



Design of a Novel Series of Hetero-Binuclear Superhalogen Anions $MM'X_4^-$ ($M = \text{Li, Na}$; $M' = \text{Be, Mg, Ca}$; $X = \text{Cl, Br}$)

Hui Yang¹, Hui-Min He², Ning Li^{1*}, Shang Jiang¹, Min-Jun Pang¹, Ying Li³ and Jian-Guo Zhao^{1*}

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, $MM'X_4^-$ ($M = \text{Li, Na}$; $M' = \text{Be, Mg, Ca}$; $X = \text{Cl, Br}$) 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 LiCaCl_4^- 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.

OPEN ACCESS

Edited by:

Iwona Anusiewicz,
University of Gdansk, Poland

Reviewed by:

Jakub Brzeski,
University of Pittsburgh, United States
Shi-Bo Cheng,
Shandong University, China

*Correspondence:

Ning Li
lin224@nenu.edu.cn
Jian-Guo Zhao
jgzhaooshi@163.com

Specialty section:

This article was submitted to
Physical Chemistry and Chemical
Physics,
a section of the journal
Frontiers in Chemistry

Received: 05 May 2022

Accepted: 07 June 2022

Published: 01 July 2022

Citation:

Yang H, He H-M, Li N, Jiang S,
Pang M-J, Li Y and Zhao J-G (2022)
Design of a Novel Series of Hetero-
Binuclear Superhalogen Anions
 $MM'X_4^-$ ($M = \text{Li, Na}$; $M' = \text{Be, Mg, Ca}$;
 $X = \text{Cl, Br}$).
Front. Chem. 10:936936.
doi: 10.3389/fchem.2022.936936

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 BF_4^- , AlCl_4^- , and AsF_6^- , and other superhalogen anions have been confirmed to be stable in crystalline solids or gaseous molecules.

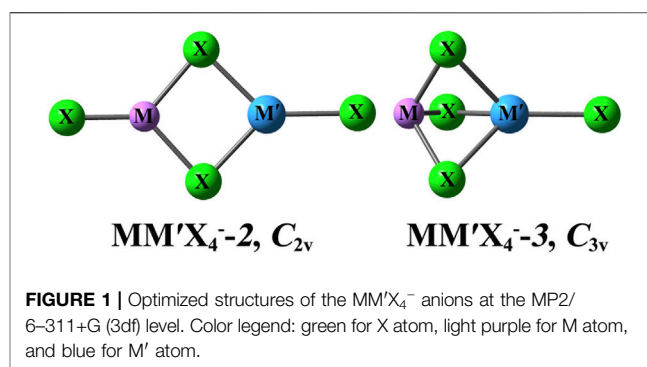
In 1981, Gutsev and Boldyrev proposed the representative formula MX_{k+1} for a class of superhalogens, in which M represents the central main group atom, K is the highest valence of M atom, and X is the halogen atom (Gutsev and Boldyrev, 1981). In 1999, the superhalogen anions MX_2^- ($M = \text{Li, Na}$; $X = \text{Cl, Br, and I}$) 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 BO_2 superhalogen (Zhai et al., 2007) and the VDE value of the MX_3^- ($M = \text{Be, Mg, Ca}$; $X = \text{Cl, Br}$) 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 MX_{k+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; Czaplá, 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 (Smuczynska and Skurski, 2009), nine-electron ligands (Sikorska et al., 2011), hydroxyl groups (Świercz and Anusiewicz, 2011), and electrophilic substituents (Anusiewicz, 2009a). In addition, $M@Nk$ -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. These clusters have higher EAs than their superhalogen 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., O_2 (Bartlett and Lohmann, 1962), noble gas atom (Bartlett, 1962), and $(H_2O)_n$ 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 $MM'X_4^-$ ($M = Li, Na; M' = Be, Mg, Ca; X = Cl, Br$) 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 $MM'X_4^-$ ($M = Li, Na; M' = Be, Mg, Ca; X = Cl, Br$) 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 $MM'X_4^-$ 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 $MM'X_4^-$ anions are depicted schematically in **Figure 1**. The relative energies, the lowest vibrational frequencies, bond lengths, and angles are listed in **Tables 1, 2**. As shown in the figure, each $MM'X_4^-$ 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 ν (cm^{-1}), total NBO charges on the MCl subunit ($|e|$), vertical detachment energies VDE (eV), bond lengths (\AA), and select bond angles (degree) of the $\text{MM}'\text{Cl}_4^-$ ($M = \text{Li, Na}; M' = \text{Be, Mg, Ca}$) anions.

Isomer	Symmetry	E_{rel}	ν	Q^a	VDE	$\text{Cl}_t\text{-M}$	M-Cl_b	$\text{Cl}_b\text{-M}'$	$\text{M}'\text{-Cl}_t'$	$\angle\text{Cl}_b\text{M}'\text{Cl}_t'$
LiBeCl_4^- -2	C_{2v}	0.00	24	-0.073	6.240	2.146	2.427	1.940	1.888	123.6
LiBeCl_4^- -3	C_{3v}	9.09	127	0.049	6.275		2.292	2.197	1.923	117.6
LiMgCl_4^- -3	C_{3v}	0.00	86	-0.017	6.700		2.325	2.425	2.266	124.5
LiMgCl_4^- -2	C_{2v}	4.48	21	-0.075	6.180	2.150	2.459	2.289	2.242	129.3
LiCaCl_4^- -3	C_{3v}	0.00	65	-0.066	6.799		2.327	2.691	2.559	129.7
LiCaCl_4^- -2	C_{2v}	10.92	20	-0.080	6.042	2.156	2.447	2.566	2.536	134.4
NaBeCl_4^- -2	C_{2v}	0.00	22	-0.039	6.116	2.503	2.772	1.940	1.891	122.4
NaBeCl_4^- -3	C_{3v}	10.36	113	0.088	5.946		2.620	2.103	1.940	115.0
NaMgCl_4^- -3	C_{3v}	0.00	79	0.025	6.573		2.657	2.420	2.277	121.0
NaMgCl_4^- -2	C_{2v}	4.42	21	-0.038	6.081	2.504	2.805	2.291	2.242	127.4
NaCaCl_4^- -3	C_{3v}	0.00	63	0.003	6.786		2.664	2.688	2.565	125.8
NaCaCl_4^- -2	C_{2v}	11.12	19	-0.040	5.998	2.509	2.804	2.570	2.534	131.8

^a Cl_tM for isomer $\text{MM}'\text{Cl}_4^-$ -2 and MCl_b , for $\text{MM}'\text{Cl}_4^-$ -3.

Italics values represents that the number of bridging X atoms.

TABLE 2 | Relative energies E_{rel} (kcal/mol), the lowest vibrational frequencies ν (cm^{-1}), total NBO charges on MBr subunit ($|e|$), vertical detachment energies VDE (eV), bond lengths (\AA), and select bond angles (degree) of the $\text{MM}'\text{Br}_4^-$ ($M = \text{Li, Na}; M' = \text{Be, Mg, Ca}$) anions.

Isomer	Symmetry	E_{rel}	ν	Q^a	VDE	$\text{Br}_t\text{-M}$	M-Br_b	$\text{Br}_b\text{-M}'$	$\text{M}'\text{-br}_t'$	$\angle\text{Br}_b\text{M}'\text{Br}_t'$
LiBeBr_4^- -2	C_{2v}	0.00	14	-0.087	5.792	2.312	2.584	2.103	2.051	123.2
LiBeBr_4^- -3	C_{3v}	7.93	77	0.060	5.795		2.452	2.275	2.089	116.8
LiMgBr_4^- -3	C_{3v}	0.00	53	-0.020	6.174		2.491	2.592	2.423	123.5
LiMgBr_4^- -2	C_{2v}	3.88	13	-0.089	5.750	2.313	2.616	2.448	2.398	128.5
LiCaBr_4^- -3	C_{3v}	0.00	42	-0.002	6.296		2.492	2.852	2.713	128.5
LiCaBr_4^- -2	C_{2v}	10.36	12	-0.100	5.650	2.317	2.609	2.721	2.690	133.1
NaBeBr_4^- -2	C_{2v}	0.00	13	-0.046	5.730	2.658	2.930	2.103	2.054	122.1
NaBeBr_4^- -3	C_{3v}	9.50	73	0.106	5.470		2.777	2.272	2.105	114.4
NaMgBr_4^- -3	C_{3v}	0.00	50	0.032	6.080		2.817	2.587	2.434	120.1
NaMgBr_4^- -2	C_{2v}	3.77	13	-0.048	5.707	2.658	2.962	2.449	2.399	126.5
NaCaBr_4^- -3	C_{3v}	0.00	40	0.001	6.322		2.822	2.850	2.718	124.8
NaCaBr_4^- -2	C_{2v}	10.27	12	-0.051	5.640	2.662	2.961	2.726	2.687	130.8

^a Br_tM for isomer $\text{MM}'\text{Br}_4^-$ -2 and MBr_b , for $\text{MM}'\text{Br}_4^-$ -3.

Italics 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 $\text{MM}'\text{F}_4^-$ 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 $\text{MM}'\text{X}_4^-$ are termed $\text{MM}'\text{X}_4^-$ -2 and $\text{MM}'\text{X}_4^-$ -3, respectively. For the sake of convenience, the terminal X atoms that bind with M and M' atoms are named X_t and X_t' , respectively, and the bridging X atom that connects M and M' atoms is named X_b .

It can be seen in **Figure 1** that the $\text{MM}'\text{Cl}_4^-$ -2 and $\text{MM}'\text{Cl}_4^-$ -3 isomers possess planar and three-dimensional structures with C_{2v} and C_{3v} symmetries, respectively. From the data in **Table 1**, it is found that for $\text{MM}'\text{Cl}_4^-$ -2 and $\text{MM}'\text{Cl}_4^-$ -3 isomers, when M' atom varies from Be to Ca, the $\text{Cl}_t\text{-M}$ and M-Cl_b bond lengths change very little, while the $\angle\text{Cl}_b\text{M}'\text{Cl}_t'$ angle showed a tendency of increasing; for example, the orders of $\angle\text{Cl}_b\text{M}'\text{Cl}_t'$ angle in $\text{NaM}'\text{Cl}_4^-$ -2 and $\text{NaM}'\text{Cl}_4^-$ -3 are $122.4^\circ < 127.4^\circ < 131.8^\circ$ and $115.0^\circ < 121.0^\circ < 125.8^\circ$ with varying M' atoms, respectively. Thus, the $\text{MM}'\text{Cl}_4^-$ -2 and $\text{MM}'\text{Cl}_4^-$ -3 structures tend to elongate along the $\text{M-M}'$ axis

with the increasing radius of M' atoms. Besides, the $\text{Cl}_t\text{-M}$ bond is shorter than the M-Cl_b bond in $\text{MM}'\text{Cl}_4^-$ -2 isomers. For instance, the $\text{Cl}_t\text{-Na}$ bonds are about 2.80 \AA , while the Na-Cl_b bonds are 2.50 \AA in $\text{NaM}'\text{Cl}_4^-$ -2 isomers. On the other hand, when the M atom goes from Li to Na, the $\text{Cl}_b\text{-M}'$ and $\text{M}'\text{-Cl}_t'$ bond lengths also show minor difference in $\text{MM}'\text{Cl}_4^-$ anions, but the $\angle\text{Cl}_b\text{M}'\text{Cl}_t'$ angles show a decrease, e.g., the $\angle\text{Cl}_b\text{M}'\text{Cl}_t'$ angles of LiBeCl_4^- -2 and LiBeCl_4^- -3 are 1.4 and 1.6° larger than that of the corresponding NaBeCl_4^- -2 and NaBeCl_4^- -3, respectively. In addition, the total NBO charges of Cl_tM subunits are in the range of -0.080–0.088 $|e|$, which are close to zero (see **Table 1**); consequently, the total NBO charges of $M'\text{Cl}_3$ subunits approximate -1. In this sense, the $\text{MM}'\text{Cl}_4^-$ structures can be regarded as a combination of an MCl molecule and a superhalogen anion $M'\text{Cl}_3^-$.

$\text{MM}'\text{Br}_4^-$ series show similar structural characteristics with $\text{MM}'\text{Cl}_4^-$ anions. From the data in **Tables 1, 2**, it is noticed that $\angle\text{X}_b\text{M}'\text{X}_t'$ angles of $\text{MM}'\text{Cl}_4^-$ anions are always larger than that of the corresponding $\text{MM}'\text{Br}_4^-$ anions; for example, the $\angle\text{Cl}_b\text{M}'\text{Cl}_t'$ angles of NaMgCl_4^- -3 and NaMgCl_4^- -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 $MM'X_4^-$ ($M = \text{Li, Na; } M' = \text{Be, Mg, Ca, } X = \text{Cl, Br}$) and $M'X_3^-$ ($M' = \text{Be, Mg, Ca, } X = \text{Cl, Br}$).

anion	VDE	anion	VDE	anion	VDE
LiBeCl_4^-	6.275	NaBeCl_4^-	6.116	BeCl_3^-	6.184
LiMgCl_4^-	6.700	NaMgCl_4^-	6.573	MgCl_3^-	6.685
LiCaCl_4^-	6.799	NaCaCl_4^-	6.786	CaCl_3^-	6.741
LiBeBr_4^-	5.795	NaBeBr_4^-	5.730	BeBr_3^-	5.643
LiMgBr_4^-	6.174	NaMgBr_4^-	6.080	MgBr_3^-	6.140
LiCaBr_4^-	6.296	NaCaBr_4^-	6.322	CaBr_3^-	6.243

$\angle \text{Br}_b \text{M}' \text{Br}_t'$ angles of NaMgBr_4^- -3 (120.1°) and NaMgBr_4^- -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 Mg_2F_5^- (Anusiewicz and Skurski, 2007) and heteronuclear ones $\text{NaM}'\text{F}_4^-$ ($M' = \text{Mg, Ca}$) (Yang et al., 2017). $MM'X_4^-$ anions also follow this rule except the MBeX_4^- series. However, MBeX_4^- 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 MBeX_4^- anions than in structure 3 of $MMgX_4^-$ and $\text{MCA}X_4^-$. This can be confirmed by the shorter $\text{Cl}_b\text{-Cl}_b$ and $\text{Br}_b\text{-Br}_b$ distance in structures 3 of MBeX_4^- than $MMgX_4^-$ and $\text{MCA}X_4^-$; for example, the $\text{Cl}_b\text{-Cl}_b$ and $\text{Br}_b\text{-Br}_b$ distances in LiBeCl_4^- -3 and LiBeBr_4^- -3 are 0.226 Å and 0.229 Å shorter than that in LiMgCl_4^- -3 and LiMgBr_4^- -3, respectively. Thereby, MBeX_4^- -3 is less stable than the MBeX_4^- -2.

Vertical Electron Detachment Energies (VDEs)

The VDE values of $MM'X_4^-$ 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 LiMgCl_4^- -3 and LiMgCl_4^- -2 are greater than those of NaMgCl_4^- -3 and NaMgCl_4^- -2, respectively. However, the only one exception is the VDE values of isomers LiCaBr_4^- -3 and NaCaBr_4^- -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).

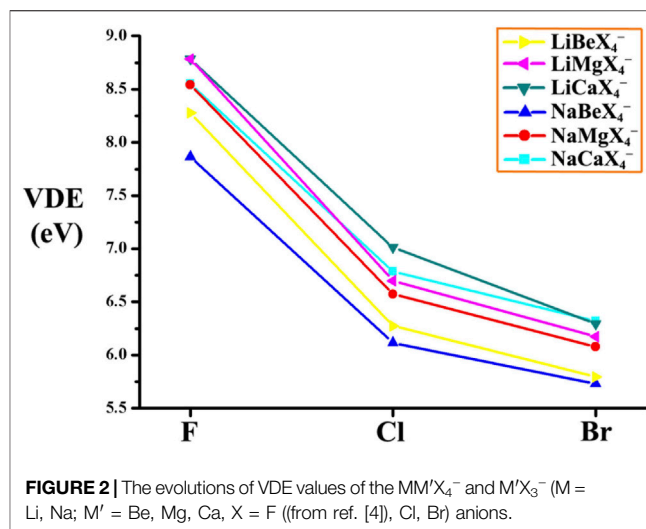


FIGURE 2 | The evolutions of VDE values of the $MM'X_4^-$ and $M'X_3^-$ ($M = \text{Li, Na; } M' = \text{Be, Mg, Ca, } X = \text{F}$ (from ref. [4]), Cl, Br) anions.

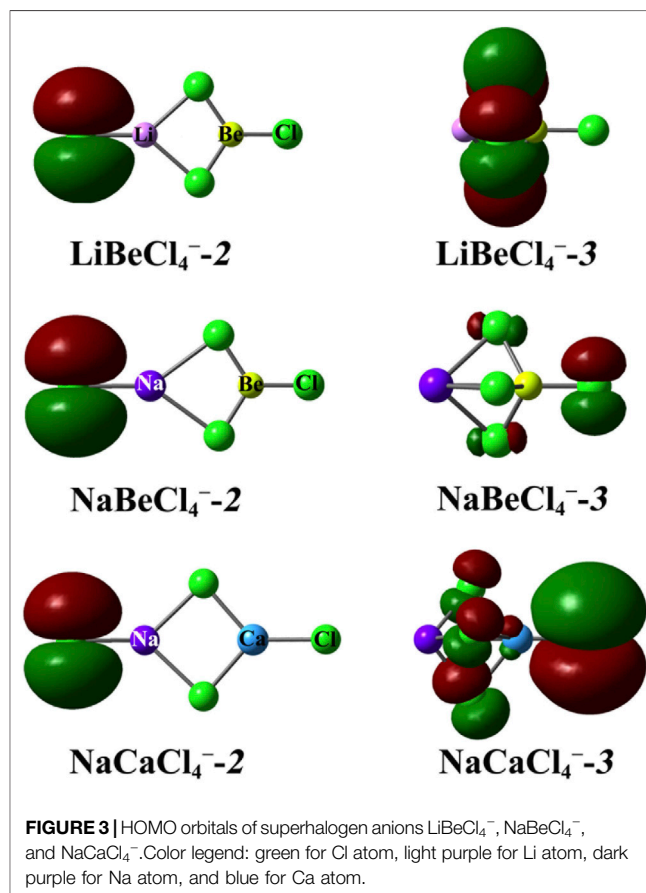


FIGURE 3 | HOMO orbitals of superhalogen anions LiBeCl_4^- , NaBeCl_4^- , and NaCaCl_4^- . Color legend: green for Cl atom, light purple for Li atom, dark purple for Na atom, and blue for Ca atom.

- (2) The largest VDE values for each $MM'X_4^-$ anions are presented in Table 3. From the table, the VDE values increase in the order: $\text{MBeX}_4^- \rightarrow \text{MMgX}_4^- \rightarrow \text{MCA}X_4^-$. Hence, the hetero-binuclear superhalogen anion $MM'X_4^-$ 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 $M'X_3^-$ is also necessary. For this reason, the VDE values of $M'X_3^-$ ($X = Cl, Br$) 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 $M'X_3^-$ also increase from BeX_3^- to CaX_3^- . Besides, the mononuclear anions $M'X_3^-$ 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 $MM'X_4^-$ ($X = F$ (Yang et al., 2017), Cl, Br) species show a decreasing order: $MM'F_4^- > MM'Cl_4^- > MM'Br_4^-$. 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 $LiM'X_4^-$, the VDE values of $LiM'X_4^-$ -3 are always larger than those of $LiM'X_4^-$ -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_t 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_t atom has a higher VDE value than isomer $NaBeX_4^-$ -3, which goes on the X_t' atom (see **Figure 3**). As to $NaMgX_4^-$ and $NaCaX_4^-$ species, the situation is similar to that of the $LiM'X_4^-$ anions. However, unlike $LiM'X_4^-$ -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 $MM'X_4^-$ ($M = Li, Na; M' = Be, Mg, Ca; X = Cl, Br$) 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 . Thereby, 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_t ligand atom instead of the X_t' 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.

FUNDING

This work was supported by the Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (2021L370, 2020L0507, and 2020L0516), the National Natural Science Foundation of China (Grant Nos. 21573089 and 51872057), the Doctoral Scientific Foundation Research Foundation of Shanxi Datong University (Grant Nos. 2019-B-11 and 2017-B-04), and the Basic Research Project Fund of Shanxi Province (20210302124491 and 20210302123341).

REFERENCES

- Anusiewicz, I., and Skurski, P. (2007). Unusual Structures of $Mg_2F_5^-$ Superhalogen Anion. *Chem. Phys. Lett.* 440, 41–44. doi:10.1016/j.cplett.2007.04.016
- Anusiewicz, I., Sobczyk, M., Dąbkowska, I., 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). $Mg_2Cl_5^-$ and $Mg_3Cl_7^-$ 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: SO_3F , SO_2F_3 , and SOF_5 .

- Int. J. Mass Spectrom.* 218, 207–215. doi:10.1016/s1387-3806(02)00713-3
- Bartlett, N., and Lohmann, D. H. (1962). Fluorides of the Noble Metals. Part II. Dioxygenyl Hexafluoroplatinate(V), $O_2 + [PtF_6]^+$. *J. Chem. Soc.* 0, 5253–5261. doi:10.1039/jr9620005253
- Bartlett, N. (1962). Xenon Hexafluoroplatinate (V) $Xe^+[PtF_6]^-$. *Chem. Soc.* 218.
- 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 Hyperhalogens. *Phys. Chem. Chem. Phys.* 21, 20156–20165. doi:10.1039/c9cp01284b
- 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 External Field-Engineered Hyperhalogen. *J. Phys. Chem. Lett.* 13, 3942–3948. doi:10.1021/acs.jpcllett.2c00916
- Elliott, B. M., Koyle, E., Boldyrev, A. I., Wang, X.-B., and Wang, L.-S. (2005). MX₃-Superhalogens (M = Be, Mg, Ca; X = Cl, Br): A Photoelectron Spectroscopic and Ab Initio Theoretical Study. *J. Phys. Chem. A* 109, 11560–11567. doi:10.1021/jp054036v
- Feng, Y., Xu, H.-G., Zheng, W., Zhao, H., Kandalam, A. K., and Jena, P. (2011). Structures and Photoelectron Spectroscopy of $Cu_n(BO_2)_m^-$ (N, M = 1, 2) Clusters: Observation of Hyperhalogen Behavior. *J. Chem. Phys.* 134, 094309. doi:10.1063/1.3556818
- Freza, S., and Skurski, P. (2010). Enormously Large (Approaching 14 eV!) Electron Binding Energies of $[HnFn+1]^-$ (N = 1-5, 7, 9, 12) Anions. *Chem. Phys. Lett.* 487, 19–23. doi:10.1016/j.cplett.2010.01.022
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., et al. (2016). *GAUSSIAN 16*. Wallingford CT: Gaussian, Inc.
- 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- α Calculations on the Ionization Potentials of MX_k+1^- Complex Anions and the Electron Affinities of MX_k+1^- "superhalogens". *Chem. Phys.* 56, 277–283. doi:10.1016/0301-0104(81)80150-4
- Gutsev, G. L., Rao, B. K., Jena, P., Wang, X.-B., and Wang, L.-S. (1999). Origin of the Unusual Stability of MnO_4^- . *Chem. Phys. Lett.* 312, 598–605. doi:10.1016/s0009-2614(99)00976-8
- Gutsev, G. L., Jena, P., Zhai, H.-J., and Wang, L.-S. (2001). Electronic Structure of Chromium Oxides, CrO_n^- and CrO_n (N=1-5) from Photoelectron Spectroscopy and Density Functional Theory Calculations. *J. Chem. Phys.* 115, 7935–7944. doi:10.1063/1.1405438
- Gutsev, G. L., Weatherford, C. A., Johnson, L. E., and Jena, P. (2012). Structure and Properties of the Aluminum Borates $Al(BO_2)_n$ and $Al(BO_2)_n^-$, (N = 1-4). *J. Comput. Chem.* 33, 416–424. doi:10.1002/jcc.21984
- Kim, H., Lim, J., Sohail, M., and Nazeeruddin, M. K. (2022). Superhalogen Passivation for Efficient and Stable Perovskite Solar Cells. *Sol. RRL*, 2200013. doi:10.1002/solr.202200013
- Koirala, P., Willis, M., Kiran, B., Kandalam, A. K., and Jena, P. (2010). Superhalogen Properties of Fluorinated Coinage Metal Clusters. *J. Phys. Chem. C* 114, 16018–16024. doi:10.1021/jp101807s
- Li, J., Huang, H.-C., Wang, J., Zhao, Y., Chen, J., Bu, Y.-X., et al. (2019). Polymeric Tungsten Carbide Nanoclusters: Structural Evolution, Ligand Modulation, and Assembled Nanomaterials. *Nanoscale* 11, 19903–19911. doi:10.1039/c9nr05613k
- Li, J., Zhao, Y., Bu, Y.-F., Chen, J., Wei, Q., and Cheng, S.-B. (2020). On the Theoretical Construction of Nb₂N₂-Based Superatoms by External Field Strategies. *Chem. Phys. Lett.* 754, 137709. doi:10.1016/j.cplett.2020.137709
- Lu, S.-J., Wu, L.-S., and Lin, F. (2019). Structural, Bonding, and Superhalogen Properties of $Au_4X_4^-/0$ (X = F, Cl, Br, and I) Clusters. *Theor. Chem. Acc.* 138, 51. doi:10.1007/s00214-019-2442-1
- Marchaj, M., Freza, S., Rybacka, O., and Skurski, P. (2013). Superhalogen Oxidizers Capable of Ionizing Water Molecules. *Chem. Phys. Lett.* 574, 13–17. doi:10.1016/j.cplett.2013.05.009
- Møller, C., and Plesset, M. S. (1934). Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* 46, 618. doi:10.1103/PhysRev.46.618
- Paduani, C., Wu, M. M., Willis, M., and Jena, P. (2011). Theoretical Study of the Stability and Electronic Structure of $Al(BH_4)_n=1\rightarrow 4$ and $Al(BF_4)_n=1\rightarrow 4$ and Their Hyperhalogen Behavior. *J. Phys. Chem. A* 115, 10237–10243. doi:10.1021/jp206330d
- Pathak, 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/jp2000392
- Smuczynska, S., and Skurski, P. (2009). Halogenoids as Ligands in Superhalogen Anions. *Inorg. Chem.* 48, 10231–10238. doi:10.1021/ci901253r
- 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 Molecule 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
- Świercz, I., and Anusiewicz, I. (2011). Neutral and Anionic Superhalogen Hydroxides. *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., Ganteför, 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, FeX_4^- and MX_3^- (M=Mn, Fe, 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 Hetero-Binuclear Anions $MM''F_4^-$ and $MM''F_5^-$ (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 Cyanide And/or Isocyanide 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 Superatoms $MM'(BO_2)_-$ (M = Na, Mg; M' = Mg, Al; N = 4-6). *Polyhedron* 209, 115456. doi:10.1016/j.poly.2021.115456
- Zakrzewski, V. G., Dolgounitcheva, O., and Ortiz, J. V. (1996). Ionization Energies of Anthracene, Phenanthrene, and Naphthalene. *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: $M@Au_{12}^{-}$ ($M = V, Nb, \text{ and } Ta$). *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 BO_2^{-} : 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.jpcllett.9b03794

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's Note: All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors, and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Copyright © 2022 Yang, He, Li, Jiang, Pang, Li and Zhao. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.