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Article

Halogenoids as Ligands in Superhalogen Anions

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The superhalogen compounds are of great importance in chemistry due to their enormously high electron affinities (approaching 13 eV). The utilizing halogenoids as ligands in the superhalogen anionic species is proposed and discussed on the basis of the *ab initio* outer valence Green function (OVGF) theoretical results. The representative species, such as LiX_2^-, NaX_2^-, BeX_3^-, MgX_3^-, CaX_3^-, BX_4^-, and AlX_4^- (where X stands for a halogenoid group), were designed and studied at the OVGF/6-311+G(3df)//MP2/6-311+G(d) level. It was found that the halogenoids (CN, NC, OCN, NCO, SCN, and NCS) might be used as ligands while designing novel superhalogen anions. The lowest and highest electron binding energies for the species considered were found for the $Na(NCS)_2^-$ (5.010 eV) and $Al(NC)_4^-$ (9.209 eV), respectively. The desired range of the electronic stability of the resulting species might be achieved by the proper choice of the central metal atom and the halogenoid ligand.

1. Introduction

Superhalogens are extraordinary inorganic compounds exhibiting enormously high electron affinities (spanning the 3.6–13 eV range)[1,2]. The existence of such species was predicted in 1981 by Boldyrev and Gutsev who employed theoretical chemistry methods to support their hypothesis[1]. Moreover, they introduced a simple formula for one class of superhalogens, MX_{k+1}, where M is a main group or transition metal atom, X is a halogen atom, and k is the maximal formal valence of the atom M. Since the early 1980s, many other theoretical efforts have been undertaken to estimate the vertical electron detachment energies (VDEs) of various anions having superhalogens as their neutral parents (see refs 3–11 and references cited therein). In 1999 dramatic progress was made in investigating superhalogen systems due to the joined theoretical and experimental effort that resulted in an excellent report comprising of the first experimental photoelectron spectra of superhalogens (measured by the Wang's group) together with their theoretical interpretations

provided by Boldyrev and Simons[12]. In particular, the photoelectron spectra of MX_2^- (where M = Li, Na, and X = Cl, Br, I) anions have been obtained and assigned on the basis of ab initio outer valence Green function (OVGF) calculations. An excellent agreement between experimentally and theoretically estimated values of VDEs has been achieved, and all the anions have proven to be superhalogen−based species since their electron binding energies were found to be greater than 3.62 eV (see ref 12). Since then, many other superhalogen anions have been proposed, examined experimentally, and characterized theoretically, e.g., MX_3^- (M = Be, Mg, Ca; X = Cl, Br)[13], the oxygen-based BO_2^-[14], MCl_4^- (M = Sc, Y, La)[15], and even larger species, such as $Na_xCl_{x+1}^-$ ($x = 1-4$)[16].

Exploring various new superhalogen species is primarily focused on studying larger molecular clusters which are capable of forming strongly bound anions. The purpose of these efforts is to provide reliable data and predictions considering the possible use of such compounds as electron acceptors in the production of organic superconductors as well as the role they can play in synthesis (e.g., in oxidation of counterpart systems with high ionization potentials).[17,18] However, we believe that the designing of new superhalogen species, albeit useful, should be more systematic and focused

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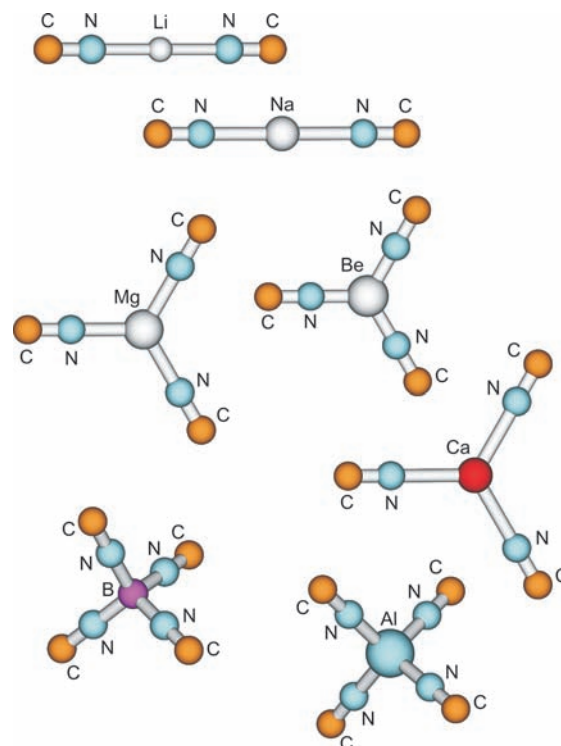(18) Wudl, F. *Acc. Chem. Res.* **1984**, *17*, 227–232.
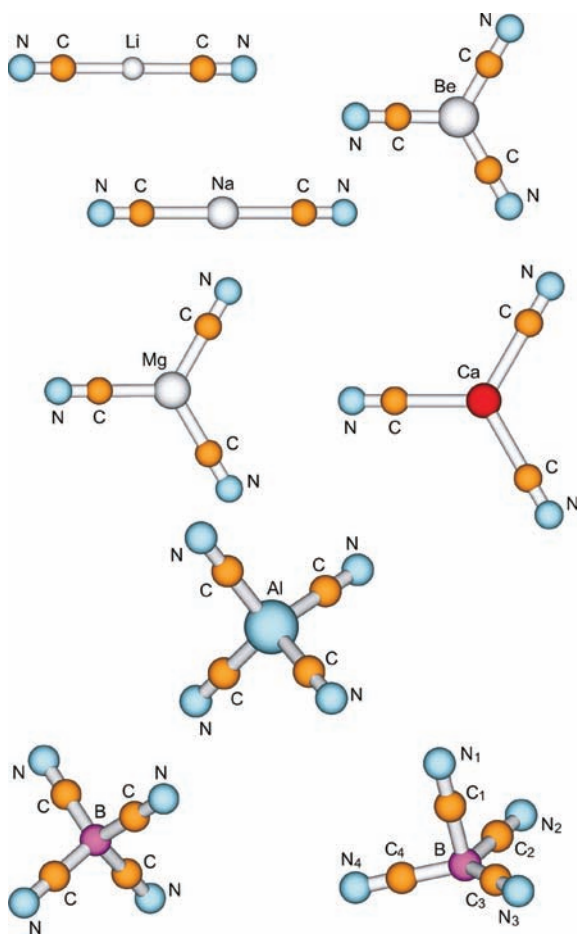
Figure 1. The equilibrium structures of the anionic superhalogen species containing the CN groups as ligands (obtained at the MP2/6-311+G(d) level).

Figure 2. The equilibrium structures of the anionic superhalogen species containing the NC groups as ligands (obtained at the MP2/6-311+G(d) level).

on certain classes of such systems. Therefore, we redirected our research into exploring more unusual superhalogens in which the central atom and/or halogen ligands are replaced with hydrogen atom and various functional groups, respectively. First of all, we reported our findings for HF_2^-, HCl_2^-, HBr_2^-, and $H_2F_3^-$ and proved that the hydrogen atom may play a central atom role in superhalogen anions.[19] Then, we considered species containing various ligands (such as NaX_2^-, where X = F, Cl, Br) and concluded that introducing various ligands into superhalogen anions reduces their electronic stabilities.[20]

Our main goal in this contribution is to point out that the presence of halogen atoms in superhalogen species is not necessary since the alternative ligands might be applied instead. Hence, we demonstrate that the halogen ligands (F, Cl, Br, I) might be replaced with the so-called halogenoids (e.g., CN, SCN, OCN), and the electronic stabilities of the resulting anions may even exceed those obtained with the VII main group elements. We believe that the vertical electron binding energies (characterizing the superhalogen anions) that 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.

2. Methods

Since our main goal was to estimate the electronic stability (i.e., the vertical electron detachment energies, VDE) for the LiX_2^-, NaX_2^-, BeX_3^-, MgX_3^-, CaX_3^-, BX_4^-, and AlX_4^- anions possessing halogenoids as ligands (X = CN, NC, OCN, NCO, SCN, NCS), we limited our geometry optimization calculations to the closed-shell anionic species for which we also obtained harmonic vibrational frequencies at their minimum energy structures. For this purpose we applied second-order Møller–Plesset (MP2) perturbational method with the 6-311+G(d) basis sets.[21,22] Providing reliable vertical electron detachment energies of the anions studied requires using more accurate treatment, thus we decided to perform *direct* calculations of the electron binding energies. A *direct* scheme was based on applying the outer valence Green function (OVGF) method.[23−27] The OVGF approximation remains valid only for outer valence ionizations for which the pole strengths (PSs) are greater than 0.80−0.85.[28] 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 0.89).

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Table 1. MP2 Geometrical Parameters and the OVGF/6-311+G(3df) Vertical Electron Detachment Energies (VDE) for the Superhalogen Anions Containing CN Groups As Ligands[a]

Li(CN)$_2^-$	(D$_{\infty h}$)	**VDE = 7.233 eV** (0.907)	
r(LiC) = 2.043 Å		r(CN) = 1.188 Å	
Na(CN)$_2^-$	(D$_{\infty h}$)	**VDE = 7.090 eV** (0.906)	
r(NaC) = 2.399 Å		r(CN) = 1.189 Å	
Be(CN)$_3^-$	(D$_{3h}$)	**VDE = 8.137 eV** (0.899)	
r(BeC) = 1.738 Å		r(CN) = 1.183 Å	∠(CBeC) = 120°
Mg(CN)$_3^-$	(D$_{3h}$)	**VDE = 8.244 eV** (0.900)	
r(MgC) = 2.134 Å		r(CN) = 1.185 Å	∠(CMgC) = 120°
Ca(CN)$_3^-$	(D$_{3h}$)	**VDE = 8.119 eV** (0.903)	
r(CaC) = 2.495 Å		r(CN) = 1.187 Å	∠(CCaC) = 120°
B(CN)$_4^-$	(T$_d$)	**VDE = 8.562 eV** (0.893)	
r(BC) = 1.594 Å		r(CN) = 1.179 Å	∠(CBC) = 109.471°
	(C$_{3v}$)	**VDE = 7.509 eV** (0.890)	
r(BC$_1$) = 1.609 Å		r(C$_1$N$_1$) = 1.181 Å	∠(C$_1$BC$_2$) = 90° ∠(C$_2$BC$_3$) = 120°
Al(CN)$_4^-$	(T$_d$)	**VDE = 8.942 eV** (0.895)	
r(AlC) = 1.975 Å		r(CN) = 1.182 Å	∠(CAlC) = 109.471°

[a] Pole strengths (PS) are given in parentheses.

Table 2. MP2 Geometrical Parameters and the OVGF/6-311+G(3df) Vertical Electron Detachment Energies (VDE) for the Superhalogen Anions Containing NC Groups As Ligands[a]

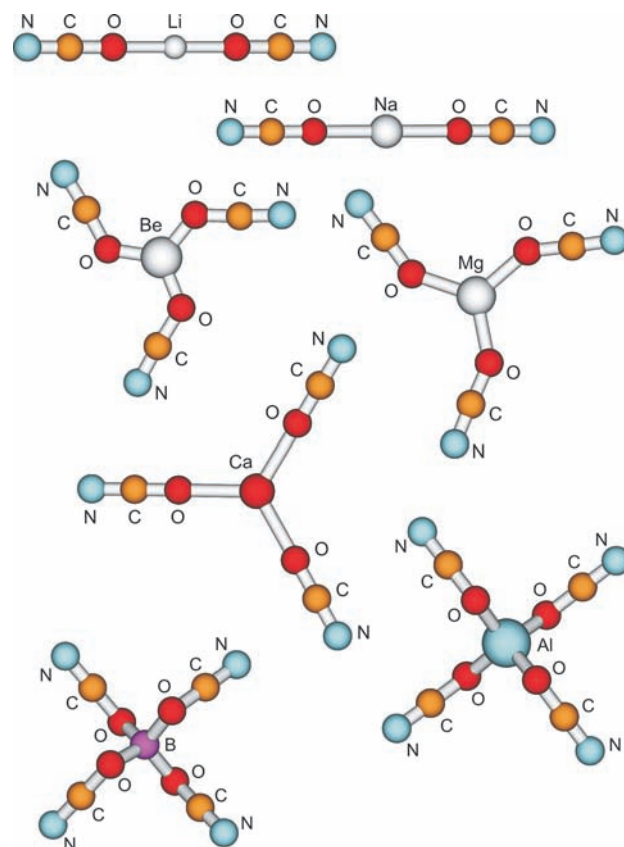|			
Li(NC)$_2^-$	(D$_{\infty h}$)	**VDE = 7.434 eV** (0.906)	
r(LiN) = 1.900 Å	r(NC) = 1.191 Å		
Na(NC)$_2^-$	(D$_{\infty h}$)	**VDE = 5.871 eV** (0.893)	
r(NaN) = 2.262 Å	r(NC) = 1.192 Å		
Be(NC)$_3^-$	(D$_{3h}$)	**VDE = 8.244 eV** (0.900)	
r(BeN) = 1.619 Å	r(NC) = 1.188 Å	∠(NBeN) = 120°	
Mg(NC)$_3^-$	(D$_{3h}$)	**VDE = 8.411 eV** (0.902)	
r(MgN) = 2.005 Å	r(NC) = 1.190 Å	∠(NMgN) = 120°	
Ca(NC)$_3^-$	(D$_{3h}$)	**VDE = 6.956 eV** (0.891)	
r(CaN) = 2.355 Å	r(NC) = 1.192 Å	∠(NCaN) = 120°	
B(NC)$_4^-$	(T$_d$)	**VDE = 8.826 eV** (0.902)	
r(BN) = 1.518 Å	r(NC) = 1.187 Å	∠(NBN) = 109.471°	
Al(NC)$_4^-$	(T$_d$)	**VDE = 9.209 eV** (0.899)	
r(AlN) = 1.853 Å	r(NC) = 1.189 Å	∠(NAlN) = 109.471°	

[a] Pole strengths (PS) are given in parentheses.

As far as the basis sets are concerned, we applied the 6-311+G(3df) basis sets[21,22] while estimating vertical electron detachment energies at various levels since analogous basis sets have been used by others for superhalogen anions and provided an excellent agreement between such calculated and experimentally measured VDEs.[10,12,16]

All calculations were performed with the Gaussian 03 program.[29]

3. Results

While exploring the possibility of using halogenoids as ligands in superhalogen anions we decided to focus on a few most extensively utilized in chemistry species, namely CN,

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Figure 3. The equilibrium structures of the anionic superhalogen species containing the OCN groups as ligands (obtained at the MP2/6-311+G(d) level).

OCN, and SCN as well as their isomers: NC, NCO, and NCS, respectively. Our choice of the halogenoids studied was dictated by their large electron affinities[30] and importance in chemical synthesis as well as their versatile applications. These illustrative applications cover their use in the production of polyurethanes,[31] a wide range of copolymers and abrasion-resistance polymers,[32] semiconductor

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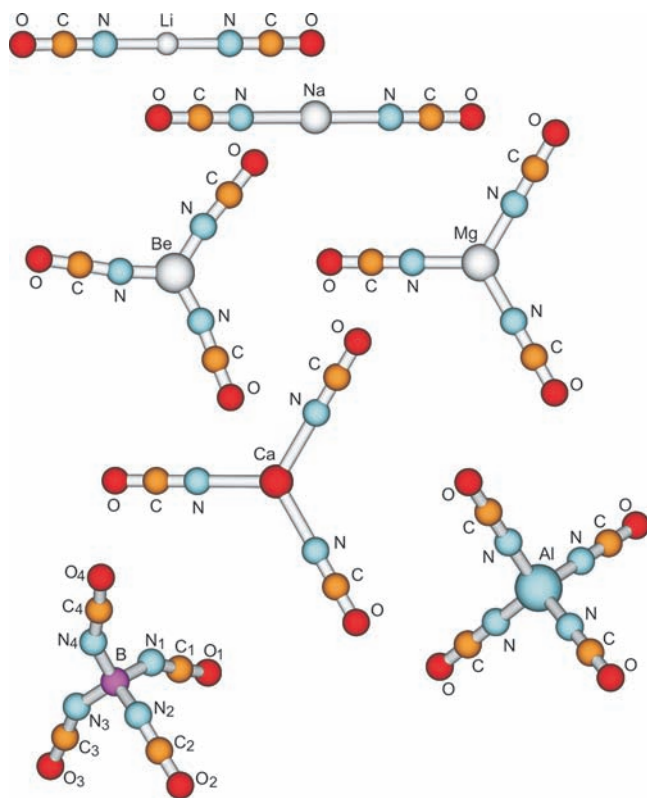
Figure 4. The equilibrium structures of the anionic superhalogen species containing the NCO groups as ligands (obtained at the MP2/6-311+G(d) level).

photoreceptors,[33] and solid polymer electrolytes.[34] It might also be useful to recall that the term *pseudohalogen* (halogenoid) was first introduced by Birckenbach in 1925[35] and further developed and justified in a series of papers.[36–38] According to the present knowledge, a small species can be classified as halogenoid when it fulfills certain criteria[39,40] with respect to a halogen-like chemical behavior, such as forming (i) strongly bound univalent radical, (ii) a singly charged anion, and (iii) a pseudohalogen-hydrogen acid, etc.

In the following sections we describe our results for several representative superhalogen anions LiX_2^-, NaX_2^-, BeX_3^-, MgX_3^-, CaX_3^-, BX_4^-, and AlX_4^- possessing halogenoids as ligands (X = CN, NC, OCN, NCO, SCN, NCS).

3.1. −CN and −NC Halogenoids As Ligands. The exploration of the potential energy surface (PES) of the anions possessing cyanide (−CN) and isocyanide (-NC) groups led to a series of minimum energy structures which are depicted in Figures 1 and 2. The corresponding geometrical parameters are gathered in Tables 1 and 2,

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while harmonic vibrational frequencies are provided in the Supporting Information (Tables S1 and S2) . We located only one minimum energy structure for each of the species studied except $B(CN)_4^-$ for which two stable isomers were found.

The anions containing I A group central atoms (Li and Na) are $D_{\infty h}$-symmetry linear species which is rather typical for superhalogen anions in which an alkali metal atom plays a central atom role [12,20]. The carbon−nitrogen separation in $M(CN)_2^-$ and $M(NC)_2^-$ (where M = Li, Na) spans the 1.188−1.192 Å range which is only slightly larger than the C−N bond length found for the CN^- anion (1.1862 Å [41]). This observation remains valid also for the anions having Be, Mg, Ca, B, and Al central atoms and CN (or NC) ligands. Indeed, the C−N distance is never larger than 1.192 Å (see Tables 1 and 2) which indicates that the anions studied can unquestionably be considered as the species consisting of CN (or NC) functional groups bound to a metal atom.

The alkaline earth metal atoms (Be, Mg, Ca) form planar triangular D_{3h}-symmetry negatively charged structures with the CN and NC ligands, see Figures 1 and 2. The anions containing III A group elements are tetrahedral (T_d-symmetry). However, in the case of $B(CN)_4^-$, two minimum energy structures were found: one tetrahedral (global minimum) and another one possessing C_{3v}-symmetry (see the bottom left and right part of the Figure 1, respectively). The latter $B(CN)_4^-$ structure is significantly higher in energy (by 34 kcal/mol) than the former so one should not expect its presence in the bulk (while at room temperature).

The vertical electron detachment energies calculated for the anions having CN or NC groups as ligands are very large. The CN ligands lead to the species with the VDEs in the ca. 7.1−8.9 eV range with the smallest (7.090 eV) value for the $Na(CN)_2^-$ and the largest (8.942 eV) for the $Al(CN)_4^-$ anion, see Table 1. It should also be noticed that the electronic stability of these superhalogen anions increases with the increasing number of the electronegative CN ligands. Similar behavior we observe for the anions in which the NC groups play ligand role. Namely, the superhalogen anions with the NC groups are characterized by the VDEs in the 7.4−9.2 eV range, except the $Na(NC)_4^-$ for which we predict the electronic stability of 5.871 eV, see Table 2. The VDEs of the anions possessing the NC ligands also grow with the increasing number of the strongly electronegative isocyanide groups (with the exception of the $Ca(NC)_3^-$), as it was observed in the case of the $M(CN)_n^-$ (M = Li, Na, Be, Mg, Ca, B, Al; n = 2−4), and the largest vertical electron binding energy (exceeding 9 eV) corresponds to the $Al(NC)_4^-$ (9.209 eV, see Table 2).

The results that we demonstrate in this section lead us to the conclusion that the use of the CN and NC functional groups as ligands while designing novel superhalogen anions is very promising and should allow for obtaining the chemical species having very large electronic stabilities (approximately spanning the 7−9 eV range).

3.2. −OCN and −NCO Halogenoids As Ligands. The minimum energy structures that we found for

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Table 3. MP2 Geometrical Parameters and the OVGF/6-311+G(3df) Vertical Electron Detachment Energies (VDE) for the Superhalogen Anions Containing OCN Groups As Ligands[a]

Li(OCN)$_2$$^-$	(D$_{\infty h}$)	**VDE = 6.070 eV** (0.907)		
r(LiO) = 1.756 Å		r(OC) = 1.247 Å	r(CN) = 1.193 Å	
Na(OCN)$_2$$^-$	(D$_{\infty h}$)	**VDE = 5.849 eV** (0.908)		
r(NaO) = 2.131 Å		r(OC) = 1.246 Å	r(CN) = 1.195 Å	
Be(OCN)$_3$$^-$	(C$_{3h}$)	**VDE = 7.423 eV** (0.905)		
r(BeO) = 1.538 Å		r(OC) = 1.271 Å	r(CN) = 1.184 Å	∠(OBeO) = 120°
∠(BeOC) = 127.012°		∠(OCN) = 177.047°		
Mg(OCN)$_3$$^-$	(C$_{3h}$)	**VDE = 7.333 eV** (0.906)		
r(MgO) = 1.900 Å		r(OC) = 1.260 Å	r(CN) = 1.187 Å	∠(OMgO) = 120°
∠(MgOC) = 145.252°		∠(OCN) = 178.612°		
Ca(OCN)$_3$$^-$	(D$_{3h}$)	**VDE = 6.961 eV** (0.905)		
r(CaO) = 2.191 Å		r(OC) = 1.231 Å	r(CN) = 1.190 Å	∠(OCaO) = 120°
B(OCN)$_4$$^-$	(D$_{2d}$)	**VDE = 8.083 eV** (0.903)		
r(BO) = 1.470 Å		r(OC) = 1.285 Å	r(CN) = 1.181 Å	∠(OBO) = 113.201°
∠(BOC) = 118.339°		∠(OCN) = 176.622°		
Al(OCN)$_4$$^-$	(D$_{2d}$)	**VDE = 8.237 eV** (0.905)		
r(AlO) = 1.771 Å		r(OC) = 1.275 Å	r(CN) = 1.182 Å	∠(OAlO) = 107.410°
∠(AlOC) = 131.726°		∠(OCN) = 177.728°		

[a] Pole strengths (PS) are given in parentheses.

Table 4. MP2 Geometrical Parameters and the OVGF/6-311+G(3df) Vertical Electron Detachment Energies (VDE) for the Superhalogen Anions Containing NCO Groups As Ligands[a]

Li(NCO)$_2$$^-$	(D$_{\infty h}$)	**VDE = 5.747 eV** (0.904)		
r(LiN) = 1.864 Å		r(NC) = 1.205 Å	r(CO) = 1.212 Å	
Na(NCO)$_2$$^-$	(D$_{\infty h}$)	**VDE = 5.619 eV** (0.907)		
r(NaN) = 2.228 Å		r(NC) = 1.206 Å	r(CO) = 1.214 Å	
Be(NCO)$_3$$^-$	(C$_{3h}$)	**VDE = 6.342 eV** (0.898)		
r(BeN) = 1.605 Å		r(NC) = 1.200 Å	r(CO) = 1.200 Å	∠(NBeN) = 120°
∠(BeNC) = 172.534°		∠(NCO) = 179.000°		
Mg(NCO)$_3$$^-$	(D$_{3h}$)	**VDE = 6.578 eV** (0.900)		
r(MgN) = 1.977 Å		r(NC) = 1.204 Å	r(CO) = 1.201 Å	∠(NMgN) = 120°
Ca(NCO)$_3$$^-$	(D$_{3h}$)	**VDE = 6.517 eV** (0.902)		
r(CaN) = 2.325 Å		r(NC) = 1.209 Å	r(CO) = 1.203 Å	∠(NCaN) = 120°
B(NCO)$_4$$^-$	(C$_s$)	**VDE = 6.561 eV** (0.898)		
r(BN$_1$) = 1.527 Å	r(BN$_2$) = 1.527 Å	r(BN$_3$) = 1.523 Å	r(BN$_4$) = 1.520 Å	
r(N$_1$C$_1$) = 1.203 Å	r(N$_2$C$_2$) = 1.203 Å	r(N$_3$C$_3$) = 1.202 Å	r(N$_4$C$_4$) = 1.202 Å	
r(C$_1$O$_1$) = 1.194 Å	r(C$_2$O$_2$) = 1.194 Å	r(C$_3$O$_3$) = 1.195 Å	r(C$_4$O$_4$) = 1.194 Å	
∠(N$_1$BN$_2$) = 109.749°	∠(N$_2$BN$_3$) = 110.112°	∠(N$_3$BN$_4$) = 108.371°	∠(N$_1$BN$_4$) = 109.234°	
∠(BN$_1$C$_1$) = 148.966°	∠(BN$_2$C$_2$) = 148.966°	∠(BN$_3$C$_3$) = 149.370°	∠(BN$_4$C$_4$) = 147.593°	
∠(N$_1$C$_1$O$_1$) = 175.495°	∠(N$_2$C$_2$O$_2$) = 175.495°	∠(N$_3$C$_3$O$_3$) = 175.434°	∠(N$_4$C$_4$O$_4$) = 175.179°	
∠(BN$_1$C$_1$O$_1$) = −179.910°	∠(BN$_2$C$_2$O$_2$) = 179.910°	∠(BN$_3$C$_3$O$_3$) = −180°	∠(BO$_4$C$_4$N$_4$) = 180°	
∠(N$_3$BN$_2$N$_1$) = 121.368°	∠(N$_4$BN$_3$N$_1$) = 119.424°			
Al(NCO)$_4$$^-$	(D$_{2d}$)	**VDE = 7.107 eV** (0.897)		
r(AlN) = 1.833 Å		r(NC) = 1.201 Å	r(CO) = 1.194 Å	∠(NAlN) = 109.498°
∠(AlNC) = 174.907°		∠(NCO) = 179.365°		

[a] Pole strengths (PS) are given in parentheses.

Li(OCN)$_2$$^-$, Na(OCN)$_2$$^-$, Li(NCO)$_2$$^-$, and Na(NCO)$_2$$^-$ are linear, see Figures 3 and 4. The corresponding bond lengths are gathered in Tables 3 and 4, while the harmonic vibrational frequencies are collected in Tables S3 and S4 (provided in the Supporting Information). The exploration of the PES for the anionic BeX$_3$$^-$, MgX$_3$$^-$, and CaX$_3$$^-$ (X = OCN, NCO), however, does not resemble the situation we observed for the superhalogen anions with the CN and NC ligands (see the preceding section). Only the structures of the Ca(OCN)$_3$$^-$, Mg(NCO)$_3$$^-$, and Ca(NCO)$_3$$^-$ are perfectly triangular (D$_{3h}$-symmetry) while the remaining MX$_3$$^-$ (M = Be, Mg; X = OCN, NCO) anions possess lower symmetry (C$_{3h}$). As it can be seen in Figure 3 the OCN ligands in Be(OCN)$_3$$^-$ and Mg(OCN)$_3$$^-$ are localized in a bent manner around the central atoms while in the case of Be(NCO)$_3$$^-$ the structure seems almost triangular (the deformations breaking the D$_{3h}$-symmetry are very small, see Table 4 and Figure 4). The anions containing B and Al as central atoms and four OCN or NCO ligands possess D$_{2d}$-symmetry with the exception of the B(NCO)$_4$$^-$ which

is of C$_S$-symmetry (see Figures 3 and 4). Such a situation is quite different than that observed for the species containing CN and NC ligands for which all the most stable species of MX$_4$$^-$ type (M = B, Al) were found tetrahedral.

It should also be noted that the OCN and NCO ligands remain linear or pseudolinear when built into the superhalogen anions studied. Indeed, the cyanate and isocyanate groups are perfectly linear in Li(OCN)$_2$$^-$, Na(OCN)$_2$$^-$, Li(NCO)$_2$$^-$, Na(NCO)$_2$$^-$, Ca(OCN)$_3$$^-$, Mg(NCO)$_3$$^-$, and Ca(NCO)$_3$$^-$. The deviations from linearity in the remaining anions, however, are relatively small and not exceeding 4° (see the OCN and NCO valence angles collected in Tables 3 and 4) which is consistent with the linear (or quasi-linear) shape of these functional groups reported by Leung and Streitwieser [42].

The vertical electron detachment energies calculated for the superhalogen anions with the cyanate and

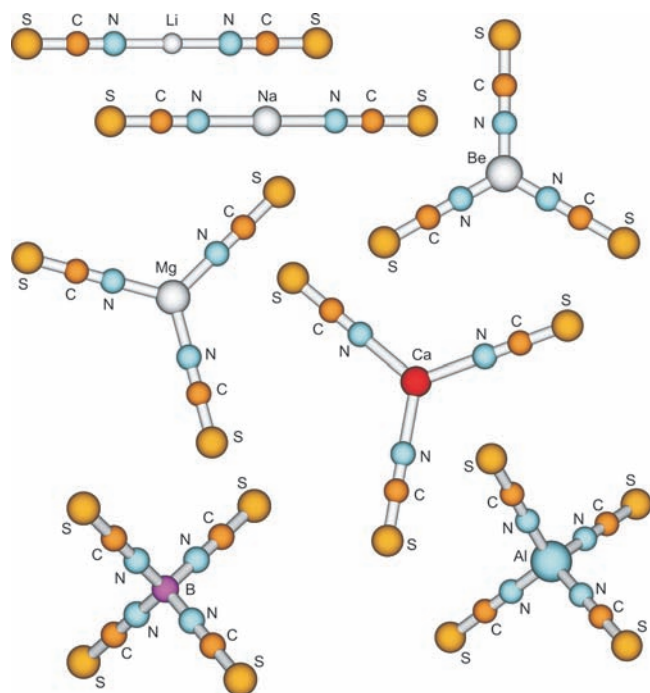(42) Leung, S. S.-W.; Streitwieser, A. *J. Comput. Chem.* **1998,** *19,* 1325–1336.
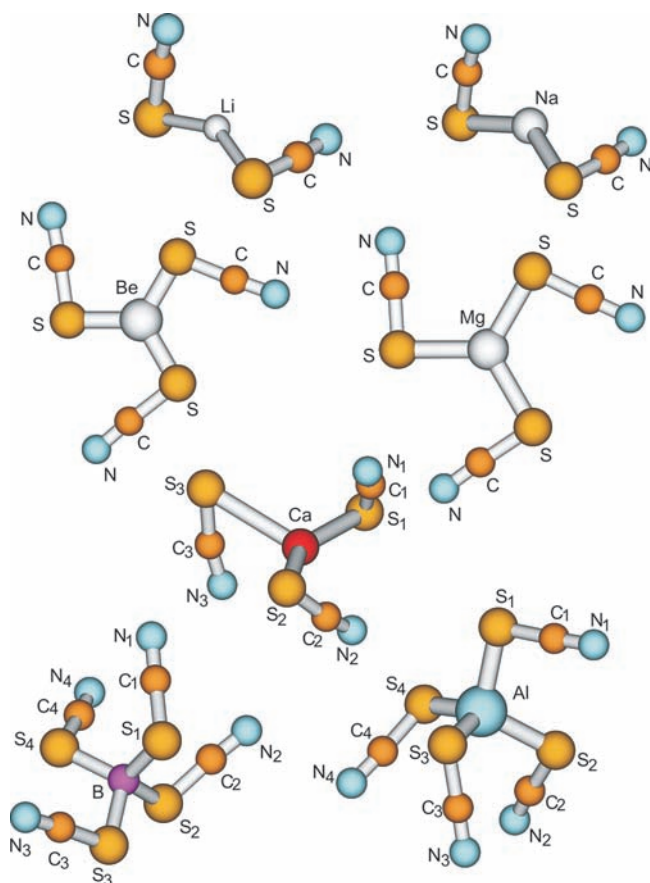
Figure 5. The equilibrium structures of the anionic superhalogen species containing the SCN groups as ligands (obtained at the MP2/6-311+G(d) level).

isocyanate ligands are gathered in Tables 3 and 4. The VDEs for the anions possessing the OCN groups as ligands span the 5.8−8.2 eV range with the largest value of 8.237 eV found for $Al(OCN)_4{}^-$ and the smallest (5.849 eV) for $Na(OCN)_2{}^-$. A very similar situation we observe for the species containing NCO ligands whose VDEs we calculated to be in the 5.6−7.1 eV range. Again, the largest VDE value corresponds to the anion containing the aluminum as a central atom (7.107 eV), while the smallest electronic stability was found for the species containing sodium (5.619 eV, see Table 4). One should also note that the VDE for the $MX_n{}^-$ (M = Li, Na, Be, Mg, Ca; X = OCN, NCO; n = 2−4) usually grows with the increasing number of the ligands which is justified by the electronegative character of the cyanate and isocyanate groups.

The results we demonstrate for the species containing OCN and NCO groups as ligands lead to the conclusion that these groups allow for designing the superhalogen anions with the VDEs in the 5−8 eV range.

3.3. −SCN and −NCS Halogenoids As Ligands. The exploration of the PES of the anionic $M(SCN)_n{}^-$ and $M(NCS)_n{}^-$ (where M = Li, Na, Be, Mg, Ca, B, Al; n = 2−4) led to the minimum energy structures depicted in Figures 5 and 6. The corresponding geometrical parameters for these structures are collected in Tables 5 and 6, while the harmonic vibrational frequencies are gathered in Tables S5 and S6 (provided in the Supporting Information). The general observation is that the anions

Figure 6. The equilibrium structures of the anionic superhalogen species containing the NCS groups as ligands (obtained at the MP2/6-311+G(d) level).

possessing isothiocyanate NCS groups are more symmetrical than those with the thiocyanate SCN groups. Indeed, the anions containing Li and Na are $D_{\infty h}$-symmetry linear species when the NCS groups are used as ligands, while those with the SCN groups are of C_2-symmetry. The anions in which the II A element (Be, Mg, Ca) plays a central atom role (i.e., $Be(NCS)_3{}^-$, $Mg(NCS)_3{}^-$, $Ca(NCS)_3{}^-$) are perfectly triangular (D_{3h}-symmetry) with the NCS ligands (see Figure 6 and Table 6). By contrast, their corresponding species utilizing the SCN groups as ligands are either planar C_{3h}-symmetry structures (($Be(SCN)_3{}^-$, $Mg(SCN)_3{}^-$) or nonplanar asymmetrical ($Ca(SCN)_3{}^-$). Similar situations we observe while comparing $B(NCS)_4{}^-$ and $Al(NCS)_4{}^-$ with $B(SCN)_4{}^-$ and $Al(SCN)_4{}^-$; the anions utilizing isothiocyanate ligands are tetrahedral (T_d), while those with the SCN groups are strongly deformed structures with no symmetry elements.

Our calculations indicate that the linear geometry of NCS group is preferred when it is built into the super-halogen anionic structure. However, as pointed out by Oláh et al. [43] and Veszprémi et al. [44], the SCN group itself usually prefers bent structure. Indeed, the S−C−N valence angle we found for the anionic species studied in this contribution was never equal to 180° (see Table 5). Namely, the deviations from the linearity we observed were in the 2−13° range with the largest corresponding to the $Ca(SCN)_3{}^-$ anion in which the SCN valence angles of ca. 167° were found.

The vertical electron detachment energies that we calculated for the anions containing the SCN ligands

(43) Oláh, J.; Van Alsenoy, C.; Veszprémi, T. *J. Phys. Chem. A* **2004**, *108*, 8400–8406.

(44) Veszprémi, T.; Pasinszki, T.; Fehér, M. *J. Am. Chem. Soc.* **1994**, *116*, 6303–6306.

Table 5. MP2 Geometrical Parameters and the OVGF/6-311+G(3df) Vertical Electron Detachment Energies (VDE) for the Superhalogen Anions Containing SCN Groups As Ligands[a]

Li(SCN)₂⁻ (C₂)	**VDE = 5.215 eV** (0.898)		
r(LiS) = 2.355 Å	r(SC) = 1.664 Å	r(CN) = 1.195 Å	∠(LiSC) = 65.451°
∠(SCN) = 172.310°	∠(LiSCN) = −1.237°		
Na(SCN)₂⁻ (C₂)	**VDE = 5.176 eV** (0.899)		
r(NaS) = 2.823 Å	r(SC) = 1.657 Å	r(CN) = 1.197 Å	∠(NaSC) = 61.396°
∠(SCN) = 171.820°	∠(NaSCN) = −0.805°		
Be(SCN)₃⁻ (C₃ₕ)	**VDE = 6.195 eV** (0.894)		
r(BeS) = 2.002 Å	r(SC) = 1.688 Å	r(CN) = 1.185 Å	∠(SBeS) = 120°
∠(BeSC) = 98.146°	∠(SCN) = 177.489°		
Mg(SCN)₃⁻ (C₃ₕ)	**VDE = 6.314 eV** (0.894)		
r(MgS) = 2.388 Å	r(SC) = 1.685 Å	r(CN) = 1.186 Å	∠(SMgS) = 120°
∠(MgSC) = 93.626°	∠(SCN) = 178.206°		
Ca(SCN)₃⁻ (C₁)	**VDE = 5.840 eV** (0.895)		
r(CaS₁) = 2.967 Å	r(CaS₂) = 2.967 Å	r(CaS₃) = 2.971 Å	r(S₁C₁) = 1.649 Å
r(S₂C₂) = 1.648 Å	r(S₃C₃) = 1.648 Å	r(C₁N₁) = 1.203 Å	r(C₂N₂) = 1.203 Å
r(C₃N₃) = 1.203 Å	∠(S₁CaS₂) = 152.052°	∠(S₂CaS₃) = 99.698°	∠(S₃CaS₄) = 104.809°
∠(CaS₁C₁) = 61.335°	∠(CaS₂C₂) = 61.421°	∠(CaS₃C₃) = 61.130°	∠(S₁C₁N₁) = 166.929°
∠(S₂C₂N₂) = 166.886°	∠(S₃C₃N₃) = 166.901°	∠(CaS₁C₁N₁) = −0.031°	∠(CaS₂C₂N₂) = 0.056°
∠(CaS₃C₃N₃) = −0.369°	∠(S₁CaS₃) = 151.089°		
B(SCN)₄⁻ (C₁)	**VDE = 6.000 eV** (0.893)		
r(BS₁) = 1.916 Å	r(BS₂) = 1.935 Å	r(BS₃) = 1.935 Å	r(BS₄) = 1.930 Å
r(S₁C₁) = 1.690 Å	r(S₂C₂) = 1.687 Å	r(S₃C₃) = 1.692 Å	r(S₄C₄) = 1.688 Å
r(C₁N₁) = 1.183 Å	r(C₂N₂) = 1.184 Å	r(C₃N₃) = 1.184 Å	r(C₄N₄) = 1.184 Å
∠(S₁BS₂) = 114.799°	∠(S₂BS₃) = 100.361°	∠(S₃BS₄) = 109.169°	∠(S₁BS₄) = 113.522°
∠(BS₁C₁) = 101.207°	∠(BS₂C₂) = 101.861°	∠(BS₃C₃) = 100.197°	∠(BS₄C₄) = 100.079°
∠(S₁C₁N₁) = 175.278°	∠(S₂C₂N₂) = 174.941°	∠(S₃C₃N₃) = 176.654°	∠(S₄C₄N₄) = 175.351°
∠(BS₁C₁N₁) = 153.560°	∠(BS₂C₂N₂) = 168.689°	∠(BS₃C₃N₃) = 177.093°	∠(BS₄C₄N₄) = 156.206°
∠(S₃BS₂S₁) = -112.453°	∠(S₄BS₃S₁) = -122.280°		
Al(SCN)₄⁻ (C₁)	**VDE = 6.511 eV** (0.891)		
r(AlS₁) = 2.275 Å	r(AlS₂) = 2.260 Å	r(AlS₃) = 2.253 Å	r(AlS₄) = 2.263 Å
r(S₁C₁) = 1.688 Å	r(S₂C₂) = 1.690 Å	r(S₃C₃) = 1.690 Å	r(S₄C₄) = 1.688 Å
r(C₁N₁) = 1.184 Å	r(C₂N₂) = 1.184 Å	r(C₃N₃) = 1.184 Å	r(C₄N₄) = 1.184 Å
∠(S₁AlS₂) = 108.574°	∠(S₂AlS₃) = 112.468°	∠(S₃AlS₄) = 113.934°	∠(S₁AlS₄) = 101.646°
∠(AlS₁C₁) = 95.649°	∠(AlS₂C₂) = 97.037°	∠(AlS₃C₃) = 97.463°	∠(AlS₄C₄) = 99.173°
∠(S₁C₁N₁) = 178.215°	∠(S₂C₂N₂) = 176.076°	∠(S₃C₃N₃) = 176.655°	∠(S₄C₄N₄) = 176.074°
∠(AlS₁C₁N₁) = 163.133°	∠(AlS₂C₂N₂) = 161.967°	∠(AlS₃C₃N₃) = 160.072°	
∠(AlS₄C₄N₄) = 164.049°	∠(S₃AlS₂S₁) = −117.056°	∠(S₄AlS₃S₁) = −110.955°	

[a] Pole strengths (PS) are given in parentheses.

Table 6. MP2 Geometrical Parameters and the OVGF/6-311+G(3df) Vertical Electron Detachment Energies (VDE) for the Superhalogen Anions Containing NCS Groups As Ligands[a]

Li(NCS)₂⁻ (D∞ₕ)	**VDE = 5.113 eV** (0.897)		
r(LiN) = 1.879 Å	r(NC) = 1.197 Å	r(CS) = 1.626 Å	
Na(NCS)₂⁻ (D∞ₕ)	**VDE = 5.010 eV** (0.898)		
r(NaN) = 2.245 Å	r(NC) = 1.198 Å	r(CS) = 1.631 Å	
Be(NCS)₃⁻ (D₃ₕ)	**VDE = 5.702 eV** (0.891)		
r(BeN) = 1.604 Å	r(NC) = 1.197 Å	r(CS) = 1.604 Å	∠(NBeN) = 120°
Mg(NCS)₃⁻ (D₃ₕ)	**VDE = 5.833 eV** (0.893)		
r(MgN) = 1.985 Å	r(NC) = 1.200 Å	r(CS) = 1.608 Å	∠(NMgN) = 120°
Ca(NCS)₃⁻ (D₃ₕ)	**VDE = 5.782 eV** (0.894)		
r(CaN) = 2.340 Å	r(NC) = 1.203 Å	r(CS) = 1.612 Å	∠(NCaN) = 120°
B(NCS)₄⁻ (Tᵈ)	**VDE = 6.009 eV** (0.890)		
r(BN) = 1.509 Å	r(NC) = 1.194 Å	r(CS) = 1.596 Å	∠(NBN) = 109.471°
Al(NCS)₄⁻ (Tᵈ)	**VDE = 6.260 eV** (0.890)		
r(AlN) = 1.834 Å	r(NC) = 1.200 Å	r(CS) = 1.594 Å	∠(NAlN) = 109.471°

[a] Pole strengths (PS) are given in parentheses.

are in the 5.2−6.5 eV range, while those for the negatively charged species with the NCS ligands span the 5.0−6.3 eV range (see Tables 5 and 6). Similarly to the results we obtained for the CN, NC, OCN, and NCO ligands, the largest VDEs were found for the anions with the aluminum central atom (6.511 eV for Al(SCN)₄⁻ and 6.260 eV for Al(NCS)₄⁻). Again, the larger number of the ligands the larger electronic stability of the anion (which is caused by the collective effects described by Boldyrev and Gutsev, see refs 1 and 3). Also, one may notice that the VDE range that can be obtained by designing the superhalogen ligands using thiocyanate

and isothiocyanate groups is narrower than with the CN (NC) or OCN (NCO) ligands (see previous sections for comparison).

4. Summary and Conclusions

The anionic species LiX₂⁻, NaX₂⁻, BeX₃⁻, MgX₃⁻, CaX₃⁻, BX₄⁻, and AlX₄⁻ (where X = CN, NC, OCN, NCO, SCN, NCS) were studied using *ab initio* methods, and their vertical electron detachment energies were calculated at the OVGF/6-311+G(3df) level.

The VDEs that we obtained strongly depend on the type of the ligand and central atom used. Namely, the use of the CN

and NC ligands leads to very large electronic stabilities of the resulting anions (approximately spanning the 7−9 eV range), while utilizing the OCN and NCO groups as ligands allows for obtaining the anionic species with the electron binding energies in the 5−8 eV range. In this comparison, the SCN and NCS ligands seem much 'weaker' in a sense that the resulting anions are less electronically stable (although re-main 'strongly bound anions' in a conventional meaning) and their VDEs span the 5.0−6.5 eV range. The trend in the VDEs of the resulting superhalogen anions can be related to the electron binding energies of the pure ligands. Indeed, the CN molecule is the strongest electron acceptor (among the ligands considered) and binds an excess electron by 3.862 ± 0.004 eV.[45] The electron affinities of the NCO and NCS species are smaller (3.609 ± 0.005 and 3.537 ± 0.005 eV, respectively[45]) which is consistent with our estimates of the electron binding energies of the superhalogen anions utilizing these molecules as ligands.

As indicated by our results, the VDE range one can obtain utilizing the SCN (or NCS) groups as ligands in superhalogen anions is narrower than that available when the CN (NC) or OCN (NCO) ligands are used. Also, the geometrical struc-tures of the anionic M(SCN)$_n$ (M = Li,Na,Be,Mg,Ca,B,Al; n = 2−4) are expected to be much more complex than those with CN, NC, OCN, or NCO groups. The relative simplicity of the geometrical structures of the superhalogen anions involving the CN (NC) ligands comparing to those with the OCN and SCN groups might be related to the symmetry and nature of the highest occupied molecular orbital (HOMO)

for the isolated ligands. Indeed, the HOMO for CN is of σ-symmetry, while the highest occupied MOs for the pure OCN and SCN are π-symmetry orbitals. In addition, in the SCN molecule, the lone pair of S is located perpendi-cular to the molecular axis of SCN which causes the bent structure.[45]

The most strongly bound anions we found using halogen-oids as ligands are those with the aluminum playing a central atom role. Hence, the largest vertical electron detachment energies reported in this contribution (approaching or even exceeding 9 eV) correspond to Al(CN)$_4{}^-$ and Al(NC)$_4{}^-$ (8.942 and 9.209 eV, respectively).

The general conclusion that can be derived from our results is that the halogenoids may play the ligand role in the superhalogen anions. More specifically, the use of such halogenoids as CN, NC, OCN, NCO, SCN, and NCS instead of much more commonly utilized halogen atoms (F, Cl, Br) should be feasible and promising while designing the novel superhalogen anions since the desired range of the electronic stability might be achieved (by the proper choice of the central metal atom and the type of the ligand).

Supporting Information Available: Tables containing non-scaled harmonic vibrational frequencies calculated for all the anionic species (Tables S1−S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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