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The crystal structure of *catena*-((μ$_2$-4,4′-bipyridine-κ^2*N*:*N*′)-bis(4-fluorobenzoato-κ^{1}O)-copper(II)), $C_{24}H_{16}F_2N_2O_4Cu$

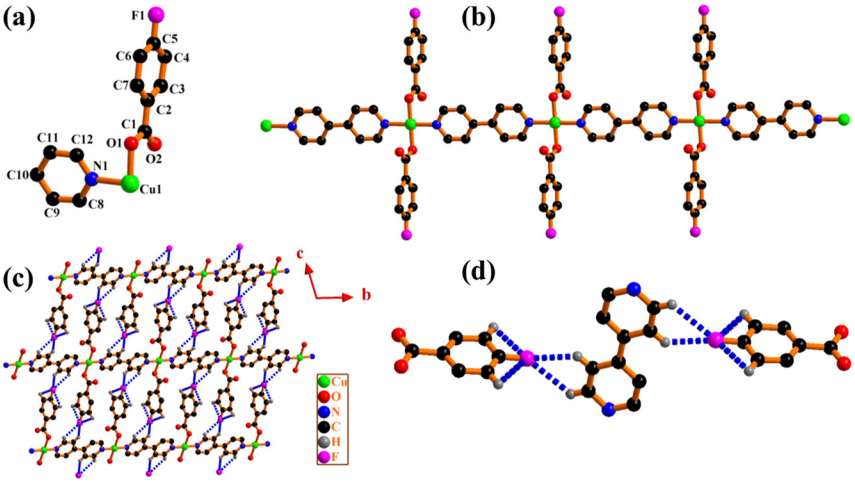

Figure 1: The crystal structure of (I). (a) The asymmetric structural unit of I, showing the atom numbering scheme; (b) view of the one-dimensional chain structure in I; (c) view of the two-dimensional hydrogen bond C–H···F interactions in I, the H···F hydrogen bonds are shown as blue dashed lines; (d) view of the enlargement C–H···F hydrogen bonds interactions between fba^- and bpy ligands with the H···F bonds shown as blue dashed lines.

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Abstract

$C_{24}H_{16}F_2N_2O_4Cu$, triclinic, $P\bar{1}$ (no. 2), a = 5.3203(6) Å, b = 9.0861(11) Å, c = 11.5282(10) Å, α = 103.718(9)°, β = 97.964(9)°, γ = 98.771(10)°, V = 526.12(10) Å^3, Z = 1, $R_{gt}(F)$ = 0.0497, $wR_{ref}(F^2)$ = 0.1000, T = 298 K.

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Table 1 contains the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

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Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.25 × 0.20 × 0.12 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.09 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB Mini (ROW), ω scans
θ_{max}, completeness:	25.1°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	2671, 1878, 0.027
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1644
$N(param)_{refined}$:	167
Programs:	Rigaku,[1] Olex2,[2] SHELX[3,4]

1 Source of materials

All chemicals were purchased from commercial sources and used as received. A mixture of $Cu(NO_3)_2$ (1.0 mL, 0.10 mol L^{-1} $Cu(NO_3)_2$ solution, 0.10 mmol), 4-fluorobenzoic acid (4-fluorobenzoic acid is abbreviated as Hfba) (0.0282 g, 0.20 mmol), 4,4′-bipyridine (4,4′-bipyridine is abbreviated as bpy) (0.0156 g, 0.1 mmol), NaOH (1.0 mL, 0.05 mol L^{-1} NaOH solution, 0.05 mmol), and H_2O/anhydrous ethanol (3.0 mL/7.0 mL) was added to a 25 mL Teflon-lined stainless steel reactor and heated at 393 K for 3 days. After cooling to room temperature at a rate of 283 K h^{-1}, blue block-shaped crystals of I were collected by filtration, washed with anhydrous

ethanol and dried in air. Phase pure crystals were obtained by manual separation (Yield: 22.41 mg, ca. 45 % based on 4-fluorobenzoic acid).

2 Experimental details

CrysAlisPro 1.171.39.46 (Rigaku Oxford Diffraction, 2018) empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was used.[1] Using Olex2,[2] the structure was solved with the ShelXT structure solution program and refined with the ShelXL[4] refinement package. Carbon-bound hydrogen atoms were placed in calculated positions (d = 0.93 Å for CH and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C) for –CH). During the structure refinement process, the Olex2 software prompts that some carbon and fluorine atoms on the carboxylic acid ligand may be split due to the large size of the ellipsoid. So the disordered atoms (C3, C4, C6, C7 and F1) were split in two parts and refined with an occupancy ratio of 0.531(7):0.469(7). The SADI and EADP instructions from ShelXL have been applied to constrain the disordered atoms associated C–C, C–F distances and their anisotropic displacement parameters. The structure was examined using the ADDSYM subroutine of PLATON.[5]

Halogen bonding was defined by the IUPAC in 2013 although the first adduct formed with a halogen bond was reported more than two centuries ago.[6] Halogen bonding forms between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity. Like hydrogen bonding, halogen bonding also has a strong orientation *via* electrostatic interaction or charge-transfer which can reduce localized heating of materials.[7–10] Based on this, halogen bonding has been used in molecular or anion recognition, self-assembly, organic synthesis, and catalysis.[11] However, so far the effect of halogen bonding on the performance of MOF (metal-organic framework) or CP (coordination polymer) or XOF (halogen organic framework, X = F, Cl, Br, I) has not been systematically analyzed. A reason for this oversight is that the number of halogen-containing MOF or CP or XOF is far fewer than the corresponding CHON-containing moieties.[12,13] Therefore, the synthesis of additional halogen-containing MOF or CP or XOF and a summary of the effects of intermolecular halogen bonding is important for the design of next-generation MOF or CP or XOF materials.[14,15] Using 4-fluorobenzoic acid bonds to any metal as the structural model for retrieval, it was found about 120 crystal structure hits in the Cambridge Crystal Structural Database (ConQuest 2022.3.0, CSD), in which there are a total of 7 crystal structures containing imidazole-based bridging ligands. On the basis of the above analysis, it has been further found that pyridine- or imidazole-based bridging ligands often act as a rigid μ_2 bridging and fba^- serve as carboxylate monodentate coordination, while 4-position fluorine atom *via* halogen···halogen interaction constructs supramolecular structures in MOFs or CPs or XOFs.[16–22] To the best of our ability, no crystal structures with the combinations of fba^-, bpy and metal ions are reported. More importantly, Hfba and its derivatives have been found to possess widespread biological activities, many of them have been developed as medical and functional materials. Based on the above considerations, the title compound (Figure) was obtained expectedly as the product of an attempted synthesis of a network complex of Cu(II) using mixed H_2O/anhydrous ethanol as the solvent.

4-Fluorobenzoic acid (abbreviated as Hfba) is usually served as an intermediate of the fungicide flumorph, pesticides and pharmaceuticals. It can also be used for the synthesis of CPs or MOFs. The Hfba can bond to metal ions by bridging and chelating modes *via* O atoms of the deprotonated carboxylate functional group. Furthermore, the aromatic benzene ring of Hfba may participate in the formation of $\pi\cdots\pi$, X–H$\cdots\pi$ and X–F$\cdots\pi$ (X = C, O) stacking interactions whilst the two oxygen atoms may play the part of the acceptors or donors to construct intermolecular and intramolecular hydrogen bonds (O–H···O, C–H···O, C–H···F). In particular, the 4-position F atom can play a key role in the formation strong hydrogen bonding and F···F interactions. Therefore, Hfdba is an excellent candidate for assembling novel CPs/MOFs by incorporating appropriate metal ions neutral nitrogen-containing auxiliary ligand in different forms, which can afford to products possessing interesting topological structures, ranging from chains and sheets to three-dimensional (3D) porous structures. Cu(II) can exhibit variable coordination numbers (4–6) and geometries, and therefore, structural diversities in copper(II) based CPs or MOFs will inevitably occur. Moreover, Cu^{2+} ions have a strong affinity both for pyridines and carboxylates, making it possible to combine Hfdba and bpy ligands in the same framework. In addition, it is known that a strategy to increase the chemical stability of CPs/MOFs is to strengthen the metal-ligand bond using linkers such as inflexible neutral nitrogen-containing pyridine, pyrazolates or imidazolates instead of carboxylates. In this work, we used Hfba and bib as organic ligands for Cu(II) centers. These combinations afforded an one-dimensional CPs, $[Cu(fba)_2(bpy)]_n$ (I), which has been synthesized by hydrothermal methods and characterized by single-crystal X-ray diffraction (SCXRD).

The single crystal X-ray diffraction (SCXRD) data have indicated that I is an one-dimension (1D) type coordination polymer. The asymmetric unit of I is consisted of a half of the formula as {[Cu(fba)$_2$(bpy)], i.e., a half of Cu^{2+}, a half of neutral auxiliary bpy ligand, and a deprotonated carboxylate $Hfba^-$ ligand. Each Cu^{2+} cation is located at the 1c site, it is tetracoordinated to two O atoms (O1 and O1^i) of two symmetry-related fba^- ligands and 2 N atoms (N1 and N1^i) (symmetry code: i = 2 – *x*, 1 – *y*, 2 – *z*) from 2 symmetry-related bpy ligands, respectively, resulting in a perfect tetrahedral {CuN_2O_2} geometry configuration with bond lengths of N1–O1 = N1^i–O1^i = 2.83(4) Å and N1–O1^i = N1^i–O1 = 2.80(6) Å, and with bond angles of N1–Cu1–N1^i = O1–Cu1–O1^i = 180.00°, O1–N1–O1^i = O1–N1^i–O1^i = 86.46(2)°, and N1–O1–N1^i = N1–O1^i–N1^i = 93.53(8)°. The Cu–O bond distances are 1.931(2) (Cu1–O1 = Cu1–O1^i) and the Zn–N bond lengths are 2.055(3) (Cu1–N1 = Cu1–N1^i), and both of within the normal range. The N(O)–Cu–O(N) angles fall in the 89.44(10)°–180.0° range, i.e., O1–Cu1–N1°=°O1^i–Cu1–N1^i = 90.56(10)°, O1–Cu1–N1^i = O1^i–Cu1–N1 = 89.44(10)°, and N1–Cu1–N1^i = O1–Cu1–O1^i = 180.0°. The detailed coordination modes of the fba^- and bpy ligands are listed in Figure. The deprotonated carboxylate of the fba^- anion coordinates with Cu(II) in a monodentate bridging mode and the bpy ligands feature a linear conformation for the bridging mode (μ_2) with a dihedral angle between the two coordinated pyridine rings of N1/C8/C9/C10/C11/C12 and N1^i/C8^i/C9^i/C10^i/C11^i/C12^i, and N1^{ii}/C8^{ii}/C9^{ii}/C10^{ii}/C11^{ii}/C12^{ii} (symmetry code: ii 1 – *x*, 2 – *y*, 2 – *z*) of 0.0°, and between the two phenyl rings of two symmetry-related fba^- C2/C3/C4/C5/C6/C7 and C2^i/C3^i/C4^i/C5^i/C6^i/C7^i also of 0.0°. While a dihedral angle of 2 hexagonal pyridine rings of bpy with six-membered benzene ring of fba^- are also 83.24(4)° (N1/C8/C9/C10/C11/C12 and C2/C3/C4/C5/C6/C7, N1^{ii}/C8^{ii}/C9^{ii}/C10^{ii}/C11^{ii}/C12^{ii} and C2/C3/C4/C5/C6/C7). It is interesting to note that the bond length Cu1–O2 is 2.83(4) Å too lager to normal coordination bond distance range. Thus two symmetrical related fba^- ligands are bound to each Cu^{2+} cation in an upside-down fashion with their deprotonated carboxylate oxygen atom (O1 and O1^i), resulting in substructural blocks {[Cu(fba)]$_2$}. These neighboring {[Cu(fba)]$_2$} units are further interconnected through the μ_2 bpy bridge to generate an infinite chain with a Cu···Cu separation of 11.20(7) Å.

In the crystal of I the analysis of potential hydrogen bonds and schemes with $d(D\cdots A) < R(D) + R(A) + 0.50$, $d(H\cdots A) < R(H) + R(A) - 0.12$ Ang., $D–H\cdots A > 100.0°$ are calculated by PLATON software. The calculation results indicate that there are no classic hydrogen bonds found except for C–H···O and C–H···F interactions. All potential hydrogen bond acceptors and donors participate in no classic hydrogen bonds interactions. In detail, two intramolecular hydrogen bonding C–H···O are formed between C12 and O1 (C12–H12···O1, C12 as donor, O1 as acceptor; bond distances: C12–H12 = 0.93, H12···O1 = 2.34, and C12···O1 = 2.891(5) Å; bond angle: C12–H12···O1 = 118°), and between C8 and O1 (C8–H8···O1, C8 as donor, O1 as acceptor; bond distances: C8–H8 = 0.93, H8···O1 = 2.31, and C8···O1 = 2.876(5) Å; bond angle: C8–H8···O1 = 119°). Moreover, these 1D chains are further interconnected by the weak non-classical intermolecular C–H···O (C11–H11···O2^{iii}, C12–H12···O2^{iii}, symmetry code: iii –1 + *x*, *y*, *z*) hydrogen bonds involved in the fba^- and bpy ligands. The separations of *d*(O···H) and *d*(C···O), and the angle of C–H···O are ranged from 2.48 to 2.55 Å and 3.096(5) to 3.139(5) Å, and 121–124°. Interestingly, four significant hydrogen bonds C–H···F lie in I, i.e., C4–H4···F1^{iv} (C4 as donor, F1^{iv} as acceptor; bond distances: C4–H4 = 0.93, H4···F1^{iv} = 2.55(3), and C4···F1^{iv} = 2.36(9) Å; bond angle: C4–H4···F1^{iv} = 68°), C6–H6···F1^{iv} (C6 as donor, F1^{iv} as acceptor; bond distances: C6–H6 = 0.93, H6···F1^{iv} = 2.50, and C6···F1^{iv} = 2.33(2) Å; bond angle: C6–H6···F1^{iv} = 69°), C8–H8···F1^{iv} (C8 as donor, F1^{iv} as acceptor; bond distances: C8–H8 = 0.93, H8···F1^{iv} = 2.64(7), and C8···F1^{iv} = 3.25(8) Å; bond angle: C8–H8···F1^{iv} = 124°), and C9–H9···F1^{iv} (C9 as donor, F1^{iv} as acceptor; bond distances: C9–H9 = 0.93, H9···F1^{iv} = 2.58(1), and C9···F1^{iv} = 3.21(7) Å; bond angle: C12–H12···F2^{iv} = 136°) (symmetry code: iv –1 + *x*, –1 + *y*, –1 + *z*), resulting in a supramolecular two-dimensional C–H···F hydrogen bonding network (Figure 1).

In addition, it doesn't obviously exist either offset face-to-face $\pi\cdots\pi$ or edge-to-face C–H···π stacking interactions. It is worth mentioning that the adjacent one-dimensional chains linked together dependent not only by two pairs of C–H···F, but also by a kind of edge-to-face C–F···π stacking interactions, i.e. between the pyridine (six-membered ring, Cg1: N1/C8/C9/C10/C11/C12) and C5–F1 bond of the fba^- ligand (C5–F1···Cg1^v, symmetry code: v 1 – *x*, 1 – *y*, 1 – *z*). The C5–F1···Cg1^v(Y–X···Cg) dihedral angle is 121.6(18)°, and with a F1···Cg1^v (X···Cg) distance of 3.93(3) Å, a X-perp distance of 3.470 Å, and a C5···Cg1^v (Y···Cg) distance of 4.815(6) Å, respectively. However, their contribution to the overall lattice energy must be very small. Thus a supramolecular 3D network fragment is formed by C–H···X (X = O or F) and C–F···π interactions stabilizing the coordination polymer. Furthermore, PLATON[5] analysis shows that the unit cell contains no residual solvent accessible void.

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