Competition between chalcogen bond and halogen bond interactions in $\text{YOX}_4: \text{NH}_3$ ($\text{Y} = \text{S, Se}; \text{X} = \text{F, Cl, Br}$) complexes: An ab initio investigation

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Abstract Using ab initio calculations, the geometries, interaction energies and bonding properties of chalcogen bond and halogen bond interactions between $\text{YOX}_4$ ($\text{Y} = \text{S, Se}; \text{X} = \text{F, Cl, Br}$) and $\text{NH}_3$ molecules are studied. These binary complexes are formed through the interaction of a positive electrostatic potential region ($\sigma$-hole) on the $\text{YOX}_4$ with the negative region in the $\text{NH}_3$. The ab initio calculations are carried out at the MP2/aug-cc-pVTZ level, through analysis of molecular electrostatic potentials, quantum theory of atoms in molecules and natural bond orbital methods. Our results indicate that even though the chalcogen and halogen bonds are mainly dominated by electrostatic effects, but the polarization and dispersion effects also make important contributions to the total interaction energy of these complexes. The examination of interaction energies suggests that the chalcogen bond is always favored over the halogen bond for all of the binary $\text{YOX}_4: \text{NH}_3$ complexes.

Keywords Halogen bond · Chalcogen bond · Electrostatic potential · Ab initio · Competition

Introduction

Characterization and proper understanding of the nature of noncovalent interactions are very important as they play critical roles in various fields of chemistry and biochemistry [1]. Noncovalent interactions are responsible for the formation, stability and biological activity of many macromolecules in living systems. A detailed comprehension of the noncovalent interactions is also of great importance for aiding self-assembly synthesis and new drugs design as well as for understanding molecular cluster formation [2–4]. Of the various noncovalent interactions, the hydrogen bond (HB) is perhaps the most widely studied and best understood case. It is generally formulated as $\text{A-H} \cdots \text{Z}$ interaction, in which the H atom of the Lewis acid, A-H, acts as a bridge to an electron-rich site of the Lewis base (Z). Besides the HB, there are also other important noncovalent interactions. Halogen bond [5–9] is an important noncovalent interaction analogues to the HB, in which a halogen atom serves a similar function as bridge between two molecules. This is very surprising since covalently bonded halogen atoms are usually negatively charged and thus would not be expected to interact attractively with other negative site. However, a detailed analysis of the electrostatic potential around the halogen atoms indicates the existence of an electron-deficient region, called as “$\sigma$-hole” [10–20], directed toward the electron donor. The presence or absence and the magnitude of a $\sigma$-hole depend upon several factors, including the polarizability and electronegativity of the halogen atom and the electron-withdrawing ability of the remainder of the molecule. For a given negative site, the strength of halogen bond interactions usually correlate linearly with the magnitude of the $\sigma$-hole potential on the halogen atom and more polarizable halogens (Br and I) tend to form
stronger halogen bonds than less polarizable ones (F and Cl). Halogen bonds interactions have been studied both theoretically [21–25] and experimentally [26–29] and their potential applications in various fields of supramolecular chemistry and biochemistry have increasingly been recognized in recent years.

Work over the years has shown that the σ-hole concept is not limited only to halogen atoms and can be also extended to the covalently bonded groups 14–16 atoms [11, 18–20, 30, 31]. For example, there are numerous evidences that indicate the Group 16 atoms (chalcogen group) are able to form σ-hole bond interaction with potential electron donors [32–38]. The resulting “chalcogen bond” is highly directional and is comparable in strength to that of the HB. The tendency to form chalcogen bonds with Lewis bases increases in the order of O < S < Se < Te. Due to its high electronegativity and less polarizability, the oxygen rarely participates in the formation of chalcogen bonds [11]. Like halogen bonds, chalcogen bonds share fundamental characteristics with the HB. For example, while the stability of the chalcogen bonding is mainly due to the electrostatic effects [39, 40], but the polarization, charge transfer and dispersion effects have also significant contributions [41–44]. The strength of chalcogen bonds can be tuned by substitution effects [34, 45], i.e., an electron-withdrawing group in the chalcogen donor tends to increase the strength of the chalcogen bond. And finally, they show synergic or cooperative effects with itself [46] and other types of interactions [47–49].

When two or more noncovalent interactions coexist in a complex, they will compete with each other. For example, Alkorta and coworkers [50] investigated the competition between the hydrogen bond and halogen bond in complexes of hypohalous acids with nitrogen bases (NH₃, N₂, and NCH). Their results demonstrated that both types of interactions can compete with each other and the electrostatic effects are of importance in mutual influence of the two interactions. Our recent study [51] indicated that halogen and pnictogen bonds interactions can compete with each other in 1:1 and 1:2 complexes of YOF₂X (X = F, Cl, Br, I; Y = P, As) with ammonia.

The aim of the present study was to investigate the competition between the chalcogen and halogen bonds interactions. We selected YOX₄ (Y = S, Se; X = F, Cl, Br) as the Lewis acid to interact with NH₃. Particular attention is paid to study the geometry, interaction energy and the nature of the halogen or chalcogen bonds interactions in the binary YOX₄:NH₃ complexes. The results of the present study may be important for the extension and future applications of the σ-hole bonds as a useful tool for design and synthesis of supramolecular systems with desired properties.

### Computational details

Full geometry optimizations and the corresponding harmonic frequency calculations were carried out at MP2/aug-cc-pVTZ level of theory using the Gaussian 09 electronic structure package [52]. The interaction energy was calculated at the same level as the difference of the total energy of the complexes and the sum of the isolated monomers in their complex geometry. The basis set superposition error (BSSE) was corrected for all calculations by using the counterpoise method [53]. The characteristic of the interactions was analyzed by the following energy decomposition scheme [54]:

$$E_{\text{int}} = E_{\text{elst}} + E_{\text{exch-rep}} + E_{\text{pol}} + E_{\text{disp}}$$

where $E_{\text{elst}}$, $E_{\text{exch-rep}}$, $E_{\text{pol}}$ and $E_{\text{disp}}$ correspond to electrostatic, exchange-repulsion, polarization and dispersion terms, respectively. All energy decompositions were carried out at the MP2/aug-cc-pVDZ with the GAMESS package [55] using the MP2/aug-cc-pVTZ optimized structures.

Molecular electrostatic potentials (MEPs) were computed on the 0.001 electrons/Bohr³ contour of the electronic density using the WFA-SAS program [56]. The electron densities of the monomers and complexes were analyzed using wave functions generated at the MP2/aug-cc-pVTZ level employing the AIM2000 program [57]. Natural bond orbital (NBO) analysis was performed by the NBO 3.1 module [58] in Gaussian 09. Since MP2 orbitals are nonexistent, the charge transfer energies were evaluated at the HF/aug-cc-pVTZ level. Electron density difference plots upon complex formation were obtained as the difference between the electron density of the complex and those of the isolated monomers at their geometry in the complex using the Multiwfn program [59].

### Results and Discussion

#### Monomers

The optimized structures of the isolated YOX₄ (Y = S, Se; X = F, Cl, Br) monomers are depicted in Figure S1 of Supporting Information. It is seen that these molecules all adopt a distorted trigonal bipyramid structure, in which the oxygen atom is located on the equator. The halogen atoms on the equator (Xₑq) have a little shorter bond distances than those of halogen atoms on the axis (Xₘ). The optimized S = O, S–Fₑq and S–Fₘ bonds in the SOF₄ are
calculated to be 1.425, 1.558 and 1.613 Å, respectively, which are in good agreement with experimental 1.409 Å, 1.539 and 1.596 Å values [60].

Figure 1 shows the MEP maps, on the 0.001 electrons/bohr³ contour, of the isolated YOX₄ molecules. As evident, there is a distinct negative MEP region on the oxygen atomic surface, corresponding to its lone-pair electrons. The MEP of YOX₄ molecules also shows two buildups of positive potentials (σ-hole), located at the outer side of the Y atom, along each Y–Xₑq bonds. This is surprising, since there is usually a σ-hole region associated with each covalently bonded chalcogen atom. This may be due to the distorted trigonal bipyramid structure of YOX₄ molecules as noted above and the sp³d hybridization of the chalcogen atom in these systems. The calculated positive electrostatic potential maximum (Vₛ,max) for these σ-holes are given in Fig. 1. In all cases, the Vₛ,max value associated with the Se atom is larger than that of S counterpart, which is due to the smaller electronegativity and larger polarizability of the Se atom than S one. Moreover, one can see that Y–O bond can generate an additional σ-hole region opposite to the oxygen atom. These σ-holes for a given chalcogen atom vary as X = F > Cl > Br. Besides, the MEP maps of YOX₄ molecules indicate that there is a σ-hole region on each halogen X atom, along the Y–X bond extension. For a given Y atom, the estimated Vₛ,max value associated with the halogen atoms tends to increase as the size of the halogen atom increases. Note that due to the high electronegativity, axial fluorine atoms of YOF₄ do not have a σ-hole on their surface. Another interesting result is that the σ-hole region of the axial halogen atoms shows a smaller positive value than those of equatorial ones, which can be attributed to their greater degree of sp-hybridization along the Y–X bond. As a result, the YOX₄ molecules can exhibit two different types of halogen-bonding interactions with potential electron donors.

**Binary complexes**

Three different interaction modes are considered for the possible complexes between the YOX₄ and NH₃ molecules (Fig. 2). The configuration (I) corresponds to the chalcogen bond interaction where the lone-pair electrons of ammonia point toward the σ-hole region on the chalcogen atom of YOX₄, along with the Y–Xₑq. The other two configurations (II and III) arise from the halogen bond formation between the σ-hole associated with the equatorial or axial halogen atoms of YOX₄ and NH₃. It should be noted that all attempts to locate a chalcogen-bonded complex through the σ-hole of Y–O bond led to configuration II after full geometry optimization. Hence, we considered only the chalcogen-bonding interactions along the extension of the Y–Xₑq.

The geometric and energetic results of the optimized complexes are summarized in Table 1 (see Figure S2 of the Supporting Information for a representation of the optimized structures). In all cases, the interaction of NH₃ induces a significant distortion of the YOX₄ molecule. The
calculated Y···N binding distances in the chalcogen-bonded complexes vary between 1.959 Å for the SOF₄:NH₃ complex to 2.139 Å for SeOBr₄:NH₃. In fact, these distances are short enough to consider them as the covalent bonds. Besides, these chalcogen bond distances are shorter than those of SOXY:NH₃ (X,Y = F, Cl) [36] or YOX₂X₂:NH₃ (Y = S, Se; X = F, Cl, Br) [61] complexes. All of the chalcogen bonds have a favorable linear arrangement, with ∠X−Y···N values between 166° and 170°. One can see that for a given X atom, the SeOX₄ complexes have a larger Y···N distance than the SOX₄ counterparts, which is due to the larger Van der Waals (VdW) radius of Se atom (1.9 Å) compared to S (1.8 Å) [62]. The type of the halogen atom in the YOX₄ has also a significant influence on the Y···N binding distances, and for a given Y atom, the chalcogen bond distance increases as the size of the halogen atom increases. The interaction energies of these chalcogen-bonded complexes range from −18.34 kcal/mol in the SOBr₂:NH₃ to −36.18 kcal/mol in the SeOF₂:NH₃ one. The interaction energies of the Se complexes are always more negative than those of S counterparts, in agreement with the electrostatic potential values obtained on these atoms (Fig. 1).

The calculated X···N binding distances in the halogen-bonded YOX₄:NH₃ complexes are in the range of 2.253–3.109 Å and 2.1310–3.125 Å for Y = S and Se, respectively (Table 1). Most of these values are much shorter than the sum of the vdW radii of the interacting atoms, which imply the formation of quite strong halogen bond interactions in these complexes. It is important to note that due to the high electronegativity of axial fluorine atoms, we did not find a stable halogen-bonded complex between YOF₄ and NH₃ with configuration III. Consistent with earlier studies [17–19], the interaction energies of the halogen-bonded complexes become more negative as the size of the halogen atom increases. Thus, in each series, the YOBr₄ molecule forms the strongest halogen-bonding interactions. Besides, for given X and Y atoms, the halogen-bonded complexes in configuration II are more stable than those of configuration III. This is due to the larger σ-hole potential on the equatorial halogen atoms than on the axial ones, which favors a stronger halogen bond interaction between the YOX₄ and NH₃ molecules. Overall, the examination of interaction energies in Table 1 suggests that the chalcogen bond is always more preferable over the halogen bond for all of these binary YOX₄:NH₃ complexes.

Table 2 shows the interaction energy decomposition analysis of the YOX₄:NH₃ complexes. It is seen that all electrostatic, polarization and dispersion energies are stabilizing and together account for the stability of the title complexes. For the chalcogen- and halogen-bonded complexes, the electrostatic interaction is the largest stabilizing term contributing to the total energy. The polarization component Epol makes also an important contribution in all complexes especially for the chalcogen-bonded complexes with the Se atom, indicating a significant perturbation of electron density distribution in these complexes. Although the electrostatic interaction is identified as the major contributing factor for the stability of the least stable fluorine-bonded complexes, the dispersion energy Edisp is comparable to the Eexch-rep in these complexes. The Eexch-rep term, which is sum of the exchange and repulsive energy terms

![Fig. 2 Different interaction modes between YOX₄ and NH₃ molecules: Chalcogen bond (I) and halogen bond (II and III)](image)

**Table 1** Binding distances (R, Å), binding angles θ (°) and BSSE-corrected interaction energies (Eint, kcal/mol) of YOX₄:NH₃ complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>R</th>
<th>θ</th>
<th>Eint</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOF₄:NH₃</td>
<td>1.959</td>
<td>168</td>
<td>−29.69</td>
</tr>
<tr>
<td>SOCl₂:NH₃</td>
<td>2.021</td>
<td>170</td>
<td>−22.41</td>
</tr>
<tr>
<td>SOBr₂:NH₃</td>
<td>2.064</td>
<td>168</td>
<td>−18.34</td>
</tr>
<tr>
<td>SeOCl₂:NH₃</td>
<td>2.048</td>
<td>166</td>
<td>−36.18</td>
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<td>SeOCl₄:NH₃</td>
<td>2.111</td>
<td>169</td>
<td>−25.16</td>
</tr>
<tr>
<td>SeOBr₂:NH₃</td>
<td>2.139</td>
<td>170</td>
<td>−21.84</td>
</tr>
<tr>
<td>Configuration II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOF₄:NH₃</td>
<td>3.109</td>
<td>179</td>
<td>−1.03</td>
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<tr>
<td>SOCl₂:NH₃</td>
<td>2.462</td>
<td>178</td>
<td>−6.96</td>
</tr>
<tr>
<td>SOBr₂:NH₃</td>
<td>2.253</td>
<td>179</td>
<td>−14.37</td>
</tr>
<tr>
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<td>178</td>
<td>−6.01</td>
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<td>SeOBr₂:NH₃</td>
<td>2.310</td>
<td>179</td>
<td>−11.84</td>
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<td>Configuration III</td>
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<td></td>
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<tr>
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<td>2.859</td>
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<td>−2.52</td>
</tr>
<tr>
<td>SOBr₂:NH₃</td>
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<td>−6.09</td>
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<tr>
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<td>−2.58</td>
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<tr>
<td>SeOBr₂:NH₃</td>
<td>2.469</td>
<td>178</td>
<td>−6.22</td>
</tr>
</tbody>
</table>

*In the complexes with configuration I, the binding angle refers to the X−Y···N angle, while in the complexes with configurations II or III, it corresponds to the Y−X···N angle.*
resulting from the Pauli exclusion principle, has also a significant contribution to the total interaction energies of the YOX₄:NH₃ complexes. For all the complexes, the absolute value of each energy term decreases as the strength of the interaction decreases.

The topology analysis of the electron density by means of the quantum theory of atoms in molecules (QTAIM) provides a useful tool to confirm the formation of a σ-hole interaction in the title complexes. Moreover, this methodology allows characterizing the nature of σ-hole interactions as an open- or closed-shell interaction. Table 3 lists the calculated electron density, \( \rho_{\text{BCP}} \), its Laplacian, \( \nabla^2 \rho_{\text{BCP}} \), and the total electron energy density, \( H_{\text{BCP}} \), at the Y···N and X···N BCPs of YOX₄:NH₃ complexes. One can see that the \( \rho_{\text{BCP}} \) values at the Y···N BCPs are large, with values between 0.095 and 0.135 au. The electron densities at the X···N BCPs range from 0.005 to 0.071 au, and are within the range proposed for other halogen-bonded complexes [8, 9, 23, 25]. Moreover, the \( \rho_{\text{BCP}} \) is often used as a descriptor of the strength of the corresponding interaction. As Fig. 3 indicates, the electron densities at the BCPs and the binding distances of the YOX₄:NH₃ complexes exhibit an exponential relationship, similar to the one described by other σ-hole-bonded complexes [63–65]. A comparison of the \( \rho_{\text{BCP}} \) values in the chalcogen- and halogen-bonded complexes also indicates that in each series; the most stable complexes are the ones showing the largest \( \rho_{\text{BCP}} \) values.
indicating the covalent character of the Y···N bonds. On the other hand, one can see that the values of $\nabla^2 \rho_{BCP}$ at the X···N BCPs are all positive. Thus, these interactions can be classified as closed-shell interactions. In addition, the calculated $H_{BCP}$ values for the $X = \text{Cl}$ and Br halogen-bonded complexes are negative, which means that these halogen bonds have some covalent character.

The other valuable method to analyze the nature of interaction is the NBO theory. The formation of chalcogen- and halogen-bonding interactions is usually associated with an orbital interaction between the lone pair of the electron donor and the antibonding orbital of the Lewis acid [41, 45]. A similar interaction is also evident for the binary complexes studied here. Table 4 summarizes the amount of charge transfer in the halogen-bonded complexes and the Wiberg bond index (WBI) values on formation of the YOX$_4$:NH$_3$ complexes. The estimated $E^{(2)}$ values associated with the n(N) → σ$_{Y-X}^*$ interaction of the chalcogen-bonded complexes are about 60 kcal/mol. Interestingly, the NBO program describes the strongly bonded chalcogen-bonded SeOF$_4$:NH$_3$, SeOCl$_4$:NH$_3$ and SOF$_4$:NH$_3$ complexes as a single molecule. The calculated $E^{(2)}$ value for the SeOBr$_4$:NH$_3$ complex is 58.0 kcal/mol, which is 2.6 kcal/mol smaller than that of SOBr$_4$:NH$_3$. This means that the orbital interaction decreases with the size of the chalcogen atom. In the case of the halogen-bonded complexes, the $E^{(2)}$ values associated with n(N) → σ$_{X-Y}^*$ interactions are in the range of 0.10–49.01 kcal/mol and increase as the size of the halogen atom increases, which is similar to the tendency observed for the interaction energy. For a given YOX$_4$:NH$_3$ complex, the amount of orbital interaction energy is always more important for chalcogen-bonded complexes than halogen-bonded ones. In addition, the halogen-bonded complexes in configuration II show a larger $E^{(2)}$ value than ones in configuration III.

As Table 4 indicates, the formation of the title complexes leads also to a net charge transfer from the NH$_3$ to YOX$_4$ molecule. One can see that the amount of charge transfer, especially in the complexes with configuration I, is large and varies between 0.282 and 0.359 e. For a given Y, the amount of charge transfer values decrease as the size of the halogen atom increases. On the other hand, the amount of charge transfer in the halogen-bonded complexes increases in the order $X = \text{Br} > \text{Cl} > \text{F}$, which is the order of increasing interaction energies of these complexes. The examination of the results of Table 4 shows that the flow of the charge transfer in the halogen-bonded complexes is smaller than those of chalcogen-bonded ones. The WBI values at the Y···N bonds range from 0.345 to 0.470, while those of X···N bonds are between 0.002 and 0.199. This supports that the former interactions are stronger than the latter ones.

Figure 4 indicates the computed electron density difference (EDD) plots of the YOBBr$_4$:NH$_3$ complexes, where red and blue regions correspond to a decrease and an increase of the electron density, respectively. As evident, a decrease of the electron density (red area) is found for the σ-hole region on the Y atom of the chalcogen-bonded complexes, which reflects the polarization of Y atom by the electric field of NH$_3$ molecule. This region is getting larger with the increase of chalcogen atom size, which is in agreement with the polarizability of Y atom in the YOX$_4$ molecule. This feature is similar to that observed in other σ-hole-bonded complexes [36]. The EDD plots also show that polarization effects caused by the positive σ-hole developed on the chalcogen atom tend to shift electron density from adjacent hydrogen atoms onto the N atom of NH$_3$ and hence increase the electron density (blue area) around the nitrogen atom. In the case of the halogen-bonded complexes, it is also evident that there is a significant electron density shift around the interacting halogen atoms. As expected, such electron density shifts are more important for the halogen-bonded complexes with configuration II than those with III, due to the larger σ-hole potential associated with the equatorial halogen atoms. These results are in agreement with the trend obtained for the interaction energies of these complexes and may suggest that the degree of the electron density shifts around the σ-hole

Table 4  NBO charge transfer energy ($E^{(2)}$, kcal/mol), amount of net charge transferred ($\Delta q_{CT}$, e) and Wiberg bond index (WBI) of SOX$_4$:NH$_3$ complexes

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$E^{(2)}$</th>
<th>$\Delta q_{CT}$</th>
<th>WBI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOF$_4$:NH$_3$</td>
<td>a</td>
<td>0.359</td>
<td>0.470</td>
</tr>
<tr>
<td>SOCl$_2$:NH$_3$</td>
<td>63.5</td>
<td>0.342</td>
<td>0.419</td>
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<td>SOBr$_4$:NH$_3$</td>
<td>60.6</td>
<td>0.323</td>
<td>0.376</td>
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<tr>
<td>SeOF$_4$:NH$_3$</td>
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<td>0.320</td>
<td>0.427</td>
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<td>SeOCl$_2$:NH$_3$</td>
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</tr>
<tr>
<td>SeOBr$_4$:NH$_3$</td>
<td>58.0</td>
<td>0.282</td>
<td>0.345</td>
</tr>
<tr>
<td>Configuration II</td>
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<td>SOF$_4$:NH$_3$</td>
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<td>0.002</td>
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<td>0.199</td>
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<td>0.002</td>
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<td>0.073</td>
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<tr>
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<td>0.138</td>
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<tr>
<td>SeOBr$_4$:NH$_3$</td>
<td>28.06</td>
<td>0.101</td>
<td>0.118</td>
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$^a$ Due to the strong interaction, NBO program treats these complexes as a single molecule.
region can be regarded as a good criterion to quantify the strength of the σ-hole bonds interactions.

Conclusion

An ab initio study was performed at the MP2/aug-cc-pVTZ level to investigate the possible chalcogen and halogen bonds interactions between YOX₄ (X = F, Cl, Br) and NH₃ molecules. The examination of interaction energies suggested that the chalcogen bond is always more preferable over the halogen bond for all these studied complexes. The results of interaction energy decomposition analysis indicated that for all the complexes considered, the electrostatic interaction is the largest stabilizing term contributing to the total energy and the polarization component $E_{\text{pol}}$ and $E_{\text{disp}}$ make also an important contribution. All the strong chalcogen-bonded complexes were characterized by a negative $\nabla^2 \rho_{\text{BCP}}$ and $H_{\text{BCP}}$ values, indicating that the Y···N interactions have a covalent nature. The orbital interaction between the lone pair of the NH₃ and the antibonding orbital of the Lewis acid was also identified as an important factor for the stability of these complexes. For a given YOX₄:NH₃ complex, the amount of orbital interaction energy is always more important for chalcogen-bonded complexes than halogen-bonded ones.

References


