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STRUCTURAL CHARACTERIZATION OF TWO COPPER(II) BISHEXAFLUOROACETYLACETONATE COMPLEXES WITH N-DONOR LIGANDS

Y.-C. Wang, G.-F. Wang*, and Z.-R. Liu

The synthesis and characterization of two copper complexes, Cu(*hfac*)$_2$($\boldsymbol{L}^1$)$_2$ (**1**) and Cu(*hfac*)$_2$($\boldsymbol{L}^2$)$_2$ (**2**) ($\boldsymbol{L}^1$ = (*E*)-3-(4-(1*H*-benzo[*d*]imidazol-1-yl)phenyl)-1-([1,1′-biphenyl]-4-yl)prop-2-en-1-one, $\boldsymbol{L}^2$ = (*E*)-3-(4-(1*H*-imidazol-1-yl)phenyl)-1-phenylprop-2-en-1-one) are reported. These complexes are characterized by elemental analyses, IR and single crystal X-ray diffraction analyses. The Cu(II) ions of **1** and **2** are both in a distorted octahedral environment with four O atoms of the *hfac* ligands and two N atoms from two ***L*** ligands. The supramolecular structures of **1** and **2** are stabilized by hydrogen bonds between the adjacent molecules. In addition, F···F interactions and π–π stacking interactions are also responsible for the stability of the structure in complex **2**.

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Keywords: synthesis, supramolecular arrangements, copper complex, crystal structure, coordination compound, hydrogen bond.

The rational design and synthesis of novel complexes has been the subject of extensive investigation mainly due to potential applications for new inorganic materials, chemical and biochemical catalytic systems, as well as their fascinating geometric aspects [1-5]. Unsaturated metal complex Cu(*hfac*)$_2$ has proven to be very useful in the preparation of materials, including oxide and thin metallic films by the chemical vapor deposition (CVD) technique. Moreover, the reactive copper(II) β-diketonate moiety may be ligated with an N-heterocyclic ligand, such as midazole, ethynylpyridine [6], in which the fluorine atoms in Cu(*hfac*)$_2$ could be used as hydrogen bond acceptors, providing another crystal engineering design tool for assembling building blocks by means of the C–F…H–C hydrogen bonding system.

As a part of our study on the coordination chemistry of copper complexes [7-10], we report here the synthesis and structural characterization of two copper(II) bishexafluoroacetylacetonate complexes with the N-heterocyclic ligand: Cu(*hfac*)$_2$($\boldsymbol{L}^1$)$_2$ (**1**), Cu(*hfac*)$_2$($\boldsymbol{L}^2$)$_2$ (**2**) ($\boldsymbol{L}^1$ = (*E*)-3-(4-(1*H*-benzo[*d*]imidazol-1-yl)phenyl)-1-([1,1′-biphenyl]-4-yl)prop-2-en-1-one, $\boldsymbol{L}^2$ = (*E*)-3-(4-(1*H*-imidazol-1-yl)phenyl)-1-phenylprop-2-en-1-one).

EXPERIMENTAL

Materials and methods. Reagents and solvents employed were commercially available and used as received. Ligands $\boldsymbol{L}^1$ and $\boldsymbol{L}^2$ were prepared according to the modified literature procedure [11]. Elemental analyses (C, H, and N) were

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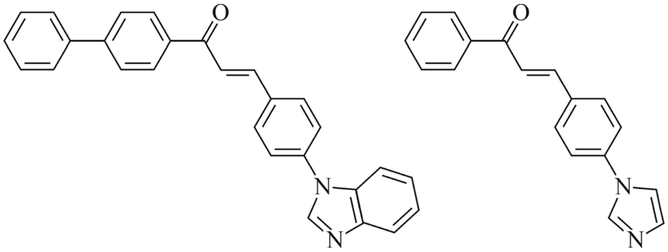
performed on a Vario EL-III analyzer. IR spectra were recorded on a Bruker Vector 22 spectrophotometer as KBr pellets in the range 400-4000 cm^{-1}.

Synthesis of Cu(*hfac*)$_2$(*L*^{1})$_2$ (1). To a CH_2Cl_2 solution (20 ml) of Cu(*hfac*)$_2$·4H_2O (55 mg, 0.10 mmol), ***L*^{1}** (80 mg, 0.2 mmol) in CH_2Cl_2 was added slowly. The mixture was stirred for 0.5 h and the resulting light green solution filtrated was kept at room temperature for several days. Green crystals suitable for X-ray crystallography formed upon evaporation of the solvent. Yield: 52%. Elemental analyses: chemical formula $C_{66}H_{42}CuF_{12}N_4O_6$; calculated, %: C 62.00, H 3.31, N, 4.38; found, %: C 61.83, H 3.22, N 4.47. IR (KBr, cm^{-1}): 3130, 2959, 1663, 1607, 1554, 1524, 1457, 1423, 1338, 1318, 1259, 1192, 1146, 1081, 1032, 1012, 995, 973, 874, 823, 793, 743, 663, 621, 579, 530, 484.



Scheme 1. Structure of L^1 and L^2 ligands.

Synthesis of Cu(*hfac*)$_2$(*L*^{2})$_2$ (2). To a CH_2Cl_2 solution (20 ml) of Cu(*hfac*)$_2$·4H_2O (55 mg, 0.10 mmol), ***L*^{2}** (54 mg, 0.2 mmol) in CH_2Cl_2 was added slowly. The mixture was stirred for 0.5 h and the resulting light green solution filtrated was kept at room temperature for several days. Green crystals suitable for X-ray crystallography formed upon evaporation of the solvent. Yield: 58%. Elemental analyses: chemical formula $C_{46}H_{30}CuF_{12}N_4O_6$; calculated, %: C 53.84, H 2.95, N 5.46; found, %: C 53.62, H 2.83, N 5.61. IR (KBr, cm^{-1}): 3134, 2959, 1663, 1605, 1552, 1526, 1431, 1340, 1311, 1257, 1213, 1132, 1063, 1016, 983, 964, 831, 790, 770, 718, 689, 663, 619, 583, 523.

X-ray crystallography. Green crystals of **1** and **2** suitable for X-ray diffraction were grown by slow evaporation from EtOH–CH_2Cl_2 after 2 weeks. X-ray crystallographic data of **1** and **2** were recorded on an Agilent Technology SuperNova Eos Dual system with a (MoK_α, $\lambda = 0.71073$ Å) micro focus source and focusing multilayer mirror optics. The data were collected at a temperature of 293 K and processed using CrysAlis^{Pro} [12]. The structures were solved by direct methods [13] with the SHELXTL (version 6.10) program [14] and refined by full matrix least-squares techniques on F^2 with SHELXTL [14]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were generated geometrically. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. CCDC numbers: 1503369 and 1503370 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, 12 Union Road Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk. The details of crystal data and refinement for **1** and **2** are given in Table 1. Selected bond distances and bond angles are listed in Table 2.

RESULTS AND DISCUSSION

The reaction between Cu(*hfac*)$_2$ and N-donor ligands in CH_2Cl_2–EtOH leads to the formation of mononuclear copper complexes **1** and **2** in moderate yields. Elemental analyses of **1** and **2** were fully consistent with their formulations. The IR spectra showed the characteristic band corresponding to carbonyl stretching frequencies at *ca*. 1663 cm^{-1}.

The structures of **1** and **2** were confirmed by X-ray diffraction analyses, as shown in Figs. 1-2, respectively. Complex **1** crystallizes in the monoclinic space group $P2_1/c$, where the asymmetric unit consists of one crystallographically independent Cu(II) ion, two *hfac* ligands, and two ***L*^{1}** ligands. The Cu(II) centre is octahedrally coordinated by four oxygen atoms (O1, O2, O1#1, O2#1) from two *hfac* ligands (Cu–O = 2.032(2)-2.313(3) Å) and two nitrogen (N1, N1#1) atoms from two ***L*^{1}** ligands(Cu–N = 1.988(3) Å).

TABLE 1. Crystallographic Data and Structure Refinement Parameters for **1** and **2**

Formula	$C_{66}H_{42}CuF_{12}N_4O_6$	$C_{46}H_{30}CuF_{12}N_4O_6$
Molar weight, g/mol	1278.59	1026.28
Crystal system	Monoclinic	Triclinic
Space group; Z	$P2(1)/c$; 2	$P\overline{1}$; 1
Wavelength, Å	0.71073	0.71073
Temperature, K	293(2)	293(2)
a, b, c, Å	10.9196(6), 15.6285(9), 19.9290(9)	8.6364(6), 8.8282(4), 14.9719(8)
α, β, γ, deg.	β 123.225(2)	97.318(4), 106.628(6), 95.198(5)
V, Å^3	2845.0(3)	1075.13(11)
Range of h, k, l	–13 / 11, –19 / 14, –24 / 23	–10 / 9, –10 / 10, –18 / 17
2θ range, deg.	3.21 to 25.68	2.94 to 25.49
d_{calc}, g/cm^3	0.482	0.616
$F(000)$	1302	519
Reflections measured / unique (R_{int})	12459 / 5399 (0.0328)	8297 / 4005 (0.0278)
Max. and min. transmission	0.9014 and 0.8809	0.8816 and 0.8563
Data / restrains / parameters	5399 / 0 / 403	4005 / 46 / 341
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices $I > 2\sigma(I)$	0.0619, 0.1488	0.0658, 0.1755
R indices (all data)	0.0843, 0.1670	0.0811, 0.1896
Goodness-of-fit on F^2	1.022	1.096
Absorption coefficient, mm^{-1}	0.482	0.616
Largest diff. peak and hole, e/Å^3	0.765 and –0.658	0.681 and –0.622

TABLE 2. Selected Bond Distances (Å) and Bond Angles (deg.) for **1** and **2**

1		**2**	
Cu(1)–N(1)$^{\#1}$	1.988(3)	Cu(1)–N(1)	2.001(3)
Cu(1)–N(1)	1.988(3)	Cu(1)–N(1)$^{\#2}$	2.001(3)
Cu(1)–O(1)$^{\#1}$	2.032(2)	Cu(1)–O(2)	2.077(3)
Cu(1)–O(1)	2.032(2)	Cu(1)–O(2)$^{\#2}$	2.077(3)
Cu(1)–O(2)$^{\#1}$	2.312(3)	Cu(1)–O(1)	2.225(3)
Cu(1)–O(2)	2.313(3)	Cu(1)–O(1)$^{\#2}$	2.225(3)
N(1)$^{\#1}$–Cu(1)–N(1)	180.00(15)	N(1)–Cu(1)–N(1)$^{\#2}$	180.000(1)
N(1)$^{\#1}$–Cu(1)–O(1)$^{\#1}$	92.68(11)	N(1)–Cu(1)–O(2)	89.24(13)
N(1)–Cu(1)–O(1)$^{\#1}$	87.32(11)	N(1)$^{\#2}$–Cu(1)–O(2)	90.76(13)
N(1)$^{\#1}$–Cu(1)–O(1)	87.32(11)	N(1)–Cu(1)–O(2)$^{\#2}$	90.76(13)
N(1)–Cu(1)–O(1)	92.68(11)	N(1)#2–Cu(1)–O(2)$^{\#2}$	89.24(13)
O(1)$^{\#1}$–Cu(1)–O(1)	180.000(1)	O(2)–Cu(1)–O(2)$^{\#2}$	180.00(17)
N(1)$^{\#1}$–Cu(1)–O(2)$^{\#1}$	87.74(11)	N(1)–Cu(1)–O(1)	90.38(13)
N(1)–Cu(1)–O(2)$^{\#1}$	92.26(11)	N(1)$^{\#2}$–Cu(1)–O(1)	89.62(13)
O(1)$^{\#1}$–Cu(1)–O(2)$^{\#1}$	84.93(10)	O(2)–Cu(1)–O(1)	87.02(11)
O(1)–Cu(1)–O(2)$^{\#1}$	95.07(10)	O(2)$^{\#2}$–Cu(1)–O(1)	92.98(11)
N(1)$^{\#1}$–Cu(1)–O(2)	92.26(11)	N(1)–Cu(1)–O(1)$^{\#2}$	89.62(13)
N(1)–Cu(1)–O(2)	87.74(11)	N(1)$^{\#2}$–Cu(1)–O(1)$^{\#2}$	90.38(13)
O(1)$^{\#1}$–Cu(1)–O(2)	95.07(10)	O(2)–Cu(1)–O(1)$^{\#2}$	92.98(11)
O(1)–Cu(1)–O(2)	84.93(10)	O(2)$^{\#2}$–Cu(1)–O(1)$^{\#2}$	87.02(11)
O(2)#1–Cu(1)–O(2)	180.0	O(1)–Cu(1)–O(1)$^{\#2}$	180.0

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x-1, -y, -z-1$; $^{\#2}$ $-x+2, -y, -z+1$.

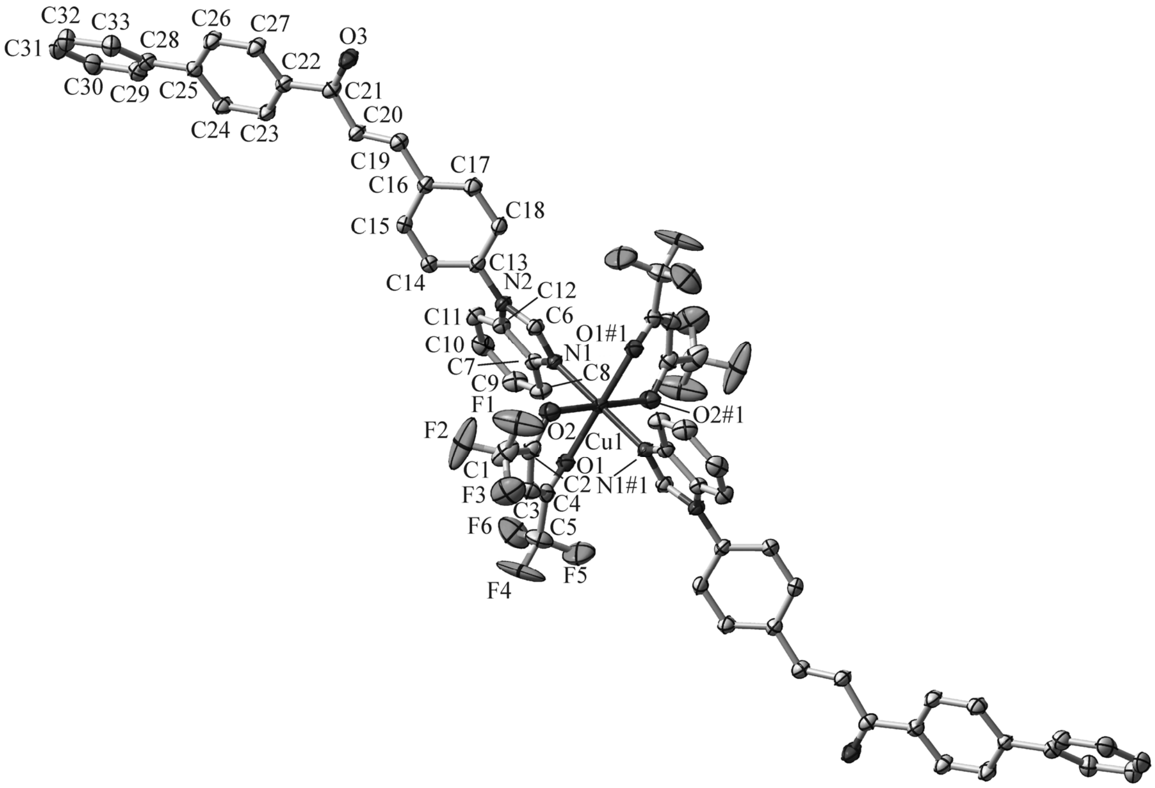


Fig. 1. Coordination environments of complex **1** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Symmetry codes: $^{\#1}$ –*x*–1, –*y*, –1–*z*.

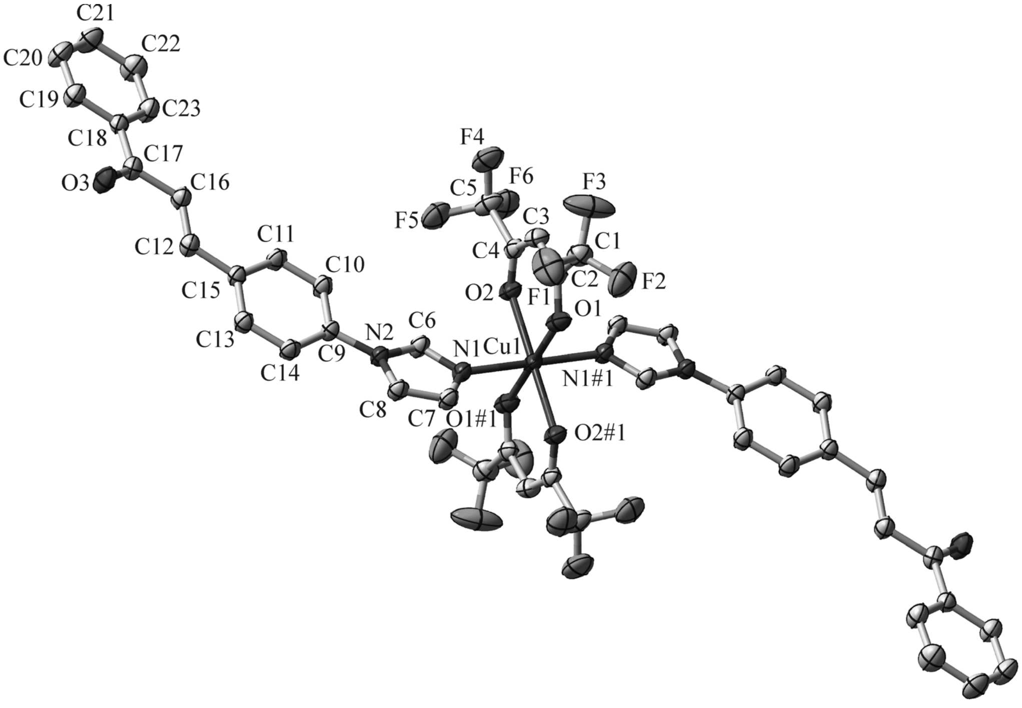


Fig. 2. Coordination environments of complex **2** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Symmetry codes: $^{\#1}$ 2–*x*, –*y*, 1–*z*.

Complex **2** crystallizes in the triclinic space group $P\overline{1}$. Each copper atom has an octahedrally coordinated geometry, bonded by four oxygen atoms from two *hfac* ligands and two nitrogen atoms from two $\boldsymbol{L^1}$ ligands. The Cu–O bond lengths in

1 are in the ranges 2.077(3)-2.225(3) Å and the Cu–N bond lengths are 2.001(3) Å, which are similar to those observed in the reported literature [8-10].

It is noted that in the crystal systems of **1** and **2**, a large quantity of hydrogen bonds are formed between the hydrogen and oxygen atoms (or fluorine atoms) in the complexes (Table 3, Figs. 3 and 4). The lengths of these bonds are very different, varying from 2.34 Å to 2.67 Å, which reflects the strength difference of these bonds. Obviously, these hydrogen bonds are responsible for the stability of a three-dimensional structure of the crystal.

Additionally, the crystal packing of **2** is stabilized by F···F interactions (F2···F4$'^{\mathrm{i}}$ = 2.757(11) Å, symmetry codes: $^{\mathrm{i}}$ *x*, *y*–1, *z*) and aromatic π···π stacking interactions. Intermolecular π···π interactions are evident between the six-membered rings, with a *Cg*1···*Cg*2$^{\mathrm{i}}$ distances of 3.907(7) Å (*Cg*1 and *Cg*2 are the centroids of the C9 ~ C14 and C18 ~ C23 benzene rings, respectively).

TABLE 3. Intra- and Intermolecular Interactions for **1** and **2** (Å, deg.)

Complex	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA	Symmetry operations
1	C3–H3···F3	0.93	2.48	2.800(6)	100	*x*, *y*, *z*
	C3–H3···F4	0.93	2.34	2.711(7)	103	*x*, *y*, *z*
	C15–H15···F6	0.93	2.64	3.376(7)	137	1–*x*, 1/2+*y*, –1/2–*z*
	C23–H23···F4	0.93	2.67	3.244(6)	121	1–*x*, 1/2+*y*, –1/2–*z*
	C32–H32···O3	0.93	2.62	3.365(7)	137	*x*, 3/2–*y*, 1/2+*z*
2	C3–H3···F3	0.93	2.39	2.749(7)	103	*x*, *y*, *z*
	C3–H3···F4	0.93	2.38	2.752(9)	103	*x*, *y*, *z*
	C3–H3···F6′	0.93	2.51	2.823(11)	100	*x*, *y*, *z*
	C6–H6···O2	0.93	2.58	2.976(6)	106	*x*, *y*, *z*
	C7–H7···F3	0.93	2.62	3.307(7)	131	*x*+1, *y*, *z*
	C8–H8···O3	0.93	2.51	3.413(5)	164	2–*x*, 1–*y*, –*z*
	C14–H14···O3	0.93	2.66	3.431(6)	141	2–*x*, 1–*y*, –*z*
	C16–H16···F1	0.93	2.60	3.478(7)	158	*x*, *y*+1, *z*
	C22–H22···F4′	0.93	2.51	3.421(12)	165	*x*, *y*+1, *z*
	F2···F4′			2.757(11)		*x*, *y*–1, *z*

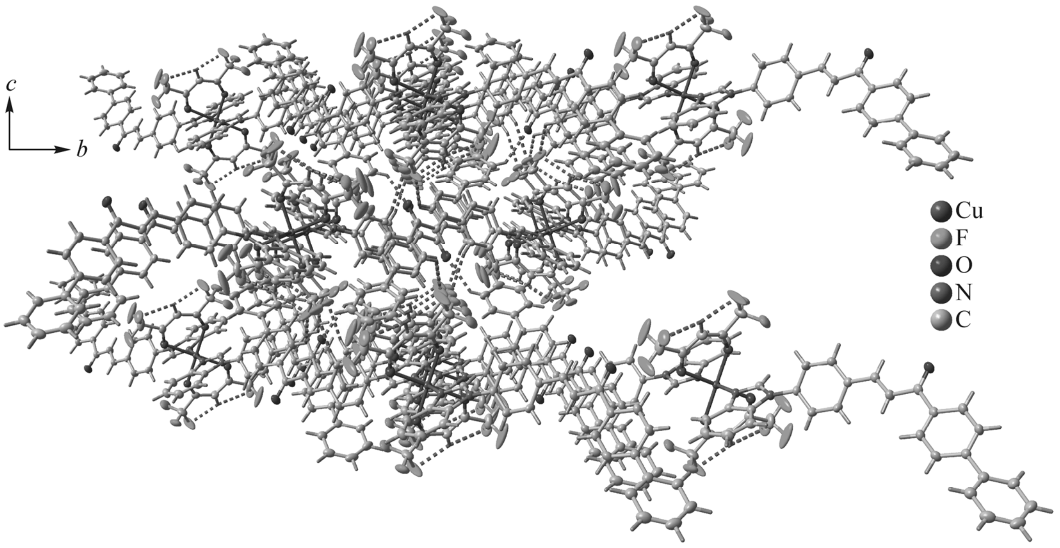


Fig. 3. Three-dimensional packing diagram of **1** along the *a* axis.

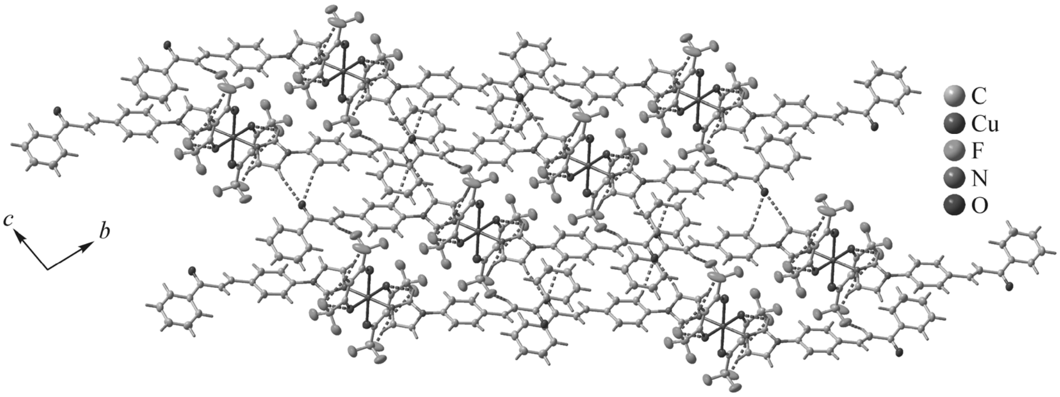


Fig. 4. Three-dimensional packing diagram of **2** along the *a* axis. Disordered atoms are omitted for clarity.

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REFERENCES

1. Qilong Zhu, Chongbin Tian, Chaojun Shen, et al. *CrystEngComm*, **2013**, *15*, 2120-2126.
2. T. W.-S. Chow, Y. Liu, and C.-M. Che. *Chem. Commun*., **2011**, *47*, 11204-11206.
3. J. Wang, S. L. H. Higgins, B. S. J. Winkel, et al. *Chem. Commun*., **2011**, *47*, 9786-9788.
4. L.-X. Xie, X.-W. Hou, Y.-T. Fan, et al. *Cryst. Growth Des*., **2012**, *12*, 1282-1291.
5. Z.-Z. Wen, X.-L. Wen, S.-L. Cai, et al. *CrystEngComm*, **2013**, *15*, 5359-5367.
6. S. Delgado, A. Muňoz, M. E. Medina, et al. *Inorg. Chim. Acta*, **2006**, *359*, 109-117.
7. G.-F. Wang, X. Zhang, S.-W. Sun, et al. *Z. Naturforsch.*, **2015**, *70B*, 617-623.
8. S.-W. Sun, X. Zhang, and G.-F. Wang. *Crystallogr. Rep.*, **2015**, *60*, 1044-1048.
9. G.-F. Wang, S.-W.,Sun, K.Qian, et al. *Z. Kristallogr. New Cryst. Struct.*, **2015**, *230*, 101/102.
10. G.-F. Wang. *Z. Naturforsch.*, **2015**, *70B*, 165-169.
11. S. K. Patle, N. Kawathekar, M. Zaveri, et al. *Med. Chem. Res*., **2013**, *22*, 1756-1761.
12. CrysAlis$^{\mathrm{Pro}}$ Version 1.171.35.19. Agilent Technologies Inc., Santa Clara, CA, USA, **2011**.
13. P. T. Beurskens, G. Admiraal. G. Beurskens, et al. The DIRDIF Program System, Technical Report of the Crystallography Laboratory. University of Nijmegen, The Netherlands, 92, **1992**.
14. G. M. Sheldrick. Program for Crystal Structure Solution and Refinement. University of Göttingen, Germany, **2000**.