Supporting Information

Synthesis, structure and magnetic properties of ACo$_5$(SeO$_3$)$_4$(OH)$_2$F (A = Rb, Cs): the first compounds with a distorted 2-uniform lattice (T29)

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Fig. S8 The magnetization curves (*M*) were measured in the range of -1 to 1 T at 2 K, with the applied magnetic field (*H*) oriented both parallel and perpendicular to the c-axis for $RbCo_5(SeO_3)_4(OH)_2F$.

Table S1 Elements ratio of $ACo_5(SeO_3)_4(OH)_2F$ (*A* = Rb, Cs) determined by EDS.

Table S2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $ACo_5(SeO_3)_4(OH)_2F$ (*A* = Rb, Cs).

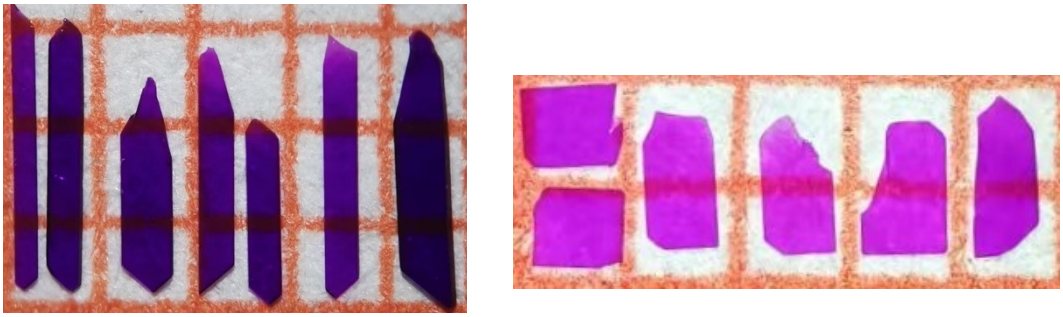
Table S3 Anisotropic displacement parameters of $ACo_5(SeO_3)_4(OH)_2F$ (*A* = Rb, Cs).

Table S4 Selected bond lengths [Å] and bond angles for $RbCo_5(SeO_3)_4(OH)_2F$.

Table S5 Selected bond lengths [Å] and bond angles for $CsCo_5(SeO_3)_4(OH)_2F$.

Table S6 Bond Valence Sum (BVS) of $ACo_5(SeO_3)_4(OH)_2F$ (*A* = Rb, Cs).

Table S7 A comparison of the Co···Co distances (Å) in $ACo_5(SeO_3)_4(OH)_2F$ (*A* = Rb and Cs).



(a)$RbCo_5$ **(b)$CsCo_5$**

Fig. S1. Single crystals of (a) $RbCo_5(SeO_3)_4(OH)_2F$ (**$RbCo_5$**) and (b) $CsCo_5(SeO_3)_4(OH)_2F$ (**$CsCo_5$**).

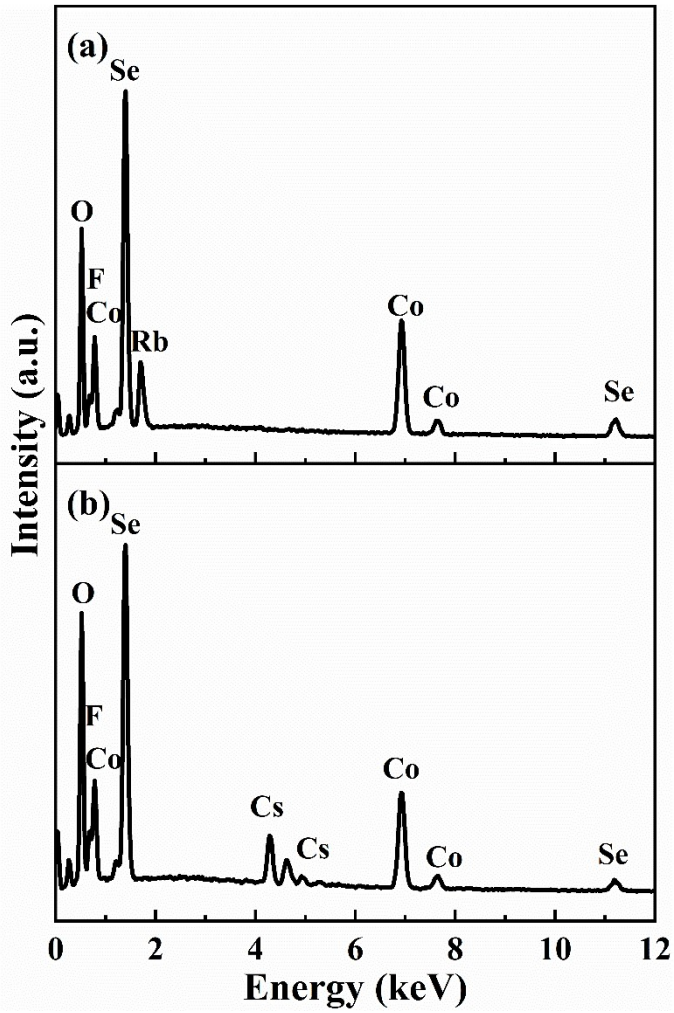


Fig. S2 The energy-dispersive spectrometry (EDS) elemental analyses of (a) $RbCo_5(SeO_3)_4(OH)_2F$, (b) $CsCo_5(SeO_3)_4(OH)_2F$.

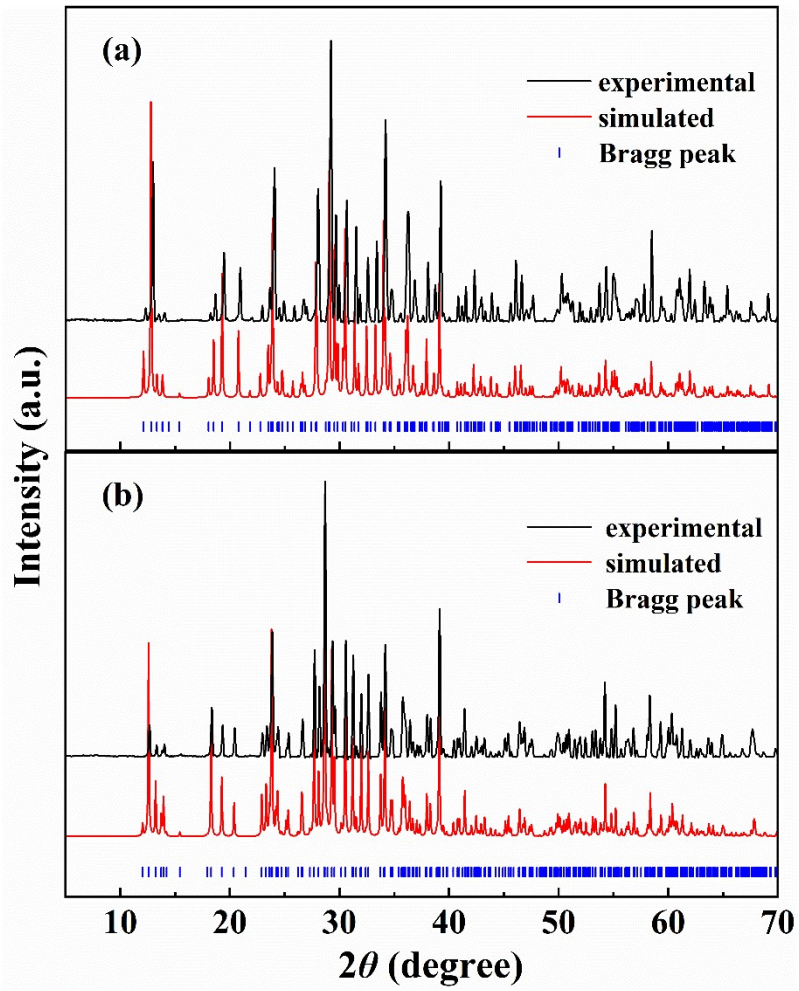


Fig. S3 Experimental (Black line), Simulated (Red line) and Bragg peak (Blue line) powder X-ray diffraction patterns of (a) $RbCo_5(SeO_3)_4(OH)_2F$, (b) $CsCo_5(SeO_3)_4(OH)_2F$.

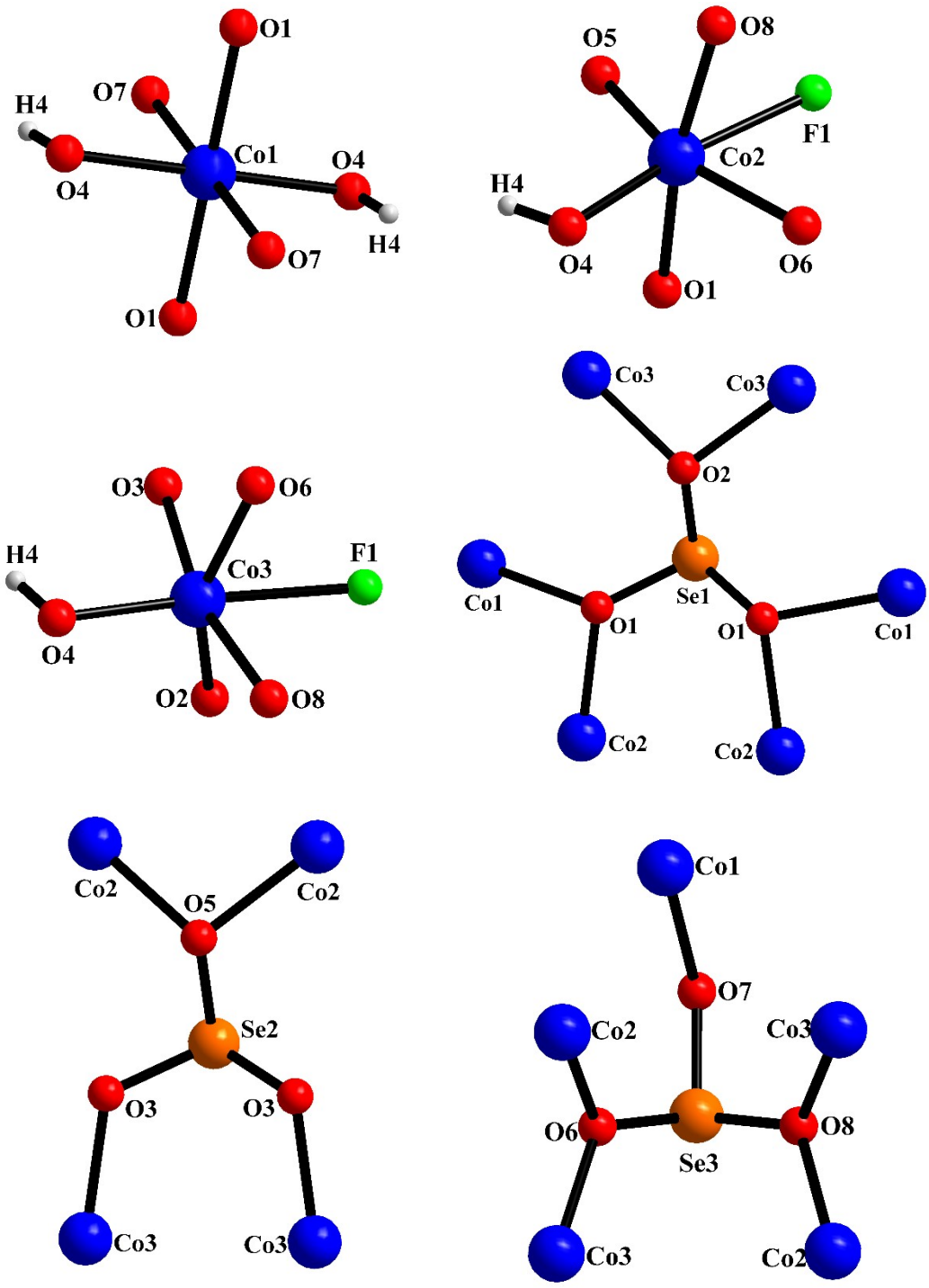


Fig. S4 View of the oxygen and fluorine coordination environments for Co and Se.

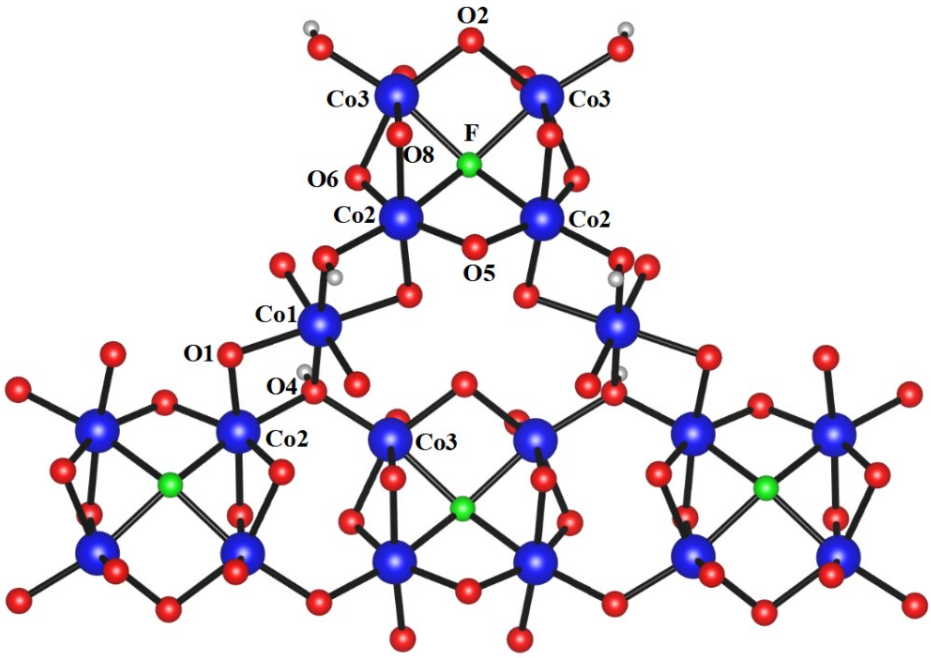


Fig. S5 The connection of $CoO_4(OH)F$ and $CoO_4(OH)_2$ octahedra within the zigzag-like chain.

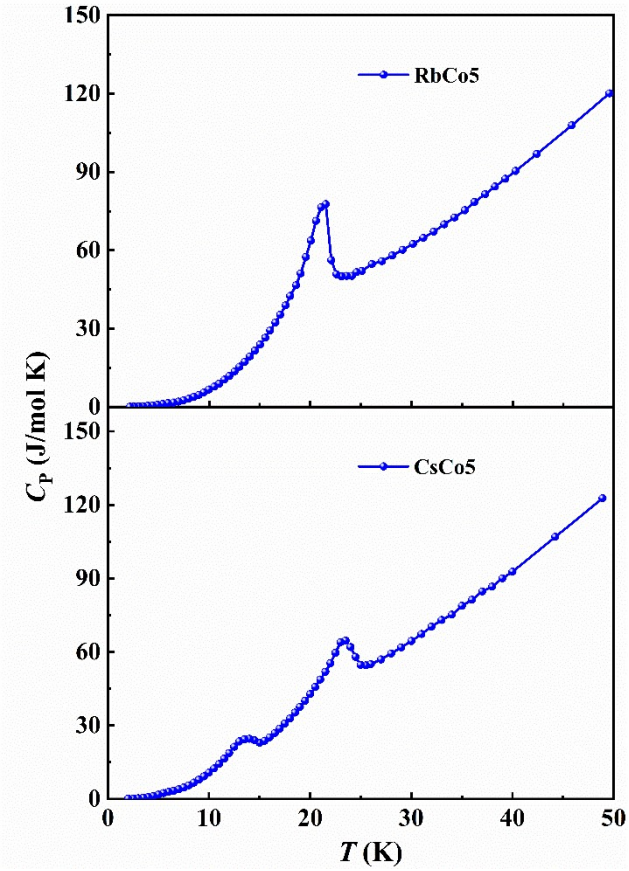


Fig. S6 The specific heat measured at zero magnetic field for (a) $RbCo_5(SeO_3)_4(OH)_2F$, (b) $CsCo_5(SeO_3)_4(OH)_2F$.

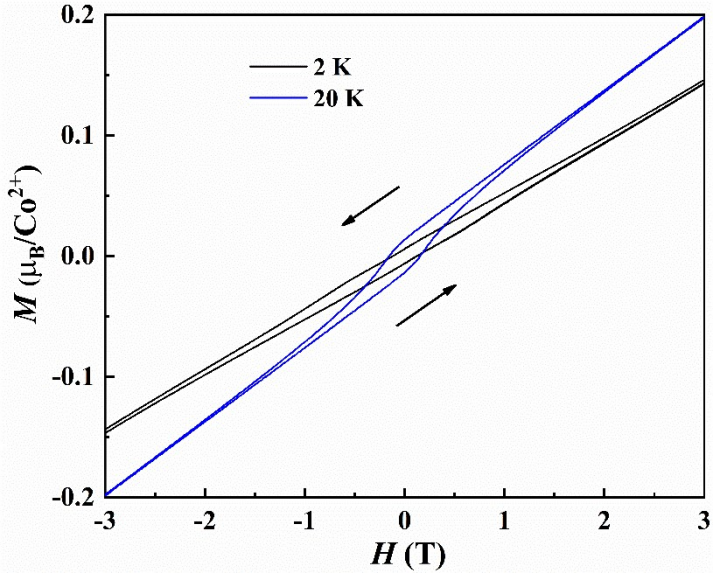


Fig. S7 The hysteresis loop measured at 2 K and 20 K for $CsCo_5(SeO_3)_4(OH)_2F$.

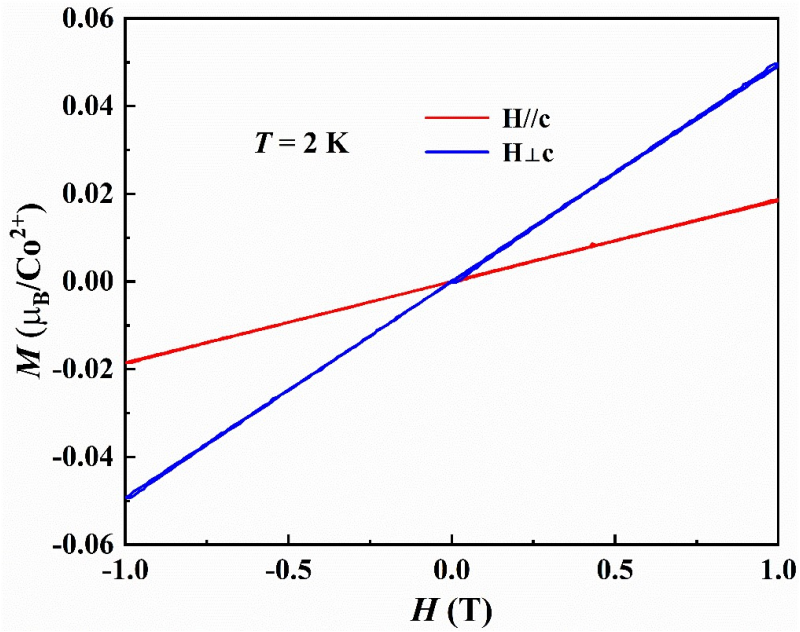


Fig. S8 The magnetization curves (*M*) were measured in the range of -1 to 1 T at 2 K, with the applied magnetic field (*H*) oriented both parallel and perpendicular to the c-axis for $RbCo_5(SeO_3)_4(OH)_2F$.

Table S1 Elements ratio of $ACo_5(SeO_3)_4(OH)_2F$ (A = Rb, Cs) determined by EDS.

Elements %	$RbCo_5$	$CsCo_5$
A	4.0	3.8
Co	18.2	18.4
Se	16.5	16.3
O	56.6	56.6
F	4.7	4.9
Ratio of A/Co/Se	1/4.6/4.1	1/4.8/4.3

Table S2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $ACo_5(SeO_3)_4(OH)_2F$ (A = Rb, Cs). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Co1	10000	10000	10000	4.93(12)
Co2	328.6(6)	6311.2(3)	3310.2(6)	4.44(9)
Co3	8177.2(6)	8735.3(3)	5695.4(5)	4.47(10)
Se1	56.4(6)	7500	-367.5(5)	3.80(9)
Se2	4335.1(6)	7500	5301.1(6)	4.68(10)
Se3	-2920.4(4)	4466.0(2)	2313.3(4)	4.22(8)
O1	-814(3)	6507.2(15)	462(3)	6.5(4)
O2	-1577(4)	7500	-2562(4)	5.9(6)
O3	5289(3)	8513.2(15)	4673(3)	8.2(4)
O4	8325(3)	10029.9(14)	7171(3)	5.5(4)
O5	2152(4)	7500	3464(4)	5.1(6)
O6	-2234(3)	5648.9(14)	3080(3)	6.0(4)
O7	-2413(3)	4375.8(15)	432(3)	7.2(4)
O8	-1115(3)	3770.5(14)	3866(3)	6.2(4)
F1	-1347(4)	7500	3962(3)	6.0(5)
Rb1	-4720.8(6)	7500	1133.6(6)	10.23(10)

Atom	*x*	*y*	*z*	U(eq)
Co1	0	5000	0	4.24(15)
Co2	461.7(8)	3683.3(4)	3360.9(7)	3.69(12)
Co3	8243.0(8)	3719.1(4)	5741.7(7)	3.69(12)
Se1	10141.5(8)	2500	9632.9(7)	2.95(12)
Se2	4393.7(8)	2500	5332.4(8)	3.57(12)
Se3	-2877.5(5)	5484.5(3)	2369.3(5)	3.67(10)
O1	9322(4)	3483.7(19)	10526(4)	4.9(4)
O2	8465(6)	2500	7482(5)	4.9(4)
O3	5375(4)	3506(2)	4738(4)	7.0(6)
O4	8327(4)	5018(2)	7181(4)	5.8(5)
O5	2268(5)	2500	3487(5)	5.2(8)
O6	-2071(4)	4335.2(19)	3185(4)	5.5(5)
O7	-2405(4)	5561(2)	450(4)	6.4(6)
O8	-1177(4)	6236.5(19)	3821(4)	5.4(5)
F1	-1220(5)	2500	4031(5)	6.4(6)
Cs1	-4602.6(5)	2500	933.1(5)	6.92(9)

Table S3 Anisotropic displacement parameters (Å^2 x 10^3) of ACo$_5$(SeO$_3$)$_4$(OH)$_2$F (A = Rb, Cs). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12].

Atom	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**
Co1	6.9(3)	4.1(3)	4.2(3)	0.0(2)	2.7(2)	-0.2(2)
Co2	5.7(2)	4.08(18)	4.2(2)	0.10(14)	2.57(16)	-0.27(15)
Co3	5.1(2)	4.45(18)	4.1(2)	-0.07(14)	2.13(17)	-0.55(15)
Se1	4.5(2)	3.72(18)	3.6(2)	0	2.03(16)	0
Se2	4.5(2)	4.97(19)	5.2(2)	0	2.66(17)	0
Se3	4.38(15)	4.38(14)	4.08(15)	-0.03(10)	1.84(12)	-0.37(10)
O1	10.3(11)	4.2(9)	5.7(11)	1.7(8)	3.8(9)	-1.7(8)
O2	7.2(15)	6.8(13)	3.5(14)	0	1.8(12)	0
O3	7.6(11)	5.5(9)	11.7(12)	2.7(8)	3.9(9)	-1.2(8)
O4	4.3(11)	6.1(10)	6.4(11)	0.7(8)	2.5(9)	1.5(8)
O5	6.5(15)	5.2(13)	3.6(14)	0	1.6(12)	0
O6	7.2(10)	5.1(9)	5.1(11)	-2.1(7)	1.8(9)	-1.9(8)
O7	9.2(11)	9.1(10)	4.2(11)	-1.4(8)	3.4(9)	-2.0(8)
O8	7.0(11)	8.1(10)	3.3(10)	2.0(8)	1.8(9)	2.1(8)
F1	5.8(12)	4.8(11)	6.8(13)	0	1.8(10)	0
Rb1	8.5(2)	11.00(19)	8.2(2)	0	-0.21(17)	0
Atom	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**
Co1	4.8(4)	3.0(3)	5.3(4)	0.1(3)	2.2(3)	0.4(3)
Co2	3.7(2)	2.3(2)	5.3(3)	-0.09(18)	1.8(2)	0.33(18)
Co3	3.0(3)	2.3(2)	5.8(3)	-0.15(18)	1.6(2)	-0.76(18)
Se1	2.7(2)	2.0(2)	4.3(3)	0	1.5(2)	0
Se2	1.9(2)	3.2(2)	5.7(3)	0	1.3(2)	0
Se3	2.41(19)	2.99(18)	5.3(2)	0.15(13)	1.05(15)	0.65(13)
O1	6.3(11)	2.9(10)	3.8(12)	-1.3(10)	-0.3(9)	-0.7(10)
O2	6.3(11)	2.9(10)	3.8(12)	-1.3(10)	-0.3(9)	-0.7(10)
O3	3.7(13)	5.6(13)	10.2(16)	2.0(10)	0.8(11)	-0.8(10)
O4	3.4(13)	6.9(13)	7.1(15)	-1.1(10)	2.0(11)	-1.2(10)

Atom	U11	U22	U33	U23	U13	U12
O5	3.1(18)	4.8(18)	6(2)	0	-0.4(15)	0
O6	5.8(13)	2.3(13)	9.8(15)	1.2(10)	4.6(11)	1.0(10)
O7	8.0(14)	8.6(14)	4.0(15)	0.8(10)	3.9(11)	0.8(10)
O8	3.8(13)	7.0(14)	3.6(14)	-2.4(10)	-0.9(11)	-1.8(10)
F1	6.7(16)	4.4(15)	7.6(18)	0	2.0(13)	0
Cs1	4.11(17)	6.76(17)	8.11(19)	0	0.03(13)	0

Table S4 Selected bond lengths [Å] and bond angles for $RbCo_5(SeO_3)_4(OH)_2F$.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
Rb1-F1	2.659(3)	Co1-O4^{10}	2.107(2)
Rb1-O3^{4}	3.103(2)	Co1-O4	2.107(2)
Rb1-O3^{5}	3.103(2)	Co1-O7^{11}	2.130(2)
Rb1-O6	3.113(2)	Co1-O7^{7}	2.130(2)
Rb1-O6^{1}	3.113(2)	Co1-O1^{7}	2.163(2)
Rb1-O7^{3}	3.211(2)	Co1-O1^{11}	2.163(2)
Rb1-O7^{6}	3.211(2)	Co2-O6	2.054(2)
Rb1-O1	3.428(2)	Co2-O5	2.060(2)
Rb1-O1^{1}	3.428(2)	Co2-O8^{12}	2.083(2)
Rb1-O5^{4}	3.487(3)	Co2-O4^{13}	2.085(2)
Se1-O2	1.700(3)	Co2-O1	2.098(2)
Se1-O1	1.708(2)	Co2-F1	2.196(2)
Se1-O1^{1}	1.708(2)	Co3-O3	2.020(2)
Se2-O3	1.684(2)	Co3-O4	2.057(2)
Se2-O3^{1}	1.684(2)	Co3-O8^{7}	2.091(2)
Se2-O5	1.723(3)	Co3-O2^{8}	2.105(2)
Se3-O7	1.674(2)	Co3-O6^{9}	2.134(2)
Se3-O6	1.691(2)	Co3-F1^{2}	2.251(2)
Se3-O8	1.709(2)	Co3-Co2^{9}	2.910(5)

Symmetry transformations used to generate equivalent atoms:

^{1}+X, 3/2-Y, +Z; ^{2}1+X, +Y, +Z; ^{3}-1-X, 1-Y, -Z; ^{4}-1+X, +Y, +Z; ^{5}-1+X, 3/2-Y, +Z; ^{6}-1-X, 1/2+Y, -Z; ^{7}1-X, 1/2+Y, 1-Z; ^{8}1+X, +Y, 1+Z; ^{9}1+X, 3/2-Y, +Z; ^{10}2-X, 2-Y, 2-Z; ^{11}1+X, 3/2-Y, 1+Z; ^{12}-X, 1-Y, 1-Z; ^{13}1-X, -1/2+Y, 1-Z.

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
F1-Rb1-O3^{4}	64.32(6)	O4^{10}-Co1-O7^{7}	88.01(8)
F1-Rb1-O3^{5}	64.32(6)	O4-Co1-O7^{7}	91.99(8)
O3^{4}-Rb1-O3^{5}	51.39(7)	O7^{11}-Co1-O7^{7}	180
F1-Rb1-O6	52.21(4)	O4^{10}-Co1-O1^{7}	96.02(8)
O3^{4}-Rb1-O6	95.80(5)	O4-Co1-O1^{7}	83.98(8)
O3^{5}-Rb1-O6	54.29(5)	O7^{11}-Co1-O1^{7}	88.72(7)
F1-Rb1-O6^{1}	52.21(4)	O7^{7}-Co1-O1^{7}	91.28(7)
O3^{4}-Rb1-O6^{1}	54.29(5)	O4^{10}-Co1-O1^{11}	83.98(8)
O3^{5}-Rb1-O6^{1}	95.80(5)	O4-Co1-O1^{11}	96.02(8)
O6-Rb1-O6^{1}	104.30(8)	O7^{11}-Co1-O1^{11}	91.28(7)
F1-Rb1-O7^{3}	127.21(4)	O7^{7}-Co1-O1^{11}	88.72(7)
O3^{4}-Rb1-O7^{3}	117.10(5)	O1^{7}-Co1-O1^{11}	180
O3^{5}-Rb1-O7^{3}	77.46(5)	O6-Co2-O5	155.33(8)
O6-Rb1-O7^{3}	76.33(5)	O6-Co2-O8^{12}	86.86(8)
O6^{1}-Rb1-O7^{3}	171.34(5)	O5-Co2-O8^{12}	93.82(10)
F1-Rb1-O7^{6}	127.21(4)	O6-Co2-O4^{13}	97.73(8)
O3^{4}-Rb1-O7^{6}	77.46(5)	O5-Co2-O4^{13}	106.29(8)
O3^{5}-Rb1-O7^{6}	117.10(5)	O8^{12}-Co2-O4^{13}	101.21(8)
O6-Rb1-O7^{6}	171.34(5)	O6-Co2-O1	88.48(8)
O6^{1}-Rb1-O7^{6}	76.33(5)	O5-Co2-O1	87.59(10)
O7^{3}-Rb1-O7^{6}	101.72(8)	O8^{12}-Co2-O1	171.76(8)
F1-Rb1-O1	62.47(6)	O4^{13}-Co2-O1	86.15(8)
O3^{4}-Rb1-O1	126.71(6)	O6-Co2-F1	74.40(7)
O3^{5}-Rb1-O1	105.32(5)	O5-Co2-F1	81.96(8)
O6-Rb1-O1	52.30(5)	O8^{12}-Co2-F1	74.88(8)
O6^{1}-Rb1-O1	89.76(5)	O4^{13}-Co2-F1	171.24(7)
O7^{3}-Rb1-O1	97.23(5)	O1-Co2-F1	97.32(8)
O7^{6}-Rb1-O1	136.24(5)	O3-Co3-O4	99.59(8)
F1-Rb1-O1^{1}	62.47(6)	O3-Co3-O8^{7}	165.11(8)
O3^{4}-Rb1-O1^{1}	105.32(5)	O4-Co3-O8^{7}	93.54(8)
O3^{5}-Rb1-O1^{1}	126.71(6)	O3-Co3-O2^{8}	87.77(10)
O6-Rb1-O1^{1}	89.76(5)	O4-Co3-O2^{8}	107.93(8)

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O6[1]-Rb1-O1[1]	52.30(5)	O8[7]-Co3-O2[8]	94.88(10)
O7[3]-Rb1-O1[1]	136.24(5)	O3-Co3-O6[9]	86.07(8)
O7[6]-Rb1-O1[1]	97.22(5)	O4-Co3-O6[9]	100.72(8)
O1-Rb1-O1[1]	45.23(6)	O8[7]-Co3-O6[9]	84.61(8)
F1-Rb1-O5[4]	99.73(7)	O2[8]-Co3-O6[9]	151.31(8)
O3[4]-Rb1-O5[4]	45.14(6)	O3-Co3-F1[2]	92.51(9)
O3[5]-Rb1-O5[4]	45.14(6)	O4-Co3-F1[2]	165.37(8)
O6-Rb1-O5[4]	97.70(5)	O8[7]-Co3-F1[2]	73.55(8)
O6[1]-Rb1-O5[4]	97.69(5)	O2[8]-Co3-F1[2]	80.57(8)
O7[3]-Rb1-O5[4]	73.71(5)	O6[9]-Co3-F1[2]	71.76(7)
O7[6]-Rb1-O5[4]	73.71(5)	Co2-F1-Co2[1]	91.92(8)
O1-Rb1-O5[4]	149.96(5)	Co2-F1-Co3[4]	154.64(13)
O1[1]-Rb1-O5[4]	149.96(5)	Co2[1]-F1-Co3[4]	81.74(3)
O2-Se1-O1	99.26(10)	Co2-F1-Co3[5]	81.74(3)
O2-Se1-O1[1]	99.26(10)	Co2[1]-F1-Co3[5]	154.64(13)
O1-Se1-O1[1]	101.03(13)	Co3[4]-F1-Co3[5]	93.53(8)
O3-Se2-O3[1]	106.05(14)	Co3-O4-Co2[7]	120.24(9)
O3-Se2-O5	97.11(10)	Co3-O4-Co1	117.90(9)
O3[1]-Se2-O5	97.11(10)	Co2[7]-O4-Co1	94.34(8)
O7-Se3-O6	104.13(10)	Co2-O1-Co1[13]	92.34(8)
O7-Se3-O8	102.39(10)	Co2-O5-Co2[1]	100.05(12)
O6-Se3-O8	101.27(10)	Co2-O6-Co3[5]	88.02(8)
O4[10]-Co1-O4	180	Co2[12]-O8-Co3[13]	88.38(9)
O4[10]-Co1-O7[11]	91.99(8)	Co3[14]-O2-Co3[15]	102.42(12)
O4-Co1-O7[11]	88.01(8)		

Symmetry transformations used to generate equivalent atoms:

[1]+X, 3/2-Y, +Z; [2]1+X, +Y, +Z; [3]-1-X, 1-Y, -Z; [4]-1+X, +Y, +Z; [5]-1+X, 3/2-Y, +Z; [6]-1-X, 1/2+Y, -Z; [7]1-X, 1/2+Y, 1-Z; [8]1+X, +Y, 1+Z; [9]1+X, 3/2-Y, +Z; [10]2-X, 2-Y, 2-Z; [11]1+X, 3/2-Y, 1+Z; [12]-X, 1-Y, 1-Z; [13]1-X, -1/2+Y, 1-Z; [14]-1+X, 3/2-Y, -1+Z; [15]-1+X, +Y, -1+Z.

Table S5 Selected bond lengths [Å] and bond angles for $CsCo_5(SeO_3)_4(OH)_2F$.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
Cs1-F1	2.823(3)	Co1-O7	2.106(3)
Cs1-O6[1]	3.222(3)	Co1-O7[9]	2.106(3)
Cs1-O6	3.222(3)	Co1-O4[6]	2.121(3)
Cs1-O3[2]	3.289(3)	Co1-O4[10]	2.121(3)
Cs1-O3[3]	3.289(3)	Co1-O1[6]	2.169(3)
Cs1-O7[4]	3.351(3)	Co1-O1[10]	2.169(3)
Cs1-O7[5]	3.351(3)	Co2-O6	2.057(3)
Cs1-O1[6]	3.355(3)	Co2-O5	2.067(2)
Cs1-O1[7]	3.355(3)	Co2-O4[10]	2.077(3)
Cs1-O5[2]	3.606(4)	Co2-O8[11]	2.088(3)
Se1-O1[1]	1.709(3)	Co2-O1[6]	2.100(3)
Se1-O1	1.709(3)	Co2-F1	2.207(2)
Se1-O2	1.710(4)	Co2-Co3[2]	2.926(7)
Se2-O3	1.681(3)	Co3-O3	2.036(3)
Se2-O3[1]	1.681(3)	Co3-O4	2.064(3)
Se2-O5	1.732(4)	Co3-O2	2.098(3)
Se3-O7	1.675(3)	Co3-O6[12]	2.108(3)
Se3-O6	1.693(3)	Co3-O8[10]	2.112(3)
Se3-O8	1.705(3)	Co3-F1[12]	2.243(2)

Symmetry transformations used to generate equivalent atoms:

[1]+X, 1/2-Y, +Z; [2]-1+X, +Y, +Z; [3]-1+X, 1/2-Y, +Z; [4]-1-X, -1/2+Y, -Z; [5]-1-X, 1-Y, -Z; [6]-1+X, +Y, -1+Z; [7]-1+X, 1/2-Y, -1+Z; [8]-2+X, +Y, -1+Z; [9]-X, 1-Y, -Z; [10]1-X, 1-Y, 1-Z; [11]-X, 1-Y, 1-Z; [12]1+X, +Y, +Z.

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
F1-Cs1-O6[1]	49.70(5)	O7-Co1-O4[13]	92.95(11)
F1-Cs1-O6	49.70(5)	O7[12]-Co1-O4[13]	87.05(11)
O6[1]-Cs1-O6	99.37(10)	O4[6]-Co1-O4[13]	180.00(14)
F1-Cs1-O3[2]	60.80(7)	O7-Co1-O1[6]	91.50(10)
O6[1]-Cs1-O3[2]	90.41(7)	O7[12]-Co1-O1[6]	88.50(10)
O6-Cs1-O3[2]	51.89(7)	O4[6]-Co1-O1[6]	96.81(10)
F1-Cs1-O3[3]	60.80(7)	O4[13]-Co1-O1[6]	83.19(10)
O6[1]-Cs1-O3[3]	51.89(7)	O7-Co1-O1[13]	88.50(10)
O6-Cs1-O3[3]	90.41(7)	O7[12]-Co1-O1[13]	91.50(10)
O3[2]-Cs1-O3[3]	48.33(9)	O4[6]-Co1-O1[13]	83.19(10)
F1-Cs1-O7[4]	124.96(5)	O4[13]-Co1-O1[13]	96.81(10)
O6[1]-Cs1-O7[4]	77.53(7)	O1[6]-Co1-O1[13]	180
O6-Cs1-O7[4]	164.74(7)	O6-Co2-O5	155.08(11)
O3[2]-Cs1-O7[4]	112.92(7)	O6-Co2-O4[13]	95.54(11)
O3[3]-Cs1-O7[4]	75.85(7)	O5-Co2-O4[13]	108.72(11)
F1-Cs1-O7[5]	124.96(5)	O6-Co2-O8[14]	85.89(11)
O6[1]-Cs1-O7[5]	164.74(7)	O5-Co2-O8[14]	94.27(13)
O6-Cs1-O7[5]	77.52(7)	O4[13]-Co2-O8[14]	102.14(11)
O3[2]-Cs1-O7[5]	75.85(7)	O6-Co2-O1[6]	88.16(11)
O3[3]-Cs1-O7[5]	112.92(7)	O5-Co2-O1[6]	87.93(13)
O7[4]-Cs1-O7[5]	101.48(10)	O4[13]-Co2-O1[6]	86.00(11)
F1-Cs1-O1[6]	61.97(8)	O8[14]-Co2-O1[6]	170.33(11)
O6[1]-Cs1-O1[6]	89.11(7)	O6-Co2-F1	73.88(10)
O6-Cs1-O1[6]	52.12(7)	O5-Co2-F1	82.13(10)
O3[2]-Cs1-O1[6]	102.69(7)	O4[13]-Co2-F1	169.00(10)
O3[3]-Cs1-O1[6]	122.75(7)	O8[14]-Co2-F1	74.57(11)
O7[4]-Cs1-O1[6]	141.77(6)	O1[6]-Co2-F1	96.45(12)
O7[5]-Cs1-O1[6]	100.24(6)	O3-Co3-O4	98.63(11)
F1-Cs1-O1[7]	61.97(8)	O3-Co3-O2	88.20(13)
O6[1]-Cs1-O1[7]	52.12(7)	O4-Co3-O2	108.52(12)
O6-Cs1-O1[7]	89.11(7)	O3-Co3-O6[11]	86.86(11)

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O3^{2}-Cs1-O1^{7}	122.75(7)	O4-Co3-O6^{11}	99.49(11)
O3^{3}-Cs1-O1^{7}	102.69(7)	O2-Co3-O6^{11}	151.97(11)
O7^{4}-Cs1-O1^{7}	100.24(6)	O3-Co3-O8^{13}	165.79(12)
O7^{5}-Cs1-O1^{7}	141.77(6)	O4-Co3-O8^{13}	93.63(11)
O1^{6}-Cs1-O1^{7}	46.22(9)	O2-Co3-O8^{13}	94.73(13)
F1-Cs1-O5^{2}	94.94(9)	O6^{11}-Co3-O8^{13}	84.03(11)
O6^{1}-Cs1-O5^{2}	93.97(6)	O3-Co3-F1^{11}	93.45(12)
O6-Cs1-O5^{2}	93.97(6)	O4-Co3-F1^{11}	165.00(10)
O3^{2}-Cs1-O5^{2}	43.44(7)	O2-Co3-F1^{11}	80.59(11)
O3^{3}-Cs1-O5^{2}	43.44(7)	O6^{11}-Co3-F1^{11}	72.20(10)
O7^{4}-Cs1-O5^{2}	71.52(6)	O8^{13}-Co3-F1^{11}	73.39(11)
O7^{5}-Cs1-O5^{2}	71.52(6)	Co2-F1-Co2^{1}	91.71(12)
O1^{6}-Cs1-O5^{2}	145.91(6)	Co2-F1-Co3^{2}	82.20(4)
O1^{7}-Cs1-O5^{2}	145.91(6)	Co2^{1}-F1-Co3^{2}	155.29(17)
O1^{1}-Se1-O1	100.78(18)	Co2-F1-Co3^{3}	155.29(17)
O1^{1}-Se1-O2	99.21(13)	Co2^{1}-F1-Co3^{3}	82.20(4)
O1-Se1-O2	99.21(13)	Co3^{2}-F1-Co3^{3}	93.37(12)
O3-Se2-O3^{1}	106.41(19)	Co2-O5-Co2^{1}	100.04(16)
O3-Se2-O5	97.63(13)	Co3-O4-Co2^{13}	121.43(13)
O3^{1}-Se2-O5	97.62(13)	Co3-O4-Co1^{10}	116.98(13)
O7-Se3-O6	103.55(13)	Co2^{13}-O4-Co1^{10}	94.87(11)
O7-Se3-O8	102.48(13)	Co2^{10}-O1-Co1^{10}	92.84(10)
O6-Se3-O8	101.65(14)	Co3^{1}-O2-Co3	102.12(17)
O7-Co1-O7^{12}	180	Co2^{14}-O8-Co3^{13}	88.31(11)
O7-Co1-O4^{6}	87.05(11)	Co2-O6-Co3^{2}	89.25(11)
O7^{12}-Co1-O4^{6}	92.95(11)		

Symmetry transformations used to generate equivalent atoms:

^{1}+X, 1/2-Y, +Z; ^{2}-1+X, +Y, +Z; ^{3}-1+X, 1/2-Y, +Z; ^{4}-1-X, -1/2+Y, -Z; ^{5}-1-X, 1-Y, -Z; ^{6}-1+X, +Y, -1+Z; ^{7}-1+X, 1/2-Y, -1+Z; ^{8}-2+X, +Y, -1+Z; ^{9}2+X, +Y, 1+Z; ^{10}1+X, +Y, 1+Z; ^{11}1+X, +Y, +Z; ^{12}-X, 1-Y, -Z; ^{13}1-X, 1-Y, 1-Z; ^{14}-X, 1-Y, 1-Z.

Table S6 Bond Valence Sum (BVS) of ACo$_5$(SeO$_3$)$_4$(OH)$_2$F (A = Rb and Cs).

Atom	$RbCo_5$	$CsCo_5$	[a]CN	Valence
A(1)[a]	1.010	1.046	10	+1
Co(1)	1.827	1.833	6	+2
Co(2)	1.996	1.980	6	+2
Co(3)	1.948	1.937	6	+2
Se(1)	3.995	3.949	3	+4
Se(2)	4.087	4.079	3	+4
Se(3)	4.149	4.151	3	+4
O(1)	1.977	2.005	4	-2
O(2)	2.010	1.985	3	-2
O(3)	1.924	1.911	3	-2
O(4)	1.046	1.031	3	-1
O(5)	2.046	2.004	4	-2
O(6)	2.162	2.188	4	-2
O(7)	1.832	1.852	3	-2
O(8)	2.005	1.996	3	-2
F(1)	1.088	1.089	5	-1

[a] CN: coordination number.

Table S7 A comparison of the Co···Co distances (Å) in ACo$_5$(SeO$_3$)$_4$(OH)$_2$F (A = Rb and Cs).

	$RbCo_5$	$CsCo_5$
Co1-Co2	3.074	3.093
Co1-Co3	3.567	3.569
Co2-Co2	3.157	3.168
Co2-Co3	2.910	2.926
Co2-Co3	3.591	3.612
Co3-Co3	3.280	3.264
Interlayer	5.442	5.473