Supporting Information

for

From 'halogen' to 'tetrel' bond: Matrix isolation IR spectroscopic and quantum mechanical studies on effect of central atom substitution in donor tetrahalogens on binary complex formation with formic acid

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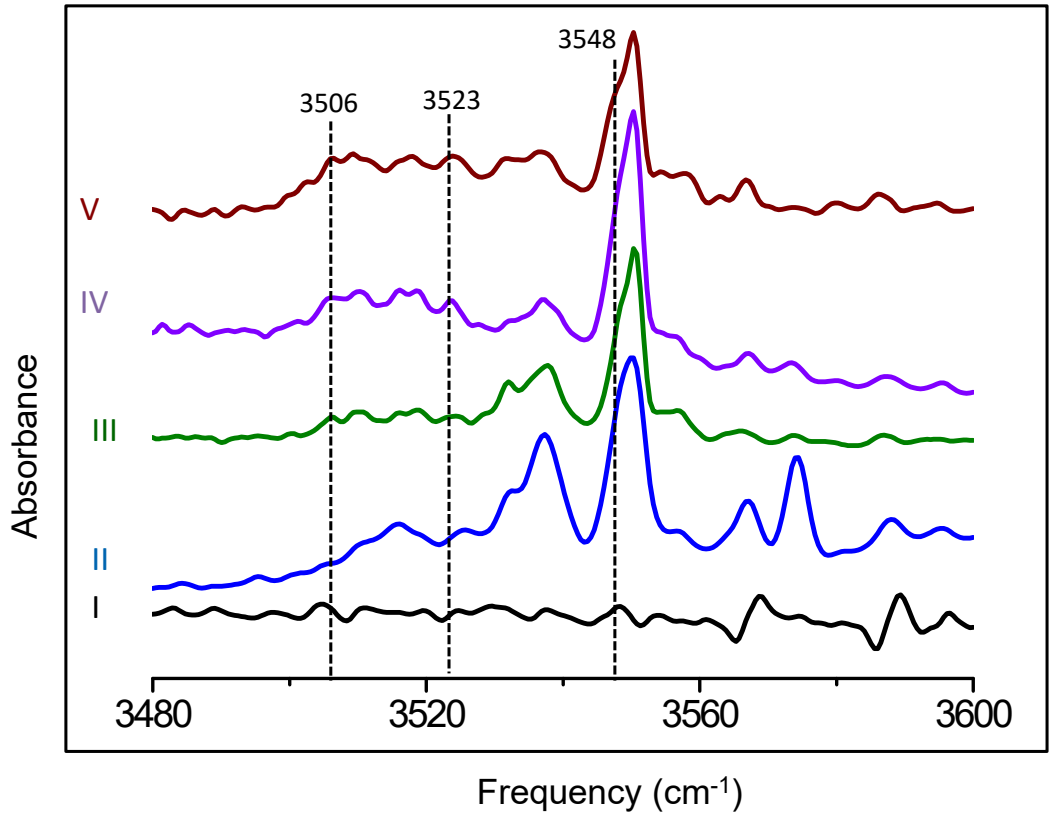

Figure S1: Infrared spectra in the $\nu_{O\text{-}H}$ region of Formic Acid (FA) depicting complex formation with $SiCl_4$ in Argon matrix. Trace I (black) depicts the $SiCl_4$ monomer ($SiCl_4$:Ar = 1:200) after annealing the matrix. Trace II (blue) depicts FA monomer (FA:Ar = 1:2000) after annealing. Traces III (green), IV (violet) and V (wine) depict FA- $SiCl_4$ mixtures in different concentration ratios (FA:$SiCl_4$:Ar = 1:2:2000, 1:5:2000 and 1:10:2000, respectively) after annealing. The positions of newly developed bands corresponding to formation of the FA-$SiCl_4$ complex have been marked with dotted lines.

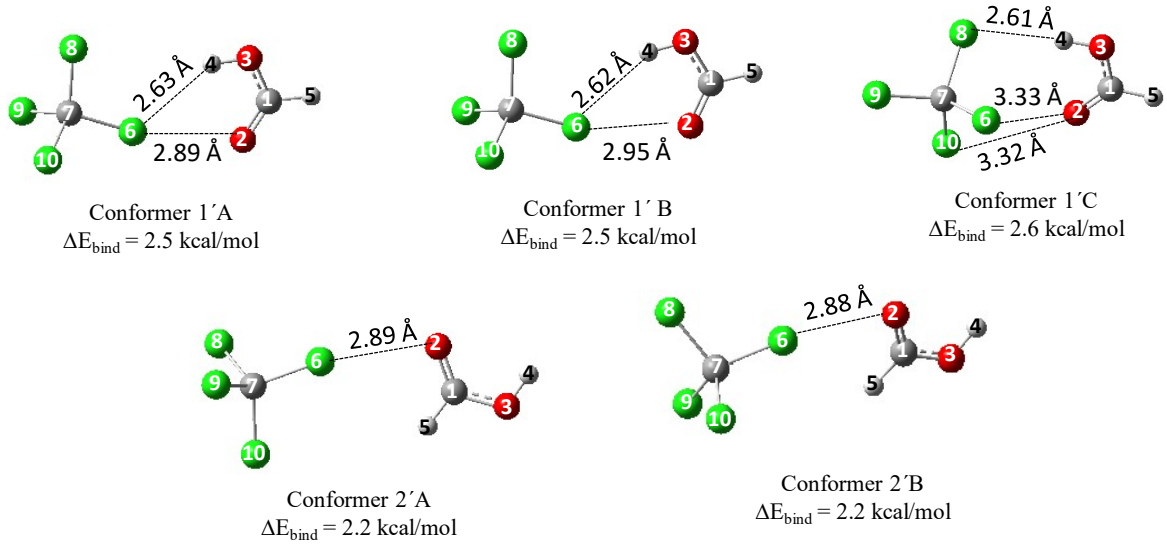

Figure S2: Optimized geometries and binding energies (ΔE_{bind}) of different conformers of the FA-CCl_4 complex (1:1) calculated at the M062X/6-31G++(d,p) level of theory. Relevant distance parameters are depicted in the figure.

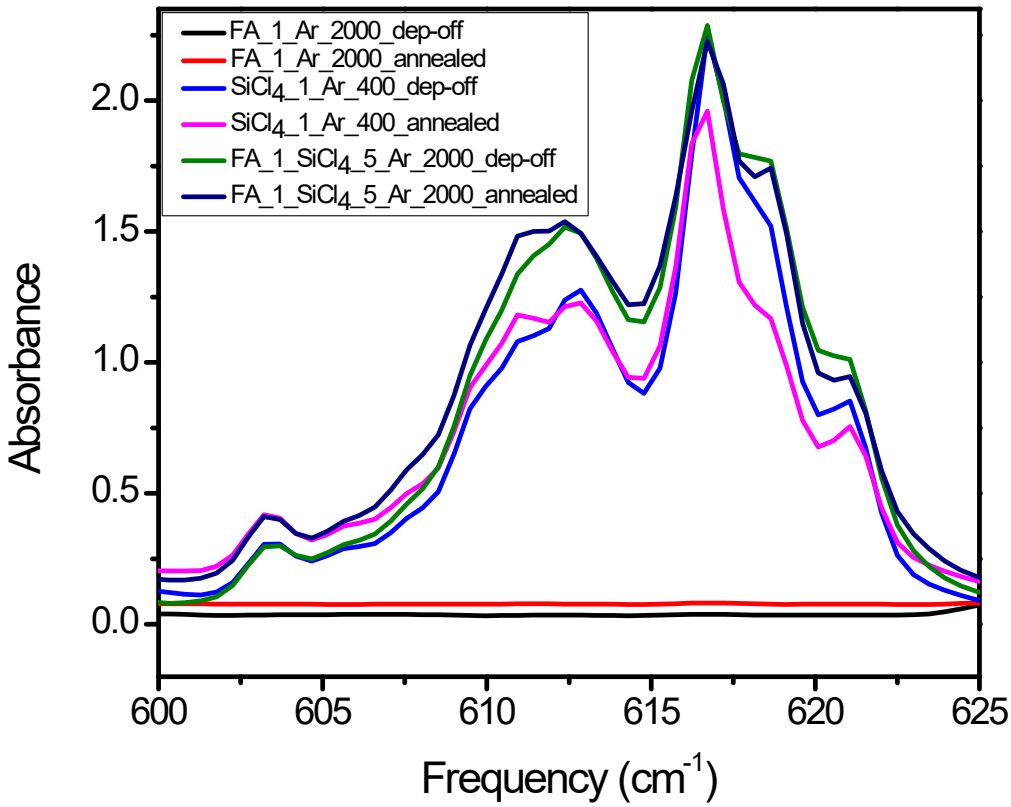

Figure S3: Infrared spectra in the $\nu_{Si\text{-}Cl}$ region of $SiCl_4$ for different concentrations of FA and $SiCl_4$ in Argon matrix (mentioned in the figure). "Dep-off" refers to the spectra of the as-deposited matrix.

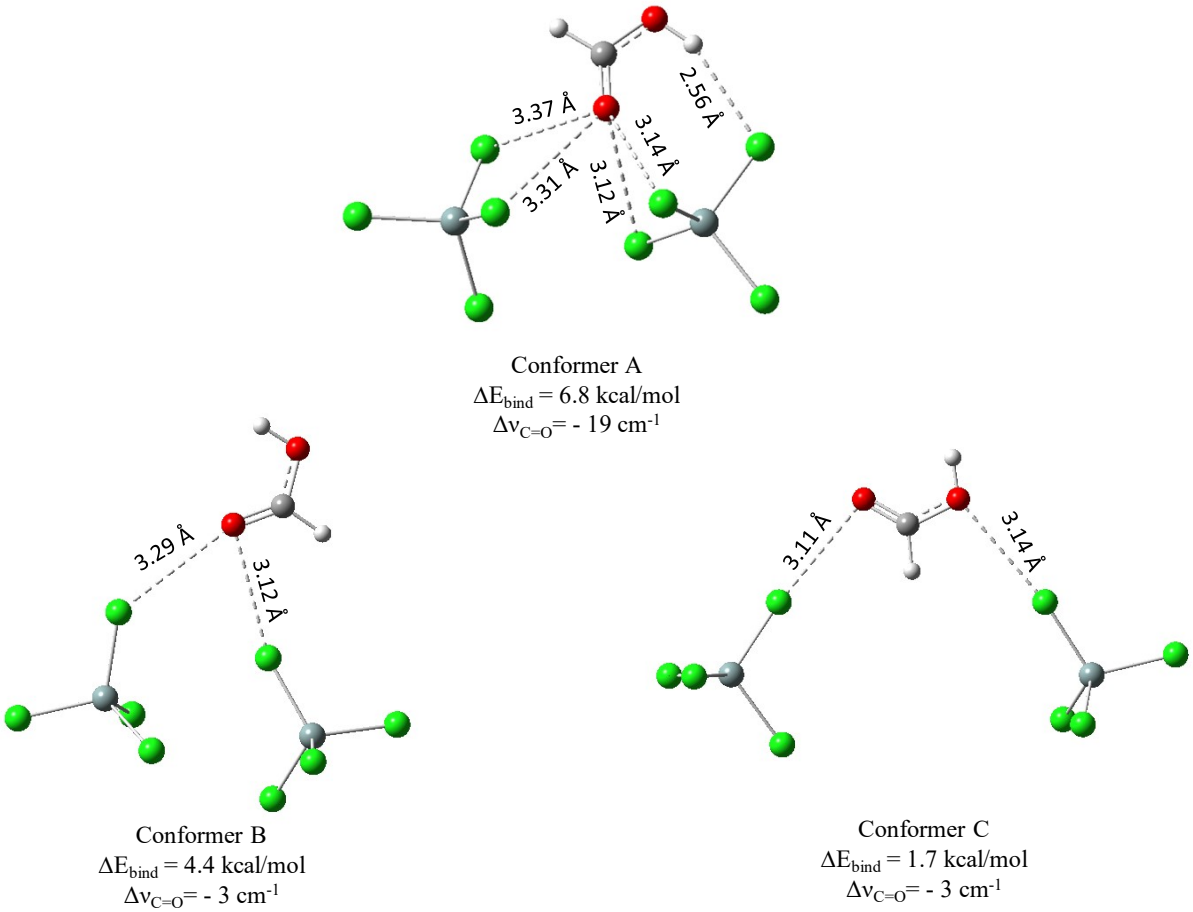

Figure S4: Optimized geometries of some of the conformers of the 1:2 FA-$SiCl_4$ complex calculated at M062X/6-31G++(d,p) level of theory with their corresponding $\nu_{C=O}$ spectral shift and binding energies (ΔE_{bind}). Different distance parameters have been also shown in the figure.

Table S1: Predictions of binding energy and geometry as well as relevant data from AIM and NBO analyses obtained at MP2/6-31G++(d,p) level of theory for optimized structures of FA-$SiCl_4$ complexes.

Predicted parameters (FA-$SiCl_4$)	Conformer 1A	Conformer 2A	Conformer 3A
ΔE_{bind} (kcal/mol)	1.3	1.1	0.4
O2···Cl10(Å)	3.47	3.32	-
O2···Cl8(Å)	3.25	3.24	-
O2···Cl6(Å)	3.25	3.24	3.27
O2···Si7(Å)	3.35	3.28	5.22
H4···Cl10(Å)	2.52	-	-
H4···Cl8(Å)	-	-	-
H4···Cl6(Å)	-	-	-
Si7-Cl10-O2(deg)	69.4	70.9	-
Si7-Cl8-O2(deg)	75.0	73.0	-
Si7-Cl6-O2(deg)	75.0	73.0	160.6
O3-H4-Cl10(deg)	165.8	-	-
O3-H4-Cl8(deg)	-	-	-
O3-H4-Cl6(deg)	-	-	-
Cl9-Si-O2(deg)	177.1	178.9	-
ρ_{BCP}(O2···Cl6)(a.u)	0.0076	0.0078	0.0068
ρ_{BCP}(O2···Cl8)(a.u)	0.0076	0.0078	-
ρ_{BCP}(O2···Cl10)(a.u)	0.0064	0.0078	-
ρ_{BCP}(H4···Cl10)(a.u)	0.0111	-	-
ρ_{BCP}(H4···Cl6)(a.u)	-	-	-
ρ_{BCP}(H4···Cl8)(a.u)	-	-	-
ρ_{BCP}(O2···Si7)(a.u)	-	0.0074	-
n(O2)→σ*(Si7-Cl10) (kcal/mol)	0.3	0.43	-

n(O2)→σ*(Si7-Cl8) (kcal/mol)	0.3	0.39	-
n(O2)→σ*(Si7-Cl6) (kcal/mol)	0.3	0.39	0.2
n(O2)→σ*(Cl9-Si7) (kcal/mol)	1.67	2.04	-
n(Cl10)→σ*(O3-H4) (kcal/mol)	5.59	-	-
n(Cl8)→σ*(O3-H4) (kcal/mol)	-	-	-
n(Cl6)→σ*(O3-H4) (kcal/mol)	-	-	-

Table S2: Predictions of binding energy, spectral shifts, geometry, as well as relevant data from AIM and NBO analyses obtained at ωB97XD/6-31G++(d,p) level of theory for optimized structures of FA-$SiCl_4$ complexes.

Predicted parameters (FA-$SiCl_4$)	Conformer 1A	Conformer 1B	Conformer 2A	Conformer 2B	Conformer 3A	Conformer 3B
ΔE_{bind} (kcal/mol)	2.7	2.7	2.2	2.2	0.8	1.2
$\Delta\nu_{C=O}$ (cm^{-1})	-9	-8	-7	-6	-3	-3
$\Delta\nu_{C-O}$ (cm^{-1})	+15	+15	+9	+8	+3	+7
O2···Cl10(Å)	3.59	3.45	3.44	3.41	-	-
O2···Cl8(Å)	3.43	3.44	3.41	3.43	-	-
O2···Cl6(Å)	3.44	3.59	3.41	3.43	3.13	3.14
O2···Si7(Å)	3.56	3.56	3.46	3.47	5.46	5.30
H4···Cl10(Å)	2.60	-	-	-	-	-
H4···Cl8(Å)	-	-	-	-	-	-
H4···Cl6(Å)	-	2.60	-	-	-	2.73
Si7-Cl10-O2(deg)	72.5	76.3	73.4	74.5	-	-
Si7-Cl8-O2(deg)	76.5	76.5	74.2	74.0	-	-
Si7-Cl6-O2(deg)	76.3	72.6	74.2	74.0	160.1	147.7
O3-H4-Cl10(deg)	166.6	-	-	-	-	-
O3-H4-Cl8(deg)	-	-	-	-	-	-
O3-H4-Cl6(deg)	-	166.4	-	-	-	165.8
Cl9-Si-O2(deg)	178.2	178.2	180.0	180.0	-	-
ρ_{BCP}(O2···Cl6)(a.u)	0.0050	0.0050	0.0057	0.0055	0.0056	-
ρ_{BCP}(O2···Cl8)(a.u)	0.0056	0.0056	0.0057	0.0060	-	-
ρ_{BCP}(O2···Cl10)(a.u)	0.0050	0.0050	0.0061	0.0060	-	-
ρ_{BCP}(H4···Cl10)(a.u)	0.0094	-	-	-	-	-
ρ_{BCP}(H4···Cl6)(a.u)	-	0.0094	-	-	-	0.0074
ρ_{BCP}(H4···Cl8)(a.u)	-	-	-	-	-	-
ρ_{BCP}(O2···Si7)(a.u)	-	-	0.0056	0.0056	-	-

n(O2)→σ*(Si7-Cl10) (kcal/mol)	0.15	0.09	0.23	0.17	-	-
n(O2)→σ*(Si7-Cl8) (kcal/mol)	0.11	0.11	0.21	0.22	-	-
n(O2)→σ*(Si7-Cl6) (kcal/mol)	0.09	0.14	0.21	0.22	0.21	0.08
n(O2)→σ*(Cl9-Si7) (kcal/mol)	0.95	0.95	1.31	1.27	-	-
n(Cl10)→σ*(O3-H4) (kcal/mol)	4.31	-	-	-	-	-
n(Cl8)→σ*(O3-H4) (kcal/mol)	-	-	-	-	-	-
n(Cl6)→σ*(O3-H4) (kcal/mol)	-	4.27	-	-	-	2.91

Table S3: Experimental and calculated $\nu_{C=O}$ and ν_{C-O} band positions of FA and their spectral shifts for different conformers of the binary FA-$SiCl_4$ complex at the M062X/6-311++G(d,p), MP2/6-311++G(d,p) and ωB97XD/6-311++G(d,p) levels of theory.

Conformer	Calculated band positions (cm^{-1})						Calculated spectral shifts (cm^{-1})					
	M06-2X		MP2		ωB97XD		M06-2X		MP2		ωB97XD	
	$\nu_{C=O}$	ν_{C-O}	$\nu_{C=O}$	ν_{C-O}	$\nu_{C=O}$	ν_{C-O}	$\Delta\nu_{C=O}$	$\Delta\nu_{C-O}$	$\Delta\nu_{C=O}$	$\Delta\nu_{C-O}$	$\Delta\nu_{C=O}$	$\Delta\nu_{C-O}$
FA monomer	1879	1169	1807	1143	1859	1163	-	-	-	-	-	-
1A	1862	1190	1800	1161	1847	1177	-17	+21	-7	+18	-12	+14
1B	1863	1182	-	-	1847	1177	-16	+13	-	-	-12	+14
2A	1864	1181	1804	1151	1848	1169	-15	+12	-3	+8	-11	+6
2B	1864	1180	-	-	1849	1169	-15	+11	-	-	-10	+6
3A	1878	1172	1806	1144	1856	1167	-1	+3	-1	+1	-3	+4
3B	-	-	-	-	1856	1169	-	-	-	-	-3	+6

Table S4: Experimental and calculated ν_{O-H} band positions of FA in the monomer and different conformers of the binary FA-$SiCl_4$ complex at the M062X/ 6-31G++(d,p), MP2/6-31G++(d,p) and ωB97XD/6-31G++(d,p) levels of theory.

Conformer	Calculated ν_{O-H} band positions (cm^{-1})			Calculated spectral shift (cm^{-1})			Experimental ν_{O-H} band positions (cm^{-1})	Experimental spectral shift (cm^{-1})
	M06-2X	MP2	ωB97XD	M06-2X	MP2	ωB97XD		
FA monomer	3810	3786	3826	-	-	-	3550	-
1A	3768	3754	3774	-42	-32	-52		
1B	3780	-	3775	-30	-	-51		
2A	3808	3782	3826	-2	-4	0	3506	-44
2B	3819	-	3823	+9	-	-3	3523	-27
3A	3798	3784	3824	-12	-2	-2	3548	-2
3B	3785	-	3793	-25	-	-33		