Structure and Stability of Small Lithium-Chloride $Li_nCl_m^{(0,+1)}$ ($n \geq m$, n = 1-6, m = 1-3) Clusters

Milan Milovanović [*a)], *Suzana Veličković* [b)], *Filip Veljković* [b)], *Stanka Jerosimić* [a)]

[a)] University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12-16, P.O.Box 47, PAC 105305, 11158 Belgrade, Republic of Serbia

[b)] University of Belgrade - Vinča Institute of Nuclear Sciences P. O. Box 522, 11001 Belgrade, Republic of Serbia

Table S1. Bond lengths of $LiCl^{(0,+1)}$ (in angstroms) calculated with B3LYP and coupled-cluster methods, in different basis sets.

Table S2. Bond lengths (C_{2v} point group) of Li_2Cl (in angstroms) and the Li-Cl-Li angle (in degrees) calculated with B3LYP and coupled-cluster methods, in different basis sets.

Table S3. Geometrical parameters (D_{2h} point group) of Li_2Cl_2: bond lengths (in angstroms) and angles (in degrees) calculated with B3LYP and coupled-cluster methods in different basis sets.

Table S4. The range of heater's temperature and the range of intensities of the most abundant isotope for Li^+, Li_nCl^+ (n = 2-6), and $Li_nCl_{n-1}^+$ (n = 3-5).

Table S5. Relative energies (that include zero-point vibrational energies *ZPVE*), *ZPVE*, and low/imaginary frequencies of the neutral clusters at B3LYP/ cc-pVQZ level. ΔE and *ZPVE* are in kJ mol^{-1}, frequencies in cm^{-1}.

Table S6. Relative energies (that include zero-point vibrational energies *ZPVE*), *ZPVE*, and low/imaginary frequencies of the cationic clusters at B3LYP/ cc-pVQZ level. ΔE and *ZPVE* are in kJ mol^{-1}, frequencies in cm^{-1}.

Table S7. The occupation numbers of valence *s* and *p* natural atomic orbitals in the molecular environment for all chlorine and lithium atoms.

Figure S1. The charge distribution and the highest occupied NBO for cationic Li_nCl_m clusters.

Table S1. Bond lengths of $LiCl^{(0,+1)}$ (in angstroms) calculated with B3LYP and coupled-cluster methods, in different basis sets.

		Bond length				
	Basis set / Method	B3LYP	RCCSD[a)]	RCCSD(T)[a)]	RCCSD	RCCSD(T)
LiCl	cc-pVTZ	2.023	2.041	2.043	2.029	2.029
	cc-pVQZ	2.021	2.038	2.040	2.021	2.021
	aug-cc-pVTZ	2.024	2.046	2.049	2.026	2.029
	aug-cc-pVQZ	2.021	2.040	2.043	2.018	2.021
	cc-pwCVTZ	2.018	2.034	2.035	2.021	2.021
	cc-pwCVQZ	2.021	2.035	2.037	2.019	2.021
	aug-cc-pwCVTZ	2.021	2.040	2.043	2.026	2.028
	aug-cc-pwCVQZ	2.021	2.038	2.040	2.021	2.023
	Experimental	2.021 [b)]				
$LiCl^+$	cc-pVTZ	2.395	2.419	2.420	2.397	2.398
	cc-pVQZ	2.382	2.412	2.414	2.382	2.382
	aug-cc-pVTZ	2.390	2.422	2.425	2.382	2.382
	aug-cc-pVQZ	2.382	2.414	2.417	2.367	2.368
	cc-pwCVTZ	2.382	2.413	2.414	2.392	2.392
	cc-pwCVQZ	2.382	2.409	2.411	2.382	2.382
	aug-cc-pwCVTZ	2.382	2.416	2.419	2.394	2.396
	aug-cc-pwCVQZ	2.382	2.412	2.415	2.382	2.383

a) Coupled cluster methods that include the correlation of only valence electrons.
b) Rounded value from Ref.[75]

Table S2. Bond length (C_{2v} point group) of Li_2Cl (in angstroms) and the Li-Cl-Li angle (in degrees) calculated with B3LYP and coupled-cluster methods, in different basis sets.

		Li-Cl Bond length				
	Basis set / Method	B3LYP	RCCSD[a)]	RCCSD(T)[a)]	RCCSD	RCCSD(T)
Li_2Cl	cc-pVTZ	2.178	2.198	2.199	2.180	2.181
	cc-pVQZ	2.173	2.192	2.194	2.170	2.172
	aug-cc-pVTZ	2.177	2.201	2.204	2.175	2.177
	aug-cc-pVQZ	2.174	2.194	2.196	2.164	2.165
	cc-pwCVTZ	2.173	2.191	2.192	2.176	2.177
	cc-pwCVQZ	2.173	2.189	2.191	2.171	2.172
	aug-cc-pwCVTZ	2.174	2.195	2.198	2.178	2.181
	aug-cc-pwCVQZ	2.174	2.191	2.194	2.173	2.174
		Angle Li–Cl–Li				
	cc-pVTZ	76.1	74.7	74.7	74.0	74.0
	cc-pVQZ	76.3	75.0	75.0	73.2	73.2
	aug-cc-pVTZ	76.3	74.8	74.8	74.2	74.3
	aug-cc-pVQZ	76.3	75.0	75.0	73.6	73.6
	cc-pwCVTZ	76.3	74.8	74.9	74.5	74.6
	cc-pwCVQZ	76.4	75.0	75.0	74.8	74.8
	aug-cc-pwCVTZ	76.2	74.9	74.9	74.7	74.6
	aug-cc-pwCVQZ	76.4	75.0	75.0	74.7	74.7

Table S3. Geometrical parameters (D_{2h} point group) of Li_2Cl_2: bond lengths (in angstroms) and angles (in degrees) calculated with B3LYP and coupled-cluster methods in different basis sets.

	Bond Li–Cl	Bond Cl–Cl	Angle Cl–Li–Cl
B3LYP/cc-pVTZ	2.202	3.592	109.3
B3LYP/aug-cc-pVTZ	2.201	3.587	109.2
B3LYP/cc-pVQZ	2.198	3.582	109.2
RCCSD(T)/cc-pwCVTZ	2.194	3.564	108.6
Experimental [a)]	2.23 ± 0.03	3.61 ± 0.03	108 ± 4
[a)] Ref.[77]			

Table S4. The range of heater's temperature and the range of intensities of the most abundant isotope for Li^+, Li_nCl^+ (n = 2-6), and $Li_nCl_{n-1}^+$ (n = 3-5).

Ion clusters	The range of heater's temperature (K)	The range of intensity of cluster ions (a. u.)
Li^+	1800 – 2700	400.000 – 1.450.000
Li_2Cl^+	1837 – 2676	2500 – 192.000
Li_3Cl^+	2283 – 2445	1400 – 16000
Li_4Cl^+	2157 – 2385	1680 – 16200
Li_5Cl^+	2285 – 2445	800 – 14000
Li_6Cl^+	1895 – 2155	7000 – 50.000
$Li_3Cl_2^+$	1953 – 2576	2300 – 180.000
$Li_4Cl_3^+$	1953 – 2272	1350 – 6150
$Li_5Cl_4^+$	2184 – 2418	1350 - 5000

Table S5. Relative energies (that include zero-point vibrational energies *ZPVE*), *ZPVE*, and low/imaginary frequencies of the neutral clusters at B3LYP/ cc-pVQZ level. ΔE and *ZPVE* are in kJ mol^{-1}, frequencies in cm^{-1}.

Species	Label	ΔE	*ZPVE*	Low / imaginary frequencies
LiCl	**1.1.n.1** ($C_{\infty v}$, $^1\Sigma^+$)	0.0	3.84	/
Li_2Cl	**2.1.n.1** (C_{2v}, $^2A_1$)	0.0	6.89	/
	2.1.n.2	77.3	4.52	/
Li_3Cl	**3.1.n.1** (C_{2v}, $^1A_1$)	0.0	10.71	/
	3.1.n.2	55.0	9.27	/
Li_4Cl	**4.1.n.1** (C_s, $^2A'$)	0.0	12.91	/
	4.1.n.2	12.9	12.73	26*i*
Li_5Cl	**5.1.n.1** (C_{2v}, $^1A_1$)	0.0	16.12	/
	5.1.n.2	16.4	16.98	/
Li_6Cl	**6.1.n.1** (C_s, $^2A'$)	0.0	20.64	/
	6.1.n.2	20.0	19.96	/
	6.1.n.3	22.7	19.42	/
Li_2Cl_2	**2.2.n.1** (D_{2h}, ^1A_g)	0.0	13.18	/
Li_3Cl_2	**3.2.n.1** (C_{2v}, $^2A_1$)	0.0	15.20	/
	3.2.n.2	12.8	14.38	37
	3.2.n.3	39.3	14.50	/
Li_4Cl_2	**4.2.n.1** (C_{2v}, $^1A_1$)	0.0	18.29	/
	4.2.n.2	24.0	18.97	/
	4.2.n.3	26.9	19.35	/
	4.2.n.4	37.6	18.10	/
Li_5Cl_2	**5.2.n.1** (C_s, $^2A'$)	0.0	22.82	/
	5.2.n.2	10.2	21.34	24
	5.2.n.3	10.9	21.69	27
	5.2.n.4	11.9	21.35	/
	5.2.n.5	12.3	20.82	45
	5.2.n.6	13.2	19.66	32
	5.2.n.7	16.2	21.28	23, 45
	5.2.n.8	18.9	21.74	/
	5.2.n.9	19.6	19.81	/
	5.2.n.10	29.0	19.51	18*i*
	5.2.n.11	29.8	19.19	21, 42
Li_3Cl_3	**3.3.n.1** (D_{3h}, $^1A_1'$)	0.0	20.23	/
	3.3.n.2	52.0	20.44	/
Li_4Cl_3	**4.3.n.1** (C_{3v}, $^2A_1$)	0.0	25.12	/
	4.3.n.2	16.7	21.74	39
	4.3.n.3	28.0	22.36	24
	4.3.n.4	29.3	21.32	21*i*
	4.3.n.5	29.8	21.99	15
	4.3.n.6	55.6	23.31	/

Table S6. Relative energies (that include zero-point vibrational energies *ZPVE*), *ZPVE*, and low/imaginary frequencies of the cationic clusters at B3LYP/ cc-pVQZ level. Δ*E* and *ZPVE* are in kJ mol^{-1}, frequencies in cm^{-1}.

Species	Label	Δ*E* [a)]	*ZPVE* [a)]	Low / imaginary frequencies
$LiCl^+$	**1.1.c.1** ($C_{\infty v}$, $^2\Pi$)	0.0	2.00	/
Li_2Cl^+	**2.1.c.1** ($D_{\infty h}$, $^1\sum_g^+$)	0.0	5.99	48, 48
Li_3Cl^+	**3.1.c.1** (C_1, ^2A)	0.0	7.21	34
	3.1.c.2	29.5	9.00	/
Li_4Cl^+	**4.1.c.1** (C_{3v}, $^1A_1$)	0.0	14.41	/
	4.1.c.2	7.9	10.63	29, 33, 47
	4.1.c.3	9.8	11.91	35
	4.1.c.4	120.9	8.12	31, 31
Li_5Cl^+	**5.1.c.1** (C_s, $^2A'$)	0.0	16.66	/
	5.1.c.2	31.2	14.13	34
	5.1.c.3	34.4	12.44	14, 15, 41
	5.1.c.4	43.3	12.14	19, 36, 38, 41
	5.1.c.5	45.3	13.18	34, 50
Li_6Cl^+	**6.1.c.1** (C_s, $^1A'$)	0.0	20.75	/
	6.1.c.2	9.6	19.87	47
	6.1.c.3	29.2	17.80	31, 31
	6.1.c.4	40.8	15.35	14, 14, 18, 46, 46
	6.1.c.5	50.7	17.58	28
	6.1.c.6	67.3	15.30	14, 19, 22, 24, 37
$Li_2Cl_2^+$	**2.2.c.1** (D_{2h}, $^2B_{1u}$)	0.0	8.90	34
	2.2.c.2	48.0	7.59	24, 28
$Li_3Cl_2^+$	**3.2.c.1** ($D_{\infty h}$, $^1\sum_g^+$)	0.0	12.00	20, 21, 30, 30
	3.2.c.2	9.2	16.85	/
	3.2.c.3	11.5	14.57	43
$Li_4Cl_2^+$	**4.2.c.1** (C_s, $^2A'$)	0.0	18.77	/
	4.2.c.2	20.6	16.34	17, 27
	4.2.c.3	27.4	13.79	4, 4, 20, 20
	4.2.c.4	31.1	13.89	12, 27, 31, 34
	4.2.c.5	34.7	13.61	14, 14, 21, 21, 41, 41
	4.2.c.6	40.1	16.21	31
	4.2.c.7	50.6	15.82	39
	4.2.c.8	63.0	13.50	28, 31, 35, 38
$Li_5Cl_2^+$	**5.2.c.1** (C_s, $^1A'$)	0.0	23.30	/
	5.2.c.2	39.4	18.12	11, 26, 29, 32
	5.2.c.3	51.0	20.00	25, 28
	5.2.c.4	54.0	19.84	36, 42
	5.2.c.5	54.3	17.14	4, 7, 18, 19, 41
	5.2.c.6	55.4	20.83	23, 44, 46
	5.2.c.7	59.2	19.55	/
	5.2.c.8	59.6	19.75	29, 30, 46
	5.2.c.9	70.8	19.29	41, 47
	5.2.c.10	73.3	21.09	/

	5.2.c.11	76.8	16.98	19, 22, 27, 31, 38
$Li_3Cl_3^+$	**3.3.c.1** (C_s, $^2A''$)	0.0	18.94	/
	3.3.c.2	4.6	14.37	17, 24, 30, 45
	3.3.c.3	11.2	16.56	30
	3.3.c.4	12.3	16.93	34
	3.3.c.5	63.2	16.08	4*i*, 7
$Li_4Cl_3^+$	**4.3.c.1** (C_{3v}, $^1A_1$)	0.0	25.22	/
	4.3.c.2	51.9	20.41	11, 17, 29, 31
	4.3.c.3	56.0	22.11	29*i*, 43
	4.3.c.4	64.5	18.17	12, 16, 19, 22, 26
	4.3.c.5	75.5	22.52	27, 27

Table S7. The occupation numbers of valence *s* and *p* natural atomic orbitals in the molecular environment for all chlorine and lithium atoms.

Li_nCl_m	∑Cl (3*s*)	∑Cl (3*p*)	∑Cl (3*s* + 3*p*)	Ideal ∑Cl	∑ Li (2*s*)	∑ Li (2*p*)	∑ Li (2*s* + 2*p*)	Ideal∑Li
LiCl	1.99	5.92	7.91	8	0.03	0.04	0.07	0
Li_2Cl	1.98	5.91	7.89	8	0.88	0.16	1.04	1
Li_3Cl	1.96	5.93	7.89	8	1.99	0.21	2.2	2
Li_4Cl	1.96	5.93	7.89	8	2.76	0.31	3.07	3
Li_5Cl	1.95	5.93	7.88	8	3.78	0.29	4.07	4
Li_6Cl	1.95	5.92	7.87	8	4.44	0.59	5.03	5
…								
Li_2Cl_2	3.96	11.80	15.76	16	0.16	0.06	0.22	0
Li_3Cl_2	3.94	11.82	15.76	16	0.98	0.19	1.17	1
Li_4Cl_2	3.92	11.84	15.76	16	2.01	0.19	2.20	2
Li_5Cl_2	3.92	11.82	15.74	16	2.69	0.47	3.16	3
…								
Li_3Cl_3	5.91	17.70	23.61	24	0.24	0.06	0.30	0
Li_4Cl_3	5.88	17.70	23.58	24	1.02	0.17	1.19	1
…								
$LiCl^+$	2.00	4.94	6.94	7	0.02	0.04	0.06	0
Li_2Cl^+	1.99	5.96	7.95	8	0.02	0.02	0.04	0
Li_3Cl^+	1.98	5.96	7.94	8	0.90	0.15	1.05	1
Li_4Cl^+	1.96	5.89	7.85	8	1.72	0.33	2.05	2
Li_5Cl^+	1.96	5.90	7.86	8	2.53	0.60	3.13	3
Li_6Cl^+	1.95	5.91	7.86	8	3.48	0.58	4.06	4
…								
$Li_2Cl_2^+$	3.98	10.90	14.88	15	0.06	0.02	0.08	0
$Li_3Cl_2^+$	3.96	11.90	15.86	16	0.08	0.03	0.11	0
$Li_4Cl_2^+$	3.94	11.80	15.74	16	0.93	0.25	1.18	1
$Li_5Cl_2^+$	3.92	11.92	15.74	16	1.84	0.33	2.17	2
…								
$Li_3Cl_3^+$	5.93	16.75	22.68	23	0.18	0.04	0.22	0
$Li_4Cl_3^+$	5.91	17.70	23.61	24	0.26	0.06	0.32	0
…								

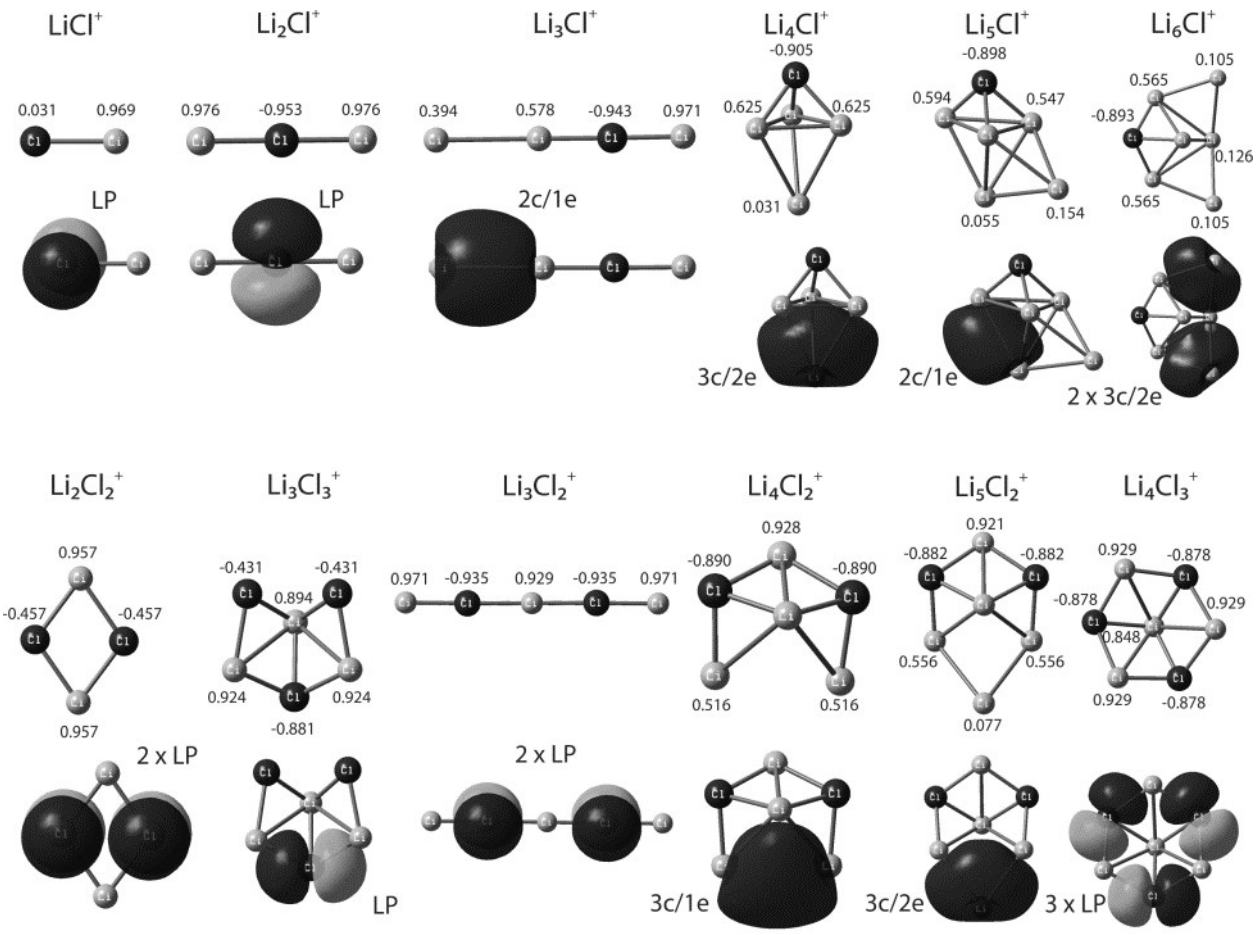

Figure S1. The charge distribution and the highest occupied NBO for cationic Li_nCl_m clusters.