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4,4′-Bipyridine-1,1′-diium tetrachloridodifluoridostannate(IV) monohydrate

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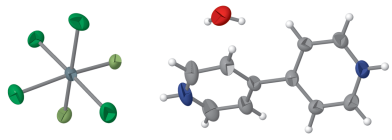
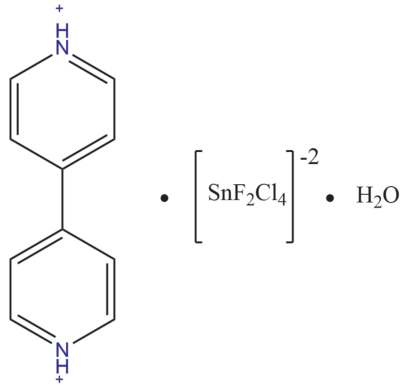
Structural data: full structural data are available from iucrdata.iucr.org

In the title hydrated salt, $(C_{10}H_{10}N_2)[SnF_2Cl_4]\cdot H_2O$, the dihedral angle between the pyridinium rings in the cation is 40.5 (4)° and the F atoms in the octahedral complex anion have a *cis* disposition [F—Sn—F = 85.32 (17)°]. In the extended structure, alternating cationic and anionic layers occur, linked by extensive hydrogen bonding, with water molecules inserted between the layers.

3D view



Chemical scheme



Structure description

The title compound, $(C_{10}H_{10}N_2^{2+})[SnF_2Cl_4]^{2-}\cdot H_2O$, crystallizes in the non-centrosymmetric orthorhombic space group $Pna2_1$ with one cation, one anion and one water molecule in the asymmetric unit (Fig. 1). The bipyridinium cation exhibits structural parameters indicative of protonation: the inter-ring C—C bond length is 1.476 (7) Å, while the average intra-ring C—C bond length is 1.384 (3) Å, reflecting aromatic conjugation. The C—N bonds measure 1.341 (9) Å or less, which are shorter than those in neutral bipyridine, due to the cationic charge. Angular distortions are observed with C—C—C angles in the range 117.9 (5)°–121.0 (6)° and C—N—C angles of 122.4 (5) and 123.0 (6)°, in agreement with literature data (*e.g.*, Horiacha *et al.*, 2022). The dihedral angle between the C1–C5/N1 and C6–C10/N2 pyridinium rings is 40.5 (4)°, which can be attributed to intramolecular (steric) interactions (Gheribi *et al.*, 2022). The $[SnF_2Cl_4]^{2-}$ anion adopts a distorted octahedral coordination sphere around the Sn^{IV} atom, with Sn—Cl bond lengths ranging from 2.383 (2) to 2.418 (2) Å and Sn—F bonds of 2.030 (4) and 2.096 (4) Å. The bond angles deviate somewhat from ideal octahedral values, with notable examples being 87.98 (13)° for F1—Sn1—F2 and 93.84 (8)° for Cl2—Sn1—Cl4, consistent with previous reports (Bruhn & Preetz, 1996).

The extended structure reveals alternating layers of cations and anions separated by interstitial water molecules (Fig. 2). Eight hydrogen bonds consolidate the tri-periodic

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···F2^{i}	0.86	1.79	2.629 (6)	163
N2—H2···F1	0.86	2.32	2.989 (6)	134
N2—H2···O1W^{ii}	0.86	2.11	2.819 (10)	140
O1W—H1WA···Cl1^{iii}	0.85	2.51	3.324 (8)	159
O1W—H1WB···Cl4^{ii}	0.85	2.72	3.366 (8)	134
O1W—H1WB···F2^{iv}	0.85	2.32	2.906 (9)	126
C1—H1A···Cl3^{iv}	0.93	2.82	3.473 (6)	128
C9—H9···F1^{ii}	0.93	2.44	3.109 (9)	129

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+1, -y+1, z+\frac{1}{2}$; (iii) $x-1, y, z$; (iv) $-x+1, -y+1, z-\frac{1}{2}$.

network (Table 1), including one strong (N1—H1···F2), two moderate (N2—H2···O1W and O1W—H1WA···Cl1), and five weak interactions (O1W—H1WB···Cl4, O1W—H1WB···F2, N2—H2···F1, C1—H1A···Cl3 and C9—H9···F1). Water molecules mediate cyclic motifs in the *bc* plane *via* O1W—H···Cl/F interactions, generating a supramolecular $R_4^4(12)$ graph-set motif (Fig. 3). Intralayer

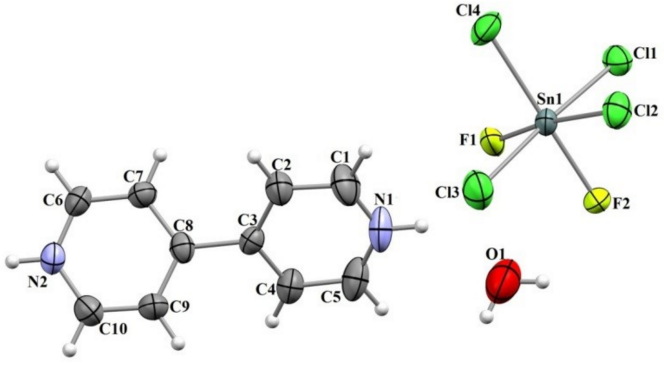


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_{10}H_{10}N_2)[SnCl_4F_2]\cdot H_2O$
M_r	474.71
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	293
a, b, c (Å)	7.5641 (2), 26.5989 (5), 7.9422 (2)
V (Å^3)	1597.94 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.28
Crystal size (mm)	0.08 × 0.08 × 0.07
Data collection	
Diffractometer	Bruker SMART APEXII area detector
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.852, 0.852
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16855, 7535, 6299
R_{int}	0.030
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.837
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.107, 1.04
No. of reflections	7535
No. of parameters	182
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.11, −2.00
Absolute structure	Ad
Absolute structure parameter	0.06 (4)

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *OLEX2.solve* (Bourhis *et al.*, 2015), *SHELXL2019/3* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

cohesion is ensured by weak π–π stacking interactions with centroid–centroid distances of 3.950 (4) Å, while interlayer bridging is provided by a Sn—Cl4···Cg($2-x, 1-y, -\frac{1}{2}+z$) halogen···π contact [Cl···π = 3.472 (4) Å, Sn—Cl···π = 110.42 (9)°] linking the $[SnF_2Cl_4]^{2-}$ anion to the N2 ring of the bipyridinium cation. The crystal packing is thus supported by

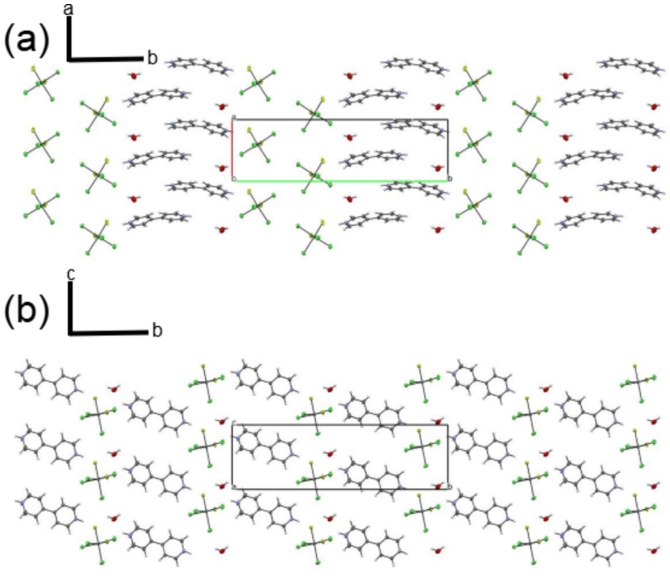


Figure 2
Projection of the crystal packing on (*a*) the *ab* plane and (*b*) the *bc* plane.

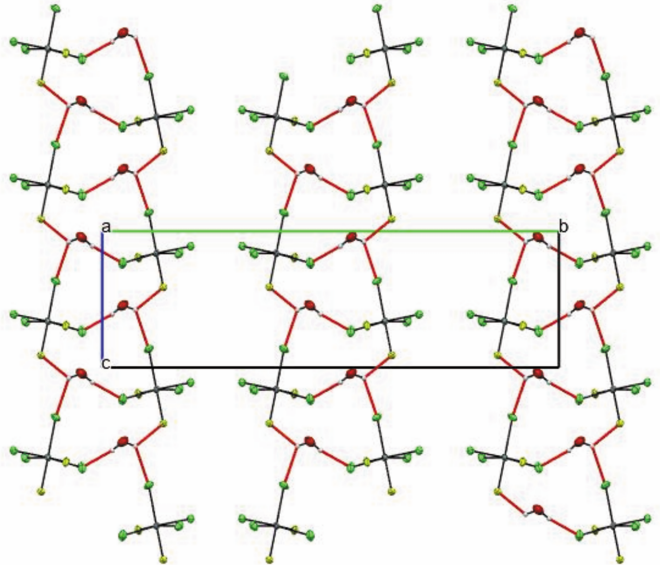


Figure 3
Sequence of $R_4^4(12)$ loops in the structure.

directional hydrogen bonds, face-to-face π-stacking within cationic layers, and anion–cation halogen$\cdots\pi$ contacts.

Synthesis and crystallization

Tin(II) fluoride (1.56 mmol) was combined with 4,4′-bipyridine (1.56 mmol) in a 1:1 molar ratio. A few drops of hydrochloric acid were added to the mixture in a minimal volume of distilled water to facilitate dissolution. After thorough stirring, the solution was transferred into a Biotage microwave vial (2–5 ml) and heated in an oven at 393 K for three days. Upon gradual cooling to room temperature, prismatic crystals of the title compound formed and were isolated under an optical microscope for further analysis.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal studied was refined as a two-component inversion twin.

Acknowledgements

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full crystallographic data

IUCrData (2025). **10**, x250596 [https://doi.org/10.1107/S2414314625005966]

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Crystal data

$(C_{10}H_{10}N_2)[SnCl_4F_2]\cdot H_2O$
M_r = 474.71
Orthorhombic, $Pna2_1$
a = 7.5641 (2) Å
b = 26.5989 (5) Å
c = 7.9422 (2) Å
V = 1597.94 (7) Å^3
Z = 4
$F(000)$ = 920
D_x = 1.973 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6299 reflections
θ = 1.5–36.5°
μ = 2.28 mm^{-1}
T = 293 K
Prism, colourless
0.08 × 0.08 × 0.07 mm

Data collection

Bruker SMART APEXII area detector diffractometer
ω and φ scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.852, T_{max} = 0.852
16855 measured reflections
7535 independent reflections
6299 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 36.5°, θ_{min} = 1.5°
h = −11→12
k = −44→20
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.107
S = 1.04
7535 reflections
182 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0043P)^2 + 2.4611P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 1.11 e Å^{-3}
$\Delta\rho_{min}$ = −2.00 e Å^{-3}
Absolute structure: ad
Absolute structure parameter: 0.06 (4)

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.

Refinement. Refined as a 2-component inversion twin. Hydrogen atoms on the aromatic rings were geometrically positioned and refined as riding atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.5711 (7)	0.22347 (18)	0.5432 (7)	0.0394 (10)
H1	0.567363	0.192734	0.510167	0.047*
N2	0.6786 (8)	0.4709 (2)	0.7922 (10)	0.0567 (16)
H2	0.697543	0.501502	0.822841	0.068*
C1	0.5305 (8)	0.2597 (2)	0.4340 (8)	0.0389 (11)
H1A	0.495469	0.251527	0.325148	0.047*
C2	0.5406 (8)	0.3090 (2)	0.4830 (7)	0.0355 (10)
H2A	0.511969	0.334401	0.407206	0.043*
C3	0.5935 (6)	0.32135 (16)	0.6459 (10)	0.0321 (10)
C4	0.6285 (8)	0.2819 (2)	0.7580 (8)	0.0383 (11)
H4	0.659405	0.288740	0.868982	0.046*
C5	0.6171 (9)	0.2333 (2)	0.7030 (8)	0.0437 (13)
H5	0.641172	0.206937	0.776600	0.052*
C6	0.6192 (7)	0.37422 (19)	0.6967 (7)	0.0337 (11)
C7	0.6957 (9)	0.4080 (2)	0.5833 (9)	0.0449 (13)
H7	0.724699	0.398189	0.474367	0.054*
C8	0.7270 (10)	0.4569 (2)	0.6390 (15)	0.061 (2)
H8	0.782381	0.479812	0.568010	0.073*
C9	0.6021 (9)	0.4396 (3)	0.9022 (11)	0.0561 (19)
H9	0.569590	0.451008	1.008552	0.067*
C10	0.5717 (9)	0.3902 (2)	0.8562 (10)	0.0440 (13)
H10	0.519959	0.367892	0.931787	0.053*
Sn1	0.90313 (4)	0.61887 (2)	0.66064 (6)	0.03161 (8)
Cl1	1.0622 (3)	0.54461 (7)	0.7330 (3)	0.0588 (5)
Cl2	1.16953 (18)	0.66810 (5)	0.6621 (3)	0.0487 (3)
Cl3	0.7297 (2)	0.69369 (5)	0.6093 (2)	0.0436 (3)
Cl4	0.9182 (3)	0.60193 (8)	0.3643 (2)	0.0545 (4)
F1	0.6661 (6)	0.57916 (12)	0.6921 (6)	0.0594 (12)
F2	0.8830 (6)	0.63386 (14)	0.9106 (5)	0.0449 (8)
O1W	0.2936 (11)	0.4547 (3)	0.5435 (9)	0.081 (2)
H1WA	0.259704	0.478305	0.608329	0.122*
H1WB	0.250934	0.426975	0.577499	0.122*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.045 (3)	0.028 (2)	0.045 (3)	0.0004 (17)	−0.001 (2)	−0.0094 (18)
N2	0.052 (3)	0.037 (3)	0.081 (5)	−0.008 (2)	0.002 (3)	−0.024 (3)
C1	0.044 (3)	0.037 (3)	0.036 (3)	−0.001 (2)	−0.002 (2)	−0.009 (2)
C2	0.040 (2)	0.034 (2)	0.032 (2)	0.001 (2)	−0.005 (2)	−0.0021 (19)
C3	0.0323 (17)	0.0280 (16)	0.036 (3)	−0.0013 (14)	0.005 (2)	−0.005 (2)
C4	0.046 (3)	0.035 (2)	0.034 (3)	0.001 (2)	−0.005 (2)	−0.001 (2)
C5	0.055 (3)	0.033 (2)	0.043 (4)	0.001 (2)	−0.001 (2)	0.003 (2)
C6	0.033 (2)	0.031 (2)	0.037 (3)	−0.0004 (15)	−0.0019 (17)	−0.0056 (17)
C7	0.050 (3)	0.033 (2)	0.052 (4)	−0.006 (2)	0.003 (3)	−0.005 (2)

C8	0.059 (4)	0.039 (3)	0.085 (7)	−0.018 (3)	0.011 (4)	−0.003 (4)
C9	0.052 (4)	0.049 (4)	0.068 (5)	−0.001 (3)	0.009 (3)	−0.028 (3)
C10	0.047 (3)	0.037 (3)	0.049 (3)	−0.004 (2)	0.001 (3)	−0.013 (2)
Sn1	0.03949 (14)	0.02310 (11)	0.03226 (13)	−0.00219 (10)	−0.00508 (19)	−0.00433 (15)
Cl1	0.0618 (10)	0.0384 (7)	0.0760 (12)	0.0042 (7)	−0.0140 (8)	−0.0060 (7)
Cl2	0.0445 (6)	0.0452 (6)	0.0565 (8)	−0.0130 (5)	0.0003 (10)	−0.0090 (10)
Cl3	0.0535 (8)	0.0351 (6)	0.0422 (7)	0.0112 (5)	0.0033 (6)	−0.0005 (5)
Cl4	0.0669 (10)	0.0578 (9)	0.0387 (8)	0.0074 (8)	−0.0084 (7)	−0.0199 (7)
F1	0.095 (3)	0.0278 (13)	0.055 (3)	−0.0150 (16)	−0.033 (2)	0.0077 (15)
F2	0.071 (2)	0.0327 (15)	0.0306 (16)	−0.0019 (16)	0.0021 (16)	−0.0019 (13)
O1W	0.102 (5)	0.074 (4)	0.067 (4)	−0.022 (4)	−0.009 (4)	0.025 (3)

Geometric parameters (Å, º)

N1—H1	0.8593	C6—C10	1.384 (9)
N1—C1	1.332 (8)	C7—H7	0.9300
N1—C5	1.341 (9)	C7—C8	1.394 (9)
N2—H2	0.8611	C8—H8	0.9300
N2—C8	1.325 (13)	C9—H9	0.9300
N2—C9	1.338 (12)	C9—C10	1.385 (9)
C1—H1A	0.9300	C10—H10	0.9300
C1—C2	1.372 (8)	Sn1—Cl1	2.3831 (18)
C2—H2A	0.9300	Sn1—Cl2	2.4032 (12)
C2—C3	1.393 (9)	Sn1—Cl3	2.4183 (14)
C3—C4	1.401 (8)	Sn1—Cl4	2.3994 (17)
C3—C6	1.476 (7)	Sn1—F1	2.096 (4)
C4—H4	0.9300	Sn1—F2	2.030 (4)
C4—C5	1.368 (9)	O1W—H1WA	0.8512
C5—H5	0.9300	O1W—H1WB	0.8498
C6—C7	1.397 (9)		
C1—N1—H1	118.8	C8—C7—H7	121.1
C1—N1—C5	122.4 (5)	N2—C8—C7	120.5 (7)
C5—N1—H1	118.8	N2—C8—H8	119.8
C8—N2—H2	118.7	C7—C8—H8	119.8
C8—N2—C9	123.0 (6)	N2—C9—H9	120.3
C9—N2—H2	118.3	N2—C9—C10	119.3 (7)
N1—C1—H1A	120.2	C10—C9—H9	120.3
N1—C1—C2	119.6 (5)	C6—C10—C9	119.3 (7)
C2—C1—H1A	120.2	C6—C10—H10	120.3
C1—C2—H2A	119.8	C9—C10—H10	120.3
C1—C2—C3	120.3 (5)	Cl1—Sn1—Cl2	91.56 (6)
C3—C2—H2A	119.8	Cl1—Sn1—Cl3	175.29 (7)
C2—C3—C4	117.9 (5)	Cl1—Sn1—Cl4	93.27 (7)
C2—C3—C6	121.0 (5)	Cl2—Sn1—Cl3	90.42 (5)
C4—C3—C6	121.0 (6)	Cl4—Sn1—Cl2	93.84 (8)
C3—C4—H4	120.2	Cl4—Sn1—Cl3	90.87 (6)
C5—C4—C3	119.6 (6)	F1—Sn1—Cl1	89.16 (12)

C5—C4—H4	120.2	F1—Sn1—Cl2	172.46 (14)
N1—C5—C4	120.1 (6)	F1—Sn1—Cl3	88.32 (12)
N1—C5—H5	119.9	F1—Sn1—Cl4	93.60 (14)
C4—C5—H5	119.9	F2—Sn1—Cl1	87.98 (13)
C7—C6—C3	119.4 (5)	F2—Sn1—Cl2	87.21 (13)
C10—C6—C3	120.5 (6)	F2—Sn1—Cl3	87.85 (12)
C10—C6—C7	120.0 (5)	F2—Sn1—Cl4	178.34 (13)
C6—C7—H7	121.1	F2—Sn1—F1	85.32 (17)
C8—C7—C6	117.8 (7)	H1WA—O1W—H1WB	109.4
N1—C1—C2—C3	0.2 (9)	C3—C6—C10—C9	178.1 (6)
N2—C9—C10—C6	−0.8 (11)	C4—C3—C6—C7	138.5 (6)
C1—N1—C5—C4	−1.9 (10)	C4—C3—C6—C10	−40.1 (8)
C1—C2—C3—C4	−2.5 (8)	C5—N1—C1—C2	2.1 (9)
C1—C2—C3—C6	174.9 (5)	C6—C3—C4—C5	−174.8 (5)
C2—C3—C4—C5	2.7 (8)	C6—C7—C8—N2	−2.7 (11)
C2—C3—C6—C7	−38.8 (7)	C7—C6—C10—C9	−0.5 (10)
C2—C3—C6—C10	142.5 (6)	C8—N2—C9—C10	0.2 (12)
C3—C4—C5—N1	−0.6 (9)	C9—N2—C8—C7	1.6 (13)
C3—C6—C7—C8	−176.4 (6)	C10—C6—C7—C8	2.2 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···F2^{i}	0.86	1.79	2.629 (6)	163
N2—H2···F1	0.86	2.32	2.989 (6)	134
N2—H2···O1*W*^{ii}	0.86	2.11	2.819 (10)	140
O1*W*—H1*WA*···Cl1^{iii}	0.85	2.51	3.324 (8)	159
O1*W*—H1*WB*···Cl4^{ii}	0.85	2.72	3.366 (8)	134
O1*W*—H1*WB*···F2^{iv}	0.85	2.32	2.906 (9)	126
C1—H1*A*···Cl3^{iv}	0.93	2.82	3.473 (6)	128
C9—H9···F1^{ii}	0.93	2.44	3.109 (9)	129

Symmetry codes: (i) −*x*+3/2, *y*−1/2, *z*−1/2; (ii) −*x*+1, −*y*+1, *z*+1/2; (iii) *x*−1, *y*, *z*; (iv) −*x*+1, −*y*+1, *z*−1/2.