Design of a Novel Series of Hetero-Binuclear Superhalogen Anions MM′X₄⁻ (M = Li, Na; M′ = Be, Mg, Ca; X = Cl, Br)

Hui Yang¹, Hui-Min He², Ning Li¹*, Shang Jiang¹, Min-Jun Pang¹, Ying Li³ and Jian-Guo Zhao¹*  
¹Institute of Carbon Materials Science, Shanxi Datong University, Datong, China, ²Physics Department, Taiyuan Normal University, Taiyuan, China, ³Institute of Theoretical Chemistry, College of Chemistry, Jilin University, Changchun, China

A series of hetero-binuclear superatom motifs involving chloride/bromide ligands, that is, MM′X₄⁻ (M = Li, Na; M′ = Be, Mg, Ca; X = Cl, Br) anions, have been characterized by using many-body perturbation theory calculations. Large vertical electron detachment energies (VDEs, 5.470–6.799 eV) confirm the superhalogen identity of these anions. A larger VDE value can be obtained by introducing small M or large M′ central atoms and small halogen ligand atoms. Thus, one isomer of LiCaCl₄⁻ possesses the largest VDE value. Besides, when the extra electron is shared by all ligand atoms or three bridging ligand atoms, the isomers have relatively larger VDE values.

Keywords: superhalogen, chloride or bromine ligands, binuclear, vertical electron detachment energy, theoretical calculation

INTRODUCTION

Superhalogens are unusual molecules possessing higher electron affinity (EA) than those of any halogen atom (Gutsev and Boldyrev, 1981). They were first proposed by Gutsev and Boldyrev in 1981 and verified by a variety of theoretical chemical methods (Gutsev and Boldyrev, 1981). Meanwhile, a new class of highly stable anions (superhalogen anions) were also reported. Now, superhalogen anions have been proved to possess very large vertical electron detachment energies (VDEs) (Anusiewicz et al., 2003; Koirala et al., 2010; Yang et al., 2017; Li et al., 2019; Li et al., 2020; Zhao et al., 2020), even approaching 14 eV in certain systems (Freza and Skurski, 2010). Moreover, it is found that the superhalogen anions have much high stability, such as BF₄⁻, AlCl₄⁻, and AsF₆⁻, and other superhalogen anions have been confirmed to be stable in crystalline solids or gaseous molecules.

In 1981, Gutsev and Boldyrev proposed the representative formula MXₖ₊₁ for a class of superhalogens, in which M represents the central main group atom, K is the highest valence of M atom, and X is the halogen atom (Gutsev and Boldyrev, 1981). In 1999, the superhalogen anions MX₃⁻ (M = Li, Na; X = Cl, Br, and I) were reported by Wang et al., and their VDE values were experimentally measured for the first time and theoretically calculated applying the outer valence Green function (OVGF) method, which are consistent with each other well (Wang et al., 1999). Shortly afterward, the EA value of the BO₂ superhalogen (Zhai et al., 2007) and the VDE value of the MX₅⁻ (M = Be, Mg, Ca; X = Cl, Br) superhalogen anion (Elliott et al., 2005) were determined by the same experimental means. During subsequent studies on superhalogens and their corresponding anions, the central atom M of MXₖ₊₁ formula was no longer limited to the main group metal atoms...
(Anusiewicz et al., 2003; Elliott et al., 2005), and the transition metal atoms (Gutsev et al., 1999; Gutsev et al., 2001; Yang et al., 2003), coinage metal atoms (Feng et al., 2011; Lu et al., 2019), and nonmetal atoms (Arnold et al., 2002) could act as central atoms to construct superhalogens. In addition, the researchers found that increasing the number of central atoms benefits the dispersion of extra negative charges without increasing the repulsion between ligands. Therefore, some binuclear/multinuclear superhalogen anions have been proposed by experimental synthesis or theoretical prediction (Anusiewicz and Skurski, 2007; Anusiewicz, 2008; Czapla, 2017; Yang et al., 2017; Yang et al., 2018).

Besides, it is realized that halogen atoms are not the necessary units for the construction of superhalogens. In recent years, the ligands of superhalogens have been extended from halogen atoms to oxygen atoms (Gutsev et al., 1999; Zhai et al., 2007), acid functional groups (Anusiewicz, 2009b), various monovalent groups (Smucznyska and Skurski, 2009), nine-electron ligands (Sikorska et al., 2011), hydroxyl groups (Anusiewicz and Skurski, 2011), and electrophilic substituents (Anusiewicz, 2009a). In addition, Mg@Nk-type superhalogens with inclusion complexes of metal (Zhai et al., 2004) and carborane cage superhalogens (Pathak et al., 2011) have also been proposed. 

Recently, a new class of cluster was designed in which the central atom was modified by superhalogen ligands replacing the halogen ligands; thus, they are termed “hyperhalogen” (Willis et al., 2010). Subsequently, many hyperhalogens with various geometries of superhalogen ligands have been proposed (Paduani et al., 2011; Gutsev et al., 2012; Sun et al., 2015; Sun et al., 2016; Yang et al., 2021; Dong et al., 2022).

Superhalogens play an important role in chemistry given the strong oxidation capability. For example, they can be used as capable oxidants to oxidize substances that have relatively high ionization potentials (e.g., O₂ (Bartlett and Lohmann, 1962), noble gas atom (Bartlett, 1962), and (H₂O)₅ clusters (Marchaj et al., 2013)). They can also be used to synthesize and prepare noble gas compounds (Saha et al., 2018; Chang et al., 2019), supersalts (Giri et al., 2014a), ion battery electrolytes (Giri et al., 2014b), ionic liquids (Srivastava et al., 2021), liquid crystalline molecules (Srivastava, 2021), solar cells (Kim et al., 2022), and so on. Therefore, exploring various new species classified as superhalogens and studying their structures, stability, and properties has become a significant and attractive research topic in recent years.

To the best of our knowledge, most hitherto proposed superhalogens are mono- or homo-nuclear. The hetero-nuclear superhalogens involving different central atoms, however, have received very little attention. The investigation on the influence of different ligands on hetero-nuclear superhalogen properties, however, has not been reported yet. In this research, we aim to design a new class of superhalogen anions with two different central atoms using chloride or bromine atoms as ligands. Consequently, the MM’X₄⁻ (M = Li, Na; M’ = Be, Mg, Ca; X = Cl, Br) anions have been proposed and systematically investigated. The considerable VDE values of these anions confirm their superhalogen identity. The geometric features and relative stability of these anions were analyzed. Meanwhile, the correlations between their VDEs and structural features, ligand and central atoms, and extra electron distribution are also revealed. The present investigation predicts a new member of superhalogens and conduces to the development of new strong oxidizing agents.

**COMPUTATIONAL DETAILS**

Initially, the structures of the MM’X₄⁻ (M = Li, Na; M’ = Be, Mg, Ca; X = Cl, Br) anions were built by considering all the possible connection between M, M’, and X atoms. Then, all the constructed structures of anions were optimized using the Møller–Plesset perturbation method (MP2) (Møller and Plesset, 1934) together with the 6–311+G (3df) basis set (Yang et al., 2017; Yang et al., 2018). Meanwhile, frequency analysis was performed at the same computational level to ensure that the obtained structures are stable on potential energy surfaces without imaginary frequency. Natural bond orbital (NBO) (Reed et al., 1985) and single-point energy calculations were carried out at the same level.

The vertical electron detachment energies (VDEs) of the MM’X₄⁻ anions were calculated applying the outer valence Green function (OVGF) approximation (Cederbaum, 1975) with the 6–311+G (3df) basis set. The smallest pole strength (PS) in our study is 0.90, justifying the validity of the OVGF method (Zakrzewski et al., 1996).

The above-mentioned calculations were performed using the GAUSSIAN 16 program package (Frisch et al., 2016). The plots of molecular structures and orbitals were generated with the GaussView program (Dennington et al., 2016).

**RESULTS AND DISCUSSION**

**Geometrical Structures and Relative Stability**

The optimized geometries of MM’X₄⁻ anions are depicted schematically in **Figure 1**. The relative energies, the lowest vibrational frequencies, bond lengths, and angles are listed in **Table 1, 2**. As shown in the figure, each MM’X₄⁻ anion has two types of structures, that is, central atoms M and M’ are connected...


**TABLE 1** | Relative energies $E_{rel}$ (kcal/mol), the lowest vibrational frequencies $\nu$ (cm⁻¹), total NBO charges on the MCI subunit $|e|$, vertical detachment energies VDE (eV), bond lengths (Å), and select bond angles (degree) of the MM$^+$Cl⁻ anions.

| Isomer          | Symmetry | $E_{rel}$ | $\nu$ | $|e|$ | VDE | Cl-M | Cl-M | $\angle$Cl-M | $\angle$Cl-M | LiBeCl₄ -2 | C₂ᵥ  | 0.00 | 24 | -0.073 | 6.240 | 2.146 | 2.427 | 1.940 | 1.888 | 123.6 |
|-----------------|----------|-----------|-------|------|-----|------|------|--------------|--------------| LiBeCl₄ -3 | C₂ᵥ  | 9.09 | 127 | 0.049 | 6.275 | 2.292 | 2.197 | 1.923 | 117.6 |
| LiMgCl₄ -3      | C₂ᵥ      | 0.00 | 86 | -0.017 | 6.700 | 2.325 | 2.425 | 2.266 | 124.5 |
| LiMgCl₄ -2      | C₂ᵥ      | 4.48 | 21 | -0.075 | 6.180 | 2.150 | 2.459 | 2.299 | 129.3 |
| LiCaBr₄ -3      | C₂ᵥ      | 0.00 | 65 | -0.066 | 6.799 | 2.327 | 2.691 | 2.559 | 129.7 |
| LiCaBr₄ -2      | C₂ᵥ      | 10.92 | 20 | -0.080 | 6.042 | 2.156 | 2.447 | 2.566 | 134.4 |
| NaBeCl₄ -2      | C₂ᵥ      | 0.00 | 22 | -0.039 | 6.116 | 2.503 | 2.772 | 1.940 | 1.891 | 122.4 |
| NaBeCl₄ -3      | C₂ᵥ      | 10.36 | 113 | 0.088 | 5.946 | 2.620 | 2.103 | 1.940 | 115.0 |
| NaMgCl₄ -2      | C₂ᵥ      | 0.00 | 79 | 0.025 | 6.573 | 2.657 | 2.420 | 2.277 | 121.0 |
| NaMgCl₄ -3      | C₂ᵥ      | 4.42 | 21 | -0.038 | 6.081 | 2.504 | 2.805 | 2.291 | 2.242 | 127.4 |
| NaCaBr₄ -3      | C₂ᵥ      | 0.00 | 63 | 0.003 | 6.786 | 2.664 | 2.688 | 2.565 | 125.8 |
| NaCaBr₄ -2      | C₂ᵥ      | 11.12 | 19 | -0.040 | 5.998 | 2.509 | 2.804 | 2.570 | 2.534 | 131.8 |

*Cl-M for isomer MM$^+$Cl⁻ -2 and MCI₂ for MM$^+$Cl⁻ -3.

Italian values represents that the number of bridging X atoms.

**TABLE 2** | Relative energies $E_{rel}$ (kcal/mol), the lowest vibrational frequencies $\nu$ (cm⁻¹), total NBO charges on MBr subunit $|e|$, vertical detachment energies VDE (eV), bond lengths (Å), and select bond angles (degree) of the MM$^+$Br⁻ anions.

| Isomer          | Symmetry | $E_{rel}$ | $\nu$ | $|e|$ | VDE | Br-M | Br-M | $\angle$Br-M | $\angle$Br-M | LiBeCl₄ -2 | C₂ᵥ  | 0.00 | 14 | -0.087 | 5.792 | 2.312 | 2.584 | 2.103 | 2.051 | 123.2 |
|-----------------|----------|-----------|-------|------|-----|------|------|--------------|--------------| LiBeCl₄ -3 | C₂ᵥ  | 7.93 | 77 | 0.060 | 5.795 | 2.452 | 2.275 | 2.089 | 116.8 |
| LiMgBr₄ -3      | C₂ᵥ      | 0.00 | 53 | -0.020 | 6.174 | 2.491 | 2.502 | 2.423 | 123.5 |
| LiMgBr₄ -2      | C₂ᵥ      | 3.88 | 13 | -0.089 | 5.750 | 2.313 | 2.616 | 2.448 | 2.398 | 128.5 |
| LiCaBr₄ -3      | C₂ᵥ      | 0.00 | 42 | -0.020 | 6.296 | 2.492 | 2.852 | 2.713 | 128.5 |
| LiCaBr₄ -2      | C₂ᵥ      | 10.36 | 12 | -0.100 | 5.660 | 2.317 | 2.609 | 2.721 | 2.690 | 133.1 |
| NaBeCl₄ -2      | C₂ᵥ      | 0.00 | 13 | -0.046 | 5.730 | 2.658 | 2.930 | 2.103 | 2.054 | 122.1 |
| NaBeCl₄ -3      | C₂ᵥ      | 9.50 | 73 | 0.106 | 5.470 | 2.777 | 2.272 | 2.105 | 114.4 |
| NaMgBr₄ -3      | C₂ᵥ      | 0.00 | 50 | 0.032 | 6.080 | 2.817 | 2.587 | 2.434 | 120.1 |
| NaMgBr₄ -2      | C₂ᵥ      | 3.77 | 13 | -0.048 | 5.707 | 2.658 | 2.962 | 2.449 | 2.399 | 126.5 |
| NaCaBr₄ -3      | C₂ᵥ      | 0.00 | 40 | 0.001 | 6.322 | 2.982 | 2.850 | 2.718 | 124.8 |
| NaCaBr₄ -2      | C₂ᵥ      | 10.27 | 12 | -0.051 | 5.640 | 2.662 | 2.961 | 2.726 | 2.687 | 130.8 |

*BnM for isomer MM$^+$Br⁻ -2 and MBr₂ for MM$^+$Br⁻ -3.

Italian values represents that the number of bridging X atoms.

by two or three bridging X atoms. Notably, these two structures are also presented in the superhalogen anions with F ligands (Yang et al., 2017). Unlike MMF₂⁻ anions (Yang et al., 2017), the structures involving one bridging ligand atom are not stable, which turn to the above two types of structures after optimization. In terms of the number of bridging X atoms, the isomers of MMX₂⁻ are termed MMX₂⁻ -2 and MMX₂⁻ -3, respectively. For the sake of convenience, the terminal X atoms that bind with M and M' atoms are named X₁ and X₂, respectively, and the bridging X atom that connects M and M' atoms is named X₀.

It can be seen in Figure 1 that the MM$^+$Cl⁻ -2 and MM$^+$Cl⁻ -3 isomers possess planar and three-dimensional structures with C₂ᵥ and C₃ᵥ symmetries, respectively. From the data in Table 1, it is found that for MM$^+$Cl⁻ -2 and MM$^+$Cl⁻ -3 isomers, when M' atom varies from Be to Ca, the Cl-M and M-Cl bond lengths change very little, while the $\angle$Cl-MCl angle showed a tendency of increasing; for example, the orders of $\angle$Cl-MCl angle in NaMCl₄ -2 and NaMCl₄ -3 are 122.4° < 127.4° < 130.8° < 115.0° < 121.0° < 125.8° with varying M' atoms, respectively. Thus, the MM$^+$Cl⁻ -2 and MM$^+$Cl⁻ -3 structures tend to elongate along the M-M' axis with the increasing radius of M' atoms. Besides, the Cl-M bond is shorter than the M-Cl₀ bond in MM$^+$Cl⁺ -2 isomers. For instance, the Cl₀-Na bonds are about 2.80 Å, while the Na-Cl₀ bonds are 2.50 Å in NaMCl₄ -2 isomers. On the other hand, when the M atom goes from Li to Na, the Cl₀-M' and M'-Cl₀' bond lengths also show minor difference in MM$^+$Cl⁺ anions, but the $\angle$Cl₀M'Cl₀' angles show a decrease, e.g., the $\angle$Cl₀M'Cl₀' angles of LiBeCl₄ -2 and LiBeCl₄ -3 are 1.4° and 1.6° larger than that of the corresponding NaBeCl₄ -2 and NaBeCl₄ -3, respectively. In addition, the total NBO charges of Cl₀M subunits are in the range of -0.080 to -0.088|e|, which are close to zero (see Table 1); consequently, the total NBO charges of M'Cl₀ subunits approximate -1. In this sense, the MM$^+$Cl⁻ structures can be regarded as a combination of an MCl molecule and a superhalogen anion MCl₃⁺.

MM$^+$Br⁻ series show similar structural characteristics with MM$^+$Cl⁻ anions. From the data in Tables 1, 2, it is noticed that $\angle$X₀MX₂ -2 angles of MM$^+$Cl⁻ anions are always larger than that of the corresponding MM$^+$Br⁻ anions; for example, the $\angle$Cl₀M'Cl₀' angles of NaMCl₄ -3 and NaMCl₄ -2 are 121.0° and 127.4°, respectively, which are larger than the
TABLE 3 | The largest vertical detachment energies VDE (eV) of superhalogen anions MM’X₄⁻ (M = Li, Na; M’ = Be, Mg, Ca, X = Cl, Br) and M’X₃⁻ (M’ = Be, Mg, Ca, X = Cl, Br).

| anion | VDE | anion | VDE | anion | VDE |
|-------|-----|-------|-----|-------|-----|
| LiBeCl₄⁻ | 6.275 | NaBeCl₄⁻ | 6.116 | BeCl₂⁻ | 6.184 |
| LiMgCl₄⁻ | 6.700 | NaMgCl₂⁻ | 6.573 | MgCl₂⁻ | 6.685 |
| LiCaCl₄⁻ | 6.799 | NaCaCl₂⁻ | 6.786 | CaCl₂⁻ | 6.741 |
| LiBeBr₄⁻ | 5.795 | NaBeBr₂⁻ | 5.730 | BeBr₂⁻ | 5.643 |
| LiMgBr₄⁻ | 6.174 | NaMgBr₂⁻ | 6.080 | MgBr₂⁻ | 6.140 |
| LiCaBr₄⁻ | 6.296 | NaCaBr₂⁻ | 6.322 | CaBr₂⁻ | 6.243 |

zBr₂M’Br₃⁻ angles of NaMgBr₄⁻-3 (120.1°) and NaMgBr₄⁻-2 (126.5°), respectively.

It is reported that the isomers could exhibit higher stability with more bridging ligands in the previous studies on the dual-nuclear superhalogen anions with F ligands, such as homonuclear MgF₄⁻ (Anusiewicz and Skurski, 2007) and heteronuclear ones NaMF₃⁻ (M’ = Mg, Ca) (Yang et al., 2017). MM’X₄⁻ anions also follow this rule except the MBeX₄⁻ series. However, MBeX₄⁻ anions show a reverse trend; that is, structure 2 is more stable than structure 3. In other words, Be atoms are more likely to bond with three ligands than four ligands. This may be due to the smaller atomic radius of the central Be atom, the three bridging ligands are more crowded in structure 3 of MBeX₄⁻ anions than in structure 3 of MMgX₄⁻ and MCaX₄⁻. This can be confirmed by the shorter Clₖ-Clₖ and Brₖ-Brₖ distance in structures 3 of MBeX₄⁻ than MMgX₄⁻ and MCaX₄⁻; for example, the Clₖ-Clₖ and Brₖ-Brₖ distances in LiBeCl₄⁻-3 and LiBeBr₄⁻-3 are 0.226 Å and 0.229 Å shorter than that in LiMgCl₄⁻-3 and LiMgBr₄⁻-3, respectively. Thereby, MBeX₄⁻-3 is less stable than the MBeX₄⁻-2.

Vertical Electron Detachment Energies (VDEs)
The VDE values of MM’X₄⁻ anions are gathered in Tables 1, 2. As one can notice, all anions have considerable VDE values (5.470–6.799 eV) exceeding the electron affinity of the Cl atom; thus undoubtedly, these anions can be identified as superhalogen anions. In addition, it is found that the factors affecting the VDE values of these studied anions were as follows:

1. When the M atom varies from the Li atom to Na atom, the VDE values of the studied anions show a tendency of decreasing in similar structures. For example, the VDE values of the isomers LiMgCl₄⁻-3 and LiMgCl₄⁻-2 are greater than those of NaMgCl₄⁻-3 and NaMgCl₄⁻-2, respectively. However, the only one exception is the VDE values of isomers LiCaBr₄⁻-3 and NaCaBr₄⁻-3. This is probably due to the different extra electron distribution of these two isomers, which will be discussed in the following. Therefore, the hetero-binuclear superhalogen anions with large VDE values could be constructed by introducing small alkali metal atoms into the system. It is worth noting that the same trend was found for the other hetero-binuclear anions with the F atom, cyanide, and isocyanide as ligands (Yang et al., 2017; Yang et al., 2018).

2. The largest VDE values for each MM’X₄⁻ anions are presented in Table 3. From the table, the VDE values increase in the order: MBeX₄⁻→MMgX₄⁻→MCaX₄⁻. Hence, the hetero-binuclear superhalogen anion MM’X₄⁻ could possess a larger VDE value by involving larger alkaline earth metal atoms. Note that it also holds true for...
the superhalogen anions with other ligands (Yang et al., 2017; Yang et al., 2018).

As pointed out earlier, the MM$X_4^-$ anions can be regarded as MX ($M'X_3$); thus, the comparison between MM$X_4^-$ anions and their corresponding mononuclear superhalogen anions M$X_4^-$ is also necessary. For this reason, the VDE values of M$X_4^-$ ($X = \mathrm{Cl}, \mathrm{Br}$) anions were also calculated at the same level and are listed in Table 3 as well. From the table, the VDE values of mononuclear anions M$X_4^-$ also increase from $\mathrm{BeX}_3^-$ to $\mathrm{CaX}_3^-$.

Besides, the mononuclear anions M$X_4^-$ possess lower VDE values than their corresponding hetero-nuclear anions MM$X_4^-$ (except for NaBeCl$_4$ and NaMgX$_4$ series). So again, the superhalogen anions could gain larger VDE values by increasing the number of central atoms.

(3) The relationship between the VDE values and the ligand atoms is plotted in Figure 2. The six curves show similar varying trends, that is, the largest VDE values of each MM$X_4^-$ ($X = \mathrm{F}$ (Yang et al., 2017)), Cl, Br) species show a decreasing order: MM$\mathrm{F}_4^-$ > MM$\mathrm{Cl}_4^-$ > MM$\mathrm{Br}_4^-$.

This may be attributed to the different electronegativity of $X$ atoms. To be specific, the $F$ atom possesses larger electronegativity and stronger electron-accepting ability than Cl and Br atoms, which is more beneficial for the anions to bind with the extra electron. Thereby, the larger electronegativity the ligand atom possesses, the higher VDE value the MM$X_4^-$ anion has.

(4) For the two isomers of Li$M'X_4^-$, the VDE values of Li$M'X_4^-$-3 are always larger than those of Li$M'X_4^-$-2. This is probably due to the fact that the extra electron distribution in two isomers is different. To analyze this clearly, the highest occupied molecular orbitals (HOMOs) of some representative MM$X_4^-$ isomers are depicted in Figure 3. As can be seen from the figure, the extra electron is confined to a single $X_i$ atom in LiBeCl$_4$-2, while localized on the three bridging $X_b$ atoms in LiBeCl$_4$-3, which is a benefit for the extra negative charge dispersion, and thus, LiBeCl$_4$-3 possesses a larger VDE value. For NaBeX$_4^-$ anions, the extra electrons of two isomers are all distributed on the terminal $X$ atom. Interestingly, the isomer NaBeX$_4^-$-2 in which the extra electron goes on $X_i$ atom has a higher VDE value than isomer NaBeX$_4^-$-3, which goes on the $X_b$ atom (see Figure 3). As to NaMgX$_4^-$ and NaCaX$_4^-$ species, the situation is similar to that of the Li$M'X_4^-$ anions. However, unlike Li$M'X_4^-$-3 and NaMgX$_4^-$-3, the extra electron is shared by all $X$ ligand atoms instead of three $X_b$ ligands in NaCaX$_4^-$-3, which leads to the extra negative charge being more evenly distributed (see Figure 3), and, hence, a relatively larger VDE values for these isomers. This may also explain why NaCaBr$_4^-$-3 exhibits larger VDE values than LiCaBr$_4^-$-3. Therefore, the extra electron distribution is an important factor affecting the VDE values of the hetero-binuclear superhalogen anions.

**CONCLUSION**

Our systematic investigation of the MM$X_4^-$ ($M = \mathrm{Li}, \mathrm{Na}; M' = \mathrm{Be}, \mathrm{Mg}, \mathrm{Ca}; X = \mathrm{Cl}, \mathrm{Br}$) species has theoretically proposed a series of hetero-binuclear superhalogen anions. The results show that these heteronuclear superhalogen anions could gain larger VDE values by involving a smaller alkali metal atom $M$, a larger alkaline earth metal atom $M'$, and a higher electronegative ligand atom $X$.

Therefore, of all the anions studied, an isomer of LiCaCl$_4^-$ anions possesses the largest VDE value (6.799 eV).

Moreover, the extra electron distribution is a very influential factor in the VDE values of structural isomers. For the NaBeX$_4^-$ anions, the isomers have larger VDE values when the extra electron is distributed on the terminal $X$ ligand atom instead of the $X_i$ ligand atom. For the other anions, the isomers possess larger VDE values when the extra electron is shared by all ligand atoms or three bridging ligand atoms.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article supplementary material; further inquiries can be directed to the corresponding authors.

**AUTHOR CONTRIBUTIONS**

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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**REFERENCES**

Anusiewicz, I., and Skurski, P. (2007). Unusual Structures of Mg$_2$Cl$_5$: Superhalogen Anion. Chem. Phys. Lett. 440, 41–44. doi:10.1016/j.cplett.2007.04.016

Anusiewicz, I., Sobczyk, M., Dąbrowska, L., and Skurski, P. (2003). An Ab Initio Study on MgX$_3^-$ and CaX$_3^-$ Superhalogen Anions (X=F, Cl, Br). Chem. Phys. 291, 171–180. doi:10.1016/s0301-0104(03)00208-8

Anusiewicz, I. (2008). Mg$_2$Cl$_5$ - and Mg$_3$Cl$_7$ - Superhalogen Anions. Aust. J. Chem. 61, 712–717. doi:10.1071/CH08212

Anusiewicz, I. (2009a). Electrophilic Substituents as Ligands in Superhalogen Anions. J. Phys. Chem. A 113, 6511–6516. doi:10.1021/jp901910q

Anusiewicz, I. (2009b). Superhalogen Anions Utilizing Acidic Functional Groups as Ligands. J. Phys. Chem. A 113, 11429–11434. doi:10.1021/jp907246w

Arnold, S. T., Miller, T. M., and Viggiano, A. A. (2002). A Theoretical Study of High Electron Affinity Sulfur Oxyfluorides: SOF$_3$, SO$_2$F$_3$, and SOF$_5$. Anusiewicz, I., Sobczyk, M., and Dąbrowska, L. (2004). Theoretical Study of Mg$_2$Cl$_5$ Superhalogen Anion. J. Chem. Phys. Lett. 440, 41–44. doi:10.1016/j.cplett.2007.04.016

Anusiewicz, I., and Skurski, P. (2007). Unusual Structures of Mg$_2$Cl$_5$: Superhalogen Anion. Chem. Phys. Lett. 440, 41–44. doi:10.1016/j.cplett.2007.04.016
Yang et al. Hetero-Binuclear Superhalogen Anions

Bartlett, N., and Lohmann, D. H. (1962). Fluorides of the Noble Metals. Part II. Dioxogenyl Hexafluoroplutinate(V), O2 + [PtF6]–. J. Chem. Soc. 0, 5253–5261. doi:10.1039/j96200005253

Bartlett, N. (1962). Xenon Hexafluoroplutinate (V) XeF6. Chem. Soc. 218, 207–215. doi:10.1039/s1387-3806(02)00713-3

Cederbaum, L. S. (1975). One-body Green’s Function for Atoms and Molecules: Theory and Application. J. Phys. B 8, 290–303. doi:10.1088/0022-3700/8/2/018

Chang, X.-T., Li, Y., Liu, J.-Y., Ma, H.-D., and Wu, D. (2019). Noble Gas Insertion Compounds of Hydrogenated and Lithiated Hyperhalogenes. Phys. Chem. Chem. Phys. 21, 20156–20165. doi:10.1039/c8cp01284b

Czapla, M. (2017). Dinuclear Superhalogen Anions Containing Two Different Central Atoms. J. Fluor. Chem. 199, 97–102. doi:10.1016/j.jfluchem.2017.05.003

Dennington, R., Keith, T., and Millam, J. (2016). GaussView version 6. Shawnee Mission, KS: Semichem Inc.

Dong, X.-X., Zhao, Y., Li, J., Wang, H., Bu, Y., and Cheng, S.-B. (2022). Dual

Gutsev, G. L., Weatherford, C. A., Johnson, L. E., and Jena, P. (2012). Structure and

Elliott, B. M., Koyle, E., Boldyrev, A. I., Wang, X.-B., and Wang, L.-S. (2005). MX3–

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A.,

Giri, S., Behera, S., and Jena, P. (2014a). Superalkalis and Superhalogens as Building Blocks of Supersalts. J. Phys. Chem. A 118, 638–645. doi:10.1021/jp4115095

Giri, S., Behera, S., and Jena, P. (2014b). Superhalogens as Building Blocks of Halogen-free Electrolytes in Lithium-Ion Batteries. Angew. Chem. Int. Ed. 53, 13916–13919. doi:10.1002/anie.201408648

Gutsev, G. L., and Boldyrev, A. I. (1981). DVM-x

Padhik, B., Samanta, D., Ahuja, R., and Jena, P. (2011). Borane Derivatives: A New Class of Super- and Hyperhalogens. ChemPhysChem 12, 2423–2428. doi:10.1002/cphc.201100320

Reed, A. E., Weinstock, R. B., and Weinhold, F. (1985). Natural Population Analysis. J. Chem. Phys. 83, 735–746. doi:10.1063/1.449486

Saha, R., Mandal, B., and Chattaraj, P. K. (2018). HNgBeF3 (Ng = Ar-Rn): Superhalogen-Supported Noble Gas Insertion Compounds. Int. J. Quantum Chem. 118, e25499. doi:10.1002/qua.25499

Sikorska, C., Freza, S., Skurski, P., and Anusiewicz, I. (2011). Theoretical Search for Alternative Nine-Electron Ligands Suitable for Superhalogen Anions. J. Phys. Chem. A 115, 2077–2085. doi:10.1021/jp200393w

Smuczyńska, S., and Skurski, P. (2009). Halogenoids as Ligands in Superhalogen Anions. Inorg. Chem. 48, 10231–10238. doi:10.1021/ic901253r

Srivastava, A. K., Kumar, A., and Misra, N. (2021). Superhalogens as Building Blocks of Ionic Liquids. J. Phys. Chem. A 125, 2146–2153. doi:10.1021/acs.jpca.1c00599

Srivastava, A. K. (2021). Prediction of Novel Liquid Crystalline Molecular-Based on BO2 Superhalogen. J. Mol. Liq. 344, 117968. doi:10.1016/j.molliq.2021.117968

Sun, W.-M., Hou, D., Wu, D., Li, X.-H., Li, Y., Chen, J.-H., et al. (2015). Theoretical Characterization of a Series of N5-Based Aromatic Hyperhalogen Anions. Dalton Trans. 44, 19901–19908. doi:10.1039/c5dt03575a

Sun, W.-M., Li, X.-H., Li, Y., Wu, D., Li, C.-Y., Chen, J.-H., et al. (2016). Can Fluorinated Molecular Cages Be Utilized as Building Blocks of Hyperhalogens? ChemPhysChem 17, 1468–1474. doi:10.1002/cphc.201600052

Świernacz, I., and Anusiewicz, I. (2011). Neutral and Anionic Superhalogen Hydrides. Chem. Phys. 383, 93–100. doi:10.1016/j.chemphys.2011.04.018

Wang, X.-B., Ding, C.-F., Wang, L.-S., Boldyrev, A. I., and Simons, J. (1999). First Experimental Photoelectron Spectra of Superhalogens and Their Theoretical Interpretations. J. Chem. Phys. 110, 4763–4771. doi:10.1063/1.478386

Willis, M., Götz, M., Kandalam, A. K., Ganteor, G. F., and Jena, P. (2010). Hyperhalogens: Discovery of a New Class of Highly Electronegative Species. Angew. Chem. Int. Ed. 49, 8966–8970. doi:10.1002/anie.201002212

Yang, X., Wang, X.-B., Wang, L.-S., Niu, S., and Ichiye, T. (2003). On the Electronic Structures of Gaseous Transition Metal Halide Complexes, FeX4– and MX3– (M=Fe, Mn, Co, Ni, X=Cl, Br). Using Photoelectron Spectroscopy and Density Functional Calculations. J. Chem. Phys. 119, 8311–8320. doi:10.1063/1.1610431

Yang, H., Li, Y., He, H.-M., Tong, J., Wu, D., and Li, Z.-R. (2017). Superhalogen Properties of Hydrogenated Anions MM′F4– and MM′F5– (M=Li, Na, M′=Be, Mg, Ca; M′=B, Al, Ga). Chem. Phys. Lett. 684, 273–278. doi:10.1016/j.cplett.2017.07.010

Yang, H., Li, Y., He, H.-M., Yu, D., Wu, D., and Li, Z.-R. (2018). Hetero-binuclear Superhalogen Anions with Cyandene And/or Icosaneide as Ligands. Chem. Phys. Lett. 713, 203–209. doi:10.1016/j.cplett.2018.10.039

Yang, H., Li, Y., Zhao, J.-G., Xing, B.-Y., He, H.-M., Jiang, S., et al. (2021). On Structure and Hyperhalogen Properties of Hetero-Binuclear Superatom MM′(BO2)− (M = Na, Mg; M′ = Mg, Al; N = 4–6). Polyhedron 209, 115456. doi:10.1016/j.poly.2021.115456

Zakrzewski, V. G., Dolgonosicheva, O., and Ortiz, J. V. (1996). Ionization Energies of Anthracene, Phenanthrene, and Naphtacene. J. Chem. Phys. 105, 8748–8753. doi:10.1063/1.472654
Zhai, H.-J., Li, J., and Wang, L.-S. (2004). Icosahedral Gold Cage Clusters: M@Au12−(M = V, Nb, and Ta). *J. Chem. Phys.* 121, 8369–8374. doi:10.1063/1.1799574
Zhai, H.-J., Wang, L.-M., Li, S.-D., and Wang, L.-S. (2007). Vibrationally Resolved Photoelectron Spectroscopy of BO− and BO2−: A Joint Experimental and Theoretical Study. *J. Phys. Chem. A* 111, 1030–1035. doi:10.1021/jp0666939
Zhao, Y., Wang, J., Huang, H.-C., Li, J., Dong, X.-X., Chen, J., et al. (2020). Tuning the Electronic Properties and Performance of Low-Temperature CO Oxidation of the Gold Cluster by Oriented External Electronic Field. *J. Phys. Chem. Lett.* 11, 1093–1099. doi:10.1021/acs.jpclett.9b03794

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