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Series of Metal−Nonmetal−Metal Sandwich Compounds: Out-of-Plane σ-Aromaticity and Electric Properties

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A new class of metal−nonmetal−metal sandwich structures $M_3-CO_3-M'_3$ (M, M′ = Li, Na, K) with all real frequencies is obtained at the second-order Möller−Plesset theory (MP2) method with the 6-311+G (2d) basis set. Because the sandwich molecule $M_3-CO_3-M'_3$ is composed of superatoms (M_3, CO_3, and M'_3), it is a sandwich "superomolecule". The superatoms M_3 and M'_3 are electron donors and CO_3 is the acceptor, and then there is a strong charge transfer between M_3 (or M'_3) and CO_3 superatom, so $M_3-CO_3-M'_3$ can be denoted as $M_3^+CO_3^{2-}M'^+_3$. Owing to the CO_3^{2-} anion in the middle repulsing the valence electrons of two metal rings (M_3 and M'_3) forming a pair of excess electrons, the compound with excess electrons is also a novel electride. In metal−nonmetal−metal sandwich compound $M_3^+CO_3^{2-}M'^+_3$, superatom units M_3^+ and M'^+_3 exhibit unusual σ-aromaticity: the maximum negative nucleus-independent chemical shift (NICS_{max}) value of each aromatic ring (M_3^+ or M'^+_3) does not locate at the center of the ring plane but locates outside the ring plane. The distance value from the center of the M_3^+ or M'^+_3 ring plane to the point with NICS_{max} ranges from 0.8 to 1.9 Å. This shows a notable out-of-plane σ-aromaticity for these sandwich compounds. What is the reason? We find that the out-of-plane σ-aromaticity of M_3^+ (or M'^+_3) results from the action of $CO_3^{2-}M'^+_3$ (or $M_3^+CO_3^{2-}$). For electric property, on account of excess electrons, the sandwich electride $M_3-CO_3-M'_3$ without the central symmetry can exhibit large static first hyperpolarizability (β_0). For $Na_3-CO_3-K_3$, the β_0 value is close to 56 000 au.

Introduction

Sandwich compounds, because of their interesting geometric structures and unusual physical and chemical properties, have attracted intense attention. Up to now, a number of sandwich compounds have been studied in both theory and experiment.[1−19] For example, the famous nonmetal−metal−nonmetal sandwich compounds metallocenes have found important applications in fundamental research and material science.[1−8] $[Al_4MAl_4]^{q-}$, a typical all-metal sandwich structure, was designed with transition-metal atom or main-group metal atom (M) in the middle.[15,16] The metal−nonmetal−metal sandwich molecules such as Li_3-O-Li_3[17−19] and Li_3-N_3-Be[20] are special ones. Under the action of the central nonmetal atom(s), electron cloud(s) of metal ring(s) are pushed out and distended. The metal−nonmetal−metal sandwich molecule with the distended electron cloud(s) exhibits several extraordinary properties that are different from those of nonmetal−metal−nonmetal and all-metal sandwich compounds without the distended electron cloud.

The sandwich compound composed of superatom(s) is interesting. At present, several sandwich structures composed of superatom(s) have been studied such as $[Al_4MAl_4]^{q-}$, Li_3-O-Li_3, Li_3-N_3-Be, and so on. Each of them containing two or more superatom subunits connected to each other through chemical bonds (such as ionic bond and covalent bond) can be viewed as "superomolecules".[20] This word is different from "supermolecule" or "superamolecule". The known sandwich superomolecules are with only one kind of atom in the middle.[8,13−20] However, the sandwich superomolecules with different atoms, especially the different nonmetal atoms in the center, have not yet been investigated.

Herein, we predict a novel class of metal−nonmetal−metal sandwich molecules $M_3-CO_3-M'_3$ (M, M′ = Li, Na, K), which are special sandwich superomolecules. Owing to their interesting metal−nonmetal−metal sandwich structures and superatom subunits, what extraordinary properties can these sandwich compounds exhibit? In this article, interesting answers will be given.

Computation Details

The geometries of $M_3-CO_3-M'_3$ (M, M′ = Li, Na, K) with all real frequencies are obtained by the MP2 method with the 6-311+G (2d) basis set. The natural bond orbital (NBO)[21] analysis at the MP2 level is performed to provide insight into the bonding nature of the $M_3-CO_3-M'_3$ molecule. The interaction energies (E_{int}) and bond energies (E_{b}) are calculated using the MP2/6-311+G (2d) level. The counterpoise (CP) procedure[22] is adopted to eliminate the basis set superposition error (BSSE),[23] as illustrated by the following formula

$$E_{\text{int}} = E_{\text{ABC}}(X_{\text{ABC}}) - E_{\text{A}}(X_{\text{ABC}}) - E_{\text{B}}(X_{\text{ABC}}) - E_{\text{C}}(X_{\text{ABC}}) \quad (1)$$

$$E_{\text{b}}(\text{A-BA}) = E_{\text{A}}(X_{\text{ABA}}) + E_{\text{BA}}(X_{\text{ABA}}) - E_{\text{ABA}}(X_{\text{ABA}}) \quad (2)$$

$$E_{\text{b}}(\text{A-BCBA}) = E_{\text{A}}(X_{\text{ABCBA}}) + E_{\text{BCBA}}(X_{\text{ABCBA}}) - E_{\text{ABCBA}}(X_{\text{ABCBA}}) \quad (3)$$

The same basis set, X_{ABC}, X_{ABA}, or X_{ABCBA}, is used for the subunit calculation and for the compound calculation.

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The aromaticity is investigated by the nucleus-independent chemical shift (NICS)[24] theory at the MP2/6-311G** level. The static (hyper)polarizabilities of $M_3-CO_3-M'_3$ (M, M′ = Li, Na, K) are obtained by a finite field (EF) approach with an electric field magnitude of 0.001 au at the MP2 level,[25] and the 6-311+G (d) basis set is employed for the C, O atoms, and the 6-311+G (3df) basis set is used for the alkali atoms. The transition energy, ΔE, oscillator strength, f_0, and the difference of the dipole moment, $\Delta\mu$, between ground and excited states are estimated by the configuration interaction with single excitations (CIS) method.

The total energy of a molecular system in the presence of a homogeneous electric field can be written as[26]

$$\mathrm{E} = \mathrm{E}^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma \qquad (4)$$

where E^0 is the molecular energy without the electric field and F_α is a component of the strength on the α direction of applied electrostatic field; μ_α, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the dipole, polarizability, and the first hyperpolarizability, respectively.

The polarizability (α_0) is defined as follows

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (5)$$

The static first hyperpolarizability is noted as

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \qquad (6)$$

Where

$$\beta_i = \frac{3}{5}(\beta_{iii} + \beta_{ijj} + \beta_{ikk}), \quad i, j, k = x, y, z$$

All of the calculations were performed with the GAUSSIAN 03 program package.[27] The 3D plots of molecular orbitals are generated with the GAUSSVIEW program[28] (Gaussian, Inc., Pittsburgh, PA).

Results and Discussions

A. Geometric Structures and Natural Bond Orbital Charges. A novel class of molecules $M_3-CO_3-M'_3$ (M, M′ = Li, Na, K) are designed. They are of the new metal−nonmetal−metal type. The triangular Li_3 cluster is a typical superalkali because its IP (ionization potential) value is appreciably lower than that of Li atom.[29] Similarly, the triangular Na_3 and K_3 cluster are superalkalis too. The trifurcate CO_3 cluster[30] can also be viewed as a superatom. Therefore, the $M_3-CO_3-M'_3$ containing three superatoms is a "superomolecule".[20]

Herein, isomers of $M_3-CO_3-M_3$ (M = Li, Na, K) are obtained by the MP2 method with the 6-311+G (2d) basis set and illustrated in Figure S1 of the Supporting Information. There are three types of isomers, sandwichlike, towerlike, and chainlike. The relative energy (E_{rel}) between corresponding different type isomers is less than 24 kcal/mol. (See Table S1 in the Supporting Information.) It shows that stabilities of different type isomers are not obviously different, and when M changes from Li, to Na, to K the energies are similar for three type isomers. Moreover, when M = M′ = K, E_{rel} differences for three type isomers are about 1 kcal/mol. For sandwichlike isomers, interaction energies (E_{int}) are −362.98 to −420.01 kcal/mol (Table 1), which shows their large stabilities. We also obtain the sandwichlike $Li_3CO_3Li_3CO_3Li_3$ structure by the B3LYP/6-311+G (2d) method, and the structure is illustrated in Figure S2 of the Supporting Information. For the purpose of comparison, the bond energies (E_b) of $Li_3-CO_3Li_3CO_3Li_3$ and $Li_3-CO_3Li_3$ are calculated and listed in Table S2 of the Supporting Information. The E_b of $Li_3CO_3Li_3CO_3Li_3$ is 218.20 kcal/mol, which is larger than 129.73 kcal/mol for $Li_3CO_3Li_3$. This indicates that $Li_3CO_3Li_3CO_3Li_3$ is more stable than $Li_3CO_3Li_3$, and the sandwich $Li_3CO_3Li_3$ may exist in bulk. The sandwichlike isomers may exhibit unusual out-of-plane σ-aromaticity. We are interested in their special structures with unusual σ-aromaticity.

TABLE 1: Interaction Energy (E_{int}) for $M_3CO_3M'_3$ (M, M′ = Li, Na, K)

$M_3CO_3M'_3$	E_{int} (kcal/mol)
$Li_3CO_3Li_3$	−420.01
$Li_3CO_3Na_3$	−399.51
$Li_3CO_3K_3$	−395.67
$Na_3CO_3Na_3$	−375.27
$Na_3CO_3K_3$	−370.68
$K_3CO_3K_3$	−362.98

Six geometries obtained of this kind of sandwich compounds $M_3-CO_3-M'_3$ (M, M′ = Li, Na, K) are illustrated in Figure 1. As shown in Figure 1, there are two structure forms, eclipsed form for $Li_3-CO_3-Li_3$ and staggered form for the other five structures, according to the orientation of two metal rings M_3 and M'_3. (CO_3 is always eclipsed with M_3 in the six structures.)

The geometric parameters of these sandwich structures are given in Table 2. From Table 2, for $M_3-CO_3-M'_3$ (M = M′ = Li, Na, K), the M−M or M′−M′ bond length increases with increasing atomic number of M or M′, for instance, 2.996 (M = Li) < 3.517 (M = Na) < 4.179 Å (M = K) for M−M bond length. For $Li_3-CO_3-M'_3$ (M′ = Na, K), the Li−Li bond length almost does not change (3.027 and 3.028 Å), and M′−M′ bond length for M′ = Na is smaller by about 0.6 Å than that for M′ = K. For $Na_3-CO_3-K_3$, the Na−Na and K−K bond lengths are close to those in $Na_3-CO_3-Na_3$ and $K_3-CO_3-K_3$, respectively. For the layer distances, the d_1 (eclipsed form between M_3 and CO_3 plane) ranges from 1.80 to 2.20 Å, and d_2 (staggered form between M'_3 and CO_3 plane except for $Li_3-CO_3-Li_3$) ranges from 1.80 to 1.96 Å.

For $M_3-CO_3-M'_3$, the superatoms M_3 and M'_3 are electron donors, and CO_3 is the acceptor, and then there is a strong charge transfer between M_3 (or M'_3) and CO_3 superatom, so $M_3-CO_3-M'_3$ is a charge-separated system. From Table 2, the sum of NBO charges is close to +1 for M_3, −2 for CO_3, and +1 for M'_3, respectively. The valence is +1 for M_3, −2 for CO_3, and +1 for M'_3. There is a typical ionic bond between M_3 (or M'_3) and CO_3 superatom subunit, and thus $M_3-CO_3-M'_3$ can be denoted as $M_3^+CO_3^{2-}M_3'^+$.

B. Out-of-Plane σ-Aromaticity and its Nature. NICS, proposed by Schleyer and coworkers,[24] is an efficient and simple criterion for probing aromaticity, which is based on the negative of the magnetic shielding computed at or above the geometrical centers of rings or clusters. Systems with negative NICS values are aromatic. For a simple π-aromatic system, such as benzene, the $NICS_{max}$ is located above its plane of about 1.0 Å, and, obviously, it exhibits the out-of-plane π-aromaticity, a common characteristic for the simple π-aromatic system. The isolated regular triangular Li_3^+, Na_3^+, and K_3^+ cations all possess the in-plane σ-aromaticity[29,31] because the $NICS_{max}$ is located at the center of plane. However, in our previous work, for Li_3^+ of

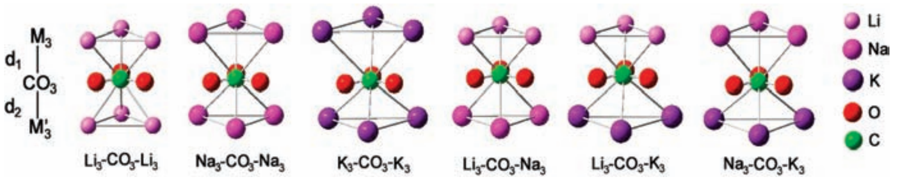

Figure 1. Six optimized structures of $M_3{-}CO_3{-}M_3'$ (M, M′ = Li, Na, K) are classified into two forms, eclipsed form for $Li_3{-}CO_3{-}Li_3$ and staggered form for the other five structures.

TABLE 2: M−M/M′−M′ Bond Lengths (angstroms), Layer Distances d_1/d_2 (angstroms) between M_3/M_3' and CO_3 Layer, and NBO Charges on M_3, M_3', and CO_3

$M_3{-}CO_3{-}M_3'$		geometric parameters				NBO charge[a]		
M	M′	M−M	M′−M′	d_1	d_2	M_3	CO_3	M_3'
Li	Li	2.996	2.996	1.86	1.86	1.00	−2.00	1.00
Na	Na	3.517	3.514	2.20	1.80	0.98	−1.92	0.95
K	K	4.179	4.103	2.33	1.82	1.03	−2.04	1.01
Li	Na	3.027	3.491	1.80	1.96	0.99	−1.94	0.95
Li	K	3.028	4.124	1.80	1.94	0.98	−2.01	1.03
Na	K	3.506	4.116	2.20	1.84	0.98	−1.99	1.00

[a] NBO charge for each subunit (M_3, M_3', and CO_3) is the sum of the NBO charges on atoms of each subunit.

TABLE 3: Nucleus-Independent Chemical Shift (NICS) (ppm) with the MP2/6-311G Level[a]**

a.[b]

$M_3^+CO_3^{2-}M_3'^+$							
M_3^+				$M_3'^+$			
M	NICS(0)	$NICS_{max}$	L_1	M′	NICS(0)	$NICS_{max}$	L_2
Li	−6.2	−9.5	0.8	Li	−6.2	−9.5	0.8
Na	−5.5	−8.3	0.9	Na	−6.1	−8.3	0.9
K	3.8	−5.2	1.9	K	1.6	−4.9	1.9
Li	−3.9	−8.4	1.0	Na	−7.0	−8.8	0.8
Li	−1.7	−7.9	1.2	K	−4.1	−6.6	1.2
Na	−2.1	−7.3	1.2	K	−1.7	−5.9	1.5

b.[c]

species	$NICS_{max}$	L_1
Li_3^+	−11.1	0
$CO_3^{2-}Li_3^+$	−9.3	1.0
$Li_3^+\cdots Li_3^+$	−7.7	0.6
$Li_3^+CO_3^{2-}Li_3^+$	−9.5	0.8

[a] NICS (0) is the NICS at the center of $M_3^+/M_3'^+$ ring plane. L_1/L_2 (angstroms) is the distance from the center of the $M_3^+/M_3'^+$ ring plane to the point with $NICS_{max}$. [b] $M_3^+CO_3^{2-}M_3'^+$ (M, M′ = Li, Na, K). [c] $Li_3^+CO_3^{2-}Li_3^+$ and its subunits.

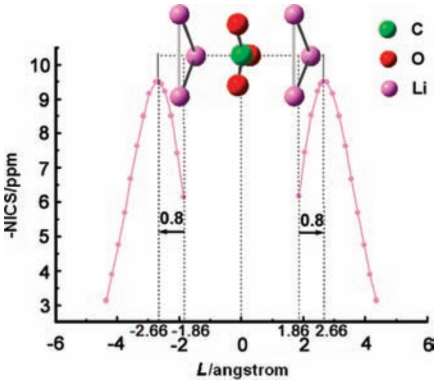

Figure 2. Relationship between the NICS value and the distance from the center of each Li_3^+ ring plane (L) for $Li_3^+CO_3^{2-}Li_3^+$.

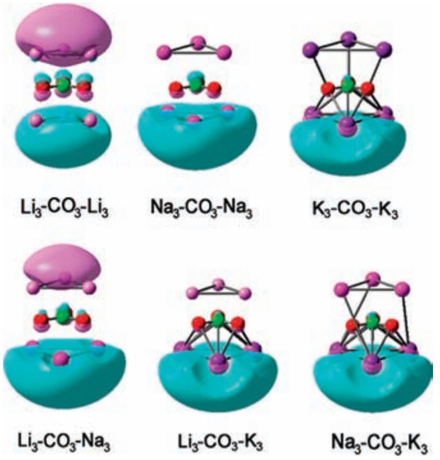

Figure 3. HOMOs for $M_3{-}CO_3{-}M_3'$ (M, M′ = Li, Na, K) in which the σ-electron clouds of M_3 and M_3' are distended.

metal−nonmetal−metal sandwich $Li_3{-}O{-}Li_3$ (D_{3d}), the $NICS_{max}$ is located above its plane, so the special out-of-plane σ-aromaticity was observed.

In the novel metal−nonmetal−metal sandwich $M_3^+CO_3^{2-}M_3'^+$ (M, M′ = Li, Na, K), can the out-of-plane σ-aromaticity be observed? To answer this question, we place ghost atoms at, above, and below each geometrical center for both M_3^+ and $M_3'^+$ rings of $M_3^+CO_3^{2-}M_3'^+$ (M, M′ = Li, Na, K) to calculate the NICS values, and the results indicate that the $NICS_{max}$ of each aromatic ring (M_3^+ or $M_3'^+$) in $M_3^+CO_3^{2-}M_3'^+$ is not located at the center of the ring plane but located outside the ring plane. The distance L_1/L_2 value from the center of the $M_3^+/M_3'^+$ ring plane to the point with $NICS_{max}$ ranges from 0.8 to 1.9 Å. (See Table 3a.) This shows that the out-of-plane σ-aromaticity indeed exists in these metal−nonmetal−metal sandwich compounds.

Taking $Li_3^+CO_3^{2-}Li_3^+$ as an example, the relationship between the NICS value and the distance from the center of each Li_3^+ ring plane is depicted in Figure 2. Clearly, the $NICS_{max}$ value, −9.5 ppm, for each Li_3^+ ring is located outside the plane of about 0.8 Å, but the NICS value at the center of the ring plane is only −6.2 ppm. Notably, a large out-of-plane component ($NICS_{zz}$) of $NICS_{max}$ relates to the out-of-plane aromaticity. The isolated Li_3^+ ring has a $NICS_{max}$ of −10.4 ppm and small out-of-plane component $NICS_{zz}$ of −3.2 ppm (only 31% of $NICS_{max}$), which shows in-plane aromaticity. In $Li_3^+CO_3^{2-}Li_3^+$, the Li_3^+ ring has a $NICS_{max}$ of −9.5 ppm and large out-of-plane component $NICS_{zz}$ of −4.8 ppm (over 50% of $NICS_{max}$), which shows out-of-plane aromaticity.

Interestingly, the σ-electron cloud of HOMO from Figure 3 is almost pushed out from the Li_3^+ ring planes of $Li_3^+CO_3^{2-}Li_3^+$ with the out-of-plane σ-aromaticity. Therefore, this exhibits a correlation between the pushed σ-electron cloud and the out-of-plane σ-aromaticity. Similar correlation is also served for sandwich compounds $M_3^+CO_3^{2-}M_3'^+$ (M, M′ = Li, Na, K) with the pushed σ-electron cloud besides $Li_3^+CO_3^{2-}Li_3^+$.

What causes the out-of-plane σ-electron cloud and σ-aromaticity for Li_3^+ ring?

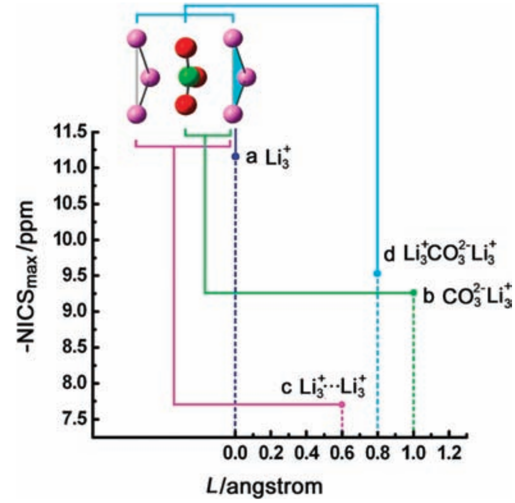

Figure 4. Relationship between the $\mathrm{NICS_{max}}$ and the distance (L) from the center of Li_3^+ ring plane (right side) to the point with the $\mathrm{NICS_{max}}$ for (a) Li_3^+, (b) $CO_3^{2-}Li_3^+$, (c) $Li_3^+\cdots Li_3^+$, and (d) $Li_3^+CO_3^{2-}Li_3^+$.

In our previous work on the D_{3d} Li_3-O-Li_3, the out-of-plane σ-aromaticity of Li_3^+ was reported.[19] For $M_3^+CO_3^{2-}M_3'^+$ (M, M′ = Li, Na, K), to reveal the actions leading to the out-of-plane σ-aromaticity for M_3^+ and $M_3'^+$ deeply, still taking $Li_3^+CO_3^{2-}Li_3^+$ as an example, the NICS values are also calculated for Li_3^+ in three designed model systems: isolated Li_3^+, $CO_3^{2-}Li_3^+$, and $Li_3^+\cdots Li_3^+$ (obtained by removing other subunit(s) from the $Li_3^+CO_3^{2-}Li_3^+$ structure), listed in Table 3b and depicted in Figure 4. From these results, for the isolated Li_3^+, the $\mathrm{NICS_{max}}$ value of about −11.1 ppm is located at the geometric center of the Li_3^+ ring plane, showing the in-plane σ-aromaticity, which is a common case. (See Figure 4a). However, for $CO_3^{2-}Li_3^+$, the $\mathrm{NICS_{max}}$ value of about −9.3 ppm is not located at the geometric center of the Li_3^+ ring plane but located outside the Li_3^+ ring plane of about 1.0 Å. (See Figure 4b.) This shows that CO_3^{2-} repulses the electron cloud of the Li_3^+ ring, bringing on the out-of-plane σ-aromaticity of Li_3^+. Noticeably, for the $Li_3^+\cdots Li_3^+$ long-range interaction system, the $\mathrm{NICS_{max}}$ value of about −7.7 ppm is located outside the Li_3^+ ring plane of about 0.6 Å. (See Figure 4c.) This new result indicates that the long-range repulsion between electron clouds of two Li_3^+ rings may also lead to the out-of-plane σ-aromaticity of Li_3^+. For the whole structure $Li_3^+CO_3^{2-}Li_3^+$, the distance value of about 0.8 Å from the Li_3^+ ring plane to the point with its $\mathrm{NICS_{max}}$ is less than not only 1.0 Å for the $CO_3^{2-}Li_3^+$ model system but also the sum of 0.6 Å for $Li_3^+\cdots Li_3^+$ and 1.0 Å for $CO_3^{2-}Li_3^+$ model systems, which can be clearly seen in Figure 4. This indicates that $Li_3^+CO_3^{2-}$ repulsing the electron cloud of the Li_3^+ ring is different from Li_3^+ and CO_3^{2-} repulsing the electron cloud of the Li_3^+ ring, respectively, which is because of a mutual effect between Li_3^+ and CO_3^{2-}. In $Li_3^+CO_3^{2-}$, the effect of CO_3^{2-} part repulsing the electron cloud of the Li_3^+ ring is decreased by the Li_3^+ part of $Li_3^+CO_3^{2-}$, and the effect of the Li_3^+ part repulsing the electron cloud of the Li_3^+ ring is screened by the CO_3^{2-} part. Therefore, for the whole structure $Li_3^+CO_3^{2-}Li_3^+$, the distance value of about 0.8 Å from the Li_3^+ ring plane to the point with its $\mathrm{NICS_{max}}$ is less than not only 1.0 Å from CO_3^{2-} but also the sum of 0.6 Å from Li_3^+ and 1.0 Å from CO_3^{2-}. Similarly, $M_3^+CO_3^{2-}/CO_3^{2-}M_3'^+$ leads to the out-of-plane σ-aromaticity of $M_3'^+/M_3^+$ in sandwich compounds $M_3^+CO_3^{2-}M_3'^+$ (M, M′ = Li, Na, K) besides $Li_3^+CO_3^{2-}Li_3^+$.

To show the effects of subunits on the σ-electron cloud of HOMO for $Li_3^+CO_3^{2-}Li_3^+$ and its subunits, the HOMOs are illustrated in Figure 5. For isolated Li_3^+ (a), the σ-electron cloud of HOMO locates symmetrically around the ring plane, which relates to the in-plane σ-aromaticity. However, for $CO_3^{2-}Li_3^+$ (b), the σ-electron cloud of HOMO for Li_3^+ ring is distended strongly and asymmetrically around the ring plane by the repulsion of the CO_3^{2-} anion, which relates to strong out-of-plane σ-aromaticity. Then, for $Li_3^+\cdots Li_3^+$ (c), the σ-electron cloud of each Li_3^+ ring is slightly distended, forming an asymmetrical σ-electron cloud because of the long-range repulsion between σ-electron clouds of two Li_3^+ rings, which relates to slight out-of-plane σ-aromaticity. For $Li_3^+CO_3^{2-}Li_3^+$ (d), the σ-electron cloud of the HOMO for the Li_3^+ ring is also pushed out by $Li_3^+CO_3^{2-}$. As shown in Figure 5, the extent of the distention of the electron cloud of the Li_3^+ ring for part d is weaker than that for part b, which is because the effect of the CO_3^{2-} part repulsing the electron cloud of the Li_3^+ ring is decreased by the Li_3^+ part of $Li_3^+CO_3^{2-}$, and the effect of the Li_3^+ part repulsing the electron cloud of the Li_3^+ ring is screened by the CO_3^{2-} part. Therefore, this relates to the obvious out-of-plane σ-aromaticity for $Li_3^+CO_3^{2-}Li_3^+$. (See Table 3b.)

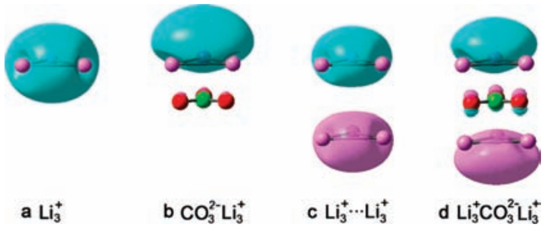

Figure 5. HOMOs of isolated (a) Li_3^+, (b) $CO_3^{2-}Li_3^+$, (c) $Li_3^+\cdots Li_3^+$, and (d) $Li_3^+CO_3^{2-}Li_3^+$ (a, b, and c model systems obtained from the structure $Li_3^+CO_3^{2-}Li_3^+$) show the change of the σ-electron cloud of Li_3^+ ring.

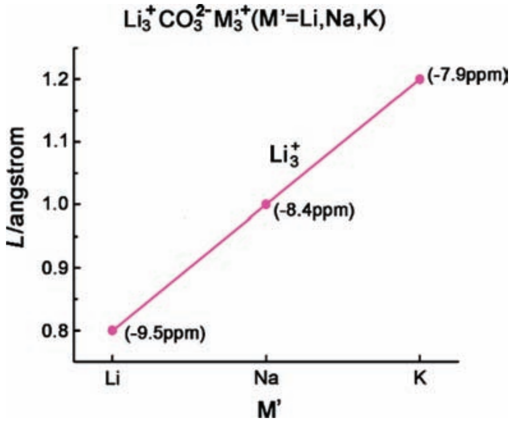

Figure 6. Distance (L) from the center of the Li_3^+ ring plane to its $\mathrm{NICS_{max}}$ (in bracket) increases with increasing atomic number of alkali metal of the other ring $M_3'^+$.

Does the alkali-metal atomic number effect the out-of-plane σ-aromaticity?

For $Li_3^+CO_3^{2-}M_3'^+$, as shown in Table 3a, when M′ changes from Li to K, the distance (L_1) from the center of the Li_3^+ ring plane to its $\mathrm{NICS_{max}}$ is about 0.8 (M′ = Li), 1.0 (M′ = Na), and 1.2 Å (M′ = K). It shows that the larger the atomic number of alkali-metal of $M_3'^+$ ring, the more notable the out-of-plane σ-aromaticity of Li_3^+. (See Figure 6.) This may be because the long-range repulsion between the electron clouds of Li_3^+ and $M_3'^+$ increases with increasing atomic number of M′. We also found that the $\mathrm{NICS_{max}}$ value of Li_3^+ decreases (−9.5 for M′ = Li, −8.4 for M′ = Na, and −7.9 ppm for M′ = K) with increasing M′−M′ bond length (2.996 for M′ = Li, 3.491 for M′ = Na, and 4.124 Å for M′ = K).

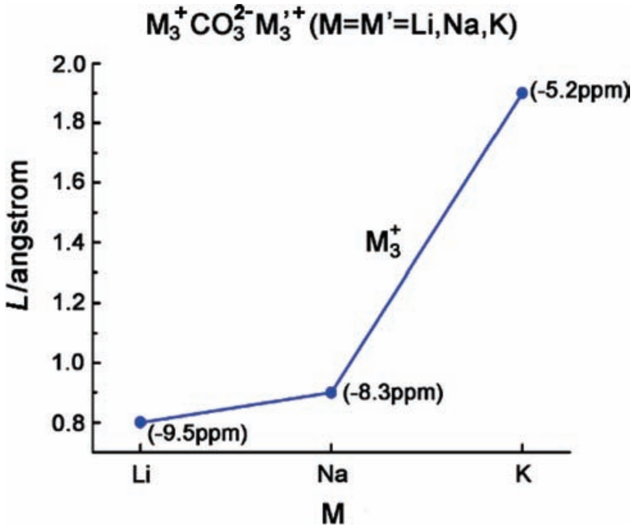

Figure 7. Distance (L) from the center of the M_3^+ ring plane to its $NICS_{max}$ (in bracket) increases with increasing atomic number of M.

For $M_3^+CO_3^{2-}M_3'^+$, when both M and M′ change from Li to K at the same time, the distances from the center of the M_3^+ ring plane to its $NICS_{max}$ are 0.8, 0.9, and 1.9 Å. (See Table 3a.) Obviously, the distance from the center of the M_3^+ ring plane to the $NICS_{max}$ increases with increasing atomic number of M. (See Figure 7.) Increasing the atomic number of M accompanied by the increase in the electron number of M enhances the repulsion between the electron clouds of the M_3^+ and $M_3'^+$ rings. Simultaneously, increasing the atomic number of M accompanied by the decrease in the ionization potential of M (5.39, 5.14, and 4.34 eV for Li, Na, and K atoms, respectively) enhances the distention of the electron cloud of the M_3^+ ring by the repulsion of the CO_3^{2-} anion. Therefore, for $M_3^+CO_3^{2-}M_3'^+$ (M = M′ = Li, Na, K), the out-of-plane σ-aromaticity increases with increasing atomic number of alkali-metal M. Moreover, the $M_3'^+$ ring is similar to the M_3^+ ring on the out-of-plane σ-aromaticity.

C. Electride Characteristic and Electric Properties. Electrides[32] are ionic salts in which anionic sites are occupied solely by excess electrons. $M_3-CO_3-M_3'$ (M, M′ = Li, Na, K) are novel sandwich superomolecular electrides because of the CO_3^{2-} in the middle repulsing the valence electrons of two metal rings forming a pair of excess electrons. Because excess electron may cause large NLO responses,[33] it is expected that $M_3-CO_3-M_3'$ without the central symmetry may exhibit a large NLO response. Their crucial transition designations are from s- to p-type orbitals of excess electrons. (See Figure 8.) Their transitions are excess electrons transitions, so the large first hyperpolarizabilities (β_0) values may be exhibited. The electric properties of $M_3-CO_3-M_3'$ (M, M′ = Li, Na, K) are given in Table 4.

From Table 4, for M = M′ = Li, Na, and K, the polarizability (α) value increases with increasing atomic number of M. In particular, β_0 values are 6 (M = Li) < 7905 (M = Na) < 36 988 au (M = K). β_0 significantly increases with increasing atomic number of M of superalkali rings, as shown in Figure 9. It is known that β_0 is correlated to oscillator strength (f_0), difference of dipole moment ($\Delta\mu$), and transition energy (ΔE). Also, from Table 4, one can see that increasing β_0 relates to the increasing f_0 and decreasing ΔE.

For M = Li, M′ = Li, Na, and K, as shown in Table 4, when only M′ changes from Li to K, the α value is increasing. The β_0 value also increases with increasing atomic number of M′ (Figure 9), which can relate to the decreasing ΔE. In particular, $M_3-CO_3-M_3'$ with different superalkali rings may exhibit the large first hyperpolarizability. For example, the β_0 value of $Na_3-CO_3-K_3$ is about 5.6 × 10^4 au, which is larger than that of not only $Na_3-CO_3-Na_3$ but also $K_3-CO_3-K_3$. It is also larger than those of studied electrides.[33] This may be beneficial to design high-performance NLO materials.

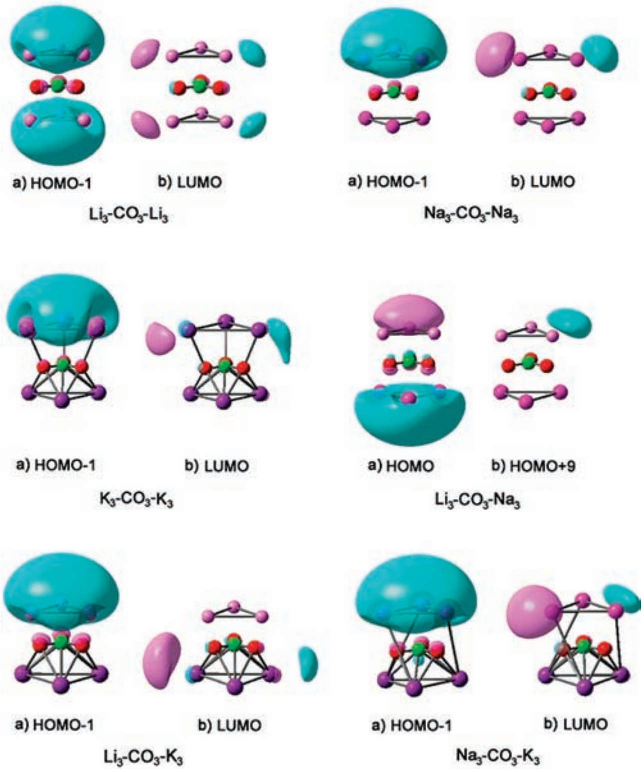

Figure 8. Crucial transition designation a → b for $M_3-CO_3-M_3'$ (M, M′ = Li, Na, K).

TABLE 4: Polarizability, α (au), First Hyperpolarizability, β_0 (au), Oscillator Strength, f_0, Difference of Dipole Moment, $\Delta\mu$ (debye), between the Ground and the Excited States, and the Transition Energy, ΔE (electronvolts), for $M_3-CO_3-M_3'$ (M, M′ = Li, Na, K)

$M_3-CO_3-M_3'$		α^a	β_0^a	f_0	$\Delta\mu$	ΔE
M	M′					
Li	Li	440	6	1.1584	1.8712	2.194
Na	Na	723	7905	1.4076	1.7486	2.037
K	K	1424	36 988	1.6805	4.8646	1.544
Li	Na	583	7922	0.9358	2.6517	2.150
Li	K	992	15 508	0.4624	1.8175	1.908
Na	K	1195	55 881	1.0452	4.4548	2.006

[a] MP2 method with 6-311+G (d) for C, O atoms, and 6-311+G (3df) for the alkali atoms.

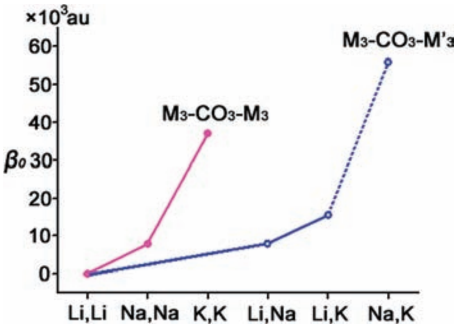

Figure 9. Relationship between β_0 and the atomic number of alkali-metal for $M_3-CO_3-M_3'$ (M, M′ = Li, Na, K).

Conclusions

A class of compounds $M_3{-}CO_3{-}M'_3$ (M, M′ = Li, Na, K) are designed utilizing the superalkali (Li_3, Na_3, and K_3) and superatom CO_3. $M_3{-}CO_3{-}M'_3$ is a charge-separated system by strong charge transfer and can be denoted as $M_3{}^+CO_3{}^{2-}M_3{}^+$. These compounds are of the metal−nonmetal−metal sandwich structures. In the special sandwich structures, the $CO_3{}^{2-}$ anion in the middle repulses the valence electrons of two metal rings to produce excess electrons, conferring the electride characteristics on these sandwich $M_3{-}CO_3{-}M'_3$ (M, M′ = Li, Na, K).

In $M_3{-}CO_3{-}M'_3$ (M, M′ = Li, Na, K), $Li_3{}^+$, $Na_3{}^+$, and $K_3{}^+$ present not the in-plane σ-aromaticity like the isolated ones but the out-of-plane σ-aromaticity, which is unusual in these compounds. Their NICS_{max} values are located outside the superalkali cation ring plane of about 0.8 to 1.9 Å. By studying the model systems, isolated $Li_3{}^+$, $CO_3{}^{2-}Li_3{}^+$, and $Li_3{}^+\cdots Li_3{}^+$, we find that both $CO_3{}^{2-}$ and $Li_3{}^+$ can lead to out-of-plane σ-aromaticity of $Li_3{}^+$. However, in the whole structure $Li_3{}^+CO_3{}^{2-}Li_3{}^+$, the distance from the $Li_3{}^+$ ring plane to the point with its NICS_{max} is less than the sum of those in the $CO_3{}^{2-}Li_3{}^+$ and $Li_3{}^+\cdots Li_3{}^+$ model systems, which is because there is a mutual effect between $CO_3{}^{2-}$ and $Li_3{}^+$ of $Li_3{}^+CO_3{}^{2-}$: the $CO_3{}^{2-}$ part repulsing the electron cloud of the $Li_3{}^+$ ring is decreased by the $Li_3{}^+$ part, and the $Li_3{}^+$ part repulsing the electron cloud of the $Li_3{}^+$ ring is screened by the $CO_3{}^{2-}$ part. This case also exists in $M_3{}^+CO_3{}^{2-}M'^+_3$ (M, M′ = Li, Na, K) beside $Li_3{}^+CO_3{}^{2-}Li_3{}^+$.

Owing to excess electrons, the sandwich superomolecular electride $M_3{-}CO_3{-}M'_3$ without the central symmetry may exhibit the large first hyperpolarizability. In particular, $Na_3{-}CO_3{-}K_3$ with different superalkali rings exhibits the largest first hyperpolarizability, 5.6×10^4 au.

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Supporting Information Available: Structures and relative energies of isomers of $M_3{-}CO_3{-}M'_3$ (M, M′ = Li, Na, K). This material is available free of charge via the Internet at http://pubs.acs.org.

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