

Zhiwei Mao, Kehua Zhang, Lian Zhou and Wensheng Zou*

The crystal structure of 1-(4-carboxybutyl)-3-methyl-1*H*-imidazol-3-ium hexafluoridophosphate, $C_9H_{15}F_6N_2O_2P$

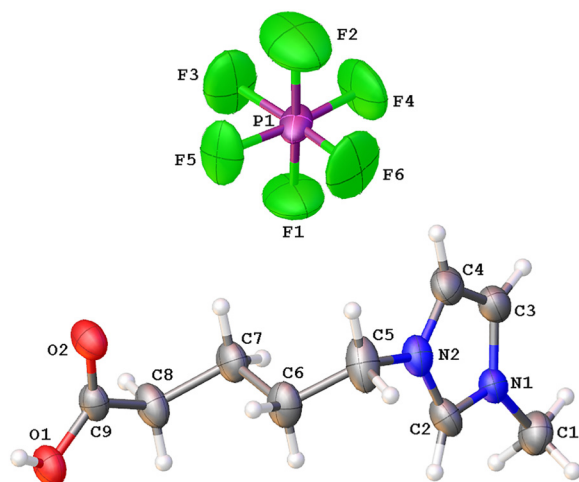


Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.19 × 0.16 × 0.12 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.27 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 Venture, φ and ω
$\theta_{\max}$, completeness:	27.2°, 97 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	3889, 2911, 0.053
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1284
$N(\text{param})_{\text{refined}}$:	247
Programs:	Bruker [1], Olex2 [2]

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Abstract

$C_9H_{15}F_6N_2O_2P$, triclinic, $P\bar{1}$ (no. 2), $a = 8.678(8)$ Å, $b = 9.085(9)$ Å, $c = 10.279(8)$ Å, $\alpha = 84.23(2)^\circ$, $\beta = 79.02(2)^\circ$, $\gamma = 62.103(14)^\circ$, $V = 62.10(1)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0730$, $wR_{\text{ref}}(F^2) = 0.1663$, $T = 296$ K.

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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.

*Corresponding author: Wensheng Zou, Key Laboratory of Functional Molecule Design and Interface Process, Anhui Jianzhu University, Hefei 230601, P.R. China, E-mail: wsou@ahjzu.edu.cn. <https://orcid.org/0000-0002-4872-8071>

Zhiwei Mao and Kehua Zhang, Key Laboratory of Functional Molecule Design and Interface Process, Anhui Jianzhu University, Hefei 230601, P.R. China, E-mail: 1602116754@qq.com (Z. Mao), zkhzhang@163.com (K. Zhang)

Lian Zhou, Faculty of Energy and Electric Engineering, Qinghai University, Xining 810016, P.R. China, E-mail: zhoulianminai@126.com

1 Source of material

The compound was obtained using commercial 1-(4-carboxybutyl)-3-methyl-1*H*-imidazol-3-ium bromide through anion exchanging with potassium hexafluorophosphate. An amount of 0.01 mol 1-(4-carboxybutyl)-3-methyl-1*H*-imidazol-3-ium bromide, 0.01 mol potassium hexafluorophosphate and 10 mL distilled water were added to a 25 mL round-bottom flask. After being stirred by a magnetic stirrer for about 24 h, the mixture was transferred to a separatory funnel and extracted with 10 mL CH_2Cl_2 , the organic phase was placed at room temperature and evaporated slow, finally the colorless crystals suitable for single crystal X-ray diffraction were obtained after about one week. ¹H NMR (d-DMSO, 400 M) δ ppm: 9.905 (s, 1H), 7.742 (s, 1H), 7.680 (s, 1H), 4.164 (t, 2H), 3.839 (s, 3H), 2.256 (t, 2H), 1.797 (m, 2H), 1.459 (m, 2H).

2 Experimental details

All H atoms were located at their calculated positions, with O–H = 0.82 (carboxyl) Å and C–H = 0.92 (methylene), 0.93 (imidazole ring) or 0.96 (methyl) Å, and refined isotropically through a riding model, with $U_{\text{iso}}(H) = 1.5 U_{\text{eq}}(O, C)$ for carboxyl and methyl H atoms and $1.2 U_{\text{eq}}(C)$ for methylene H atoms. The hexafluorophosphate group is disordered over two positions with site occupancy ratio of 0.49:0.51 [3].

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} ^a /U _{eq}
P1 ^a	0.6864 (8)	0.6905 (6)	0.6787 (6)	0.070 (3)
P1A ^b	0.6911 (8)	0.6845 (8)	0.6821 (5)	0.078 (3)
F1 ^a	0.6865 (15)	0.5310 (11)	0.6461 (18)	0.173 (5)
F1A ^b	0.8864 (11)	0.5407 (10)	0.6866 (16)	0.154 (4)
F2 ^a	0.6875 (18)	0.8546 (13)	0.6797 (18)	0.215 (7)
F2A ^b	0.5040 (13)	0.8177 (14)	0.6928 (19)	0.190 (6)
F3 ^a	0.5742 (12)	0.778 (2)	0.5601 (10)	0.182 (5)
F3A ^b	0.6201 (18)	0.5720 (18)	0.7808 (11)	0.186 (5)
F4 ^a	0.8559 (12)	0.6384 (18)	0.5766 (13)	0.173 (5)
F4A ^b	0.6627 (15)	0.6139 (18)	0.5684 (10)	0.144 (5)
F5 ^a	0.5054 (10)	0.7541 (15)	0.7685 (6)	0.127 (4)
F5A ^b	0.7060 (11)	0.7685 (14)	0.8059 (8)	0.115 (4)
F6 ^a	0.7783 (16)	0.615 (2)	0.7978 (12)	0.203 (6)
F6A ^b	0.7846 (19)	0.776 (2)	0.6014 (12)	0.174 (5)
O1	0.0895 (3)	0.2974 (3)	0.9392 (2)	0.0685 (9)
H1	0.012857	0.369700	0.989837	0.103*
O2	0.1877 (3)	0.4874 (4)	0.9003 (2)	0.0718 (9)
N1	1.1115 (3)	−0.1327 (4)	0.6653 (3)	0.0555 (9)
N2	0.9185 (4)	0.0707 (4)	0.7950 (3)	0.0630 (10)
C1	1.2153 (5)	−0.3003 (5)	0.6060 (4)	0.0766 (13)
H1A	1.298342	−0.297029	0.530799	0.115*
H1B	1.277792	−0.378605	0.670581	0.115*
H1C	1.136985	−0.333934	0.578310	0.115*
C2	0.9832 (4)	−0.0913 (6)	0.7721 (4)	0.0653 (12)
H2	0.945801	−0.163497	0.821687	0.078*
C3	1.1267 (5)	0.0073 (6)	0.6216 (4)	0.0672 (12)
H3	1.205876	0.014433	0.549380	0.081*
C4	1.0071 (5)	0.1332 (6)	0.7011 (4)	0.0714 (12)
H4	0.988258	0.243076	0.693443	0.086*
C5	0.7743 (5)	0.1668 (6)	0.9046 (4)	0.0913 (17)
H5A	0.812516	0.121243	0.988852	0.110*
H5B	0.753829	0.281643	0.898684	0.110*
C6	0.6050 (5)	0.1634 (6)	0.9013 (4)	0.0744 (13)
H6A	0.519576	0.224798	0.976565	0.089*
H6B	0.625130	0.048741	0.912191	0.089*
C7	0.5241 (4)	0.2351 (5)	0.7758 (4)	0.0647 (12)
H7A	0.504503	0.349501	0.763386	0.078*
H7B	0.606991	0.172219	0.700082	0.078*
C8	0.3502 (4)	0.2306 (5)	0.7809 (4)	0.0713 (13)
H8A	0.316353	0.258292	0.693618	0.086*
H8B	0.367800	0.117990	0.802715	0.086*
C9	0.2016 (4)	0.3476 (5)	0.8797 (3)	0.0549 (11)

^aOccupancy: 0.507(9), ^boccupancy: 0.493(9).

3 Comment

Ionic liquids (ILs) are the important functional materials, they can be applied in the industry and research fields of catalysis [4], extraction [5], liquid crystals and electrochemistry [6]. So focusing on the attentions from the researchers in decades, and many novel ILs with functional organics were designed and synthesized such as amino acid

[7] and carboxylic acid [8]. In this work, the bromide anion of 1-(4-carboxybutyl)-3-methyl-1H-imidazol-3-ium bromide was exchanged by hexafluorophosphate group, then yielded hexafluorophosphate salt ionic liquid containing imidazole – carboxylic acid.

Single crystal X-ray diffraction clearly reveals that the Br[−] anions are completely substituted by hexafluorophosphate groups without residual Br[−] anions. In addition, there are no other guest molecules of solvents in the asymmetric unit of the structure. The carboxyl group connects imidazole ring by the twist-arrangement of four methylene groups. The bond distances between O atom and C atom are 1.254(6) and 1.289(5) Å for C5–O2 and C5–O1, respectively. They are close to each other, embodying the delocalized state for the C=O and C–O bonds of carboxyl, agreeing with others in the coordination polymer [9].

No classical hydrogen bonds exist in the structure of this compound. The hexafluorophosphate group and imidazole – carboxylic acid interact through C–H...F hydrogen bond with D or R²₂(8) style. On the other hand, two molecules of imidazole – carboxylic acid associate by O–H...O hydrogen bond R²₂(8) style from two carboxyls to form a dimer. Through those hydrogen bonds, the molecules are connected one by one to create a stable 3-dimensional network with ABAB fashion along *b* axis. The centroids distance between the centroid of one imidazole ring and the adjacent one is 8.878(8) Å, revealing that no π...π interactions are present in the crystals.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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