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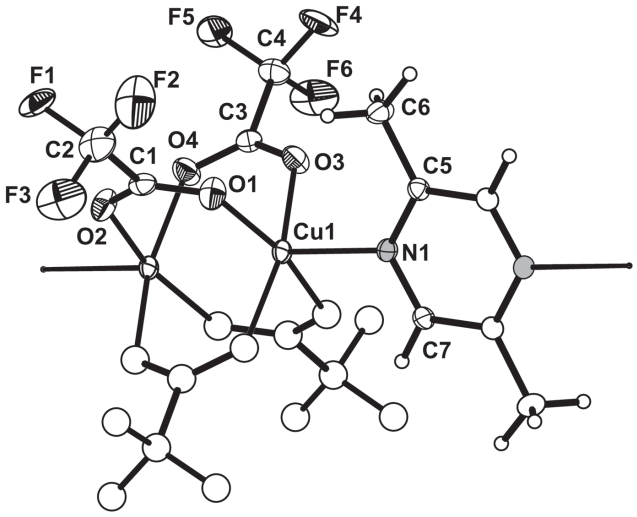
Crystal structure of *catena*-poly[tetrakis(μ_2-trifluoroacetato-κ^2O:O')(μ_2-2,5-dimethylpyrazine-κ^2N,N')dicopper(II)], $C_7H_4CuF_6NO_4$



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Abstract

$C_7H_4CuF_6NO_4$, triclinic, $P\bar{1}$ (no. 2), $a = 8.5122(5)$ Å, $b = 8.5458(6)$ Å, $c = 8.8674(6)$ Å, $\alpha = 75.042(3)°$, $\beta = 68.601(2)°$, $\gamma = 89.809(3)°$, $V = 577.26(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0247$, $wR_{ref}(F^2) = 0.0625$, $T = 152.41$ K.

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A part of the title structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.11 × 0.10 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.98 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12313, 2373, 0.040
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2162
$N(param)_{refined}$:	201
Programs:	Bruker [1], SHELX [2], Diamond [3], Olex2 [4]

Source of material

All reagents were of analytical grade and used as purchased. A mixture of copper oxide (0.002 mol, 0.1638 g), trifluoroacetic acid (HTFA) (0.005 mol, 0.614 g) and H_2O (25 mL) were added to the round bottom flask in turn. After refluxing for 1 h, 2,5-dimethylpyrazine (DMP) (0.004 mol, 0.396 g) was added and mixed with stirring. The mixture was heated under reflux for 3 h, and then the solution was cooled, filtered and recrystallized. Green block crystals of the title compound were obtained after 1 month.

Experimental details

Absorption corrections were applied by using multi-scan program [1]. Hydrogen atoms were generated geometrically and refined isotropically with a riding model (including free rotating group about the methyl). The U_{iso} values were constrained to be $1.5U_{eq}$(C) for the methyl H atoms and $1.2U_{eq}$ for others. The F atoms of one trifluoromethyl group have been refined with the instruction PART due to disorder. The occupancy of the F atoms is refined as free variable, and the displacement parameters of the F atoms were restrained to be more reasonable by means of the instruction RIGU.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.35990(3)	0.48376(3)	0.64634(3)	0.01308(9)
F1[a]	0.874(2)	0.1717(15)	0.687(2)	0.039(2)
F2[a]	0.672(3)	0.172(4)	0.917(2)	0.069(5)
F3[a]	0.853(3)	0.3764(17)	0.784(4)	0.065(4)
F4	0.2095(2)	0.00008(18)	0.5769(2)	0.0449(4)
F5	0.4283(2)	0.01750(18)	0.3555(2)	0.0435(4)
F6	0.2204(2)	0.1558(2)	0.3423(3)	0.0560(5)
O1	0.50898(18)	0.36244(19)	0.74919(19)	0.0231(3)
O2	0.73672(19)	0.38546(19)	0.51141(19)	0.0236(3)
O3	0.29996(18)	0.28875(18)	0.59147(19)	0.0216(3)
O4	0.52910(19)	0.31296(18)	0.35387(19)	0.0228(3)
N1	0.14058(19)	0.4814(2)	0.8672(2)	0.0133(3)
C1	0.6568(3)	0.3429(2)	0.6666(3)	0.0178(4)
C2	0.7568(3)	0.2600(3)	0.7727(3)	0.0330(6)
C3	0.3892(2)	0.2485(2)	0.4639(2)	0.0161(4)
C4	0.3113(3)	0.1027(3)	0.4344(3)	0.0251(5)
C5	0.0643(2)	0.3537(2)	1.0019(2)	0.0135(4)
C6	0.1313(3)	0.1915(2)	1.0052(3)	0.0221(5)
H6B	0.126447	0.156633	0.909901	0.033*
H6A	0.062204	0.111593	1.110942	0.033*
H6C	0.249056	0.199833	0.997047	0.033*
C7	0.0766(2)	0.6245(2)	0.8661(2)	0.0147(4)
H7	0.129803	0.715167	0.771106	0.018*
F2A[b]	0.656(2)	0.1325(14)	0.9013(19)	0.050(2)
F1A[b]	0.8906(19)	0.203(3)	0.6933(19)	0.066(3)
F3A[b]	0.792(3)	0.3625(16)	0.847(3)	0.071(3)

[a]Occupancy: 0.44(5), [b]Occupancy: 0.56(5).

Comment

Compounds containing trifluoromethyl have attracted much attention due to their excellent performance in application, such as pharmaceuticals, agricultural chemistry and materials science [5–11]. A trifluoromethyl group, for example, is known to enhance lipid solubility and metabolic stability of a molecule, and to lead to reduced side effects [12]. Moreover, the presence of this strongly electron-withdrawing group on the 2-position of a chromen-4-one skeleton has been found to have a major impact on the reactivity of the pyrone ring towards nitrogen-, sulfur- and carbon-based nucleophiles [13]. Pyrazines, such as 2,5-dimethylpyrazine (DMP), are an important class of heterocyclic compounds and have important applications [14].

Single-crystal X-ray diffraction analysis reveals that the title complex exhibits a one-dimensional chain coordination polymer (see the figure). The asymmetric unit of the title compound consists of $[Cu(TFA)_2\ (DMP)_{0.5}]$ (see the figure). The central Cu ion exhibits a distorted octahedron coordination. Four oxygen atoms from four different TFA anions (O1, O2A, O3 and O4A) are in equatorial position, whereas, one axial position is occupied by one nitrogen atom (N1) from DMP neutral ligand, whereas the 6th position keeps unoccupied. All the four equatorial O atoms form a plane, yet the Cu(II) ion is not in the equatorial plane, and the maximal deviation from the least-squares plane is 0.26 Å. The bite angles of O—Cu—O are in the range of 88.18(7)° and 90.38(7)°. The angle of N1—Cu1—Cu1A is 174.91(5)° that is almost linear. The presence of single μ_2-DMP bridge links adjacent metal atoms to form polymeric chains of six-coordinate Cu(II) polyhedra [15, 16]. The TFA ligands adopt the coordination fashion that is typical for such complexes. There are two independent five-membered chelate rings in the bridging coordination conformation. The coordination plane comprising Cu1, O3, C3, O4 and Cu1A make a dihedral angle of 46.77° with the plane formed by the DMP ligand. The Cu—N distance is 2.1522(15) Å that is similar to a previously described structure [17]. The bond lengths of Cu1—O1, Cu1—O2A, Cu1—O3, Cu1—O4A are 1.9659(15) Å, 1.9770(15) Å, 1.9697(15) Å and 1.9795(15) Å, respectively, that fall within the normal range [18]. The Cu1—Cu1A distance is 2.7599(5) Å, which is slightly longer than 2.6307(9)–2.6325(10) Å in $[C_{30}H_{32}N_4O_8S_2Cu_2]$ [19].

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