Supporting information of

Planar Pentacoordinate *s*-Block Metals

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Table S1. The lowest vibrational frequencies in cm^{-1} and the number of the imaginary frequencies in parentheses for the D_{5h} structures of the AM_5 (A and M are alkali metals) clusters at the PBE0-D3/def2-QZVPP level.

AM_5	Frequencies				
A / M	Li	Na	K	Rb	Cs
Li	77*i* (1)	75*i* (1)	121*i* (5)	148*i* (5)	178*i* (5)
Na	**24**	41*i* (1)	54*i* (3)	50*i* (3)	77*i* (5)
K	**9**	**16**	30*i* (1)	26*i* (1)	26*i* (3)
Rb	**1**	**8**	22*i* (1)	19*i* (1)	20*i* (1)
Cs	5*i* (2)	**2**	13*i* (1)	13*i* (1)	15*i* (1)

Table S2. T_1 diagnostic values of the LiM_5 (M = Na, K, Rb) clusters at the single-point CCSD(T)/def2-QZVPP level.

	T_1-diagnostic							
	A1	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**	**A8**
$LiNa_5$	0.02	0.02	0.02	0.02	0.02	0.09	0.11	0.10
LiK_5	0.03	0.03	0.03	0.03	0.02	0.08	0.15	0.14
$LiRb_5$	0.02	0.02	0.02	0.02	0.02	0.03	0.06	0.05

Table S3. The relative energies in kcal/mol of the first three lowest-energy isomers of ppLi and ppAE computed at the CASPT2/def2-TZVPP optimization and CASPT2/def2-QZVPP//PBE0-D3/def2-QZVPP single-point calculations.

	CASPT2/def2-TZVPP			CASPT2/def2-QZVPP//PBE0-D3/def2-QZVPP		
	A1	**A2**	**A3**	**A1**	**A2**	**A3**
$LiNa_5$	0.0	3.2	2.5	0.0	3.0	5.0
LiK_5	0.0	-0.5	-0.7	0.0	-2.8	0.1
$LiRb_5$	0.0	-1.4	0.8	0.0	-2.1	-1.3
	AE1	**AE2**	**AE3**	**AE1**	**AE2**	**AE3**
$MgLi_5^+$	0.0	4.1	4.3	0.0	4.7	5.1
$MgNa_5^+$	0.0	4.1	–[a]	0.0	5.1	5.2
CaK_5^+	0.0	3.0	4.9	0.0	4.9	6.4
$CaRb_5^+$	0.0	1.8	3.3	0.0	3.9	5.6
$SrRb_5^+$	0.0	2.0	2.9	0.0	5.1	2.5
$SrCs_5^+$	0.0	1.0	1.4	0.0	3.7	4.3

[a]Turning into **AE1** in the optimized process.

Table S4. The lowest vibrational frequencies in cm^{-1} and the number of the imaginary frequencies in parentheses for the D_{5h} structures of the AEM_5^+ (AE is an alkaline earth metal and M is an alkali metal) clusters at the PBE0-D3/def2-QZVPP level.

AEM_5^+	Frequencies				
AE / M	Be	Mg	Ca	Sr	Ba
Li	58*i* (2)	**67**	77*i* (3)	130*i* (3)	115*i* (2)
Na	26*i* (2)	**26**	35*i* (1)	38*i* (2)	77*i* (5)
K	26*i* (2)	12*i* (2)	**15**	10*i* (1)	36*i* (3)
Rb	18*i* (2)	10*i* (2)	**7**	**8.6**	18*i* (1)
Cs	14*i* (2)	9*i* (2)	3*i* (2)	**4.7**	12*i* (1)

Table S5. T_1 diagnostic values of the Li_5Mg^+, Na_5Mg^+, K_5Ca^+, $CaRb_5^+$, Rb_5Sr^+, and $SrCs_5^+$ clusters at the single-point CCSD(T)/def2-QZVPP level.

	T_1-diagnostic							
	AE1	**AE2**	**AE3**	**AE4**	**AE5**	**AE6**	**AE7**	**AE8**
Li_5Mg^+	0.02	0.02	0.03	0.01	0.09	-	0.02	0.06
Na_5Mg^+	0.02	0.03	0.03	0.03	0.07	0.03	0.03	0.05
K_5Ca^+	0.02	0.04	0.03	0.03	0.14	0.15	0.03	0.03
$CaRb_5^+$	0.02	0.04	0.03	0.04	0.15	0.15	0.03	0.03
Rb_5Sr^+	0.03	0.04	0.04	0.17	0.11	0.04	0.04	0.04
$SrCs_5^+$	0.03	0.03	0.03	0.15	0.09	0.03	0.03	0.03

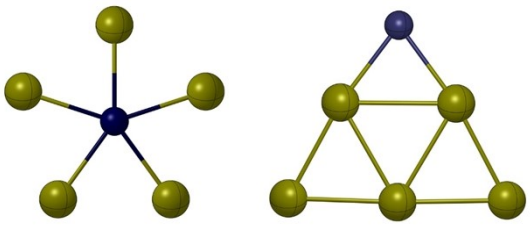


Figure S1. Relative energies (in kcal/mol) between ppNa and the C_{2v} lower-energy isomers in NaM_5 (M = K, (Rb), [Cs]) clusters computed at the CCSD(T)/def2-QZVPP//PBE0-D3/def2-QZVPP level. Total energies were corrected by the zero-point energies (ZPE) calculated at the PBE0-D3 level. Point groups and spectroscopic states are also given.

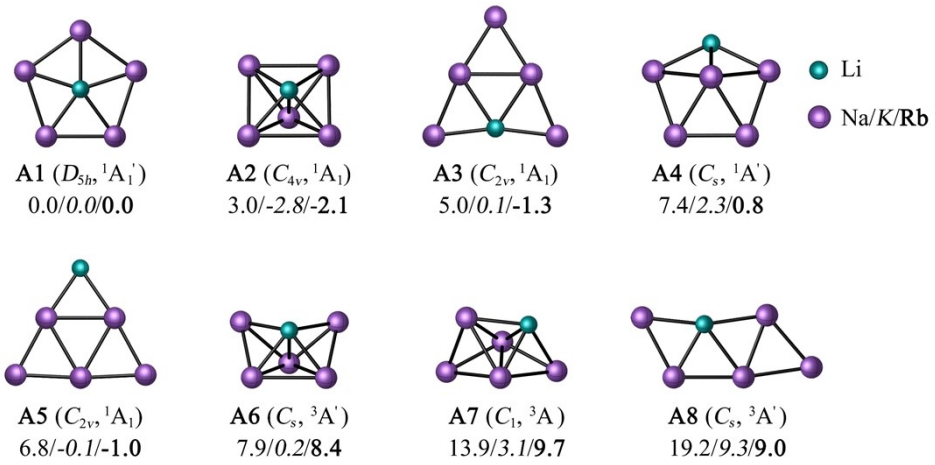


Figure S2. Structure and relative energies in kcal/mol of the low-lying energy isomers of LiM_5 (M = Na/*K*/**Rb**) computed at CASPT2/def2-QZVPP//PBE0-D3/def2-QZVPP. The point group and spectroscopic states were given in parenthesis.

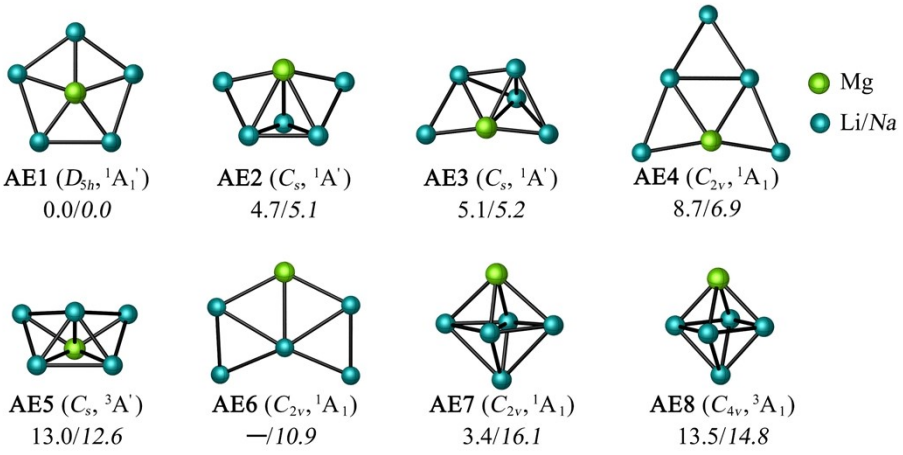


Figure S3. Structure and relative energies in kcal/mol of the low-lying energy isomers of M_5Mg^+ (M = Li/*Na*) computed at CASPT2/def2-QZVPP//PBE0-D3/def2-QZVPP. The point group and spectroscopic states were given in parenthesis. "–" converges to **AE2**.

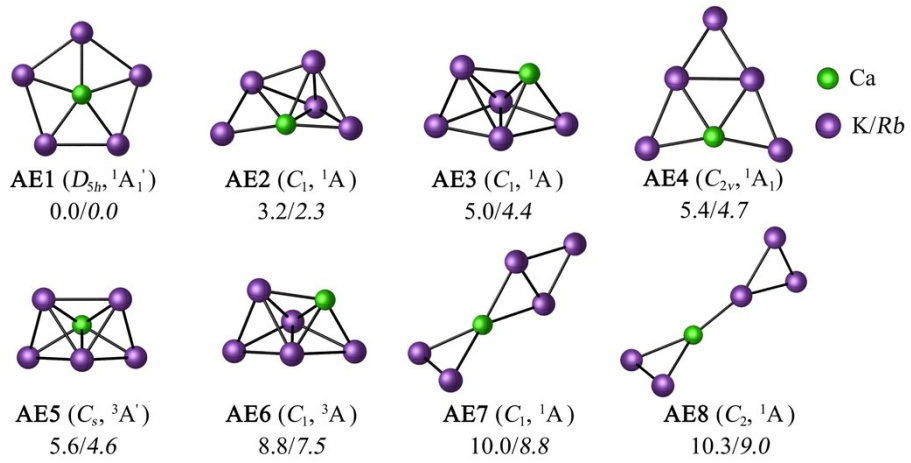


Figure S4. Structure and relative energies in kcal/mol of the low-lying energy isomers of CaK_5^+ and $CaRb_5^+$ computed at CCSD(T)/def2-QZVPP//PBE0-D3/def2-QZVPP. The energy of CCSD(T) is corrected by zero-point energy of PBE0-D3/def2-QZVPP. The point group and spectroscopic states were given in parenthesis.

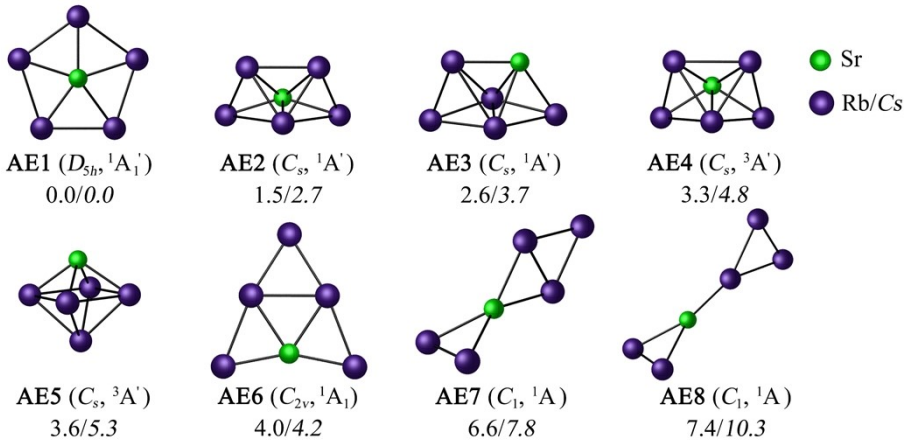


Figure S5. Structure and relative energies in kcal/mol of the low-lying energy isomers of $SrRb_5^+$ and $SrCs_5^+$ computed at CCSD(T)/def2-QZVPP//PBE0-D3/def2-QZVPP. The energy of CCSD(T) is corrected by zero-point energy of PBE0-D3/def2-QZVPP. The point group and spectroscopic states were given in parenthesis.

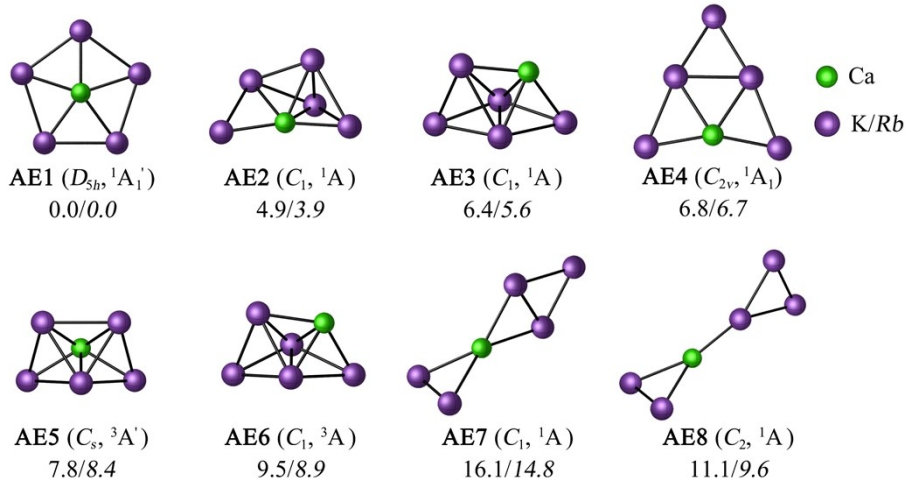


Figure S6. Structure and relative energies in kcal/mol of the low-lying energy isomers of CaK_5^+ and $CaRb_5^+$ computed at CASPT2/def2-QZVPP//PBE0-D3/def2-QZVPP. The point group and spectroscopic states were given in parenthesis.

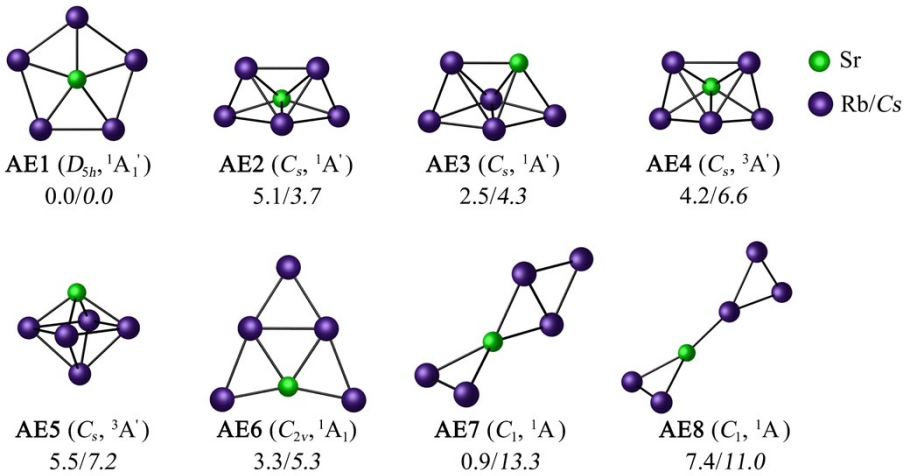
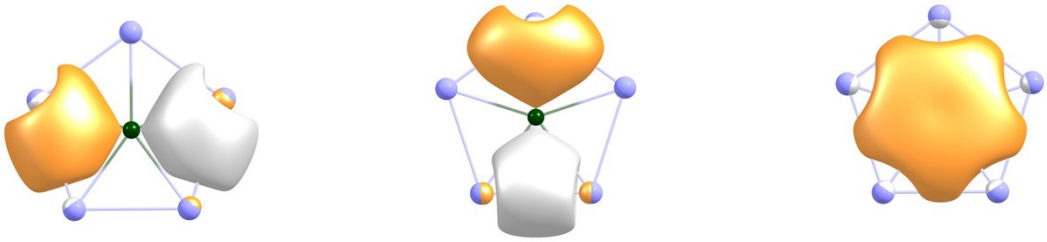
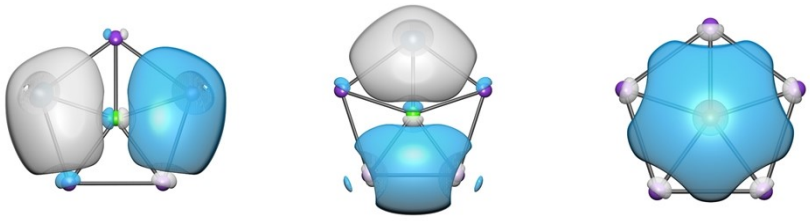


Figure S7. Structure and relative energies in kcal/mol of the low-lying energy isomers of $SrRb_5^+$ and $SrCs_5^+$ computed at CASPT2/def2-QZVPP//PBE0-D3/def2-QZVPP. The point group and spectroscopic states were given in parenthesis.



	HOMO	HOMO′	HOMO-1
	ε	ε	ε
$LiNa_5$	-3.4	-3.4	-4.6
LiK_5	-2.8	-2.8	-3.8
$MgLi_5^+$	-7.1	-7.1	-9.5
$MgNa_5^+$	-6.6	-6.6	-8.9
CaK_5^+	-5.3	-5.3	-6.9
$CaRb_5^+$	-5.1	-5.1	-6.7
$SrRb_5^+$	-5.0	-5.0	-6.5
$SrCs_5^+$	-4.7	-4.7	-6.2

Figure S8. Three molecular orbitals and their corresponding energies (ε, eV) in ppLi and ppAE isomers.



3 × 6c-2e σ bonds ON = 2.00 |e|

Figure S9. The orbitals recovered in AdNDP analysis in ppLi and ppAE, ON refers to occupation number.

Coordinates of ppLi and ppAE
PBE0-D3/def2-QZVPP level

$LiNa_5$

Na	0.000000	3.110810	-0.000000
Na	-2.958556	0.961293	-0.000000
Li	0.000000	0.000000	0.000000
Na	-1.828488	-2.516698	-0.000000
Na	2.958556	0.961293	-0.000000
Na	1.828488	-2.516698	-0.000000

LiK_5

K	-0.000000	3.797096	0.000000
K	3.611253	1.173367	0.000000
Li	0.000000	0.000000	0.000000
K	2.231877	-3.071915	0.000000
K	-3.611253	1.173367	0.000000
K	-2.231877	-3.071915	0.000000

$LiRb_5$

Rb	0.000000	4.026182	0.000000
Rb	-3.829127	1.244159	0.000000
Li	0.000000	0.000000	0.000000
Rb	-2.366530	-3.257250	0.000000
Rb	3.829127	1.244159	0.000000
Rb	2.366530	-3.257249	0.000000

Li_5Mg^+

Li	-0.000000	2.887777	0.000000
Li	1.697393	-2.336261	0.000000
Li	-2.746439	0.892372	0.000000
Li	2.746439	0.892372	0.000000
Mg	0.000000	0.000000	0.000000
Li	-1.697393	-2.336261	0.000000

Na_5Mg^+

Na	0.000000	3.234468	-0.000000
Na	1.901173	-2.616740	-0.000000
Na	-3.076162	0.999506	-0.000000
Na	3.076162	0.999506	-0.000000
Mg	0.000000	0.000000	0.000000
Na	-1.901173	-2.616740	-0.000000

K_5Ca^+

K	-0.000000	4.123352	0.000000
K	2.423646	-3.335862	0.000000
K	-3.921541	1.274186	0.000000
K	3.921541	1.274186	0.000000
Ca	0.000000	0.000000	0.000000
K	-2.423646	-3.335862	0.000000

$CaRb_5^+$

Ca	0.000000	0.000000	0.000000
Rb	0.000000	4.336895	-0.000000
Rb	2.549163	-3.508622	-0.000000
Rb	-4.124632	1.340174	-0.000000
Rb	-2.549163	-3.508622	-0.000000
Rb	4.124632	1.340174	-0.000000

Rb_5Sr^+

Rb	0.000000	4.490004	-0.000000
Rb	2.639158	-3.632489	-0.000000
Rb	-4.270247	1.387487	-0.000000
Rb	-2.639158	-3.632489	-0.000000
Rb	4.270247	1.387487	-0.000000
Sr	0.000000	0.000000	0.000000

$SrCs_5^+$

Cs	0.000000	4.763923	-0.000000
Cs	2.800164	-3.854095	-0.000000
Cs	-4.530760	1.472133	-0.000000
Cs	-2.800164	-3.854095	-0.000000
Cs	4.530760	1.472133	-0.000000
Sr	0.000000	0.000000	0.000000