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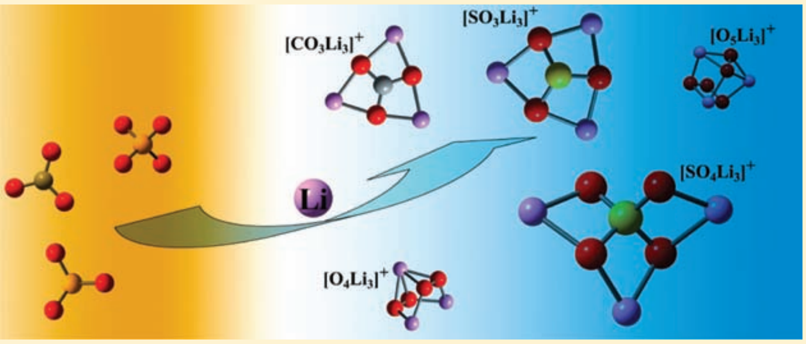
Theoretical Study on Polynuclear Superalkali Cations with Various Functional Groups as the Central Core

Jing Tong,[†,‡] Ying Li,[†] Di Wu,*[,†] and Zhi-Jian Wu*[,‡]

[†]Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130023, People's Republic of China

[‡]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

Ⓢ *Supporting Information*



ABSTRACT: A new series of polynuclear superalkali cations YLi_3^+ (Y = CO_3, SO_3, SO_4, O_4, and O_5) has been created when the central group is surrounded by alkali atoms. The structural characteristics and stabilities of these systems are provided on the basis of ab initio methods. In the lowest-energy structure of the $CO_3Li_3^+$, $SO_3Li_3^+$, and $SO_4Li_3^+$ cations, the central Y (Y = CO_3, SO_3, and SO_4) group features a slight distortion. The global minima of $O_4Li_3^+$ and $O_5Li_3^+$ are of the forms $O_2^-(Li^+)_3O_2^-$ and $O_2^-(Li^+)_3O_3^-$, respectively, both of which contain two monovalent ion units. The structural integrity of the central Y group and the arrangement of the lithium ligands are two influencing factors on the vertical electron affinities (EA_{vert}) for the YLi_3^+ species. The YLi_3^+ cation, with its lithium ligands being distributed evenly or far from each other, tends to exhibit a low EA_{vert} value, whereas a greater extent of cleavage of the central Y group leads to a higher EA_{vert} value and even makes some species lose their superalkali nature.

I. INTRODUCTION

Superalkali clusters are extraordinary compounds exhibiting lower ionization potentials (IPs) than those (5.39−3.89 eV)[1] of alkali-metal atoms. A lot of theoretical and experimental investigations have been carried out extensively to obtain more evidence and insight into the specific structural and electronic properties of these systems.[2−7] Most superalkali clusters investigated are hyperalkalized molecules of the ML_{k+n} type (where L is an alkali-metal atom, k is the maximal formal valence of the central atom M, and $n \geq 1$), which was introduced by Gutsev and Boldyrev.[3] The first evidence of such kinds of clusters is the Li_3O molecule, which was observed by mass spectrometric measurements over solid lithium oxide as early as 1979 and later indicated to be quite stable thermodynamically toward dissociation or loss of an electron by Schleyer and Wuerthwein.[8,9] The studies on such systems of interest also include, for example, XLi_2 (X = F, Cl, Br, and I),[10−15] OM_3 (M = Li, Na, and K),[16−20] NLi_4,[2] BLi_6,[21] etc.

Superalkali clusters are well-known for their ability to form unusual charge-transfer salts with a moiety possessing relatively low electron affinity. A crystal salt $Li_3O^+NO_2^-$ containing a singly charged superalkali cation Li_3O^+ was reported as early as 1938.[22] Afterward, using single-crystal X-ray diffraction, the true nature of the compound Na_3NO_3 was discovered to be sodium oxide nitrite, $Na_3O^+(NO_2)^-$,[23−25] where the superalkali cation Na_3O^+ can be detected in experiment.[26] In addition, superalkali structures can mimic the characteristics of alkali metals and maintain their structural and electronic integrities when combined with other species. Theoretical considerations have predicted some superatom compounds, such as BLi_6X (X = F, LiF_2, BeF_3, and BF_4),[27] $Al_{13}(K_3O)$, and $Al_{13}(Na_3O)$,[28] where the superalkali clusters serve as elementary molecular building units. Interest in superalkali clusters has increased in the last 2 decades, and a number of new types of superalkali clusters were predicted and characterized. In 2003, Alexandrova and Boldyrev reported that the Li_3 radical can be considered as a superalkali.[7] Recently, the Na_2X (X = SCN, OCN, and CN) species serving as building blocks have been predicted to possess superalkali nature with low IPs.[29] In our previous work, a series of

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binuclear superalkali cations with the $M_2Li_{2k+1}^+$ (M = F, O, N, C, and B for $k = 1-5$, respectively) formula were investigated in detail.[30,31]

Although the above developments bring out various low-IP superalkali clusters, limited investigation on the polynuclear superalkali clusters with multivalent functional groups as the central core is reported. Can the functional groups enable the polynuclear superalkali clusters to exhibit lower IPs than the traditional superalkali clusters of the ML_{k+n} type? Can the structural integrities of the functional groups be maintained inside the superalkali clusters? What about the influence of the different functional groups together with their behavior on the geometrical structures and IPs of polynuclear superalkali clusters? The consideration has motivated us to take a closer look at various polynuclear superalkali cations of this type and to investigate their structural and superalkali characteristics. Herein, the familiar CO_3^{2-}, SO_3^{2-}, and SO_4^{2-} dianions were chosen to play the role of the central core of superalkali cations.

In a precursory work, a combined experimental and theoretical effort was made to investigate the O_4^{2-} and O_5^{2-} dianions, which are analogous to the well-known inorganic anions SO_3^{2-} and SO_4^{2-}, respectively, and can be stabilized in the forms of $M^+O_4^{2-}$ and $M^+O_5^{2-}$ (M = Li, Na, K, and Cs) in the gas phase.[32,33] Moreover, the calculations proved that the FLi_3O_4 salt unit formed out of the FLi_3^{2+} dication and the O_4^{2-} dianion is stable toward any dissociation channel.[34] Clearly, the synthesis of any molecule containing O_4^{2-} or O_5^{2-} dianion would represent a major breakthrough in making even more oxygen-rich compounds. Such molecules containing more than three covalently bound oxygen atoms will have a great potential as high-density oxygen storage. Hence, in this contribution, we also select the O_4^{2-} and O_5^{2-} dianions as the central core of a kind of superalkali cation. Of course, such compounds, if made, would add candidates to the research on superatoms and offer potential building blocks for the assembly of new materials in which strong electron donors are involved.

In this article, we theoretically present a series of superalkali cations YLi_3^+ (Y = CO_3, SO_3, SO_4, O_4, and O_5). The main objectives of this contribution are (1) to exhibit the various structures of the polynuclear YLi_3^+ cations and explore the different behaviors of the Y functional groups in such species, (2) to calculate the vertical electron affinities (EA_{vert}) of the YLi_3^+ cations and discuss whether these species possess superalkali characteristics, or not (3) to search the correlation between the EA_{vert} values and the structural features and reveal the chief factors in lowering the EA_{vert} value. We hope that these results can be used as references on a variety of polynuclear superatoms, and such novel superalkali clusters may greatly enrich our knowledge and global view of the superalkali species.

II. THEORY AND COMPUTATIONS

The randomized algorithms[30,31,35−37] were used to search all of the minima structures of the YLi_3^+ (Y = CO_3, SO_3, SO_4, O_4, and O_5) cations. In this method, all atoms are placed at a common initial point in geometrical space and then tossed randomly within a sphere. Such a "zero" input structure can avoid biasing the search. The radius of the sphere varies from 2.0 to 7.0 Å for $CO_3Li_3^+$, $SO_3Li_3^+$, and $O_4Li_3^+$ and from 2.5 to 8.0 Å for $SO_4Li_3^+$ and $O_5Li_3^+$. A lot of starting geometries were obtained at the B3LYP/STO-3G level until no new minima appeared. To ensure that all of the minima have been located, randomized searches were implemented again in the region of one structure found above to do an intensive search for additional minima. The minima at the B3LYP/STO-3G level are then reoptimized at the MP2(full)/6-311+G(3df) level, followed by vibrational frequency calculations.

In addition, CCSD(T)/6-311+G(3df) single-point computations on these stable points were carried out.

The EA_{vert} values for these YLi_3^+ cations, which can reflect the IPs of their corresponding neutral species, were obtained and assigned on the basis of the restricted outer-valence Green function (OVGF)[38−43] method with the 6-311+G(3df) basis set. Natural bond orbital (NBO)[44] analyses were performed at the MP2/6-311+G(3df) level.

All calculations were performed using the *GAUSSIAN 09* program package.[45] Dimensional plots of molecular structures were generated with the *GaussView* program.[46]

III. RESULTS AND DISCUSSION

The optimized geometries of various isomers and the selected geometrical parameters of $CO_3Li_3^+$, $SO_3Li_3^+$, $SO_4Li_3^+$, $O_4Li_3^+$, and $O_5Li_3^+$ are shown in Figures 1−5, respectively. The symmetries, relative energies, lowest frequencies, highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) gaps, and the EA_{vert} values of these species are gathered in Tables 1−5, respectively. For convenience, we name the minimum-energy structures of YLi_3^+ **A**−**E**, ..., respectively. The total energies of these structures increased in the order **A** < **B** < **C** < **D** < **E** < ..., at the CCSD(T)/6-311+G(3df) level of theory.

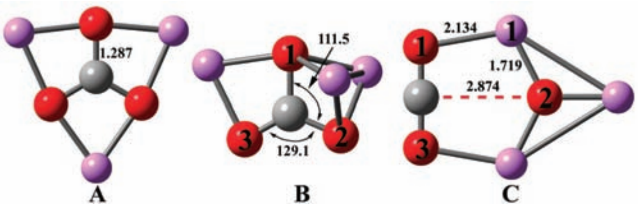

Figure 1. Three equilibrium structures of superalkali cation $CO_3Li_3^+$. Color legend: C, gray; O, red; Li, purple.

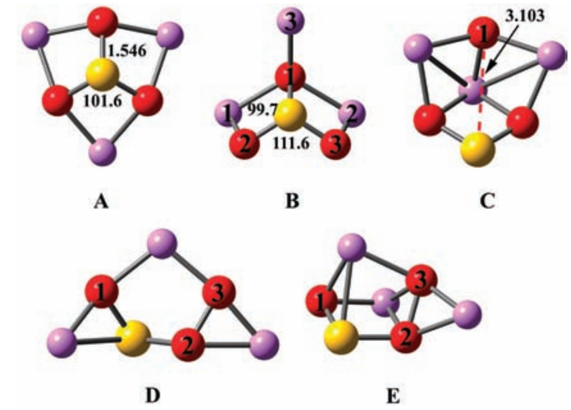

Figure 2. Five equilibrium structures of superalkali cation $SO_3Li_3^+$. Color legend: S, yellow; O, red; Li, purple.

To explore the thermodynamic driving force for dissociation for these cationic systems, the zero-point-corrected dissociation energies of selected fragmentation channels are obtained at the MP2(full)/6-311+G(3df) level and listed in Tables S1−S5 (Supporting Information), respectively. The NBO charges of the YLi_3^+ (Y = CO_3, SO_3, SO_4, O_4, and O_5) cations are shown

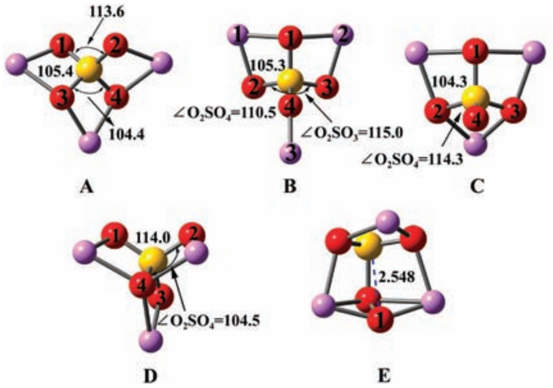

Figure 3. Five equilibrium structures of superalkali cation $SO_4Li_3^+$. Color legend: S, yellow; O, red; Li, purple.

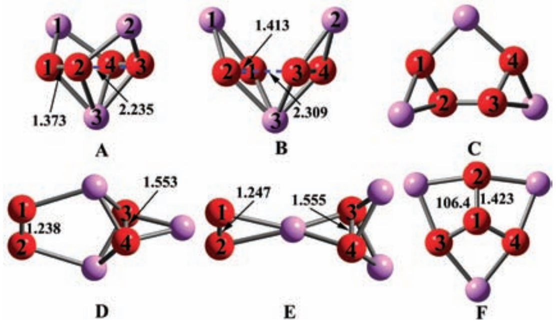

Figure 4. Six equilibrium structures of superalkali cation $O_4Li_3^+$. Color legend: O, red; Li, purple.

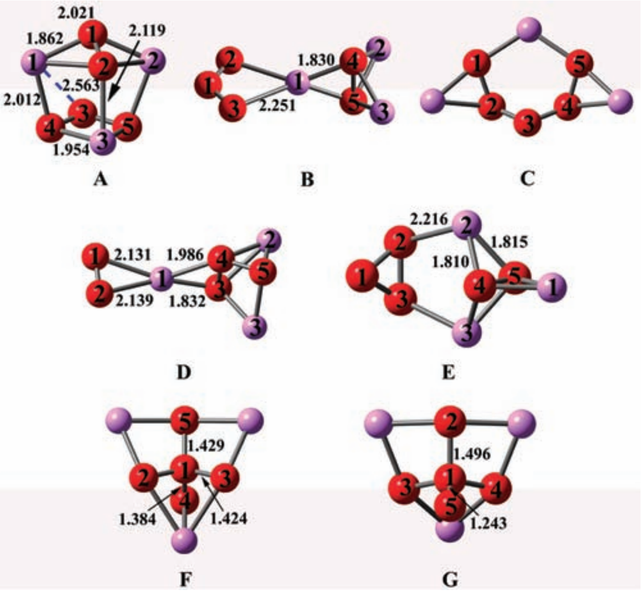

Figure 5. Seven equilibrium structures of superalkali cation $O_5Li_3^+$. Color legend: O, red; Li, purple.

in Figures S1−S5 (Supporting Information). In addition, the YLi_3^+ isomers, which are more than 100 kcal/mol higher in total energy than the global minima, are shown in Figures S6−S9 (Supporting Information), and their structures and properties are not discussed in detail here.

In the following subsections, the structural features, together with the EA_{vert} values of the isomers for each YLi_3^+ cation, are discussed in detail.

Table 1. Symmetry Point Groups, Relative Energies E_{rel} (in kcal/mol), Lowest Vibrational Frequencies (ν_1, in cm^{-1}), HOMO−LUMO Gaps (in eV), EA_{vert} (in eV), and Average C−O Bond Lengths [R_{C-O}, in Å] of the $CO_3Li_3^+$ Cations

isomer	symmetry	E_{rel} (kcal/mol)	ν_1 (cm^{-1})	gap (eV)	EA_{vert} (eV)	R_{C-O} (Å)
A	D_{3h}	0.00	174.7	13.9	3.03	1.287
B	C_s	32.34	140.3	12.9	3.70	1.297
C	C_{2v}	51.66	31.1	10.8	3.34	1.164

III.1. $CO_3Li_3^+$.

Three forms of $CO_3Li_3^+$ cations are illustrated in Figure 1. The D_{3h}-symmetrical **A** is the most stable structure in which three lithium atoms and the CO_3^{2-} group are coplanar, featuring the lithium atoms bonded on each O−O side, respectively. The structural integrity of the CO_3^{2-} group is found to be maintained inside isomer **A** with a C−O bond length of 1.287 Å and a O−C−O angle of 120°.

The next isomer **B** is 32.34 kcal/mol less stable than **A**. The average C−O bond of 1.297 Å in **B** is longer by 0.01 Å than that involved in isomer **A**. In addition, the angle O−C−O in the free CO_3^{2-} ion is 120°, while the ∠O1CO2 and ∠O2CO3 angles are 111.5° and 129.1°, respectively, in isomer **B**. Clearly, the CO_3^{2-} group is distorted from its D_{3h} structure in **B** because of the asymmetrical arrangement of the lithium ligands.

Isomer **C** is of C_{2v} symmetry, where four atoms of the CO_3 group are linked via two lithium atoms. The middle C−O2 distance of 2.874 Å is much longer than that of the lowest-energy isomer **A**, and the bridged O1−Li1 distance of 2.134 Å is relatively long compared with the O2−Li1 bond length of 1.719 Å. This indicates that this structure is composed of CO_2 and OLi_3^+ units. Hence, isomer **C** can be characterized as $(CO_2)(OLi_3)^+$, which is also supported by NBO analyses. From Figure S1 in the Supporting Information, the NBO charges on the CO_2 and OLi_3^+ units are 0.054 and 0.946, respectively.

As can be seen from Figure S6 in the Supporting Information, in the cases of isomers **D** and **E**, the CO_3^{2-} core is also distorted significantly from the planar D_{3h} structure to a three-dimensional geometry. Therefore, the stabilities of isomers of $CO_3Li_3^+$ are closely related to the structure of CO_3^{2-} core. The preferred structure for $CO_3Li_3^+$ is **A**, and the second is structure **B**, in both of which the distortion of the CO_3^{2-} ion is slight. As for the other isomers, the CO_3^{2-} ion is significantly distorted compared with **A** and **B**. Thus, the structural isomers with the integral CO_3^{2-} core will have a higher stability than the structural isomers with a distorted CO_3^{2-} core.

The gap between HOMO and LUMO is a useful quantity for examining the stability of the clusters. It is found that systems with larger HOMO−LUMO energy gaps are less reactive. From Table 1, the HOMO−LUMO gaps of $CO_3Li_3^+$ are as large as 10.8−13.9 eV. Note that the lowest-energy structure **A** exhibits the largest HOMO−LUMO gap of 13.9 eV, which is much larger than that of mononuclear superalkali cation OLi_3^+ [10.58 eV at the same MP2/6-311+G(3df) level]. This suggests an enhanced stability of $CO_3Li_3^+$. In addition, the dissociation reactions shown in Table S1 in the Supporting Information are all endothermic, indicating the stabilities of the $CO_3Li_3^+$ cations with respect to elimination of Li^+ or O_2.

As can be seen from Table 1, the EA_{vert} values of the $CO_3Li_3^+$ cations are all lower than the IP = 3.90 eV of the cesium atom and greatly lower than the IP = 5.34 eV of the lithium ligand. Thus, the studied $CO_3Li_3^+$ species should be classified as superalkali cations, and the corresponding neutral CO_3Li_3

Table 2. Symmetry Point Groups, Relative Energies E_{rel} (in kcal/mol), Lowest Vibrational Frequencies (ν_1, in cm^{-1}), HOMO−LUMO Gaps (in eV), EA_{vert} (in eV), and Average S−O Bond Lengths [R_{S-O}, in Å] of the $SO_3Li_3^+$ Cations

isomer	symmetry	E_{rel}(kcal/mol)	ν_1(cm^{-1})	gap (eV)	EA_{vert} (eV)	R_{S-O} (Å)	SO_3^{2-} (condensed phase data)[a]
A	C_{3v}	0.00	191.7	11.7	3.28	1.546	R_{S-O} = 1.51 Å
B	C_s	23.07	106.4	10.8	3.80	1.553	∠OSO = 106°
C	C_1	71.70	43.9	5.8	6.07	2.077	
D	C_1	95.96	95.6	9.9	3.13	1.931	
E	C_1	96.04	131.5	9.7	3.49	1.964	

[a] The structural data are from ref 47.

Table 3. Symmetry Point Groups, Relative Energies E_{rel} (in kcal/mol), Lowest Vibrational Frequencies (ν_1, in cm^{-1}), HOMO−LUMO Gaps (in eV), EA_{vert} (in eV), and Average S−O Bond Lengths [R_{S-O}, in Å] of the $SO_4Li_3^+$ Cations

isomer	symmetry	E_{rel}(kcal/mol)	ν_1(cm^{-1})	gap (eV)	EA_{vert} (eV)	R_{S-O} (Å)	SO_4^{2-} (condensed phase data)[a]
A	C_2	0.00	133.0	13.5	3.34	1.486	R_{S-O} = 1.49 Å
B	C_s	2.40	61.7	13.0	3.17	1.481	∠OSO = 109.5°
C	C_{3v}	5.47	145.5	13.3	3.48	1.489	
D	C_{3v}	8.07	129.6	13.0	3.71	1.489	
E	C_s	76.86	64.2	9.7	3.46	1.815	

[a] The structural data are from ref 47.

Table 4. Symmetry Point Groups, Relative Energies E_{rel} (in kcal/mol), Lowest Vibrational Frequencies (ν_1, in cm^{-1}), HOMO−LUMO Gaps (in eV), and EA_{vert} (in eV) of the $O_4Li_3^+$ Cations

isomer	symmetry	E_{rel}(kcal/mol)	ν_1 (cm^{-1})	gap (eV)	EA_{vert} (eV)
A	C_{2v}	0.00	115.9	9.4	4.85
B	C_{2v}	3.48	127.2	8.4	5.29
C	C_2	3.61	106.5	12.6	3.08
D	C_{2v}	7.07	80.8	10.5	6.39
E	C_{2v}	8.35	31.5	10.8	6.09
F	C_{3v}	12.82	153.0	13.3	3.20

Table 5. Symmetry Point Groups, Relative Energies E_{rel} (in kcal/mol), Lowest Vibrational Frequencies (ν_1, in cm^{-1}), HOMO−LUMO Gaps (in eV), and EA_{vert} (in eV) of the $O_5Li_3^+$ Cations

isomer	symmetry	E_{rel}(kcal/mol)	ν_1(cm^{-1})	gap (eV)	EA_{vert} (eV)
A	C_s	0.00	133.5	7.0	6.84
B	C_{2v}	5.81	14.6	9.6	6.46
C	C_s	8.07	87.9	12.9	3.02
D	C_1	19.68	20.4	10.2	6.39
E	C_s	39.82	70.8	12.6	3.11
F	C_s	81.28	73.0	13.6	3.27
G	C_{3v}	82.64	103.0	12.2	3.55

species can be regarded as superalkali clusters. Among the three $CO_3Li_3^+$ cations, isomer **A**$^+$ shows the lowest EA_{vert} value of 3.03 eV, which might be related to its higher molecular symmetry (D_{3h}) and even distribution of the lithium ligands. As one can notice, the three ligand lithium atoms are not linked in isomer **A** and distribute far away from each other around the CO_3^{2-} ion. From Figure 1, the lithium ligands tend to link each other in structures **B** and **C**, which is a disadvantage for these two isomers to evenly disperse the excess positive charge. As a result, their EA_{vert} values are 3.70 and 3.34 eV, respectively, which are a bit higher than that of **A** without Li−Li connections.

III.2. $SO_3Li_3^+$.

Eight structures are identified for superalkali cations $SO_3Li_3^+$, and the first five low-energy structures are illustrated in Figure 2. The **A** form is the most stable isomer of $SO_3Li_3^+$ and exhibits a cap-shaped structure with C_{3v} symmetry. In this structure, three ligand lithium atoms attach respectively to each O−O side of the central SO_3^{2-} core. From Figure 2 and Table 2, the S−O bond length of 1.546 Å and ∠OSO of 101.6° in **A** are very close to the corresponding crystal data (R_{S-O} = 1.51 Å; ∠OSO = 106°).[47] Clearly, the SO_3^{2-} group has a very slight distortion in **A** after interaction with the lithium ligands.

The less favorable structure of $SO_3Li_3^+$, **B**, is higher in energy by 23.07 kcal/mol than **A**. In isomer **B**, the average S−O bond length of 1.553 Å is longer by 0.007 Å than that in **A**, and the bond angle ∠O1SO2 of 99.7° is smaller, and the bond angle ∠O2SO3 of 111.6° is larger, than the angle value (101.6°) in isomer **A**. As can be seen from Figure 2, structure **B** features that the Li1(2) atom attaches to the O−O side, and the Li3 atom is linked to the O1 atom. Hence, the SO_3^{2-} group in **B** is distorted from the C_{3v} geometry because of the uneven interaction with the lithium ligands.

The next stable isomer **C** is 48.63 kcal/mol less stable than **B**. In this C_1 structure, the S−O1 distance of 3.103 Å is about twice as long as that in isolated SO_3^{2-}, and the average S−O distance of 2.077 Å is much longer compared to the corresponding crystal data (1.51 Å). Obviously, the SO_3^{2-} group in **C** is broken into two parts, which are bridged by the lithium ligands.

In the two structures **D** and **E**, the SO_3^{2-} groups present chainlike structures, featuring the sulfur atom inserted into the O_3 cluster, thereby forming an O_2SO segment. The average S−O distances (R_{S-O}) in **D** and **E** are 1.931 and 1.964 Å, respectively. From Figure S2 in the Supporting Information, the NBO charges on the O_2SO unit are −1.648 and −1.579 for **D** and **E**, respectively. So, both isomers **D** and **E** can be regarded as structures in which the O_2SO^{2-} core is surrounded by three Li^+ cations. Hence, the difference in the total energy between **D** and **E** is only 0.08 kcal/mol.

Similar to $CO_3Li_3^+$, the first two low-energy isomers of $SO_3Li_3^+$, namely, **A** and **B**, have slightly distorted SO_3^{2-} cores. From Table 2, the HOMO−LUMO gaps of $SO_3Li_3^+$ are in the range of 5.8−11.7 eV. Note that the most stable isomer **A** possesses the largest gap among all of the $SO_3Li_3^+$ species. From Table S2 in the Supporting Information, all of the isomers of $SO_3Li_3^+$ are stable with respect to loss of a Li^+ cation or an O_2 molecule.

It is confirmed theoretically that the $SO_3Li_3^+$ species have very low EA_{vert} values in the range of 3.13–3.80 eV except isomer **C**. Interestingly, it is found that the EA_{vert} value of an isomer is closely related to the distribution of lithium ligands. One key to lower EA_{vert} is to distribute the lithium ligands as evenly as possible around the central core, which benefits a more even distribution of the excess positive charge. In addition, another important factor in lowering the EA_{vert} value is to distribute the lithium ligands far from each other, which helps to disperse the excess positive charge and therefore reduce the repulsion interaction. Among the five isomers, **D** shows the lowest EA_{vert} of 3.13 eV. This might be related to its chainlike O_2SO segment, which can distribute three lithium atoms as far as possible from each other. Isomer **A**, with three lithiun ligands evenly distributed, has the second lowest EA_{vert} of 3.28 eV. It is noteworthy that the SO_3 group was cleaved by the lithium atoms in isomer **C**, resulting in a high EA_{vert} value of 6.07 eV of this structure. Consequently, isomer **C** loses the superalkali characteristics.

III.3. $SO_4Li_3^+$.

Five structures for superalkali cation $SO_4Li_3^+$ are presented in Figure 3. The C_2 isomer **A** is the lowest-energy structure of $SO_4Li_3^+$ at the MP2(full)/6-311+G(3df) level of theory. The average S–O bond length (R_{S-O}) of 1.486 Å for **A** is very close to the corresponding crystal data (1.49 Å)[47] which is also listed in Table 3. From Figure 3, the bond angles ∠O1SO2, ∠O1SO3, and ∠O3SO4 in isomer **A** are 113.6°, 105.4°, and 104.4°, respectively. Clearly, the differences in ∠OSO between the optimized structure of **A** and the crystal data (109.5°)[47] never exceed 5.1°. Hence, the structural integrity of SO_4^{2-} is found to be maintained inside isomer **A**.

The less favorable structure of $SO_4Li_3^+$, **B**, is higher in energy by 2.40 kcal/mol than **A**. In isomer **B** of C_s symmetry, the Li1(2) atom attaches to the O–O side, and the Li3 atom is linked to the O4 atom. The average S–O bond length (R_{S-O}) of 1.481 Å is shorter by 0.005 Å than that in **A**, and the bond angles ∠O1SO2, ∠O2SO4, and ∠O2SO3 are 105.3°, 110.5°, and 115.0°, respectively. It is clear from these results that the central SO_4^{2-} group is distorted slightly in isomer **B**.

The difference in the total energy between the two isomers **C** and **D** is only 2.60 kcal/mol. Both of the species have average S–O bond lengths (R_{S-O}) of 1.489 Å, which are also close to the crystal data (1.49 Å). From Figure 3, the SO_4^{2-} groups are distorted differently in these two complexes. In isomer **C**, the S–O1(2,3) bond length of 1.513 Å is longer and the S–O4 bond length of 1.418 Å is shorter than the crystal data (1.49 Å). Oppositely, in isomer **D**, the S–O1(2,3) bond length of 1.459 Å is shorter and the S–O4 bond length of 1.579 Å is longer compared with the crystal data. Hence, the SO_4 tetrahedron is shortened along the S–O4 axis for **C** and elongated along the S–O4 axis for **D**. Both isomers **C** and **D** have C_{3v} symmetry and a pyramidal SO_4^{2-} core. From Figure 3, three lithium atoms are attached to the bottom edge (i.e., O1–O2, O2–O3, and O1–O3) of the pyramidal SO_4^{2-} core in the former and are bonded to the side edge (i.e., O1–O4, O2–O4, and O3–O4) of the SO_4^{2-} core in the latter. Hence, the bond angle ∠O1SO2 of 104.3° is much smaller than ∠O2SO4 of 114.3° in isomer **C**, whereas the reverse is observed for the bond angles ∠O1SO2 (114.0°) and ∠O2SO4 (104.5°) in **D**.

The least favorable structure of $SO_4Li_3^+$ is isomer **E** with C_s symmetry, which is found to have far higher energy than the first four species (see Table 3). Note that the S–O1 distance of 2.548 Å is much longer than the other S–O bonds; hence, the central SO_4^{2-} group is distorted severely in this structure.

It can be clearly seen that the structural integrity of the SO_4^{2-} group is maintained inside the first four isomers **A**–**D** of $Li_3SO_4^+$ and is broken in the last isomer **E**. It can be concluded from these tendencies that the geometry of the SO_4^{2-} core strongly affects the stability of $SO_4Li_3^+$. As listed in Table 3, the HOMO–LUMO gaps of $SO_4Li_3^+$ are in the range of 9.7–13.5 eV, and the most stable isomer **A** and the least stable isomer **E** exhibit the largest and the lowest gap values among all of the $SO_4Li_3^+$ species, respectively. As can be seen from Table S3 in the Supporting Information, dissociating a Li^+ cation or an O_2 molecule from the $SO_4Li_3^+$ cations requires significant 275.8–358.8 and 68.1–151.1 kcal/mol, respectively, indicating the stabilities of $SO_4Li_3^+$ with respect to emission of Li^+ or O_2.

As is shown in Table 3, the EA_{vert} values for the $SO_4Li_3^+$ cations are in the 3.17–3.71 eV range, which are all lower than the IP = 3.9 eV of the cesium atom and greatly lower than the IP of the lithium ligand. In addition, isomer **B** with lithium ligands distributed far from each other shows the lowest EA_{vert} value.

III.4. $O_4Li_3^+$.

In precursory work, Adamantides et al. theoretically predicted the covalently bound cyclic (D_{2h}) form of O_4.[48] Subsequent theoretical studies have also identified a D_{3h} form analogous to SO_3.[49,50] However, both of the structures are highly unstable and were found to be ~5.3 and ~6.5 eV higher in energy, respectively, than two separate O_2 molecules. Recently, two species containing oxygen dianion O_4^{2-} have been reported, namely, MO_4^- (M = Li, Na, and K)[32] and FLi_3O_4.[34] The $O_2^-M^+O_2^-$ isomer was found to be more stable than the $M^+O_4^{2-}$ isomer by ~2.4–2.9 eV in energy. As for FLi_3O_4, the isomer containing a rectangular structure of O_4^{2-} is lower in energy compared to the isomer containing the pyramidal C_{3v}-symmetrical O_4^{2-} dianion.

In this contribution, six structures are obtained for the $O_4Li_3^+$ cations (see Figure 4). The lowest-energy structure of $O_4Li_3^+$ is isomer **A** with C_{2v} symmetry, which contains a covalently bound cyclic O_4^{2-} dianion. The second isomer **B**, which is only 3.48 kcal/mol less stable than **A**, presents similar structural characteristics. In both structures, we found that the O_4^{2-} dianion had a rectangular shape with two short O–O distances and two long O–O distances. This conclusion is also consistent with the results calculated by Elliott and Boldyrev.[34] The short O1–O2 bond length and the long O2–O3 bond length in isomer **A** are 1.373 and 2.235 Å, respectively, which are slightly shorter than those in **B** with a O1–O2 bond length of 1.413 Å and a O2–O3 bond length of 2.309 Å. Besides, the Li1(2) atom is attached to the long O–O bond (i.e., O1–O4 and O2–O3) in the former and attached to the short O–O bond (i.e., O1–O2 and O3–O4) in the latter. Another Li3 atom attaches to one face of the planar O_4 unit in both structures. A natural population analysis clearly shows that the pyramidal O_4 group carries an effective charge close to −2 [−1.64 for **A** and −1.63 for **B** at the MP2/6-311+G(3df) level]. Hence, the O_4^{2-} unit can be considered as the core of the superalkali cation $O_4Li_3^+$. From another viewpoint, both structures **A** and **B** can also be considered as two O_2^- anions linked via lithium atoms, but the O_4^{2-} core is not completely cleaved.

Isomer **C** is found to be only 3.61 kcal/mol higher in energy than **A**. Similar to the structure **D** of $SO_3Li_3^+$, the O1, O2, O3, and O4 atoms in this structure are connected successively and represent a spiral-type chainlike array; therefore, it exhibits C_2 symmetry. From the NBO results, isomer **C** can be characterized as $O_4^{2-}(Li^+)_3$, and the O_4^{2-} unit can be considered as the core of superalkali cation $O_4Li_3^+$. Although O_4^{2-} in isomer **C** presents a peculiar chainlike geometry, it maintains the integrity and is not cleaved by lithium atoms.

Both isomers **D** and **E** have C_{2v} symmetry with two O_2 units separated by lithium bridge atoms. Different from the condition in isomers **A** and **B**, the NBO charges on the O_4 group in **D** and **E** are not averaged over two O_2 units. From Figure S4 in the Supporting Information, the charges on the O1−O2 and O3−O4 units in **D** are 0.085 and −1.635, respectively, so this structure can be regarded as the O_2 molecule bound to the $(Li^+)_3O_2^{2-}$ unit. This description is also valid for isomer **E**. Hence, the difference in the total energy between **D** and **E** is only 1.28 kcal/mol. The O1−O2 bond length of 1.238 Å and the O3−O4 bond length of 1.553 Å in isomer **D** are very close to the corresponding parameters of isomer **E** with a O1−O2 bond length of 1.247 Å and a O3−O4 bond length of 1.555 Å. Clearly, in structures **D** and **E**, the O_4 unit has been completely cleaved by lithium atoms.

The least favorable structure of $O_4Li_3^+$ is **F** with C_{3v} symmetry, which is 12.82 kcal/mol less stable than **A**. Our optimized geometrical parameters are presented in Figure 4. The calculated O1−O2(3,4) bond length (1.423 Å) and bond angle ∠O2O1O3 (106.4°) for the O_4^{2-} dianion in isomer **F** are close to the corresponding crystal data of the SO_3^{2-} dianion (R_{S-O} = 1.51 Å; ∠OSO = 106°).[47] In addition, the geometrical parameters of the pyramidal O_4^{2-} core are found to be reasonable when compared to the isoelectronic and isostructural SO_3^{2-} core in isomer **A** of $SO_3Li_3^+$ (R_{S-O} = 1.546 Å; ∠OSO = 101.6°), suggesting that chemical species containing an O_4^{2-} dianion may exist. However, we found that this structure of $O_4Li_3^+$ containing the pyramidal O_4^{2-} dianion is not only less stable than the structures with rectangular O_4^{2-} dianion but also less stable than the structure with chainlike covalently bound O_4^{2-} dianion.

From Table 4, all of the $O_4Li_3^+$ species show large HOMO−LUMO gaps ranging from 8.4 to 13.3 eV. In addition, from the discussion above, the preferential order for the $O_4Li_3^+$ structures is containing rectangular O_4^{2-} dianion (**A** and **B**) > chainlike O_4^{2-} dianion (**C**) > separated O_2 and O_2^{2-} units (**D** and **E**) > pyramidal O_4^{2-} dianion (**F**). It is found that the structures (**A** and **B**) containing two O_2^- anions are more stable than the structures (**D** and **E**) containing one O_2 molecule and one O_2^{2-} dianion. Also, note that our theoretical study predicts the first compound containing the chainlike covalently bound O_4^{2-} dianion, which is not only more stable than the form containing previously found pyramidal O_4^{2-} dianion but also more stable than the isomers containing separate O_2 units. This might provide new candidates for oxygen-rich species and offer potential as models for understanding oxygen-storage properties.

For the $O_4Li_3^+$ cations, the dissociation channels of $O_4Li_3^+ \rightarrow Li^+ + Li_2O_4$, $O_4Li_3^+ \rightarrow Li_3O_2^+ + O_2$, and $O_4Li_3^+ \rightarrow O_3 + Li_3O^+$ are considered. As shown in Table S4 in the Supporting Information, the $O_4Li_3^+$ cations are stable upon loss of Li^+ or O_3 with positive dissociation energies. The preferred channel for $O_4Li_3^+$ is the emission of an O_2 molecule, and only isomers **A** and **B** exhibit positive dissociation energies (see Table S4 in the Supporting Information).

Similar to superalkali cations $SO_3Li_3^+$, the lowest EA_{vert} value (3.08 eV) for the $O_4Li_3^+$ cations is found for isomer **C** including a chainlike O_4^{2-} unit, in which the ligand lithium atoms distribute as far as possible from each other. From Figure 4, isomer **F** has an arrangement of the lithium ligands similar to that of **C**, and it shows the second low EA_{vert} value of 3.20 eV. In structures **A** and **B**, the central O_4^{2-} groups can be considered as partially cleaved by lithium atoms. Hence, these two isomers show relatively higher EA_{vert} values, that is, 4.85 and 5.29 eV, respectively. However, these EA_{vert} values are lower than the IP = 5.34 eV of the ligand lithium atoms, so isomers **A** and **B** still possess superalkali nature. The EA_{vert} values of 6.39 eV for **D** and 6.09 eV for **E** are much higher than the IP = 5.39 eV of the lithium ligand. Hence, these two isomers with separate O_2 and O_2^{2-} units cannot be considered as superalkali cations.

III.5. $O_5Li_3^+$. The experimental and ab initio investigations on the MO_5^+ (M = Li, Na, and K) species[32] have shown that the C_{2v} structures with separate O_2^- and O_3^- units are more stable than the covalently bound C_{3v} structures containing a pyramidal structure of the O_5^{2-} dianion. In this Article, we found that both the separated and tetrahedral covalently bound O_5^{2-} dianions could be part of the $O_5Li_3^+$ ions. More importantly, we present the theoretical evidence for a novel structure of $O_5Li_3^+$, which contains an unforeseen chainlike O_5^{2-} dianion and is a true minimum.

The first seven low-energy structures for $O_5Li_3^+$ are illustrated in Figure 5. The global minimum-energy structure **A** possesses C_s symmetry, in which two separate O_2 and O_3 units interact with three bridged lithium atoms (see Figure 5). The bridged O−Li bond lengths of **A** are 1.862−2.119 Å except that the O3−Li1 distance of 2.563 Å is relatively long. From Figure S5 in the Supporting Information, the O_2 and O_3 units carry −0.874 and −0.669 NBO charges, respectively, so isomer **A** can be characterized as $O_2^-(Li^+)_3O_3^-$.

The less favorable structure of $O_5Li_3^+$, **B**, is found to be higher in energy by 5.81 kcal/mol than **A**. The structure **B** is of C_{2v} symmetry, with two separate O_2 and O_3 units located on opposite sides of a central Li^+ cation and another two Li^+ cations linked to the O_2 unit. This species can be characterized as $O_3[O_2^{2-}(Li^+)_3]$, with the O_3 molecule bound to an apex of the $O_2^{2-}(Li^+)_3$ unit, which is also supported by NBO analyses. The O4(5)−Li1 bond length of 1.830 Å is far shorter than the O2(3)−Li1 bond length of 2.251 Å.

In the next stable isomer **C** with C_s symmetry, the O1, O2, O3, O4, and O5 atoms are connected successively, thereby forming a chainlike array. As can be seen from Figure S5 in the Supporting Information, the NBO charge on the O_5 unit is −1.678, so isomer **C** can be regarded as an integrated O_5^{2-} ion bound by three ligand lithium atoms.

The C_1-symmetrical **D** is found to have separate O_2 and O_3^{2-} units bridged via a Li^+ cation, as shown in Figure 5. Differently from structure **B**, it can be characterized as $O_2Li^+O_3^{2-}(Li^+)_2$, which is also supported by the NBO charges (see Figure S5 in the Supporting Information). The bridged O−Li bond lengths of **D** are 1.832−2.139 Å.

Similar to **B**, isomer **E** also has separate O_3 and O_2^{2-} units, which are linked via two Li^+ cations. From another viewpoint, structure **E** can also be considered as an O_3 molecule bound to the $O_2^{2-}(Li^+)_3$ unit. The O5−Li2(3) bond length of 1.815 Å and the O4−Li2(3) bond length of 1.810 Å are far shorter than the O2−Li2 (O3−Li3) bond length of 2.216 Å.

The optimized geometries of the least favorable structures **F** and **G** are quite similar to those of isomers **B** and **C** of $SO_4Li_3^+$, respectively. Both structures **F** and **G** contain the tetrahedral O_5^{2-} dianions, and they exhibit geometrical parameters very similar to each other. As a result, the total energy difference between them is very small (1.36 kcal/mol). From Figure 5, the average O1−O(2,3,4,5) bond lengths in isomers **F** and **G** are 1.415 and 1.432 Å, respectively, which are close to the corresponding data of the SO_4^{2-} dianion (R_{S-O} = 1.49 Å).[47] Although isomers **F** and **G** are 81.28 and 82.64 kcal/mol less stable than **A**, respectively, these two forms containing tetrahedral covalently bound O_5^{2-} dianion are true minima on the potential energy surfaces. Furthermore, the integrated tetrahedral O_5^{2-} dianion adds candidates to the core of superalkali clusters.

From the discussions above, it is found that the preferential order for the $O_5Li_3^+$ isomers is containing two separate units (**A**, **B**, **D**, and **E**) > tetrahedral O_5^{2-} dianion (**F** and **G**), which is in line with the conclusions by Boldyrev et al. that the $O_2^-M^+O_3^-$ form is more stable than the covalently bound species $M^+O_5^{2-}$.[32] In addition, it is also found that the structure (**A**) containing separate O_2^- and O_3^- anions is more stable than the structures (**B**, **D**, and **E**) containing one molecule and one dianion (O_2 and O_3^{2-} or O_3 and O_2^{2-}). Note that the structure containing a novel chainlike O_5^{2-} dianion was found for the $O_5Li_3^+$ cation, which is more stable than the forms containing a tetrahedral covalently bound O_5^{2-} dianion. As collected in Table 5, the HOMO−LUMO gaps of $O_5Li_3^+$ are in the range of 7.0−13.6 eV, which are as large as those of other YLi_3^+ cations. From Tables S5 in the Supporting Information, dissociating a Li^+ cation from each $O_5Li_3^+$ isomer is endothermic. However, only two isomers of $O_5Li_3^+$, namely, **A** and **B**, show stabilities with respect to emission of an O_2 or O_3 molecule.

The EA_{vert} values for the $O_5Li_3^+$ cations are listed in Table 5. Isomer **C** including a chainlike O_5^{2-} unit is found to possess the lowest EA_{vert} value (3.02 eV). This observation is consistent with the above investigation on superalkali cation $O_4Li_3^+$. In addition, isomers **F** and **G** with O_5^{2-} tetrahedra also show low EA_{vert} values, that is, 3.27 and 3.55 eV, respectively. From Table 5, the $O_5Li_3^+$ species with well-separated O_5^{2-} dianions (**A**, **B**, and **D**) have very high EA_{vert} values in the range of 6.39−6.84 eV except that isomer **E** shows the second lowest EA_{vert} value of 3.11 eV. Hence, isomers **A**, **B**, and **D** cannot be considered to exhibit superalkali nature.

IV. CONCLUSIONS AND OUTLOOK

Our systematic calculations on the YLi_3^+ (Y = CO_3, SO_3, SO_4, O_4, and O_5) cations have theoretically predicted a new type of polynuclear superalkali species. Careful analyses of the geometries and energetic properties of YLi_3^+ showed that the stabilities of these cations were related to the structural characteristics of the central core. The structural integrity of the central Y group maintains inside the preferred structures of the $CO_3Li_3^+$, $SO_3Li_3^+$, and $SO_4Li_3^+$ cations. Besides, the less the central group is distorted, the higher stability of the isomer exhibits. However, in the global minima of the $O_4Li_3^+$ and $O_5Li_3^+$ cations, both of the central cores can be considered as two monovalent ion units (i.e., O_2^- and O_2^- in $O_4Li_3^+$; O_2^- and O_3^- in $O_5Li_3^+$). That is, the most stable $O_4Li_3^+$ and $O_5Li_3^+$ species are actually of the $O_2^-(Li^+)_3O_2^-$ and $O_2^-(Li^+)_3O_3^-$ forms, respectively. According to the positive dissociation energies, the lowest-energy isomer of each YLi_3^+ cation is stable with regard to loss of Li^+, O_2 or O_3 molecule.

The EA_{vert} values for these YLi_3^+ cations at the OVGF/6-311+G(3df) level are closely related to the structural characteristics of the central core and the arrangement of the lithium ligands. For the $CO_3Li_3^+$, $SO_3Li_3^+$, and $SO_4Li_3^+$ cations, most isomers exhibit lower EA_{vert} values than the IP = 5.39 eV of the ligand lithium atom except that isomer **E** of $SO_3Li_3^+$ including a totally cleaved central group shows a relatively higher EA_{vert} value of 6.07 eV. For the $O_4Li_3^+$ and $O_5Li_3^+$ cations, isomers containing completely cleaved O_4^{2-} and O_5^{2-} dianions usually have high EA_{vert} values and therefore cannot be regarded as superalkali species. In addition, distributing the lithium ligands evenly and far from each other is found to be another key factor to a lower EA_{vert} value.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected dissociation channels and calculated dissociation energies of the YLi_3^+ (Y = CO_3, SO_3, SO_4, O_4, and O_5) cations, high-energy structures of the YLi_3^+ cations, and NBO charges on each atom of the YLi_3^+ cations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wud@mail.jlu.edu.cn (D.W.), zjwu@ciac.jl.cn (Z.-J.W.).

Notes

The authors declare no competing financial interest.

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