

# $N_4Mg_6M$ (M=Li, Na, K) superalkalis for $CO_2$ activation

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## Abstract

Superatoms have exciting properties, including diverse functionalization, redox activity, and magnetic ordering, so the resulting cluster-assembled solids hold the promise of high tunability, atomic precision, and robust architectures. By utilizing adamantane-like clusters as building blocks, a new class of superatoms  $N_4Mg_6M$  (M=Li, Na, K) is proposed here. The studied superalkalis feature low adiabatic ionization energies (AIE), an antibonding character in the interactions between magnesium-nitrogen atoms, and highly delocalized HOMO. Consequently, the  $N_4Mg_6M$  superalkalis might easily lose their HOMO electrons when interacting with superhalogen electrophiles to form stable superatom [superalkali]<sup>+</sup>[superhalogen]<sup>-</sup> compounds. Moreover, studied superalkalis interact strongly with carbon dioxide, and the resulting  $N_4Mg_6M/CO_2$  systems represent two strongly interacting ionic fragments (i.e.,  $N_4Mg_6M^+$  and  $CO_2^-$ ). In turn, the electron affinity of the  $N_2$  molecule (of -1.8 eV) is substantially lower than observed for carbon dioxide (EA=-0.6 eV) and consequently, the  $N_2$  was found to form the weakly bound  $[N_4Mg_6M][N_2]$  complex rather than the desired ionic  $[N_4Mg_6M]^+[N_2]^-$  product. Thus, the  $N_4Mg_6M$  superalkalis have high selectivity over  $N_2$  when it comes to  $CO_2$  reduction and also are themselves stable. We believe that the results described within this paper will be useful for understanding  $CO_2$  activation, which is the first step for producing fuels from  $CO_2$ . Moreover, we demonstrate that designing novel superatomic systems and exploring their physicochemical features might be used to create desirable functional materials.

**Keywords:** ionization energy, superalkali, superhalogen, anion, catalyst, carbon dioxide activation

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## 1 Introduction

Reducing agents play an essential role in chemical synthesis. Strong reductors have low ionization energies (IEs). Among the periodic table elements, alkali metal atoms exhibit the lowest ionization energies (5.39–3.89 eV). It was found, however, that a class of molecular clusters has even lower IEs than those of the alkali metal atoms. These polyatomic systems were named “superalkalis” by Gutsev and Boldyrev in 1982.<sup>1</sup> As a superatom type, superalkalis can behave as alkali metal atoms if combined with halogens or superhalogens to create supersalts.<sup>2-3</sup> Since superalkalis have stronger reducibility than the alkali metal atoms, they might activate stable CO<sub>2</sub> and N<sub>2</sub> molecules.<sup>4-5</sup> Moreover, they can be used as hydrogen<sup>6</sup> and noble-gas-trapping agents<sup>7</sup>, as well as building blocks of nanoscale materials (e.g., nonlinear optical materials).<sup>8</sup>

Initially, superalkalis were designed by ligating a *k*-valent electronegative central atom (M) with *k*+1 alkali-metal atoms (L) based on the ML<sub>*k*+1</sub> formula.<sup>1</sup> Typical examples of such superalkalis are FLi<sub>2</sub><sup>9</sup>, OLi<sub>3</sub><sup>10 11</sup>, and CLi<sub>5</sub><sup>12</sup>. In the ML<sub>*k*+1</sub> species, *k* is the number of valence electrons required to close the electronic shell of the electronegative M atom, and thus one more alkali metal atom (L) will provide an extra valence electron for the electronic shell of the M atom. Subsequently, the ML<sub>*k*+1</sub> molecular system exhibits a high tendency to lose one valence electron, forming a very stable cation with the positive charges distributed over all the *k*+1 alkali atoms (L). Since the early 1980s, the scope of superalkalis has been expanded through the introduction of binuclear superalkali species (M<sub>2</sub>L<sub>2*k*+1</sub>)<sup>13-14</sup> and polynuclear superalkalis (YL<sub>*k*+1</sub>, where *k* is the valence state of the anionic groups/clusters) with various polyatomic groups (Y)<sup>15-16</sup> as the central cores. More recently, a lot of effort has been devoted to proposing more unique superalkali species, including non-metallic superalkali cations<sup>17</sup>, aromatic superalkali species<sup>18</sup>, and organo-zintl superalkalis.<sup>19</sup> Despite these achievements, it is still desired to design and characterize more attempts to obtain novel superalkali species to enrich the superalkali family.

The advantage of superatomic materials compared to conventional bulk species is the tunability of the physicochemical characteristics (such as thermal transport, redox activity, electric and magnetic properties) of individual superatoms. The synthesis of superatomic based materials depicts

a challenge for experimental chemistry. Up to now, only a few superatom based bulk materials have been synthesized.<sup>20-25</sup> An excellent recent review<sup>26</sup> has explored the experimental work on superatom synthesis and the assembly of superatomic crystals.

Inspired by recent success of computational design of superalkalis for carbon dioxide activation, which is the first step for producing fuels from CO<sub>2</sub>,<sup>4-5</sup> we design novel superalkalis and explore their possible applications as the building blocks of superatom compounds and catalysts for CO<sub>2</sub> activation. To obtain novel superalkalis, here we propose a N<sub>4</sub>Mg<sub>6</sub>M formula (where M is an alkali metal atom). Explicitly, we designed superalkali systems by decorating electronegative nitrogen atoms with electropositive alkaline earth metal (magnesium) and alkali metal atoms. In such systems, the twelve valence electrons from the Mg atoms will fully close the atomic shells of four nitrogen atoms, and one additional electron will be accommodated within the metal network, leading to low ionization energies. The resulting N<sub>4</sub>Mg<sub>6</sub>M systems were investigated to verify whether they are thermodynamically stable and feature lower ionization energies than those of alkali metal atoms. In the last step, we explored the feasibility of applying the designed systems as efficient reducing agents to activate CO<sub>2</sub>/N<sub>2</sub> molecules and as building blocks to assemble ionic superatom compounds. This contribution firstly introduces N<sub>4</sub>Mg<sub>6</sub>M members into the superalkali family and might assist with further systematic research on the design and synthesis of such species with N<sub>4</sub>Mg<sub>6</sub>M building blocks.

## 2 Computational details

Geometrical optimizations and the harmonic vibrational frequencies for all studied species were obtained by performing the second-order Møller-Plesset (MP2) perturbational method with the Pople split-valence basis sets of triple zeta quality (6-311+G(d)).<sup>27</sup> The coupled-cluster method with single, double and non-iterative triple excitations, CCSD(T), with the 6-311+G(3df) basis was used to estimate the final energies of the N<sub>4</sub>Mg<sub>6</sub>M species (M=Li, Na, K) at their equilibrium geometries obtained with the MP2/6-311+G(d) approach (i.e., CCSD(T)/6-311+G(3df)//MP2/6-311+G(d)). The stabilities of non-charged and ionic N<sub>4</sub>Mg<sub>6</sub>M species were examined by calculating their binding energies per atom ( $E_b$ ) at the CCSD(T)/6-311+G(3df) level, defined as given in Equations 1-3.

$$E_b(N_4Mg_6M)=[6 \cdot E(Mg) + 4 \cdot E(N) + E(Li) - E(N_4Mg_6M)]/11 \quad (1)$$

$$E_b(N_4Mg_6M^+)=[6 \cdot E(Mg) + 4 \cdot E(N) + E(Li^+) - E(N_4Mg_6M^+)]/11 \quad (2)$$

$$E_b(N_4Mg_6M^-)=[6 \cdot E(Mg) + 3 \cdot E(N) + E(Li) + E(N^-) - E(N_4Mg_6M^-)]/11 \quad (3)$$

The adiabatic electron affinity (AEA) indicates the ability of the neutral system to attach an extra electron to form a stable anion. The AEA was calculated by subtracting the total electronic energies of the neutral ( $E_{neu}$ ) and anionic species ( $E_{an}$ ) at each equilibrium geometry ( $r_{e,0}$  and  $r_{e,-}$ , respectively; Equation 4). To check if the neutral system can detach an electron to form a stable cationic system, we obtained the adiabatic ionization energy (AIE). The AIE was estimated as the electronic energy differences between the cation ( $E_{cat}$ ) and neutral ( $E_{neu}$ ) at each equilibrium geometry ( $r_{e,+}$  and  $r_{e,0}$ , respectively; Equation 5). The vertical detachment energy (VDE) is defined as the minimum energy needed to eject an electron from the anion in its ground state and was estimated as the electronic energy differences between the neutral and negative ion, both at the equilibrium geometry of the anion ( $r_{e,-}$ ; Equation 6).

$$AEA = E_{neu}(r_{e,0}) - E_{an}(r_{e,-}) \quad (4)$$

$$AIE = E_{cat}(r_{e,+}) - E_{neu}(r_{e,0}) \quad (5)$$

$$VDE = E_{neu}(r_{e,-}) - E_{an}(r_{e,-}) \quad (6)$$

The adiabatic electron affinities (AEAs), adiabatic ionization energies (AIEs), and vertical electron detachment energies (VDEs) were calculated using the CCSD(T)/6-311+G(3df)//MP2/6-311+G(d) approach and comprising zero-point energy corrections. The intramolecular interaction energies ( $E_{int}$ ) of the  $N_4Mg_6M/Y$  systems ( $M=Li, Na, K; Y=CO_2, N_2, AlF_4, AlCl_4$ ) were obtained at the CCSD(T)/6-311+G(d) level of theory. To eliminate the basis set superposition error (BSSE) effect, we used the counterpoise procedure, in which the same basis set ( $E_{N_4M_6M/Y}$ ) was applied for the subunit energy ( $E_{N_4M_6M}$  and  $E_Y$ ) computations as for the complex energy ( $E_{N_4M_6M/Y}$ ) estimation; Equation 4.

$$E_{int} = E_{N_4Mg_6M/Y}(X_{N_4Mg_6M/Y}) - E_{N_4Mg_6M}(X_{N_4Mg_6M/Y}) - E_Y(X_{N_4Mg_6M/Y}) \quad (4)$$

All calculations were performed with the Gaussian 16 (Rev. C.01) software.<sup>28</sup> Multiwfn v.3.6<sup>29</sup> was applied for wavefunction analyses. The frontier molecular orbitals were generated with the ChemCraft v.1.8 program<sup>30</sup>, and the contour values used in the plots were obtained with the OpenCubeMan r.0.01<sup>31</sup> using a fraction of electron ( $F_e$ ) density equal to 0.8.

### 3 Results and discussion

We designed magnesium-nitrogen-based molecules with an adamantane-like, thus diamondoid,  $[N_4Mg_6]$  scaffold. The latter is free of inversion symmetry as it possesses a tetrahedral shape. Lower molecular symmetry and delocalization of electronic states are appreciated by the decoration of the  $N_4Mg_6$  cage with alkali metal atom (M). The steric influence of the alkali metal atom determines the molecular structure of the cluster core and the catalytic nature of the compound. There are two positions within the  $N_4Mg_6$  cage where alkali metal atom attaching might occur; the  $N_1$ -position, where  $N_4Mg_6$  molecule retains a threefold rotation axis and encapsulated position where a plane of symmetry remains intact. The harmonic vibrational frequencies of studied  $N_4Mg_6M^{0,+,-}$  clusters (M=Li, Na, K) are all positive, indicating that the predicted structures in Table I are minima on the potential energy surface.

#### 3.1 The neutral $N_4Mg_6M$ species (M=Li, Na, K)

The ground state structures of  $Mg_6N_4M$  species possess  $C_{3v}$  symmetry with the alkali atoms connected to the  $N_4Mg_6$  diamondoid through a single M-N bond (of 1.811 Å ( $N_4Mg_6Li$ ), 2.173 Å ( $N_4Mg_6Na$ ), and 2.507 Å ( $N_4Mg_6K$ )); see *Figure 2*. The HOMO–LUMO gaps of the most stable  $N_4Mg_6Li$ ,  $N_4Mg_6Na$ , and  $N_4Mg_6K$  systems read 3.958, 3.752, 3.662 eV, respectively, implying the chemical stability of these molecules. Their  $E_b$  values are in the 3.05–3.12 eV range, confirming their thermodynamic stability. Moreover, it is observed that these  $E_b$  values decrease in the order 3.12 eV ( $N_4Mg_6Li$ ) > 3.06 eV ( $N_4Mg_6Na$ ) > 3.05 eV ( $N_4Mg_6K$ ), demonstrating the effect of composition and size on the cohesion of these molecules.

*Table I* Adiabatic ionization energy (AIE, in eV), adiabatic electron affinity (AEA, in eV) values for the ground state  $N_4Mg_6M$  systems. The lowest vibrational frequencies ( $V_1$ , in  $cm^{-1}$ ), HOMO–

LUMO gaps (GAP, in eV), and binding energies per atom ( $E_b$ , in eV), for the most stable  $N_4Mg_6M^{0/+/-}$  (M=Li, Na, K). For higher energy isomers see supporting information.

Species	AIE	AEA	neutral			cation			anion		
			$V_1$	GAP	$E_b$	$V_1$	GAP	$E_b$	$V_1$	GAP	$E_b$
<b><math>N_4Mg_6Li</math></b>	4.710	1.598	124	3.958	3.12	123	6.669	3.20	78	2.601	3.20
<b><math>N_4Mg_6Na</math></b>	4.564	1.530	77	3.752	3.06	86	6.571	3.09	44	2.397	3.13
<b><math>N_4Mg_6K</math></b>	4.414	1.448	58	3.662	3.05	65	6.654	3.04	37	2.116	3.12

The  $N_4Mg_6M$  systems are thermodynamically stable due to both attractive electrostatic interaction between electropositive metal atoms and electronegative nitrogen atoms, and covalent-like interactions between magnesium atoms. The magnesium-magnesium interaction in  $N_4Mg_6Li$ ,  $N_4Mg_6Na$ , and  $N_4Mg_6K$  leads to short Mg–Mg distances (2.943–3.015 Å), which are near to the bond length of the covalently bounded  $Mg_2^{2+}$  cation (2.922 Å as calculated at the same theory level). Moreover, the Mg–Mg bonding character can be seen from their HOMOs, where the excess valence electron delocalizes over the whole cluster, benefiting the thermodynamic stability of these open-shell systems. The alkali metal atoms ensure a better electron delocalization in comparison to  $N_4Mg_6$  cage structure. As depicted in Figure S1, the  $N_4Mg_6$   $T_d$ -symmetry structure (labeled **B** in Figure S1) is higher in energy (by 5 kcal/mol) than  $C_s$ -symmetry planar isomer (labeled **A** in Figure S1), which mimics the  $N_2Mg_6$  subunit interacting with the  $N_2$  molecule. The  $N_4Mg_6M$  are thermodynamically stable and not sustainable to  $N_2$  loss. The thermodynamic stability of the  $N_4Mg_6M$  systems was examined by calculating the Gibbs free ( $\Delta G_r^{298}$ ) energies of the fragmentation channels of  $N_4Mg_6M \rightarrow M + N_2Mg_6 + N_2$ ,  $N_4Mg_6M \rightarrow M + 2NMg_3 + N_2$ , and  $N_4Mg_6M \rightarrow MMg + 5Mg + 2N_2$  (where M is alkali metal atom). From Table II, it can be seen that all the dissociation reactions are endothermic. The positive dissociation energies of these fragmentation channels demonstrate that the  $N_4Mg_6M$  species possess thermodynamic stability with respect to the elimination of  $N_2$ . Furthermore, it is observed that the lighter the alkali metal atom, the larger the thermodynamic stability of the  $N_4Mg_6M$  system (with larger  $\Delta G_r^{298}$  values).

*Table II* Free enthalpies ( $\Delta H_r^{298}$  in kcal/mol), entropies ( $\Delta S_r^{298}$  in cal/(mol·K)), and Gibbs free ( $\Delta G_r^{298}$  in kcal/mol) energies of the fragmentation reactions (at  $T = 298.15$  K,  $p = 1$  atm) obtained at the CCSD(T)/6-311+G(3df) level of theory for the  $N_4Mg_6M$  ( $M=Li, Na, K$ ) ground states.

Fragmentation path	$\Delta H_r^{298}$	$\Delta S_r^{298}$	$\Delta G_r^{298}$
$N_4Mg_6Li \rightarrow Li + N_2Mg_6 + N_2$	55.96	35.66	45.32
$N_4Mg_6Li \rightarrow Li + 2NMg_3 + N_2$	120.52	123.80	83.61
$N_4Mg_6Li \rightarrow LiMg + 5Mg + 2N_2$	216.02	321.51	120.16
$N_4Mg_6Na \rightarrow Na + N_2Mg_6 + N_2$	38.96	35.09	28.50
$N_4Mg_6Na \rightarrow Na + 2NMg_3 + N_2$	103.53	123.23	66.79
$N_4Mg_6Na \rightarrow NaMg + 5Mg + 2N_2$	196.50	234.21	126.67
$N_4Mg_6K \rightarrow K + N_2Mg_6 + N_2$	37.68	80.78	13.59
$N_4Mg_6K \rightarrow K + 2NMg_3 + N_2$	102.24	239.66	30.79
$N_4Mg_6K \rightarrow KMg + 5Mg + 2N_2$	184.34	328.50	86.40

The  $N_4Mg_6M$  ( $M=Li, Na, K$ ) species comprise 33 valence electrons ( $4 \times 5 + 6 \times 2 + 1$ ), thus one additional electron than needed for the octet shell closure, in analogy to alkali atoms. Their ionization energies obtained at the CCSD(T)/6-311+G(3df) level of theory reads 4.710 eV ( $N_4Mg_6Li$ ), 4.564 eV ( $N_4Mg_6Na$ ), 4.414 eV ( $N_4Mg_6K$ ) and are smaller than those of lithium atom (5.39 eV), which emphasize their superalkali nature. This conclusion is supported by the antibonding character of the highest occupied molecular orbitals in similarity to the HOMOs reported for typical superalkalis in the past.<sup>1</sup> In particular, the HOMOs consist mainly of the s orbitals of the magnesium atoms and indicate an antibonding character in the interactions between Mg-N atoms, which implies their low ionization energies.

The HOMOs of  $N_4Mg_6M$  ( $M=Li, Na, K$ ) species are highly delocalized over the whole clusters so as to reduce the repulsion among the electrons. The highly diffuse HOMO also implies that the extra electron is loosely bound by the nuclei, giving rise to the low IE values. The electron delocalization is also confirmed by the electron localization function (ELF) analysis and is yet to be discussed in section 3.4. To conclude, the  $N_4Mg_6M$  ( $M=Li, Na, K$ ) seems to possess excellent reducing potential and can be used in the synthesis of unusual charge-transfer salts with the counterpart possessing relatively low electron affinity.

### 3.2 The $\text{N}_4\text{Mg}_6\text{M}^-$ anions (M=Li, Na, K)

The equilibrium structures of the  $\text{N}_4\text{Mg}_6\text{M}^-$  anions are depicted in Figure 3, while the corresponding geometrical parameters are provided in Figure S8 of supporting information. The lowest energy  $\text{N}_4\text{Mg}_6\text{M}^-$  structures are highly symmetry ( $C_{3v}$ ) species with the alkali atom localized on the top and with the M–N bond lengths equal to 1.805 Å ( $\text{N}_4\text{Mg}_6\text{Li}^-$ ), 2.157 Å ( $\text{N}_4\text{Mg}_6\text{Na}^-$ ), and 2.469 Å ( $\text{N}_4\text{Mg}_6\text{K}^-$ ). The alkali–nitrogen distances are shortened compared to those found for the corresponding neutral species, which is likely caused by an effective bonding of excess electron. The adiabatic electron affinity of  $\text{N}_4\text{Mg}_6\text{M}$  molecules read 1.598 eV ( $\text{N}_4\text{Mg}_6\text{Li}$ ), 1.530 eV ( $\text{N}_4\text{Mg}_6\text{Na}$ ), and 1.448 eV ( $\text{N}_4\text{Mg}_6\text{K}$ ), which confirms that the excess electron is strongly bound in each  $\text{N}_4\text{Mg}_6\text{M}^-$  anion. These species might be considered as double-Rydberg (DR) anions. DR anions, such as the  $\text{LiFLi}^-$  or the  $\text{NH}_4^-$ , consist of a closed-shell cation core (i.e., parent cation) plus two extra electrons described by Rydberg orbitals.<sup>32-33</sup> The highest occupied molecular orbital (HOMO) for the bound  $\text{N}_4\text{Mg}_6\text{M}^-$  anions are depicted in Figure 3 and show the involvement of the diffuse Rydberg-like orbitals. The  $\text{N}_4\text{Mg}_6\text{M}^-$  anions might be seen as consisting of geometrically and electronically stable parent cations (i.e.,  $\text{N}_4\text{Mg}_6\text{M}^+$ ) around which a pair of electrons move in diffuse orbitals.

Moreover, we found additional bound states for the  $\text{N}_4\text{Mg}_6\text{Li}^-$  and  $\text{N}_4\text{Mg}_6\text{Na}^-$  anions to be  $T_d$ -symmetry with alkali atom localized in the center. These excited anionic states are adiabatically bound by 0.750 eV and -2.727 eV with respect to the neutral  $\text{N}_4\text{Mg}_6\text{Li}$  and  $\text{N}_4\text{Mg}_6\text{Na}$  molecules, respectively (see Figure 3). The HOMO holding the excess electron in the  $\text{N}_4\text{Mg}_6\text{Li}^-$  excited state reflects substantial contributions from the s-symmetry magnesium AOs with non-negligible contributions from the p-symmetry nitrogen AOs. The delocalization of an excess electron over the  $\text{N}_4\text{Mg}_6$  cage suggests significant electronic stability of the  $\text{N}_4\text{Mg}_6\text{Li}^-$  excited state. In turn, one might be tempted to classify the  $\text{N}_4\text{Mg}_6\text{Na}^-$  excited state as a metastable anion (due to the negative AEA value). However, the vertical electron detachment energy (VDE) of the  $\text{N}_4\text{Mg}_6\text{Na}^-$  excited state is 1.960 eV, implying that this anion might exist at very low temperatures in the gas phase (because of the kinetic barrier related to bond breaking and structural reorganization).



The charge distributions analysed by the NBO approach are listed in Table III. The extra electron in the anions was filled mostly in the 1s orbital of alkali metal atom, 2p orbital of three magnesium atoms ( $\text{Mg}_{1,3,5}$ ), and 3p orbital of nitrogen atoms. The electron density for alkali metal atoms has been increased by 0.272  $e$  ( $\text{N}_4\text{Mg}_6\text{Li}^-$ ), 0.326  $e$  ( $\text{N}_4\text{Mg}_6\text{Na}^-$ ), 0.425  $e$  ( $\text{N}_4\text{Mg}_6\text{K}^-$ ) in comparison to radical forms. As the alkali metal atom becomes less positive, the anionic structure becomes more stable. The magnesium atoms (i.e.,  $\text{Mg}_{2,4,6}$ ) that are further away from the M atom have more positive charges than that of the closer magnesium atoms (i.e.,  $\text{Mg}_{1,3,5}$ ). The positive charges on the three magnesium atoms ( $\text{Mg}_{2,4,6}$ ) tend to be equal for all radical species (1.7  $e$ ) and are essentially unchanged with the addition of an extra electron. In turn, electron density for the magnesium atoms ( $\text{Mg}_{1,3,5}$ ) near the  $\text{N}_1$  atom has been reduced by 0.05-0.09  $e$  for anionic forms. Finally, a comparison between the radical parent and anionic daughter indicates an increase in the electron density of the nitrogen atoms of ca. 0.15  $e$  and 0.09  $e$  for the  $\text{N}_1$  and  $\text{N}_{2,3,4}$  atoms, respectively.

Table III Atomic charges by NBO analysis (in  $e$ ) for the  $\text{N}_4\text{Mg}_6\text{M}^{0/+}$  (M=Li, Na, K) ground states.

Species	$\text{N}_4\text{Mg}_6\text{Li}$			$\text{N}_4\text{Mg}_6\text{Na}$			$\text{N}_4\text{Mg}_6\text{K}$		
	cation	neutral	anion	cation	neutral	anion	cation	neutral	anion
<b>M</b>	0.983	0.615	0.343	0.974	0.585	0.259	0.990	0.734	0.309
<b>Mg<sub>1,3,5</sub></b>	1.757	1.614	1.527	1.754	1.621	1.542	1.749	1.575	1.524
<b>Mg<sub>2,4,6</sub></b>	1.771	1.737	1.734	1.768	1.738	1.734	1.765	1.728	1.733
<b>N<sub>1</sub></b>	-2.741	-2.741	-2.885	-2.711	-2.734	-2.880	-2.706	-2.719	-2.871
<b>N<sub>2,3,4</sub></b>	-2.608	-2.642	-2.746	-2.610	-2.643	-2.736	-2.609	-2.642	-2.736

### 3.3 The $\text{N}_4\text{Mg}_6\text{M}^+$ cations (M=Li, Na, K)

The ionization (electron loss) of the  $\text{N}_4\text{Mg}_6\text{M}$  species does not lead to significant geometry relaxation of the structures. The M– $\text{N}_1$  bond lengths in  $\text{Mg}_6\text{N}_4\text{M}$  elongates by 0.046-0.109 Å when the  $\text{N}_4\text{Mg}_6\text{M}^+$  cations are produced while the  $\text{N}_1$ – $\text{Mg}_{1-3}$  distances increase by 0.018-0.036 Å. All  $\text{N}_4\text{Mg}_6\text{M}^+$  cations have a large HOMO-LUMO energy gap (of 6.571-6.669 eV) and show a significant increase in GAP values (by ca. 3.0 eV) as compared to non-charged  $\text{N}_4\text{Mg}_6\text{M}$  species. Besides

obtained HOMO-LUMO gaps are larger than the experimental GAPs of fullerene (GAP=1.57 eV for  $C_{60}$ )<sup>34</sup> and chemically inert  $Al_{13}^-$  anion (GAP=1.87 eV)<sup>35</sup>, suggesting their superatom nature.<sup>4</sup> Thus, the designed cations might be considered to be highly chemically stable superatoms. This conclusion is also confirmed by the estimated binding energies per atom ( $E_b$ ). Explicitly, the  $E_b$  values of the  $N_4Mg_6M^+$  cations are in the 3.04-3.20 eV range, implying their stability upon dissociation into atomic parts.

The stability of the cations is guaranteed by their large HOMO-LUMO gaps, binding energies per atom, as well as the strong ionic interactions between electronegative nitrogen atoms and electropositive metal atoms. The NBO computations empathize that the nitrogen atoms hold negative charges (i.e., cover the range from -2.741 to -2.608  $e$ ) and the positive charges are distributed on the metal atoms in each  $N_4Mg_6M^+$  cation. Alkali metal atoms always carry positive charges of the 0.974-0.990  $e$  range, while the magnesium atoms hold the charge of the 1.749-1.771  $e$ . The enhanced electronic stability of  $N_4Mg_6M^+$  cations is related to ionic interactions between positively charged metal atoms and negatively charged nitrogen atoms, which is discussed in the following section.

### 3.4 Electron localization function (ELF) maps analysis

ELF is a measure of the degree of electron localization; the normalized ELF =1.0 represents fully localized electrons, ELF = 0.5 corresponds to a free electron gas, and small values stand for low electron densities. For light elements with s and p electrons (such as lithium and magnesium), localized electrons exhibit  $ELF \geq 0.7$ . The blue circles around the metal atoms separate the core electrons from the valence electrons. Figure 5 illustrates the ELF maps of the representative  $N_4Mg_6Li^{0,+,-}$  systems (in the three different planes) to visualize the electron distributions and the bonding features. Since our main attention focuses on the electron flow between nitrogen and alkali/magnesium atoms, we selected three planes for the display of the ELF, which include  $Mg_1$ - $Mg_3$ - $Mg_5$  (left column in Figure 5),  $N_1$ - $N_2$ - $N_4$  (middle column in Figure 5), and  $Li$ - $N_2$ - $Mg_4$  (right column in Figure 5) atoms. The small, middle, and big red circles are the atomic nuclei of the Mg, N, and Li atoms, respectively. The  $Mg_1$ - $Mg_3$ - $Mg_5$  plane of the species (right column in Figure 5) has a

green area in the center of the three Mg atoms, corresponding to electron-gas-like pair probability. Simultaneously, a bowed-out green area appears on the outside of the Li atom in an  $\text{N}_4\text{Mg}_6\text{Li}^-$  anion. This change identifies the existence of the excess electron bonding in the anionic  $\text{N}_4\text{Mg}_6\text{Li}^-$  system. In addition, the ELF analysis of non-charged  $\text{N}_4\text{Mg}_6\text{Li}$  cluster shows that there are only core basins and valence basins around the nitrogen and metal atoms in the system, whereas valence basins located between the N and Mg/Li atoms could not be found, indicating that the covalent bonds do not form between N and Li or Mg atoms. Similar observations are also found for the  $\text{N}_4\text{Mg}_6\text{Li}^-$  anion and  $\text{N}_4\text{Mg}_6\text{Li}^+$  cation. It is clear that the metal atoms form naked cations, and the  $\text{N}_4\text{Mg}_6\text{Li}^+$  cation is formed by ionically bonding  $\text{Li}^+$  and  $\text{Mg}^{2+}$  cations with  $\text{N}^{3-}$  anions.

As has been previously observed for superalkalis<sup>36</sup>, there is electron delocalization in these systems that lends further support to their high stability. As shown in the  $\text{N}_1\text{-N}_2\text{-N}_4$  and  $\text{Li-N}_2\text{-Mg}_4$  planes in Figure 5, the electron delocalization (ELF=0.5, colored in green) reduces with the change of the ionization from anion through neutral to cation. This indicates that the stability of  $\text{N}_4\text{Mg}_6\text{Li}^{0,-}$  becomes lower with the change of the charge from anion to neutral, which is in agreement with the diagram representing relative stability of non-charged and ionic  $\text{N}_4\text{Mg}_6\text{Li}$  species; see *Figure 3*.

### 3.5 Application for carbon dioxide activation

Carbon dioxide, a significant contributor to global warming, is a covalently bonded linear molecule. The first step involved in transforming  $\text{CO}_2$  into fuel is to activate  $\text{CO}_2$  (i.e., convert from the linear to a bent structure). The  $\text{CO}_2$  bending can be accomplished by adding an electron as  $\text{CO}_2^-$  has a bent geometry with a valence angle of  $137.3^\circ$  (as depicted in Figure 6). Recent studies suggest that superalkalis might form superalkali/ $\text{CO}_2$  complexes in which negatively charged  $\text{CO}_2$  is stabilized by the superalkali cation.<sup>4-5</sup> To test the catalytic features of the  $\text{N}_4\text{Mg}_6\text{M}$  superalkalis, we analyze their potential applications for  $\text{CO}_2$  activation. The  $\text{CO}_2$  molecule was combined with each  $\text{N}_4\text{Mg}_6\text{M}$  system in various relative orientations, and the resulted low-energy  $\text{N}_4\text{Mg}_6\text{M}/\text{CO}_2$  structures are provided in Figure 6. The lowest vibrational frequencies, HOMO–LUMO gaps, interaction energies ( $E_{\text{int}}$ ), and NBO charges ( $Q$ ) on the  $\text{CO}_2$  counterpart are collected in Table IV.

*Table IV* The lowest vibrational frequencies ( $V_1$ , in  $\text{cm}^{-1}$ ), relative energies ( $E_r$ , in kcal/mol), interaction energies ( $E_{\text{int}}$ , in kcal/mol) and HOMO–LUMO gaps (GAP, in eV), NBO charges on the  $\text{CO}_2/\text{N}_2$  and  $\text{AlF}_4/\text{AlCl}_4$  subunits ( $Q$ , in  $e$ ) of the low-energy  $\text{N}_4\text{Mg}_6\text{M}/\text{Y}$  isomers ( $E_r$  within 6 kcal/mol;  $\text{M}=\text{Li}, \text{Na}, \text{K}$ ;  $\text{Y}=\text{CO}_2, \text{N}_2, \text{AlF}_4, \text{AlCl}_4$ ).

Species	isomer	$E_r$	$V_1$	$E_{\text{int}}$	GAP	$Q$
$\text{N}_4\text{Mg}_6\text{Li}/\text{CO}_2$	A	0.00	47	-36.27	3.980	-0.799
$\text{N}_4\text{Mg}_6\text{Li}/\text{CO}_2$	B	0.97	39	-35.29	4.343	-0.792
$\text{N}_4\text{Mg}_6\text{Li}/\text{CO}_2$	C	2.48	69	-33.79	4.382	-0.870
$\text{N}_4\text{Mg}_6\text{Na}/\text{CO}_2$	A	0.00	46	-36.98	3.768	-0.803
$\text{N}_4\text{Mg}_6\text{Na}/\text{CO}_2$	B	1.08	38	-35.90	4.114	-0.795
$\text{N}_4\text{Mg}_6\text{Na}/\text{CO}_2$	C	3.19	46	-33.79	4.788	-0.863
$\text{N}_4\text{Mg}_6\text{K}/\text{CO}_2$	A	0.00	46	-37.76	3.788	-0.806
$\text{N}_4\text{Mg}_6\text{K}/\text{CO}_2$	B	1.02	37	-36.73	4.091	-0.797
$\text{N}_4\text{Mg}_6\text{K}/\text{CO}_2$	C	1.66	43	-36.09	4.349	-0.869
$\text{N}_4\text{Mg}_6\text{Li}/\text{N}_2$	A	0.00	25	-3.41	4.164	0.021
$\text{N}_4\text{Mg}_6\text{Li}/\text{N}_2$	B	1.31	10	-2.11	4.003	0.017
$\text{N}_4\text{Mg}_6\text{Li}/\text{N}_2$	C	2.99	5	-0.42	3.961	-0.002
$\text{N}_4\text{Mg}_6\text{Li}/\text{N}_2$	D	3.29	20	-0.12	3.839	0.013
$\text{N}_4\text{Mg}_6\text{Na}/\text{N}_2$	A	0.00	9	-1.89	3.783	0.016
$\text{N}_4\text{Mg}_6\text{Na}/\text{N}_2$	B	0.74	17	-1.14	4.001	0.014
$\text{N}_4\text{Mg}_6\text{Na}/\text{N}_2$	C	1.45	6	-0.43	3.756	-0.003
$\text{N}_4\text{Mg}_6\text{Na}/\text{N}_2$	D	1.88	19	0.00	3.694	0.010
$\text{N}_4\text{Mg}_6\text{K}/\text{N}_2$	A	0.00	9	-1.76	3.654	0.016
$\text{N}_4\text{Mg}_6\text{K}/\text{N}_2$	B	0.49	4	-1.27	3.840	0.003
$\text{N}_4\text{Mg}_6\text{K}/\text{N}_2$	C	0.73	1	-1.03	3.673	0.007
$\text{N}_4\text{Mg}_6\text{K}/\text{N}_2$	D	0.94	6	-0.82	3.647	0.006
$\text{N}_4\text{Mg}_6\text{K}/\text{N}_2$	E	2.07	19	0.32	3.533	0.010
$\text{N}_4\text{Mg}_6\text{Li}/\text{AlF}_4$	A	0.00	64	-201.27	6.782	-0.956
$\text{N}_4\text{Mg}_6\text{Li}/\text{AlCl}_4$	A	0.00	24	-134.33	6.847	-0.877
$\text{N}_4\text{Mg}_6\text{Li}/\text{AlCl}_4$	B	3.47	15	-130.87	6.746	-0.881
$\text{N}_4\text{Mg}_6\text{Li}/\text{AlCl}_4$	C	4.81	10	-129.52	6.861	-0.883
$\text{N}_4\text{Mg}_6\text{Na}/\text{AlF}_4$	A	0.00	58	-194.88	6.546	-0.960
$\text{N}_4\text{Mg}_6\text{Na}/\text{AlF}_4$	B	4.33	51	-190.55	5.532	-0.952
$\text{N}_4\text{Mg}_6\text{Na}/\text{AlCl}_4$	A	0.00	14	-130.71	6.647	-0.894
$\text{N}_4\text{Mg}_6\text{Na}/\text{AlCl}_4$	B	2.27	8	-128.44	6.600	-0.896
$\text{N}_4\text{Mg}_6\text{Na}/\text{AlCl}_4$	C	3.43	12	-127.27	6.745	-0.906
$\text{N}_4\text{Mg}_6\text{Na}/\text{AlCl}_4$	D	4.00	53	-126.71	6.402	-0.888
$\text{N}_4\text{Mg}_6\text{K}/\text{AlF}_4$	A	0.00	51	-196.79	6.450	-0.961
$\text{N}_4\text{Mg}_6\text{K}/\text{AlF}_4$	B	5.72	44	-191.07	6.003	-0.954
$\text{N}_4\text{Mg}_6\text{K}/\text{AlCl}_4$	A	0.00	18	-129.63	6.546	-0.910
$\text{N}_4\text{Mg}_6\text{K}/\text{AlCl}_4$	B	0.61	57	-129.02	6.260	-0.896
$\text{N}_4\text{Mg}_6\text{K}/\text{AlCl}_4$	C	1.19	12	-128.44	6.534	-0.913

All the  $\text{N}_4\text{Mg}_6\text{M}/\text{CO}_2$  complexes ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ) were fully optimized without any symmetry constraints. The computation of harmonic vibrational frequency reveals that there are no imaginary frequencies in all considered systems, implying that they are dynamically stable and belong to minima in the corresponding potential energy surface. As for energetic stability, all  $\text{N}_4\text{Mg}_6\text{M}/\text{CO}_2$  systems

hold negative  $E_{\text{int}}$  values (Table IV), which indicates that they are energetically stable concerning fragmentations leading to their isolated subunits (i.e.,  $\text{N}_4\text{Mg}_6\text{M}$  and  $\text{CO}_2$ ).

The  $\text{CO}_2$  binds to  $\text{N}_4\text{Mg}_6\text{M}$  species through C-N bonding interaction. The C-N bond length is in the 1.452-1.454 Å range, implying the formation of a single bond between C and N in all cases. The O-C bonds are extended to 1.223-1.224 and 1.335-1.336 Å; see Figure 6. These are about 8% longer than that in  $\text{CO}_2^-$ . In addition, the O-C-O angle is  $125^\circ$  resulting in a structure that is 9% more bent than the isolated  $\text{CO}_2^-$  anion. Thus, the stretching of the O-C bonds as well as the bending of the O-C-O angle weaken the O-C bonds of  $\text{CO}_2$ , making it easy to activate. The NBO charge transfer from designed superalkalis to  $\text{CO}_2$  molecule is from  $-0.799 e$  to  $-0.806 e$ , suggesting  $\text{CO}_2$  reduction upon its interaction with each superalkali. The obtained HOMO-LUMO gaps cover the 3.768-3.980 eV range indicating the chemical stability of these complexes. These results suggest that the designed superalkalis might be used as efficient catalysts for  $\text{CO}_2$  activation.

### 3.6 Nitrogen as an interacting counterpart

In view of the reducibility of  $\text{N}_4\text{Mg}_6\text{M}$  superalkalis (M=Li, Na, K), they indicate potential applications in activating carbon dioxide. This is not a trivial task as the electron affinity of this greenhouse gas is  $-0.6 \text{ eV}$ ,<sup>37</sup> and the corresponding anion is metastable. In order to demonstrate that the ionic nature of superalkali/Y compounds is the result of the strong reducing ability of superalkali subunit, we extended our studies to cover three additional compounds (i.e.,  $\text{N}_4\text{Mg}_6\text{Li}/\text{N}_2$ ,  $\text{N}_4\text{Mg}_6\text{Na}/\text{N}_2$ , and  $\text{N}_4\text{Mg}_6\text{K}/\text{N}_2$ ) in which carbon dioxide was replaced with nitrogen gas molecule with EA value of  $-1.8 \text{ eV}$ .<sup>38</sup> The  $\text{N}_2$  molecule, as characterized by significantly lower electron affinity, is expected to interact more weakly with the  $\text{N}_4\text{Mg}_6\text{M}$  superalkalis than the  $\text{CO}_2$  system does.

Upon  $\text{N}_2$  gaining an electron, the N-N bond is stretched from 1.120 Å to 1.199 Å. As shown in Figure 7, upon interaction with each of  $\text{N}_4\text{Mg}_6\text{M}$  superalkalis, the N-N bond length (of 1.120 Å) remains unchanged in  $\text{N}_4\text{Mg}_6\text{M}/\text{N}_2$  systems at their global minima. This negligible geometry modification (of 0.001 Å) is accompanied by hardly any charge flow between interacting subunits as NBO charges range from  $-0.002 e$  to  $0.021 e$ . These results imply that, contrary to the  $\text{CO}_2$  molecule,

the N<sub>2</sub> does not undergo an electron transfer from the superalkali upon interaction. This was further confirmed by the interaction energy ( $E_{\text{int}}$ ) analysis, which shows that the Mg<sub>6</sub>N<sub>4</sub>M/N<sub>2</sub> are weakly bound complexes with  $E_{\text{int}}$  from -3.41 kcal/mol to 0.32 kcal/mol, while the CO<sub>2</sub> forms ionic compounds with each of N<sub>4</sub>Mg<sub>6</sub>M superalkalis ( $E_{\text{int}}$  is always below -33 kcal/mol). Hence, the N<sub>4</sub>Mg<sub>6</sub>M superalkalis have high selectivity over N<sub>2</sub> when it comes to CO<sub>2</sub> reduction. A similar observation was made in the case of Mg<sub>3</sub>Al and Li<sub>3</sub>F<sub>2</sub> superalkalis.<sup>4, 39</sup>

In summary, carbon dioxide interacts with the N<sub>4</sub>Mg<sub>6</sub>M superalkalis, and the most stable isomers of the N<sub>4</sub>Mg<sub>6</sub>M/CO<sub>2</sub> systems represent two strongly interacting ionic fragments (i.e., N<sub>4</sub>Mg<sub>6</sub>M<sup>+</sup> and CO<sub>2</sub><sup>-</sup>). The electron affinity of N<sub>2</sub> molecule (of -1.8 eV), however, is substantially lower than those observed for carbon dioxide (AIE=-0.6 eV), which results in a N<sub>4</sub>Mg<sub>6</sub>M inability to its effective ionization. Consequently, the N<sub>2</sub> was found to form the weakly bound [N<sub>4</sub>Mg<sub>6</sub>M][N<sub>2</sub>] complex (as its lowest energy isomer) rather than the desired ionic [N<sub>4</sub>Mg<sub>6</sub>M]<sup>+</sup>[N<sub>2</sub>]<sup>-</sup> product.

### 3.7 Superatomic compounds formation

The superalkalis represent an unusual class of stable species that exhibit low ionization energies (even for the removal of multiple electrons), enabling their classification as superdonor superatoms. The electron-rich superalkalis transfer charge to an electron-accepting unit (e.g., superhalogen) to produce solids.<sup>25, 40</sup> These superatomic compounds are formed through electron transfer between the electrically neutral building blocks, while the internal structures of the constituent subunit maintain unchanged. In this contribution, we decided to investigate interactions between N<sub>4</sub>Mg<sub>6</sub>M superalkalis and two chosen superhalogens (i.e., AlCl<sub>4</sub> and AlF<sub>4</sub>) as representative strong electron acceptors for the charge-transfer superatom compounds. We chose AlCl<sub>4</sub> and AlF<sub>4</sub> molecules, as they are typical and structurally simple superhalogens, and their electron affinities (i.e., 6.102 eV (AlCl<sub>4</sub>) and 8.108 eV (AlF<sub>4</sub>) at the CCSD(T)/6-311+G(3df) level) seemed to be suitable.

All the resulting N<sub>4</sub>Mg<sub>6</sub>M/superhalogen geometrical structures depicted in Figures 8-10 are minima on the potential energy surface at MP2/6-311+G(d) level of theory. The stability of designed superatom compounds is confirmed by both highly negative interaction energies and relatively large

HOMO-LUMO gaps (Table IV). Charge transfer between interacting counterparts reads 0.96  $e$  for  $N_4Mg_6M/AlF_4$  species and covers the 0.88-0.91  $e$  range for  $N_4Mg_6M/AlCl_4$  systems. Hence, we accomplished, that the  $N_4Mg_6M$  superalkalis might easily lose their HOMO electrons when interacting with  $AlX_4$  electrophiles to form a stable ionic [superalkali]<sup>+</sup>[superhalogen]<sup>-</sup> compounds. The ionic binding character between  $N_4Mg_6M$  and  $AlX_4$  guarantees the electronic integrity of  $N_4Mg_6M^+$  cations inside the  $N_4Mg_6M/AlX_4$  compounds. Moreover, from Figures 8-10, the structural identity of the  $N_4Mg_6M^+$  cations are maintained in the  $N_4Mg_6M/AlX_4$  systems as well.

As shown in Table 2, the HOMO–LUMO gaps of 4.449–6.847 eV for the  $N_4Mg_6M/AlX_4$  compounds are significantly large compared with those of 1.29 and 2.54 eV for the previously reported  $Al_{13}-K$ <sup>41</sup>  $BF_4-Mg_3Al$ <sup>4</sup> respectively, indicating the enhanced chemical stability of the studied superatom compounds. Besides, these ionic compounds also possess relatively large bond energies of 130-201 kcal/mol, comparable to (or larger) typical ionic bond energies. Hence, the  $N_4Mg_6M^+$  cations and superhalogen anions are expected to be strongly bound together and subsequently form stable superatom compounds.

In solid lattices, we would expect higher binding energies than between a pair of clusters. Earlier studies on superatomic cluster binary and bulk assemblies have shown that even in case of weak binary assembly interactions, high cohesive energies and a strong charge transfer can be achieved for corresponding binary bulk assemblies.<sup>42</sup> A high lattice energy and shorter distances between the clusters in the solid-state materials lead to stronger binding energies, such as more orbital overlap, stronger charge transfer, and enhanced long-range interactions.<sup>42</sup> Therefore, further investigations on the  $N_4Mg_6M/AlX_4$  solids should consider the role of the lattice structure in stabilizing these materials.

As we reported in the past<sup>43</sup>, the electronic affinity of superhalogens depends on the ligands of which those systems consist, and the larger atomic number of halogen atoms used as ligands results in the smaller EA of the resulting superhalogen. In particular, the adiabatic electronic affinity of  $AlF_4$  (AEA=8.108 eV) decreases by 2 eV when fluorine atoms are replaced with chlorine ligands (AEA of

6.102 eV). Thus,  $\text{AlCl}_4$  superhalogen, albeit characterized by large AEA, forms less stable compounds than  $\text{AlF}_4$  when combined with  $\text{N}_4\text{Mg}_6\text{M}$  superalkalis. In the case of each  $\text{N}_4\text{Mg}_6\text{M}-\text{AlF}_4$  /  $\text{N}_4\text{Mg}_6\text{M}-\text{AlCl}_4$  pair considered, we observed the weaker interactions between  $\text{N}_4\text{Mg}_6\text{M}$  and  $\text{AlX}_4$  subunits with replacing F atoms with Cl ligands, which is also accompanied by the charge flow decrease (Table IV). The distance between interacting subunits are in the 1.832-2.032 Å and 2.252-2.512 Å ranges for  $\text{N}_4\text{Mg}_6\text{M}-\text{AlF}_4$  and  $\text{N}_4\text{Mg}_6\text{M}-\text{AlCl}_4$  systems, respectively. Note that two factors determine the respective interaction energies: the electron affinity of superhalogen and the distance between interacting subunits. A larger EA of the superhalogen will yield stronger interaction, while a greater distance between interacting subunits will yield weaker interaction energy. In the case of  $\text{N}_4\text{Mg}_6\text{M}-\text{AlX}_4$  species, both EA and the distance between interacting subunits seem to play an important role, with interaction energy strengthening as EA gets larger and cation-anion distance gets smaller.

### 3.8 Competition between the IE of superalkalis and EA of Y on the stability of $\text{N}_4\text{Mg}_6\text{M}-\text{Y}$ species

The designed  $\text{N}_4\text{Mg}_6\text{M}$  superalkalis donate charge to  $\text{CO}_2$ ,  $\text{AlF}_4$ ,  $\text{AlCl}_4$  molecules, however, to a varying degree. In particular, the charge transfer results in  $\text{CO}_2$  bending and the C-O bonds weakness, hence making it easier to break. To indicate the dominant factor for  $\text{CO}_2$  activation and superatom compounds formation, we perform the comparison of relationship between the IE of superalkali, the amount of charge transfer to Y and the electron affinity of Y counterpart. The smaller IE of the superalkali leads the larger amount of charged transferred to  $\text{CO}_2$  molecule (-0.799, -0.803, -0.806 e for  $\text{N}_4\text{Mg}_6\text{Li}-\text{CO}_2$ ,  $\text{N}_4\text{Mg}_6\text{Na}-\text{CO}_2$ , and  $\text{N}_4\text{Mg}_6\text{K}-\text{CO}_2$ , respectively; see Figure 11). The relationship between IE of superalkali and amount of charged transfer to Y counterpart is also the case of the  $\text{N}_4\text{Mg}_6\text{M}-\text{AlX}_4$  superatom compounds. As soon as electron affinity of Y is considered, the  $\text{N}_4\text{Mg}_6\text{M}/\text{Y}$  systems show a monotonic increase in the amount of charge transfer with an increase in electron affinity of Y subunits; Figure 11. The stability of  $\text{N}_4\text{Mg}_6\text{M}/\text{Y}$  complexes increases gradually in the order  $\text{N}_4\text{Mg}_6\text{M}/\text{N}_2 < \text{N}_4\text{Mg}_6\text{M}/\text{CO}_2 < \text{N}_4\text{Mg}_6\text{M}/\text{AlCl}_4 < \text{N}_4\text{Mg}_6\text{M}/\text{AlF}_4$ , which is largely related to the electron affinity of the Y subunit therein. Therefore, both ionization energy of superalkali and electron



affinity of the molecule the superalkali is combined with are dominant factors for predicting the stability of certain species. Nevertheless, the  $N_4Mg_6M$  superalkali systems as enormously strong reducing agents are predicted to be capable to form ionic compounds when combined with nearly any neutral molecule whose electron affinity exceeds  $-0.6$  eV.

#### 4 Conclusions

In this contribution, we designed novel superalkali systems and examined their performance as reducing agents. Based on our results, we conclude as follows:

- (i) The adiabatic ionization energies obtained at the CCSD(T)/6-311+G(3df) level of theory read  $4.710$  ( $N_4Mg_6Li$ ),  $4.564$  ( $N_4Mg_6Na$ ),  $4.414$  eV ( $N_4Mg_6K$ ) and are smaller than those of the sodium atom ( $5.14$  eV at the same theory level), which emphasize their superalkali nature. This conclusion is also confirmed by their large HOMO-LUMO gaps and binding energies per atom.
- (ii) In superalkali/ $CO_2$  complexes, the O–C–O bond angle was smaller (by 9%) than that in the  $CO_2^-$  anion, and the amount of charge transfer reads c.a.  $0.8 e$  and increase with the ionization energy of superalkali decrease. The charge transfer made possible by low IE of superalkali seems to play a role in  $CO_2$  activation; a superalkali with a smaller IE should transfer an electron to carbon dioxide easily compared to one with a larger IE. Forming a bonding interaction between carbon and the electronegative atoms of reductant would also bend the linear  $CO_2$  structure.
- (iii) The  $N_4Mg_6M$  superalkalis form superatom compounds with superhalogens in which  $N_4Mg_6M^+$  cations maintain their structural integrity. These ionic compounds possess relatively large bond energies (of 130-201 kcal/mol), which are comparable (or even larger) than typical ionic bond energies. Hence, adamantane-like  $N_4Mg_6M$  cations and superhalogen anions are expected to form strongly bound superatom compounds, and consequently, to serve as building blocks for cluster-assembled materials. Further investigations should consider the role of lattice structure is stabilizing these materials.

## Supplementary material

See supplementary material for the geometrical structures of the studied superalkalis and superalkali/Y complexes.

## Dedication

This paper is dedicated to Iwona Anusiewicz, who is outstanding physical chemist. Iwona Anusiewicz has mentored and inspired many students, including one of the authors, to pursue careers in physical chemistry, during her academic career at University of Gdansk.

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## Data Availability Statement

The data that supports the findings of this study are available within the article and its supplementary material.

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## Figure captions:

Figure 1 The  $N_4Mg_6$  cage and its frontier orbitals (contour value=0.02).

Figure 2 The ground states of non-charged  $N_4Mg_6Li$ ,  $N_4Mg_6Na$ , and  $N_4Mg_6K$  species and their HOMOs (plotted with a fraction of electron density equal to 0.8). Adiabatic ionization energies (AIE, in eV) and bond lengths (in Å) are also provided.

Figure 3 The CCSD(T)/6-311+G(3df)//MP2/6-311+G(d) energy diagram showing relative stability of  $N_4Mg_6Li$  and  $N_4Mg_6Na$  and their ions (with respect to the anionic  $N_4Mg_6Li^-$  and  $N_4Mg_6Na^-$ , respectively, whose energies were taken as zero) and frontier molecular orbitals (LUMO or HOMO; plotted with a fraction of electron density equal to 0.8) for  $N_4Mg_6Li^{0,+,-}$  and  $N_4Mg_6Na^{0,+,-}$  species.

Figure 4 The ground states of the  $N_4Mg_6Li^+$ ,  $N_4Mg_6Na^+$ , and  $N_4Mg_6K^+$  cations. The bond distances in Å and NBO charges (in green) in  $e$ .

Figure 5 Cut-plane electron localization functions (ELF) of  $N_4Mg_6Li^-$  (top),  $N_4Mg_6Li$  (middle), and  $N_4Mg_6Li^+$  (bottom) in the plane of  $Mg_1-Mg_3-Mg_5$  (left column),  $N_1-N_2-N_4$  (middle column), and  $Li-N_2-Mg_4$  (right column). The big red circles are lithium atoms.

Figure 6 The MP2/6-311+G(d) equilibrium structures of  $N_4Mg_6M/CO_2$  ( $M=Li, Na, K$ ) systems, neutral  $CO_2$ , and  $CO_2^-$  anion. The CCSD(T)/6-311+G(d) relative energies ( $E_r$ , in kcal/mol) are obtained for  $N_4Mg_6M/CO_2$  complexes with respect to the corresponding global minimum (**A**, in red frames). Bond distances are expressed in Å.

Figure 7 Low-energy isomers of  $N_4Mg_6Li/N_2$  (left column),  $N_4Mg_6Na/N_2$  (middle column), and  $N_4Mg_6K/N_2$  (right column) complexes. The structures of neutral  $N_2$  and anionic  $N_2^-$  are also provided for comparison. For higher energy isomers see supporting information.

Figure 8 Equilibrium structures of  $N_4Mg_6Li$ /superhalogen species. The CCSD(T)/6-311+G(d) relative zero-point corrected energies ( $E_r$ , in kcal/mol) are obtained for  $N_4Mg_6Li$ /superhalogen systems with respect to the corresponding global minimum (**A**, in red frames). Bond distances are expressed in Å.

Figure 9 Equilibrium structures of  $N_4Mg_6Na$ /superhalogen species. The CCSD(T)/6-311+G(d) relative zero-point corrected energies ( $E_r$ , in kcal/mol) are obtained for  $N_4Mg_6Na$ /superhalogen systems with respect to the corresponding global minimum (**A**, in red frames). Bond distances are expressed in Å.

Figure 10 Equilibrium structures of  $N_4Mg_6K$ /superhalogen species. The CCSD(T)/6-311+G(d) relative zero-point corrected energies ( $E_r$ , in kcal/mol) are obtained for  $N_4Mg_6K$ /superhalogen systems with respect to the corresponding global minimum (**A**, in red frames). Bond distances are expressed in Å.

Figure 11 Interaction energy ( $E_{int}$  in kcal/mol) and charge flow ( $Q$  in  $e$ ) between superalkalis and **Y** counterparts.