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Superhalogen Anions Utilizing Acidic Functional Groups As Ligands

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The vertical electron detachment energies (VDE) of several NaL_2^- and MgL_3^- anions (where *L*= -ClO$_4$, -ClO$_3$, -ClO$_2$, -ClO, -NO$_3$, -PO$_3$, -H$_2$PO$_4$, -HSO$_4$, -HCO$_3$, -SH) were calculated at the outer valence Green function level with the 6-311++G(3df,3pd) basis sets. It was shown that various acidic functional groups may act as ligands in superhalogen anions whose electronic stabilities always exceed 4 eV. The largest values of the electron binding energies were found for the anions containing -ClO$_4$ ligands (VDE=7.8−8.9 eV). The VDE dependencies on the origin of the ligand used (whether it is a functional group derived from strong or weak acid), chemical constitution of acidic functional groups and the electronegativity of the ligand's central atom were observed and discussed.

1. Introduction

This is the second article in which we describe our efforts to study the possibility of forming stable anions of superhalogen nature with alternative (to F, Cl, Br, I) ligands. Superhalogens are molecules possessing very large electron binding energies, exceeding the 3.61 eV atomic electron affinity of chlorine.[1] Because molecules exhibiting extremal characteristics are of a great importance in chemistry, the superhalogen species have been extensively studied in the past, primarily by Boldyrev, Gutsev, and Ortiz (see refs 2−7 and references cited therein). In addition, a simple formula for one class of these compounds has been established, MX_{k+1}, where M is a main group atom (including hydrogen[8]) or transition-metal atom, X stands for a halogen atom (or hydrogen atom[9,10]) 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 $(M_nL_{nk+1})^-$,[11,12] which allows us to cover also polynuclear superhalogen anions, possessing more than one central atom.

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. Namely, $Xe^+[PtF_6]^-$ species was synthesized in 1962 by Bartlett as a representative system.[13] Since then, the molecules possessing high electron affinities are widely used in the production of organic metals and organic superconductors.[14]

The electron binding energies of many superhalogen anions have been estimated both theoretically and experimentally. Many of them have been obtained by Boldyrev's and Wang's groups (e.g., $LiCl_2^-$, $NaBr_2^-$, $MgCl_3^-$, $Na_xCl_{x+1}^-$ (x = 1−4), BO_2^-, MCl_4^- (M = Sc, Y, La)),[15−19] Skurski's group (e.g., $BeCl_3^-$, CaF_3^-, $AlFCl_3^-$, $Ta_3F_{16}^-$)[20−26] and Gutsev.[27,28] Recently, Wu and co-workers predicted theoretically that superhalogens can serve as components of novel nontraditional superalkali−superhalogen solid salts with special bonding nature and properties.[29−31] 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 extraordinarily large NLO responses.[30]

In the preceding article,[32] we described the vertical electron binding energies for anions having electrophiles as ligands. In particular, we focused our studies on the NaL_2^- and MgL_3^- (where L = −NO$_2$, −SHO$_3$, −CF$_3$, −CCl$_3$, −COOH, −CHO, −CONH$_2$, −COOCH$_3$). It was found that some of the electrophilic functional groups (−NO$_2$, −CF$_3$, −CCl$_3$, −SHO$_3$, and −COOH) lead to anions having relatively large VDEs.

In this contribution, we present the ab initio results for 20 negatively charged species exhibiting superhalogen nature and having Na or Mg as the metal component in the ML_{k+1}^- and acidic functional groups as ligands (L = −ClO$_4$, −ClO$_3$, −ClO$_2$, −ClO, −NO$_3$, −PO$_3$, −H$_2$PO$_4$, −HSO$_4$, −HCO$_3$, −SH). We believe that the vertical electron binding energies we provide in this work might be found useful for experimental chemists, especially those who design new materials in which the strong electron acceptors are involved. However, one should keep in mind that the species whose existence is proposed in this contribution might be unstable in condensed phases.

2. Methods

We present the equilibrium geometrical structures of the NaL_2^- and MgL_3^- (where L = −ClO$_4$, −ClO$_3$, −ClO$_2$, −ClO, −NO$_3$, −PO$_3$, −H$_2$PO$_4$, −HSO$_4$, −HCO$_3$, −SH) 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 all 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 (*B* approximation).[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 the use of the OVGF method (the smallest PS found for the states studied in this work is 0.88, Table 1). 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 because analogous basis sets have been used

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

species and symmetry	VDE [eV](OVGF)	PS	VDE [eV](MP2)
$Na(ClO_4)_2^- D_{2d}$	7.843	(0.899)	8.498
$Mg(ClO_4)_3^- C_3$	8.914	(0.889)	7.642
$Na(ClO_3)_2^- C_2$	6.650	(0.908)	6.167
$Mg(ClO_3)_3^- C_3$	7.555	(0.903)	7.192
$Na(ClO_2)_2^- D_{2d}$	4.747	(0.908)	4.273
$Mg(ClO_2)_3^- D_3$	5.298	(0.904)	4.264
$Na(ClO)_2^- C_{2h}$	4.982	(0.907)	4.246
$Mg(ClO)_3^- C_{3h}$	6.146	(0.906)	6.211
$Na(NO_3)_2^- D_{2d}$	6.689	(0.900)	6.262
$Mg(NO_3)_3^- D_3$	8.293	(0.884)	8.388
$Na(PO_3)_2^- D_{2d}$	7.613	(0.906)	7.235
$Mg(PO_3)_3^- D_3$	8.676	(0.902)	7.672
$Na(HSO_4)_2^- C_2$	7.318	(0.903)	6.966
$Mg(HSO_4)_3^- C_3$	8.606	(0.893)	9.170
$Na(H_2PO_4)_2^- C_2$	6.264	(0.906)	5.751
$Mg(H_2PO_4)_3^- C_3$	7.234	(0.897)	7.679
$Na(HCO_3)_2^- C_2$	6.783	(0.902)	6.579
$Mg(HCO_3)_3^- C_3$	7.379	(0.898)	7.374
$Na(SH)_2^- C_2$	4.281	(0.903)	4.205
$Mg(SH)_3^- C_3$	5.112	(0.897)	5.084

[a] See Figures 1−6 for geometrical structures. The VDEs are calculated with the OVGF and MP2 methods using the 6-311++G(3df,3pd) basis sets. Pole strengths (PS) in parentheses.

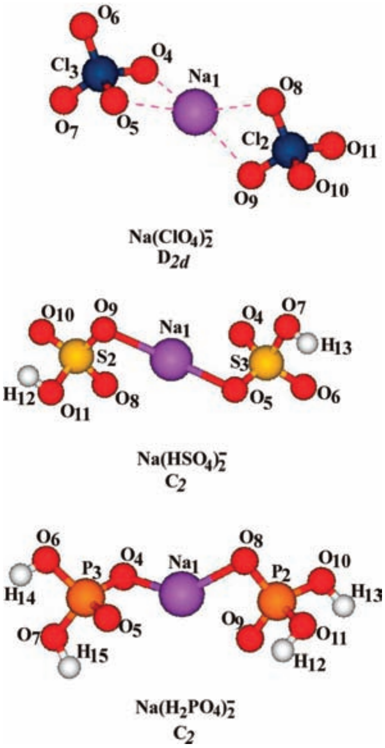

Figure 1. MP2/6-311+G(d,p) equilibrium geometries of the $Na(ClO_4)_2^-$, $Na(HSO_4)_2^-$, and $Na(H_2PO_4)_2^-$ anions.

by others for superhalogen anions and provided an excellent agreement between such calculated and experimentally measured VDEs.[15,17−21]

The vertical electron detachment energies were also calculated with the MP2 method (for comparison).

All calculations were performed with the *Gaussian03* program.[41]

3. Results

The main purpose of this work is to verify whether the acidic functional groups may replace halogen ligands in superhalogen anions. According to our earlier findings, considering the possibility of using the electrophilic substituents as potential ligands[32] in superhalogen anions, the sulfonic acid functional groups ($-HSO_3$) and nitro groups ($-NO_2$) might be especially promising ligands in designing novel species. Because the $-HSO_3$ and $-NO_2$ can be viewed as acidic functional groups, we decided to check the usefulness of other ligands of those types in the construction of superhalogen anions. Therefore, we have arbitrary chosen several well-known acidic functional groups (i.e., $-ClO_4$, $-ClO_3$, $-ClO_2$, $-ClO$, $-NO_3$, $-PO_3$, $-H_2PO_4$, $-HSO_4$, $-HCO_3$, $-SH$) and we designed the hypothetical anionic species according to the $(ML_{k+1})^-$ formula and using sodium and magnesium as central atoms. The choice of Na or Mg 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 relatively strongly bound superhalogen anions.

We consider the vertical electron binding energies calculated with the OVGF method as more reliable than those calculated with the MP2 method. Indeed, we found the VDE^{MP2} to be either underestimated or overestimated in comparison with the OVGF-calculated values for the species described in this work. Hence, we limited our discussion to the results obtained at the OVGF/6-311++G(3df,3pd) level, whereas the VDEs calculated with the MP2 method are only gathered in Table 1 for comparison.

3.1. MP2 Equilibrium Geometries.

Because it was not our goal to explore the potential energy surface searching for higher energy isomers, we limited our theoretical investigation to the most stable anionic species. We begin our discussion from the anions with ligands that possess tetrahedral geometrical structure and we subsequently move to the acidic functional groups consisting of a smaller number of atoms.

3.1.1. $-ClO_4$, $-HSO_4$, and $-H_2PO_4$ Ligands.

The equilibrium structures of NaL_2^- and MgL_3^- (L = $-ClO_4$, $-HSO_4$, and $-H_2PO_4$) are depicted in Figures 1 and 2, whereas the corresponding geometrical parameters and harmonic vibrational frequencies are gathered in Table S1 of the Supporting Information. On the basis of our MP2/6-311++G(d,p) calculations, we found that the mentioned above oxoacidic functional groups of chlorine, sulfur, and phosphorus connect to the central atom (sodium or magnesium) through the oxygen atoms. This is consistent with our earlier findings for electrophilic substituents (i.e., $-NO_2$ and $-HSO_3$),[32] in which the central atom (Na or Mg) was linked to the ligands through the oxygen atoms. Such a configuration leads to D_{2d}-symmetry species for $Na(ClO_4)_2^-$ and C_2-symmetry anions for $Na(HSO_4)_2^-$ and $Na(H_2PO_4)_2^-$ (Figure 1). As far as $Mg(ClO_4)_3^-$, $Mg(HSO_4)_2^-$, and $Mg(H_2PO_4)_3^-$ are concerned, we found that each of these anions possesses C_3 symmetry (Figure 2). The C_3-symmetry species of $Mg(HSO_4)_2^-$ and $Mg(H_2PO_4)_3^-$ contain intramolecular hydrogen bonds additionally stabilizing their structures. As a result, the ligands are connected not only to the central atom but also between one another (forming a ligand cage that surrounds the center of the system).

The sodium−oxygen and magnesium−oxygen bond lengths for NaL_2^- and MgL_3^- anions (L = $-H_2PO_4$, $-HSO_4$, and $-ClO_4$) are within 2.299−2.377 Å and 1.915−2.115 Å range, respectively, and we found the largest Na−O and Mg−O separation for $Na(ClO_4)_2^-$ and $Mg(ClO_4)_3^-$ species (Table S1 of the Supporting Information). Data collected in Table S1 demonstrate that the Na−O distance increases with an increase of the electronegativity of the ligand's central atom. One may notice the same tendency for the Mg−O distance in MgL_3^- species (Table S1 of the Supporting Information).

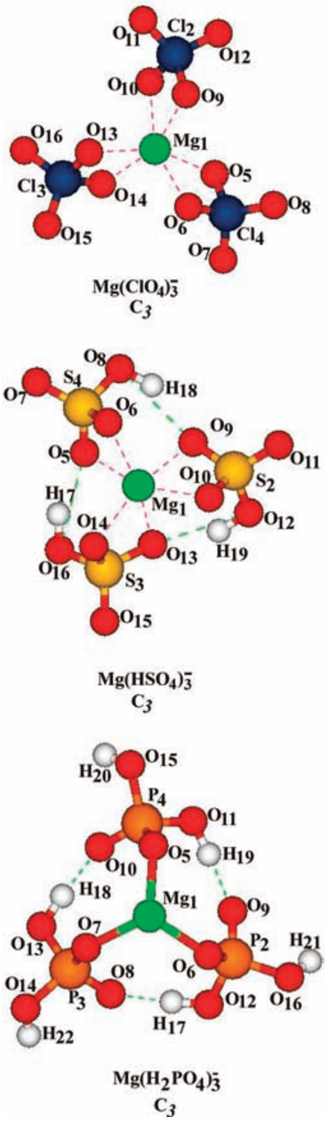

Figure 2. MP2/6-311+G(d,p) equilibrium geometries of the $Mg(ClO_4)_3^-$, $Mg(HSO_4)_3^-$, and $Mg(H_2PO_4)_3^-$ anions.

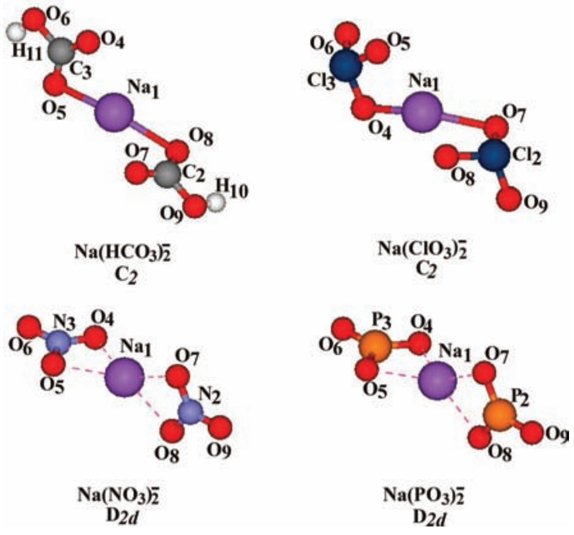

Figure 3. MP2/6-311++G(d,p) equilibrium geometries of $Na(HCO_3)_2^-$, $Na(ClO_3)_2^-$, $Na(NO_3)_2^-$, and $Na(PO_3)_2^-$ anions.

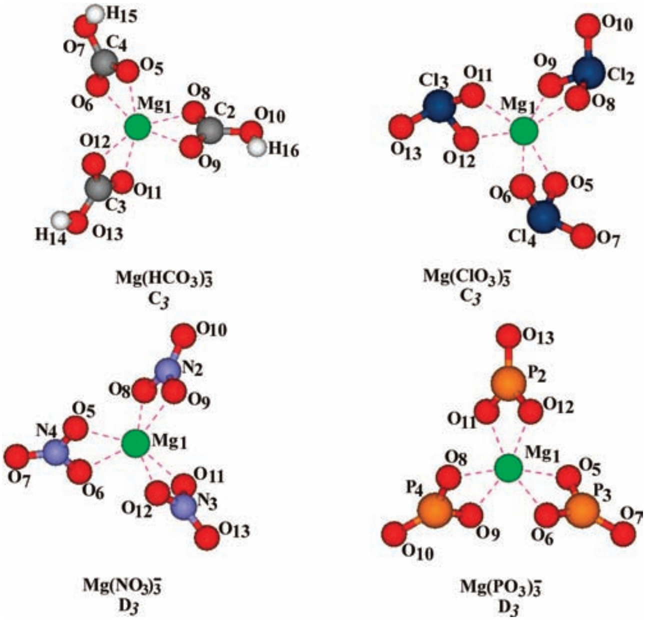

Figure 4. MP2/6-311++G(d,p) equilibrium geometries of $Mg(HCO_3)_3^-$, $Mg(ClO_3)_3^-$, $Mg(NO_3)_3^-$, and $Mg(PO_3)_3^-$ anions.

3.1.2. $-HCO_3$, $-ClO_3$, $-NO_3$, and $-PO_3$ Ligands. The MP2 equilibrium geometries of NaL_2^- and MgL_3^- (L = $-HCO_3$, $-ClO_3$, $-NO_3$, and $-PO_3$) are depicted in Figures 3 and 4, whereas the corresponding geometrical parameters and harmonic vibrational frequencies are gathered in Table S1 of the Supporting Information. We found that oxoacidic functional groups containing carbon, nitrogen, and phosphorus in NaL_2^- and MgL_3^- systems are planar, whereas the chlorate group is pyramidal. Such geometrical structures of the ligands lead to the D_{2d}-symmetry $Na(PO_3)_2^-$ and $Na(NO_3)_2^-$ species, C_2-symmetry $Na(HCO_3)_2^-$ and $Na(ClO_3)_2^-$ systems, D_3-symmetry $Mg(PO_3)_3^-$ and $Mg(NO_3)_3^-$ anions, and C_3-symmetry $Mg(HCO_3)_3^-$ and $Mg(ClO_3)_3^-$ compounds (Figures 3 and 4).

The sodium−oxygen and magnesium−oxygen bond lengths for NaL_2^- and MgL_3^- anions (L = $-ClO_3$, $-NO_3$, and $-PO_3$) are within the 2.362−2.407 Å and 2.114−2.156 Å range respectively, and we found the largest Na−O and Mg−O separations for $Na(PO_3)_2^-$ and $Mg(PO_3)_3^-$ species (Table S1 of the Supporting Information), which might be explained by the strength of the corresponding HL acid (discussion below in the section 3.2).

The Na−O and Mg−O bond lengths for the $Na(HCO_3)_2^-$ and $Mg(HCO_3)_3^-$ are 2.488 Å and 2.143 Å respectively, which seems relatively long when compared to analogous distances in $Na(PO_3)_2^-$ and $Mg(PO_3)_3^-$ species. This can be explained by the fact that carbon (central atom in $-HCO_3$) is more electronegative than phosphorus in the $-PO_3$ group. This observation on the dependencies of the metal−oxygen bond length on the electonegativity of the ligand's central atom is consistent with our earlier findings (section 3.1.1). Unlike in the quasi-tetrahedral $-HSO_4$ and $-H_2PO_4$ ligands, the planar geometry of the bicarbonate groups prevents forming of intramolecular hydrogen bonds (Figures 3 and 4).

3.1.3. $-ClO_2$ Ligands. Because the chlorite functional group resembles the previously studied nitro group,[32] the $-ClO_2$ ligands connect to the central metal atom (sodium or magnesium) through the oxygen atoms. The MP2-optimized equilibrium D_{2d}-symmetry structure of $Na(ClO_2)_2^-$ and D_3-symmetry structure of $Mg(ClO_2)_3^-$ are shown in Figure 5. The corresponding geometrical parameters and harmonic vibrational frequencies are collected in Table S1 of the Supporting Information. As it was previously stated, such geometrical

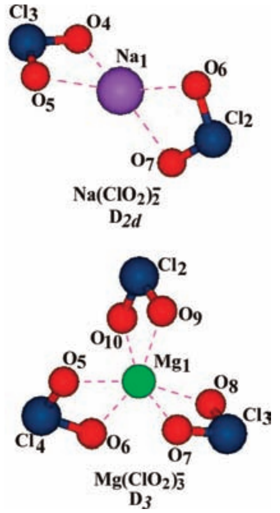

Figure 5. MP2/6-311++G(d,p) equilibrium geometries of $Na(ClO_2)_2^-$ and $Mg(ClO_2)_3^-$ anions.

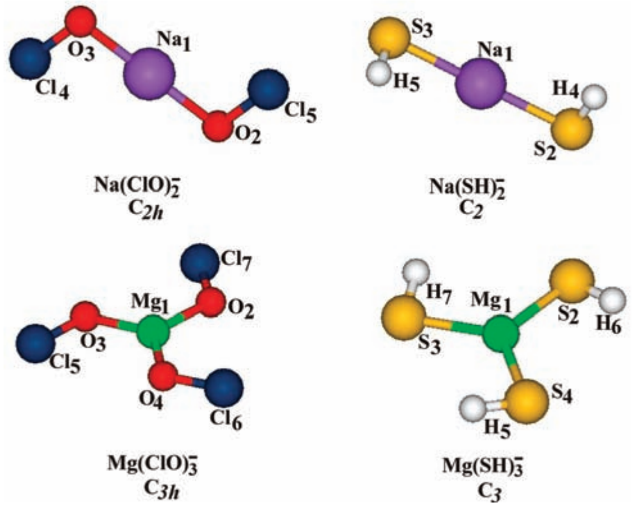

Figure 6. MP2/6-311++G(d,p) equilibrium geometries of $Na(ClO)_2^-$, $Na(SH)_2^-$, $Mg(ClO)_3^-$, and $Mg(SH)_3^-$ anions.

structures (with two ligands' oxygen atoms pointing toward the Na or Mg) allow for larger number of the stabilizing bonding interactions among the central atom and ligands.

The Na−O and Mg−O bond lengths for $Na(ClO_2)_2^-$ and $Mg(ClO_2)_3^-$ are 2.422 and 2.149 Å respectively, and these bonds seem relatively long when compared to analogous distances in $Na(ClO_3)_2^-$ and $Mg(ClO_3)_3^-$ species. Such geometrical structures allow for a relatively large number of the stabilizing bonding interactions among the central atom and the ligands.

3.1.4. −ClO and −SH Ligands. According to our findings, the diatomic −ClO and −SH ligands are connected to the central atom (Na or Mg) through the oxygen and sulfur, respectively. The equilibrium geometries of NaL_2^- and MgL_3^- (L = −ClO and −SH) are depicted in Figure 6, whereas the corresponding geometrical parameters and harmonic vibrational frequencies are gathered in Table S1 of the Supporting Information.

On the basis of our calculations, we found that the $Na(ClO)_2^-$ anion is planar and possesses C_{2h} symmetry, whereas the −SH groups are perpendicular to each other in $Na(SH)_2^-$, which results in C_2 symmetry. Similarly, the use of −ClO ligands leads to the planar structure of the $Mg(ClO)_3^-$anion, whereas employing the −SH groups results in the nonplanar equilibrium geometry of $Mg(SH)_3^-$ (Figure 6).

The Na−O and Mg−O bond lengths for $Na(ClO)_2^-$ and $Mg(ClO)_3^-$ are 2.193 Å and 1.926 Å respectively, and they are much shorter than those found for the NaL_2^- and MgL_3^- (L = $-ClO_4$, $-ClO_3$, $-ClO_2$) species. Because the bisulfide functional groups are linked directly to the metal (Na or Mg) atom through sulfur, the Na−S and Mg−S bond lengths in $Na(SH)_2^-$ and $Mg(SH)_3^-$ are 2.614 Å and 2.382 Å, respectively (Table S1 of the Supporting Information).

3.2. Vertical Electron Detachment Energies. The vertical electron detachment energies of NaL_2^- and MgL_3^- (where L = $-ClO_4$, $-ClO_3$, $-ClO_2$, −ClO, $-NO_3$, $-PO_3$, $-H_2PO_4$, $-HSO_4$, $-HCO_3$, −SH) anions calculated at the OVGF/6-311++G(3df,3pd) level are collected in Table 1 and Table S1 of the Supporting Information. On the basis of our experience, we consider the VDEs calculated at the OVGF level with the 6-311++G(3df,3pd) basis sets as reliable values and we move on to the discussion of these results.

The largest VDE among the systems considered was found for the $Na(ClO_4)_2^-$ (7.843 eV) and for $Mg(ClO_4)_3^-$ (8.914 eV), which is even larger than the VDE of NaF_2^- (6.644 eV)[22] and MgF_3^- (8.793 eV).[21] The fact that the ClO_4 ligand leads to the anions whose VDEs exceed the corresponding values for the anions containing fluorine ligands seems surprising at a first glance. Usually, in the case of superhalogens, the presence of the F atoms as ligands ensured the highest possible electronic stability that one could achieve using a particular central atom. However, the usefulness of the ClO_4 ligands might be explained by at least two observations: (i) the ClO_4 functional group consists of five strongly electronegative atoms. Certainly, the electronegativity of a single F atom is larger than the electronegativity of Cl or O, but replacing *one* fluorine atom with the ligand containing *five* electronegative atoms (one chlorine and four oxygen atoms) has to cause the VDE increase in the resulting superhalogen anion. (ii) Significantly larger spatial extent of the ClO_4 functional group (comparing to that of the single fluorine atom) allows for a more effective delocalization of the excess negative charge in the monoanionic system (which increases the electronic stability of the anion). However, the $-ClO_4$ ligand contains halogen atom (Cl), whereas one of our goals was to propose a ligand *not* containing *any* halogens. Among such functional groups studied in this work, the most promising is the $-PO_3$, which leads to the VDEs in the 7.6−8.6 eV range (Table 1). One should notice that such large vertical electron detachment energies also approach or even exceed those for the corresponding anions utilizing fluorine atoms as ligands.

The analysis of the results calculated for the $Na(ClO_2)_2^-$−-$Na(ClO_3)_2^-$−$Na(ClO_4)_2^-$ series and the $Mg(ClO_2)_3^-$−$Mg(ClO_3)_3^-$−$Mg(ClO_4)_3^-$ series of compounds indicates that the increasing number of oxygen atoms in ligands leads to the higher VDE (i.e., the highest VDE corresponds to the $Na(ClO_4)_2^-$ and $Mg(ClO_4)_3^-$ species, each of which contains five-atomic ligands involving four oxygen atoms). However, this tendency is not general because the $Na(ClO)_2^-$ and $Mg(ClO)_3^-$ anions are characterized by higher VDEs than the $Na(ClO_2)_2^-$ and $Mg(ClO_2)_3^-$, respectively (Table 1).

A similar trend can be observed for the anions with oxoacid functional groups containing either sulfur ($-HSO_4$ and $-HSO_3$) or nitrogen ($-NO_3$ and $-NO_2$) as ligands in superhalogen anions (the results for HSO_4 and NO_3 ligands are gathered in Table 1, whereas those for HSO_3 and NO_2 have been recently described in ref 32). Namely, the VDE calculated for $Na(HSO_4)_2^-$ exceeds by 1.27 eV the VDE found for $Na(HSO_3)_2^-$, whereas the electron binding energy for $Mg(HSO_4)_3^-$ is larger (by 1.84 eV) than that of $Mg(HSO_3)_3^-$. Analogously, the VDE differences between $Na(NO_3)_2^-$ and $Na(NO_2)_2^-$ and between $Mg(NO_3)_3^-$ and $Mg(NO_2)_3^-$ are 1.54 and 1.79 eV, respectively.

The electronegativity of the central atom in each complex ligand studied may also be related to the vertical electron detachment energy of the resulting superhalogen anion. Indeed, the VDE calculated for the $Na(ClO_4)_2^-$−$Na(HSO_4)_2^-$−$Na(HCO_3)_2^-$−$Na(H_2PO_4)_2^-$ series and for the $Mg(ClO_4)_3^-$−$Mg(HSO_4)_3^-$−$Mg(HCO_3)_3^-$−$Mg(H_2PO_4)_3^-$ series of species decreases from 7.843 to 6.264 eV (for the anions containing sodium) and from 8.914 to 7.234 eV (for the species containing magnesium), which is consistent with the electronegativity decrease in the Cl−S−C−P series of atoms.

For the species involving four-atomic ligands of XO_3 type (where X stands for Cl, N, P), an additional tendency can be observed. In the $Na(ClO_3)_2^-$−$Na(NO_3)_2^-$−$Na(PO_3)_2^-$ and $Mg(ClO_3)_3^-$−$Mg(NO_3)_3^-$−$Mg(PO_3)_3^-$ series, the VDE increases with the strength of the corresponding HL acid (where L = $-ClO_3$, $-NO_3$, $-PO_3$). The strongest acid among listed above is HPO_3 whose strength is comparable to that of hydroiodic acid[42] ($pK_a(HI) \approx -10$).[43] The HNO_3 and $HClO_3$ are less acidic and their pK_a are ca. −1.3 and −1, respectively.[44] According to this, the vertical electron detachment energies increase from 6.65 eV for $Na(ClO_3)_2^-$ to 7.61 eV for $Na(PO_3)_2^-$ and from 7.56 eV for $Mg(ClO_3)_3^-$ to 8.68 eV for $Mg(PO_3)_3^-$ (Table 1).

The VDEs of $Na(SH)_2^-$ and $Mg(SH)_3^-$ are the smallest among all systems studied in this work (4.281 and 5.112 eV respectively, Table 1). This is consistent with our earlier observation considering the dependence of the VDE of the superhalogen anion on the strength of the corresponding HL acid (where L is an acidic functional group playing a ligand role). Hydrogen sulfide (H_2S) is the weakest acid among all nonoxoacids known in inorganic chemistry ($pK_a(H_2S) \approx 7$)[45] and thus the −SH functional groups might lead to lower VDE values when used as ligands in superhalogen anions.

4. Summary

The vertical electron detachment energies of superhalogens anions NaL_2^- and MgL_3^- (where L = $-ClO_4$, $-ClO_3$, $-ClO_2$, $-ClO$, $-NO_3$, $-PO_3$, $-H_2PO_4$, $-HSO_4$, $-HCO_3$, $-SH$) were calculated at the OVGF/-6-311++G(3df,3pd) level. On the basis of these results, we conclude as follows:

(i) Our best estimates of the vertical electron detachment energies (VDEs) are: 7.843 eV ($Na(ClO_4)_2^-$), 7.613 eV ($Na(PO_3)_2^-$), 7.318 ($Na(HSO_4)_2^-$), 6.783 $Na(HCO_3)_2^-$), 6.689 ($Na(NO_3)_2^-$), 6.264 ($Na(H_2PO_4)_2^-$), 6.650 ($Na(ClO_3)_2^-$), 4.982 ($Na(ClO)_2^-$), 4.747 ($Na(ClO_2)_2^-$), 4.281 ($Na(SH)_2^-$), 8.914 eV ($Mg(ClO_4)_3^-$), 8.676 eV ($Mg(PO_3)_3^-$), 8.606 ($Mg(HSO_4)_3^-$), 8.293 ($Mg(NO_3)_3^-$), 7.379 $Mg(HCO_3)_3^-$), 7.555 ($Mg(ClO_3)_3^-$), 7.234 ($Mg(H_2PO_4)_3^-$), 6.146 ($Mg(ClO)_3^-$), 5.298 ($Mg(ClO_2)_3^-$), and 5.112 ($Mg(SH)_3^-$).

(ii) All of the negatively charged species studied in this work have proven to possess electron binding energies exceeding 4.2 and approaching 9 eV. Therefore, their neutral parents may be viewed as potentially useful strong electron acceptors.

(iii) The superhalogen anions involving acidic functional groups as ligands exhibit the dependence of their VDEs on the strength of the underlying HL acids. The largest VDEs are found for the anions utilizing the ClO_4 ligands ($HClO_4$ is the strongest acid), whereas the smallest for the anions possessing SH groups (H_2S is the weakest acid originating from the ligands considered).

Therefore, we recommend using acidic functional groups as ligands in designing novel superhalogen anions. We believe that our conclusions (as well as the structures 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: VDEs (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 of the Supporting Information). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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