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A Novel Class of Compounds—Superalkalides: $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, and K; en = Ethylenediamine) with Excellent Nonlinear Optical Properties and High Stabilities

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Abstract:

With the aid of *ab initio* calculations at the MP2 level of theory, we designed a novel class of inorganic salts, $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, and K), by using the M'_3O superalkalis. These compounds are the first examples of inorganic salt where superalkali occupies the anionic site, termed as superalkalides. The electronic structure features of the $M^+(en)_3M'_3O^-$ superalkalides are very similar to those of the corresponding $M^+(en)_3M'^-$ alkalides which have been reported by Zurek (*J. Am. Chem. Soc.* **2011**, *133*, 4829). In this study, the calculated NLO properties of $M^+(en)_3M'_3O^-$ and $M^+(en)_3M'^-$ (M, M' = Li, Na, and K) show that both superalkalides and alkalides have significantly large first hyperpolarizabilities (β_0) with the values in the range of $7.80\times10^3 \sim 9.16\times10^4$ au and $7.95\times10^3 \sim 1.84\times10^5$ au, respectively. The computations on the stabilities of $M^+(en)_3M'_3O^-$ and $M^+(en)_3M'^-$ demonstrate that the $M^+(en)_3M'_3O^-$ superalkalides have preference in stability than the corresponding $M^+(en)_3M'^-$ alkalides because of the existences of the hydrogen bonds in $M^+(en)_3M'_3O^-$. Therefore, the designed superalkalides, $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, and K), with excellent nonlinear optical properties and high stabilities are greatly promising candidates for NLO materials. We hope that this article could attract more research interest in superatom chemistry and further experimental researches.

1. Introduction

Over the last several decades, a great deal of interests has been concentrated on the design and synthesis of novel materials with excellent nolinear optical (NLO) properties because of their important applications in the photoelectronics and photonics fields.[1-14] Two kinds of promising strategies for enhancing NLO response of materials were discovered in previous researches. One approach is to increase the degree of charge transfer in molecular complexes. Following this way, many species with large NLO response have been characterized as important candidates for NLO utilizations, including molecules with extended[3,4] or twisted[5] π-electron systems, donor-π-conjugated bridge-acceptor (D-π-A) or donor-acceptor (D-A) frameworks,[6,7] transition-metal-ligand compounds,[8-11] X-type chiral π-conjugated oligomers,[12] and octupolar molecules.[13,14]

Another practical approach is introducing loosely bound excess electrons into different systems to prepare materials with unique NLO properties. The earliest investigation of systems containing diffuse excess electrons can date back to the observation of alkali metals dissolved in gaseous ammonia.[15-18] Ever since this discovery, a large amount of researches focused on the conceptually related systems: excess electrons in water,[19] electrides,[20-34] and alkalides,[35-43] and revealed that some of these systems exhibit striking NLO responses with a significantly large first hyperpolarizability (β_0).[19,30-34,41-43]

Electrides are a kind of untraditional ionic salts in which alkali metals ionize to bound alkali cations and “excess” electrons occupying the anionic sites.[20,21] The first synthesized crystalline organic electride is $Cs^+(18\text{-crown-}6)_2e^-$.[22,23] Since then, Dye’s group have synthesized and characterized a series of crystalline organic electrides with C-O bond or C-N bonds in complexants.[24-28] Meanwhile, inorganic electride with thermal stability and low reactivity towards air was also designed and synthesized.[29]

Resembling electrides, alkalides are another kind of novel ionic salts where anionic sites are occupied by alkali metal anions (Na^-, K^-, Rb^-, or Cs^-),[35] namely, the excess electron being located on alkali metal. Because of the small electron affinity of alkali metals (e.g. <0.62 eV for Li), [44] the excess electron is loosely bound in alkalide compound. Na^+(cryptand-[2.2.2])Na^- is the first prepared example for alkalide.[36] In 1999, room-temperature stable alkalides, K^+(aza222)Na^- and K^+(aza222)K^-, were successfully synthesized.[37]

Recently, many theoretical studies on the NLO properities of various electrides and alkalides have been performed. For example, our group has carried out investigations on Li@calix[4]pyrrole,[30] Li^+(calix[4]pyrrole)M'^- (M = Li, Na, and K),[38] $Li(NH_3)_{(n)}Na$(n = 1 - 4),[40] (M^+@n^6adz)M'^- (M, M′ = Li, Na, K; n = 2, 3),[41] M^{2+}(H_5Azacrytand$[2.2.2]^-$)M'^- $\cdot 2MeNH_2$(abbreviated MH_5Aza222M')(M= Be, Mg, Ca; M'= Li, Na, K),[43] $(M_3O)^+(e@C_{20}F_{20})^-$(M = Na, K),[25] and so on. It should be noted that various electrides and alkalides have different complexants, including cuplike calix[4]pyrrole complexant,[30,38,45,46] saddle[4]pyrrole complexant,[42] flexible ammonia complexant,[39,40] cagelike adamanzane[41] and H_5Azacrytand[2.2.2][43] complexants, and so on. Despite of the diversity in complexant, metal atoms introduced in those complexants to form electrides and alkalides are only alkalis or alkaline earth in periodic table. Exploring new metals to construct systems with diffuse excess electrons is a meaning way to extend the related field.

"Superatoms" are a type of atom clusters that seem to exhibit some of the properties of element atoms. Since Bergeron et al.[47,48] found that the clusters of Al_{13} and Al_{14} behave like a single iodine atom and an alkaline earth atom, respectively, superatoms have attracted more and more attention because they provide a thrilling prospect of serving as building block to construct new materials.

Superalkalis are one kind of typical superatoms, which have been theoretically and experimentally studied for over two decades.[49-57] Many superalkalis-doped molecules with loosely bound excess electrons have been theoretically investigated.[34,46,58] For example, single-caged superalkali electride salt molecules $(M_3O)^+(e@C_{20}F_{20})^-$(M = Na, K)[34] have been constructed and demonstrated to possess not only excellent nonlinear optical properties but also high stabilities. A series of new superalkali-based alkalides with large NLO responses were also designed,[46,58] including $Li_3(NH_3)_nNa$(n = 1 - 4), Li_3^+(calix[4]pyrrole)M^-, Li_3O^+(calix[4]pyrrole)M^-, and M_3O^+(calix[4]pyrrole)K^- (M = Li, Na, and K). It should be noticed that superalkalis serve as cations in those investigated superalkalis-doped systems.

To our best knowledge, there are no superalkali-based alkalide where superalkali occupies the anionic site. Such alkalide is termed as superalkalide. It can be expected that superalkalides might exhibit more excellent NLO properties than the above mentioned superalkali-based alkalides do because the larger volume of superalkali than alkali makes the bind of the excess electron to the superalkali core more loose, and results in the electron density distribution more diffuse and more easily polarized. Therefore, superalkalide might be a novel class of promising species with large NLO response.

The flip side of the more loosely bound of excess electron in superalkalis is that finding appropriate complexant to construct superalkalide should be of challenge. The complexant in superalkalide has to be much insensitive towards reduction. Dye's group pointed out that complexants with C-N bond are more suitable than those with C-O bond for the synthesis of thermally stable alkalides.[21] For example, Na^+(cryptand-[2.2.2])Na^-[36] is very unstable due to the reductive cleavage of the C-O bond in complexants, while K^+(aza222)Na^- and K^+(aza222)K^- with C-N bond instead of C-O bond can be synthesized at and above room temperature.[37] Another alkalide with complexants containing C-N bonds, $Li^+(en)_2Na^-$(en = ethylenediamine), has also been synthesized by Dye's group.[59] Subsequently Zurek has theoretically studied $M(en)_3^{\delta+}\cdot M^{\delta-}$ (M = Na, K, Rb, or Cs),[60] and demonstrated that the systems of $M(en)_3^+$ and $M(en)_3$ in which alkali metal atoms are chelated by three ethylenediamine molecules are more stable than the corresponding cationic and neutral systems where alkalis are chelated by one, two, or four ethylenediamine molecules.

Based on the above review of literatures about alkalides, we attempt to design a novel kind of superalkalides, $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, and K), where about one unit of electron charge transfers from the $M(en)_3$ fragment to the M'_3O superalkali to give an excess electron diffusing around M'_3O. Considering M'_3O has larger size and smaller IP value than that of the corresponding M' alkali atom in $M^+(en)_3M'^-$, it can be expected that the excess electron in $M^+(en)_3M'_3O^-$ would be more diffuse and more easily polarized which will cause considerable NLO response for the molecule $M^+(en)_3M'_3O^-$. In addition, the extra interaction between the oxygen atom of M'_3O^- and the hydrogen atoms of $M^+(en)_3$ will make $M^+(en)_3M'_3O^-$ significantly more stable than $M^+(en)_3M'^-$. For the purpose of comparison, here we have also re-calculated the structures of $M^+(en)_3M'^-$ (M, M' = Li, Na, and K) and estimated their NLO properties which have never been reported to our best knowledge.

As we expected, the present theoretical investigation show that the novel compounds, $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, and K), are a new class of alkalide where the anionic site is occupied by superalkali atom. All $M^+(en)_3M'_3O^-$ are more stable than $M^+(en)_3M'^-$ due to the formation of hydrogen bond between M'_3O^- and $M^+(en)_3$. Moreover, $M^+(en)_3M'_3O^-$ exhibit excellent NLO properties. We hope that this article could extend the field of superatom chemistry.

2. Computational Details

In this work, the second-order Møller-Plesset (MP2) method with the 6-31G(d) basis set was applied to optimize the geometrical structures of $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ (M, M'= Li, Na, and K). All reported $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ structures are genuine minima on the potential energy surface (PES) without imaginary vibrational frequencies. To understand the stabilities of those compounds, the interaction energies (E_{int}) were evaluated at the MP2/6-31G(d) and MP2/6-311++G(d, p) levels as well as the MP2/6-31G(d) level along with the PCM solvation model, based on the optimized geometries. The E_{int} is the energy difference between the compounds $M^+(en)_3M'^-$/$M^+(en)_3M'_3O^-$ and the sum of the subunits $M(en)_3$ and M'/M'_3O. To eliminate the basis-set superposition error (BSSE) in the interaction energy calculation, the counterpoise (CP)[61,62] correction is used as shown in eq. (1),

$$E_{\text{int}} = E_{\text{AB}}(X_{\text{AB}}) - [E_{\text{A}}(X_{\text{AB}}) + E_{\text{B}}(X_{\text{AB}})] \quad (1)$$

where the same basis set, X_{AB}, is used for both the subunit energy calculations (E_{A} and E_{B}) and the compound energy (E_{AB}) calculation.

To understand the property of the interaction between $M(en)_3$ and M'/M'_3O, we estimated the noncovalent interaction according to the method proposed by Yang's group[63] which indicates that the noncovalent interaction can be isolated as regions with low density and low reduced density gradient (RDG). The following eq. (2) defines the RDG which is denoted as s,

$$s = 1/(2(3\pi^2)^{1/3})|\nabla \rho|/\rho^{4/3} \tag{2}$$

where ρ is the electron density. For clarity, in the text, the scatter diagram of the RDG versus sign(λ_2)ρ is used to illustrate the noncovalent interaction, where sign(λ_2)ρ equals the electron density multiplied by the sign of the second hessian eigenvalue. It should be noted that Multiwfn software was employed for RDG analysis with medium quality grid which covers the whole system by about 512000 points in total.

Besides, the natural bond orbital (NBO) charges[64] and the vertical ionization energies (VIE) were calculated by using the MP2 method with the 6-311++G basis set for C, H, and N atoms, and the 6-311++G(3df) basis set for the alkali atoms and oxygen atoms. The VIE is calculated as:

$$\mathrm{VIE} = E[\mathrm{Mol}^{+}] - E[\mathrm{opt\ Mol}] \tag{3}$$

where E[opt Mol] and $E[\mathrm{Mol}^{+}]$ are the energies of an optimized neutral molecule and the its cation with the same geometrical structure as the neutral molecule, respectively.

To precisely explore the electron structural features, electron localization function (ELF) and localized orbital locator (LOL) of these systems were analyzed. The ELF, proposed initially by Becke,[65] is used to measure electron localization in molecular systems. The LOL, proposed by Schmider and Becke,[66] is applied to locate and characterize bond effect in terms of kinetic energy contributions, revealing localized electron locations without explicitly obtaining localized orbital.

With regards to the calculation of the first hyperpolarizabilities of the investigated systems, the MP2 method is suitable for calculating the first hyperpolarizability.[31,32,38,40,41,67-69] Maroulis et al. pointed out that improvement for accurate prediction of the polarizability was obtained by addition of suitable diffuse functions rather than polarization functions.[70] And some previous work have proven that the 6-311++G basis set is sufficient in reproducing hyperpolarizabilities.[38,40] In the present work, the first hyperpolarizabilities were evaluated by finite field (FF) approach at the MP2 level with the 6-311++G basis set for the (en)$_3$ framework and the 6-311++G(3df) basis set for the alkali and oxygen atoms. The magnitude of the applied electric field is chosen as 0.001 au for the calculation of the first hyperpolarizability, which has been proved to be the most adequate value for the numerical differentiation in several similar studies.[31,32,38,40,41,67-69]

In the FF approach, it is well known that the total energy of a molecule in a weak static electric field (F) can be expressed as follows:

$$E = E^{(0)} - \mu_i F_i - \frac{1}{2}\alpha_{ij} F_i F_j - \frac{1}{6}\beta_{ijk} F_i F_j F_k - \ldots \qquad (4)$$

in which $E^{(0)}$ is the total energy of the molecule in the absence of the applied electric field, F_i is the cartesian component of the field, and μ, α, and β are the dipole moment, the linear polarizability, and the first hyperpolarizability, respectively. For a molecule, the average dipole moment (μ_0) and polarizability (α_0) are defined as follows:

$$\mu_0 = \left(\sum_{i=1}^{3} \mu_i^2\right)^{1/2} \qquad (5)$$

$$\alpha_0 = \frac{1}{3}\sum_{i=1}^{3} \alpha_{ii} \qquad (6)$$

the first hyperpolarizability is defined as:

$$\beta_0 = \left(\sum_{i=1}^{3} \beta_i^2\right)^{1/2} \qquad (7)$$

in which

$$\beta_i = \frac{3}{5}(\beta_{iii} + \beta_{i,i+1,i+1} + \beta_{i,i+2,i+2}),\ i = i + 3 \qquad (8)$$

where $i = 1$ for x, $i = 2$ for y, $i = 3$ for z.

Moreover, the transition energy ΔE, oscillator strength f_0 and the difference of the dipole moment $\Delta\mu$, between the ground state and the crucial excited state which has the largest oscillator strength, are calculated by employing the configuration interaction singles (CIS) method with the same basis set as that of the calculation of the first hyperpolarizabilities.

All calculations are carried out using the Gaussian 09 program package.[71] And the NBO 5.0 program is also performed to refine the NBO charge.[72] The molecular structures and orbitals are plotted with the GaussView program.[73] The fchk files produced by Gaussian 09 are used as inputs for Multiwfn 3.3.5 software[74] to analyze the above mentioned LOL,ELF, as well as RDG.

3. Results and Discussions

3.1 Equilibrium Geometry and Stability

In $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$, the alkali cation M^+ are chelated by three chiral ethylenediamine ligands. Zurek pointed out that the D_3 structure of $M^+(en)_3$ can have four conformers for both the Δ and the Λ stereoisomer.[60] According to the orientations of the C-C bonds in the three en rings: either parallel (*lel*) or oblique (*ob*) to the C_3-axis of the $M^+(en)_3$ structure, the four conformers can be distinguished as *lel*$_3$, *lel*$_2$*ob*, *lelob*$_2$, and *ob*$_3$, respectively. Zurek indicated that the reaction energies, optical absorption spectra, and NMR chemical shieldings of the four conformers are very similar.[60] Therefore in this work, the initial input structures for $M^+(en)_3M'^-$ and

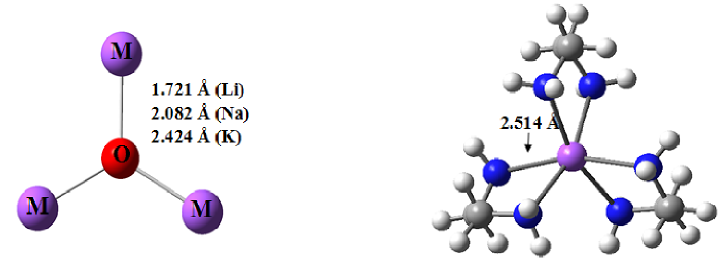
Table 1. The geometrical parameters for $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ (M , M' = Li, Na, and K) molecules.

		$M^+(en)_3M'^-$				**$M^+(en)_3M'_3O^-$**						
M	**M'**	**C-C**	**C-N**	**M-N**	**M-M'**	**C-C**	**C-N**	**M-N**	**M-O**	**O-H**	**M'-O**	**d**
Li	**Li**	1.522	1.469	2.252	4.947	1.522	1.467	2.236	3.833	2.022	1.798	0.895
			1.472	2.265			1.472	2.262				
Li	**Na**	1.521	1.469	2.258	5.170	1.524	1.465	2.231	3.729	1.923	2.202	1.173
			1.472	2.264			1.471	2.256				
Li	**K**	1.521	1.470	2.260	5.711	1.525	1.462	2.226	3.587	1.785	2.535	1.223
			1.472	2.268			1.470	2.253				
Na	**Li**	1.523	1.469	2.507	4.986	1.524	1.467	2.495	3.971	2.045	1.798	0.900
			1.474	2.522			1.475	2.517				
Na	**Na**	1.523	1.470	2.511	5.228	1.525	1.467	2.488	3.860	1.942	2.203	1.183
			1.474	2.524			1.475	2.514				
Na	**K**	1.522	1.471	2.512	5.763	1.526	1.462	2.485	3.697	1.795	2.536	1.229
			1.474	2.530			1.474	2.509				
K	**Li**	1.523	1.470	2.871-2.887	4.293	1.524	1.467	2.833	4.273	2.057	1.797	0.897
			1.473	2.925-3.029			1.477	2.925				
K	**Na**	1.523	1.470	2.878	4.993	1.525	1.465	2.823	4.154	1.950	2.203	1.185
			1.474	2.928			1.476	2.923				
K	**K**	1.523	1.470	2.886	5.522	1.526	1.462	2.819	3.989	1.805	2.537	1.239
			1.474	2.937			1.476	2.923				

$D_{C\text{-}C}$=1.528 Å $D_{C\text{-}N}$=1.468, 1.462 Å in sole ethylenediamine molecule, which is optimized at MP2/6-31G(d) level.

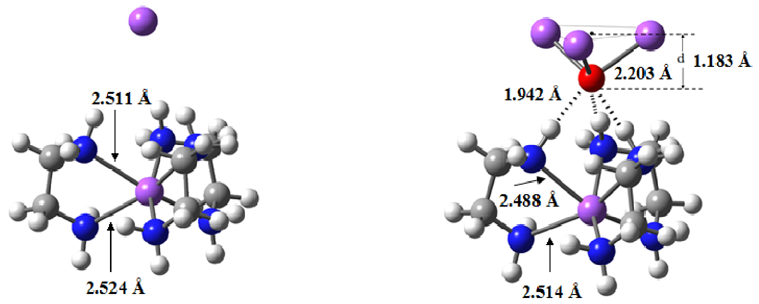
$M^+(en)_3M'_3O^-$ are designed basing upon the *lel*$_3$ $M^+(en)_3$ conformer. The optimized structures of $Na^+(en)_3Na^-$ and $Na^+(en)_3Na_3O^-$ are presented in Figure 1 as examples along with the structures of $Na(en)_3$ and M'_3O (M' = Li, Na, and K). Table 1 collects the optimized geometrical parameters for $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, and K). It should be noted that all structures listed in Table 1 has the symmetry of C_3 except for $K^+(en)_3Li^-$ whose structure is no symmetry (C_1).

As shown in Figure 1a and d, the structure of Na_3O slightly deviates from a plane to a triangle cone shape when it approaches to $Na(en)_3$ to give the superalkalide compound $Na^+(en)_3Na_3O^-$. The bond length of O-Na in Na_3O correspondingly elongates from 2.082 Å to 2.203 Å during the process. Similar trends are found in the formations of other eight $M^+(en)_3M'_3O^-$ superalkalides as shown in Table 1. Despite the structure distortion, the distance of O-M' in $M^+(en)_3M'_3O^-$ shows that a chemical bond indeed exists between O atom and each M' atom, which indicates that M'_3O superalkali keeps its integrity as an element during the interaction with $M(en)_3$ to form $M^+(en)_3M'_3O^-$.



D_{3h} M_3O (M=Li, Na, and K)
(a)

D_3 $Na(en)_3$
(b)



C_3 $Na^+(en)_3Na^-$
(c)

C_3 $Na^+(en)_3Na_3O^-$
(d)

Figure 1. Optimized geometrical structures of M_3O(M=Li, Na, and K), $Na(en)_3$, $Na^+(en)_3Na^-$, and $Na^+(en)_3Na_3O^-$.

The structures of the electride, alkalide, and superalkalide ionic salts, namely, $Na(en)_3$, $Na^+(en)_3Na^-$, and $Na^+(en)_3Na_3O^-$ are listed in Figure 1b, c, and d. It can be seen that the sizes of the $Na(en)_3$ fragments in $Na(en)_3$ and $Na^+(en)_3Na^-$ salts are nearly the same. However, when the anionic site is occupied by the Na_3O superalkali, the length of the Na-N bonds close to the Na_3O in the $Na(en)_3$ fragment reduce from 2.514 Å to 2.488 Å. In other words, the introduction of Na_3O to $Na(en)_3$ to form $Na^+(en)_3Na_3O^-$ substantially compresses the sphere of the $Na(en)_3$ fragment. The compression should make the electrostatic interaction between the central metal ion Na^+ and en ligands stronger than those in the $Na(en)_3$ and $Na^+(en)_3Na^-$ salts, and result in higher stability of the $Na(en)_3$ fragment in the $Na^+(en)_3Na_3O^-$ salt. Such compressions also exist in other superalkalides (seeing Table 1).

Furthermore, it can be seen in Figure 1d and Table 1 that in $M^+(en)_3M'_3O^-$ the distances between the oxygen of M'_3O and the neighboring hydrogens of en ligands are in the range of 1.785~2.057 Å, which suggest the existence of hydrogen bonds in $M^+(en)_3M'_3O^-$. It can be expected that the presents of these hydrogen bonds in $M^+(en)_3M'_3O^-$ should provide excess stability for $M^+(en)_3M'_3O^-$ comparing to that for $M^+(en)_3M'^-$. The interaction energies (E_{int}) between $M^+(en)_3$ and M'^-/M'_3O^- were also calculated at the MP2/6-31G(d) level to explore the stabilities of $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$. Table 2 show that the values of E_{int} are in the range of -15.06~-23.20 kcal/mol for $M^+(en)_3M'^-$, and -37.27~-52.35 kcal/mol for $M^+(en)_3M'_3O^-$, respectively, indicating the remarkable stabilities of the alkalides and superalkalides under investigation. In addition, the E_{int} values of $M^+(en)_3M'_3O^-$ are over twice as large as those of $M^+(en)_3M'^-$, confirming the mentioned suggestion that superalkalide $M^+(en)_3M'_3O^-$ is more stable than the corresponding alkalide $M^+(en)_3M'^-$.

A larger triple-ζ basis set with polarization as well as diffuse functions, 6-311++G(d, p), were also used for all atoms to evaluate the dependence of E_{int} on basis set size. However, it is found that larger basis set nearly do not change the E_{int} (Table 2), therefore, the E_{int} at the MP2/6-31G(d) level is reliable.

In addition, the solvation effect on the E_{int} is also estimated for the corresponding alkalide and superalkalide by the polarizable continuum (PCM) modes at the

MP2/6-31G(d) level. The dielectric constant is 12.9 for the ethylenediamine liquid. The values of E_{int} increase by about 20-35 kcal/molafter considering the solvent effect (Table 2), indicating that the solvent effect is significant on the E_{int}. However, the solvated superalkalide $M^+(en)_3M'_3O^-$ is also much more stable than the corresponding alkalide $M^+(en)_3M'^{\cdot-}$.

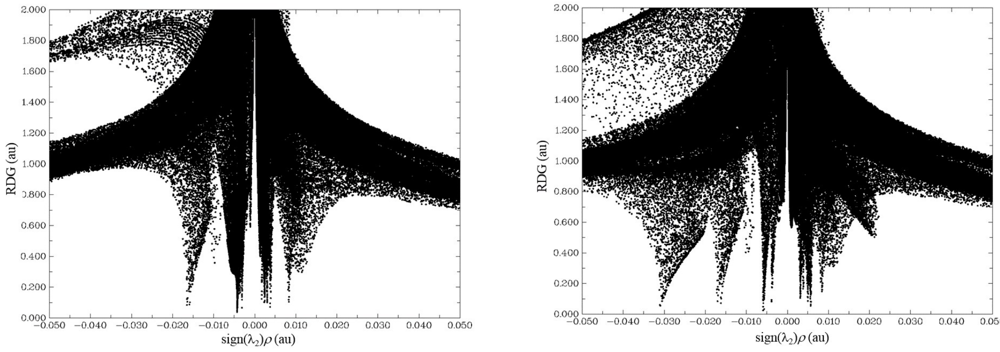
Table 2. NBO charges Q on M, M', O, the sum of charges on M'_3O, the VIE values and the interaction energies E_{int} (kcal/mol) of the $M^+(en)_3M'^{\cdot-}$ and $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, and K) molecules.

		$M^+(en)_3M'^{\cdot-}$						**$M^+(en)_3M'_3O^-$**							
M	**M'**	**Q_M**	**$Q_{M'}$**	**VIE**	**E_{int}^a**	**E_{int}^b**	**E_{int}^c**	**Q_M**	**$Q_{M'}$**	**Q_O**	**$Q_{M'3O}$**	**VIE**	**E_{int}^a**	**E_{int}^b**	**E_{int}^c**
Li	**Li**	0.811	-0.766	3.058	-23.20	-22.83	6.35	0.794	0.335	-1.919	-0.914	3.203	-39.09	-39.57	-2.54
Li	**Na**	0.806	-0.817	2.909	-20.49	-19.74	1.71	0.791	0.341	-1.884	-0.861	3.159	-49.54	-51.95	-15.93
Li	**K**	0.797	-0.830	2.715	-15.06	-16.68	4.04	0.783	0.341	-1.802	-0.779	2.620	-52.35	-54.75	-28.18
Na	**Li**	0.854	-0.822	3.328	-23.12	-23.00	6.53	0.848	0.335	-1.923	-0.918	3.326	-38.39	-39.20	-2.47
Na	**Na**	0.852	-0.848	2.883	-20.50	-19.97	1.89	0.844	0.341	-1.891	-0.867	3.261	-48.59	-51.32	-15.60
Na	**K**	0.835	-0.847	2.687	-15.22	-16.82	4.27	0.835	0.341	-1.807	-0.784	2.832	-50.96	-54.09	-27.38
K	**Li**	0.857	-0.845	3.213	-22.46	-23.74	6.46	0.916	0.336	-1.927	-0.918	3.316	-37.27	-38.68	-2.56
K	**Na**	0.888	-0.866	3.140	-20.06	-20.56	1.73	0.912	0.342	-1.895	-0.869	3.257	-47.23	-50.49	-14.94
K	**K**	0.856	-0.843	2.474	-15.31	-17.33	4.12	0.904	0.342	-1.814	-0.787	2.828	-49.22	-53.12	-25.82

E_{int}^a is predicted at the MP2/6-31G(d) level;

E_{int}^b is predicted at the MP2/6-311++G(d,p) level;

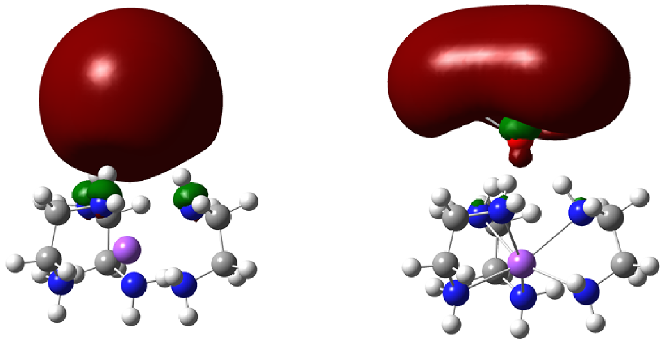
E_{int}^c is predicted by the polarizable continuum (PCM) modes at the MP2/6-31G(d) level.



$Na^+(en)_3Na^-$ $Na^+(en)_3Na_3O^-$

Figure 2. Sign(λ_2)ρ ~ RDG maps for $Na^+(en)_3Na^-$ and $Na^+(en)_3Na_3O^-$.

Whether the excess stability of $M^+(en)_3M'_3O^-$ relative to $M^+(en)_3M'^{\cdot-}$ is caused by the hydrogen bonds is verified by the calculated RDG. Figure 2 plots the RDG versus sign(λ_2)ρ for $Na^+(en)_3Na^-$ and $Na^+(en)_3Na_3O^-$. Yang's group[63] proposed that noncovalent interactions can be isolated as regions with low density and low reduced gradient. Surfaces with very low density values (i.e., $\rho < 0.005$ au) generally map to weak dispersion interactions; surfaces with slightly higher density values (i.e., 0.005 au $< \rho <$ 0.05 au) map to strong noncovalent interactions including both attractive H-bonding (negative λ_2) and steric clashes (positive λ_2). Figure 2 shows that, for $Na^+(en)_3Na_3O^-$, the density values of spikes in the region of RDG < 0.5 au and $-0.02 < \mathrm{sign}(\lambda_2)\rho < 0.02$ as well as the region RDG < 0.5 au and $\mathrm{sign}(\lambda_2)\rho < -0.02$ are comparable, indicating that both weak dispersion interaction and hydrogen bond interaction exist in this superalkalide. When it comes to $Na^+(en)_3Na^-$, the spikes only distribute in the region of RDG < 0.5 au and $-0.02 < \mathrm{sign}(\lambda_2)\rho < 0.02$ and its density value in this region is comparable to that in $Na^+(en)_3Na_3O^-$. Therefore, the RDG calculation substantiate that the hydrogen bonds in the superalkalide systems, $M^+(en)_3M'_3O^-$, play an important role in their preference in the stability than the alkalide systems, $M^+(en)_3M'^-$.



$Na^+(en)_3Na^-$ $Na^+(en)_3Na_3O^-$

Figure 3. HOMOs (isovalue = 0.02) of $Na^+(en)_3Na^-$ and $Na^+(en)_3Na_3O^-$.

3.2 Electronic Structure Features

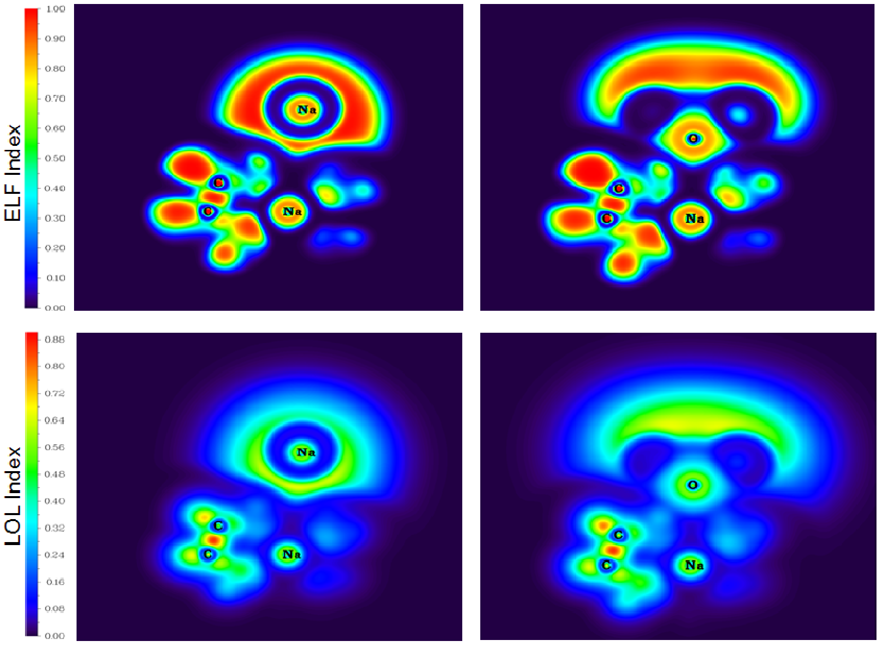
Table 2 collects the results of NBO analyses and VIE calculations on the compounds under investigation. For $M^+(en)_3M'^-$, the NBO analyses show that natural atomic charges on the M' atoms in the range of -0.766e to -0.866e, which indicate that

$M^+(en)_3M'^-$ are typical alkalides. The results are consistent with that of the theoretical study on $M(en)_3^{\delta+}M^{\delta-}$ performed by Zurek.[60] In $M^+(en)_3M'^-$, the excess electron located on M' originates from the outer *s* valence electron of M which is the center of the $(en)_3$ cavity. In the cavity, all the lone pairs of N atoms in the three en ligands direct toward the center and synergistically push away the outer *s* electron of M to M' to form alkali anion. The highest occupied molecular orbital (HOMO) of $Na^+(en)_3Na^-$ is displayed in Figure 3 for example. It is shown that the excess electron occupies the HOMO which enwraps the whole Na and looks like a hat on the $Na^+(en)_3$ fragment. The HOMOs of other $M^+(en)_3M'^-$ are very similar to that of $Na^+(en)_3Na^-$. The calculated VIEs for $M^+(en)_3M'^-$ are in the range of 2.474~3.328 eV which are close to the VIEs for $M^+@(n^6adz)M'^-$ alkalides (M, M' = Li, Na, and K).[41] The small VIE values indicate that the excess electrons in $M^+(en)_3M'^-$ are very diffuse and suggest that $M^+(en)_3M'^-$ might have good NLO response.

The NBO analyses for $M^+(en)_3M'_3O^-$ show that the substitution of superalkalis M'_3O for M' in $M^+(en)_3M'^-$ have negligible impact on the charge distribution. The positive charge center for $M^+(en)_3M'_3O^-$ still locate on the metal inside the $(en)_3$ cavity, and the natural atomic charge on M'_3O is nearly the same as that on M' in $M^+(en)_3M'^-$. For example, the natural atomic charges on Na^+ and Na^- of $Na^+(en)_3Na^-$ are 0.852e and -0.848e, respectively, and those on Na^+ and Na_3O^- of $Na^+(en)_3Na_3O^-$ are 0.844e and -0.867e, respectively. The electron cloud of HOMO of $Na^+(en)_3Na_3O^-$ distributes over the whole Na_3O framework and its shape is very similar to that of $Na^+(en)_3Na^-$ as shown in Figure 3. The NBO analyses and HOMO electron cloud distributions suggest that these novel superalkalides might exhibit excellent NLO properties. The calculated VIEs for $M^+(en)_3M'_3O^-$, in the range of 2.620~3.326 eV (Table 2), provide another support for such suggestion. It can be found in Table 2 that the VIE value of $M^+(en)_3M'_3O^-$ is larger than that of the corresponding $M^+(en)_3M'^-$. For example, the VIE for $Na^+(en)_3Na_3O^-$ is 3.261 eV, while it is 2.883 eV for $Na^+(en)_3Na^-$. The larger VIE values for $M^+(en)_3M'_3O^-$ implies that the excess electron in $M^+(en)_3M'_3O^-$ is bound more tightly than that in $M^+(en)_3M'^-$. This may origin from the hydrogen bonds in $M^+(en)_3M'_3O^-$ which increases the stability of $M^+(en)_3M'_3O^-$ and synergistically strengthens the bound effect to the excess electron.

To further reveal the electronic localized property of $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$, the ELF and LOL are calculated. Figure 4 depicts the results of ELF and LOL for $Na^+(en)_3Na^-$ and $Na^+(en)_3Na_3O^-$ as examples, while the results for other alkalides and superalkalides are displayed in the Supporting Information (SI). The cut-plane representation of both ELF and LOL is selected along a plane through Na^+, Na^-, and one of C-C bond of the $(en)_3$ cavity for $Na^+(en)_3Na^-$ and Na^+, O, and one of C-C bond of the $(en)_3$ cavity for $Na^+(en)_3Na_3O^-$, respectively.

As shown in Figure 4, the electron distribution shape around Na/Na_3O is consistent with the corresponding shape of HOMO shown in Figure 3. It demonstrates, again, that the excess electron in the alkalide/superalkalide is located on the Na/Na_3O to form alkali/superalkali metal anion. In addition, the ELF and LOL values for the area between Na^-/Na_3O^- and $Na^+(en)_3$ are very small, indicating that the existence of electrostatic force instead of covalent interaction between the two fragments.



$Na^+(en)_3Na^-$ $Na^+(en)_3Na_3O^-$

Figure 4. Cut-plane ELF and LOL of complexes $Na^+(en)_3Na^-$ and $Na^+(en)_3Na_3O^-$.

Therefore, both $Na^+(en)_3Na^-$ and $Na^+(en)_3Na_3O^-$ are proved to be ionic compounds.

And again, the same findings can be applied to other $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ compounds.

Table 3. Polarizability α_0 (au), the first hyperpolarizability β_0 (au), the transition energy ΔE(eV), the largest oscillator strength f_0, the difference of dipole moment between the ground state and the crucial excited state $\Delta\mu$ (D) of the $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, and K) molecules.

		$M^+(en)_3M'^-$					**$M^+(en)_3M'_3O^-$**				
M	**M'**	α_0	β_0	ΔE	f_0	$\Delta\mu$	α_0	β_0	ΔE	f_0	$\Delta\mu$
Li	**Li**	466	1.29×10^4	1.864	0.314	14.542	664	1.59×10^4	1.093	0.386	4.732
Li	**Na**	548	2.76×10^4	1.769	0.280	17.011	783	9.93×10^3	1.110	0.466	3.135
Li	**K**	875	1.50×10^5	1.429	0.238	12.653	1275	6.15×10^4	0.844	0.482	4.577
Na	**Li**	466	7.95×10^3	1.845	0.309	14.372	665	1.28×10^4	1.090	0.387	4.637
Na	**Na**	549	1.99×10^4	1.755	0.274	16.836	783	7.80×10^3	1.108	0.465	3.075
Na	**K**	877	1.24×10^5	1.414	0.245	13.127	1285	6.19×10^4	0.837	0.480	4.717
K	**Li**	285	3.33×10^4	1.504	0.220	4.028	558	6.81×10^4	1.078	0.381	4.674
K	**Na**	288	3.46×10^4	1.748	0.292	9.898	665	7.20×10^4	1.097	0.458	3.130
K	**K**	723	1.84×10^5	1.412	0.274	16.975	1236	9.16×10^4	0.824	0.470	4.948

3.3 Nonlinear Optical Property

The NLO properties of $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ calculated by the MP2 method are listed in Table 3. It shows that both $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ compounds exhibit considerably large polarizability (α_0) and first hyperpolarizability (β_0). For the series of $M^+(en)_3M'^-$, $Li^+(en)_3Li^-$ has the smallest β_0 of 1.29×10^4 au and $K^+(en)_3K^-$ has the largest β_0 of 1.84×10^5 au. For $M^+(en)_3M'_3O^-$, $Na^+(en)_3Na_3O^-$ displays the smallest β_0 of 7.80×10^3 au, while $K^+(en)_3K_3O^-$ gives the largest β_0 of 9.16×10^4 au. To explore the reason why alkalides $M^+(en)_3M'^-$ and superalkalides $M^+(en)_3M'_3O^-$ possess such large β_0 values, the following two-level model[75-77] is applied:

$$\beta_0 \propto \frac{(\Delta\mu)\times f_0}{(\Delta E)^3}$$

where ΔE, f_0, and $\Delta\mu$ are the transition energy, oscillator strength, and the difference of dipole moments between the ground state and the crucial excited state with the largest oscillator strength, respectively. In the two-level expression, the third power of the transition energy is inversely proportional to the β_0 values. Hence, the transition energy (ΔE) is usually a crucial factor in effect on the first hyperpolarizability.

The crucial excited states of $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ have been estimated by the CIS method. The computed crucial excited states for $Li^+(en)_3Li^-$, $Na^+(en)_3Na^-$, $K^+(en)_3K^-$, $Li^+(en)_3Li_3O^-$, $Na^+(en)_3Na_3O^-$, and $K^+(en)_3K_3O^-$ are shown in Figure 5 as examples, and others are present in the Supporting Information. It can be found that all the electron transitions between the ground state and the crucial excited state of these alkalides and superalkalides occur on the electron populating their respective HOMO orbitals. Under the action of the lone pairs of N atoms in the $(en)_3$ fragment, the *s* valence electron of the M atom is pushed out to become an excess electron and populate the diffuse HOMO. It can be expected that the interaction between the excess electron and the M core is very weak. In addition, the small vertical ionization potentials of M'/M'_3O[78,79] suggest that the interaction between the excess electron and the M'/M'_3O core should be very weak too. Therefore, it can be anticipated that the excess electron can be easily excited. The calculated transition energies (ΔE) indeed confirm such assumption. Table 3 shows that both $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ have very small ΔE values in the range of 1.412~1.864eV and 0.824~1.110eV, respectively. According to the two-level expression, such small ΔE values should cause significantly large β_0 values for $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ in the range of 7.95×10^3~1.84×10^5 au and 7.80×10^3 ~9.16×10^4 au, respectively.

Based on the above analysis, one can see that the ability of the complexant $(en)_3$ in $M^+(en)_3M'^-$ or $M^+(en)_3M'_3O^-$ to push the *s* valence electron in M atom out to form excess electron play an crucial role in enhancing the β_0 value. The β_0 values of Li^+(calix[4]pyrrole)K^-[38] and $Li^+(en)_3K^-$ are 3.6×10^4 au and 1.50×10^5 au, respectively, which indicates that C_3-symmetric flexible complexant $(en)_3$ does better in enhancing the β_0 value of the alkalide than the C_{4v}-symmetric complexant calix[4]pyrrole does. Therefore, the C_3-symmetric flexible complexant $(en)_3$ is a promise complexant candidate for constructing novel alkalides and superalkalides.

Finally, the β_0 value of the $K^+(en)_3K'_3O^-$ compound under this investigation is 9.16×10^4 au which is very close to that of the well-known organometallic system

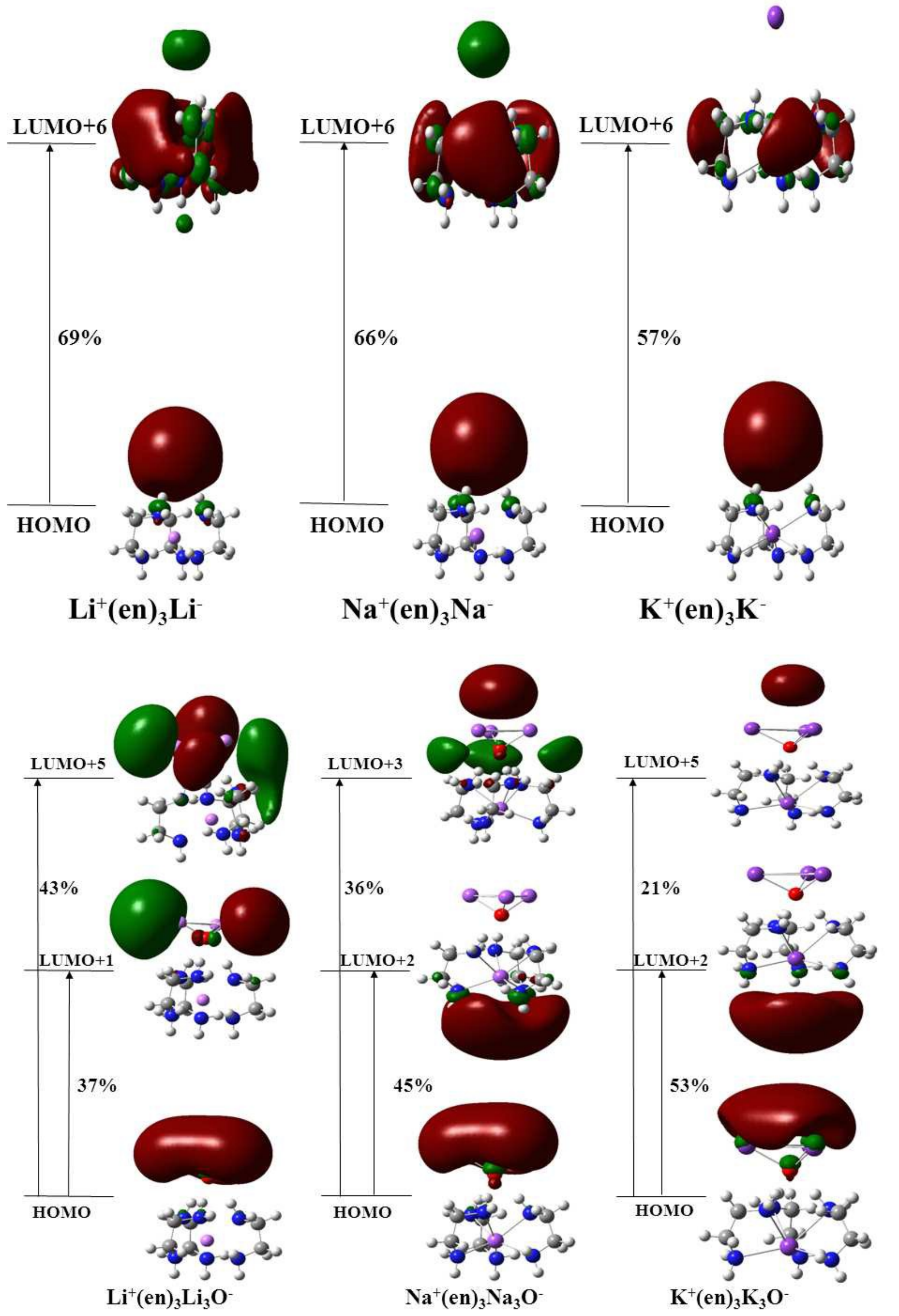


Figure 5. Crucial transition states of $Li^+(en)_3Li^-$, $Na^+(en)_3Na^-$, $K^+(en)_3K^-$, $Li^+(en)_3Li_3O^-$, $Na^+(en)_3Na_3O^-$, and $K^+(en)_3K_3O^-$ molecules, where component coefficient percentage is marked. The isovalues of the corresponding MO isosurfaces are 0.02.

Ru(trans-4,4'-dibutylaminostyryl-2,2'-bipyridine)$_3^{2+}$.[80,81] Besides, the β_0 values of the superalkalides Li$^+$(en)$_3$M'$_3$O$^-$ (M' = Li, K) are larger than that of the reported alkalides Li$^+$(calix[4]pyrrole)M$^-$.[38] These results suggest that the substitution of superalkalis for alkali metal atoms with negative charges in alkalides is a new strategy to enhance NLO response.

4. Conclusion

In this work, by using the M'$_3$O (M' = Li, Na, and K) superalkalis, a novel kind of alkalides, M$^+$(en)$_3$M'$_3$O$^-$ (M, M' = Li, Na, and K), have been designed and demonstrated to be promising inorganic salts with excellent NLO properties. Such new ionic salts are termed as superalkalides where the M'$_3$O superalkali occupies the anionic site. These superalkalides, M$^+$(en)$_3$M'$_3$O$^-$, are first examples of inorganic salt in which superalkali serves as anion.

The geometrical optimizations for M$^+$(en)$_3$M'$_3$O$^-$ show that M'$_3$O superalkali atom keep its integrity as an element in all the superalkalide compounds. The NBO analyses demonstrate that, in the M$^+$(en)$_3$M'$_3$O$^-$ ionic salts, the M'$_3$O superalkali atoms are the negative charge centers with the natural atomic charges in the range of -0.779e to -0.918e, while the M metals inside the (en)$_3$ cavity are the corresponding positive charge centers. The NBO results reveal that the M$^+$(en)$_3$M'$_3$O$^-$ compounds are indeed superalkalides. In M$^+$(en)$_3$M'$_3$O$^-$, the valence *s* electron of M is pushed out of the (en)$_3$ cavity under the repulsive action of the lone pairs of N atoms in (en)$_3$ to become an excess electron and populate the HOMO which is a diffuse *s*-type orbital enwrapping the M'$_3$O superalkali atom. Both interactions between the excess electron and the M core as well as the M'$_3$O core in M$^+$(en)$_3$M'$_3$O$^-$ are very weak. In other words, the excess electron is loosely bound and can be easily excited. Indeed, the calculated transition energies (ΔE) between the ground state and the crucial excited state with the largest oscillator strength of M$^+$(en)$_3$M'$_3$O$^-$ are very small in the range of 0.824~1.110 eV. According to the two-level expression, the small ΔE cause the considerablely large first hyperpolarizability (β_0) in the range of 7.80×10^3 ~9.16×10^4 au..

The properties of the $M^+(en)_3M'_3O^-$ (M, M' = Na, and K) superalkalides are very similar to those of the $M^+(en)_3M'^-_3$ (M, M' = Na, and K) alkalides which were theoretically investigated by Zurek.[60] In this study, we have also re-calculated the structures of $M^+(en)_3M'^-$ (M, M' = Li, Na, and K) and estimated their NLO properties for comparison. Although the β_0 values of $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ are comparable, the $M^+(en)_3M'_3O^-$ superalkalides are more promising candidates than $M^+(en)_3M'^-$ for NLO materials because of their higher stabilities. The hydrogen bonds between the oxygen of M'_3O and the neighboring hydrogens of en ligands in $M^+(en)_3M'_3O^-$ provide extra stability for $M^+(en)_3M'_3O^-$ than the corresponding $M^+(en)_3M'^-$ alkalide.

We propose the strategy of the substitution of superalkali atoms for the alkali atoms with negative charge in the alkalides to construct a novel class of compounds, termed as superalkalides. The designed superalkalides, $M^+(en)_3M'_3O^-$ (M, M' = Na, and K) exhibit not only considerable NLO responds but also significant stabilities. Further experimental researches are invited.

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Supporting Information

Figure S1. Cut-plane ELF and LOL of $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$(M, M' = Li, Na, and K) molecules. Figure S2. Crucial transition states of $M^+(en)_3M'^-$ and $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, and K) molecules, where component coefficient percentage is marked.

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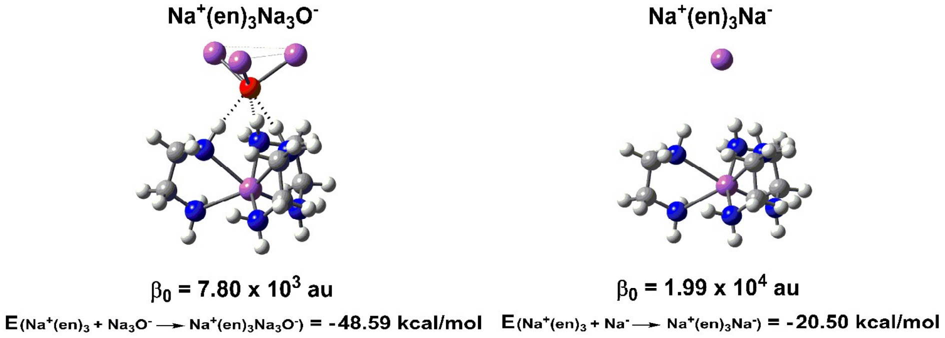
Graphic Abstract



Textual Abstract

A novel class of inorganic salts where superalkali occupies the anionic site, termed as superalkalides, $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, and K) have been designed and predicted to be candidates for NLO materials.