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Supporting Information

The structures and properties of halogen bonds involving polyvalent halogen in complexes of FXO_n (X = Cl, Br; n = 0-3)—CH_3CN

Na Cheng[a], Fuzhen Bi[a], Yongjun Liu*[a,b], Changqiao Zhang[a],Chengbu Liu[a]

[a]*Key Laboratory of Theoretical and Computational Chemistry in Universities of Shandong, School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong 250100, China*

[b]*Northwest Institute of Plateau Biology, Chinese Academy of Sciences, Xining, Qinghai 810001, China*

Table S1 The most positive electrostatic potentials (V_{max}, kcal/mol) on 0.001 a.u. surface of X in monomer FXO_n (X = Cl, Br; n = 0-3).

Complexes	V_{max}
FCl	45.1
FClO	47.7
$FClO_2$	53.1
$FClO_3$	43.1
FBr	54.4
FBrO	53.1
$FBrO_2$	57.1
$FBrO_3$	52.8

Table S2

Halogen-bonded lengths (R, Å), some key bond lengths (r, Å), angle F-Cl···N (Θ, °) and interaction energies (ΔE^{cp}, kcal/mol) for all Cl complexes at M05-2X/6-311++G(d,p) and MP2/aug-cc-pVTZ level with or without a BSSE-corrected energy expression.

		M05-2X/6-311++G(d,p)		MP2/aug-cc-pVTZ	
		without BSSE	With BSSE	without BSSE	with BSSE
FCl-CH_3CN	$R_{Cl\cdots N}$	2.579	2.594	2.473	2.514
	r_{F-Cl}	1.665	1.665	1.662	1.661
	$r_{C\equiv N}$	1.144	1.144	1.167	1.168
	$\Theta_{F-Cl\cdots N}$	180.0	180.0	180.0	180.0
	ΔE^{cp}	-6.54	-6.54	-6.55	-6.54
FClO-CH_3CN(I)	$R_{Cl\cdots N}$	2.807	2.842	2.827	2.859
	r_{F-Cl}	1.716	1.716	1.747	1.746
	r_{Cl-O}	1.500	1.499	1.488	1.488
	$r_{C\equiv N}$	1.145	1.145	1.169	1.169
	$\Theta_{F-Cl\cdots N}$	155.6	156.1	149.6	150.6
	ΔE^{cp}	-6.02	-6.02	-5.37	-5.38
FClO-CH_3CN(II)	$R_{Cl\cdots N}$	2.912	2.934	2.922	2.945
	$R_{O\cdots H}$	2.514	2.560	2.589	2.710
	r_{F-Cl}	1.702	1.702	1.727	1.728
	r_{Cl-O}	1.505	1.504	1.490	1.490
	$r_{C\equiv N}$	1.147	1.147	1.170	1.170
	$\Theta_{F-Cl\cdots N}$	160.0	160.7	155.5	156.0
	ΔE^{cp}	-6.74	-6.75	-5.48	-5.31
FClO-CH_3CN(III)	$R_{Cl\cdots N}$	2.971	2.981	2.893	2.926
	$R_{F\cdots H}$	2.507	2.591	2.507	2.580
	r_{F-Cl}	1.727	1.727	1.771	1.768
	r_{Cl-O}	1.498	1.498	1.491	1.491
	$r_{C\equiv N}$	1.147	1.147	1.170	1.170
	$\Theta_{F-Cl\cdots N}$	81.5	81.4	86.2	86.0
	ΔE^{cp}	-6.05	-6.05	-5.95	-5.93
$FClO_2$-CH_3CN(I)	$R_{Cl\cdots N}$	2.828	2.874	2.868	2.904
	r_{F-Cl}	1.737	1.738	1.783	1.783

	$r_{Cl\text{-}O1}$	1.442	1.441	1.438	1.438
	$r_{Cl\text{-}O2}$	1.442	1.441	1.438	1.438
	$r_{C\equiv N}$	1.145	1.145	1.168	1.169
	$\Theta_{F\text{-}Cl\cdots N}$	154.5	155.9	154.5	154.8
	ΔE^{cp}	-6.63	-6.66	-5.80	-5.81
$FClO_2$-CH_3CN(II)	$R_{Cl\cdots N}$	2.951	2.958	2.933	NA
	$R_{O1\cdots H}$	2.704	2.881	3.013	NA
	$r_{F\text{-}Cl}$	1.725	1.726	1.771	NA
	$r_{Cl\text{-}O1}$	1.447	1.446	1.441	NA
	$r_{Cl\text{-}O2}$	1.440	1.440	1.437	NA
	$r_{C\equiv N}$	1.147	1.147	1.170	NA
	$\Theta_{F\text{-}Cl\cdots N}$	148.9	155.0	154.9	NA
	ΔE^{cp}	-6.12	-6.18	-5.18	NA
$FClO_2$-CH_3CN(III)	$R_{Cl\cdots N}$	3.004	3.036	2.999	3.037
	$R_{F\cdots H}$	2.497	2.557	2.473	2.539
	$r_{F\text{-}Cl}$	1.750	1.749	1.804	1.802
	$r_{Cl\text{-}O1}$	1.440	1.440	1.438	1.438
	$r_{Cl\text{-}O2}$	1.442	1.442	1.441	1.441
	$r_{C\equiv N}$	1.147	1.147	1.170	1.170
	$\Theta_{F\text{-}Cl\cdots N}$	80.2	80.0	84.3	84.1
	ΔE^{cp}	-6.28	-6.28	-5.96	-5.95
$FClO_3$-CH_3CN	$R_{Cl\cdots N}$	3.026	3.055	3.047	3.094
	$r_{F\text{-}Cl}$	1.672	1.672	1.680	1.680
	$r_{Cl\text{-}O1}$	1.425	1.425	1.419	1.419
	$r_{Cl\text{-}O2}$	1.425	1.425	1.419	1.419
	$r_{Cl\text{-}O3}$	1.425	1.425	1.419	1.419
	$r_{C\equiv N1.}$	1.145	1.145	1.169	1.169
	$\Theta_{F\text{-}Cl\cdots N}$	180.0	180.0	180.0	180.0
	ΔE^{cp}	-4.27	-4.25	-3.79	-3.80

NA: the structure of complex $FClO_2$-CH_3CN(II) was not obtained at the MP2/aug-cc-pVTZ with BSSE-corrected energy expression.

Table S3 The amount of charge transfer (Q_{CT}, e) from CH_3CN to FXO_n (X = Cl, Br; n = 0-3), most significant donor-acceptor orbital interactions and their corresponding second-order perturbation stabilization energies ($\Delta E^{(2)}$, kcal/mol) for selected halogen -bonded complexes calculated at the M05-2X/6-311++G(d,p) level.

Complexes	Q_{CT}	donor	acceptor	interaction	$\Delta E^{(2)}$
FCl-CH_3CN	0.025	LP(1)N	BD*(1)F-Cl	n→σ*	10.17
FClO-CH_3CN (I)	0.008	LP(1)N	BD*(1)F-Cl	n→σ*	2.69
FClO-CH_3CN(II)	0.007	BD(3)C-N	BD*(1)F-Cl	π→σ*	2.24
FClO-CH_3CN(III)	-0.001	BD(3)C-N	BD*(1)Cl-O	π→σ*	0.76
$FClO_2$-CH_3CN(I)	0.002	LP(1)N	BD*(1)F-Cl	n→σ*	1.98
$FClO_2$-CH_3CN(II)	0.000	BD(3)C-N	BD*(1)F-Cl	π→σ*	1.24
$FClO_2$-CH_3CN(III)	-0.004	BD(3)C-N	BD*(1)Cl-O2	π→σ*	0.45
$FClO_3$-CH_3CN	-0.005	LP(1)N	BD*(1)F-Cl	n→σ*	0.54
FBr-CH_3CN	0.056	LP(1)N	BD*(1)F-Br	n→σ*	18.36
FBrO-CH_3CN (I)	0.017	LP(1)N	BD*(1)F-Br	n→σ*	5.31
FBrO-CH_3CN(II)	0.018	BD(3)C-N	BD*(1)F-Br	π→σ*	3.70
FBrO-CH_3CN(III)	0.002	BD(3)C-N	BD*(1)Br-O	π→σ*	1.04
$FBrO_2$-CH_3CN(I)	0.010	LP(1)N	BD*(1)F-Br	n→σ*	3.84
$FBrO_2$-CH_3CN(II)	0.010	BD(3)C-N	BD*(1)F-Br	π→σ*	2.65
$FBrO_2$-CH_3CN(III)	0.001	BD(3)C-N	BD*(1)Br-O2	π→σ*	0.91
$FBrO_3$-CH_3CN	0.004	LP(1)N	BD*(1)F-Br	n→σ*	2.06

BD* denotes the formally empty antibonding orbital and LP denotes the occupied lone pair.

Table S4 The binding lengths ($r_{C\cdots F}$, Å), significant orbital interactions and their corresponding second-order perturbation stabilization energies ($E^{(2)}$, kcal mol^{-1}), and some bond critical point properties (in a.u.) of the C···F interaction of complexes FXO_n-CH_3CN(III) (X = Cl, Br; n = 1, 2) at the M05-2X/6-311++G(d,p) level.

	FClO-CH_3CN(III)	$FClO_2$-CH_3CN(III)	FBrO-CH_3CN(III)	$FBrO_2$-CH_3CN(III)
$r_{C\cdots F}$	2.953	2.953	2.936	2.963
Orbital interactions	LP(3)→BD*(3)C-N	LP(3)→BD*(3)C-N	LP(3)→BD*(3)C-N	LP(3)→BD*(3)C-N
$E^{(2)}$	0.73	0.53	0.73	0.39
ρ	0.0086	0.0087	0.0090	0.0087
$\nabla^2\rho$	0.0334	0.0336	0.0350	0.0340
V_b	-0.0063	-0.0064	-0.0066	-0.0063
G_b	0.0073	0.0074	0.0077	0.0074
H_b	0.0010	0.0010	0.0011	0.0011
$\lvert V_b\rvert/G_b$	0.8630	0.8649	0.8571	0.8514

Figure S1 The M05-2X-D3 potential energy curves of complexes FCl-CH_3CN (left) and FBrO-CH_3CN(III) (right). Distance between the monomers represents the distance between X (X = Cl or Br) and N atoms.