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Electrophilic Substituents as Ligands in Superhalogen Anions

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The vertical electron detachment energies (VDE) of several NaL_2^- and MgL_3^- anions (where L = $-NO_2$, $-CF_3$, $-CCl_3$, $-SHO_3$, $-COOH$, $-COOCH_3$, $-CHO$, $-CONH_2$) were calculated at the outer valence Green function level with the 6-311++G(3df,3pd) basis sets. It was proposed that some of electrophilic substituents may act as ligands in these species, analogously to halogen atoms in superhalogen anions. The largest values of the electron binding energies were found for the anions containing $-SHO_3$ ligands (VDE = 6.0−8.2 eV) and $-CF_3$ groups (VDE = 5.2−6.6 eV).

1. Introduction

In the last decades, great progress has been achieved in the study on superhalogen anions that are stable in the gas phase. Superhalogens are molecules possessing very large electron binding energies, exceeding the 3.61 eV atomic electron affinity of chlorine.[1] In a precursory theoretical work,[2] Gutsev and Boldyrev introduced a simple formula for one class of superhalogens, MX_{k+1}, where M is a main group (including hydrogen atom[3−5]) or transition metal atom, X is a halogen atom or monovalent electronegative ligand, and *k* is the maximal formal valence of the atom M (as became clear later on, this formula is, in fact, more general and reads $(M_nL_{nk+1})^-$,[6,7] which allows us to cover also polynuclear superhalogen anions, possessing more than one central atom). Since then, the vertical electron binding energies (VDEs) of many superhalogen anions have been estimated theoretically (see refs 8−12 and references cited therein).

Superhalogens may be useful in the oxidation of counterpart systems with relatively high ionization potentials (such as O_2, Xe), and allow the synthesis of new classes of ionic compounds (e.g., $Xe^+[PtF_6]^-$). In addition, molecules possessing high electron affinities are widely used in the production of organic metals and organic superconductors.[13,14]

Experimentally, direct measurements of the high electron binding energies in the superhalogens were not possible until 1999 when the smallest superhalogens, MX_{k+1}^- (M = Li, Na; X = Cl, Br, I), were first studied by photoelectron spectroscopy (measured by the Wang's group). Ab initio outer valence Green function (OVGF) calculations were performed by Boldyrev and Simons, and an excellent agreement was found between theoretical results and experimental data.[15] All these anions have proven to be superhalogen-based species since their electron binding energies were found to be greater than 3.61 eV (see ref 15 for details).

Lately, Boldyrev's and Wang's groups reported a joint experimental and theoretical investigation on MX_3^- (M = Be, Mg, Ca; X = Cl, Br)[16] and even larger superhalogen species, such as $Na_xCl_{x+1}^-$ ($x = 1-4$)[17] using photoelectron spectroscopy and ab initio calculations. The most recent work of Wang's group provided the results for the oxygen-based BO_2^- [18] and MCl_4^- (M = Sc, Y, La)[19] superhalogen anions.

In the past few years Skurski and co-workers performed extensive theoretical studies on several superhalogen species: BeX_3^- (X = F, Cl, Br),[20] MgX_3^- and CaX_3^- (X = F, Cl, Br),[21] NaX_2^- (X = F, Cl, Br),[22] and AlX_4^- and BX_4[23] (X = F, Cl, Br)[23] as well as species with mixed halide ligands. In addition, the Skurski's group performed a theoretical search for anions possessing extremely large electron binding energies, which resulted in finding a polynuclear superhalogen anion $Ta_3F_{16}^-$ whose binding energy was estimated to be 12.63 eV (recognized as the largest excess electron binding energy of a molecular system reported thus far).[24] Most recently, it has been demonstrated that the structures of polynuclear $Mg_2X_5^-$ (X = F, Cl) and $Mg_3Cl_7^-$ anions exhibit "superhalogen nature" since their electron binding energies were found to be greater than 6.5 eV.[25,26]

Extensive research on superhalogens was also carried out by Wu and co-workers.[27−29] In particular, it has been theoretically predicted that superhalogens can serve as components of novel nontraditional superalkali−superhalogen solid salts with special bonding nature and properties. Moreover, Wu's group demonstrated that such compounds may represent a new kind of potential nonlinear optical (NLO) materials because they exhibit large bond energies and extraordinary large NLO responses.[28]

As previously stated, most superhalogen anions match the $(M_nL_{nk+1})^-$ formula (where M is an electropositive atom and L corresponds to any ligand with high EA). Since the halogens are known to have the highest EA among all the chemical elements it is natural to use them as ligands in superhalogens. Extremely high VDEs were reported for these species and several of these are beyond the direct experimental measurements by photoelectron spectroscopy: e.g., BeF_3^- (8.47 eV), AlF_4^- (9.79 eV), $Mg_2F_5^-$ (9.38 eV), $Ta_3F_{16}^-$ (12.63 eV), all with F^- ligands. In general, species with Cl^- or Br^- ligands have lower VDEs. Additionally, it was found that certain O-rich metal oxide clusters can also exhibit very high EAs.[18,30,31] Since the O and F atoms are the most electronegative elements in the periodic table, it seems clear that electronegativity of the ligands is important in construction of superhalogen anions with desired high VDEs. In organic chemistry strongly electronegative reagents are known as electrophiles. The electrophiles frequently seen in the organic syntheses are species such as $-NO_2$, $-HSO_3$, $-CHO$, $-COOH$, and $-Cl$.[32]

In this paper we present our theoretical search for superhalogen anions having electrophiles as ligands. In particular, we

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focused our studies on NaL_2^- and MgL_3^- (where L = $-NO_2$, $-SHO_3$, $-CF_3$, $-CCl_3$, $-COOH$, $-CHO$, $-CONH_2$, $-COOCH_3$). Our goal was to investigate if such species are electronically, geometrically, and thermodynamically stable and whether they exhibit large values of the electron binding energies.

2. Methods

We present geometrical structures of the NaL_2^- and MgL_3^- (where L = $-NO_2$, $-SHO_3$, $-CF_3$, $-CCl_3$, $-COOH$, $-CHO$, $-CONH_2$, $-COOCH_3$) anions for which we also calculated harmonic vibrational frequencies (these data can be found in Table S1 in the Supporting Information). For this purpose we applied the second-order Møller−Plesset (MP2) perturbational method with the 6-311+G(d) basis set for most of the species but those with hydrogen atom, for which the 6-311++G(d,p) basis set[33,34] was chosen. Providing reliable vertical electron detachment energies of the superhalogen anions requires using more accurate treatment thus we performed *direct* calculations of the electron binding energies of these species. A *direct* scheme we applied was the outer valence Green function (OVGF) method.[35−39] The OVGF approximation remains valid only for outer valence ionizations for which the pole strengths (PSs) are greater than 0.80−0.85.[40] For all states studied here, the PSs are sufficiently large to justify use of the OVGF method (the smallest PS found for the states studied in this work is 0.90; see Table S1, Supporting Information). As far as the basis sets are concerned, we applied the 6-311+G(3df) or 6-311++G(3df,3pd) (for anions containing H atoms) basis sets[33,34] while estimating VDEs since analogous basis sets have been used by others for superhalogen anions and provided an excellent agreement between such calculated and experimentally measured VDEs.[15,17−21]

All calculations were performed with the Gaussian 03 program.[41]

3. Results

The main purpose of this work is to verify if the widely used electrophilic substituents may replace halogen ligands in superhalogen anions. Therefore, we have arbitrarily chosen several well-known electrophiles ($-NO_2$, $-CF_3$, $-CCl_3$, $-SHO_3$, $-COOH$, $-COOCH_3$, $-CHO$, $-CONH_2$) and we designed the hypothetical anionic species according to the formula $(ML_{k+1})^-$ and using sodium and magnesium as central atoms. The choice of metal atoms was dictated by the desire of considering such central atoms that are representative for the alkali and alkaline earth metals which are known to form superhalogen anions. Now we move on to the discussion of each type of ligand and its usefulness in designing the anionic species exhibiting unusually large excess electron binding energies.

3.1. $-NO_2$ Ligands. The equilibrium structures of $Na(NO_2)_2^-$ and $Mg(NO_2)_3^-$ are depicted in Figure 1 while the corresponding geometrical parameters and harmonic vibrational frequencies are gathered in Table S1, Supporting Information. As described in the literature,[42] the nitro group may connect to other atoms either through its nitrogen atom or the oxygen atoms. Indeed, we found these two cases to be operative in $Na(NO_2)_2^-$ and $Mg(NO_2)_3^-$ species. The lower energy anionic structures correspond to those in which the central atom (Na or Mg) is linked to the $-NO_2$ groups through the oxygen atoms. In particular, the D_{2d} symmetry $Na(NO_2)_2^-$ in which such bonding occurs is lower in energy by 13.3 kcal/mol than its C_2 symmetry isomer. A similar situation is observed in the case of $Mg(NO_2)_3^-$ where the C_3 symmetry structure (in which the nitro groups are connected through the nitrogen with the central atom) is by 23.7 kcal/mol higher in energy than the D_3 symmetry isomer. Hence we conclude that the higher symmetry structures are preferred for the anions containing the nitro groups as ligands since they allow for the larger number of the stabilizing bonding interactions among the central atom and ligands.

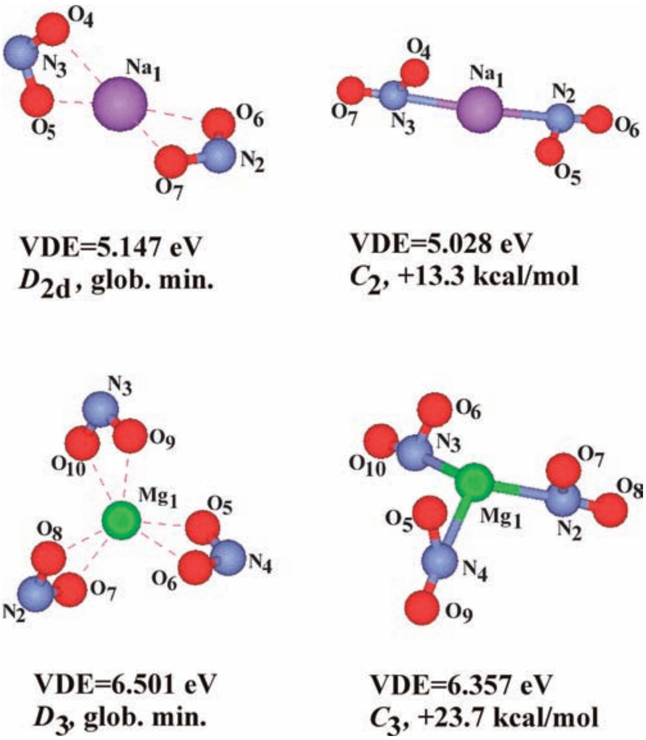

Figure 1. MP2/6-311+G(d) equilibrium geometries of the $Na(NO_2)_2^-$ and $Mg(NO_2)_3^-$ anions. The symmetry point group and the corresponding VDE (in eV) for each species are also given. For more than one isomer the relative energy (with respect to the global minimum) is shown in kcal/mol.

The results shown in Figure 1, Table 1, and Table S1 (Supporting Information) indicate that the electron binding energies (calculated as the vertical electron detachment energies) are relatively large for species containing the proper number of nitro groups connected to metal atoms. The VDEs for the $Na(NO_2)_2^-$ anions are in the 5.028−5.147 eV range, while those for the $Mg(NO_2)_3^-$ are in the 6.357−6.501 eV range. It should also be noted that the larger value of the vertical electron detachment energy corresponds to the most stable structure (in the case of both $Na(NO_2)_2^-$ and $Mg(NO_2)_3^-$). Therefore, we conclude that using the alkali or alkaline earth metals as central atoms should lead to electronic stabilities exceeding 5 eV when the nitro groups play the role of ligands. These results confirm the usefulness of the NO_2 groups in designing novel superhalogen anions. Interestingly, the superhalogens possessing nitro group as ligands do not contain *any* halogen atom, unlike almost all species of this type.

3.2. $-CF_3$ and $-CCl_3$ Ligands. The MP2-optimized equilibrium D_{3d} symmetry structures (in the case of $Na(CF_3)_2^-$ and $Na(CCl_3)_2^-$) and C_{3h} symmetry structures (for $Mg(CF_3)_3^-$ and $Mg(CCl_3)_3^-$) are shown in Figure 2. The corresponding geometrical parameters and harmonic vibrational frequencies are collected in Table S1, Supporting Information. The intuitive structures found for these anions as well as the lack of other stable isomers are the consequences of the simplicity of the $-CX_3$ (X = F, Cl) groups and the fact that its ability to connect to the central atom is limited to forming the metal−carbon bond. A relatively large number of halogen

TABLE 1: Vertical Electron Detachment Energies (VDE) for the Anions Studied in This Work[a]

species and symmetry	VDE [eV]	PS	species and symmetry	VDE [eV]	PS
$Na(NO_2)_2^-$	**5.147**	**(0.907)**	$Na(COOH)_2^-$	**4.065**	**(0.906)**
D_{2d}	5.394	(0.908)	C_2	4.391	(0.909)
	6.704	(0.894)		7.318	(0.896)
	6.724	(0.894)		7.318	(0.896)
$Mg(NO_2)_3^-$	**6.501**	(0.903)	$Mg(COOH)_3^-$	**5.204**	**(0.903)**
D_3	6.501	(0.903)	C_{3v}	5.204	(0.903)
	7.835	(0.890)		6.283	(0.906)
	7.835	(0.890)		8.061	(0.894)
$Na(CF_3)_2^-$	**5.168**	**(0.913)**	$Mg(COOCH_3)_3^-$	**5.083**	**(0.900)**
D_{3d}	5.519	(0.916)	C_{3v}	5.083	(0.900)
	10.401	(0.908)		6.051	(0.896)
	10.401	(0.908)		7.376	(0.889)
$Mg(CF_3)_3^-$	**6.593**	**(0.910)**	$Na(CHO)_2^-$	**2.793**	**(0.907)**
C_{3h}	6.593	(0.910)	C_2	2.862	(0.909)
	7.972	(0.916)		8.429	(0.888)
	11.353	(0.908)		8.432	(0.888)
$Na(CCl_3)_2^-$	**4.693**	**(0.900)**	$Mg(CHO)_3^-$	**3.831**	**(0.903)**
D_{3d}	4.924	(0.898)	C_{3h}	3.831	(0.905)
	7.236	(0.892)		4.905	(0.909)
	7.237	(0.892)		9.062	(0.885)
$Mg(CCl_3)_3^-$	**5.552**	**(0.900)**	$Na(CONH_2)_2^-$	**3.154**	**(0.904)**
C_{3h}	5.552	(0.900)	C_2	3.208	(0.905)
	6.405	(0.898)		5.888	(0.896)
	7.598	(0.890)		5.892	(0.896)
$Na(SHO_3)_2^-$	**6.048**	**(0.909)**	$Mg(CONH_2)_3^-$	**3.888**	**(0.900)**
1-C_2	6.114	(0.909)	C_1	4.305	(0.899)
	7.171	(0.900)		5.174	(0.901)
	7.174	(0.900)		5.825	(0.891)
$Mg(SHO_3)_3^-$	**6.770**	**(0.911)**			
1-C_3	6.770	(0.911)			
	7.333	(0.900)			
	7.452	(0.892)			

[a] See Figures 1−6 for geometrical structures. The VDEs are calculated with the OVGF method using the 6-311++G(3df,3pd) basis sets. Pole strengths (PS) in parentheses.

atoms (F or Cl) in these ligands let us predict their potential ability to enhance the electron binding energy of the resulting anion (due to electronegativity of the F and Cl atoms and the collective effects[8]). Indeed, the trifluoromethyl and trichloromethyl functional groups may act as very convenient ligands in superhalogen anions ensuring their large excess electron binding energies. According to our estimates, using the $-CF_3$ ligands leads to VDEs of 5.168 eV (for $Na(CF_3)_2^-$) and 6.593 eV (for $Mg(CF_3)_3^-$); see Table 1 and Figure 2. However, replacing the F atoms with Cl atoms results in the decrease of the electronic stability of such anions, which is consistent with our earlier findings.[20,21] Hence, as we expected, using the $-CCl_3$ instead of $-CF_3$ ligands reduces the VDEs to 4.693 and 5.552 eV for $Na(CCl_3)_2^-$ and $Mg(CCl_3)_3^-$, respectively. Despite this, both the $-CF_3$ and $-CCl_3$ groups should be considered as potential ligands while designing superhalogen anions exhibiting VDEs in the 4.5−6.5 eV range (depending on the central atom used).

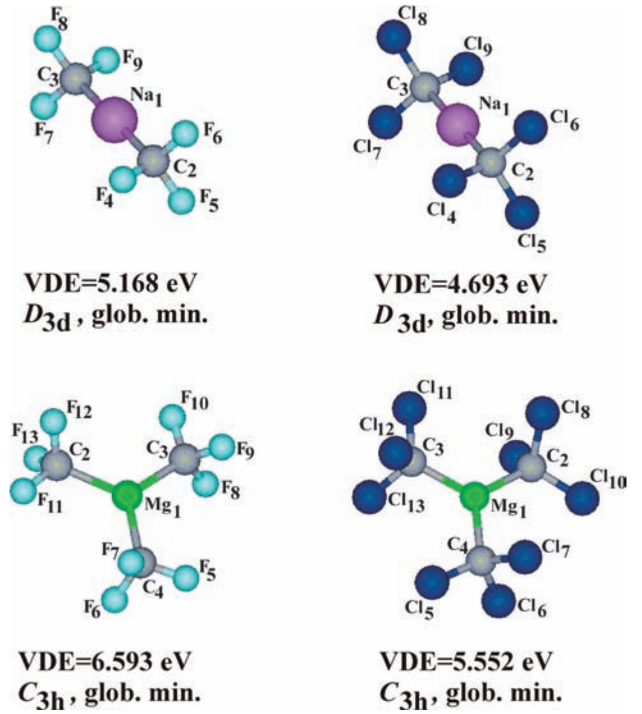

Figure 2. MP2/6-311+G(d) equilibrium geometries of the $Na(CF_3)_2^-$, $Mg(CF_3)_3^-$, $Na(CCl_3)_2^-$, and $Mg(CCl_3)_3^-$ anions. The symmetry point group and the corresponding VDE (in eV) for each species are also given. For more than one isomer the relative energy (with respect to the global minimum) is shown in kcal/mol.

3.3. $-SHO_3$ Ligands. According to our findings the sulfonic acid functional groups connect to the central metal atom (sodium or magnesium) through the oxygen atom, however, the hydrogen atoms may attach either to the sulfur atom or to one of the oxygen atoms. This allows basically for two types of isomers and we found the corresponding structures both for $Na(SHO_3)_2^-$ and $Mg(SHO_3)_3^-$. Their geometries are depicted in Figure 3 while the corresponding geometrical parameters (and the harmonic vibrational frequencies) are collected in Table S1, Supporting Information. We found two C_2 symmetry $Na(SHO_3)_2^-$ stable structures (labeled 1-C_2 and 2-C_2 in Figure 3, for the global minimum and the higher energy isomer, respectively) and two C_3 symmetry $Mg(SHO_3)_3^-$ structures (similarly labeled 1-C_3 and 2-C_3 in Figure 3, for the global minimum and the higher energy isomer, respectively). Despite which metal atom (i.e., Na or Mg) plays a central atom role, the most stable isomer is always the one containing the H atom bound to the oxygen rather than to sulfur atom, because of the

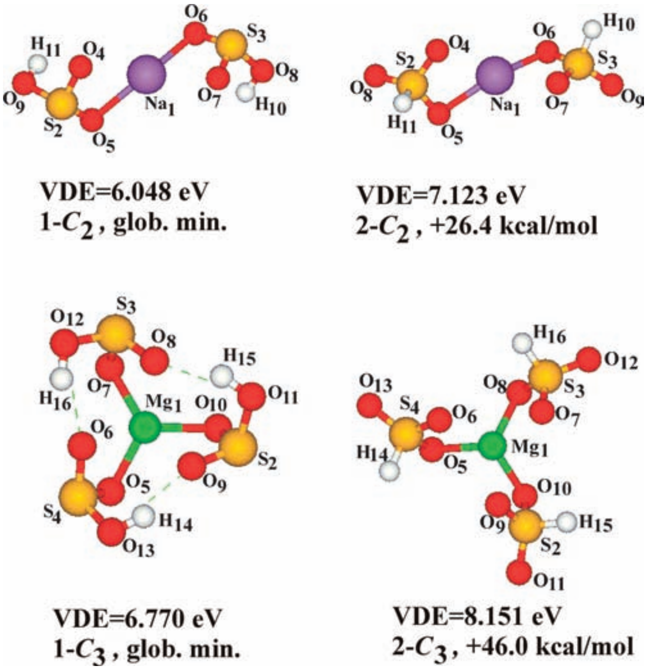

Figure 3. MP2/6-311++G(d,p) equilibrium geometries of the $Na(SHO_3)_2^-$ and $Mg(SHO_3)_3^-$ anions. The symmetry point group and the corresponding VDE (in eV) for each species are also given. For more than one isomer the relative energy (with respect to the global minimum) is shown in kcal/mol.

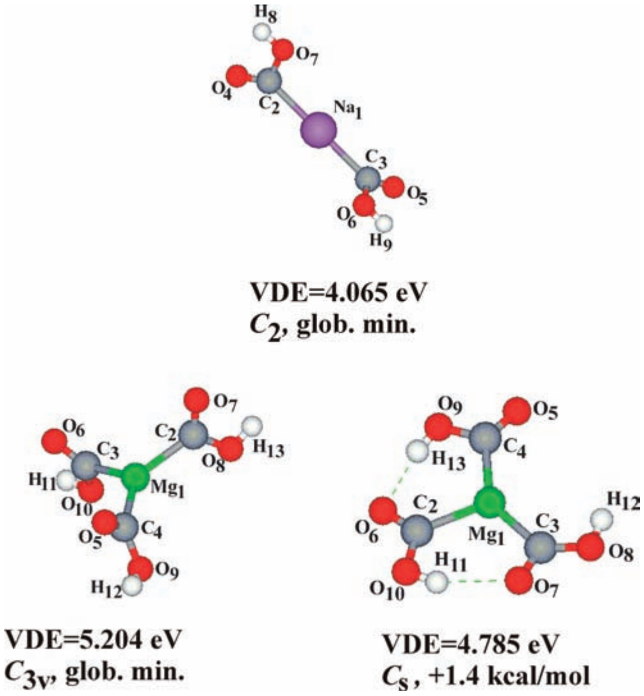

Figure 4. MP2/6-311++G(d,p) equilibrium geometries of the Na$(COOH)_2^-$ and $Mg(COOH)_3^-$ anions. The symmetry point group and the corresponding VDE (in eV) for each species are also given. For more than one isomer the relative energy (with respect to the global minimum) is shown in kcal/mol.

possibility of forming larger number of internal hydrogen bonds; see Figure 3. The energy gap between 1-C_2 and 2-C_2 $Na(SHO_3)_2^-$ structures was calculated to be 26.4 kcal/mol while the energy difference between the global minimum of Mg$(SHO_3)_3^-$ (i.e., 1-C_3 structure) and the corresponding less stable isomer (2-C_3 structure) was found to be 46.0 kcal/mol (at the MP2/6-311++G(d,p) level). For both anions, however, the larger value of the vertical electron detachment energy corresponds to the less stable isomer and reads 7.123 eV for 2-C_2 $Na(SHO_3)_2^-$ and 8.151 eV for 2-C_3 $Mg(SHO_3)_3^-$ (see Table 1 and Table S1, Supporting Information). The excess electron binding energies for the global minima of these anions (i.e., 1-C_2 $Na(SHO_3)_2^-$ and 1-C_3 $Mg(SHO_3)_3^-$) are also relatively large and were calculated to be 6.048 and 6.770 eV, respectively. Hence, we conclude that one may expect quite strong excess electron bonding (exceeding 6 eV) for the superhalogen anions containing alkali and alkaline metal central atoms when the sulfonic acid functional groups are used as ligands.

3.4. −COOH Ligands. The MP2 equilibrium structures of the $Na(COOH)_2^-$ and $Mg(COOH)_3^-$ anions are depicted in Figure 4 while the corresponding geometrical parameters and harmonic vibrational frequencies are gathered in Table S1, Supporting Information. We found only one stable structure for the system containing Na as a central atom while for the $Mg(COOH)_3^-$ anion two geometrically stable isomers were obtained. The stable structure for the $Na(COOH)_2^-$ anion is of C_2 symmetry, which corresponds to the geometrical configuration with two perpendicular COOH groups. This anion is characterized by the vertical electron detachment energy of 4.065 eV (see Table 1). The global minimum for the $Mg(COOH)_3^-$ anion possesses C_{3v} symmetry and each of its three carboxylic groups contains an internal hydrogen bond (see Figure 4 and Table 1). The C_s symmetry $Mg(COOH)_3^-$ isomer containing intramolecular hydrogen bonds (among COOH groups) is higher in energy than the global C_{3v} symmetry minimum by only 1.4 kcal/mol, which may suggest that both of these structures should be present at room temperature. As far as their electron binding energies are concerned, the VDE for the most stable C_{3v} symmetry $Mg(COOH)_3^-$ anion was calculated to be 5.204 eV while the value of 4.785 eV was found for the C_s symmetry isomer (see Table S1, Supporting Information). Therefore, we conclude that the COOH functional groups may be used as ligands in designing superhalogen anions, although one cannot expect them to exhibit extremely high electron binding energies (VDEs in the 4−5 eV range could be anticipated).

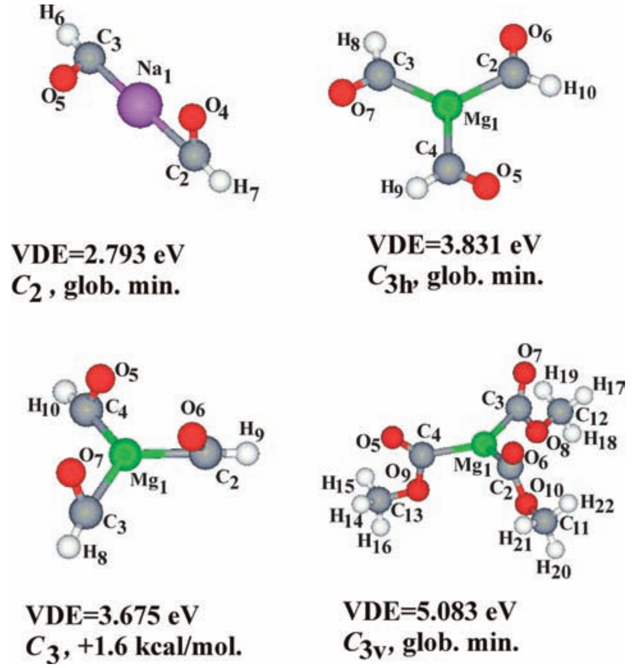

Figure 5. MP2/6-311++G(d,p) equilibrium geometries of the Na$(CHO)_2^-$, $Mg(CHO)_3^-$, and $Mg(COOCH_3)_3^-$ anions. The symmetry point group and the corresponding VDE (in eV) for each species are also given. For more than one isomer the relative energy (with respect to the global minimum) is shown in kcal/mol.

3.5. −COOCH$_3$ Ligands. Taking into account the possibility of forming stable anions of superhalogen nature having sodium or magnesium as central atoms and involving the $-COOCH_3$ functional groups as ligands led to only one species, the $Mg(COOCH_3)_3^-$ anion (see Figure 5 and Table S1, Supporting Information, where its geometrical parameters and harmonic vibrational frequencies are collected). We found the Na$(COOCH_3)_2^-$ system to be unstable thermodynamically and geometrically. The only stable structure we obtained was when the Mg atom played a central atom role and the resulting anion was found to possess a C_{3v} symmetry (like the global minimum of the $Mg(COOH)_3^-$ species described in section 3.4). Even though the vertical electron detachment energy of the Mg$(COOCH_3)_3^-$ anion was calculated to be 5.083 eV (see Table 1 and Figure 5), we do not view the $COOCH_3$ ligands as promising in designing novel superhalogen anions because the possibility of spontaneous fragmentation of such species is likely (which we conclude on the basis of the observed instability of $Na(COOCH_3)_2^-$).

3.6. −CHO Ligands. The MP2 equilibrium geometries of the $Na(CHO)_2^-$ and $Mg(CHO)_3^-$ anions are depicted in Figure 5 and the corresponding geometrical parameters and harmonic vibrational frequencies are gathered in Table S1, Supporting Information). We found only one stable anion in which the sodium atom plays a central atom role and the formyl groups are involved as ligands. This structure possesses C_2 symmetry

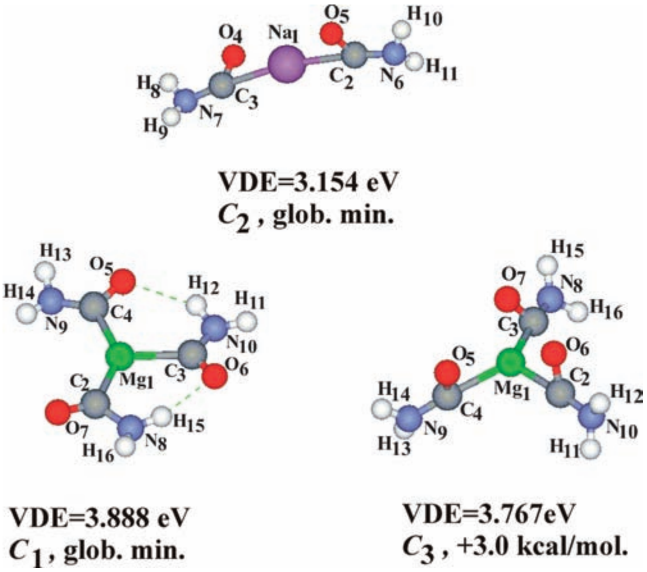

Figure 6. MP2/6-311++G(d,p) equilibrium geometries of the $Na(CONH_2)_2^-$ and $Mg(CONH_2)_3^-$ anions. The symmetry point group and the corresponding VDE (in eV) for each species are also given. For more than one isomer the relative energy (with respect to the global minimum) is shown in kcal/mol.

and exhibits a rather small value of VDE (2.793 eV, see Table 1). For the $Mg(CHO)_3^-$ species we obtained two geometrically stable isomers: the more stable structure having C_{3h} symmetry and the higher energy isomer of C_3 symmetry (see Figure 5 and Table S1, Supporting Information). The electron binding energies calculated for these two species (3.831 and 3.675 eV for the C_{3h} symmetry and C_3 symmetry, respectively) only barely exceed the electron affinity of chlorine atom (3.61 eV).[1] Thus, we do not consider the −CHO functional groups as useful ligands while proposing novel strongly bound anions of superhalogen nature.

3.7. $-CONH_2$ Ligands. The equilibrium geometries of the anionic species containing amide functional groups as ligands and sodium/magnesium as central atoms are shown in Figure 6 (the corresponding geometrical parameters and harmonic vibrational frequencies are collected in Table S1, Supporting Information). We found only one stable structure in the case of the $Na(CONH_2)_2^-$ anion and two isomers for $Mg(CONH_2)_3^-$. The $Na(CONH_2)_2^-$ anion possesses C_2 symmetry and its relatively stretched structure does not allow for forming intramolecular hydrogen bonds between the two amide groups. The vertical electron detachment energy of this anion was calculated to be 3.154 eV. The two isomers of $Mg(CONH_2)_3^-$ are characterized by similar VDE values (ca. 3.8−3.9 eV). In particular, the most stable structure (C_1 symmetry) binds an excess electron by 3.888 eV, while the higher energy isomer (C_3 symmetry) possesses VDE of 3.767 eV (see Table 1, Table S1, Supporting Information, and Figure 6). Having in mind much larger electron binding energies found for other species (see sections 3.1−3.3), we do not consider the amide functional group as a promising ligand for designing strongly bound superhalogen species.

4. Conclusions

On the basis of our ab initio calculations we conclude that some of the electrophilic functional groups are capable of playing the ligand role in superhalogen anions. We formulated such a conclusion by taking into account the following observations:

(i) The $-NO_2$ functional groups used as ligands in superhalogen anions containing sodium or magnesium as central atom lead to VDEs in the 5.03−6.50 eV range.

(ii) The superhalogen anions having $-CF_3$ or $-CCl_3$ groups as ligands exhibit the VDEs in the 4.69−6.59 eV range.

(iii) The $-SHO_3$ ligands lead to the largest vertical electron energies (among the systems studied in this work) exceeding 8 eV (VDEs in the 6.05−8.15 eV range).

(iv) The superhalogen anions possessing −COOH functional groups as ligands are less strongly bound (by 4.07−5.20 eV).

(v) The anions involving $-COOCH_3$ ligands are either geometrically unstable (i.e., $Na(COOCH_3)_2^-$) or bound by ca. 5 eV ($Mg(COOCH_3)_3^-$).

(vi) The remaining functional groups (i.e., −CHO and $-CONH_2$) lead to anions exhibiting much smaller electron binding energies (2.79−3.89 eV range).

Therefore, we recommend using $-NO_2$, $-CF_3$, $-CCl_3$, $-SHO_3$, and −COOH functional groups as ligands in designing novel superhalogen anions. We believe that our conclusions (as well as the structures and results presented in this work) might be representative for other one-center superhalogens possessing alkali or alkaline earth metals as central atoms.

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Supporting Information Available: VDE (in eV) calculated at the OVGF/6-311++G(3df,3pd) and the MP2/6-311++G(d,p) equilibrium geometries and nonscaled harmonic vibrational frequencies for anionic species (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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