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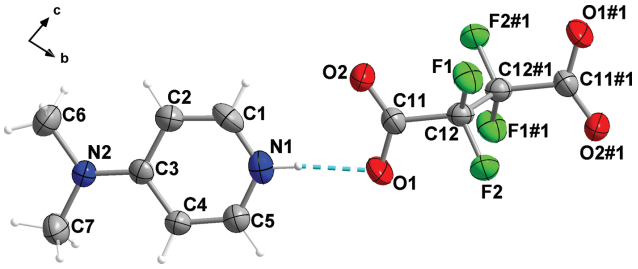
Crystal structure of bis(4-dimethylamino-pyridin-1-ium)tetrafluorosuccinate, $C_{18}H_{22}F_4N_4O_4$



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Abstract

$C_{18}H_{22}F_4N_4O_4$, triclinic, $P\bar{1}$ (no. 2), $a = 7.3295(9)$ Å, $b = 8.6026(9)$ Å, $c = 8.8041(11)$ Å, $\alpha = 77.240(4)°$, $\beta = 72.215(4)°$, $\gamma = 71.531(4)°$, $V = 496.61(10)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.1022$, $wR_{ref}(F^2) = 0.1587$, $T = 294(2)$ K.

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Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

Colorless crystals of bis(4-dimethylamino-pyridinium) tetrafluorosuccinate were prepared by dissolving the calculated amount (2:1) of 4-dimethylaminopyridine (DMAP) and tetrafluorosuccinic acid in methanol under ultrasonication. The mixture was evaporated at 278 K. After 2 days, colorless block crystals of title complex formed. Yield over 95%. The powder X-ray diffraction pattern matches well with the simulated one from single-crystal data. **Elemental analysis** (%) calcd. for $C_{11}H_{12}O_4N_2F_4$: C 42.32, H 3.87, N 24.34; found: C 42.71, H 3.74, N 24.15; **FT-IR** (KBr pellet, cm^{-1}): 3081 w, 1665, 1646 vs, 1558 m, 1363 m, 1215 m, 1122 vs, 806 m, 631 w.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.35 × 0.15 × 0.06 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.3 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	50°, >98.6%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7483, 1723, 0.075
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1215
$N(param)_{refined}$:	138
Programs:	SHELX [1], DIAMOND [2], Bruker programs [3]

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

Atom	x	y	z	U_{iso}*/U_{eq}
C11	0.1463(6)	0.8505(5)	0.8319(5)	0.0405(10)
O1	0.1108(5)	0.9107(4)	0.6975(3)	0.0594(10)
O2	0.2073(5)	0.7060(4)	0.8861(4)	0.0584(9)
C12	0.1043(6)	0.9814(5)	0.9442(5)	0.0378(10)
F1	0.2361(3)	0.9309(3)	1.0387(3)	0.0492(7)
F2	0.1335(4)	1.1285(3)	0.8572(3)	0.0501(7)
N1	0.2027(5)	0.6524(4)	0.5333(4)	0.0460(9)
H1N	0.1775	0.7293	0.5906	0.069*
C1	0.2521(6)	0.4932(6)	0.5980(5)	0.0479(12)
H1	0.2608	0.4675	0.7043	0.058*
C2	0.2897(6)	0.3689(5)	0.5117(5)	0.0435(11)
H2	0.3227	0.2595	0.5594	0.052*
C3	0.2789(6)	0.4052(5)	0.3492(5)	0.0336(9)
C4	0.2315(6)	0.5755(5)	0.2850(5)	0.0386(10)
H4	0.2273	0.6067	0.1778	0.046*
C5	0.1924(6)	0.6921(5)	0.3798(5)	0.0428(11)
H5	0.1574	0.8031	0.3371	0.051*
N2	0.3065(5)	0.2874(4)	0.2611(4)	0.0373(9)
C6	0.3515(8)	0.1125(5)	0.3287(6)	0.0572(13)
H6A	0.4778	0.0801	0.3544	0.086*
H6B	0.3566	0.0471	0.2514	0.086*
H6C	0.2498	0.0953	0.4247	0.086*
C7	0.2959(8)	0.3278(6)	0.0937(5)	0.0537(13)
H7A	0.1648	0.3947	0.0884	0.081*
H7B	0.3243	0.2276	0.0497	0.081*
H7C	0.3915	0.3877	0.0329	0.081*

Experimental details

All hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms.

Comment

4-Dimethylaminopyridine (DMAP) is a derivative of pyridine with the chemical formula $(CH_3)_2NC_5H_4N$. This colourless solid is widely used as nucleophilic catalyst for a variety of reactions [4]. This weak base has a pKa value of 9.6, and also extensively used in the field of the pharmaceutical industry due to its utility for the modification of active drug ingredients without affecting the biological activity by co-crystallization [5–8]. The protonation and the consequential positive charge on the ring nitrogen of this pyridine derivative construct the heteroatom as a strong electron acceptor, and it is habitually used which evade to utilize of non-linear optics chromophores in uncontaminated enantiomeric form through donor-acceptor cocrystalization [9–13]. This base can be introduced into multicomponent crystals to tune the luminescent properties of an organic fluorescent dye through rational control of the interaction and arrangement of chromophores within the crystal [14]. The two-component crystals formed from this base with a series of carboxylic acids are crystallized exclusively as salts [15–19]. Tetrafluorosuccinic acid is the perfluorinated analogue of succinic acid but is significantly more acidic. Compared with its hydrogenous analogues, fluorination makes its carbon chains more hydrophobic and may change the fluorescent properties of organic chromophore through hydrogen bonding [14].

The asymmetric unit of the title structure contains one 4-dimethylaminopyridinium cation and one half of a tetrafluorosuccinate dianion (*cf*. the figure). The bond lengths and angles are in the normal ranges. The crystal structure is stabilized by hydrogen bonds and $\pi\cdots\pi$ stacking interactions, in addition to van der Waals interactions. The central distance between adjoining cations is 3.549 Å, which suggests the existence of $\pi\cdots\pi$ stacking.

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