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SUPPORTING INFORMATION

Octahedral Aromaticity in $^{2S+1}A_{1g}$ X_6^q Clusters (X = Li–C and Be–Si, S = 0–3, and q = -2–+4)

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Table S1. Cartesian coordinates of optimized $^{2S+1}A_{1g}$ X_6^q clusters that are minima in the potential energy surface.

$^4A_{1g}$ Li_6^+

3	0.000000	0.000000	2.126102
3	2.126102	0.000000	0.000000
3	0.000000	-2.126102	0.000000
3	-2.126102	0.000000	0.000000
3	0.000000	2.126102	0.000000
3	0.000000	0.000000	-2.126102

$^6A_{1g}$ Li_6^+

3	0.000000	0.000000	2.200515
3	2.200515	0.000000	0.000000
3	0.000000	-2.200515	0.000000
3	-2.200515	0.000000	0.000000
3	0.000000	2.200515	0.000000
3	0.000000	0.000000	-2.200515

$^1A_{1g}$ Na_6^{2-}

11	0.000000	0.000000	2.549470
11	2.549470	0.000000	0.000000
11	0.000000	-2.549470	0.000000
11	-2.549470	0.000000	0.000000
11	0.000000	2.549470	0.000000
11	0.000000	0.000000	-2.549470

$^7A_{1g}$ Na_6^{2-}

11	0.000000	0.000000	2.750779
11	2.750779	0.000000	0.000000
11	0.000000	-2.750779	0.000000
11	-2.750779	0.000000	0.000000
11	0.000000	2.750779	0.000000
11	0.000000	0.000000	-2.750779

$^4A_{1g}$ Na_6^+

11	0.000000	0.000000	2.546869
11	2.546869	0.000000	0.000000
11	0.000000	-2.546869	0.000000
11	-2.546869	0.000000	0.000000
11	0.000000	2.546869	0.000000
11	0.000000	0.000000	-2.546869

$^7A_{1g}$ Be_6^{2-}

4	0.000000	0.000000	1.505705
4	0.000000	1.505705	0.000000
4	1.505705	0.000000	0.000000
4	0.000000	-1.505705	0.000000
4	-1.505705	0.000000	0.000000
4	0.000000	0.000000	-1.505705

$^4A_{1g}$ Be_6^-

4	0.000000	0.000000	1.431286
4	0.000000	1.431286	0.000000
4	1.431286	0.000000	0.000000
4	0.000000	-1.431286	0.000000
4	-1.431286	0.000000	0.000000
4	0.000000	0.000000	-1.431286

$^5A_{1g}$ Be_6

4	0.000000	0.000000	1.442232
4	1.442232	0.000000	0.000000
4	0.000000	-1.442232	0.000000
4	-1.442232	0.000000	0.000000
4	0.000000	1.442232	0.000000
4	0.000000	0.000000	-1.442232

$^1A_{1g}$ Be_6^{2+}

4	0.000000	0.000000	1.509343
4	1.509343	0.000000	0.000000
4	0.000000	-1.509343	0.000000
4	-1.509343	0.000000	0.000000
4	0.000000	1.509343	0.000000
4	0.000000	0.000000	-1.509343

$^2A_{1g}$ Be_6^{3+}

4	0.000000	0.000000	1.603276
4	1.603276	0.000000	0.000000
4	0.000000	-1.603276	0.000000
4	-1.603276	0.000000	0.000000
4	0.000000	1.603276	0.000000
4	0.000000	0.000000	-1.603276

$^1A_{1g}$ Mg_6^{2-}

12	0.000000	0.000000	2.432066
12	2.432066	0.000000	0.000000
12	0.000000	-2.432066	0.000000
12	-2.432066	0.000000	0.000000
12	0.000000	2.432066	0.000000
12	0.000000	0.000000	-2.432066

$^7A_{1g}$ Mg_6^{2-}

12	0.000000	0.000000	2.189541
12	2.189541	0.000000	0.000000
12	0.000000	-2.189541	0.000000
12	-2.189541	0.000000	0.000000
12	0.000000	2.189541	0.000000
12	0.000000	0.000000	-2.189541

$^{1}A_{1g}$ Mg_6

12	0.000000	0.000000	2.617914
12	2.617914	0.000000	0.000000
12	0.000000	-2.617914	0.000000
12	-2.617914	0.000000	0.000000
12	0.000000	2.617914	0.000000
12	0.000000	0.000000	-2.617914

$^{3}A_{1g}$ Mg_6^{2+}

12	0.000000	0.000000	2.411867
12	2.411867	0.000000	0.000000
12	0.000000	-2.411867	0.000000
12	-2.411867	0.000000	0.000000
12	0.000000	2.411867	0.000000
12	0.000000	0.000000	-2.411867

$^{3}A_{1g}$ B_6

5	0.000000	0.000000	1.184608
5	1.184608	0.000000	0.000000
5	0.000000	-1.184608	0.000000
5	-1.184608	0.000000	0.000000
5	0.000000	1.184608	0.000000
5	0.000000	0.000000	-1.184608

$^{1}A_{1g}$ B_6^{2+}

5	0.000000	0.000000	1.150851
5	1.150851	0.000000	0.000000
5	0.000000	-1.150851	0.000000
5	-1.150851	0.000000	0.000000
5	0.000000	1.150851	0.000000
5	0.000000	0.000000	-1.150851

$^{2}A_{1g}$ B_6^{3+}

5	0.000000	0.000000	1.185606
5	1.185606	0.000000	0.000000
5	0.000000	-1.185606	0.000000
5	-1.185606	0.000000	0.000000
5	0.000000	1.185606	0.000000
5	0.000000	0.000000	-1.185606

$^{1}A_{1g}$ B_6^{4+}

5	0.000000	0.000000	1.234009
5	1.234009	0.000000	0.000000
5	0.000000	-1.234009	0.000000
5	-1.234009	0.000000	0.000000
5	0.000000	1.234009	0.000000
5	0.000000	0.000000	-1.234009

$^{1}A_{1g}$ Al_6^{2-}

13	0.000000	0.000000	1.916201
13	1.916201	0.000000	0.000000
13	0.000000	-1.916201	0.000000
13	-1.916201	0.000000	0.000000
13	0.000000	1.916201	0.000000
13	0.000000	0.000000	-1.916201

$^{7}A_{1g}$ Al_6^{2-}

13	0.000000	0.000000	2.025754
13	2.025754	0.000000	0.000000
13	0.000000	-2.025754	0.000000
13	-2.025754	0.000000	0.000000
13	0.000000	2.025754	0.000000
13	0.000000	0.000000	-2.025754

$^{5}A_{1g}$ Al_6^{2+}

13	0.000000	0.000000	2.084238
13	2.084238	0.000000	0.000000
13	0.000000	-2.084238	0.000000
13	-2.084238	0.000000	0.000000
13	0.000000	2.084238	0.000000
13	0.000000	0.000000	-2.084238

$^{1}A_{1g}$ Si_6^{2-}

14	0.000000	0.000000	1.75681
14	1.756881	0.000000	0.00000
14	0.000000	-1.756881	0.00000
14	-1.756881	0.000000	0.00000
14	0.000000	1.756881	0.00000
14	0.000000	0.000000	-1.75681

$^{4}A_{1g}$ Si_6^{+}

14	0.000000	0.000000	1.740324
14	1.740324	0.000000	0.000000
14	0.000000	-1.740324	0.000000
14	-1.740324	0.000000	0.000000
14	0.000000	1.740324	0.000000
14	0.000000	0.000000	-1.740324

Table S2. Cartesian coordinates of optimized $^{2S+1}A_{1g}$ X_6^q clusters that are saddle-points in the potential energy surface. The number of imaginary frequencies is included.

$^{1}A_{1g}$ Li_6^{2-}

3	0.000000	0.000000	2.109438
3	2.109438	0.000000	0.000000
3	0.000000	-2.109438	0.000000
3	-2.109438	0.000000	0.000000
3	0.000000	2.109438	0.000000
3	0.000000	0.000000	-2.109438

Number of imaginary frequencies = 3

$^{5}A_{1g}$ Li_6

3	0.000000	0.000000	2.028595
3	2.028595	0.000000	0.000000
3	0.000000	-2.028595	0.000000
3	-2.028595	0.000000	0.000000
3	0.000000	2.028595	0.000000
3	0.000000	0.000000	-2.028595

Number of imaginary frequencies = 3

$^{5}A_{1g}$ Li_6^{2+}

3	0.000000	0.000000	2.505651
3	0.000000	2.505651	0.000000
3	0.000000	0.000000	-2.505651
3	0.000000	-2.505651	0.000000
3	-2.505651	0.000000	0.000000
3	2.505651	0.000000	0.000000

Number of imaginary frequencies = 3

$^{6}A_{1g}$ Na_6^{-}

11	0.000000	0.000000	2.794959
11	2.794959	0.000000	0.000000
11	0.000000	-2.794959	0.000000
11	-2.794959	0.000000	0.000000
11	0.000000	2.794959	0.000000
11	0.000000	0.000000	-2.794959

Number of imaginary frequencies = 2

$^{5}A_{1g}$ Na_6^{2+}

11	0.000000	0.000000	3.024430
11	3.024430	0.000000	0.000000
11	0.000000	-3.024430	0.000000
11	-3.024430	0.000000	0.000000
11	0.000000	3.024430	0.000000
11	0.000000	0.000000	-3.024430

Number of imaginary frequencies = 3

$^{4}A_{1g}$ Be_6^{1+}

4	0.000000	0.000000	1.473887
4	1.473887	0.000000	0.000000
4	0.000000	-1.473887	0.000000
4	-1.473887	0.000000	0.000000
4	0.000000	1.473887	0.000000
4	0.000000	0.000000	-1.473887

Number of imaginary frequencies = 3

$^{1}A_{1g}$ Be_6^{4+}

4	0.000000	0.000000	1.761753
4	1.761753	0.000000	0.000000
4	0.000000	-1.761753	0.000000
4	-1.761753	0.000000	0.000000
4	0.000000	1.761753	0.000000
4	0.000000	0.000000	-1.761753

Number of imaginary frequencies = 3

$^{7}A_{1g}$ Be_6^{4+}

4	0.000000	0.000000	1.750759
4	1.750759	0.000000	0.000000
4	0.000000	-1.750759	0.000000
4	-1.750759	0.000000	0.000000
4	0.000000	1.750759	0.000000
4	0.000000	0.000000	-1.750759

Number of imaginary frequencies = 3

$^{2}A_{1g}$ Mg_6^{-}

12	0.000000	0.000000	2.468836
12	2.468836	0.000000	0.000000
12	0.000000	-2.468836	0.000000
12	-2.468836	0.000000	0.000000
12	0.000000	2.468836	0.000000
12	0.000000	0.000000	-2.468836

Number of imaginary frequencies = 3

$^{4}A_{1g}$ Mg_6^{+}

12	0.000000	0.000000	2.261198
12	2.261198	0.000000	0.000000
12	0.000000	-2.261198	0.000000
12	-2.261198	0.000000	0.000000
12	0.000000	2.261198	0.000000
12	0.000000	0.000000	-2.261198

Number of imaginary frequencies = 3

$^{1}A_{1g}$ Mg_6^{4+}

12	0.000000	0.000000	2.491603
12	2.491603	0.000000	0.000000
12	0.000000	-2.491603	0.000000
12	-2.491603	0.000000	0.000000
12	0.000000	2.491603	0.000000
12	0.000000	0.000000	-2.491603

Number of imaginary frequencies = 6

$^{1}A_{1g}$ B_6^{2-}

5	0.000000	0.000000	1.235567
5	1.235567	0.000000	0.000000
5	0.000000	-1.235567	0.000000
5	-1.235567	0.000000	0.000000
5	0.000000	1.235567	0.000000
5	0.000000	0.000000	-1.235567

Number of imaginary frequencies = 3

$^{7}A_{1g}$ B_6^{4+}

5	0.000000	0.000000	1.40017
5	1.400117	0.000000	0.00000
5	0.000000	-1.400117	0.00000
5	-1.400117	0.000000	0.00000
5	0.000000	1.400117	0.00000
5	0.000000	0.000000	-1.40017

Number of imaginary frequencies = 6

$^{7}A_{1g}$ Al_6^{4+}

13	0.000000	0.000000	2.084372
13	2.084372	0.000000	0.000000
13	0.000000	-2.084372	0.000000
13	-2.084372	0.000000	0.000000
13	0.000000	2.084372	0.000000
13	0.000000	0.000000	-2.084372

Number of imaginary frequencies = 3

$^{1}A_{1g}$ C_6^{2-}

6	0.000000	0.000000	1.135696
6	1.135696	0.000000	0.000000
6	0.000000	-1.135696	0.000000
6	-1.135696	0.000000	0.000000
6	0.000000	1.135696	0.000000
6	0.000000	0.000000	-1.135696

Number of imaginary frequencies = 3

$^{4}A_{1g}$ C_6^{+}

6	0.000000	0.000000	1.136705
6	1.136705	0.000000	0.000000
6	0.000000	-1.136705	0.000000
6	-1.136705	0.000000	0.000000
6	0.000000	1.136705	0.000000
6	0.000000	0.000000	-1.136705

Number of imaginary frequencies = 3

$^{6}A_{1g}$ C_6^{3+}

6	0.000000	0.000000	1.109483
6	1.109483	0.000000	0.000000
6	0.000000	-1.109483	0.000000
6	-1.109483	0.000000	0.000000
6	0.000000	1.109483	0.000000
6	0.000000	0.000000	-1.109483

Number of imaginary frequencies = 3

$^{1}A_{1g}$ C_6^{4+}

6	0.000000	0.000000	1.209339
6	1.209339	0.000000	0.000000
6	0.000000	-1.209339	0.000000
6	-1.209339	0.000000	0.000000
6	0.000000	1.209339	0.000000
6	0.000000	0.000000	-1.209339

Number of imaginary frequencies = 6

$^{7}A_{1g}$ C_6^{4+}

6	0.000000	0.000000	1.168386
6	1.168386	0.000000	0.000000
6	0.000000	-1.168386	0.000000
6	-1.168386	0.000000	0.000000
6	0.000000	1.168386	0.000000
6	0.000000	0.000000	-1.168386

Number of imaginary frequencies = 6

$^{7}A_{1g}$ Si_6^{2-}

14	0.000000	0.000000	1.786330
14	1.786330	0.000000	0.000000
14	0.000000	-1.786330	0.000000
14	-1.786330	0.000000	0.000000
14	0.000000	1.786330	0.000000
14	0.000000	0.000000	-1.786330

Number of imaginary frequencies = 6

$^{1}A_{1g}$ Si_6^{4+}

14	0.000000	0.000000	1.813384
14	1.813384	0.000000	0.000000
14	0.000000	-1.813384	0.000000
14	-1.813384	0.000000	0.000000
14	0.000000	1.813384	0.000000
14	0.000000	0.000000	-1.813384

Number of imaginary frequencies = 3

$^{7}A_{1g}$ Si_6^{4+}

14	0.000000	0.000000	2.171685
14	2.171685	0.000000	0.000000
14	0.000000	-2.171685	0.000000
14	-2.171685	0.000000	0.000000
14	0.000000	2.171685	0.000000
14	0.000000	0.000000	-2.171685

Number of imaginary frequencies = 6

Table S3. Linear **c**orrelation coefficients between the different computed indices including all the possible combinations.

r^2	MCI_6	MCI_4	MCI_3	$NICS(0)_6$	$NICS(0)_3$	PDI
MCI_6	1.00					
MCI_4	0.58	1.00				
MCI_3	0.33	0.31	1.00			
$NICS(0)_6$	0.37	0.71	0.30	1.00		
$NICS(0)_3$	0.20	0.66	0.26	0.88	1.00	
PDI	0.09	0.22	0.82	0.25	0.26	1.00

Table S4. Relative energies of Li_6^+, Na_6^{2-}, Mg_6^{2-} and Al_6^{2-} between two electronic states. Values in kcal/mol.

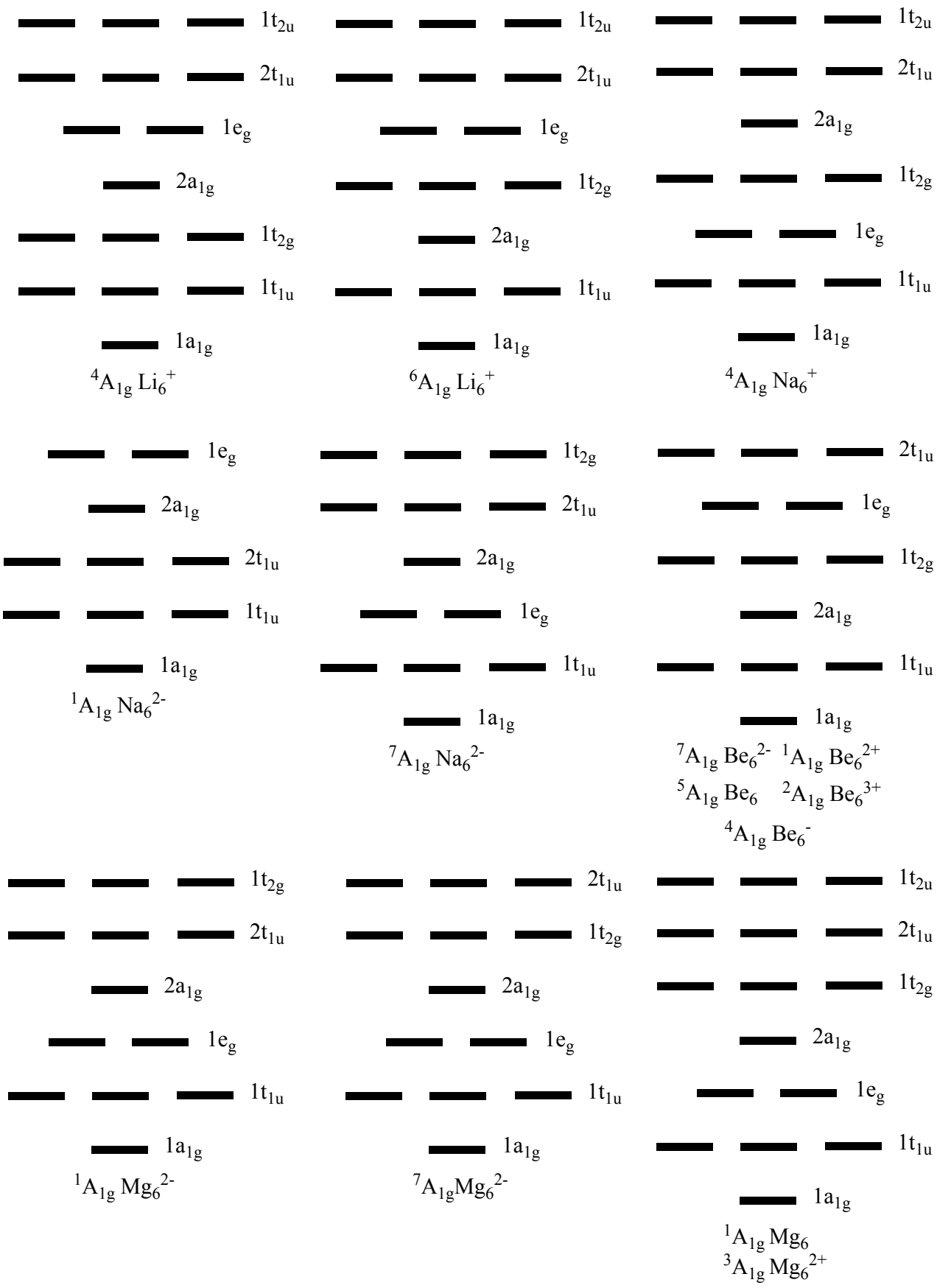
Electronic state	Li_6^+
$^4A_{1g}$	0.00
$^6A_{1g}$	62.3

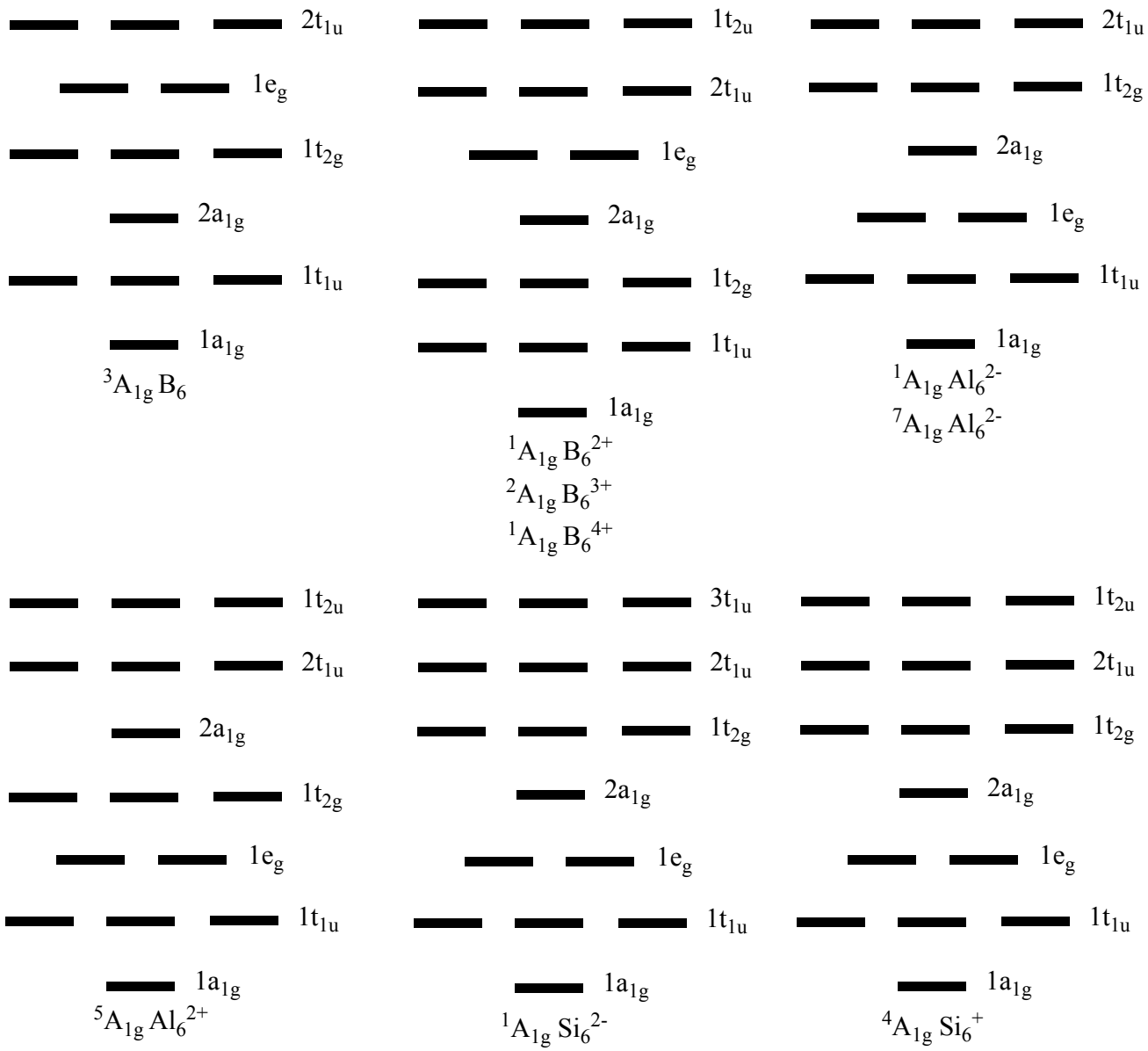
Electronic state	Na_6^{2-}	Mg_6^{2-}	Al_6^{2-}
$^1A_{1g}$	0.00	0.00	0.00
$^7A_{1g}$	40.5	35.2	44.7

Table S5. Molecular structures of octahedral clusters $^{2S+1}A_{1g}\,X_6^q$ that are saddle-points in the potential surface. Values of X−X bond distance in Å, MCI and PDI in electrons and NICS in ppm.

System	*q*	*Spin*	Electronic state	d(X–X)	MCI_6	MCI_4	MCI_3	$NICS(0)_6$	$NICS(0)_3$	PDI
Li_6	*-2*	S=0	$^1A_{1g}$	2.983	0.038	0.0466	0.0999	-13.18	-13.29	0.374
	0	S=2	$^5A_{1g}$	2.869	0.112	0.0538	0.0944	-24.00	-16.94	0.312
	2	S=2	$^5A_{1g}$	3.544	0.0245	0.0169	0.0240	-13.56	-10.84	0.197
Be_6	*1*	S=3/2	$^4A_{1g}$	2.084	0.043	0.0269	0.1396	126.80	112.94	0.548
	4	S=0	$^1A_{1g}$	2.491	0.049	0.0373	0.1090	-36.72	-29.11	0.391
	4	S=3	$^7A_{1g}$	2.476	0.055	0.0297	0.0908	-6.88	-2.50	0.391
B_6	*-2*	S=0	$^1A_{1g}$	1.747	0.059	0.057	0.153	-102.72	-85.49	0.744
	4	S=3	$^7A_{1g}$	1.980	0.059	0.051	0.120	-71.07	-57.80	0.545
C_6	*-2*	S=0	$^1A_{1g}$	1.606	0.032	0.034	0.159	-24.10	-48.37	0.786
	1	S=3/2	$^4A_{1g}$	1.608	0.050	0.046	0.148	-63.03	-70.53	0.742
	3	S=5/2	$^6A_{1g}$	1.569	0.072	0.049	0.169	-15.49	-27.90	0.771
	4	S=0	$^1A_{1g}$	1.710	0.072	0.069	0.124	-110.45	-91.27	0.688
	4	S=3	$^7A_{1g}$	1.652	0.033	0.028	0.144	3.29	-12.10	0.704
Na_6	*-1*	S=5/2	$^6A_{1g}$	3.953	0.041	0.022	0.040	3.65	5.91	0.227
	2	S=2	$^7A_{1g}$	4.277	0.017	0.019	0.040	-14.28	-11.00	0.167
Mg_6	*-1*	S=1/2	$^{21}A_{1g}$	3.491	0.030	0.018	0.054	16.05	17.45	0.337
	1	S=3/2	$^4A_{1g}$	3.198	0.046	0.034	0.081	-2.37	2.84	0.363
	4	S=0	$^1A_{1g}$	3.524	0.030	0.039	0.073	-32.40	-25.37	0.317
Al_6	*4*	S=3	$^7A_{1g}$	2.948	0.061	0.067	0.093	-58.73	-47.15	0.484
Si_6	*-2*	S=3	$^7A_{1g}$	2.526	0.055	0.052	0.131	65.41	65.76	0.818
	4	S=0	$^1A_{1g}$	2.565	0.086	0.092	0.111	54.74	38.28	0.649
	4	S=3	$^7A_{1g}$	3.071	0.059	0.027	0.107	3.85	-0.98	0.508

Figure S1. Energetic order of molecular orbitals for studied O_h $^{2S+1}A_{1g}$ X_6^q clusters that are minima (Table S1).

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1t2g
2a1g
1t1u
1a1g
3A1g B6
1t2u
2t1u
1eg
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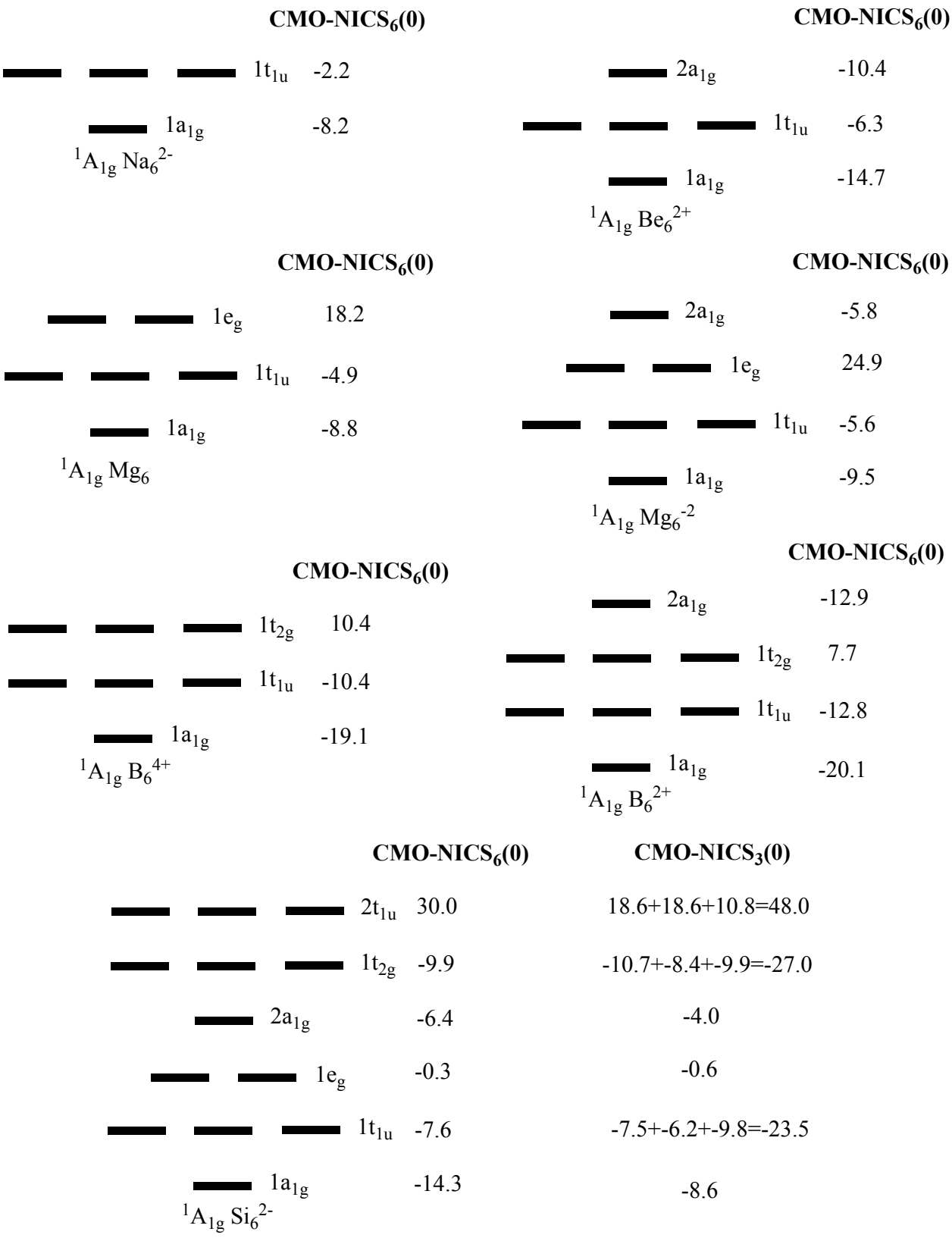
1t2g
1t1u
1a1g
1A1g B6 2+
2A1g B6 3+
1A1g B6 4+
2t1u
1t2g
2a1g
1eg
1t1u
1a1g
1A1g Al6 2-
7A1g Al6 2-
1t2u
2t1u
2a1g
1t2g
1eg
1t1u
1a1g
5A1g Al6 2+
3t1u
2t1u
1t2g
2a1g
1eg
1t1u
1a1g
1A1g Si6 2-
1t2u
2t1u
1t2g
2a1g
1eg
1t1u
1a1g
4A1g Si6 +

Figure S2. CMO-NICS for Na_6^{2-}, Be_6^{2+} [a], Mg_6^{2-}, Mg_6, B_6^{2+}, B_6^{4+}, Al_6^{2-} and Si_6^{2-} [a] in the $^1A_{1g}$ electronic state. Contributions of the core molecular orbitals are not included.



[a] CMO-NICS for $Si_6^{2-}$and Be_6^{2+} were computed using 6-311++G and aug-cc-pVQZ basis sets, respectively, due to technical problems experienced by the NBO 6.0 program when the 6-311++G(3df,3pd) basis set is used. Si_6^{2-} ($NICS(0)_3$=-10.2 and $NICS(0)_6$=14.6) – Be_6^{2+} ($NICS(0)_3$=-37.1 and $NICS(0)_6$=-50.3).