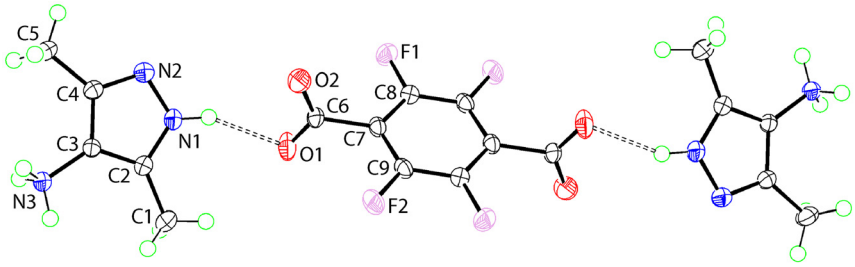
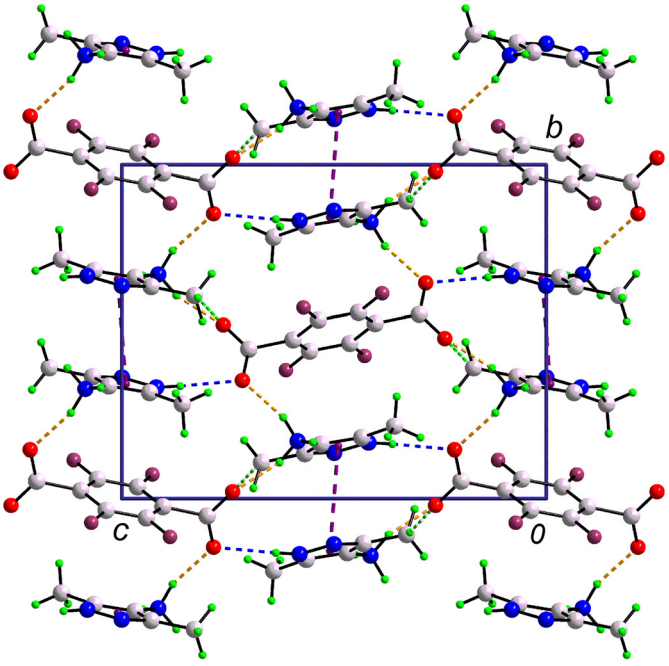
Kiyoshi Fujisawa*, Seigo Harakuni, Keigo Ageishi and Edward R. T. Tiekink*

Crystal structure of bis(3,5-dimethyl-1*H*-pyrazol-4-ammonium) tetrafluoroterephthate, $2[C_5H_{10}N_3][C_8F_4O_4]$





https://doi.org/10.1515/ncrs-2023-0333
Received July 18, 2023; accepted July 31, 2023;
published online August 21, 2023

Abstract

$2[C_5H_{10}N_3][C_8F_4O_4]$, monoclinic, $P2_1/n$ (no. 14), a = 6.1490(2) Å, b = 11.0063(3) Å, c = 14.0214(3) Å, β = 94.386(5)°, V = 946.16(5) Å^3, Z = 2, $R_{gt}(F)$ = 0.0371, $wR_{ref}(F^2)$ = 0.1127, T = 178 K.

CCDC no.: 2285587

***Corresponding authors: Kiyoshi Fujisawa**, Department of Chemistry, Ibaraki University, Mito, Ibaraki 310–8512, Japan, E-mail: kiyoshi.fujisawa.sci@vc.ibaraki.ac.jp. https://orcid.org/0000-0002-4023-0025; and **Edward R. T. Tiekink**, Research Centre for Crystalline Materials, School of Medical and Life Sciences, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, E-mail: edwardt@sunway.edu.my. https://orcid.org/0000-0003-1401-1520
Seigo Harakuni and Keigo Ageishi, Department of Chemistry, Ibaraki University, Mito, Ibaraki 310–8512, Japan, E-mail: s1g@icloud.com (S. Harakuni), ageishichem@gmail.com (K. Ageishi)

The molecular 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.

1 Source of material

Under an argon atmosphere, the reaction of 4-amino-3,5-dimethyl-1-pyrazole (0.050 g, 0.45 mmol) with tetra-

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.16 × 0.14 × 0.10 mm
Wavelength:	Mo*K*α radiation (0.71073 Å)
μ:	0.14 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB P200, ω
θ_{max}, completeness:	29.6°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6985, 2414, 0.021
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2259
$N(param)_{refined}$:	159
Programs:	CrysAlis^{PRO} [1], IL MILIONE [2], SHELX [3], WinGX/ORTEP [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
N1	0.36750 (15)	0.33299 (9)	−0.08110 (7)	0.0178 (2)
H1N	0.291 (2)	0.3370 (14)	−0.1373 (8)	0.021*
N2	0.26894 (15)	0.36280 (9)	−0.00029 (7)	0.0182 (2)
N3	0.83825 (14)	0.32853 (9)	0.08590 (6)	0.0156 (2)
H2N	0.841 (3)	0.2570 (10)	0.1197 (10)	0.023*
H3N	0.853 (3)	0.3915 (12)	0.1283 (10)	0.023*
H4N	0.955 (2)	0.3320 (15)	0.0496 (11)	0.023*
C1	0.72698 (19)	0.28321 (12)	−0.14236 (8)	0.0230 (2)
H1A	0.733071	0.194500	−0.147514	0.034*
H1B	0.874302	0.315120	−0.127015	0.034*
H1C	0.667020	0.317498	−0.203310	0.034*
C2	0.58520 (17)	0.31739 (10)	−0.06537 (7)	0.0155 (2)
C3	0.62920 (16)	0.33752 (9)	0.03093 (7)	0.0139 (2)
C4	0.43077 (17)	0.36511 (9)	0.06909 (7)	0.0155 (2)
C5	0.39585 (18)	0.39193 (11)	0.17112 (8)	0.0211 (2)
H5A	0.239157	0.398388	0.178724	0.032*
H5B	0.467426	0.468767	0.189879	0.032*
H5C	0.458021	0.326241	0.211774	0.032*
F1	−0.27376 (11)	0.38486 (7)	−0.38662 (5)	0.02198 (18)
F2	0.40163 (11)	0.57251 (7)	−0.42807 (5)	0.02257 (18)
O1	0.25345 (15)	0.35392 (8)	−0.28398 (6)	0.0240 (2)
O2	0.08167 (14)	0.52050 (9)	−0.23902 (6)	0.0265 (2)
C6	0.14165 (17)	0.44777 (10)	−0.29906 (7)	0.0157 (2)
C7	0.06848 (17)	0.47559 (9)	−0.40327 (7)	0.0145 (2)
C8	−0.13667 (17)	0.44180 (9)	−0.44222 (7)	0.0152 (2)
C9	0.20297 (17)	0.53508 (9)	−0.46292 (7)	0.0153 (2)

fluoroterephthalic acid (0.049 g, 0.21 mmol) in anhydrous methanol (10 mL) was conducted at room temperature overnight. The solvent was removed in vacuo. The colourless crystals of (I), suitable for X-ray analysis, were obtained by slow evaporation at room temperature from an anhydrous methanol and toluene solution (7:3 v/v) (0.042 g, 0.091 mmol, 43 % yield). **Anal. Calcd**. for $C_{18}H_{20}F_4N_6O_4$: C 46.96, H 4.38, N 18.25 %. Found: C 46.85, H 4.41, N 18.27 %. **^{1}H NMR** (CD_3OD, 500 MHz): δ 2.17 (s, 12H, CH_3); N–H protons were not observed. **IR** (KBr, cm^{-1}): 3197 s ν(N–H), 2894 s ν(C–H), 1639 s ν(C=O), 1607 s ν(C=O), 1466 s, 1382 s, 978 s, 728 s.

2 Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.98 Å) and refined as riding with U_{iso}(H) = 1.5U_{eq}(C). The N-bound H atoms were located in a difference Fourier map and refined with pyrazolyl–N–H = 0.88 ± 0.01 Å and ammonium–N–H = 0.91 ± 0.01 Å with U_{iso}(H) = 1.2 and 1.5U_{eq}(N), respectively.

3 Comment

Recently, covalent organic frameworks (COFs) became recognised as a new class of materials featuring linkages supported by strong covalent bonds to form two-or three-dimensional, porous and stable crystalline materials [5]. In COFs the covalent links can arise from, for example, B–O, imine–C=N and amide–C–N bond formation [6]. The title salt (I, systematic name: bis(3,5-dimethyl-1H-pyrazol-4-aminium) 2,3,5,6-tetrafluorobenzene-1,4-dicarboxylate) was generated in an on-going study into imine–C=N bond formation, employing an aliphatic or aromatic amine reacting with an aldehyde followed by dehydration. Previously, the structure of the result of C=N bond formation by the direct reaction of 4-amino-3,5-diisopropyl-1-pyrazole (L^1HpzNH_2) [7] with terephthalaldehyde (benzene-1,4-dicarboxaldehyde) was described [8]. Moreover, the structure obtained by the reaction of the less hindered methyl-substituted pyrazole viz. 4-amino-3,5-dimethyl-1-pyrazole (L^0HpzNH_2) with terephthalaldehyde in anhydrous methanol solution has also been described recently [9]. In this article, the results of the exploration of amide bond formation by the reaction of L^0HpzNH_2 with a carboxylic acid, i.e. tetrafluoroterephthalic acid, are outlined. While initially terephthalic acid was employed as the carboxylic acid source, this acid has very poor solubility in normal organic solvents such as methanol, ethanol and chloroform. Therefore, tetrafluoroterephthalic acid was evaluated as the carboxylic acid precursor, since the presence of fluoride improves the solubility in regular solvents due to the polarized $C^{\delta+}$ and $F^{\delta-}$ atoms [10, 11]. In the IR spectrum, salt (I) has a characteristic absorption band at 3197 cm^{-1}, which is assigned to N–H stretching. It is also noted that the sharp N–H_2 stretching band evident at 3345 cm^{-1} in the IR spectrum of L^0HpzNH_2 disappeared. In addition, new characteristic C=O stretching bands, split at 1639 and 1607 cm^{-1}, which are clearly shifted from those

of the other starting material, tetrafluoroterephthalic acid (1700 cm^{-1}).

The molecular structures of the constituents of salt (I) are shown in the upper view of the figure (70 % displacement ellipsoids, dashed lines indicate N–H···O hydrogen bonds and unlabelled atoms are related by the symmetry operation $-x, 1-y, 1-z$). The asymmetric-unit comprises a 3,5-dimethyl-1*H*-pyrazol-4-ammonium cation, in a general position, and half a 2,3,5,6-tetrafluorobenzene-1,4-dicarboxylate dianion, being situated about a centre of inversion. The confirmation of proton transfer during co-crystallisation is evident in the near equivalence of the C6–O1,O2 bond lengths [1.2498(13) & 1.2381(13) Å] and the wider angle at the N1 atom [C2–N1–N2 = 113.09(9)°] compared with that at the N2 atom [C4–N2–N1 = 104.80(9)°].

The pyrazolyl ring is planar to ±0.002(1) Å and an evaluation of the bond lengths within the five-membered ring is consistent with the delocalisation of π-electron density over the constituent atoms. Thus, the formally double-bonded C4–N2 [1.3376(14) Å] and C2–C3 [1.3745(13) Å] bonds are elongated and the formally single-bonded N1–N2 [1.3653(13) Å], C2–N1 [1.3509(14) Å] and C3–C4 [1.4026(14) Å] bonds are shortened; the exocyclic C3–N3 bond length is 1.4508(13) Å. The dianion is not planar with the carboxylate residues being close to orthogonal to the phenyl ring to which they are connected to, with the dihedral angle between the respective least-squares planes being 83.14(6)°. The dihedral angle between the carboxylate residue and the hydrogen bonded pyrazolyl ring is 41.84(8)°.

The crystal structure of the neutral 3,5-dimethyl-4-aminopyrazole molecule has been described [12]. There is a high degree of concordance in the geometric parameters in the pyrazolyl rings although the N1–N2 bond length of 1.353(2)° is shorter than that in (I) [1.3653(13) Å]. Further, two molecules of 3,5-dimethyl-4-aminopyrazole coordinate the cobalt(II) atom of $CoCl_2$ via the imine–N atoms to generate a tetrahedral complex [13]. Finally, a cation of 3,5-dimethyl-4-aminopyrazole with a 3,4-dicarboxy-3-hydroxybutanoate counter-anion, as a monohydrate, has been reported [14]. Here, protonation has occurred at the ring rather than at the amino–N atom in (I).

As anticipated from the compositon of (I), extensive hydrogen-bonding is evident in the crystal; all specified hydrogen bonds are charge-assisted. The connection between the pyrazolyl–N–H and the carboxylate–O1 atoms [N1–H1n···O1: H1n···O1 = 2.060(11) Å, N1···O1 = 2.8865(13) Å with angle at H1n = 154.5(11)°] is highlighted as blue-dashed bonds in the unit-cell diagram shown in the lower view of the figure. When viewed down the *a*-axis direction, the crystal comprises columns of cations and anions such that each column comprising cations is surrounded by six columns of alternatively charged species, whereas each column of anions is surrounded by six columns of cations. Hydrogen bonds linking cations within a column are of the type ammonium–N–H···N(pyrazolyl) [N3–H4n···N2^{i}: H4n···N2^{i} = 2.130(13) Å, N3···N2^{i} = 3.0176(13) Å with angle at H4*n* = 164.1(13)° for symmetry operation (i) $1+x, y, z$]. The remaining ammonium–N–H···O(carboxylate) hydrogen bonds involve two different carboxylate residues within the same column [N3–H2n···O1^{ii}: H2n···O1^{ii} = 1.928(14) Å, N3···O1^{ii} = 2.7890(13) Å with angle at H2*n* = 155.4(15)° and N3–H3n···O2^{iii} = H3n···O2^{iii} = 1.848(14) Å, N3···O2^{iii} = 2.7297(13) Å with angle at H3*n* = 161.7(13)° for (ii) $-x, 1-y, -z$ and (iii) $1-x, 1-y, -z$]. All specified contacts occur within a three-dimensional assembly. Complementing the hydrogen-bonding interactions are close methyl–C–H···O(carboxylate) [C5–H5a···O2^{iv}: H5a···O2^{iv} = 2.38 Å, C5···O2^{iv} = 3.2992(14) Å with angle at H5a = 156° for (iv) $1/2+x, 1/2-y, 1/2+z$] interactions, shown as bright-green dashed bonds in the unit-cell diagram, and π(pyrazolyl)···π-(pyrazolyl) [Cg(pyrazolyl)···Cg(pyrazolyl)^{iii} = 3.5008(7) Å] contacts between centrosymmetrically related molecules occupying different columns (purple dashed lines). Longer [3.7880(6) Å] π(pyrazolyl)···π(phenyl) contacts are also noted.

This analysis was augmented by the calculation of the Hirshfeld surfaces and of the full and delineated two-dimensional fingerprint plots with the aid of Crystal Explorer 21 [15] and standard protocols [16]. The calculations were based on the three-molecule aggregate shown in the upper view of the figure, and highlight the prominent role hydrogen plays in the molecular packing by participating in 86.0 % of all surface contacts. While H···H contacts contribute 23.5 % to the calculated surface, the greatest contribution comes from O···H/H···O contacts, reflecting, in part, the prominent role of hydrogen-bonding involving oxygen. After these, the next most dominant contacts involve fluoride with F···H/H···F contacts contributing 19.8 % to the surface but at separations greater than the van der Waals criterion. At 9.2 and 7.7 %, significant contributions are made by N···H/H···N and C···H/H···C contacts, respectively. Smaller contributions are made by F···F [3.8 %], C···C [3.7 %], N···C/C···N [3.6 %] and F···C. C···F [2.1 %] surface contacts. Naturally, when the individual ions were evaluated for their specific surface contacts, vastly different distributions of surface contacts are apparent. Thus, for the cation, the most signficant contributions to the surface about this species were H···H [35.0 %], H···O [21.3 %], H···N/N···H [13.9 %], H···F [13.5 %] and H···C/C···H [6.2 %]. For the di-anion, O···H [42.6 %], F···H [26.3 %], F···F [9.3 %] and C···H [8.8 %] surface contacts predominate.

Acknowledgments: KF is grateful for support from the joint usage/research programme "Artificial Photosynthesis" based at Osaka City University.
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: This study was financially supported by the Joint Usage/Research Center for Catalysis (Proposals 22DS0143 and 23DS0198).
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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