Electronic Supplementary Material (ESI) for RSC Advances

SUPPORTING INFORMATION PARAGRAPH

Investigation of heterodimeric and homodimeric radical cations of the series $[F_2O_2]^+$, $[F_2Cl_2]^+$, $[Cl_2O_2]^+$, $[F_4]^+$, and $[Cl_4]^+$

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Table S1 Calculated thermochemical data under standard conditions for the $[X_2]^+ + Y_2 \rightarrow [X_2Y_2]^+$ type homo- and heterodimerization reactions

Reaction	$\Delta_r E_{el,\,0K}$ [kJ mol^{-1}] [a]	$\Delta_r E_{vrt,\,298K}$ [kJ mol^{-1}] [b]	$\Delta_r S^\circ$ [J mol^{-1} K^{-1}] [b]	$\Delta_r G^\circ$ [kJ mol^{-1}]
$[F_2]^+ + F_2 \rightarrow [F_4]^+$	− 55.7	+ 5.0	− 95.1	− 24.8
$[F_2]^+ + O_2 \rightarrow [F_2O_2]^+$	− 371.0	+ 6.4	− 107.2	− 335.1
$[F_2]^+ + Cl_2 \rightarrow [F_2Cl_2]^+$	− 416.3	+4.3	− 75.1	− 392.0
$[Cl_2]^+ + F_2 \rightarrow [F_2Cl_2]^+$	− 11.2	+ 5.0 [c]	− 74.9 [c]	+ 13.6
$[Cl_2]^+ + O_2 \rightarrow [O_2Cl_2]^+$	− 67.4	+ 5.9	− 112.1	− 30.6
$[Cl_2]^+ + Cl_2 \rightarrow [Cl_4]^+$	− 76.2	+ 5.0	− 97.4	− 44.6
$[O_2]^+ + F_2 \rightarrow [F_2O_2]^+$	− 20.3	+ 5.0	− 98.1	+ 11.5
$[O_2]^+ + Cl_2 \rightarrow [O_2Cl_2]^+$	− 121.7	+ 3.8	− 103.1	− 89.7

[a] CCSD(T)/aVTZ. [b] B3LYP/aVTZ. [c] at B3LYP/aVTZ level $[F_2Cl_2]^+$ has C_{2v} symmetry.

Calculation of lattice energies using Jenkins equation[1]:

$$U_{lat} = z^+ \cdot z^- \cdot n \cdot \left(\frac{\alpha}{\sqrt[3]{V_{therm}}} + \beta\right) \text{kJ mol}^{-1}$$

with z^+, z^-: cation and anion charges; n: number of ions in the unit cell; V_{therm}: thermochemical volume; α = 117.3 nm mol−1, β = 51.9: empirical constants (for AB salts).

Calculation of lattice entropies using the Jenkins-Glasser equation[2]:

$$S^{\bullet}_{(s)} = (kV_{therm} + c) \text{J mol}^{-1}\text{K}^{-1}$$

with V_{therm}: thermochemical volume, k = 1360 nm^{-3}, c = 15: empirical constants.

Calculation of free lattice enthalpies[1] for AB salts:

$$\Delta_{lat}G^{\bullet} = U_{lat} + T\left\{\left(\frac{n_a + n_b}{2} - 4\right) \cdot R + S^{\bullet}_{(s)} - S^{\bullet}_{(g)}\right\}$$

with $n_{a/b}$ = 3 for monoatomic ions, 5 for linear polyatomic ions and 6 for non-linear polyatomic ions.

Table S2 Calculated free lattice enthalpies for $[X_2]^+$, $[X_4]$+ and $[X_2Y_2]^+$ hexafluoroantimonates using the VBT approach

Salt	V^- [nm^3] [a]	V^+ [nm^3] [b]	Crystal structures	U_{pot} [kJ mol^{-1}]	$S^\circ_{(s)}$ [J mol^{-1} K^{-1}]	$S^\circ_{(g)}$ (cation) [J mol^{-1} K^{-1}] [c]	$\Delta_{lat}G^\circ$ [kJ mol^{-1}]
$[F_2]^+[SbF_6]^-$	0.121	0.009		566.9	191.8	206.5	461.2
$[O_2]^+[SbF_6]^-$	0.121	0.009	[3]	566.9	191.8	200.1	463.1
$[Cl_2]^+[SbF_6]^-$	0.121	0.03965		535.4	233.5	227.2	435.9
$[F_4]^+[SbF_6]^-$	0.121	0.018		556.7	204.4	313.5	424.0
$[Cl_4]^+[SbF_6]^-$	0.121	0.0793	[4]	504.8	287.4	352.8	385.2
$[F_2O_2]^+[SbF_6]^-$	0.121	0.018		556.7	204.0	304.2	426.8
$[F_2Cl_2]^+[SbF_6]^-$ [d]	0.121	0.0666		513.6	270.1	354.4	388.4
$[Cl_2O_2]^+[SbF_6]^-$	0.121	0.0666	[5]	513.6	270.1	320.1	398.6

[a] V_- from ref. [2]. [b] V_+ established by subtracting anion volume from the cell volume for known cations, values for hypothetical cations estimated to be: $V_+([F_2]^+) = V_+([O_2]^+)$, $V_+([Cl_2]^+) = ½\ V_+([Cl_4]^+)$, $V_+([F_2O_2]^+) = V_+([F_4]^+) = 2\ V([O_2]^+)$ and $V_+([Cl_2F_2]^+) = V_+([Cl_2O_2]^+)$. [c] calculated at B3LYP/aVTZ level, at the same level $S^\circ_{(g)}([SbF_6]^-) = 352.3$ J mol^{-1} K^{-1}. [d] at B3LYP/aVTZ level $[F_2Cl_2]^+$ has C_{2v} symmetry.

Table S3 Computed vibrational frequencies at B3LYP and CCSD(T) level

Species	Sym.	B3LYP[a]	$^{18}O/^{37}Cl$[b]	IR[c]	Raman	aVDZ	aVTZ	aVQZ	Ref.
$[F_4]^+$									
δ_{as} ($F_2\cdots F_2$)	B_{2u}	70/35		–	–	279	312	334	
ρ ($F_2\cdots F_2$)	A_u	104/101		–	–	125	126	126	
ν ($F_2\cdots F_2$)	A_g	130/120		–	32	269	266	271	
δ_s ($F_2\cdots F_2$)	B_{3g}	216/207		–	6	270	272	279	
νa_s (F-F)	B_{1u}	1083/1073		206	–	1168	1247	1267	
ν_s (F-F)	A_g	1144/1131		–	16	933	1020	1023	
$[Cl_4]^+$									
ρ ($Cl_2\cdots Cl_2$)	A_u	50/47	49	--	–	51	54	58	57[d]
δ_{as} ($Cl_2\cdots Cl_2$)	B_{2u}	72/66	70	–	–	331	221	201	78[d]
ν ($Cl_2\cdots Cl_2$)	A_g	104/96	101	–	96	165	164	169	104[d], 175[e]
δ_s ($Cl_2\cdots Cl_2$)	B_{3g}	113/109	110	–	13	145	142	139	116[d], 241[e]
ν_{as} (Cl-Cl)	B_{1u}	560/556	545	77	–	983	957	895	563[d]
ν_s (Cl-Cl)	A_g	584/580	568	–	32	569	595	602	589[d], 578[e]
$[F_2O_2]^+$									
δ_{as} ($F_2\cdots O_2$)	B_2	106/33	103	–	–	22	71	73	
ρ ($F_2\cdots O_2$)	A_2	146/134	141	–	–	48	111	109	
ν ($F_2\cdots O_2$)	A_1	186/130	180	26	28	101	130	126	
δ_{as} (($F_2\cdots O_2$)	B_2	309/287	300	–	4	105	165	168	
ν (F-F)	A_1	1055/1038	1055	32	28	817	902	907	
ν (O-O)	A_1	1919/1892	1809	180	190	1909	1894	1918	
$[Cl_2O_2]^+$									
δ_{as} ($Cl_2\cdots O_2$)	B_2	109/94	107/107	1	3	200	330	321	116[d], 227? (193)[e]
ν ($Cl_2\cdots O_2$)	A_1	141/124	135/140	-	53	468	289	284	144[d], 263 (255)[e]
ρ ($Cl_2\cdots O_2$)	A_2	158/143	150/159	-	-	350	205	204	160[d]
δ_s ($Cl_2\cdots O_2$)	B_2	330/304	313/329	2	5	795	498	437	338[d], 414 (395)[e]
ν (Cl-Cl)	A_1	581/576	581/565	22	17	538	567	579	587[d], 593 (593)[e, f]

ν (O-O)	A_1	1684/1659	1587/1684	621	13	1765	1597	1618	1697[d], 1534 (1448)[e]
$[F_2Cl_2]^+$									
ρ (F_2··Cl_2)	$A_{(2)}$	43/11	42	–	–	8	10	–	
δ_{as} (F_2··Cl_2)	$B_{(2)}$	46/16	45	–	5	40	41	–	
ν (F_2··Cl_2)	$A_{(1)}$	82/51	81	12	**11**	60	74	–	
δ_s (F_2··Cl_2)	$B_{(2)q}$	112/94	111	-	1	72	107	–	
ν (Cl-Cl)	$A_{(1)}$	621/615	604	5	102	585	624	–	
ν (F-F)	$A_{(1)}$	1045/1031	1045	32	326	817	907	–	

[a] Harmonic/Anharmonic vibrational frequencies. [b] Isotopic frequency calculation using ^{18}O or ^{37}Cl (for $[Cl_2O_2]^+$ either ^{35}Cl or ^{16}O has been replaced). [c]Int. in km/mol. [d] B3LYP/6-311++G(3df,3pd) level.[4,5] [e] Experimental Raman frequencies, values in parentheses for $[Cl_2{}^{18}O_2]^+$.[4,5] [f] Frequency for mixed chlorine isotopomer $[{}^{35}Cl{}^{37}ClO_2]^+$: ν (Cl-Cl) = 586 cm^{-1}.

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