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References

EXPERIMENTAL

General considerations

All the experimental work and sample preparation were carried out under dried nitrogen atmosphere using standard Schlenk techniques. CH_2Cl_2, C_3Cl_5H, diethylether, petroleum ether, methanol, ethanol, D_2O, trihexylamine, and $NH(CH_2CF_3)_2$ were obtained commercially. CH_2Cl_2 was dried using an in-house solvent purification system. Mid-IR data were collected at room temperature by using a Bruker Alpha spectrometer, operating with a Platinum ATR unit with a diamond crystal. A resolution of 4 cm^{-1} and 25 scans were taken. ^{1}H-, $^{13}C\{^1H\}$- and ^{19}F-NMR spectra were collected on an JEOL ECZ400S spectrometer operating at 400, 100 and 376 MHz, respectively, in CD_3OD referenced to residual solvent peaks. The instrument was equipped with a ROYAL HFX probe. Electrospray mass spectrometry was carried out on a Micromass LCT, with samples dissolved in acetonitrile. Microanalyses were performed by Campbell Microanalytical Laboratory, University of Otago, Dunedin.

Synthesis of bis(bis(2,2,2-trifluoroethyl)amino)dihexylaminocyclopropenium chloride semihydrate, $[C_3(NHex_2)(NC_2H_4F_6)_2]Cl.0.5H_2O$. $NHex_3$ (5.056 g, 18.02 mmol) and $NH(CH_2CF_3)_2$ (8.456 g, 44.61 mmol) were dissolved in dried CH_2Cl_2 (10 mL) and added slowly to C_3Cl_5H (2.290 g, 10.69 mmol) which was dissolved in dried CH_2Cl_2 (30 mL) at 0 °C with stirring. The stirring was continued at ambient temperature for 48 h. CH_2Cl_2 was removed *in vacuo* and column chromatographic separation through silica gel column gave a white powder (0.63 g, 10% yield). A mixture of petroleum ether, CH_2Cl_2 and ethanol (4:3:1 ratio) was used as eluent. Crystals suitable for X-ray diffraction were grown by slow evaporation of an undried methanol-diethyl ether solution. ^{1}H NMR (CD_3OD, 400 MHz): 4.47 (q, $^3J_{HF}$ = 8.1 Hz, 8H, $NC\underline{H}_2CF_3$), 3.52 (t, $^3J_{HH}$ = 7.4 Hz, 4H, NCH_2), 1.70 (m, 4H, $NCH_2C\underline{H}_2CH_2$), 1.34 (m, 12H, $NCH_2CH_2(C\underline{H}_2)_3CH_3$), 0.93 (t, $^3J_{HH}$ = 6.7 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3OD, 100 MHz): 125.51 (q, $^1J_{CF}$ = 280.3 Hz, $NCH_2\underline{C}F_3$), 124.67

($\underline{C}N(CH_2CF_3)_2$) , 119.25 ($\underline{C}NHex_2$), 55.80 (q, $^2J_{CF}$ = 34.4 Hz, $N\underline{C}H_2CF_3$), 54.64 (NCH_2), 32.73 ($NCH_2\underline{C}H_2$), 29.08 ($NCH_2CH_2\underline{C}H_2$), 27.16 ($NCH_2CH_2CH_2\underline{C}H_2$), 23.73 ($NCH_2CH_2CH_2CH_2\underline{C}H_2$), 14.36 ($\underline{C}H_3$). ^{19}F NMR ($CD_3OD$, 376 MHz): –72.80 (t, $^3J_{FH}$ = 8.1 Hz). ES-MS$^+$ m/z 580.2573 (100%, M^+); calculated for $C_{23}H_{34}F_{12}N_3^+$ 580.2556. Microanalysis: Exptl C, 43.91; H, 5.64; N, 6.45. Calcd for $C_{23}H_{35}ClF_{12}N_3O_{0.5}$ C, 44.20; H, 5.64; 6.72.

X-ray Crystallography

A suitable crystal was mounted on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. Using Olex2,[1] the structure was solved with the XS structure solution program[2] using Direct Methods and refined with the XL refinement package[2] using Least Squares minimisation with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms on the methylene groups were refined isotropically at their calculated positions and methyl groups were refined as rotating groups. The water protons were located from the density difference map and refined isotropically. CCDC 1988268 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table1S. Structure refinement data for $[C_3(NHex_2)(N(CH_2CF_3)_2)_2]Cl.0.5H_2O$.

Parameter	Value	Parameter	Value
formula	$C_{46}H_{70}Cl_2F_{24}N_6O$	T [K]	119.99(10)
a [Å]	10.6228(4)	F(000)	2584
b [Å]	38.0161(17)	2ϑ range [°]	7.498–142.998
c [Å]	15.0865(5)	index ranges	$-12 \le h \le 13$
α [°]	90		$-33 \le k \le 46$
β [°]	94.999(3)		$-18 \le l \le 18$
γ [°]	90	reflections collected	26625
V [Å^3]	6069.3(4)	independent reflns	11795
Z	4	R(int)	0.0783
ρ_{calc} [g cm^{-3}]	1.368	data/restraints/parameters	11795/7/749
crystal system	monoclinic	GoF on F^2	1.002
space group	P21/n	R_1/wR_2 [$I>2\sigma(I)$]	0.0699/0.1618
shape/colour	plate/colourless	R_1/wR_2 (all data)	0.1335/0.1879
crystal size [mm]	0.234 × 0.123 × 0.025	$\Delta\rho_{max/min}$/e [Å^{-3}]	0.525/–0.337
μ [mm^{-1}]	1.974	CCDC number	1988268

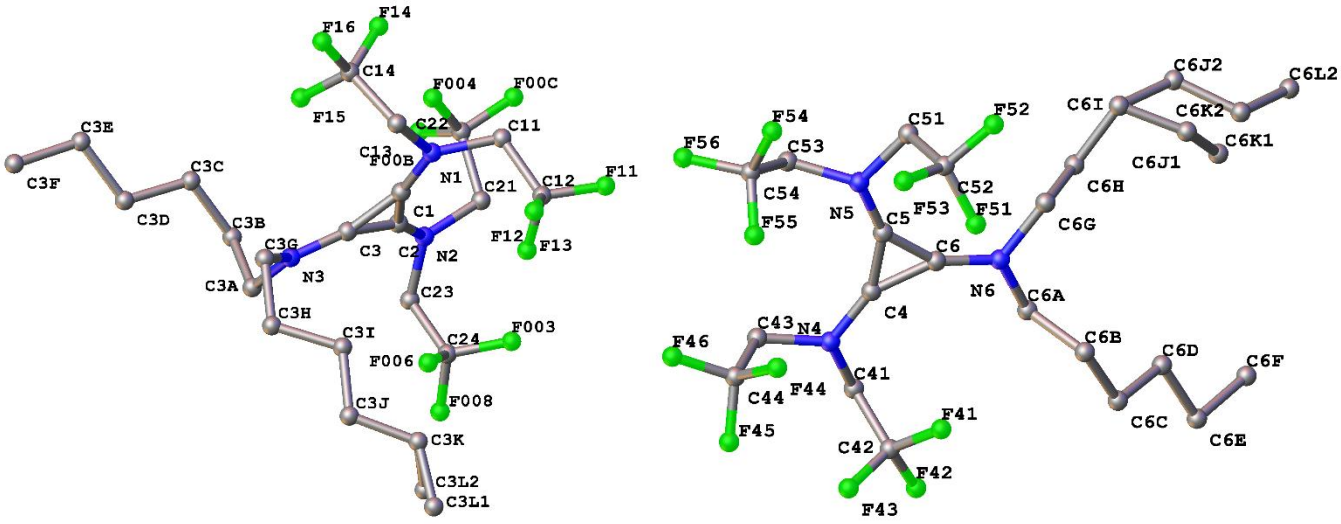

Figure 1S. Numbering scheme for the two independent cations in $[C_3(NHex_2)(N(CH_2CF_3)_2)_2]Cl.0.5H_2O$ (H atoms removed for clarity).

Table 2S. Bond distances (Å) for $[C_3(NHex_2)(N(CH_2CF_3)_2)_2]Cl.0.5H_2O$.

O1–H1A	0.79(16)	O1–H1B	0.85(2)
C1–C2	1.372(5)	C5–C4	1.357(6)
C1–C3	1.394(5)	C6–C4	1.393(6)
C3–C2	1.388(5)	C5–C6	1.367(6)
N1–C1	1.338(5)	N4–C4	1.346(5)
N1–C11	1.468(5)	N4–C41	1.451(6)
N1–C13	1.465(4)	N4–C43	1.454(6)
N2–C2	1.347(5)	N5–C5	1.362(5)
N2–C21	1.450(4)	N5–C51	1.459(5)
N2–C23	1.463(5)	N5–C53	1.461(6)
N3–C3	1.305(5)	N6–C6	1.309(6)
N3–C3A	1.477(5)	N6–C6G	1.478(6)
N3–C3G	1.473(5)	N6–C6A	1.468(6)
C11–C12	1.489(7)	C41–C42	1.492(7)
F11–C12	1.326(6)	F41–C42	1.351(6)
F12–C12	1.329(7)	F42–C42	1.319(6)
F13–C12	1.353(5)	F43–C42	1.345(7)
C13–C14	1.507(6)	C43–C44	1.491(8)
F14–C14	1.340(5)	F44–C44	1.310(7)
F15–C14	1.343(5)	F45–C44	1.303(7)
F16–C14	1.343(4)	F46–C44	1.342(7)
C21–C22	1.518(6)	C51–C52	1.500(7)
F004–C22	1.339(4)	F51–C52	1.338(5)
F00B–C22	1.327(5)	F52–C52	1.336(5)
F00C–C22	1.339(4)	F53–C52	1.331(6)
C23–C24	1.501(6)	C53–C54	1.489(7)
F003–C24	1.338(5)	F54–C54	1.325(6)
F006–C24	1.349(5)	F55–C54	1.316(6)
F008–C24	1.339(5)	F56–C54	1.352(6)
C3A–C3B	1.521(7)	C6A–C6B	1.524(8)
C3B–C3C	1.509(7)	C6B–C6C	1.543(8)
C3C–C3D	1.469(8)	C6C–C6D	1.487(8)
C3D–C3E	1.543(9)	C6D–C6E	1.542(12)
C3E–C3F	1.504(10)	C6E–C6F	1.603(13)
C3G–C3H	1.519(6)	C6G–C6H	1.456(9)
C3H–C3I	1.516(7)	C6I–C6H	1.499(8)
C3I–C3J	1.512(8)	C6I–C6J1	1.42(2)
C3J–C3K	1.498(10)	C6J1–C6K1	1.442(18)
C3K–C3L1	1.386(15)	C6K1–C6L1	1.521(19)
C3K–C3L2	1.389(17)	C6I–C6J2	1.508(13)
		C6J2–C6K2	1.452(18)
		C6L2–C6K2	1.545(19)

Table 3S. Selected bond angles (°) for $[C_3(NHex_2)(N(CH_2CF_3)_2)_2]Cl.0.5H_2O$.

H1A-O1-H1B	101(10)		
C2-C1-C3	60.2(3)	C5-C4-C6	59.6(3)
N1-C1-C2	150.2(3)	N4-C4-C5	151.5(4)
N1-C1-C3	149.6(3)	N4-C4-C6	148.9(4)
C1-C2-C3	60.7(3)	C4-C5-C6	61.5(3)
N2-C2-C1	150.7(4)	C4-C5-N5	149.4(4)
N2-C2-C3	148.6(4)	N5-C5-C6	149.1(4)
C2-C3-C1	59.1(3)	C5-C6-C4	58.9(3)
N3-C3-C1	152.2(4)	N6-C6-C4	150.8(4)
N3-C3-C2	148.7(4)	N6-C6-C5	150.2(4)

C1-N1-C13	120.7(3)	C4-N4-C41	119.4(4)
C1-N1-C11	120.1(3)	C4-N4-C43	119.4(4)
C13-N1-C11	119.2(3)	C41-N4-C43	119.0(4)
C2-N2-C21	120.4(3)	C5-N5-C51	118.2(4)
C2-N2-C23	118.1(3)	C5-N5-C53	120.2(4)
C21-N2-C23	118.4(3)	C51-N5-C53	118.0(3)
C3-N3-C3A	119.1(3)	C6-N6-C6G	121.0(4)
C3-N3-C3G	121.8(3)	C6-N6-C6A	121.9(4)
C3G-N3-C3A	119.2(3)	C6A-N6-C6G	116.9(4)
N1-C11-C12	110.2(3)	N4-C41-C42	112.0(4)
N1-C13-C14	109.8(4)	N4-C43-C44	114.6(5)
N2-C21-C22	110.3(3)	N5-C51-C52	110.1(4)
N2-C23-C24	110.6(3)	N5-C53-C54	112.8(4)
N3-C3A-C3B	111.9(3)	N6-C6A-C6B	111.7(4)
N3-C3G-C3H	112.5(3)	N6-C6G-C6H	114.7(5)

Table 4S. Hydrogen-bonding parameters for the dichloride-water cluster environment.

Hydrogen bond	Cl---C (Å)	Cl---H (Å)	Cl–H-C (°)
Cl1–H13A–C13	3.444(4)	2.6038(10)	145.0(2)
Cl1–H21B–C21	3.640(4)	2.7677(10)	150.0(3)
Cl1–H23B–C23	3.432(4)	2.4994(10)	161.3(2)
Cl2–H11B–C11	3.612(4)	2.6925(10)	158.5(2)
Cl2–H13B–C13	3.509(4)	2.6069(10)	154.7(3)
Cl2–H41B–C41	3.543(5)	2.6037(10)	163.2(3)
Cl2–H53B–C53	3.659(4)	2.7368(10)	159.2(3)

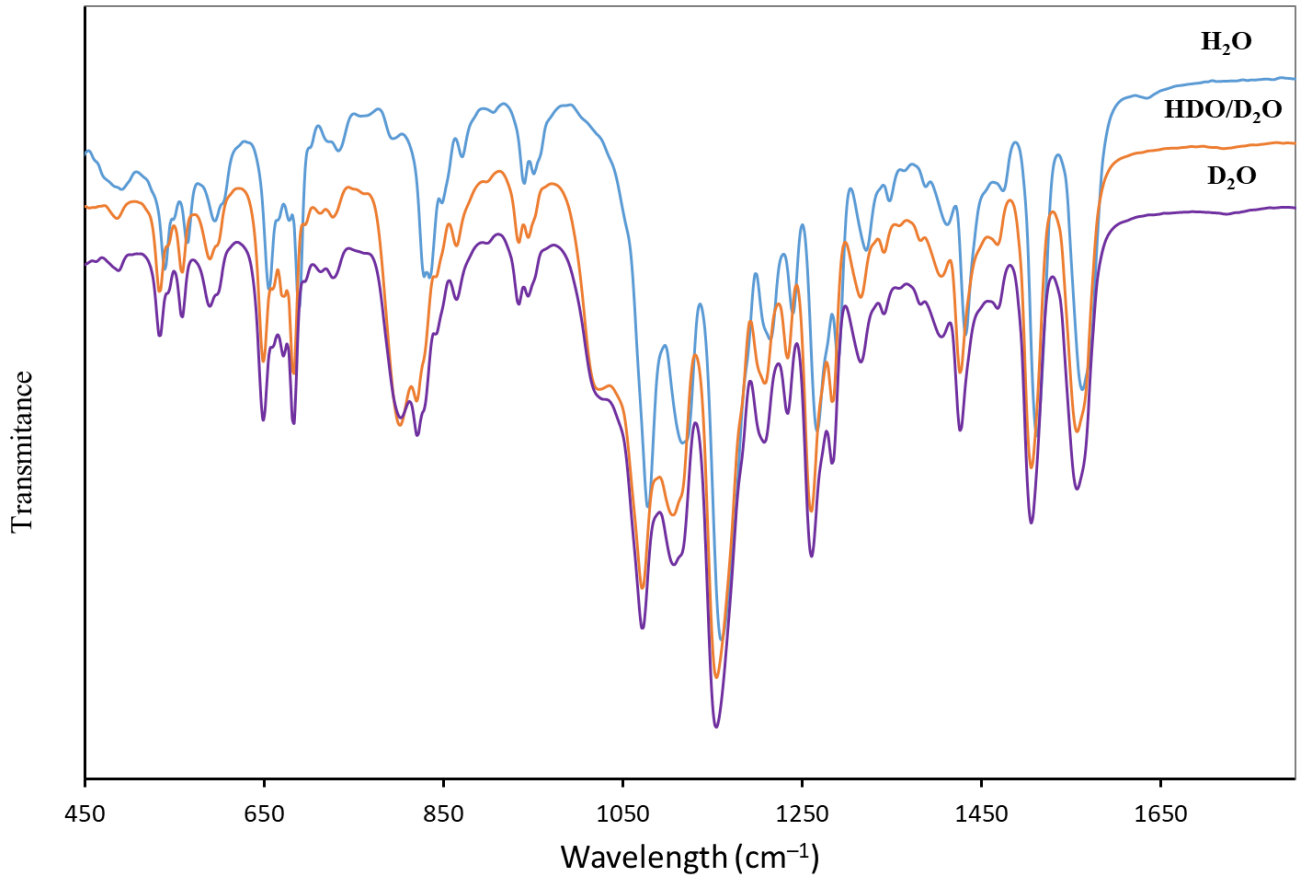

Figure 2S. Infrared spectra of $[C_3(NHex_2)(N(CH_2CF_3)_2)_2]Cl.0.5H_2O$ and the HDO and D_2O isotopomers.

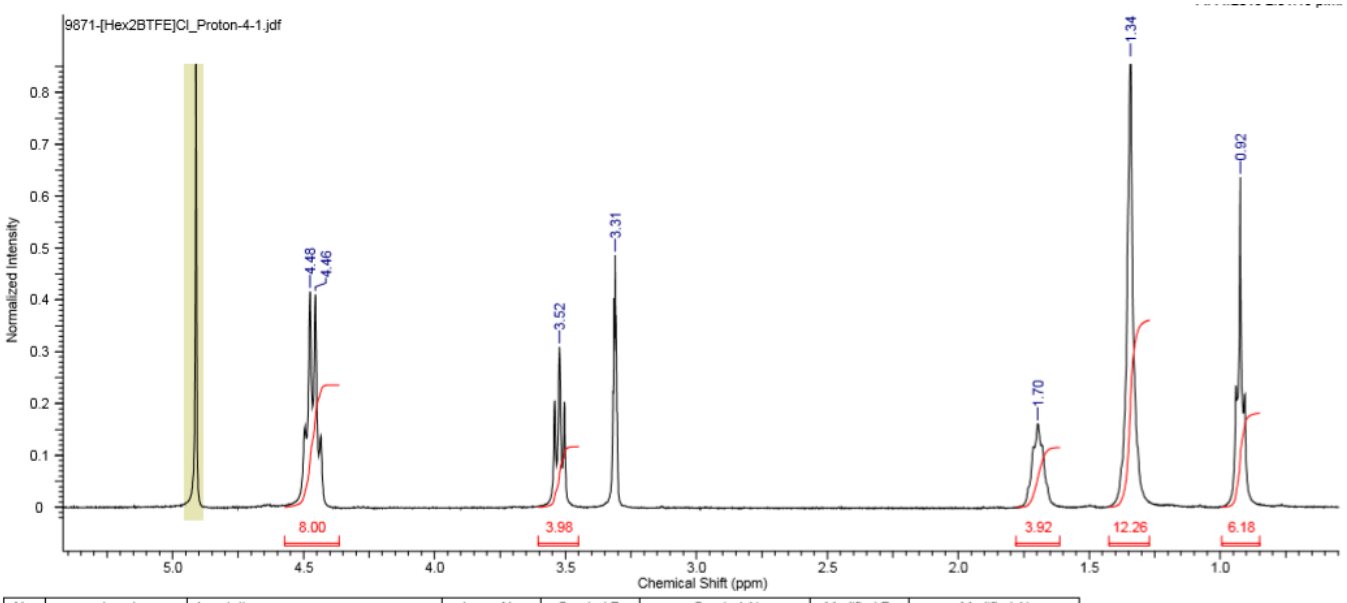

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Figure 3S. ^{1}H-NMR spectrum of $[C_3(NHex_2)(NC_2H_4F_6)_2]Cl.0.5H_2O$ in CD_3OD.

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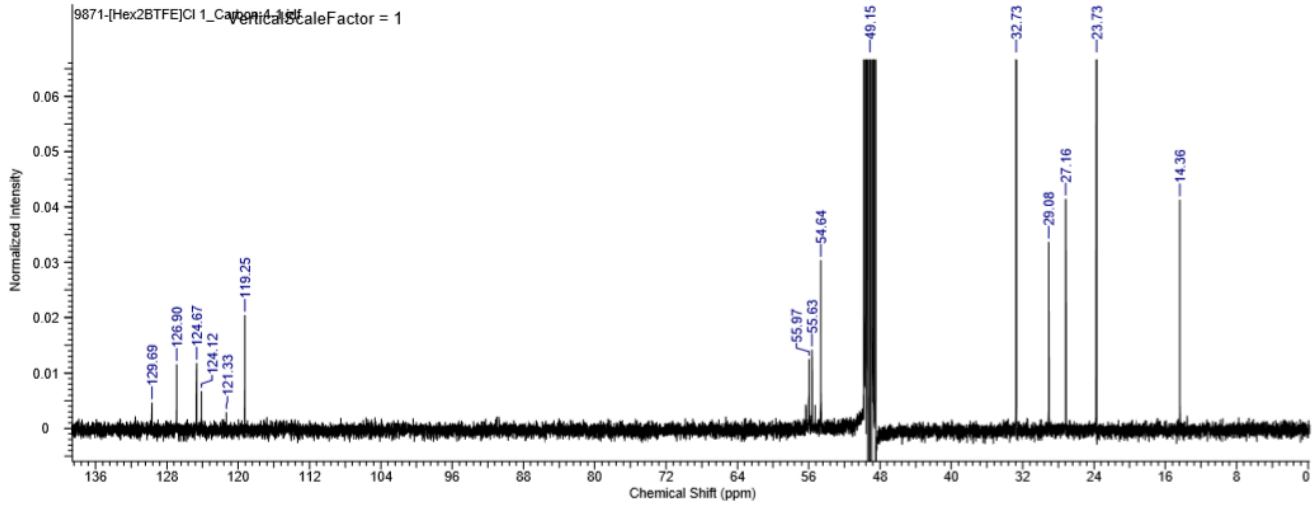

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Figure 4S. $^{13}C\{^{1}H\}$-NMR spectrum of $[C_3(NHex_2)(NC_2H_4F_6)_2]Cl.0.5H_2O$ in CD_3OD.

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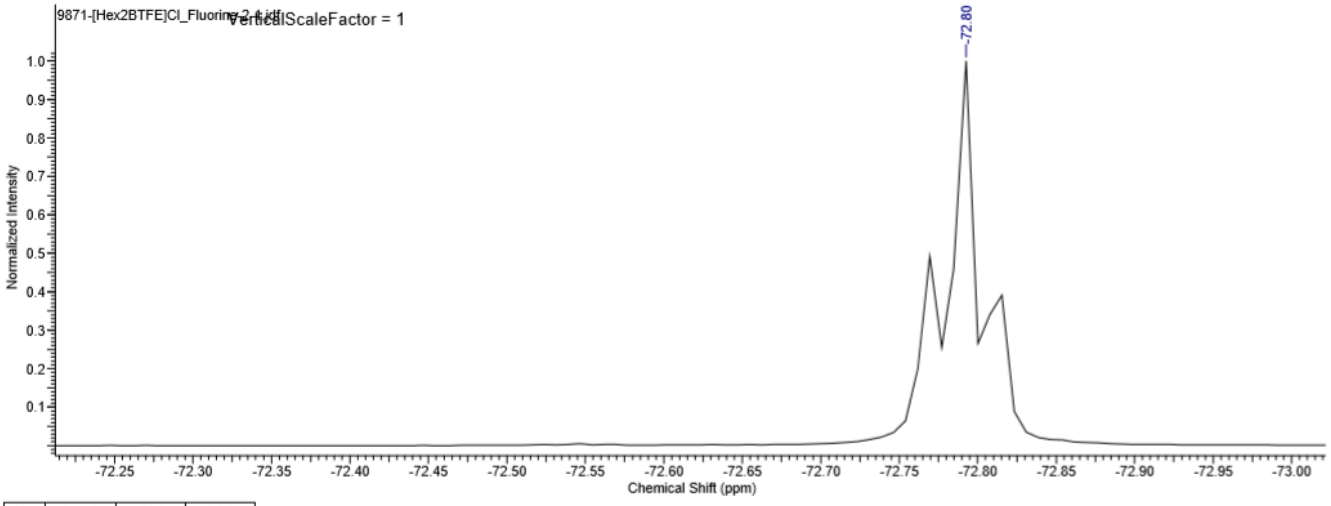

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Figure 5S. ^{19}F-NMR spectrum of $[C_3(NHex_2)(NC_2H_4F_6)_2]Cl.0.5H_2O$ in CD_3OD.

References

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst*. **2009**, *42*, 339-341.

[2] G. M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112-122.