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Crystal structure of (*R*)-3-fluoropyrrolidine hydrochloride

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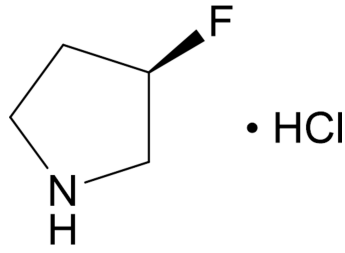
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The title compound [also called (*R*)-3-fluoropyrrolidin-1-ium chloride], $C_4H_9FN^+\cdot Cl^-$, crystallizes in the monoclinic Sohncke space group $P2_1$ (#4). The asymmetric unit contains one 3-fluoropyrrolidinium cation and one chloride anion. The pyrrolidinium ring adopts a puckered conformation, and the fluorine substituent is bonded to C3 at a distance of 1.396 (3) Å. In the crystal, the ammonium N—H groups form hydrogen bonds with the chloride anions, creating an extended hydrogen-bonded arrangement. Although 3-fluoropyrrolidinium derivatives have been investigated as chiral organic components in hybrid materials, including magnetic and ferroelectric systems, the crystallographic characterization of the hydrochloride salt itself has not been reported.

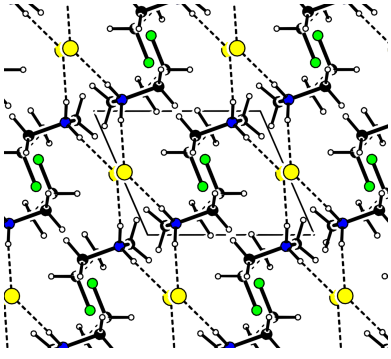
1. Chemical context

In recent years, chiral 3-fluoropyrrolidinium cations have attracted interest as the organic components in organic–inorganic hybrid materials with magnetic and ferroelectric properties. The addition of (*R*)- and (S)-3-fluoropyrrolidinium in cyanido-bridged dimetallic materials has led to the creation of homochiral multiferroic substances that exhibit ferroelectric and ferroelastic behavior (Mao *et al.*, 2022).

(*R*)- and (S)-3-fluoropyrrolidinium cations have also been integrated into quasi-two-dimensional copper(II) chloride hybrid perovskites, materials, which, with the molecule's addition, exhibit magnetic chirality (Zhang *et al.*, 2026). In addition, the cation has been used in the context of alkaline-earth-metal hybrid perovskites, one of which being [(*R*)-3-fluoropyrrolidinium]Ba(ClO4)$_3$ where molecular fluorination demonstrated an enhancement of several ferroelectric properties relative to the corresponding unsubstituted pyrrolidinium material (Zhou *et al.*, 2025). (*R*)-3-Fluoropyrrolidinium has also been used to create hexagonal perovskite-type manganese(II) chloride ferroelectrics (Ai *et al.*, 2019).



Despite the incorporation of 3-fluoropyrrolidinium in many chiral organic–inorganic hybrid materials, the hydrochloride salt of (*R*)-3-fluoropyrrolidine [also known as (*R*)-3-fluoropyrrolidinium chloride], does not have a publicly reported



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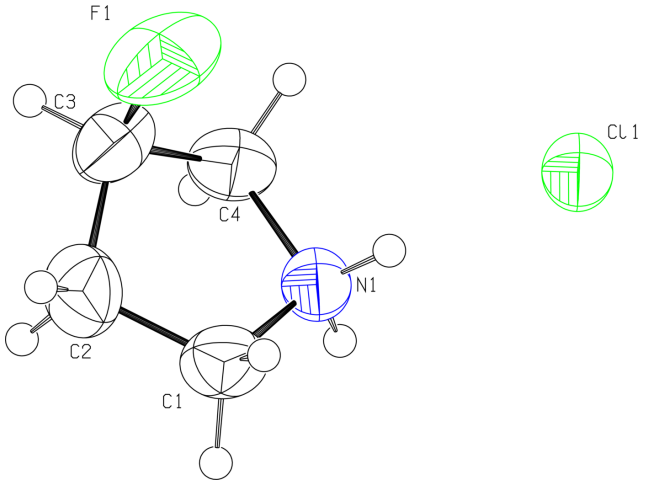


Figure 1
Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

crystal structure. The structure presented here therefore provides a crystallographic characterization of the organic salt, which enables the conformation, stereochemistry, and intermolecular interactions of the 3-fluoropyrrolidinium cation to be independently examined, not in the context of an inorganic hybrid framework.

2. Structural commentary

The title compound crystallizes in the monoclinic Sohncke space group $P2_1$ (#4). The asymmetric unit contains one (*R*)-3-fluoropyrrolidinium cation and one chloride anion (Fig. 1). Two formula units compose the unit cell. The pyrrolidinium ring has a non-planarenvelope conformation, with C3 out of plane. The C1—C2—C3—C4 and C2—C3—C4—N1 torsion angles are 36.2 (2)° and −33.8 (2)°, respectively, indicating that the five-membered ring is puckered rather than planar. The C3 atom is bonded to fluorine, with a bond length of 1.396 (3) Å, and the geometry around this carbon is approximately tetrahedral with F1—C3—C2, F1—C3—C4, and C2—C3—C4 angles of 109.2 (2), 109.1 (2), and 103.98 (16)°, respectively. The protonated nitrogen also has approximately tetrahedral geometry.

3. Supramolecular features

The cations and chloride anions are connected through N—H···Cl hydrogen bonds (Fig. 2, Table 1). Each pyrrolidinium cation contains two N—H groups, which both participate in hydrogen bonding with the chloride anions. Nearly linear, these interactions connect neighboring ions and allow for an extended hydrogen-bonded structure throughout the crystal.

4. Database survey

Unfluorinated pyrrolidine hydrochloride crystallizes in the orthorhombic space group *Pnma* (#62) with V/Z = 155.877 Å^3 (Giglmeier *et al.*, 2009). Fluorination causes V/Z to increase to 159.532 Å^3 in (*R*)-3-fluoropyrrolidine hydrochloride, though thermal expansion may account for some of the difference in volume as the crystal structure of pyrrolidine hydrochloride was collected at 200 K whereas the structure of (*R*)-3-fluoropyrrolidine hydrochloride was collected at 295 K.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl1	0.87 (3)	2.20 (3)	3.0770 (18)	178 (2)
N1—H1*B*···Cl1^{i}	0.85 (3)	2.22 (3)	3.0686 (18)	174 (2)

Symmetry code: (i) $x-1, y, z$.

5. Synthesis and crystallization

1 mmol $NiCl_2{\cdot}6H_2O$ (Thermo Scientific) and 2 mmol (*R*)-3-fluoropyrrolidine hydrochloride (Ambeed) were dissolved in 0.25 mL of methanol. Crystals were obtained by slow vapor diffusion of diethyl ether into the solution. After five days, the crystals were rinsed with the antisolvent several times and dried under vacuum. The obtained crystals were found to be recrystallized (*R*)-3-fluoropyrrolidine hydrochloride; an organic-inorganic hybrid material containing both nickel chloride and (*R*)-3-fluoropyrrolidinium did not form.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Carbon-bonded hydrogen atoms were refined using a riding model with the C—H bond length allowed to vary using the HFIX 24 (two sp^3 hydrogens for C1, C2, and C4) or HFIX 14 (one sp^3 hydrogen for C3) commands

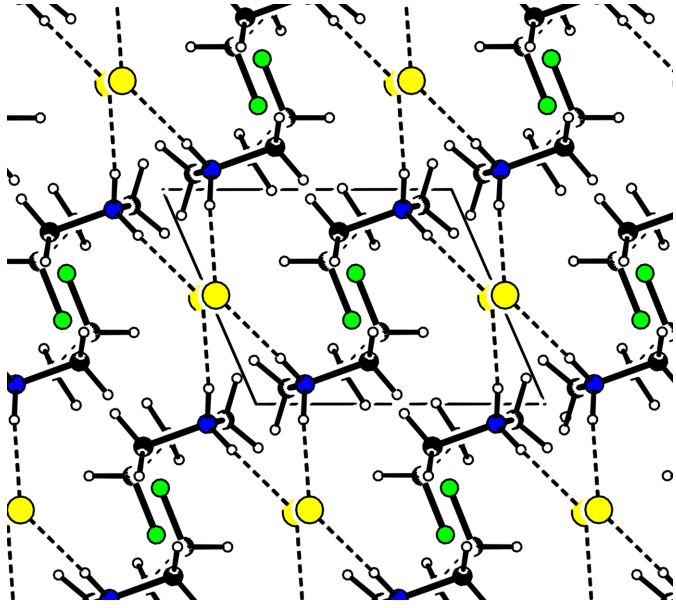


Figure 2
Hydrogen-bonding network in the title compound viewed down the *b* axis, with Cl^- ions shown in yellow.

in *SHELXL*. The positions of the nitrogen-bonded hydrogen atoms (H1*A* and H1*B*) were allowed to freely refine, and their isotropic thermal parameters were set to $1.2U_{eq}$(N). The structure was refined using the *OLEX2* GUI (Dolomanov *et al.*, 2009).

Acknowledgements

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References

Ai, Y., Chen, X.-G., Shi, P.-P., Tang, Y.-Y., Li, P.-F., Liao, W.-Q. & Xiong, R.-G. (2019). *J. Am. Chem. Soc.* **141**, 4474–4479.

Bruker (2016). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2026). *BIS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Giglmeier, H., Kerscher, T., Klüfers, P. & Mayer, P. (2009). *Acta Cryst.* E**65**, o592.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Mao, Y., Chen, X.-G., Gu, Z., Zhang, Z.-X., Song, X.-J., Gu, N. & Xiong, R. G. (2022). *Angew. Chem. Int. Ed.* **61**, e202204135.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Zhang, Z., Xu, M., Gonzalez Jimenez, J. L., Zhang, S., Xie, W., Xu, X. & Straus, D. B. (2026). *JACS* **148**, 33895–33904.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_4H_9FN^+\cdot Cl^-$
M_r	125.57
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	295
a, b, c (Å)	5.1390 (1), 10.6704 (2), 6.3479 (1)
β (°)	113.564 (1)
V (Å^3)	319.06 (1)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.50
Crystal size (mm)	0.38 × 0.21 × 0.16
Data collection	
Diffractometer	Bruker D8 Quest
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.932, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18053, 1857, 1781
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.705
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.068, 1.07
No. of reflections	1857
No. of parameters	74
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.13
Absolute structure	Flack x determined using 806 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.* (2013)
Absolute structure parameter	−0.017 (16)

Computer programs: *BIS* (Bruker, 2026), *SAINT* (Bruker, 2016), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2025/1* (Sheldrick, 2015*b*b), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

Zhou, Q.-F., Pan, L., Ni, H.-F., Ye, L.-K., Zhao, Y.-P., Luo, Q.-K., Teri, G., Luo, J.-Q., Fu, D.-W., Zhang, Z.-X., Shi, C. & Zhang, Y. (2025). *Angew. Chem. Int. Ed.* **64**, e202509006.

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Crystal structure of (*R*)-3-fluoropyrrolidine hydrochloride

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Computing details

(*R*)-3-Fluoropyrrolidin-1-ium chloride

Crystal data

$C_4H_9FN^+\cdot Cl^-$
M_r = 125.57
Monoclinic, $P2_1$
a = 5.1390 (1) Å
b = 10.6704 (2) Å
c = 6.3479 (1) Å
β = 113.564 (1)°
V = 319.06 (1) Å^3
Z = 2
$F(000)$ = 132
D_x = 1.307 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9897 reflections
θ = 3.5–28.2°
μ = 0.50 mm^{-1}
T = 295 K
Prism, brown
0.38 × 0.21 × 0.16 mm

Data collection

Bruker D8 Quest diffractometer
Radiation source: sealed tube
Flat graphite monochromator
Detector resolution: 7.40 pixels mm^{-1}
ω and phi scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.932, T_{max} = 1.000
18053 measured reflections
1857 independent reflections
1781 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 30.1°, θ_{min} = 3.5°
h = −7→7
k = −15→15
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.068
S = 1.07
1857 reflections
74 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.016P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Absolute structure: Flack x determined using 806 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.* (2013)
Absolute structure parameter: −0.017 (16)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.50723 (8)	0.66790 (4)	0.02568 (7)	0.05125 (14)
F1	0.6093 (3)	0.4266 (3)	0.5424 (3)	0.1009 (6)
N1	0.0917 (3)	0.54125 (16)	0.1987 (3)	0.0477 (3)
H1A	0.213 (6)	0.577 (2)	0.153 (4)	0.057*
H1B	−0.073 (6)	0.574 (2)	0.140 (4)	0.057*
C1	0.0736 (5)	0.4059 (3)	0.1332 (4)	0.0642 (5)
H1C	−0.120 (5)	0.3842 (6)	0.027 (3)	0.077*
H1D	0.204 (3)	0.3871 (5)	0.0589 (18)	0.077*
C2	0.1553 (6)	0.3349 (2)	0.3517 (5)	0.0704 (6)
H2A	0.259 (3)	0.264 (2)	0.3500 (5)	0.084*
H2B	−0.005 (5)	0.3108 (8)	0.3758 (9)	0.084*
C3	0.3344 (4)	0.4251 (3)	0.5356 (4)	0.0625 (5)
H3	0.3345 (4)	0.4034 (7)	0.686 (5)	0.075*
C4	0.1987 (5)	0.5491 (2)	0.4540 (4)	0.0609 (5)
H4A	0.335 (3)	0.6162 (15)	0.5129 (14)	0.073*
H4B	0.044 (3)	0.5631 (4)	0.5017 (11)	0.073*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.04294 (19)	0.0534 (2)	0.0592 (2)	0.00460 (17)	0.02232 (15)	0.0093 (3)
F1	0.0422 (6)	0.1661 (18)	0.0836 (11)	0.0214 (10)	0.0139 (7)	0.0195 (13)
N1	0.0365 (6)	0.0502 (7)	0.0559 (8)	0.0036 (6)	0.0179 (6)	0.0085 (6)
C1	0.0690 (12)	0.0578 (10)	0.0551 (11)	−0.0026 (10)	0.0135 (9)	−0.0105 (10)
C2	0.0733 (15)	0.0504 (11)	0.0848 (17)	0.0087 (10)	0.0289 (13)	0.0116 (10)
C3	0.0512 (10)	0.0869 (15)	0.0486 (10)	0.0086 (11)	0.0189 (9)	0.0120 (10)
C4	0.0596 (11)	0.0633 (12)	0.0561 (11)	−0.0061 (9)	0.0193 (9)	−0.0136 (9)

Geometric parameters (Å, º)

F1—C3	1.396 (3)	C2—H2A	0.93 (3)
N1—H1A	0.88 (3)	C2—H2B	0.93 (3)
N1—H1B	0.85 (3)	C2—C3	1.509 (4)
N1—C1	1.496 (3)	C3—H3	0.98 (3)
N1—C4	1.491 (3)	C3—C4	1.489 (4)
C1—H1C	0.98 (2)	C4—H4A	0.97 (2)
C1—H1D	0.98 (2)	C4—H4B	0.97 (2)
C1—C2	1.486 (4)		

H1A—N1—H1B	113 (2)	H2A—C2—H2B	108.9
C1—N1—H1A	107.8 (16)	C3—C2—H2A	110.8
C1—N1—H1B	109.6 (17)	C3—C2—H2B	110.8
C4—N1—H1A	109.4 (15)	F1—C3—C2	109.2 (2)
C4—N1—H1B	108.6 (18)	F1—C3—H3	111.4
C4—N1—C1	108.14 (16)	F1—C3—C4	109.1 (2)
N1—C1—H1C	110.6	C2—C3—H3	111.4
N1—C1—H1D	110.6	C4—C3—C2	103.98 (16)
H1C—C1—H1D	108.7	C4—C3—H3	111.4
C2—C1—N1	105.65 (18)	N1—C4—H4A	110.9
C2—C1—H1C	110.6	N1—C4—H4B	110.9
C2—C1—H1D	110.6	C3—C4—N1	104.23 (18)
C1—C2—H2A	110.8	C3—C4—H4A	110.9
C1—C2—H2B	110.8	C3—C4—H4B	110.9
C1—C2—C3	104.7 (2)	H4A—C4—H4B	108.9

F1—C3—C4—N1	82.6 (2)	C1—C2—C3—C4	36.2 (2)
N1—C1—C2—C3	−24.0 (2)	C2—C3—C4—N1	−33.8 (2)
C1—N1—C4—C3	19.2 (2)	C4—N1—C1—C2	3.1 (2)
C1—C2—C3—F1	−80.2 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl1	0.87 (3)	2.20 (3)	3.0770 (18)	178 (2)
N1—H1*B*···Cl1^{i}	0.85 (3)	2.22 (3)	3.0686 (18)	174 (2)

Symmetry code: (i) *x*−1, *y*, *z*.