

Table S 1. Crystal data and structure refinement for $\text{CH}_3\text{OCHCl}^+\text{SbF}_6^-$.

Identification code	chloreth
Empirical formula	C2 H4 Cl F6 O Sb
Formula weight	319.25
Temperature	125.2). K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions (deg)	a = 5.970(3) Å alpha = 90.00(3) b = 12.019(5) Å beta = 92.59(3) c = 10.994(5) Å gamma = 90.00(3)
Volume	788.1(6) Å ³
Z	4
Density (calculated)	2.657 Mg/m ³
Absorption coefficient	3.891 mm ⁻¹
F(000)	584
Crystal size	0.6 x 0.4 x 0.1 mm
Theta range for data collection	3.39 to 25.86 deg.
Index ranges	-7<=h<=7, 0<=k<=12, 0<=l<=11
Reflections collected	1774
Independent reflections	1045 [R(int) = 0.0983]
Absorption correction	DIFABS
Max. and min. transmission	1.169 and 0.624
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1045 / 0 / 104
Goodness-of-fit on F ²	1.141
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1344
R indices (all data)	R1 = 0.0439, wR2 = 0.1372
Extinction coefficient	0.004(2)
Largest diff. peak and hole	0.802 and -0.798 e.Å ⁻³

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{CH}_3\text{OCHCl}^+\text{SbF}_6^-$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Sb	6666(1)	8043(1)	844(1)	26(1)
F(1)	6434(8)	6911(4)	2011(5)	41(1)
F(2)	3886(6)	7650(5)	151(5)	50(1)
F(3)	9442(6)	8457(5)	1572(5)	41(1)
F(4)	8122(8)	7049(4)	-153(5)	45(2)
F(5)	5270(6)	9043(4)	1868(5)	38(1)
F(6)	6992(7)	9169(4)	-301(4)	42(1)
O	10630(7)	5618(5)	2041(5)	39(2)
C(1)	11555(9)	6249(6)	3148(6)	23(2)
C(2)	8831(11)	5107(7)	2176(8)	34(2)
Cl	7790(3)	4391(2)	1001(2)	48(1)

Table S 3. Bond lengths [Å] and angles [deg] for $\text{CH}_3\text{OCHCl}^+\text{SbF}_6^-$.

Sb-F(2)	1.855(4)
Sb-F(4)	1.863(5)
Sb-F(6)	1.864(5)
Sb-F(5)	1.869(5)
Sb-F(3)	1.875(4)
Sb-F(1)	1.880(5)
O-C(2)	1.252(9)
O-C(1)	1.517(9)
C(2)-Cl	1.650(9)
F(2)-Sb-F(4)	91.6(3)
F(2)-Sb-F(6)	91.5(2)
F(4)-Sb-F(6)	90.1(2)
F(2)-Sb-F(5)	89.8(2)
F(4)-Sb-F(5)	178.6(2)
F(6)-Sb-F(5)	90.2(2)
F(2)-Sb-F(3)	178.7(2)
F(4)-Sb-F(3)	89.7(2)
F(6)-Sb-F(3)	88.7(2)
F(5)-Sb-F(3)	88.9(2)
F(2)-Sb-F(1)	90.2(3)
F(4)-Sb-F(1)	89.3(2)
F(6)-Sb-F(1)	178.2(2)
F(5)-Sb-F(1)	90.3(2)
F(3)-Sb-F(1)	89.5(2)
C(2)-O-C(1)	115.7(6)
O-C(2)-Cl	117.3(6)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{CH}_3\text{OCHCl}^+\text{SbF}_6^-$.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
Sb	17 (1)	23 (1)	38 (1)	1 (1)	1 (1)	2 (1)
F (1)	32 (2)	33 (4)	59 (3)	10 (2)	8 (2)	1 (2)
F (2)	28 (2)	42 (4)	76 (4)	3 (3)	-14 (2)	-1 (2)
F (3)	24 (2)	32 (3)	65 (3)	-4 (3)	2 (2)	-2 (2)
F (4)	44 (3)	37 (4)	55 (4)	-7 (2)	8 (2)	9 (2)
F (5)	34 (2)	31 (3)	49 (3)	-4 (2)	7 (2)	8 (2)
F (6)	38 (2)	43 (3)	46 (3)	11 (2)	6 (2)	7 (2)
O	24 (2)	39 (4)	56 (4)	9 (3)	5 (2)	3 (2)
C (1)	21 (2)	13 (4)	35 (4)	-6 (3)	-10 (2)	0 (2)
C (2)	27 (3)	24 (5)	50 (6)	11 (4)	3 (3)	4 (3)
Cl	41 (1)	45 (2)	58 (2)	-4 (1)	6 (1)	-2 (1)

TableS5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{CH}_3\text{OCHCl}^+\text{SbF}_6^-$.

	x	y	z	U (eq)
H(11)	12928 (9)	6612 (6)	2955 (6)	35
H(12)	11840 (9)	5739 (6)	3809 (6)	35
H(13)	10484 (9)	6797 (6)	3380 (6)	35
H(2)	8263 (134)	4995 (78)	2963 (81)	40

Table S 6. Crystal data and structure refinement for $\text{CH}_3\text{OCHF}^+\text{SbF}_6^-$.

Identification code	fleth_psi
Empirical formula	C2 H4 F7 O Sb
Formula weight	298.80
Temperature	125(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions (deg)	a = 9.942(2) Å alpha = 90.00(3) b = 7.454(2) Å beta = 111.27(2) c = 10.297(3) Å gamma = 90.00(3)
Volume	711.1(3) Å ³
Z	4
Density (calculated)	2.791 Mg/m ³
Absorption coefficient	3.959 mm ⁻¹
F(000)	552
Crystal size	0.4 x 0.3 x 0.3 mm
Theta range for data collection	3.46 to 29.96 deg.
Index ranges	0 ≤ h ≤ 13, -10 ≤ k ≤ 10, -14 ≤ l ≤ 13
Reflections collected	4209
Independent reflections	2073 [R(int) = 0.0591]
Absorption correction	Psi-scan
Max. and min. transmission	0.9976 and 0.729
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2072 / 0 / 113
Goodness-of-fit on F ²	1.196
Final R indices [I > 2sigma(I)]	R1 = 0.0471, wR2 = 0.1446
R indices (all data)	R1 = 0.0516, wR2 = 0.1515
Extinction coefficient	0.011(2)
Largest diff. peak and hole	3.731 and -3.648 e.Å ⁻³

Table S 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{CH}_3\text{OCHF}^+\text{SbF}_6^-$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Sb	2336 (1)	2444 (1)	6566 (1)	13 (1)
F (1)	1447 (3)	805 (3)	7404 (3)	19 (1)
F (2)	3179 (3)	4107 (3)	5737 (3)	27 (1)
F (3)	895 (3)	4105 (3)	6532 (3)	29 (1)
F (4)	3749 (3)	735 (4)	6689 (4)	33 (1)
F (5)	1173 (3)	1573 (4)	4821 (3)	31 (1)
F (6)	3461 (3)	3343 (4)	8320 (3)	35 (1)
O	7862 (5)	2693 (4)	1264 (5)	20 (1)
C (1)	6269 (9)	2573 (6)	732 (10)	28 (2)
C (2)	8560 (8)	2625 (5)	2517 (8)	19 (1)
F (7)	7956 (6)	2522 (3)	3409 (4)	28 (1)

Table S 8. Bond lengths [Å] and angles [deg] for $\text{CH}_3\text{OCHF}^+\text{SbF}_6^-$.

Sb-F(5)	1.866(3)
Sb-F(4)	1.866(2)
Sb-F(2)	1.868(2)
Sb-F(6)	1.870(3)
Sb-F(3)	1.884(2)
Sb-F(1)	1.889(2)
O-C(2)	1.224(9)
O-C(1)	1.479(9)
C(1)-H(11)	0.72(7)
C(1)-H(12)	0.89(8)
C(1)-H(13)	0.71(7)
C(2)-F(7)	1.269(7)
C(2)-H(2)	0.65(9)
F(5)-Sb-F(4)	90.91(14)
F(5)-Sb-F(2)	90.81(13)
F(4)-Sb-F(2)	91.84(12)
F(5)-Sb-F(6)	178.59(12)
F(4)-Sb-F(6)	90.4(2)
F(2)-Sb-F(6)	89.62(13)
F(5)-Sb-F(3)	90.54(14)
F(4)-Sb-F(3)	176.68(11)
F(2)-Sb-F(3)	91.13(11)
F(6)-Sb-F(3)	88.11(14)
F(5)-Sb-F(1)	89.19(12)
F(4)-Sb-F(1)	89.61(11)
F(2)-Sb-F(1)	178.55(9)
F(6)-Sb-F(1)	90.34(12)
F(3)-Sb-F(1)	87.42(11)
C(2)-O-C(1)	120.7(5)
O-C(1)-H(11)	110(5)
O-C(1)-H(12)	116(5)
H(11)-C(1)-H(12)	99(6)
O-C(1)-H(13)	112(6)
H(11)-C(1)-H(13)	121(8)
H(12)-C(1)-H(13)	100(7)
O-C(2)-F(7)	121.9(7)
O-C(2)-H(2)	116(8)
F(7)-C(2)-H(2)	122(8)

Symmetry transformations used to generate equivalent atoms:

Table S 9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{CH}_3\text{OCHF}^+\text{SbF}_6^-$.
 The anisotropic displacement factor exponent takes the form:
 $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Sb	6(1)	12(1)	19(1)	0(1)	4(1)	-1(1)
F(1)	16(1)	17(1)	28(1)	4(1)	12(1)	-1(1)
F(2)	26(1)	23(1)	38(1)	7(1)	19(1)	-4(1)
F(3)	19(1)	18(1)	55(2)	8(1)	19(1)	8(1)
F(4)	17(1)	24(1)	65(2)	12(1)	23(1)	13(1)
F(5)	26(1)	43(2)	21(1)	-8(1)	4(1)	-17(1)
F(6)	25(1)	46(2)	26(1)	-9(1)	2(1)	-22(1)
O	15(2)	21(1)	27(2)	4(1)	8(1)	3(1)
C(1)	12(3)	26(3)	48(4)	-2(2)	12(3)	4(1)
C(2)	15(3)	15(2)	29(3)	-1(1)	12(2)	-1(1)
F(7)	40(2)	21(2)	34(2)	-5(1)	26(2)	-4(1)

Table S 10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{CH}_3\text{OCHF}^+\text{SbF}_6^-$.

	x	y	z	U (eq)
H (11)	6052 (71)	1654 (100)	573 (68)	30
H (12)	5857 (88)	2783 (70)	1354 (83)	30
H (13)	5949 (72)	3260 (100)	247 (68)	30
H (2)	9262 (100)	2687 (67)	2705 (88)	30