



Superalkali Li_3M ($\text{M} = \text{Cl}, \text{Br}, \text{I}$) as a Lewis base in halogen bonding: A heavier halogen is a stronger Lewis base than a lighter halogen

WenKai Tian, Qin Miao, QingZhong Li*, WenZuo Li, JianBo Cheng

The Laboratory of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, PR China

ARTICLE INFO

Article history:

Received 31 January 2013
Received in revised form 4 March 2013
Accepted 4 March 2013
Available online 14 March 2013

Keywords:

Halogen bond
Superatom
Orbital interaction
 Li_3Cl
 Li_3Br

ABSTRACT

The $\text{Li}_3\text{M}-\text{XY}$ ($\text{M} = \text{Cl}, \text{Br}, \text{and I}$; $\text{XY} = \text{ClCl}, \text{BrBr}, \text{ClF}, \text{BrCl}, \text{and BrF}$) complexes have been studied with theoretical calculations at the MP2/aug-cc-pVTZ level. The results showed that the Br atom in Li_3Br is a stronger halogen acceptor than the Cl atom in Li_3Cl when it interacts with dihalogen molecules although their strength difference is small and the Li_3I is the strongest Lewis base. To the best of our knowledge, this is the first report on halogen bonds involved with superatoms. The formation of halogen bonding has been analyzed with natural bond orbital (NBO), atoms in molecules (AIM), and energy decomposition. The results showed that the orbital interaction plays an important role for the stabilization of the complexes, which is different from conventional halogen bonds.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Halogen bonding is a non-covalent interaction between the halogen atom in one molecule and a Lewis base which has one or more electronegative centers [1]. Like hydrogen bonding, it is also of great importance in many fields such as molecular recognition, supermolecular materials, and chemical reactions [2–10]. Hernandez et al. [9] summarized the prevalence of halogenated drugs and their structural and pharmacological features, and discussed the identification and prediction of halogen bonds in protein–ligand complexes as well as how these bonds should be exploited. Metrangolo et al. presented a review on the potential applications of halogen bonding in liquid crystals, magnetic and conducting materials, and biological systems [10].

The strength of halogen bonding is dependent on the nature of halogen donor and becomes greater in order of $\text{F} < \text{Cl} < \text{Br} < \text{I}$. F seldom participates in halogen bonding although it can do when it is adjoined with electron-withdrawing groups or the Lewis base is a stronger halogen acceptor [11]. This is mainly due to the electrostatic nature of halogen bonding, which can be confirmed by examination of electrostatic potentials on the halogen's surfaces. It was found that a positive region (σ -hole) of electrostatic potential exists on the outer side of the halogen in the halogenated systems [12–16]. The σ -hole tends to become larger and more positive with the increase of the halogen size [14]. This σ -hole can be tuned through substitution of atoms or chemical groups in the vicinity

of a halogen [15]. For example, the bromine in 5-bromo-4,6-dicyano pyrimidine shows a more positive σ -hole than the corresponding one in 5-bromopyrimidine [16].

The strength of halogen bonding is also related with the nature of Lewis bases. Besides conventional electron donors such as oxygen- and nitrogen-containing molecules, the Lewis bases can also be from aromatic compounds, metal hydrides [17], radicals [18], and carbenes [19]. Nitrogen electron donors are favorable to form a halogen bond with respect to oxygen electron donors and ammonia even shows an attractive interaction with the F atom in F_2 [20]. The halogen acceptor ability of S depends greatly on its environment [21]. For example, the $\text{H}_2\text{S}-\text{XF}$ ($\text{X} = \text{Cl}$ and Br) complexes show weaker halogen bonds than the $\text{H}_2\text{O}-\text{XF}$ complexes, while the reverse result is found for the corresponding methyl-substituted molecules [22]. It was demonstrated that alkali metals in $\text{HCCBr}-\text{NCLi}$ and $\text{HCCBr}-\text{NCNa}$ complexes enhance greatly the strength of halogen bonding [23].

Recently, superatoms have attracted more and more attention because they have synthetic utility and represent potential building blocks for the assembly of novel and nanostructured materials [24–28]. Superhalogens and superalkalies are often two typical types of superatoms. Superalkalies are molecules with lower ionization potentials (IPs) than alkali atoms [29,30] and the most prominent examples are alkali metal clusters with the formula of L_{k+1}M (e.g. Li_3O , Li_4N), where L is an alkali metal atom [31]. Alexandrova and Boldyrev [32] introduced σ -aromaticity into the Li_3^+ cation and pointed out that Li_3 can be considered to be a superalkali because its IP value is appreciably lower than that of the Li atom. Although superatoms have been investigated for several

* Corresponding author. Tel./fax: +86 535 6902063.

E-mail address: liqingzhong1990@sina.com (Q. Li).

decades, as far as we know, little study is performed for halogen bonds with superatoms.

In this paper, we chose Li_3 as a superalkali to form a compound Li_3M ($\text{M} = \text{Cl}, \text{Br}, \text{and I}$) with a halogen element. Then Li_3M combines with dihalogen molecules $\text{XY} = \text{ClCl}, \text{BrBr}, \text{ClF}, \text{BrCl}, \text{and BrF}$. We paid our attention to the influence of superalkali on the strength of halogen bonding. Will there be any unexpected characteristics in these interactions? How about the nature of halogen bonding? Such study would make good sense for superatom chemistry.

2. Theoretical methods

All calculations were performed using the Gaussian 09 suite of programs [33]. The systems were optimized at the MP2 computational level in conjunction with the correlation consistent basis set aug-cc-pVTZ for all atoms, except iodine, for which the aug-cc-pVTZ-PP [34] basis set was used. The frozen core (FC) treatment was adopted in the optimization. Frequency calculations were performed at the same computational level in order to confirm that the obtained structures correspond to local minima on the potential energy surfaces. The interaction energy was calculated to be the difference between the energy of the complex and the sum of the energies of the isolated monomers in their minimum configuration. The basis set superposition error (BSSE) with the Boys–Bernardi counterpoise scheme [35] was removed from the interaction energy. The electrostatic potentials were calculated using the Surface Analysis Suite (SAS) program [36].

Topological properties of electron density were calculated using the AIM2000 [37] software for the Atoms-in-Molecules (AIM) theory. The topological analysis of the electron localization function (ELF) was performed with Multiwfn 2.01 suite of program [38]. Natural bond orbital (NBO) analysis was also performed via NBO package [39] included in the Gaussian 09 suite of programs.

Energy decomposition calculations were carried out with the ADF 2008.01 package [40]. The calculations were performed at the gradient-corrected DFT level using the functional of mPBE. No relativistic effects were considered. Double- ζ quality with a single polarization function (DZP) was employed for all atoms and no electron is frozen.

3. Results and discussion

Superatom can exhibit similar properties with one single atom [41] and Li_3 cluster is a superalkali with lower IP value [27]. Thus the Li_3 cluster can form small halogen-doped lithium clusters Li_3M ($\text{M} = \text{Cl} \text{ and } \text{Br}$), which were obtained by a thermal ionization source of modified design and selected by a magnetic sector mass spectrometer [42,43]. The ionization energies were determined to be 4.10 ± 0.25 eV for Li_3Cl and 3.92 ± 0.20 eV for Li_3Br [42,43]. Both clusters have a much lower ionization potential than that of a lithium atom (5.390 eV) [27], so they belong to the superalkali. The low ionization energies mean that they are easy to lose electrons. Thus we designed $\text{Li}_3\text{M}-\text{XY}$ ($\text{XY} = \text{dihalogen}$) systems to study the formation of halogen bond with Li_3M as the halogen acceptor. Fig. 1 shows the sketch of $\text{Li}_3\text{M}-\text{XY}$ ($\text{M} = \text{Cl}, \text{Br}, \text{and I}$; $\text{XY} = \text{ClCl}, \text{BrBr}, \text{ClF}, \text{BrCl}, \text{and BrF}$) complex. The energetic, geometrical, and spectroscopic parameters in the complexes are summarized in Table 1. These complexes display an attractive halogen–halogen contact. Such attractive contact can be understood with molecular electrostatic potentials of Li_3M and XY . It has been shown that a positive region of electrostatic potential (σ -hole) is found on the outer portion of the halogen's surface, centered on the $\text{X}-\text{Y}$ axis [21], however, the electrostatic potential of the halogen atom's surface in Li_3M is negative (blue) as shown in Fig. 2. A negative region

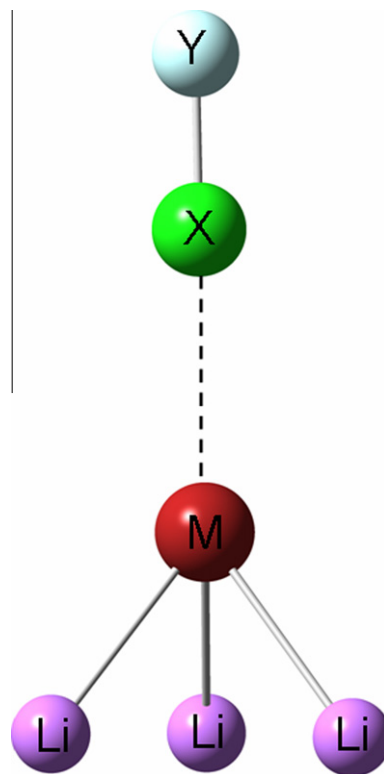


Fig. 1. The structure of $\text{Li}_3\text{M}-\text{XY}$ ($\text{M} = \text{Cl} \text{ and } \text{Br}$; $\text{XY} = \text{ClCl}, \text{BrBr}, \text{ClF}, \text{BrCl}, \text{and BrF}$) complex.

Table 1

Interaction energy (ΔE , kcal/mol) corrected for BSSE, binding distance (R , Å), changes of $\text{X}-\text{Y}$ and $\text{M}-\text{Li}$ bond lengths (Δr , Å), and frequency shifts of $\text{X}-\text{Y}$ and $\text{M}-\text{Li}$ stretch vibrations ($\Delta \nu$, cm^{-1}) in $\text{Li}_3\text{M}-\text{XY}$ complexes.

	ΔE	R	$\Delta r_{\text{X-Y}}$	$\Delta r_{\text{M-Li}}$	$\Delta \nu_{\text{X-Y}}$	$\Delta \nu_{\text{M-Li}}$
$\text{Li}_3\text{Cl}-\text{ClCl}$	-2.77	3.077	0.017	0.014	-42	-11
$\text{Li}_3\text{Cl}-\text{BrBr}$	-3.96	3.036	0.031	0.020	-43	-16
$\text{Li}_3\text{Cl}-\text{ClF}$	-4.37	2.852	0.027	0.031	-90	-22
$\text{Li}_3\text{Cl}-\text{BrCl}$	-4.41	2.995	0.033	0.026	-53	-23
$\text{Li}_3\text{Cl}-\text{BrF}$	-6.53	2.816	0.038	0.048	-94	-31
$\text{Li}_3\text{Br}-\text{ClCl}$	-2.86	3.124	0.023	0.024	-59	-9
$\text{Li}_3\text{Br}-\text{BrBr}$	-4.24	3.069	0.044	0.024	-63	-12
$\text{Li}_3\text{Br}-\text{ClF}$	-4.56	2.886	0.038	0.035	-134	-17
$\text{Li}_3\text{Br}-\text{BrCl}$	-4.69	3.033	0.047	0.031	-77	-18
$\text{Li}_3\text{Br}-\text{BrF}$	-6.99	2.869	0.052	0.046	-129	-22
$\text{Li}_3\text{I}-\text{ClCl}$	-3.13	3.183	0.038	0.021	-105	-6
$\text{Li}_3\text{I}-\text{BrBr}$	-5.03	3.087	0.088	0.029	-118	-7
$\text{Li}_3\text{I}-\text{ClF}$	-5.15	2.906	0.074	0.051	-262	-11
$\text{Li}_3\text{I}-\text{BrCl}$	-5.48	3.063	0.087	0.028	-151	-5
$\text{Li}_3\text{I}-\text{BrF}$	-8.17	2.936	0.084	0.052	-202	-13

of electrostatic potential is also found on the surface of Li_3 cluster. This provides a further evidence for the aromaticity of Li_3^+ ring [44].

One unexpected result is that the interaction energy in the Li_3Br complex is more negative than that in the Li_3Cl counterpart. For example, it is -4.37 kcal/mol for $\text{Li}_3\text{Cl}-\text{ClF}$ and -4.56 kcal/mol for $\text{Li}_3\text{Br}-\text{ClF}$. Their difference is dependent on the dihalogen molecule and is increased in order $\text{ClCl} < \text{ClF} < \text{BrBr} < \text{BrCl} < \text{BrF}$. The difference in the strength is small, but it shows that Li_3Br as a Lewis base forms a stronger halogen bonding than Li_3Cl . The result is reverse to that found in halogen-bonded $\text{DX} \cdots \text{A}^-$ ($\text{D}, \text{X}, \text{A} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) complexes [45], in which the halogen bond becomes weaker as the accepting halide varies from F^- to I^- . However, it is consistent with the ionization potentials of Li_3Cl and Li_3Br clusters. Followed by this, we want to know if Li_3I cluster is a much stronger halogen acceptor in halogen bonding than Li_3Cl and Li_3Br ones. It is found

Download English Version:

<https://daneshyari.com/en/article/5394206>

Download Persian Version:

<https://daneshyari.com/article/5394206>

[Daneshyari.com](https://daneshyari.com)