029*
N2	0.65751 (5)	0.75711 (14)	0.53373 (6)	0.01704 (17)
N3	0.78961 (5)	0.67952 (17)	0.61181 (6)	0.0208 (2)
O1	0.71204 (5)	0.42959 (14)	0.47722 (6)	0.02501 (19)
O2	0.62959 (5)	0.90531 (12)	0.55624 (6)	0.02333 (18)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0261 (5)	0.0133 (5)	0.0219 (5)	0.0016 (4)	0.0052 (4)	0.0011 (4)
C2	0.0209 (5)	0.0130 (5)	0.0204 (5)	0.0011 (4)	0.0051 (4)	0.0007 (4)
C3	0.0205 (5)	0.0150 (5)	0.0215 (5)	-0.0005 (4)	0.0041 (4)	0.0022 (4)

C4	0.0254 (6)	0.0219 (6)	0.0299 (6)	0.0018 (5)	0.0092 (5)	0.0011 (5)
C5	0.0246 (6)	0.0335 (8)	0.0367 (7)	0.0022 (5)	0.0131 (5)	0.0036 (6)
C6	0.0254 (6)	0.0329 (8)	0.0420 (8)	-0.0059 (6)	0.0098 (6)	0.0092 (7)
C7	0.0292 (6)	0.0201 (6)	0.0386 (7)	-0.0053 (5)	0.0057 (5)	0.0062 (5)
C8	0.0237 (5)	0.0145 (5)	0.0255 (5)	-0.0007 (4)	0.0036 (4)	0.0033 (4)
C9	0.0295 (6)	0.0297 (7)	0.0220 (6)	0.0023 (5)	0.0034 (5)	-0.0005 (5)
C10	0.0398 (8)	0.0476 (10)	0.0199 (6)	-0.0019 (7)	0.0009 (5)	-0.0030 (6)
C11	0.0345 (7)	0.0532 (11)	0.0230 (6)	-0.0028 (7)	-0.0006 (5)	0.0120 (6)
C12	0.0375 (8)	0.0367 (8)	0.0327 (7)	0.0066 (7)	0.0026 (6)	0.0141 (6)
C13	0.0322 (6)	0.0278 (7)	0.0262 (6)	0.0071 (5)	0.0069 (5)	0.0045 (5)
Cu1	0.01925 (10)	0.01681 (10)	0.01575 (9)	0.00118 (7)	0.00488 (6)	0.00176 (7)
F1	0.0404 (5)	0.0492 (7)	0.0705 (8)	0.0048 (5)	0.0367 (5)	0.0016 (6)
N1	0.0325 (6)	0.0093 (4)	0.0326 (6)	0.0007 (4)	0.0108 (5)	0.0011 (4)
N2	0.0204 (4)	0.0131 (4)	0.0179 (4)	0.0018 (3)	0.0040 (3)	0.0000 (3)
N3	0.0203 (4)	0.0249 (5)	0.0182 (4)	0.0027 (4)	0.0064 (3)	0.0029 (4)
O1	0.0308 (5)	0.0182 (4)	0.0284 (5)	0.0044 (4)	0.0123 (4)	0.0013 (4)
O2	0.0297 (4)	0.0122 (4)	0.0301 (5)	0.0025 (3)	0.0113 (4)	-0.0021 (3)

Geometric parameters (Å, °)

C1—O1	1.2342 (15)	C9—N3	1.3412 (19)
C1—N1	1.3649 (16)	C9—C10	1.387 (2)
C1—C2	1.4798 (17)	C9—H5	0.9500
C2—N2	1.3070 (15)	C10—C11	1.378 (3)
C2—C3	1.4493 (16)	C10—H6	0.9500
C3—C4	1.3901 (18)	C11—C12	1.378 (3)
C3—C8	1.4072 (17)	C11—H7	0.9500
C4—C5	1.386 (2)	C12—C13	1.387 (2)
C4—H1	0.9500	C12—H8	0.9500
C5—F1	1.3591 (17)	C13—N3	1.3423 (19)
C5—C6	1.382 (2)	C13—H9	0.9500
C6—C7	1.392 (2)	Cu1—N2	2.0176 (10)
C6—H2	0.9500	Cu1—N3	2.0319 (11)
C7—C8	1.3841 (18)	N1—H4	0.8800
C7—H3	0.9500	N2—O2	1.2917 (13)
C8—N1	1.4077 (17)		
O1—C1—N1	127.37 (12)	N3—C9—H5	119.0
O1—C1—C2	126.46 (12)	C10—C9—H5	119.0
N1—C1—C2	106.18 (11)	C11—C10—C9	119.13 (15)
N2—C2—C3	133.98 (11)	C11—C10—H6	120.4
N2—C2—C1	118.12 (10)	C9—C10—H6	120.4
C3—C2—C1	107.89 (10)	C10—C11—C12	119.00 (14)
C4—C3—C8	120.61 (12)	C10—C11—H7	120.5
C4—C3—C2	133.96 (12)	C12—C11—H7	120.5
C8—C3—C2	105.40 (11)	C11—C12—C13	119.13 (15)
C5—C4—C3	116.20 (13)	C11—C12—H8	120.4
C5—C4—H1	121.9	C13—C12—H8	120.4

C3—C4—H1	121.9	N3—C13—C12	122.02 (15)
F1—C5—C6	118.42 (13)	N3—C13—H9	119.0
F1—C5—C4	117.69 (14)	C12—C13—H9	119.0
C6—C5—C4	123.89 (14)	N2—Cu1—N3	88.75 (4)
C5—C6—C7	119.82 (13)	O1—Cu1—N3	89.01 (4)
C5—C6—H2	120.1	C1—N1—C8	110.49 (10)
C7—C6—H2	120.1	C1—N1—H4	124.8
C8—C7—C6	117.53 (13)	C8—N1—H4	124.8
C8—C7—H3	121.2	O2—N2—C2	120.09 (10)
C6—C7—H3	121.2	O2—N2—Cu1	124.18 (8)
C7—C8—C3	121.93 (13)	C2—N2—Cu1	115.18 (8)
C7—C8—N1	128.03 (12)	C9—N3—C13	118.66 (12)
C3—C8—N1	110.04 (11)	C9—N3—Cu1	119.59 (10)
N3—C9—C10	122.06 (15)	C13—N3—Cu1	121.74 (10)
O1—C1—C2—N2	-2.32 (19)	C4—C3—C8—N1	-178.83 (12)
N1—C1—C2—N2	177.94 (12)	C2—C3—C8—N1	-0.40 (14)
O1—C1—C2—C3	179.09 (13)	N3—C9—C10—C11	0.1 (2)
N1—C1—C2—C3	-0.65 (14)	C9—C10—C11—C12	0.5 (3)
N2—C2—C3—C4	0.5 (3)	C10—C11—C12—C13	-0.6 (3)
C1—C2—C3—C4	178.76 (14)	C11—C12—C13—N3	0.0 (2)
N2—C2—C3—C8	-177.63 (14)	O1—C1—N1—C8	-179.33 (13)
C1—C2—C3—C8	0.63 (13)	C2—C1—N1—C8	0.41 (14)
C8—C3—C4—C5	-0.3 (2)	C7—C8—N1—C1	179.97 (14)
C2—C3—C4—C5	-178.20 (14)	C3—C8—N1—C1	-0.01 (16)
C3—C4—C5—F1	179.91 (13)	C3—C2—N2—O2	-4.6 (2)
C3—C4—C5—C6	-0.4 (2)	C1—C2—N2—O2	177.27 (11)
F1—C5—C6—C7	179.92 (15)	C3—C2—N2—Cu1	167.30 (11)
C4—C5—C6—C7	0.2 (3)	C1—C2—N2—Cu1	-10.83 (14)
C5—C6—C7—C8	0.6 (2)	C10—C9—N3—C13	-0.7 (2)
C6—C7—C8—C3	-1.3 (2)	C10—C9—N3—Cu1	178.48 (12)
C6—C7—C8—N1	178.68 (14)	C12—C13—N3—C9	0.6 (2)
C4—C3—C8—C7	1.2 (2)	C12—C13—N3—Cu1	-178.54 (12)
C2—C3—C8—C7	179.62 (13)		

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the N3/C9—C13 ring

<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>
C9—H5...O1 ⁱ	0.95	2.54	3.1424 (18)	121
C12—H8...F1 ⁱⁱ	0.95	2.49	3.287 (2)	142
C13—H9...O1	0.95	2.54	3.1077 (19)	119
N1—H4...O2 ⁱⁱⁱ	0.88	2.00	2.7529 (14)	143
C6—H2...Cg1 ^{iv}	0.95	2.79	3.7076 (17)	162

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