Electronic Supporting Information

Structural Chemistry of Antimony(III) Oxalates with Lone Pairs: Polyhedral Distortion [SbO4F2], π-Conjugation [C2O4], and Birefringence Tuning

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Experimental Section

Synthesis.

The regents, $H_2C_2O_4$ (99%), SbF_3 (AR), $(NH_4)_2CO_3$ (99.99%), and $[C(NH_2)_3]_2CO_3$ (99%) were purchased commercially and used directly as raw material without further purification.

Single crystals of $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$ and $NH_4Sb(C_2O_4)F_2 \cdot H_2O$ were prepared by a solvent evaporation method. $[C(NH_2)_3]_2CO_3$, SbF_3, and $H_2C_2O_4$ were dissolved into the appropriate amount of deionized water at a ratio of 1.5: 1: 2 to synthesize $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$, and at a ratio of 0.5: 1 :1 to synthesize $NH_4Sb(C_2O_4)F_2 \cdot H_2O$. The reagents were mixed in a plastic beaker and stirred at room temperature until the solution was clear and free of bubbles. The solution evaporates of $NH_4Sb(C_2O_4)F_2 \cdot H_2O$ at room temperature for about a week, and colorless transparent crystals are obtained. The beaker of $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$ needs to be heated to 80 ℃ and kept for evaporation until block single crystals are successfully obtained. The yields of compound 1 and compound 2 are 72% and 68%, respectively.

For compound $(NH_4)_4Sb_2(C_2O_4)_3F_4 \cdot 2H_2O$, the starting materials were weighed at a molar ratio of 1:2:2, with a total mass of 1.677 g. The weighed materials were transferred into a polytetrafluoroethylene (PTFE) liner of a hydrothermal reactor (23 mL capacity). First, 3 mL of anhydrous ethanol was added, followed by 1 mL of deionized water. The mixture was stirred uniformly, though the reactants were not fully dissolved at this stage. After assembling the hydrothermal reactor, the oven temperature program was set: the holding temperature was 85 °C, the holding time was 5 days, and finally, the temperature was cooled to room temperature at a rate of 5 °C/h. Upon completion of the temperature program, the hydrothermal reactor was opened, and it was found that the product contained both small crystalline particles and partially undissolved powder. Regrettably, due to the deviation of the feed molar ratio from the stoichiometric ratio during synthesis, the pure phase of this compound was not obtained. The crystalline samples were then extracted for subsequent single-crystal X-ray diffraction testing.

Single-Crystal Structure Determination.

Single-crystal data of $NH_4Sb(C_2O_4)F_2 \cdot H_2O$, $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$ and $(NH_4)_4Sb_2(C_2O_4)_3F_4 \cdot 2H_2O$ were collected at 288 K, using a Bruker D8 Venture X-ray single crystal diffractometer. Olex2 software was used to solve the crystal structures, and a full-matrix least-squares on F^2 with SHELX was used to refine the structures.[1, 2] The space groups were examined by the PLATON program and there were no higher symmetries.[3] The crystallographic data of the two compounds are listed in Table S1 and other relevant data are listed in Tables S1−S5.

EDX

The single crystal was characterized by EDS using a JMS-7610FPlus scanning electron microscope (SEM), equipped with an Oxford X-MaxN EDS detector with a 20 mm^2 window, operated with an accelerating voltage of 20 kV and a working distance of 10 mm. Figure. S3 displays the EDX analysis of the three compounds, and the results conclusively confirm the presence of fluorine within the compound.

Powder X-ray Diffraction.

The powder XRD measurements of $NH_4Sb(C_2O_4)F_2 \cdot H_2O$ and $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O \cdot$were carried out on a Bruker D2 PHASER diffractometer (Cu Kα radiation, λ=1.5418 Å). The measurement conditions were as follows: 2θ=5−70°, step time was 0.2 s, and scanning step width was 0.03°.

Infrared Spectroscopy.

The IR absorption spectra of the two compounds were recorded using a Shimadzu Affinity-1 Fourier transform IR spectrometer in the wavenumber range of 400–4000 cm^{-1}. The samples were mixed and ground with KBr in a ratio of 1:100 to prepare the test samples.

UV–vis–NIR diffuse reflectance spectra.

UV–vis–NIR diffuse-reflectance spectroscopy data of $NH_4Sb(C_2O_4)F_2 \cdot H_2O$ and $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$ were recorded using a Shimadzu 3700DUV spectrophotometer in the wavelength range from 180 to 2600 nm at room temperature. Besides, reflectance spectra were converted to absorbance with the Kubelka-Munk function, and the optical bandgap could be obtained by the Tauc plot method.[4, 5]

Birefringence measurements.

The birefringence of $NH_4Sb(C_2O_4)F_2 \cdot H_2O$ single crystal was assessed with a polarizing microscope ZEISS Axioscope 5, equipped with a Berek compensator. The wavelength of the light source was 546 nm. The birefringence was calculated according to the formula:

$$\Delta R = \Delta n \times d,$$

in which ΔR, Δn, d, were the optical path difference, birefringence and thickness of crystal.

Thermal Analysis.

The data of thermal behavior of $NH_4Sb(C_2O_4)F_2 \cdot H_2O$ and $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$ were collected by NETZSCH STA 449C simultaneous analyzer instrument under flowing nitrogen gas, and the sample were put in closed platinum crucibles with a temperature from room temperature to 800 °C at a heating rate of 10 °C/ min.

Theoretical Calculations.

The structure of the two compounds was optimized geometrically, and the calculations of energy band structure, electronic structure, density of states (DOS) and partial density of states (PDOS) of the two compounds were computed, using the CASTEP program[6] with the density functional theory (DFT).[7-9] The Perdew-Burke-Ernzerhof (PBE) function under generalized gradient approximation (GGA) was adopted in all calculations.[10-12] The kinetic energy cut-off values for two compounds were both set as 750 eV, while the k-point separation were 0.04 Å^{-1}.

By the response electronic distribution anisotropy (REDA) method, the optical anisotropy was characterized by the REDA index (ζ)[13].The formula can be expressed as:

$$\boldsymbol{\zeta} = \sum \boldsymbol{g}\ [\boldsymbol{N_c Z_a \Delta\rho^b} / (\boldsymbol{n_1 E_0})]\ \boldsymbol{g}$$

where N_c is the coordination number of the nearest−neighbor cations to the central anion, Z_a is the formal chemical valence of the anion, $\Delta\rho^b$ is the difference between the maximum and minimum bonding electron densities of a covalent bond in an anionic group on the principal optical axis of the crystal, E_0 is the optical band gap, and $\boldsymbol{n}_1$ is the minimum refractive index.

Tables

Table S1. Crystal data and structure refinement for $NH_4Sb(C_2O_4)F_2{\cdot}H_2O$, $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2{\cdot}2H_2O$ and $(NH_4)_4Sb_2(C_2O_4)_3F_4{\cdot}2H_2O$.

Formula	$NH_4Sb(C_2O_4)F_2{\cdot}H_2O$	$[C(NH_2)_3]_3Sb(C_2O_4)_2F_2{\cdot}2H_2O$	$(NH_4)_4Sb_2(C_2O_4)_3F_4{\cdot}2H_2O$
Formula weight	283.83	552.08	691.76
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	5.0281(9)	8.3223(7)	8.6392(5)
b/Å	15.851(3)	11.0455(9)	9.8051(5)
c/Å	9.3431(16)	12.2379(8)	11.7908(6)
α/°	90	69.660(3)	90
β/°	98.079(7)	76.132(3)	94.628(2)
γ/°	90	69.725(3)	90
Volume/Å^3	737.3(2)	980.32(13)	995.52(9)
Z	4	2	2
ρ_{calc}g/cm^3	2.557	1.870	2.308
Temperature/K	288.00	288.00	288.00
F (000)	536.0	552.0	668.0
μ/mm^{-1}	3.761	1.493	2.825
2θ range for data collection/°	5.098 to 55.184	4.108 to 55.174	5.41 to 55.022
Index ranges	$-6 \le h \le 6$, $-20 \le k \le 20$, $-11 \le l \le 12$	$-10 \le h \le 10$, $-14 \le k \le 14$, $-14 \le l \le 15$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-15 \le l \le 15$
Reflections collected	18242	24593	29432
Independent reflections	1661 [R_{int} = 0.0654, R_{sigma} = 0.0321]	4497 [R_{int}= 0.0970, R_{sigma}= 0.0603]	2229 [R_{int}= 0.0554, R_{sigma}= 0.0222]
Data/restraints/parameters	1661/0/103	4497/0/269	2229/6/146
Goodness-of-fit on F^2	1.080	1.056	1.081
R_1, wR_2 ($I > 2\sigma(I)$)	0.0299/0.0682	0.0386/0.0741	0.0226/0.0599
R_1, wR_2 (all data)	0.0374/0.0729	0.0520/0.0809	0.0253/ 0.0623
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e·Å^{-3}	1.34/-0.72	0.53/-0.88	0.49/-0.69

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters ($Å^2$× 10^3) and bond valence sum (BVS) calculations for $NH_4Sb(C_2O_4)F_2{\cdot}H_2O$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	*U*(eq)	BVS
Sb1	8073.1(5)	4243.4(2)	7663.6(3)	26.81(11)	3.186
F1	4675(5)	4535.2(19)	6634(3)	44.4(7)	1.009
F2	6928(6)	3037.2(17)	7276(3)	47.1(8)	0.851
O1	2948(8)	4467(2)	11025(5)	49.9(10)	1.874
O2	5383(8)	3966(2)	9418(4)	44.4(9)	1.912
O3	8938(6)	3985.1(18)	5395(3)	31.3(7)	1.930
O4	10675(7)	4448.7(18)	3488(4)	33.8(7)	1.858
O5	4112(9)	2067(3)	9183(6)	66.4(12)	2.451
C1	4520(9)	4547(3)	10138(5)	34.2(10)	4.135
C2	9897(8)	4554(2)	4672(5)	26.0(8)	4.096
N1	836(11)	2139(3)	6012(7)	67.2(17)	5.404
H1A	154.22	2251.01	5101.13	81	1.352
H1B	2222.42	1788.71	6025.23	81	1.350
H1C	1384.22	2616.21	6461.43	81	1.353
H1D	9581.42	1899.41	6461.43	81	1.348
H5A	5286.65	1762.28	9682.33	100	1.222
H5B	4882.89	2471.56	8807.59	100	1.228

The bond valence sum (BVS) for all atoms was calculated with the following formula: $V_i = \sum s_{ij}$ and $s_{ij} = \exp[(d_0 - dij)/b]$, where s_{ij} is the valence of bond *i-j*, and d_0 and b are bond valence parameters, with values 1.955 and 0.37 for Sb-O bonds, 1.9 and 0.37 for Sb-F bonds, 1.41 and 0.37 for C-O bonds, 1.54 and 0.37 for C-C bonds, 1.014 and 0.413 for N-H bonds, respectively.

Table S3. Bond lengths [Å] and angles [°] for $NH_4Sb(C_2O_4)F_2\cdot H_2O$.

Bond	Length/Å	Bond	Length/Å
Sb1-F1	1.896(3)	C1-O1	1.230(5)
Sb1-F2	2.015(3)	C1-O2	1.253(5)
Sb1-O1^{2}	2.474(3)	C1-C1^{2}	1.549(8)
Sb1-O2	2.309(3)	C2-O3	1.262(5)
Sb1-O3	2.260(3)	C2-O4	1.235(5)
Sb1-O4^{1}	2.458(3)	C2-C2^{1}	1.539(8)

Bond	Angle/°	Bond	Angle/°
F1-Sb1-F2	85.76(14)	O2-Sb1-O3	147.16(12)
F1-Sb1-O1^{2}	79.32(14)	O3-Sb1-O4^{1}	69.35(10)
F1-Sb1-O2	80.25(14)	O1-C1-C1^{2}	116.9(5)
F1-Sb1-O3	81.20(13)	O1-C1-O2	126.2(4)
F1-Sb1-O4^{1}	80.80(12)	C1^{2}-C1-O2	116.9(5)
F2-Sb1-O1^{2}	143.06(11)	C2^{1}-C2-O3	116.9(5)
F2-Sb1-O2	76.45(11)	C2^{1}-C2-O4	117.9(4)
F2-Sb1-O3	75.37(11)	O3-C2-O4	125.2(4)
F2-Sb1-O4^{1}	143.70(11)		
O1^{2}-Sb1-O2	67.86(11)		
O1^{2}-Sb1-O3	134.00(12)		
O1^{2}-Sb1-O4^{1}	66.64(11)		
O2-Sb1-O4^{1}	133.07(11)		

Symmetry transformations used to generate equivalent atoms:

^{1}(2-x, 1-y, 1-z); ^{2}(1-x, 1-y, 2-z)

Table S4. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2× 10^3) and bond valence sum (BVS) calculations for $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$. *U*(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	*U*(eq)	BVS
Sb1	608.5(3)	3072.8(3)	6562.6(2)	30.27(10)	2.991
F1	2692(3)	2389(2)	7301(2)	40.7(5)	0.898
F2	229(3)	1287(2)	7712(2)	47.5(6)	0.642
O1	3658(4)	1133(3)	3967(3)	55.6(9)	1.602
O2	4143(4)	3614(3)	3328(3)	49.0(8)	1.601
O3	2501(4)	3931(3)	4993(2)	38.5(6)	1.857
O4	1991(4)	1523(3)	5587(2)	38.5(6)	1.927
O5	-820(4)	3519(3)	8358(2)	42.7(7)	1.795
O6	881(4)	5091(3)	6736(3)	48.2(8)	1.732
O7	-480(4)	6798(3)	7489(3)	58.5(9)	1.636
O8	-2282(4)	5143(3)	9189(3)	55.0(8)	1.628
O9	-3329(4)	1725(3)	8442(3)	63.2(10)	2.448
O10	5257(4)	5812(3)	2909(3)	58.6(9)	2.452
C1	7214(5)	1938(4)	1367(4)	38.4(9)	4.199
C2	2683(5)	-2083(4)	4878(4)	37.7(9)	4.176
C3	2945(5)	1853(4)	4627(4)	35.5(9)	4.067
C4	3229(5)	3259(4)	4267(3)	33.1(8)	4.070
C5	-205(5)	5632(4)	7488(4)	36.7(9)	4.070
C6	-1211(5)	4711(4)	8425(4)	38.1(9)	4.091
C7	-2747(5)	8412(4)	9692(4)	40.0(9)	4.196
N1	8689(4)	1526(4)	710(3)	48.1(9)	1.371
N2	6224(5)	3184(4)	1035(4)	54.4(10)	1.416
N3	6754(5)	1074(4)	2345(3)	48.7(9)	1.410
N4	2741(5)	-3284(3)	4871(3)	47.7(9)	1.414
N5	3745(5)	-1439(3)	4118(3)	48.2(9)	1.403
N6	1533(5)	-1502(4)	5642(4)	53.0(10)	1.359
N7	-2803(5)	8870(4)	8546(3)	56.9(11)	1.384
N8	-2985(4)	9274(4)	279(3)	43.9(8)	1.396
N9	-2457(5)	7116(4)	235(4)	54.9(10)	1.415

Table S5. Bond lengths [Å] and angles [°] for $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2\cdot 2H_2O$.

Bond	Length/Å	Bond	Length/Å
Sb1-F1	1.940(2)	C3-O1	1.236(5)
Sb1-F2	2.064(2)	C3-O4	1.265(5)
Sb1-O3	2.321(3)	C4-O2	1.236(5)
Sb1-O4	2.253(3)	C4-O3	1.263(4)
Sb1-O5	2.361(3)	C5-C6	1.540(6)
Sb1-O6	2.402(3)	C5-O6	1.276(5)
C1-N1	1.324(5)	C5-O7	1.228(5)
C1-N2	1.313(5)	C6-O5	1.270(5)
C1-N3	1.315(5)	C6-O8	1.229(5)
C2-N4	1.313(5)	C7-N7	1.322(5)
C2-N5	1.316(5)	C7-N8	1.319(5)
C2-N6	1.329(6)	C7-N9	1.313(5)
C3-C4	1.546(5)		

Bond	Angle/°	Bond	Angle/°
F1-Sb1-F2	80.80(10)	N4-C2-N5	120.3(4)
F1-Sb1-O3	80.02(10)	N4-C2-N6	120.1(4)
F1-Sb1-O4	84.64(10)	N5-C2-N6	119.6(4)
F1-Sb1-O5	85.07(10)	O1-C3-C4	124.6(4)
F1-Sb1-O6	78.07(10)	O1-C3-O4	124.6(4)
F2-Sb1-O3	142.35(9)	C4-C3-O4	117.0(3)
F2-Sb1-O4	75.11(10)	O3-C4-C3	115.3(3)
F2-Sb1-O5	73.05(10)	O2-C4-O3	126.3(4)
F2-Sb1-O6	135.96(10)	O2-C4-C3	118.5(3)
O3-Sb1-O4	136.49(10)	O7-C5-C6	120.5(4)
O3-Sb1-O5	69.96(9)	O7-C5-O6	124.6(4)
O3-Sb1-O6	71.09(9)	O5-C6-O5	115.7(3)
O4-Sb1-O5	147.70(10)	O8-C6-C5	124.6(4)
O4-Sb1-O6	139.47(10)	C6-C6-C6	119.7(4)
O5-Sb1-O6	67.03(10)	N7-C7-N8	119.0(4)
N1-C1-N2	118.9(4)	N7-C7-N9	120.3(4)
N1-C1-N3	120.3(4)	N8-C7-N9	120.7(4)
N2-C1-N3	120.9(4)		

Table S6. Fractional Atomic Coordinates (×10^4), Equivalent Isotropic Displacement Parameters (Å^2×10^3) and bond valence sum (BVS) calculations for $(NH_4)_4Sb_2(C_2O_4)_3F_4\cdot 2H_2O$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Sb(1)	1277.7(2)	4035.3(2)	7400.8(2)	26.61(9)	3.051
F(1)	-256(2)	4706(2)	8528.1(15)	40.5(4)	0.650
F(2)	1926(2)	5901.5(17)	7518.1(16)	36.2(4)	0.960
O(1)	-1896(2)	5450(2)	4536.5(17)	33.6(4)	1.823
O(2)	-877(3)	4967(3)	6280.4(17)	40.8(5)	1.853
O(3)	2496(2)	3781(2)	9137.7(17)	34.7(5)	1.888
O(4)	4712(3)	3261(3)	10131.1(18)	44.4(6)	1.653
O(5)	3904(2)	3817(2)	7222.6(17)	31.7(4)	1.8521
O(6)	6209(2)	3532(3)	8177.9(19)	38.8(5)	1.631
O(7)	4830(20)	6175(13)	5939(9)	54(2)	2.469
O(8)	5460(20)	5925(14)	6011(11)	50(2)	2.447
N(1)	7728(4)	1524(3)	6993(3)	48.2(7)	5.404
N(2)	-1714(3)	3207(3)	10171(2)	33.7(5)	5.400
C(1)	-797(3)	5121(3)	5233(2)	28.9(6)	4.080
C(2)	3957(3)	3547(3)	9236(2)	29.6(6)	4.056
C(3)	4787(3)	3631(3)	8123(2)	26.8(5)	4.073
H1A	-2213.04	3775.04	10604.38	40	1.350
H1B	-1971.04	3390.34	9441.38	40	1.353
H1C	-694.04	3311.04	10320.08	40	1.350
H1D	-1976.34	2352.04	10320.08	40	1.350
H2A	7537.82	1655.79	6248.01	58	1.350
H2B	8336.92	797.79	7113.81	58	1.350
H2C	8199.92	2255.79	7305.31	58	1.350
H2D	6836.32	1387.69	7305.31	58	1.350
H7A	4567.61	5485.81	6314.78	82	1.230
H7B	4072.21	6721.31	5949.18	82	1.238
H8A	5052.22	5197.03	6240.54	76	1.225
H8B	6191.52	5722.53	5598.84	76	1.221

Table S7. Bond lengths (Å) and angles (°) for $(NH_4)_4Sb_2(C_2O_4)_3F_4 \cdot 2H_2O$

Atom-Atom	Length/Å	Atom-Atom	Length/Å
Sb(1)-F(1)	2.0591(17)	O(1)-C(1)	1.247(3)
Sb(1)-F(2)	1.9153(17)	O(2)-C(1)	1.251(3)
Sb(1)-O(5)	2.305(2)	O(3)-C(2)	1.279(4)
Sb(1)-O(1)^{1}	2.440(2)	O(6)-C(3)	1.229(3)
Sb(1)-O(2)	2.376(2)	C(3)-C(2)	1.548(4)
Sb(1)-O(3)	2.240(2)	O(4)-C(2)	1.227(3)
O(5)-C(3)	1.269(3)	C(1)-C(1)^{1}	1.542(5)

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
F(1)-Sb(1)-O(5)	141.07(8)	O(3)-Sb(1)-O(2)	147.18(7)
F(1)-Sb(1)-O(1)^{1}	137.65(7)	C(3)-O(5)-Sb(1)	117.82(18)
F(1)-Sb(1)-O(2)	73.74(7)	C(1)-O(1)-Sb(1)^{1}	117.26(18)
F(1)-Sb(1)-O(3)	74.03(7)	C(1)-O(2)-Sb(1)	119.47(18)
F(2)-Sb(1)-F(1)	81.25(8)	C(2)-O(3)-Sb(1)	119.39(18)
F(2)-Sb(1)-O(5)	79.12(8)	O(5)-C(3)-C(2)	115.4(2)
F(2)-Sb(1)-O(1)^{1}	77.60(8)	O(6)-C(3)-O(5)	125.9(3)
F(2)-Sb(1)-O(2)	83.35(9)	O(6)-C(3)-C(2)	118.7(2)
F(2)-Sb(1)-O(3)	85.84(8)	O(3)-C(2)-C(3)	115.8(2)
O(5)-Sb(1)-O(1)^{1}	69.06(7)	O(4)-C(2)-O(3)	124.8(3)
O(5)-Sb(1)-O(2)	135.85(8)	O(4)-C(2)-C(3)	119.4(3)
O(2)-Sb(1)-O(1)^{1}	67.72(7)	O(1)-C(1)-O(2)	125.6(3)
O(3)-Sb(1)-O(5)	71.31(7)	O(1)-C(1)-C(1)^{1}	117.3(3)
O(3)-Sb(1)-O(1)^{1}	139.18(7)	O(2)-C(1)-C(1)^{1}	117.1(3)

Symmetry transformations used to generate equivalent atoms:

^{1}(-x,1-y,1-z)

Table S8. The calculated REDA Δ*ρ* values and contributions.

Compounds	Units	Δρ	Contributions
$NH_4Sb(C_2O_4)F_2\cdot H_2O$	NH_4^+	0.00002	0.0019
	H_2O	0.00120	0.1497
	$[SbO_4F_2]$	0.00072	0.0898
	$[C_2O_4]$	0.00607	0.7586
Total	0.00800	1.0000	1
$[C(NH_2)_3]_3Sb(C_2O_4)_2F_2\cdot 2H_2O$	$[SbO_4F_2]$	0.00001	0.0147
	$[C(NH_2)_3]$	0.00694	0.3232
	$[C_2O_4]$	0.01825	0.8501
	H_2O	-0.00373	-0.1738
Total	0.02039	1.0000	1

Table S9. Sn(II) and Sb(III) oxalates and other Oxalates.

No	Molecular formula	Space group	Birefringence (Δn)	Band gap (E_g/eV)	Coordination mode	quasi-dimensional frameworks	References
1	$K_5Sb_2(C_2O_4)_{5.5}\cdot 3H_2O$	$P2_1/n$	0.020@546 nm (exp)	3.95 (exp)	SbO_6	0D $[Sb(1)_2(C_2O_4)_5]^{4-}$ clusters, 0D$[Sb(2)(C_2O_4)_3]^{3-}$ clusters	[14]
2	$C_9H_{25}N_3\cdot In_2(C_2O_4)_4$	$P2_1$	0.041@546 nm (exp)	4.25 (exp)	InO_7	3D framework structure 12-ring channels	[15]
3	$C_9H_{25}N_3\cdot Sc_2(C_2O_4)_4\cdot{}_2H_2O$	$P2_12_12_1$	0.055@546 nm (exp)	4.54 (exp)	ScO_8	3D framework structure 16-ring channels	[15]
4	$(NH_4)_4Sb(C_2O_4)_3F_4\cdot 2H_2O$	$P2_1/c$	0.066@546 nm (cal)	2.781(cal)	SbO_4F_2	0D $[Sb_2(C_2O_4)_3F_2]^{4-}$	This work
5	$BaSb(C_2O_4)_{2.5}\cdot 3H_2O$	$\mathrm{P\bar{1}}$	0.070@546 nm (exp)	3.91 (exp)	SbO_6	0D $[Sb_2(C_2O_4)_5]^{4-}$ clusters	[14]
6	$C(NH_2)_3Cd(C_2O_4)Cl(H_2O)\cdot H_2O$	$\mathrm{P\bar{1}}$	0.075@546 nm (exp)	3.76 (exp)	CdO_5Cl	1D $\{[Cd_2(C_2O_4)_2Cl_2(H_2O)_2]^{2-}\}_\infty$ chains	[16]
7	$RbSb_2(C_2O_4)F_5$	$P2_12_12_1$	0.090@546 nm (exp)	3.96 (exp)	SbO_2F_2,$SbOF_3$	0D $[Sb_2(C_2O_4)F_5]^-$ cluster	[17]
8	$BaCd(C_2O_4)_{1.5}Cl(H_2O)_2$	$C2/\mathrm{c}$	0.096@546 nm (exp)	4.53 (exp)	CdO_5Cl	2D $\{[Cd(C_2O_4)_{1.5}Cl]^{2-}\}_\infty$ layer	[16]
9	$K_2Sb_2(C_2O_4)F_6$	$\mathrm{Pca2_1}$	0.097@546 nm (exp)	4.27 (exp)	SbO_2F_3	1D $[Sb_2(C_2O_4)_2F_6]_\infty{}^{2-}$ chains	[18]
10	$Na_4Sb_2O(C_2O_4)_4\cdot 6H_2O$	$\mathrm{I2/a}$	0.100@546 nm (exp)	3.88 (exp)	SbO_5	0D $[Sb_2O(C_2O_4)_4]^{4-}$ clusters	[14]
11	$K_2Sn(C_2O_4)_2\cdot H_2O$	$\mathrm{P\bar{1}}$	0.103@546 nm (exp)	3.74 (exp)	SnO_4	0D $[Sn(C_2O_4)_2]^{2-}$ cluster	[19]
12	$Rb_2Sb(C_2O_4)_{2.5}(H_2O)_3$	$P2_1/c$	0.110@546 nm (exp)	3.89 (exp)	SbO_6	0D $[Sb_2(C_2O_4)_5]^{4-}$ cluster	[17]
13	$NH_4Sb_2(C_2O_4)F_5$	$P2_12_12_1$	0.111@546 nm (cal)	3.85 (exp)	SbO_2F_2,$SbOF_3$	0D $[Sb_2(C_2O_4)F_5]^-$ cluster	[20]
14	$(CN_4H_7)SbC_2O_4F_2(H_2O)_{0.5}$	$\mathrm{P\bar{1}}$	0.126@546 nm (exp)	3.44 (exp)	SbO_4F_2	1D $[Sb(C_2O_4)F_2]_\infty{}^-$ chains	[21]
15	$Na_4Sn_4(C_2O_4)_3F_6$	$\mathrm{P\bar{1}}$	0.160@546 nm (exp)	3.15 (exp)	SnO_2F_2,SnO_3F	0D $[C_2O_4F_4]^{6-}$ clusters,1D $[SnC_2O_4F]_\infty{}^-$ chains	[22]
16	$RbSb(C_2O_4)F_2\cdot H_2O$	$\mathrm{P2_1/c}$	0.162@546 nm (exp)	3.83 (exp)	SbO_4F_2	1D $[Sb(C_2O_4)F_2]_\infty{}^-$ chains	[23]
17	$KSb_2C_2O_4F_5$	$P2_1/n$	0.170@546 nm (exp)	4.07 (exp)	SbO_2F_2,$SbOF_3$	0D $[Sb_2C_2O_4F_5]^-$ cluster	[24]
18	$Na_2Sb_2(C_2O_4)F_6$	$\mathrm{C2/c}$	0.188@546 nm (exp)	4.03 (exp)	SbO_3F_3	1D $[(SbF_3)_2(C_2O_4)]^{2-}$ chains	[18]
19	$NaSnC_2O_4F\cdot H_2O$	$\mathrm{P\bar{1}}$	0.189@546 nm (exp)	3.75 (exp)	SnO_3F_2	1D $[Sn_2(C_2O_4)_2F_2]_\infty{}^{2-}$ double chains	[22]
20	$K_2Sb(C_2O_4)Cl_3$	$P2_12_12_1$	0.210@546 nm (cal)	3.61 (exp)	SbO_2Cl_3	0D $[SbC_2O_4Cl_3]^{2-}$ cluster	[25]
21	$Na_3Sb(C_2O_4)_2F_2\cdot 2H_2O$	$P2_1/n$	0.210@546 nm (exp)	4.03 (exp)	SbO_4F_2	0D $[Sb(C_2O_4)_2F_2]^{3-}$ clusters	[14]
22	$Rb_2Sb(C_2O_4)Cl_3$	$P2_12_12_1$	0.220@546 nm (cal)	3.74 (exp)	SbO_2Cl_3	0D $[SbC_2O_4Cl_3]^{2-}$ cluster	[25]
23	$[C(NH_2)_3]_3Sb(C_2O_4)_2F_2\cdot 2H_2O$	$\mathrm{P\bar{1}}$	0.251@546 nm (cal)	3.29 (exp)	SbO_4F_2	0D $[Sb(C_2O_4)_2F_2]^{3-}$ clusters	This work
24	$(NH_4)_2Sb(C_2O_4)Cl_3$	$P2_12_12_1$	0.270@546 nm (cal)	3.55 (exp)	SbO_2Cl_3	0D $[SbC_2O_4Cl_3]^{2-}$ cluster	[25]
25	$(C_5H_6ON)_2[Sb_2O(C_2O_4)_3]$	$\mathrm{C2/c}$	0.279@546 nm (exp)	3.76 (exp)	SbO_6	2D $[Sb_2O(C_2O_4)_3]_n{}^{2n}$ layer	[26]
26	$K_2Sn_2(C_2O_4)_2F_2\cdot H_2O$	$P2_1/c$	0.301@546 nm (exp)	3.21 (exp)	SnO_4F	1D $[Sn_2(C_2O_4)_2F_2]_\infty{}^{2-}$ chains	[19]
27	$[C(NH_2)_3]Sb(C_2O_4)F_2\cdot H_2O$	$P2_1/\mathrm{c}$	0.323@546 nm (exp)	4.09 (exp)	SbO_4F_2	1D $[Sb(C_2O_4)F_2]_\infty{}^-$ chains	[23]
28	$Cs_2Sb_2(C_2O_4)_2F_4\cdot H_2O$	$\mathrm{P\bar{1}}$	0.325@546 nm (exp)	3.81 (exp)	SbO_4F_2	1D $[Sb_2(C_2O_4)_2F_4]_\infty{}^{2-}$ chains	[18]
29	$NH_4Sb(C_2O_4)F_2\cdot H_2O$	$P2_1/c$	0.381@546 nm (cal)	3.45 (exp)	SbO_4F_2	1D $[Sb(C_2O_4)F_2]_\infty{}^-$ chains	This work

Figures

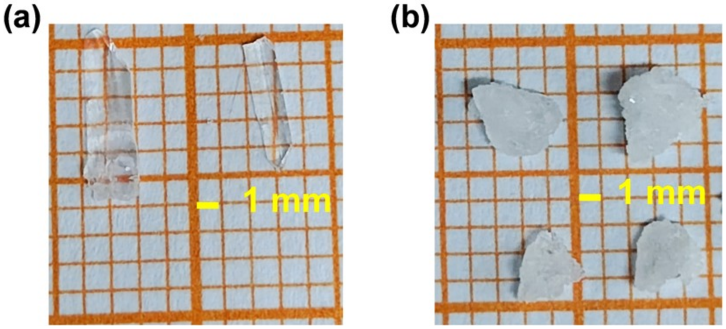

Figure S1. The photos of two compounds (a) $NH_4Sb(C_2O_4)F_2 \cdot H_2O$, and (b) $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$.

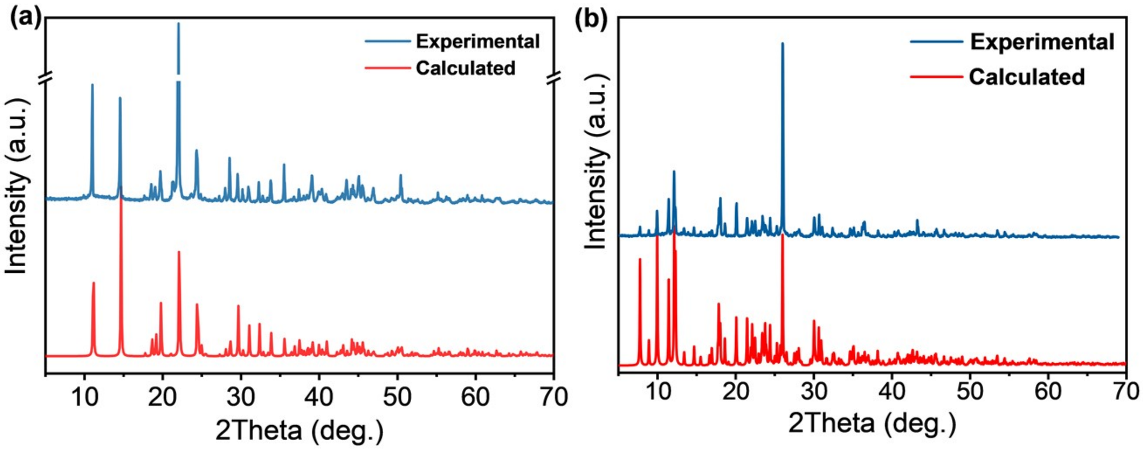

Figure S2. XRD patterns for compounds (a) $NH_4Sb(C_2O_4)F_2 \cdot H_2O$, and (b) $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$.

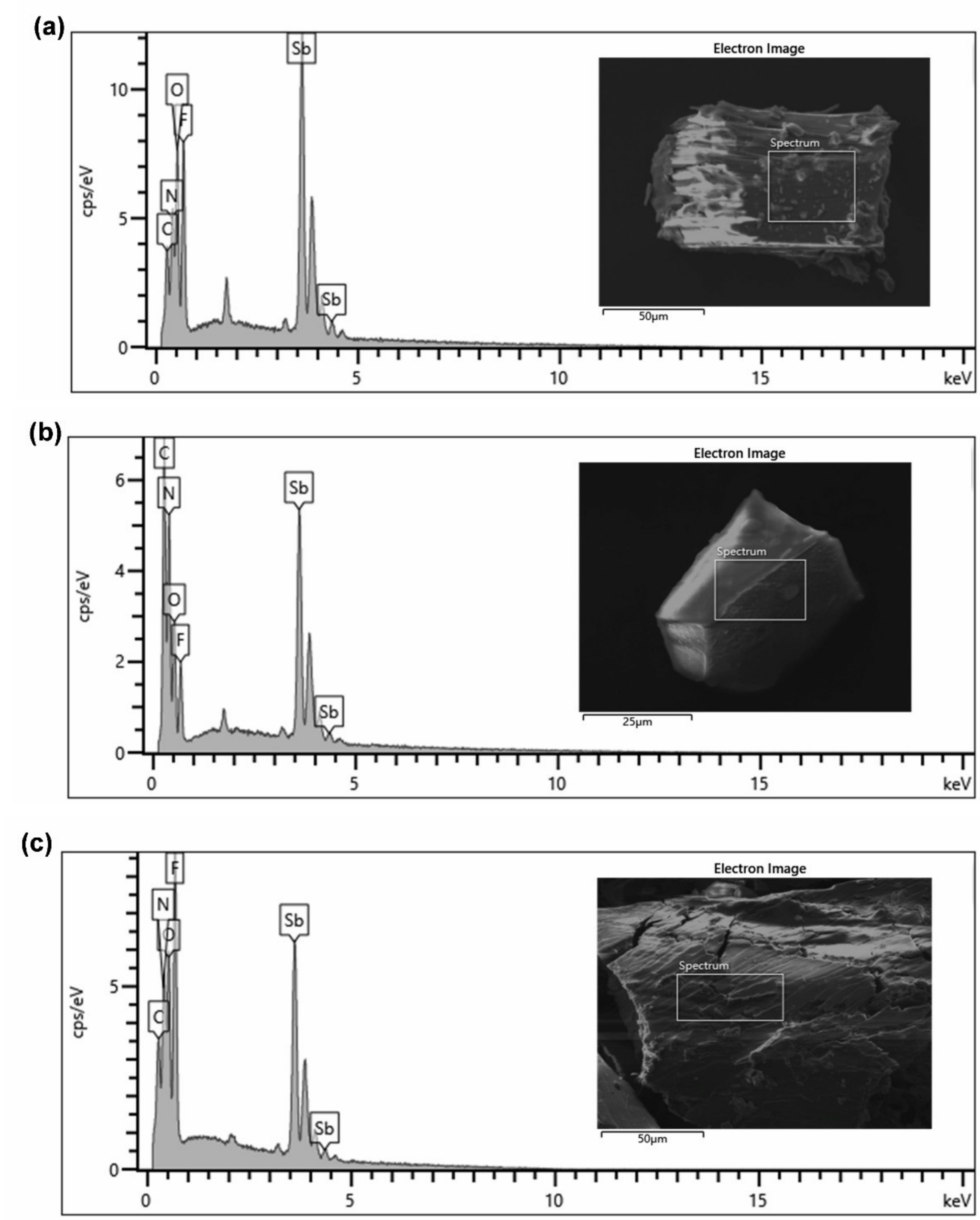

Figure S3. EDS spectrum of (a) $NH_4Sb(C_2O_4)F_2{\cdot}H_2O$, (b) $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2{\cdot}2H_2O$ and (c) $(NH_4)_4Sb_2(C_2O_4)_3F_4{\cdot}2H_2O$.

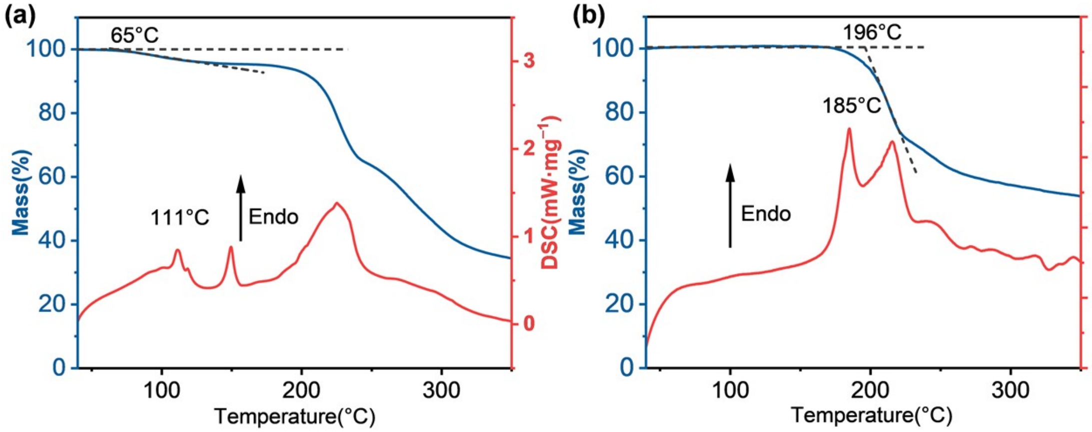

Figure S4. The TG-DSC curves of of (a) $NH_4Sb(C_2O_4)F_2 \cdot H_2O$, and (b) $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$.

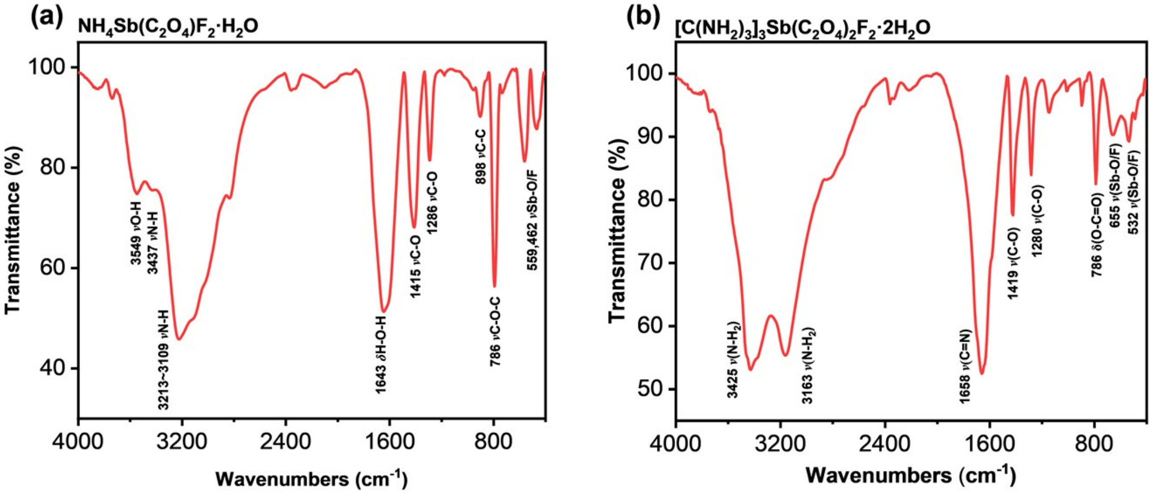

Figure S5. The IR spectra of (a) $NH_4Sb(C_2O_4)F_2 \cdot H_2O$, and (b) $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2 \cdot 2H_2O$.

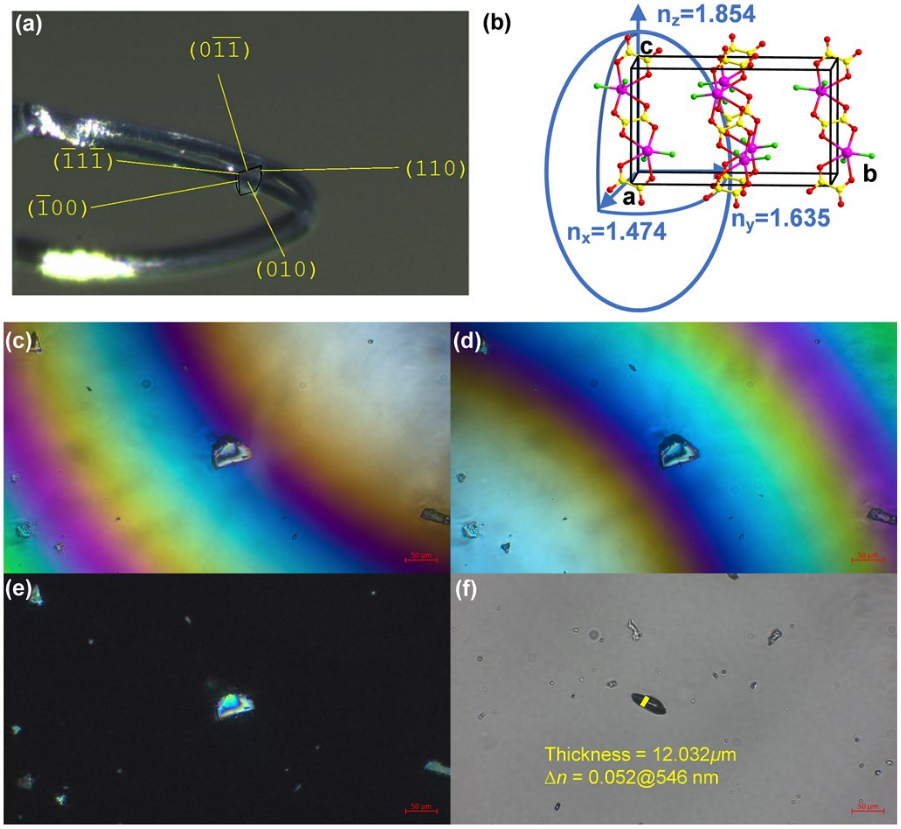

Figure S6. (a) The tested orientation of $NH_4Sb(C_2O_4)F_2 \cdot H_2O$ (compound 1) crystal plane is (010) from SD-XRD. (b) The indicatrix of optic biaxial crystal of $NH_4Sb(C_2O_4)F_2 \cdot H_2O$. (c) The positions of test crystal achromatism for compound 3. (d) The another positions of test crystal achromatism for compound 3 (e) Crystals under cross-polarized light (f) Thickness of the tested tiny crystal.

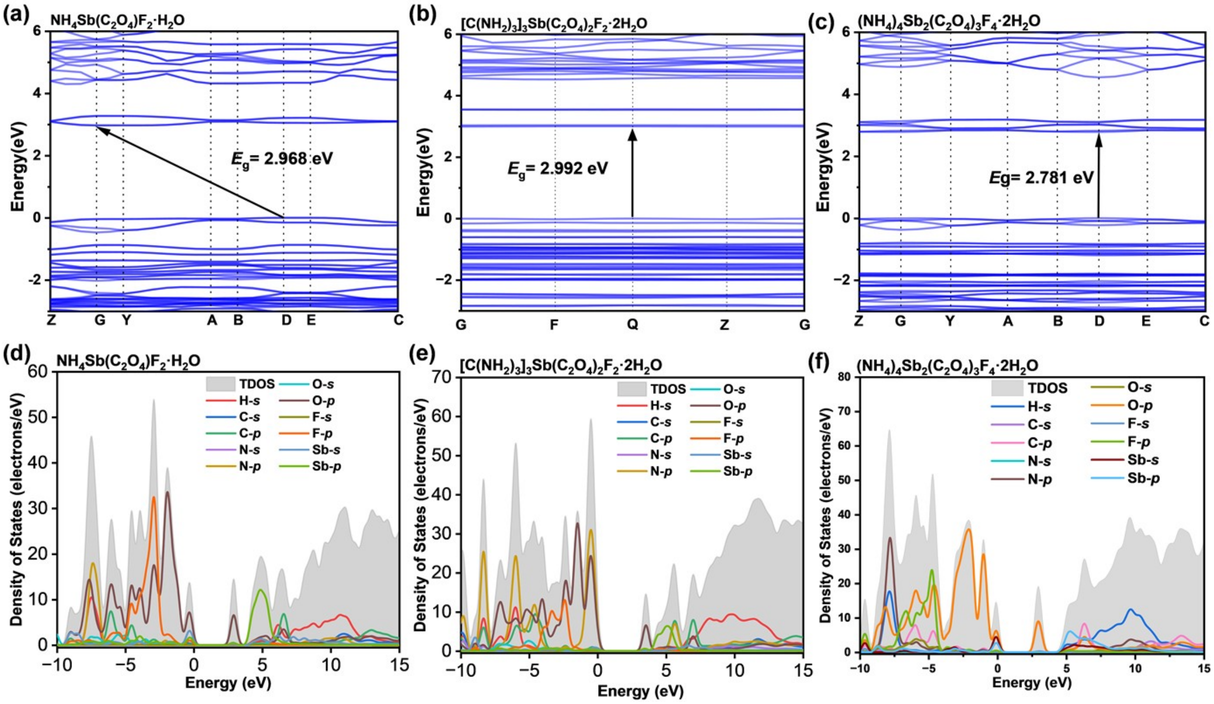

Figure S7. Calculated band structures and total and partial density of states of $NH_4Sb(C_2O_4)F_2{\cdot}H_2O$ (a), (c) and $[C(NH_2)_3]_3Sb(C_2O_4)_2F_2{\cdot}2H_2O$ (b), (e) $(NH_4)_4Sb_2(C_2O_4)_3F_4{\cdot}2H_2O$ (c), (f).

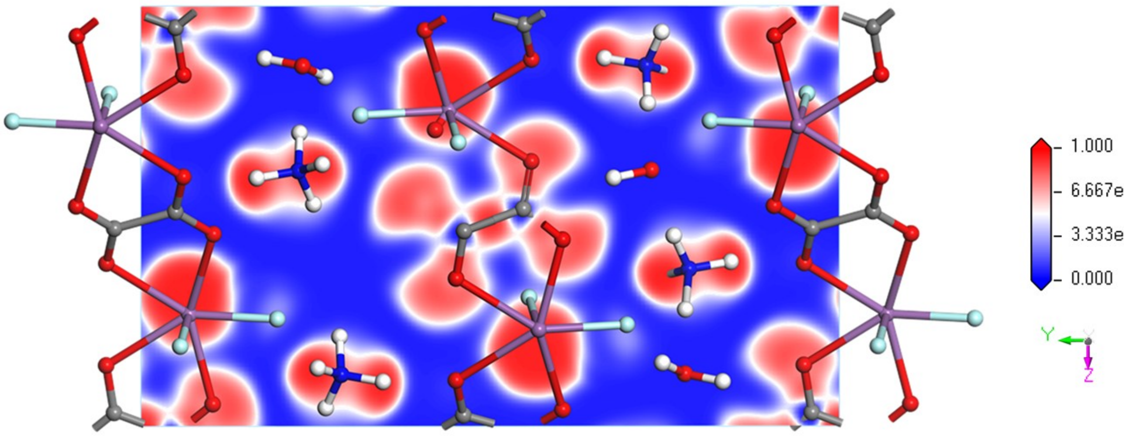

Figure S8. The electron localization function (ELF) diagram in $NH_4Sb(C_2O_4)F_2{\cdot}H_2O$.

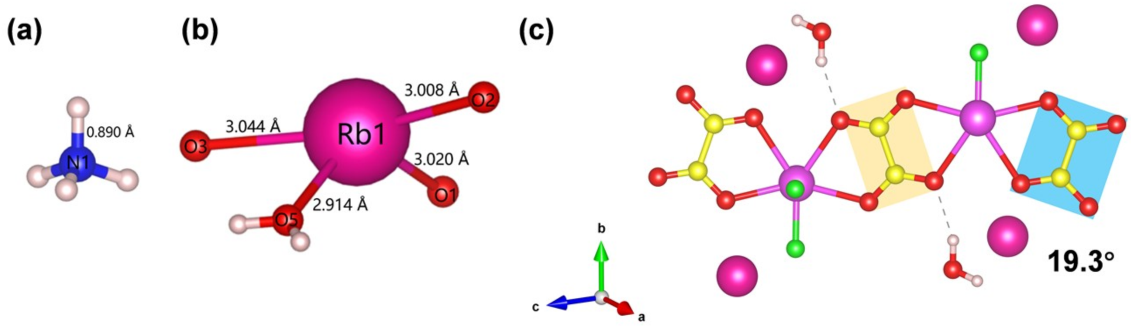

Figure S9. (a) The NH_4^+ in $NH_4Sb(C_2O_4)F_2 \cdot H_2O$. (b)The coordination of Rb in compound $RbSb(C_2O_4)F_2 \cdot H_2O$.(c) The $[Sb(C_2O_4)F_2]_\infty^-$ anionic chains in $RbSb(C_2O_4)F_2 \cdot H_2O$, the angle of two $[C_2O_4]$ planes.

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