Supporting Information for

Planar Hexacoordinate Chlorine

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Table S1. Lowest vibrational frequencies (v_{min}, in cm^{-1}) and numbers of imaginary frequencies (NIMG) for D_{6h} $X©M_6X'_6^-$ (X = F–I; M = Li–Cs; X′ = H, F–I) clusters at the PBE0-D3(BJ)/def2-TZVPP level.

System	v_{min}	NIMG	System	v_{min}	NIMG
$F©Li_6H_6^-$	201i	7	$Br©Na_6H_6^-$	5i	2
$F©Li_6F_6^-$	189i	8	$Br©Na_6F_6^-$	13i	2
$F©Li_6Cl_6^-$	185i	9	$Br©Na_6Cl_6^-$	51i	9
$F©Li_6Br_6^-$	178i	9	$Br©Na_6Br_6^-$	53i	9
$F©Li_6I_6^-$	177i	9	$Br©Na_6I_6^-$	49i	9
$Cl©Li_6H_6^-$	38	0	$I©Na_6H_6^-$	17	0
$Cl©Li_6F_6^-$	11	0	$I©Na_6F_6^-$	17	0
$Cl©Li_6Cl_6^-$	108i	8	$I©Na_6Cl_6^-$	32i	5
$Cl©Li_6Br_6^-$	97i	9	$I©Na_6Br_6^-$	40i	9
$Cl©Li_6I_6^-$	95i	9	$I©Na_6I_6^-$	37i	9
$Br©Li_6H_6^-$	24	0	$F©K_6H_6^-$	101i	8
$Br©Li_6F_6^-$	8	0	$F©K_6F_6^-$	92i	8
$Br©Li_6Cl_6^-$	77i	5	$F©K_6Cl_6^-$	93i	9
$Br©Li_6Br_6^-$	77i	8	$F©K_6Br_6^-$	93i	9
$Br©Li_6I_6^-$	69i	9	$F©K_6I_6^-$	95i	9
$I©Li_6H_6^-$	48i	1	$Cl©K_6H_6^-$	54i	8
$I©Li_6F_6^-$	36i	1	$Cl©K_6F_6^-$	44i	8
$I©Li_6Cl_6^-$	15i	2	$Cl©K_6Cl_6^-$	61i	8
$I©Li_6Br_6^-$	38i	4	$Cl©K_6Br_6^-$	62i	9
$I©Li_6I_6^-$	47i	6	$Cl©K_6I_6^-$	64i	9
$F©Na_6H_6^-$	127i	8	$Br©K_6H_6^-$	35i	8
$F©Na_6F_6^-$	118i	8	$Br©K_6F_6^-$	38i	6
$F©Na_6Cl_6^-$	127i	9	$Br©K_6Cl_6^-$	42i	8
$F©Na_6Br_6^-$	128i	9	$Br©K_6Br_6^-$	44i	9
$F©Na_6I_6^-$	129i	9	$Br©K_6I_6^-$	43i	9
$Cl©Na_6H_6^-$	46i	5	$I©K_6H_6^-$	21i	5
$Cl©Na_6F_6^-$	42i	8	$I©K_6F_6^-$	31i	4
$Cl©Na_6Cl_6^-$	73i	9	$I©K_6Cl_6^-$	29i	8
$Cl©Na_6Br_6^-$	76i	9	$I©K_6Br_6^-$	32i	9
$Cl©Na_6I_6^-$	78i	9	$I©K_6I_6^-$	31i	9

System	v_{min}	NIMG	System	v_{min}	NIMG
F©$Rb_6H_6^-$	87i	8	F©$Cs_6H_6^-$	81i	8
F©$Rb_6F_6^-$	83i	11	F©$Cs_6F_6^-$	77i	14
F©$Rb_6Cl_6^-$	80i	8	F©$Cs_6Cl_6^-$	82i	14
F©$Rb_6Br_6^-$	83i	9	F©$Cs_6Br_6^-$	81i	8
F©$Rb_6I_6^-$	83i	9	F©$Cs_6I_6^-$	79i	9
Cl©$Rb_6H_6^-$	50i	8	Cl©$Cs_6H_6^-$	29i	8
Cl©$Rb_6F_6^-$	38i	11	Cl©$Cs_6F_6^-$	44i	14
Cl©$Rb_6Cl_6^-$	53i	8	Cl©$Cs_6Cl_6^-$	43i	14
Cl©$Rb_6Br_6^-$	54i	9	Cl©$Cs_6Br_6^-$	45i	8
Cl©$Rb_6I_6^-$	55i	9	Cl©$Cs_6I_6^-$	49i	9
Br©$Rb_6H_6^-$	28i	8	Br©$Cs_6H_6^-$	21i	6
Br©$Rb_6F_6^-$	32i	9	Br©$Cs_6F_6^-$	42i	12
Br©$Rb_6Cl_6^-$	35i	8	Br©$Cs_6Cl_6^-$	25i	14
Br©$Rb_6Br_6^-$	35i	9	Br©$Cs_6Br_6^-$	29i	8
Br©$Rb_6I_6^-$	36i	9	Br©$Cs_6I_6^-$	31i	9
I©$Rb_6H_6^-$	17i	6	I©$Cs_6H_6^-$	18i	6
I©$Rb_6F_6^-$	29i	5	I©$Cs_6F_6^-$	40i	11
I©$Rb_6Cl_6^-$	23i	8	I©$Cs_6Cl_6^-$	22i	14
I©$Rb_6Br_6^-$	26i	8	I©$Cs_6Br_6^-$	16i	8
I©$Rb_6I_6^-$	26i	9	I©$Cs_6I_6^-$	21i	9

Table S2. Lowest vibrational frequencies (v_{min}, in cm^{-1}) and numbers of imaginary frequencies (NIMG) for D_{6h} X©$M_6X'_6^-$ (X = F–I; M = Be–Ba; X′ = O–Po) clusters at the PBE0-D3(BJ)/def2-TZVPP level.

System	v_{min}	NIMG	System	v_{min}	NIMG
F©$Be_6O_6^-$	160i	5	Br©$Mg_6O_6^-$	23	0
F©$Be_6S_6^-$	236i	8	Br©$Mg_6S_6^-$	59i	8
F©$Be_6Se_6^-$	236i	8	Br©$Mg_6Se_6^-$	63i	8
F©$Be_6Te_6^-$	235i	8	Br©$Mg_6Te_6^-$	68i	8
F©$Be_6Po_6^-$	237i	8	Br©$Mg_6Po_6^-$	67i	8
Cl©$Be_6O_6^-$	103i	1	I©$Mg_6O_6^-$	31i	1
Cl©$Be_6S_6^-$	152i	8	I©$Mg_6S_6^-$	28i	3
Cl©$Be_6Se_6^-$	144i	8	I©$Mg_6Se_6^-$	45i	6
Cl©$Be_6Te_6^-$	154i	8	I©$Mg_6Te_6^-$	51i	8
Cl©$Be_6Po_6^-$	155i	8	I©$Mg_6Po_6^-$	47i	8
Br©$Be_6O_6^-$	101i	1	F©$Ca_6O_6^-$	146i	8
Br©$Be_6S_6^-$	140i	5	F©$Ca_6S_6^-$	131i	9
Br©$Be_6Se_6^-$	141i	8	F©$Ca_6Se_6^-$	129i	8
Br©$Be_6Te_6^-$	128i	8	F©$Ca_6Te_6^-$	128i	9
Br©$Be_6Po_6^-$	117i	8	F©$Ca_6Po_6^-$	128i	9
I©$Be_6O_6^-$	112i	1	Cl©$Ca_6O_6^-$	100i	8
I©$Be_6S_6^-$	118i	2	Cl©$Ca_6S_6^-$	95i	8
I©$Be_6Se_6^-$	135i	5	Cl©$Ca_6Se_6^-$	94i	8
I©$Be_6Te_6^-$	133i	8	Cl©$Ca_6Te_6^-$	93i	9
I©$Be_6Po_6^-$	123i	8	Cl©$Ca_6Po_6^-$	92i	9
F©$Mg_6O_6^-$	161i	5	Br©$Ca_6O_6^-$	91i	8
F©$Mg_6S_6^-$	167i	8	Br©$Ca_6S_6^-$	68i	8
F©$Mg_6Se_6^-$	165i	8	Br©$Ca_6Se_6^-$	67i	8
F©$Mg_6Te_6^-$	162i	8	Br©$Ca_6Te_6^-$	65i	9
F©$Mg_6Po_6^-$	162i	8	Br©$Ca_6Po_6^-$	63i	9
Cl©$Mg_6O_6^-$	30i	3	I©$Ca_6O_6^-$	79i	9
Cl©$Mg_6S_6^-$	94i	8	I©$Ca_6S_6^-$	55i	8
Cl©$Mg_6Se_6^-$	100i	8	I©$Ca_6Se_6^-$	54i	8
Cl©$Mg_6Te_6^-$	104i	8	I©$Ca_6Te_6^-$	47i	9
Cl©$Mg_6Po_6^-$	104i	8	I©$Ca_6Po_6^-$	44i	9
F©$Sr_6O_6^-$	122i	11	F©$Ba_6O_6^-$	111i	11

System	v_{min}	NIMG	System	v_{min}	NIMG
F©$Sr_6S_6^-$	111i	11	F©$Ba_6S_6^-$	93i	14
F©$Sr_6Se_6^-$	110i	8	F©$Ba_6Se_6^-$	92i	11
F©$Sr_6Te_6^-$	109i	8	F©$Ba_6Te_6^-$	91i	8
F©$Sr_6Po_6^-$	110i	8	F©$Ba_6Po_6^-$	93i	8
Cl©$Sr_6O_6^-$	93i	11	Cl©$Ba_6O_6^-$	106i	11
Cl©$Sr_6S_6^-$	81i	11	Cl©$Ba_6S_6^-$ (D_{3h})	28i	7
Cl©$Sr_6Se_6^-$	81i	8	Cl©$Ba_6Se_6^-$	67i	11
Cl©$Sr_6Te_6^-$	80i	8	Cl©$Ba_6Te_6^-$	66i	8
Cl©$Sr_6Po_6^-$	80i	8	Cl©$Ba_6Po_6^-$	67i	8
Br©$Sr_6O_6^-$	68i	11	Br©$Ba_6O_6^-$	102i	11
Br©$Sr_6S_6^-$	56i	11	Br©$Ba_6S_6^-$ (C_{3v})	10	0
Br©$Sr_6Se_6^-$	56i	8	Br©$Ba_6Se_6^-$	49i	11
Br©$Sr_6Te_6^-$	55i	8	Br©$Ba_6Te_6^-$	49i	8
Br©$Sr_6Po_6^-$	55i	8	Br©$Ba_6Po_6^-$	49i	8
I©$Sr_6O_6^-$	66i	11	I©$Ba_6O_6^-$	101i	11
I©$Sr_6S_6^-$	43i	11	I©$Ba_6S_6^-$ (D_{3h})	21i	5
I©$Sr_6Se_6^-$	44i	8	I©$Ba_6Se_6^-$	39i	11
I©$Sr_6Te_6^-$	43i	8	I©$Ba_6Te_6^-$	—	—
I©$Sr_6Po_6^-$	42i	8	I©$Ba_6Po_6^-$	—	—

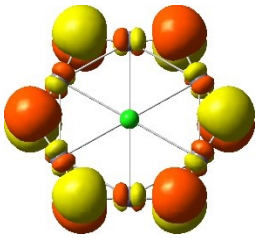
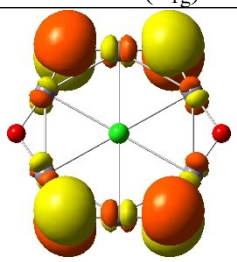
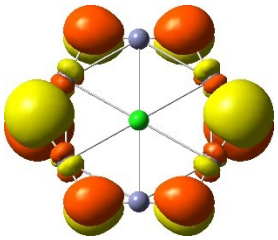
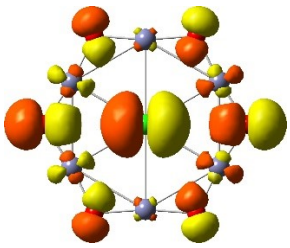
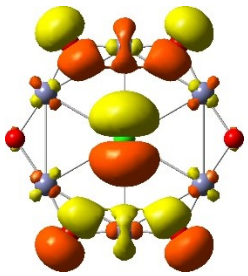
Table S3. Lowest vibrational frequencies (v_{min}, in cm^{-1}) and numbers of imaginary frequencies (NIMG) for D_{6h} $X©M_6X'_6^-$ (X = F–I; M = Zn–Hg; X′ = O–Po) clusters at the PBE0-D3(BJ)/def2-TZVPP level.

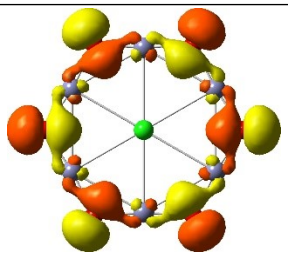
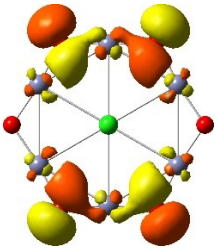
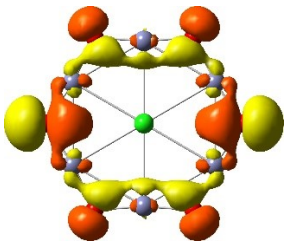
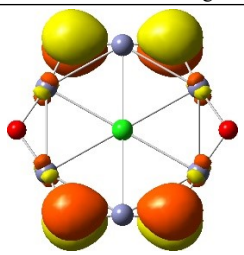
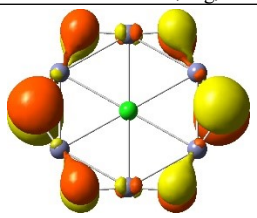
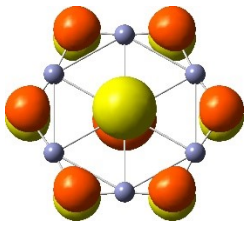
System	v_{min}	NIMG	System	v_{min}	NIMG
$F©Zn_6O_6^-$	122i	6	$Br©Cd_6O_6^-$	71i	3
$F©Zn_6S_6^-$	155i	8	$Br©Cd_6S_6^-$	31i	8
$F©Zn_6Se_6^-$	156i	8	$Br©Cd_6Se_6^-$	42i	8
$F©Zn_6Te_6^-$	153i	8	$Br©Cd_6Te_6^-$	55i	8
$F©Zn_6Po_6^-$	155i	8	$Br©Cd_6Po_6^-$	56i	8
$Cl©Zn_6O_6^-$	33	0	$I©Cd_6O_6^-$	60i	4
$Cl©Zn_6S_6^-$	62i	8	$I©Cd_6S_6^-$	27i	3
$Cl©Zn_6Se_6^-$	82i	8	$I©Cd_6Se_6^-$	22i	6
$Cl©Zn_6Te_6^-$	96i	8	$I©Cd_6Te_6^-$	33i	8
$Cl©Zn_6Po_6^-$	97i	8	$I©Cd_6Po_6^-$	36i	8
$Br©Zn_6O_6^-$	29i	1	$F©Hg_6O_6^-$	99i	5
$Br©Zn_6S_6^-$	35i	6	$F©Hg_6S_6^-$	117i	7
$Br©Zn_6Se_6^-$	44i	8	$F©Hg_6Se_6^-$	119i	7
$Br©Zn_6Te_6^-$	63i	8	$F©Hg_6Te_6^-$	109i	7
$Br©Zn_6Po_6^-$	65i	8	$F©Hg_6Po_6^-$	108i	8
$I©Zn_6O_6^-$	43i	1	$Cl©Hg_6O_6^-$	79i	3
$I©Zn_6S_6^-$	24i	4	$Cl©Hg_6S_6^-$	53i	7
$I©Zn_6Se_6^-$	40i	6	$Cl©Hg_6Se_6^-$	68i	7
$I©Zn_6Te_6^-$	46i	8	$Cl©Hg_6Te_6^-$	76i	8
$I©Zn_6Po_6^-$	45i	8	$Cl©Hg_6Po_6^-$	77i	8
$F©Cd_6O_6^-$	120i	5	$Br©Hg_6O_6^-$	75i	4
$F©Cd_6S_6^-$	132i	8	$Br©Hg_6S_6^-$	36i	5
$F©Cd_6Se_6^-$	133i	8	$Br©Hg_6Se_6^-$	38i	7
$F©Cd_6Te_6^-$	134i	8	$Br©Hg_6Te_6^-$	50i	8
$F©Cd_6Po_6^-$	135i	8	$Br©Hg_6Po_6^-$	52i	8
$Cl©Cd_6O_6^-$	77i	3	$I©Hg_6O_6^-$	69i	4
$Cl©Cd_6S_6^-$	63i	8	$I©Hg_6S_6^-$	33i	3
$Cl©Cd_6Se_6^-$	75i	8	$I©Hg_6Se_6^-$	24i	5
$Cl©Cd_6Te_6^-$	84i	8	$I©Hg_6Te_6^-$	34i	8
$Cl©Cd_6Po_6^-$	85i	8	$I©Hg_6Po_6^-$	38i	8

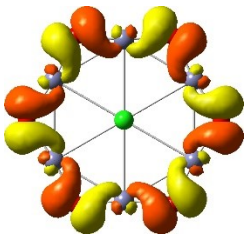
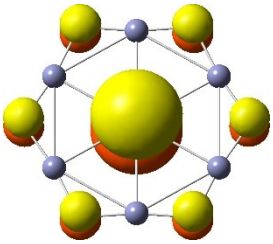
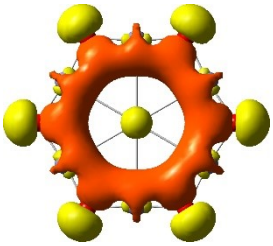
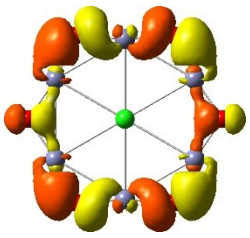
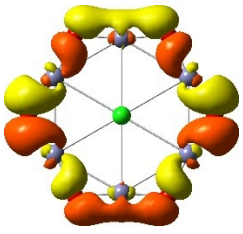
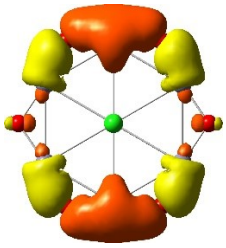
Table S4. Lowest vibrational frequency of the global-minimum structure **1** (D_{6h}, $^1A_{1g}$) of $Cl©Zn_6O_6^-$ cluster at eight theoretical levels.

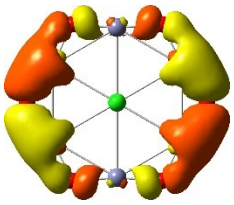
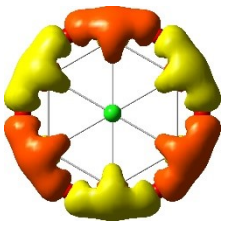
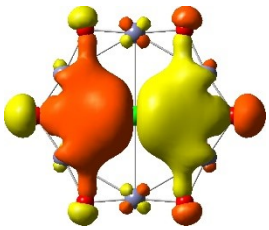
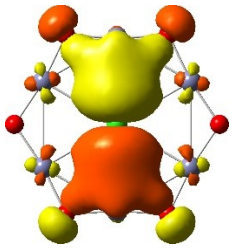
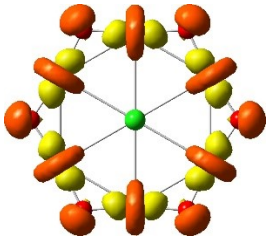
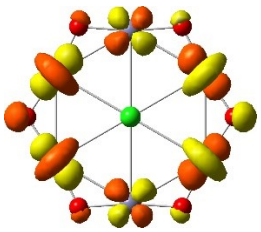
	Theoretical level	Lowest vibrational frequency (cm^{-1})
1	PBE0-D3(BJ)/aug-cc-pVTZ	29
2	BP86-D3(BJ)/aug-cc-pVTZ	15
3	B3LYP-D3(BJ)/aug-cc-pVTZ	17
4	B3PW91-D3(BJ)/aug-cc-pVTZ	23
5	TPSS-D3(BJ)/aug-cc-pVTZ	25
6	ωB97X-D/aug-cc-pVTZ	22
7	TPSSh/aug-cc-pVTZ	28
8	M06-2X/aug-cc-pVTZ	33

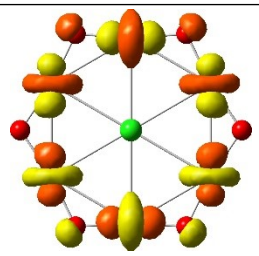
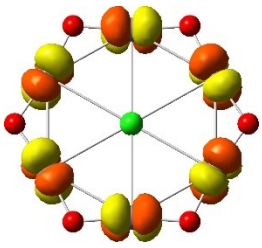
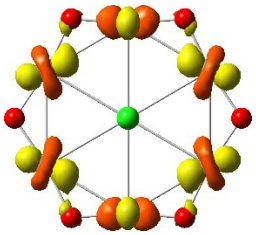
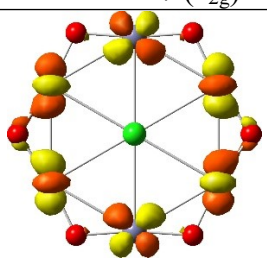
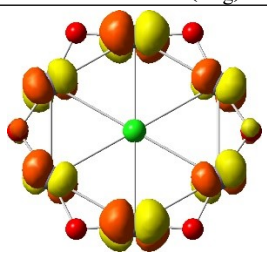
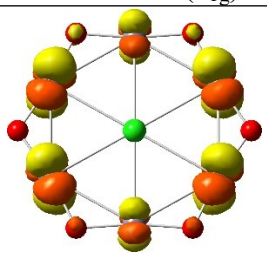
Table S5. Orbital composition analysis of the canonical molecular orbitals of the Cl©$Zn_6O_6^-$ global-minimum structure **1** (D_{6h}, $^1A_{1g}$).

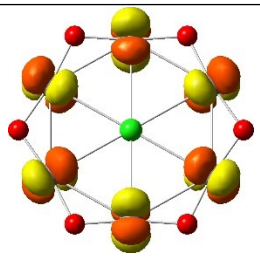
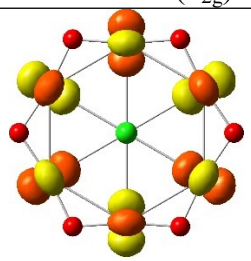
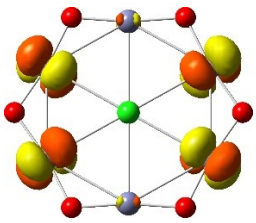
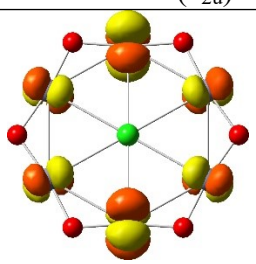
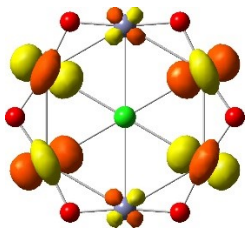
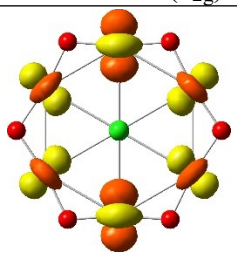
CMO	Cl (%)		Zn_6 (%)		O_6 (%)	
	3*s*/3*p*	total	3*d*/4*s*/4*p*	total	2*s*/2*p*	total
 HOMO (b_{1g})	0.00/0.00	0.00	6.36/0.00/0.00	6.36	0.00/**93.64**	**93.64**
 HOMO–1 (e_{2u})	0.00/0.00	0.00	4.31/0.00/0.00	4.31	0.00/**95.69**	**95.69**
 HOMO–1′ (e_{2u})	0.00/0.00	0.00	4.62/0.00/1.34	5.96	0.00/**94.04**	**94.04**
 HOMO–2 (e_{1u})	0.00/**36.16**	**36.16**	5.68/4.01/0.00	9.69	0.00/**54.15**	**54.15**
 HOMO–2′ (e_{1u})	0.00/**36.40**	**36.40**	6.28/2.70/0.00	8.98	0.00/**54.62**	**54.62**

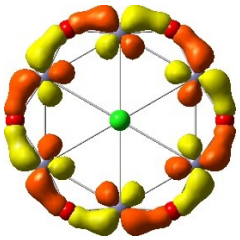
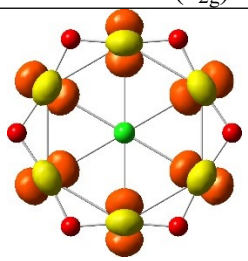
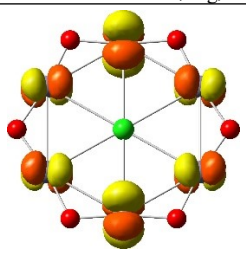
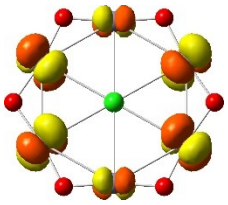
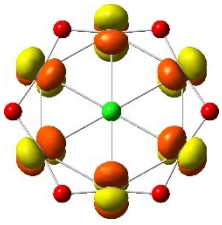
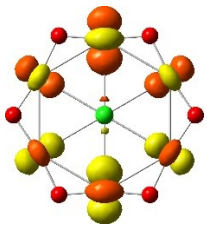
CMO	Cl (%)		Zn_6 (%)		O_6 (%)	
	3*s*/3*p*	total	3*d*/4*s*/4*p*	total	2*s*/2*p*	total
 HOMO–3 (b_{2u})	0.00/0.00	0.00	4.47/0.00/0.00	4.47	0.00/**95.53**	**95.53**
 HOMO–4 (e_{2g})	0.00/0.00	0.00	5.50/3.74/0.00	9.24	0.00/**90.76**	**90.76**
 HOMO–4′ (e_{2g})	0.00/0.00	0.00	4.81/2.52/0.00	7.33	1.22/**91.45**	**92.67**
 HOMO–5 (e_{1g})	0.00/0.00	0.00	2.10/0.00/3.56	5.66	0.00/**94.34**	**94.34**
 HOMO–5′ (e_{1g})	0.00/0.00	0.00	1.74/0.00/5.27	7.01	0.00/**92.99**	**92.99**
 HOMO–6 (a_{2u})	0.00/**32.11**	**32.11**	0.00/0.00/0.00	0.00	0.00/**67.89**	**67.89**

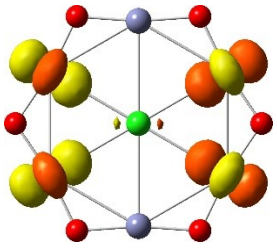
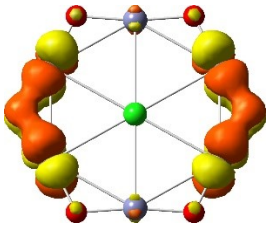
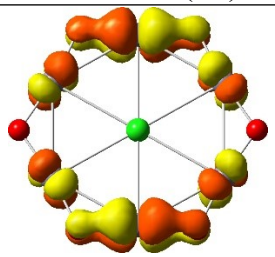
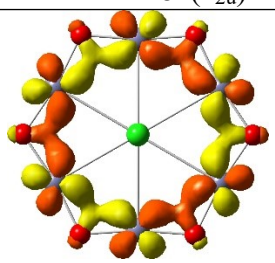
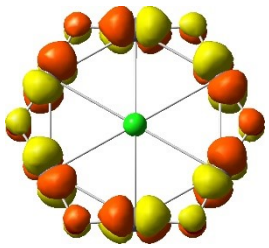
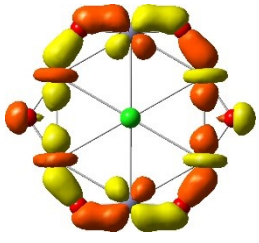
CMO	Cl (%)		Zn_6 (%)		O_6 (%)	
	3*s*/3*p*	total	3*d*/4*s*/4*p*	total	2*s*/2*p*	total
 HOMO–7 (a_{2g})	0.00/0.00	0.00	5.91/0.00/0.00	5.91	0.00/**94.09**	**94.09**
 HOMO–8 (a_{2u})	0.00/**67.92**	**67.92**	0.00/0.00/4.23	4.23	0.00/**27.85**	**27.85**
 HOMO–9 (a_{1g})	1.42/0.00	1.42	1.39/14.30/3.78	19.47	0.00/**79.11**	**79.11**
 HOMO–10 (e_{1u})	0.00/0.00	0.00	4.42/3.02/0.00	7.44	0.00/**92.56**	**92.56**
 HOMO–10′ (e_{1u})	0.00/0.00	0.00	2.24/2.13/0.00	4.37	0.00/**95.63**	**95.63**
 HOMO–11 (e_{2g})	0.00/0.00	0.00	11.21/14.57/0.00	**25.78**	0.00/**74.22**	**74.22**

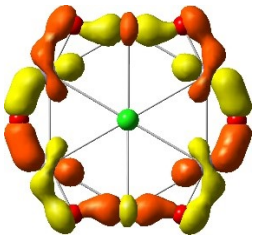
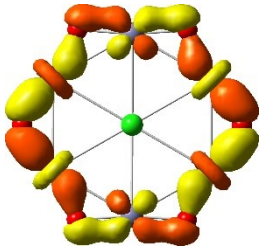
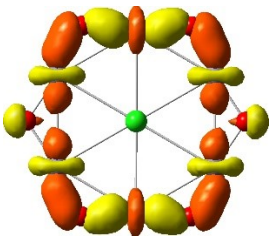
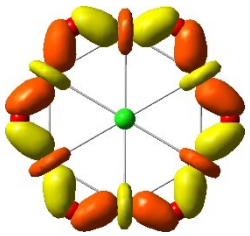
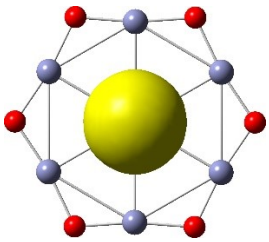
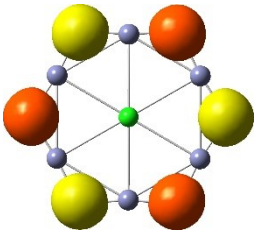
CMO	Cl (%)		Zn_6 (%)		O_6 (%)	
	3*s*/3*p*	total	3*d*/4*s*/4*p*	total	2*s*/2*p*	total
 HOMO–11′(e_{2g})	0.00/0.00	0.00	11.87/14.75/0.00	**26.62**	0.00/**73.38**	**73.38**
 HOMO–12 (b_{1u})	0.00/0.00	0.00	18.08/17.66/0.00	**35.74**	0.00/**64.26**	**64.26**
 HOMO–13 (e_{1u})	0.00/**60.42**	**60.42**	2.51/7.00/2.67	12.18	1.42/**25.98**	**27.40**
 HOMO–13′ (e_{1u})	0.00/**59.92**	**59.92**	2.94/6.95/2.87	12.76	2.10/**25.22**	**27.32**
 HOMO–14 (a_{1g})	0.00/0.00	0.00	**87.15**/0.00/0.00	**87.15**	6.71/6.14	12.85
 HOMO–15 (e_{1u})	0.00/1.37	1.37	**94.28**/2.37/0.00	**96.65**	1.98/0.00	1.98

CMO	Cl (%)		Zn_6 (%)		O_6 (%)	
	3*s*/3*p*	total	3*d*/4*s*/4*p*	total	2*s*/2*p*	total
 HOMO–15′ (e_{1u})	0.00/1.36	1.36	**94.09**/1.58/0.00	**95.67**	2.97/0.00	2.97
 HOMO–16 (a_{1u})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–17 (e_{2g})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–17′ (e_{2g})	0.00/0.00	0.00	**98.51**/0.00/0.00	**98.51**	0.00/1.49	1.49
 HOMO–18 (e_{1g})	0.00/0.00	0.00	**98.44**/0.00/0.00	**98.44**	0.00/1.56	1.56
 HOMO–18′ (e_{1g})	0.00/0.00	0.00	**97.67**/0.00/0.00	**97.67**	0.00/2.33	2.33

CMO	Cl (%)		Zn_6 (%)		O_6 (%)	
	3*s*/3*p*	total	3*d*/4*s*/4*p*	total	2*s*/2*p*	total
 HOMO–19 (b_{2g})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–20 (b_{1u})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–21 (e_{2u})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–21′ (e_{2u})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–22 (e_{2g})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–22′ (e_{2g})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00

CMO	Cl (%)		Zn_6 (%)		O_6 (%)	
	3*s*/3*p*	total	3*d*/4*s*/4*p*	total	2*s*/2*p*	total
 HOMO–23 (a_{2g})	0.00/0.00	0.00	**94.29**/0.00/0.00	**94.29**	0.00/5.71	5.71
 HOMO–24 (a_{1g})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–25 (e_{1g})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–25′ (e_{1g})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–26 (a_{2u})	0.00/0.00	0.00	**100.00**/0.00/0.00	**100.00**	0.00/0.00	0.00
 HOMO–27 (e_{1u})	0.00/1.46	1.46	**98.54**/0.00/0.00	**98.54**	0.00/0.00	0.00

CMO	Cl (%)		Zn_6 (%)		O_6 (%)	
	3*s*/3*p*	total	3*d*/4*s*/4*p*	total	2*s*/2*p*	total
 HOMO–27′ (e_{1u})	0.00/1.46	1.46	**98.54**/0.00/0.00	**98.54**	0.00/0.00	0.00
 HOMO–28(e_{2u})	0.00/0.00	0.00	**93.91**/0.00/0.00	**93.91**	0.00/6.09	6.09
 HOMO–28′ (e_{2u})	0.00/0.00	0.00	**93.96**/0.00/0.00	**93.96**	0.00/6.04	6.04
 HOMO–29 (b_{2u})	0.00/0.00	0.00	**95.77**/0.00/0.00	**95.77**	0.00/4.23	4.23
 HOMO–30 (b_{1g})	0.00/0.00	0.00	**92.50**/0.00/0.00	**92.50**	0.00/7.50	7.50
 HOMO–31 (e_{1u})	0.00/0.00	0.00	**86.18**/0.00/0.00	**86.18**	1.25/12.57	13.82

CMO	Cl (%)		Zn_6 (%)		O_6 (%)	
	3*s*/3*p*	total	3*d*/4*s*/4*p*	total	2*s*/2*p*	total
 HOMO–31′ (e_{1u})	0.00/0.00	0.00	**88.09**/0.00/0.00	**88.09**	0.00/11.91	11.91
 HOMO–32 (e_{2g})	0.00/0.00	0.00	**83.24**/0.00/0.00	**83.24**	0.00/16.76	16.76
 HOMO–32′ (e_{2g})	0.00/0.00	0.00	**83.22**/0.00/0.00	**83.22**	0.00/16.78	16.78
 HOMO–33 (b_{1u})	0.00/0.00	0.00	**79.95**/0.00/0.00	**79.95**	0.00/20.05	20.05
 HOMO–34 (a_{1g})	**100.00** /0.00	**100.00**	0.00/0.00/0.00	0.00	0.00/0.00	0.00
 HOMO–35 (b_{2u})	0.00/0.00	0.00	0.00/0.00/7.00	7.00	**93.00**/0.00	**93.00**

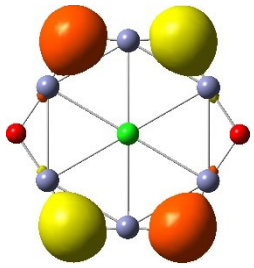
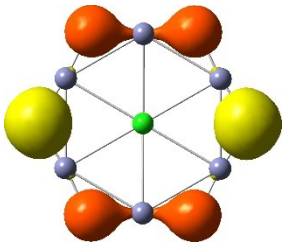
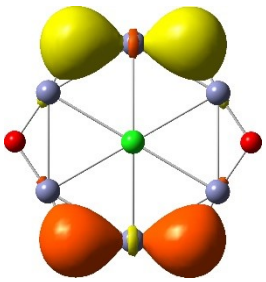
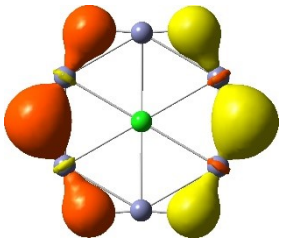
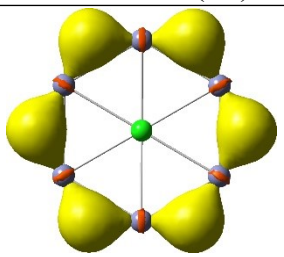
CMO	Cl (%)		Zn_6 (%)		O_6 (%)	
	3*s*/3*p*	total	3*d*/4*s*/4*p*	total	2*s*/2*p*	total
 HOMO–36 (e_{2g})	0.00/0.00	0.00	0.00/0.00/4.41	4.41	**95.59**/0.00	**95.59**
 HOMO–36′ (e_{2g})	0.00/0.00	0.00	1.13/1.19/4.65	6.97	**93.03**/0.00	**93.03**
 HOMO–37 (e_{1u})	0.00/0.00	0.00	3.12/3.54/0.00	6.66	**93.34**/0.00	**93.34**
 HOMO–37′ (e_{1u})	0.00/0.00	0.00	3.50/5.10/1.45	10.05	**89.95**/0.00	**89.95**
 HOMO–38 (a_{1g})	0.00/0.00	0.00	4.70/6.87/0.00	11.57	**88.43**/0.00	**88.43**

Table S6. Energy decomposition analysis (EDA) results for **1** using Cl and Zn_6O_6 fragments in different charge and electronic states at the PBE0/TZ2P-ZORA level. All energies are given in kcal/mol (S = singlet; D = doublet; T = triplet).

Energy Terms	Cl^- (S, $3s^2 3p_x{}^2 3p_y{}^2 3p_z{}^2$) + Zn_6O_6 (S)	Cl (D, $3s^2 3p_x{}^2 3p_y{}^2 3p_z{}^1$) + $Zn_6O_6^-$ (D)	Cl^+ (S, $3s^2 3p_x{}^2 3p_y{}^2 3p_z{}^0$) + $Zn_6O_6^{2-}$ (S)	Cl^+ (T, $3s^2 3p_x{}^2 3p_y{}^1 3p_z{}^1$) + $Zn_6O_6^{2-}$ (T)
ΔE_{int}	–76.9	–205.9	–700.0	–602.0
ΔE_{Pauli}	76.9	65.7	58.9	67.5
ΔE_{elstat}	–116.8 (75.9%)	–41.3 (15.2%)	–162.9 (21.5%)	–153.8 (23.0%)
ΔE_{oi}	**–37.0** (24.1%)	–230.3 (84.8%)	–596.0 (78.5%)	–515.7 (77.0%)

Table S7.

Interacting Quantum Atoms (IQA) energy components for D_{6h} Cl©$Zn_6O_6^-$ and Zn_6O_6 at the PBE0/TZ2P level. V^{IQA}, V_C, and V_{XC} denote the interatomic IQA interaction energy and its Coulombic and exchange–correlation components, respectively kcal/mol.

	Cl©$Zn_6O_6^-$	Zn_6O_6
V^{IQA}(Cl–Zn)	–121.7	—
V_C(Cl–Zn)	–106.9 (87.8%)	—
V_{XC}(Cl–Zn)	–14.8 (12.2%)	—
V^{IQA}(Zn–Zn)	171.2	164.7
V_C(Zn–Zn)	174.2 (98.3%)	167.9 (98.1%)
V_{XC}(Zn–Zn)	–3.0 (1.7%)	–3.2 (1.9 %)
V^{IQA}(Zn–O)	–392.8	–398.4
V_C(Zn–O)	–271.4 (69.1%)	–271.8 (68.2%)
V_{XC}(Zn–O)	–121.4 (30.9%)	–126.6 (31.8%)

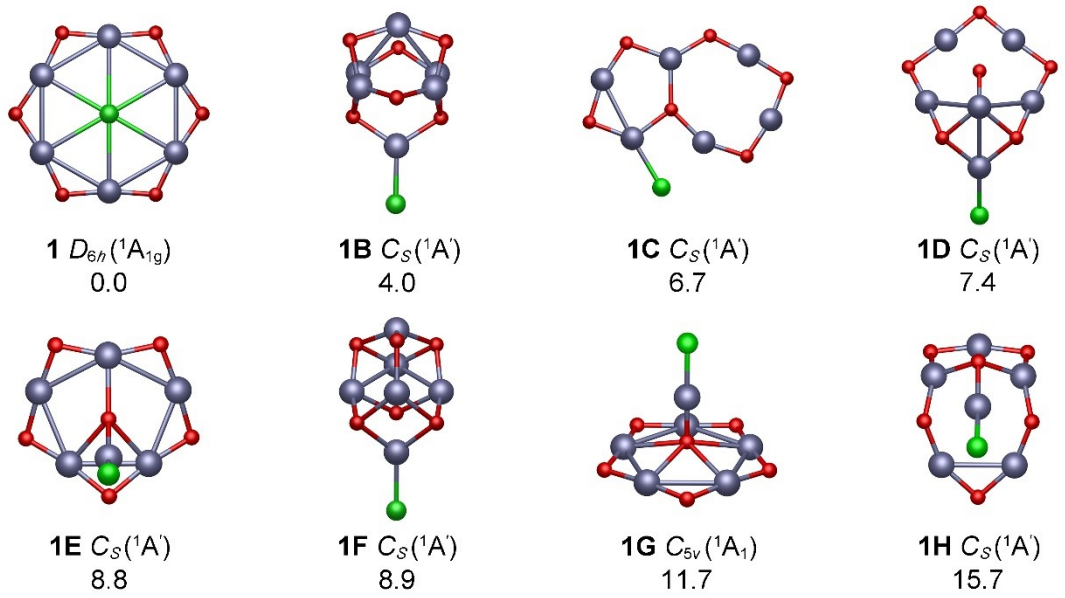


Figure S1. PBE0-D3(BJ)/aug-cc-pVTZ geometries of the eight lowest-energy isomers of Cl©$Zn_6O_6^-$. Relative energies (kcal mol^{-1}) were computed at the CCSD(T)/aug-cc-pVTZ//PBE0-D3(BJ)/aug-cc-pVTZ level and include zero-point energy (ZPE) corrections obtained at the PBE0-D3(BJ)/aug-cc-pVTZ level.

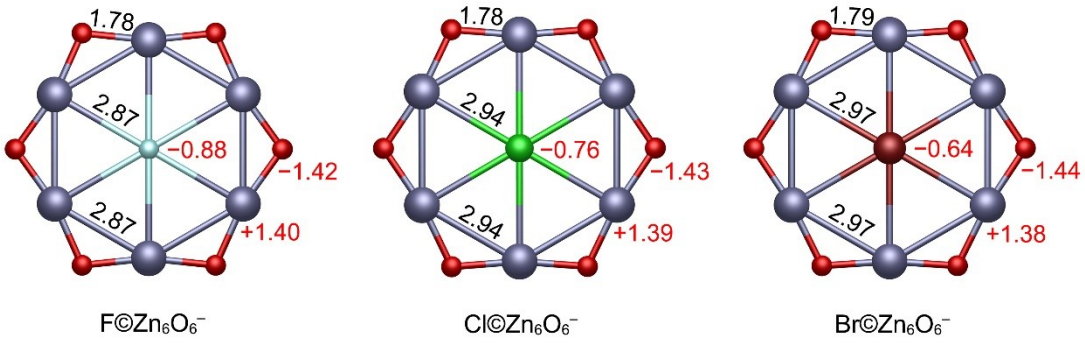


Figure S2. Bond distances (Å) and natural atomic charges (|e|, shown in red) for D_{6h} Cl©$Zn_6O_6^-$ (X = F, Cl, Br) computed at the PBE0-D3(BJ)/aug-cc-pVTZ level.

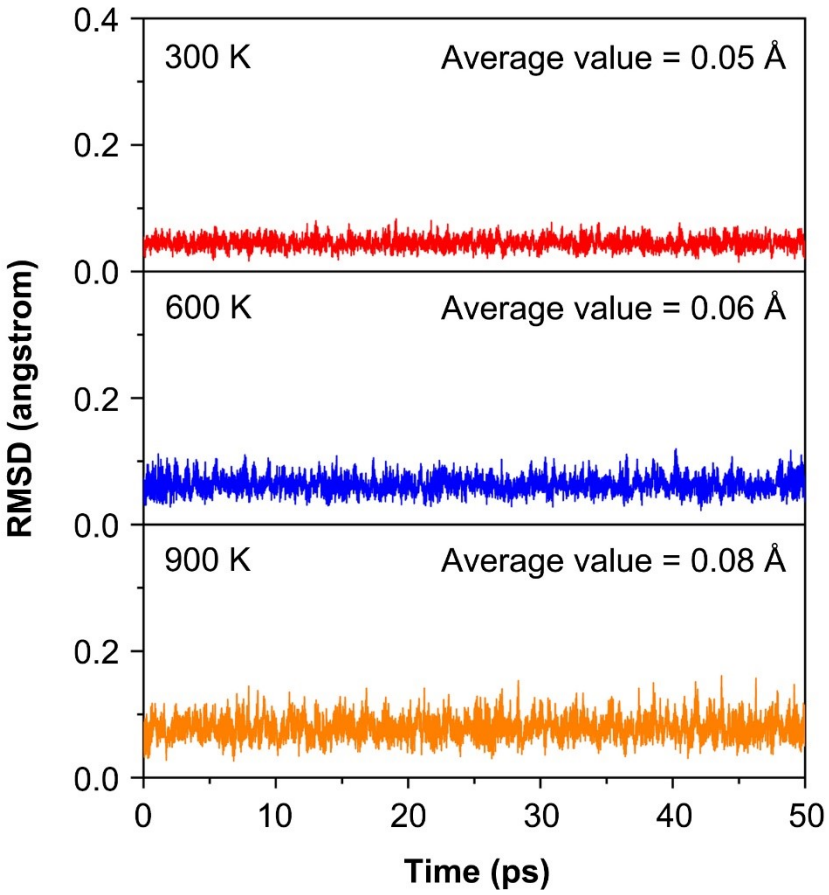


Figure S3. Root-mean-square deviation (RMSD) as a function of time during 50 ps Born–Oppenheimer molecular dynamic simulations at 300, 600, and 900 K.

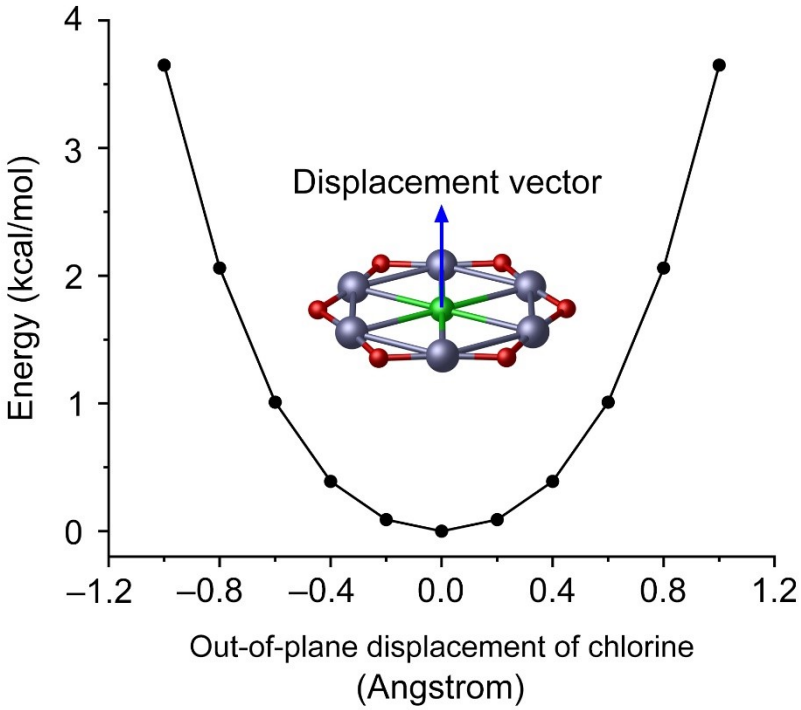
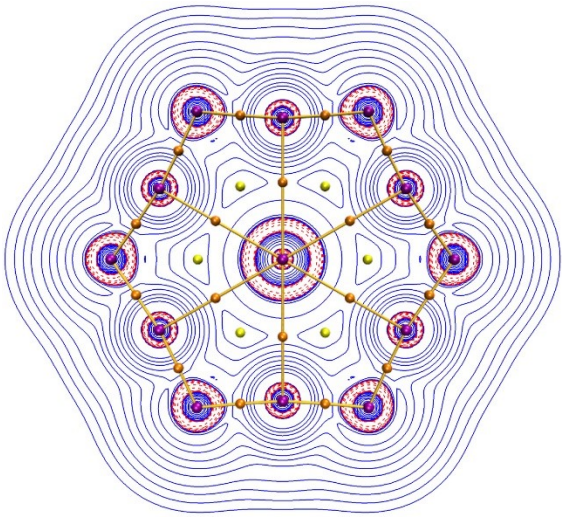


Figure S4. Potential energy curve for out-of-plane displacement of the central chlorine atom.



1 Cl©$Zn_6O_6^-$ (D_{6h}, $^1A_{1g}$)

Figure S5. Laplacian of the electron density, bond paths, and critical points for Cl©$Zn_6O_6^-$. Regions of charge concentration ($\nabla^2\rho(r) < 0$) are shown in red, whereas charge depletion ($\nabla^2\rho(r) > 0$) is shown in blue. Bond paths are depicted as brown lines; bond and ring critical points are indicated by brown and yellow dots, respectively.

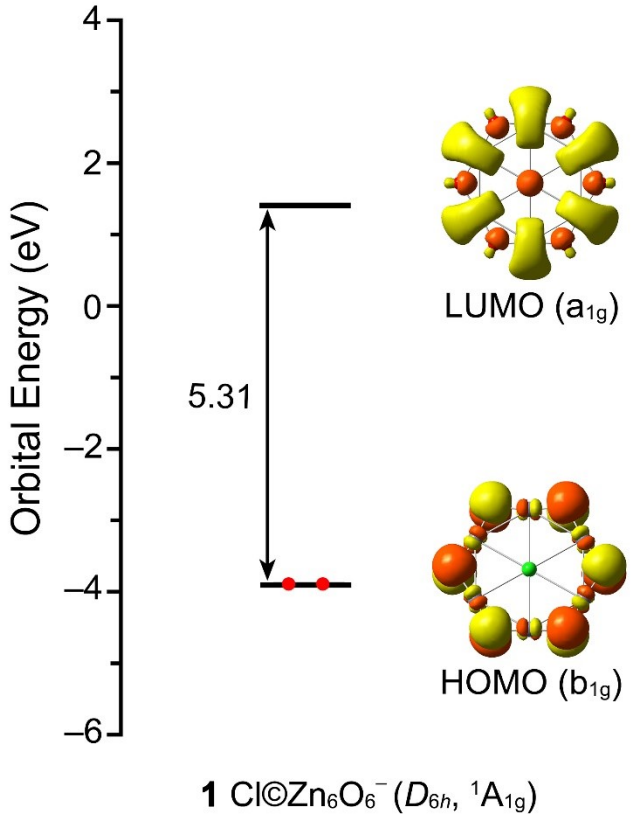


Figure S6. HOMO, LUMO, and HOMO–LUMO gap of **1**.

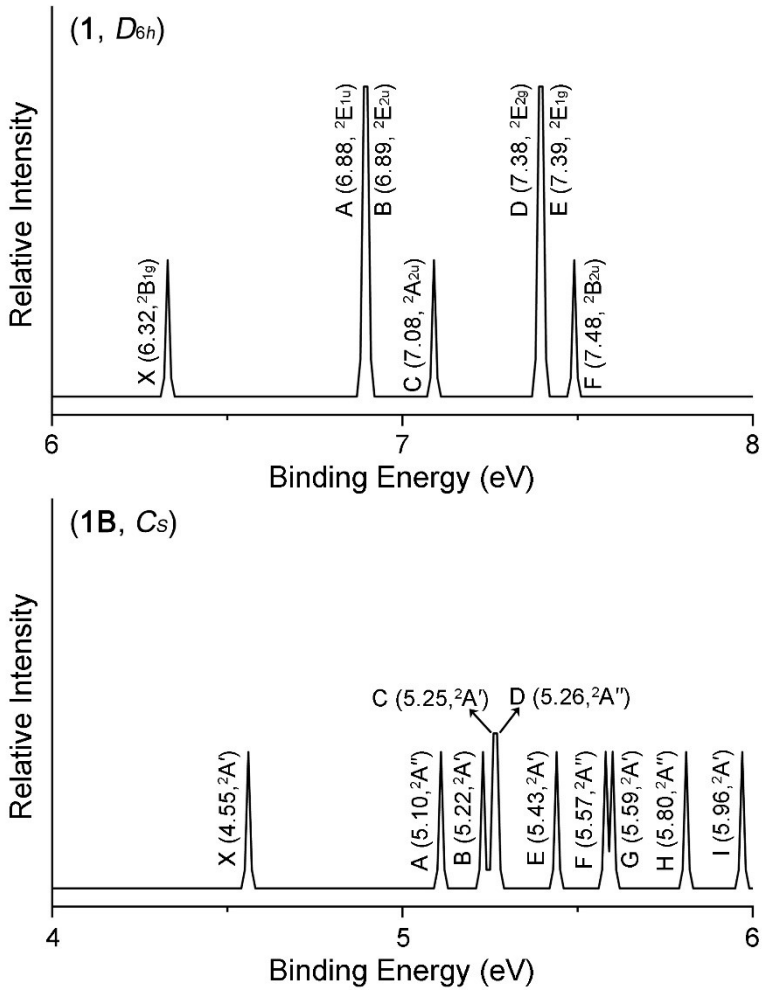


Figure S7. Photoelectron spectra of **1** and **1B** computed at the TD-PBE0/aug-cc-pVTZ level. The spectra were simulated by fitting the distributions of calculated vertical detachment energies (VDEs) with unit-area Gaussian functions with a half-width of 0.01 eV.

Cartesian coordinates of the eight lowest-energy isomers of Cl©$Zn_6O_6^-$ at the PBE0-D3(BJ)/aug-cc-pVTZ level.

1 (D_{6h}, $^1A_{1g}$)

Cl	0.00000000	0.00000000	0.00000000
Zn	0.00000000	2.94676000	0.00000000
Zn	-2.55196900	1.47338000	0.00000000
Zn	2.55196900	1.47338000	0.00000000
Zn	2.55196900	-1.47338000	0.00000000
Zn	0.00000000	-2.94676000	0.00000000
Zn	-2.55196900	-1.47338000	0.00000000
O	-3.55059900	0.00000000	0.00000000
O	-1.77529900	3.07490900	0.00000000
O	1.77529900	3.07490900	0.00000000
O	3.55059900	0.00000000	0.00000000
O	1.77529900	-3.07490900	0.00000000
O	-1.77529900	-3.07490900	0.00000000

1B (C_s, $^1A'$)

Cl	2.75811800	3.30697200	0.00000000
Zn	-1.26322200	0.62264900	1.35944100
Zn	-1.22590100	-2.02404700	0.00000000
Zn	-1.26322200	0.62264900	-1.35944100
Zn	0.72841900	-1.11254000	1.46002400
Zn	1.34397500	1.63045900	0.00000000
Zn	0.72841900	-1.11254000	-1.46002400
O	-1.26322200	-1.31353700	1.73854100
O	-1.26322200	-1.31353700	-1.73854100
O	-2.10358100	1.53860900	0.00000000
O	0.88988200	-2.31133500	0.00000000
O	0.72369600	0.76131500	1.59993800
O	0.72369600	0.76131500	-1.59993800

1C (C_s, $^1A'$)

Cl	2.73377000	2.20898600	0.00000000
Zn	0.47128400	2.54060200	0.00000000
Zn	1.70081800	-0.05159300	0.00000000
Zn	-2.17077000	2.76071800	0.00000000
Zn	-1.89275900	-0.08058600	0.00000000
Zn	-0.84448200	-3.06925500	0.00000000
Zn	1.88253800	-2.90959300	0.00000000
O	2.86860300	-1.44781700	0.00000000
O	-0.77819000	3.88158200	0.00000000

O	-3.15168400	1.30128500	0.00000000
O	-2.14525100	-1.91570100	0.00000000
O	0.59739900	-4.13815000	0.00000000
O	0.00000000	0.66111000	0.00000000

1D (C_s, ^{1}A′)

Cl	3.00828900	-3.56455900	0.00000000
Zn	1.18803900	-2.41566000	0.00000000
Zn	0.05270500	-0.16570700	2.30634600
Zn	-0.67952100	2.33702900	1.33115700
Zn	-1.05040000	-0.94013300	0.00000000
Zn	0.05270500	-0.16570700	-2.30634600
Zn	-0.67952100	2.33702900	-1.33115700
O	-1.35744200	0.84041000	0.00000000
O	0.05270500	-1.76067800	1.42394000
O	-0.13447600	1.48228100	2.89320200
O	-0.68665000	3.59038000	0.00000000
O	-0.13447600	1.48228100	-2.89320200
O	0.05270500	-1.76067800	-1.42394000

1E (C_s, ^{1}A′)

Cl	-3.94152500	-0.39255000	0.00000000
Zn	0.24766600	-1.57550200	1.36725700
Zn	0.99924300	0.81267100	2.41633600
Zn	0.70761100	2.14786400	0.00000000
Zn	0.99924300	0.81267100	-2.41633600
Zn	0.24766600	-1.57550200	-1.36725700
Zn	-1.81553200	-0.62128000	0.00000000
O	-0.09887600	0.15990200	0.00000000
O	0.99924300	-0.92972100	2.86487800
O	-0.72545300	-2.40318500	0.00000000
O	0.99924300	-0.92972100	-2.86487800
O	1.00223400	2.46671700	-1.78714200
O	1.00223400	2.46671700	1.78714200

1F (C_s, ^{1}A′)

Cl	1.91380000	3.79569700	0.00000000
Zn	0.62469900	2.01780900	0.00000000
Zn	0.20371600	-0.20748000	1.63205600
Zn	1.45313500	-1.84114200	0.00000000
Zn	-1.18727300	-2.04688800	0.00000000
Zn	-1.84304900	0.73397900	0.00000000
Zn	0.20371600	-0.20748000	-1.63205600
O	-0.66186800	1.41059900	1.43562400

O	0.20371600	-2.10126200	1.46862400
O	1.53714000	0.07308500	0.00000000
O	-2.64370100	-0.94060700	0.00000000
O	0.20371600	-2.10126200	-1.46862400
O	-0.66186800	1.41059900	-1.43562400

1G (C_{5v}, $^1A_1$)

Cl	0.00000000	0.00000000	3.88811943
O	-2.89763908	0.94150001	-0.66191004
O	0.00000000	3.04675803	-0.66191004
O	2.89763908	0.94150001	-0.66191004
O	0.00000000	0.00000000	0.02126988
O	1.79083944	-2.46487902	-0.66191004
O	-1.79083944	-2.46487902	-0.66191004
Zn	-1.39755552	1.92357015	-0.62231677
Zn	-2.26129233	-0.73473842	-0.62231677
Zn	0.00000000	-2.37766346	-0.62231677
Zn	1.39755552	1.92357015	-0.62231677
Zn	0.00000000	0.00000000	1.78567134
Zn	2.26129233	-0.73473842	-0.62231677

1H (C_s, $^1A'$)

Cl	0.53368700	3.65113800	0.00000000
Zn	-1.82615000	0.96497700	1.29585600
Zn	-1.82615000	0.96497700	-1.29585600
Zn	0.90252900	-2.99730700	0.00000000
Zn	0.83915000	1.48502000	0.00000000
Zn	0.80975300	-0.85350000	1.58991100
Zn	0.80975300	-0.85350000	-1.58991100
O	0.80975300	-2.70373400	-1.76049900
O	0.80975300	-2.70373400	1.76049900
O	1.74778000	-0.15607000	0.00000000
O	-0.16821900	0.76859000	1.88794900
O	-3.07324800	1.10268500	0.00000000
O	-0.16821900	0.76859000	-1.88794900