Struct Chem (2016) 27:1439–1447
DOI 10.1007/s11224-016-0763-4

ORIGINAL RESEARCH

Competition between chalcogen bond and halogen bond interactions in YOX_4:NH_3 (Y = S, Se; X = F, Cl, Br) complexes: An ab initio investigation

Mehdi D. Esrafili[1] · Soheila Asadollahi[1] · Yousef Dadban Shahamat[2]

Received: 1 February 2016 / Accepted: 11 April 2016 / Published online: 21 April 2016
© Springer Science+Business Media New York 2016

Abstract Using ab initio calculations, the geometries, interaction energies and bonding properties of chalcogen bond and halogen bond interactions between YOX_4 (Y = S, Se; X = F, Cl, Br) and NH_3 molecules are studied. These binary complexes are formed through the interaction of a positive electrostatic potential region (σ-hole) on the YOX_4 with the negative region in the 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 YOX_4:NH_3 complexes.

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

Electronic supplementary material The online version of this article (doi:10.1007/s11224-016-0763-4) contains supplementary material, which is available to authorized users.

✉ Mehdi D. Esrafili
esrafili@maragheh.ac.ir

[1] Laboratory of Theoretical Chemistry, Department of Chemistry, University of Maragheh, P.O. Box 5513864596, Maragheh, Iran

[2] Environmental Heath Research Center, Golestan University of Medical Sciences, Gorgan, Iran

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 A-H···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 "σ-hole" [10–20], directed toward the electron donor. The presence or absence and the magnitude of a σ-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 σ-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 (NH_3, N_2, and NCH). Li and coworkers [49] have recently reported the competition between the C···N and X···N interactions in complexes involving F_2CX (X = Se and Te) and NH_3 or 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 pnicogen bonds interactions can compete with each other in 1:1 and 1:2 complexes of YOF_2X (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 YOX_4 (Y = S, Se; X = F, Cl, Br) as the Lewis acid to interact with NH_3. Particular attention is paid to study the geometry, interaction energy and the nature of the halogen or chalcogen bonds interactions in the binary YOX_4:NH_3 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]:

$$E_{\text{int}} = E_{\text{elst}} + E_{\text{exch-rep}} + E_{\text{pol}} + E_{\text{disp}} \quad (1)$$

where E_{elst}, $E_{\text{exch-rep}}$, E_{pol} and E_{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/Bohr^3 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 YOX_4 (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 (X_{eq}) have a little shorter bond distances than those of halogen atoms on the axis (X_{ax}). The optimized S = O, S–F_{eq} and S–F_{ax} bonds in the SOF_4 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/bohr^3 contour, of the isolated YOX_4 molecules. As evident, there is a distinct negative MEP region on the oxygen atomic surface, corresponding to its lone-pair electrons. The MEP of YOX_4 molecules also shows two buildups of positive potentials (σ-hole), located at the outer side of the Y atom, along each Y–X_{eq} 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 YOX_4 molecules as noted above and the sp^{3}d hybridization of the chalcogen atom in these systems. The calculated positive electrostatic potential maximum ($V_{S,max}$) for these σ-holes are given in Fig. 1. In all cases, the $V_{S,max}$ 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 YOX_4 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 $V_{S,max}$ 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 YOF_4 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 YOX_4 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 YOX_4 and NH_3 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 YOX_4, along with the Y–X_{eq}. 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 YOX_4 and NH_3. 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–X_{eq}.

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 NH_3 induces a significant distortion of the YOX_4 molecule. The

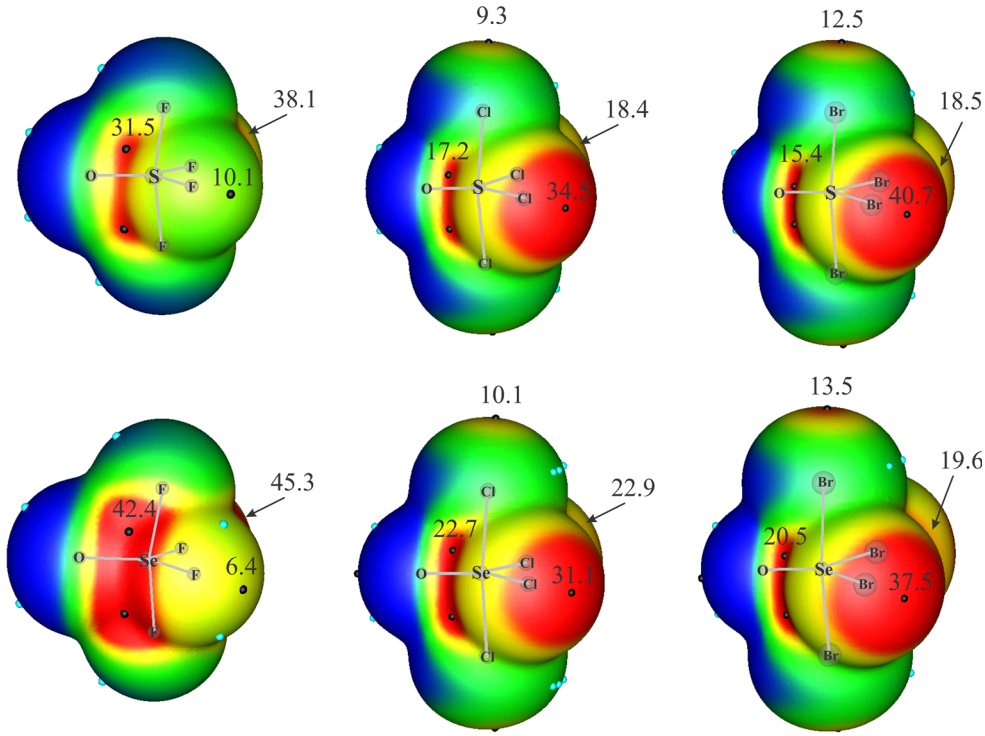

Fig. 1 Calculated MEPs of the isolated YOX_4 monomers. The color ranges, in kcal/mol, are: *red* > 12.1, 12.1 < *yellow* < 3.2, 3.2 < *green* < −6.7 and blue < −6.7. The locations of the σ-holes on the Y and X atoms are indicated with *black circles*, and their values are given in kcal/mol (Color figure online)

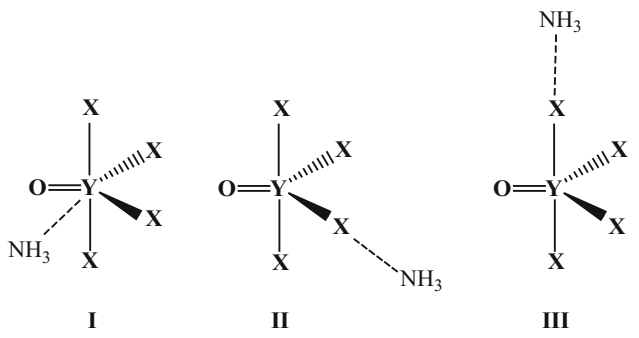

Fig. 2 Different interaction modes between YOX_4 and NH_3 molecules: Chalcogen bond (**I**) and halogen bond (**II** and **III**)

Table 1 Binding distances (R, Å), binding angles [a] (θ, °) and BSSE-corrected interaction energies (E_{int}, kcal/mol) of YOX_4:NH_3 complexes

Complex	*R*	*θ*	E_{int}
Configuration **I**			
SOF_4:NH_3	1.959	168	−29.69
$SOCl_4$:NH_3	2.021	170	−22.41
$SOBr_4$:NH_3	2.064	168	−18.34
$SeOF_4$:NH_3	2.048	166	−36.18
$SeOCl_4$:NH_3	2.111	169	−25.16
$SeOBr_4$:NH_3	2.139	170	−21.84
Configuration **II**			
SOF_4:NH_3	3.109	179	−1.03
$SOCl_4$:NH_3	2.462	178	−6.96
$SOBr_4$:NH_3	2.253	179	−14.37
$SeOF_4$:NH_3	3.123	178	−0.79
$SeOCl_4$:NH_3	2.514	178	−6.01
$SeOBr_4$:NH_3	2.310	179	−11.84
Configuration **III**			
$SOCl_4$:NH_3	2.859	176	−2.52
$SOBr_4$:NH_3	2.477	179	−6.09
$SeOCl_4$:NH_3	2.857	176	−2.58
$SeOBr_4$:NH_3	2.469	178	−6.22

[a] 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

calculated Y···N binding distances in the chalcogen-bonded complexes vary between 1.959 Å for the SOF_4:NH_3 complex to 2.139 Å for $SeOBr_4$:NH_3. 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:NH_3 (X,Y = F, Cl) [36] or YO_2X_2:NH_3 (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 $SeOX_4$ complexes have a larger Y···N distance than the SOX_4 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 YOX_4 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 $SOBr_4$:NH_3 to −36.18 kcal/mol in the $SeOF_4$:NH_3 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 YOX_4:NH_3 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 YOF_4 and NH_3 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 $YOBr_4$ 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 YOX_4 and NH_3 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 YOX_4:NH_3 complexes.

Table 2 shows the interaction energy decomposition analysis of the YOX_4:NH_3 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 E_{pol} 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 E_{disp} is comparable to the E_{elst} in these complexes. The $E_{exch\text{-}rep}$ term, which is sum of the exchange and repulsive energy terms

Table 2 Interaction energy decomposition analysis (at the MP2/aug-cc-pVDZ level) of YOX_4:NH_3 complexes

Complex	E_{elst}	$E_{exch\text{-}rep}$	E_{pol}	E_{disp}
Configuration **I**				
SOF_4:NH_3	−118.55	176.30	−86.1	−2.22
$SOCl_4$:NH_3	−105.33	160.61	−76.03	−3.02
$SOBr_4$:NH_3	−95.27	135.88	−58.04	−4.19
$SeOF_4$:NH_3	−119.41	182.51	−98.97	−2.58
$SeOCl_4$:NH_3	−107.65	172.44	−87.28	−3.79
$SeOBr_4$:NH_3	−96.48	149.65	−71.29	−4.88
Configuration **II**				
SOF_4:NH_3	−1.35	1.24	−0.27	−0.60
$SOCl_4$:NH_3	−22.47	34.00	−13.56	−4.16
$SOBr_4$:NH_3	−32.56	38.89	−18.90	−7.66
$SeOF_4$:NH_3	−1.00	1.19	−0.26	−0.65
$SeOCl_4$:NH_3	−19.55	29.50	−11.46	−3.91
$SeOBr_4$:NH_3	−29.84	33.46	−16.02	−6.61
Configuration **III**				
$SOCl_4$:NH_3	−17.44	25.06	−9.62	−2.24
$SOBr_4$:NH_3	−24.11	33.73	−12.42	−4.97
$SeOCl_4$:NH_3	−16.22	22.6	−7.48	−1.94
$SeOBr_4$:NH_3	−22.5	28.71	−10.58	−4.21

resulting from the Pauli exclusion principle, has also a significant contribution to the total interaction energies of the YOX_4:NH_3 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, ρ_{BCP}, its Laplacian, $\nabla^2\rho_{BCP}$, and the total electron energy density, H_{BCP}, at the Y···N and X···N bond critical points (BCPs) of the YOX_4:NH_3 complexes. One can see that the ρ_{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 ρ_{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 YOX_4:NH_3 complexes exhibit an exponential relationship, similar to the one described by other σ-hole-bonded complexes [63–65]. A comparison of the ρ_{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 ρ_{BCP} values.

Table 3 Electron density (ρ_{BCP}, au), its Laplacian ($\nabla^2\rho_{BCP}$, au) and total electron energy density (H_{BCP}, au) at Y···N and X···N BCPs of SOX_4:NH_3 complexes

Complex	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}
Configuration **I**			
SOF_4:NH_3	0.115	−0.226	−0.073
$SOCl_4$:NH_3	0.102	0.001	−0.055
$SOBr_4$:NH_3	0.095	0.015	−0.048
$SeOF_4$:NH_3	0.135	−0.226	−0.104
$SeOCl_4$:NH_3	0.118	−0.109	−0.071
$SeOBr_4$:NH_3	0.107	−0.055	−0.056
Configuration **II**			
SOF_4:NH_3	0.005	0.022	0.001
$SOCl_4$:NH_3	0.039	0.120	−0.002
$SOBr_4$:NH_3	0.071	0.131	−0.021
$SeOF_4$:NH_3	0.005	0.022	0.001
$SeOCl_4$:NH_3	0.035	0.113	−0.001
$SeOBr_4$:NH_3	0.063	0.114	−0.015
Configuration **III**			
$SOCl_4$:NH_3	0.020	0.070	−0.001
$SOBr_4$:NH_3	0.046	0.084	−0.005
$SeOCl_4$:NH_3	0.018	0.062	−0.001
$SeOBr_4$:NH_3	0.042	0.073	−0.004

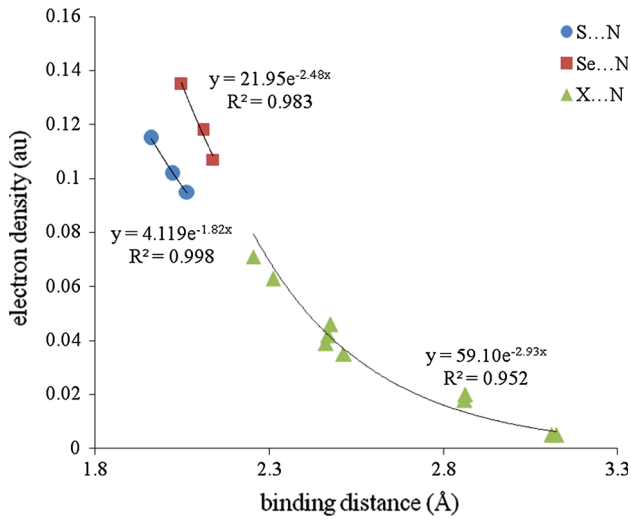

Fig. 3 Correlation between binding distances and electron densities at Y···N and X···N BCPs of YOX_4:NH_3 complexes

The Laplacian ($\nabla^2\rho_{BCP}$) and the total energy density (H_{BCP}) at the BCP are often been used to characterize the nature of interactions [66–68]. As Table 3 indicates, all chalcogen-bonded complexes have a negative $\nabla^2\rho_{BCP}$ value, except $SOCl_4$:NH_3 and $SOBr_4$:NH_3. These complexes are also characterized by a negative H_{BCP} value,

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 = 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 stabilization energies ($E^{(2)}$), net charge transfer (q_{CT}) and 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**.

Table 4 NBO charge transfer energy ($E^{(2)}$, kcal/mol), amount of net charge transferred (q_{CT}, *e*) and Wiberg bond index (WBI) of SOX_4:NH_3 complexes

Complex	$E^{(2)}$	q_{CT}	WBI
Configuration **I**			
SOF_4:NH_3	[a]	0.359	0.470
$SOCl_4$:NH_3	63.5	0.342	0.419
$SOBr_4$:NH_3	60.6	0.323	0.376
$SeOF_4$:NH_3	[a]	0.320	0.427
$SeOCl_4$:NH_3	[a]	0.305	0.374
$SeOBr_4$:NH_3	58.0	0.282	0.345
Configuration **II**			
SOF_4:NH_3	0.10	0.002	0.002
$SOCl_4$:NH_3	22.91	0.077	0.092
$SOBr_4$:NH_3	49.01	0.126	0.199
$SeOF_4$:NH_3	0.11	0.002	0.002
$SeOCl_4$:NH_3	18.00	0.065	0.073
$SeOBr_4$:NH_3	38.59	0.091	0.138
Configuration **III**			
$SOCl_4$:NH_3	3.96	0.015	0.018
$SOBr_4$:NH_3	27.96	0.098	0.119
$SeOCl_4$:NH_3	3.69	0.014	0.019
$SeOBr_4$:NH_3	28.06	0.101	0.118

[a] Due to the strong interaction, NBO program treats these complexes as a single molecule

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 = Br > Cl > 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 $YOBr_4$: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

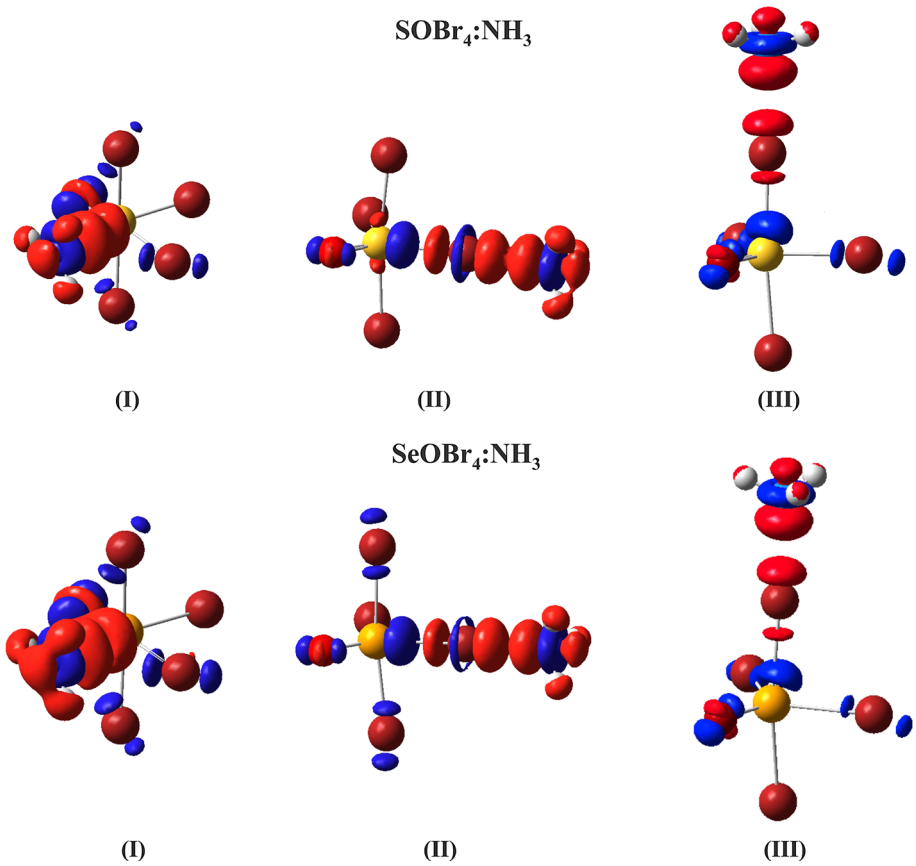

Fig. 4 Electron density difference isosurfaces (±0.005 au) for $YOBr_4$:NH_3 complexes. *Blue/red* regions represent gain/loss of density (Color figure online)

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 YOX_4 (X = F, Cl, Br) and NH_3 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_{pol} and E_{disp} make also an important contribution. All the strong chalcogen-bonded complexes were characterized by a negative $\nabla^2\rho_{BCP}$ and H_{BCP} values, indicating that the Y···N interactions have a covalent nature. The orbital interaction between the lone pair of the NH_3 and the antibonding orbital of the Lewis acid was also identified as an important factor for the stability of these complexes. 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.

References

1. Scheiner S (1997) Hydrogen bonding. A theoretical perspective. Oxford University Press, New York
2. Pochorovski I, Milić J, Kolarski D, Gropp C, Schweizer WB, Diederich F (2014) Evaluation of hydrogen-bond acceptors for redox-switchable resorc in [4] arene cavitands. J Am Chem Soc 136:3852–3858
3. Nichols DA, Hargis JC, Sanishvili R, Jaishankar P, Defrees K, Smith EW, Wang KK, Prati F, Renslo AR, Woodcock HL, Chen Y (2015) Ligand-induced proton transfer and low-barrier hydrogen bond revealed by X-ray crystallography. J Am Chem Soc 137:8086–8095
4. Nick TU, Lee W, Koßmann S, Neese F, Stubbe J, Bennati M (2015) Hydrogen bond network between amino acid radical intermediates on the proton-coupled electron transfer pathway of *E. coli* α_2 ribonucleotide reductase. J Am Chem Soc 137:289–298
5. Metrangolo P, Carcenac Y, Lahtinen M, Pilati T, Rissanen K, Vij A, Resnati G (2009) Nonporous organic solids capable of dynamically resolving mixtures of diiodoperfluoroalkanes. Science 323:1461–1464
6. Voth AR, Khuu P, Oishi K, Ho PS (2009) Halogen bonds as orthogonal molecular interactions to hydrogen bonds. Nat Chem 1:74–79
7. Metrangolo P, Murray JS, Pilati T, Politzer P, Resnati G, Terraneo G (2011) The fluorine atom as a halogen bond donor, viz. a positive site. CrystEngComm 13:6593–6596
8. Esrafili MD, Ahmadi B (2012) A theoretical investigation on the nature of Cl···N and Br···N halogen bonds in FArX···NCY complexes (X = Cl, Br and Y = H, F, Cl, Br, OH, NH_2, CH_3 and CN). Comput Theor Chem 997:77–82

9. Esrafili MD, Juyban P (2014) CNXeCl and CNXeBr species as halogen bond donors: a quantum chemical study on the structure, properties, and nature of halogen···nitrogen interactions. J Mol Model 20:2203
10. Clark T, Hennemann M, Murray JS, Politzer P (2007) Halogen bonding: the σ-hole. J Mol Model 13:291–296
11. Murray JS, Lane P, Clark T, Politzer P (2007) σ-hole bonding: molecules containing group VI atoms. J Mol Model 13:1033–1038
12. Murray JS, Concha MC, Lane P, Hobza P, Politzer P (2008) Blue shifts vs red shifts in σ-hole bonding. J Mol Model 14:699–704
13. Murray JS, Lane P, Politzer P (2008) Simultaneous σ-hole and hydrogen bonding by sulfur-and selenium-containing heterocycles. Int J Quantum Chem 108:2770–2781
14. Politzer P, Murray JS, Concha MC (2008) σ-hole bonding between like atoms; a fallacy of atomic charges. J Mol Model 14:659–665
15. Shields ZP, Murray JS, Politzer P (2010) Directional tendencies of halogen and hydrogen bonds. Int J Quantum Chem 110:2823–2832
16. Hennemann M, Murray JS, Politzer P, Riley KE, Clark T (2012) Polarization-induced σ-holes and hydrogen bonding. J Mol Model 18:2461–2469
17. Murray JS, Lane P, Clark T, Riley KE, Politzer P (2012) σ-Holes, π-holes and electrostatically-driven interactions. J Mol Model 18:541–548
18. Politzer P, Murray JS, Clark T (2013) Halogen bonding and other σ-hole interactions: a perspective. Phys Chem Chem Phys 15:11178–11189
19. Murray JS, Macaveiu L, Politzer P (2014) Factors affecting the strengths of σ-hole electrostatic potentials. J Comput Sci 5:590–596
20. Politzer P, Murray JS, Janjić GV, Zarić SD (2014) σ-Hole interactions of covalently-bonded nitrogen, phosphorus and arsenic: a survey of crystal structures. Crystals 4:12–31
21. Wang Y-H, Zou J-W, Lu Y-X, Yu Q-S, Xu H-Y (2007) Single-electron halogen bond: Ab initio study. Int J Quantum Chem 107:501–506
22. Li Q, Li R, Yi S, Li W, Cheng J (2012) The single-electron hydrogen, lithium, and halogen bonds with HBe, H_2B, and H_3C radicals as the electron donor: an ab initio study. Struct Chem 23:411–416
23. Li QZ, Li R, Liu XF, Li WZ, Cheng JB (2012) Concerted interaction between pnicogen and halogen bonds in XCl-FH_2P-NH_3 (X = F, OH, CN, NC, and FCC). ChemPhysChem 13:1205–1212
24. Zhang Y, Ma N, Wang W (2012) A new class of halogen bonds that avoids the σ-hole. Chem Phys Lett 532:27–30
25. Esrafili MD, Vakili M (2014) Halogen bonds enhanced by σ-hole and π-hole interactions: a comparative study on cooperativity and competition effects between X···N and S···N interactions in H3N···XCN···SF2 and H3N···XCN···SO2 complexes (X = F, Cl, Br and I). J Mol Model 20:2291
26. Metrangolo P, Resnati G, Pilati T, Biella S (2008) Halogen bonding in crystal engineering. Springer, Berlin
27. Cinčić D, Friščić T, Jones W (2011) Experimental and database studies of three-centered halogen bonds with bifurcated acceptors present in molecular crystals, cocrystals and salts. CrystEngComm 13:3224–3231
28. Ji B, Wang W, Deng D, Zhang Y (2011) Symmetrical bifurcated halogen bond: design and synthesis. Crys Growth Des 11:3622–3628
29. Troff RW, Mäkelä T, Topić F, Valkonen A, Raatikainen K, Rissanen K (2013) Alternative motifs for halogen bonding. Eur J Org Chem 2013:1617–1637
30. Murray JS, Lane P, Politzer P (2009) Expansion of the σ-hole concept. J Mol Model 15:723–729
31. Bundhun A, Ramasami P, Murray J, Politzer P (2013) Trends in σ-hole strengths and interactions of F_3MX molecules (M = C, Si, Ge and X = F, Cl, Br, I). J Mol Model 19:2739–2746
32. Wang W, Ji B, Zhang Y (2009) Chalcogen bond: a sister noncovalent bond to halogen bond. J Phys Chem A 113:8132–8135
33. Shishkin OV, Omelchenko IV, Kalyuzhny AL, Paponov BV (2010) Intramolecular S···O chalcogen bond in thioindirubin. Struct Chem 21:1005–1011
34. Adhikari U, Scheiner S (2014) Effects of charge and substituent on the S···N chalcogen bond. J Phys Chem A 118:3183–3192
35. Nziko VdPN, Scheiner S (2014) Chalcogen bonding between tetravalent SF_4 and amines. J Phys Chem A 118:10849–10856
36. Azofra LM, Alkorta I, Scheiner S (2015) Chalcogen bonds in complexes of SOXY (X, Y = F, Cl) with nitrogen bases. J Phys Chem A 119:535–541
37. Esrafili MD, Mohammadian-Sabet F (2015) Bifurcated chalcogen bonds: a theoretical study on the structure, strength and bonding properties. Chem Phys Lett 634:210–215
38. Esrafili MD, Mohammadian-Sabet F (2015) An ab initio study on chalcogen–chalcogen bond interactions in cyclic $(SHX)_3$ complexes (X = F, Cl, CN, NC, CCH, OH, OCH_3, NH_2). Chem Phys Lett 628:71–75
39. Li Q-Z, Li R, Guo P, Li H, Li W-Z, Cheng J-B (2012) Competition of chalcogen bond, halogen bond, and hydrogen bond in SCS–HOX and SeCSe–HOX (X = Cl and Br) complexes. Comput Theor Chem 980:56–61
40. Esrafili MD, Mohammadian-Sabet F (2015) Does single-electron chalcogen bond exist? Some theoretical insights. J Mol Model 21:65
41. Scheiner S (2013) Detailed comparison of the pnicogen bond with chalcogen, halogen, and hydrogen bonds. Int J Quantum Chem 113:1609–1620
42. Esrafili MD, Mohammadian-Sabet F (2014) Halogen-bond interactions enhanced by charge-assisted hydrogen bonds: an ab Initio study. Bull Chem Soc Jpn 87:882–889
43. Cozzolino AF, Vargas-Baca I, Mansour S, Mahmoudkhani AH (2005) The nature of the supramolecular association of 1, 2, 5-chalcogenadiazoles. J Am Chem Soc 127:3184–3190
44. Bleiholder C, Werz DB, Köppel H, Gleiter R (2006) Theoretical investigations on chalcogen-chalcogen interactions: what makes these nonbonded interactions bonding? J Am Chem Soc 128:2666–2674
45. Adhikari U, Scheiner S (2012) Substituent effects on Cl···N, S···N, and P···N noncovalent bonds. J Phys Chem A 116:3487–3497
46. Esrafili MD, Mohammadian-Sabet F (2014) Ab initio calculations of cooperativity effects on chalcogen bonding: linear clusters of $(OCS)_{2-8}$ and $(OCSe)_{2-8}$. Struct Chem 26:199–206
47. Esrafili MD, Vakili M (2014) Cooperativity effects between σ-hole interactions: a theoretical evidence for mutual influence between chalcogen bond and halogen bond interactions in F_2-S···NCX···NCY complexes (X = F, Cl, Br, I; Y = H, F, OH). Mol Phys 112:2746–2752
48. Esrafili MD, Mohammadirad N (2015) Substituent effects in cooperativity of chalcogen bonds. Mol Phys 113:3282–3290
49. Guo X, Liu Y-W, Li Q-Z, Li W-Z, Cheng J-B (2015) Competition and cooperativity between tetrel bond and chalcogen bond in complexes involving F_2CX (X = Se and Te). Chem Phys Lett 620:7–12
50. Alkorta I, Blanco F, Solimannejad M, Elguero J (2008) Competition of hydrogen bonds and halogen bonds in complexes of hypohalous acids with nitrogenated bases. J Phys Chem A 112:10856–10863

51. Esrafili MD, Mohammadirad N (2016) Characterization of σ-hole interactions in 1:1 and 1:2 complexes of YOF_2X (X = F, Cl, Br, I; Y = P, As) with ammonia: competition between halogen and pnicogen bonds. Struct Chem 27:617–625
52. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA Jr, Peralta JE, Ogliaro F, Bearpark MJ, Heyd J, Brothers EN, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell AP, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam NJ, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, in. Gaussian Inc, Wallingford
53. Boys SF, Bernardi F (1970) The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. Mol Phys 19:553–566
54. Su P, Li H (2009) Energy decomposition analysis of covalent bonds and intermolecular interactions. J Chem Phys 131:014102
55. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA (1993) General atomic and molecular electronic structure system. J Comput Chem 14:1347–1363
56. Bulat F, Toro-Labbé A, Brinck T, Murray J, Politzer P (2010) Quantitative analysis of molecular surfaces: areas, volumes, electrostatic potentials and average local ionization energies. J Mol Model 16:1679–1691
57. Biegler-Konig F, Schonbohm J, Bayles D (2001) AIM2000. J Comput Chem 22:545–559
58. Reed AE, Curtiss LA, Weinhold F (1988) Intermolecular interactions from a natural bond orbital, donor–acceptor viewpoint. Chem Rev 88:899–926
59. Lu T, Chen F (2012) Multiwfn: a multifunctional wavefunction analyzer. J Comput Chem 33:580–592
60. Hedberg L, Hedberg K (1982) Thionyl tetrafluoride. Reanalysis of the molecular structure and resolution of the multiple model problem. J Phys Chem 86:598–602
61. Esrafili MD, Mohammadian-Sabet F (2016) σ-Hole bond tunability in YO_2X_2:NH_3 and YO_2X_2: H_2O complexes (X = F, Cl, Br; Y = S, Se): trends and theoretical aspects. Struct Chem 27:617–625
62. Bondi A (1964) van der Waals volumes and radii. J Phys Chem 68:441–451
63. Alkorta I, Sánchez-Sanz G, Elguero J, Del Bene JE (2012) Exploring $(NH_2F)_2$, H_2FP: NFH_2, and $(PH_2F)_2$ potential surfaces: hydrogen bonds or pnicogen bonds? J Phys Chem A 117:183–191
64. Alkorta I, Elguero J, Del Bene JE (2013) Pnicogen bonded complexes of PO_2X (X = F, Cl) with nitrogen bases. J Phys Chem A 117:10497–10503
65. Alkorta I, Elguero J, Grabowski SJ (2015) Pnicogen and hydrogen bonds: complexes between $PH_3X^{(+)}$ and PH_2X systems. Phys Chem Chem Phys 17:3261–3272
66. Cremer D, Kraka E (1984) A description of the chemical bond in terms of local properties of electron density and energy. Croat Chem Acta 57:1259–1281
67. Rozas I, Alkorta I, Elguero J (2000) Behavior of ylides containing N, O, and C atoms as hydrogen bond acceptors. J Am Chem Soc 122:11154–11161
68. Grabowski SJ (2009) Covalent character of hydrogen bonds enhanced by π-electron delocalization. Croat Chem Acta 82:185–192