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σ -Hole Bonds and the VSEPR Model—From the Tetrahedral Structure to the Trigonal Bipyramid

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Abstract: Complexes linked by various interactions are analysed in this study. They are characterized by the tetrahedral configuration of the Lewis acid centre. Interactions, being a subject of this study, are classified as σ -hole bonds, such as the halogen, chalcogen, pnictogen, and tetrel bonds. In the case of strong interactions, the tetrahedral configuration of the Lewis acid centre changes into the trigonal bipyramid configuration. This change is in line with the Valence-Shell Electron-Pair Repulsion model, VSEPR, and this is supported here by the results of high-level ab initio calculations. The theoretical results concerning the geometries are supported mainly by the Natural Bond Orbital, NBO, method.

Keywords: σ -hole bond; valence-shell electron-pair repulsion model (VSEPR); tetrahedral configuration; trigonal bipyramid configuration; the natural bond orbital (NBO)



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1. Introduction

There are numerous phenomena in chemistry categorized by various terms. Some of these terms are ambiguous and, consequently, they are difficult to define. However, these terms are indispensable in descriptions and discussions of various reactions and processes. One can mention such terms as aromaticity, hydrogen bond, stabilization energy, electronegativity, and so on [1–6]. Even such a term as a chemical bond, which is commonly used in various studies, dissertations, and monographs, is a subject of numerous debates and polemics [7–9]. One can mention the definition recommended by the IUPAC, which states: “Chemical bond—when forces acting between two atoms or groups of atoms lead to the formation of a stable independent molecular entity, a chemical bond is considered to exist between these atoms or groups. The principal characteristic of a bond in a molecule is the existence of a region between the nuclei of constant potential contours that allows the potential energy to improve substantially by atomic contraction at the expense of only a small increase in kinetic energy. Not only directed covalent bonds characteristic of organic compounds, but also bonds such as those existing between sodium cations and chloride anions in a crystal of sodium chloride or the bonds binding aluminium to six molecules of water in its environment, and even weak bonds that link two molecules of O₂ into O₄, are to be attributed to chemical bonds” [10]. This definition makes reference to the Pauling monograph [11] and to other studies [12,13].

However, one can also refer to early Lewis concepts, where arrangements of electrons in molecular structures are taken into account [14]. Hence, so-called Lewis structures may be considered that are commonly presented in various academic books and monographs. Lewis stated that “Two electrons thus coupled together, when lying between two atomic centres, and held jointly in the shells of the two atoms, I have considered to be the chemical bond” [14]. In other words, the chemical bond is related to the occurrence of the electron pair situated between two atomic centres; this pair may be less or more moved to one of the atomic centres, which is related to the bond polarization and that determines the degree of the ionic character of the bond [15].

On the other hand, numerous inter- and intramolecular interactions are very strong and possess various characteristics of covalent bonds. As a consequence, there is no sharp border between bonds and intermolecular as well as intramolecular contacts. The hydrogen bond is an example, since it is often very strong; the covalency of this interaction was analysed in different studies [16]. Other interactions, not only hydrogen bonds, may possess numerous characteristics of covalent bonds [17]. One can mention the σ -hole and π -hole bonds, which may be often treated as counterparts of the hydrogen bond [18–21]. However, it is also very important that interactions may be treated as the preliminary stages of chemical reactions [22] and that, if they are strong enough, they change the configurations of reactants [23]. The interrelation between interactions and the Valence-Shell Electron-Pair Repulsion, VSEPR, model [24] was discussed, and it was justified that the classification of interactions may be based on the changes in the configurations of interacting centres [23]. There are other numerous studies where various kinds of interactions are analysed and compared between themselves [25–28]; in particular, those interactions that are related to the σ -hole and π -hole concepts are widely discussed in recent studies [29–32]. On the other hand, the studies related to the changes in the configurations of interacting centres are rather rare [33]. One of the studies on very strong chalcogen bonds may be mentioned here [34], which found clear trigonal bipyramid structures for the analysed chalcogen bonded complexes.

This is why two topics are analysed here: very strong interactions possessing the characteristics of covalent bonds and changes in the configurations resulting from such interactions. The following interactions classified as the σ -hole bonds are analysed in this study: tetrel, pnictogen, chalcogen, and halogen bonds. For the latter interactions, the elements of the 14th, 15th, 16th, and 17th groups, respectively, act as the Lewis acid centres. The tetrahedral systems that interact with chloride anions are discussed here, since such charge-assisted interactions possess numerous characteristics of covalent bonds. These complexes were discussed earlier [17]; however, not in terms of the VSEPR model or in terms of the changes in the configurations of interacting units. In other words, neither the relationships concerning the structures discussed here nor their characteristics that are also presented were analysed before.

2. Computational Details

The complexes connected by halogen, chalcogen, pnictogen, and tetrel bonds, where the Cl^- anion acts as the Lewis base, are analysed. The FCl and FBr electron acceptors form complexes with the latter anion by the halogen bond; the SFH and SeFH species form complexes through the chalcogen bond; similarly, the pnictogen bond links the chloride anion with the PFH₂ and AsFH₂ moieties, while the tetrel bond connects the SiFH₃ and GeFH₃ species with the Cl^- anion. In the complexes analysed here, the Z centre (Z = Cl, Br, S, Se, As, P, Si, or Ge) of the Lewis acid unit is connected to the chloride anion through the σ -hole. The latter is situated approximately at the Z-centre, in the extension of the F–Z bond. There are also σ -holes located in elongations of the H–Z bonds; however, the contacts with them are not analysed here. The above-mentioned σ -holes are characterized by the depletion of the electron charge and the positive electrostatic potential (EP); four σ -holes are observed for the Ge and Si centres, three for As and P, two for S and Se, and one for Br and Cl. Figure 1 shows two examples of EP mapped at the molecular surfaces of the AsFH₂ and FBr moieties; the σ -holes are shown there. The species containing fluorine substituents were chosen as the Lewis acid units, since the fluorine, as the electron-withdrawing substituent, enhances the σ -hole (positive EP increases) at the Z-centre in the extension of the F–Z bond. In the case of the FBr species, there is one σ -hole at the bromine centre located in the elongation of the F–Br bond, while, for the AsFH₂ moiety, there are three σ -holes at the arsenic centre; the strongest one is characterised by the greatest positive EP in the extension of the F–As bond and two in extensions of the H–As bonds (only one of them is visible in Figure 1).

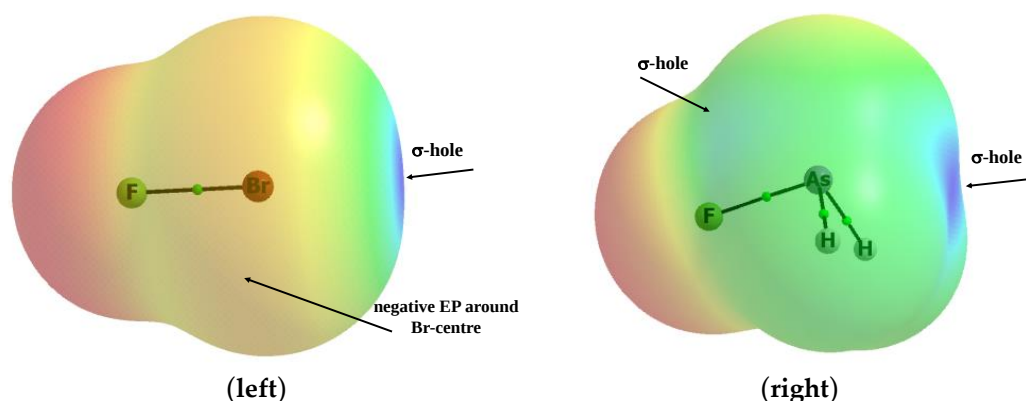


Figure 1. Electrostatic potential maps of the FBr (**left**) and AsFH₂ (**right**) species for the surfaces characterized by an electron density of 0.001 au.

The chloride anion was chosen here as an electron donor; the fluoride anion could be a better choice, since it is a stronger Lewis base [35]. However, the F-substituent is connected to the Z-centre of the Lewis acid unit to enhance the σ -hole. The interactions of such units with fluoride anions lead to the symmetrical ZH_xF₂ units ($x = 0, 1, 2$, or 3) with two equivalent Z...F contacts. Such systems may be the subject of another study.

Figure 2 presents the 2D maps of the Laplacian of electron density, $\nabla^2\rho$, for the FCl species and for the FCl...Cl[−] complex. One can see here the positive $\nabla^2\rho$ value in the extension of the F–Cl bond for the isolated FCl unit that corresponds to the σ -hole. The complexation is connected to the electron charge shifts from the chloride anion to the FCl unit that leads to the accumulation of the electron charge between the Cl centres; both chlorine centres in the complex are surrounded by areas of negative $\nabla^2\rho$ values.

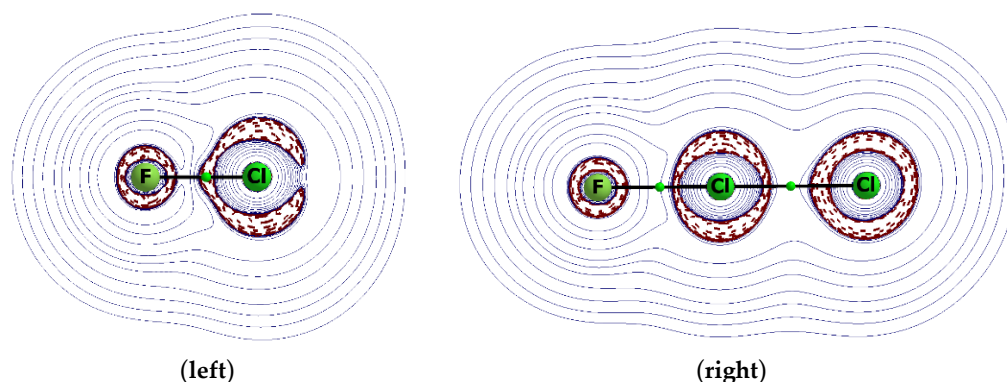


Figure 2. Maps of the Laplacian of the electron density for the F–Cl species (**left**) and for its complex, FCl...Cl[−] (**right**). The areas of negative Laplacian values are designated by the broken brown lines.

Such “closure” of the valence shell is possible, since the great electron charge shift from the chloride anion to the F–Cl Lewis acid moiety is observed (see further discussion). However, in the case of weaker interactions in the FCl...C₂H₂ and FCl...NH₃ complexes, lower charge shifts are observed and the valence shell of the Cl centre is not closed [36]. Another topic is related to the heavier halogen centres. For example, in the case of the F₃CBr species, the σ -hole is observed at the Br centre in the elongation of the C–Br bond; the large depletion of the electron charge is observed here due to the influence of F substituents [36]. The valence electron shell of the bromine centre is open, but the ring of the negative Laplacian is around its nucleus due to the inner electron shells. However, the positive total electrostatic potential, EP, at the σ -hole area is very important here; it is the sum of the electron EP and of the nucleus EP contributions. For example, at the σ -hole areas of the chlorine and bromine centres of the F₃CCl and F₃CBr moieties, the total EP is equal to +0.034 au and +0.040 au, respectively (MP2/aug-cc-pVTZ results). The valence shell for the

bromine centre is not closed in the $\text{F}_3\text{C}-\text{Br}\cdots\text{NH}_3$ and $\text{F}_3\text{C}-\text{Br}\cdots\text{OH}^-$ complexes; however, the closed rings of inner electrons are still observed here. A similar situation is observed for the isolated $\text{F}-\text{Br}$ species and for this species involved in the halogen bond interaction in the $\text{F}-\text{Br}\cdots\text{NH}_3$ complex [37], where, in both cases, the valence electron charge ring is open and the closed inner shell rings are observed.

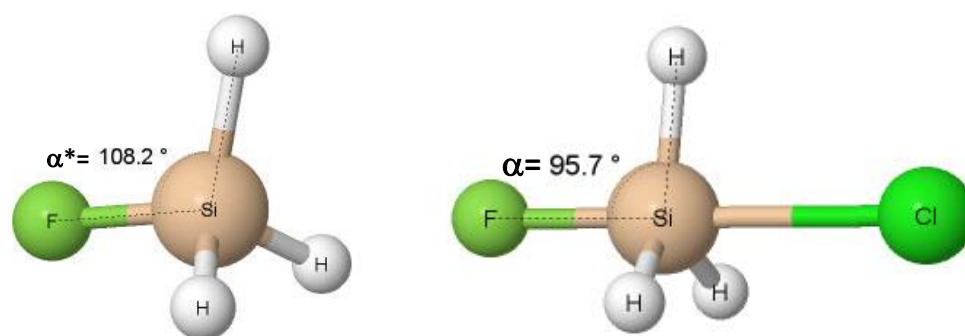
For the complexes analysed in this study, the second-order Møller–Plesset perturbation theory (MP2) [38] calculations were performed with the use of Gaussian16 [39]; the Dunning-style aug-cc-pVTZ basis set was applied [40]. Frequency calculations performed at the same computational level have shown that the optimized structures correspond to energetic minima. For the systems containing the Ge, As, Se, and Br atoms, additional calculations were carried out to check the significance of the relativistic effects; the Stuttgart/Cologne group ECP10MDF pseudopotentials were applied for these centres [41], with the corresponding Peterson AVTZ (11s12p10d2f)/[6s5p4d2f] basis sets [42]. These results that partly take into account relativistic effects are presented in this study; however, they do not differ significantly from the MP2/aug-cc-pVTZ results, where such effects are not included. For example, the interaction energy differences between both approaches, relativistic and non-relativistic, do not exceed 0.2 kcal/mol; only slight and negligible differences are observed for other parameters, with geometrical ones between them.

The interaction energy for the complexes analysed, E_{int} , was calculated as the difference between the energy of the complex and the sum of the energies of monomers, where the energies of monomers correspond to their geometries in the complex [43]. The basis set superposition error (BSSE) [44] correction was also calculated; thus, the BSSE-corrected E_{int} values are discussed hereafter. The Natural Bond Orbital (NBO) method [45,46] was also applied to analyse the electron charge shifts resulting from complexations. For the NBO calculations, the NBO 5.0 program [47] implemented in the GAMESS codes [48] was used. Additionally, the AIMAll program [49] was used to calculate the delocalization indices.

3. Results and Discussion

3.1. σ -Hole Bonds Analysed in This Study

It was pointed out in previous studies that various interactions may be treated as preliminary stages of chemical reactions [22]. For example, the hydrogen bond may initiate the proton transfer process [50,51] while the tetrel bond may lead to the $\text{S}_{\text{N}}2$ reaction [52]. It was shown also that interactions, if they are strong enough, lead to a change in the configurations of reaction centres. For example, the tetrel centre, characterized by the tetrahedral configuration, may act as the electron acceptor interacting with the Lewis base unit through the σ -hole bond. The latter interaction may lead to the change of the tetrahedral configuration of the tetrel centre into the trigonal bipyramid configuration. Scheme 1 presents an example of the SiFH_3 species that interacts strongly with the chloride anion, since the interaction energy, E_{int} , is equal to -32.6 kcal/mol (Table 1). The angle presented in Scheme 1, designated later here as the α angle, may be treated as a degree of the change of one configuration (tetrahedral) into another (trigonal bipyramid). This angle is equal to 109.5° for the “pure” tetrahedral structure characterized by the same substituents (as for methane with the same H-atoms attached to the carbon centre). In the case of various substituents, this angle is different to 109.5° , more or less. For the “pure” trigonal bipyramid configuration, the α angle is equal to 90° . Scheme 1 shows the change in this angle that is smaller, i.e., 95.7° , for the $\text{SiFH}_3\cdots\text{Cl}^-$ system than that for the isolated SiFH_3 unit, i.e., 108.2° . It is worth mentioning that, for the $\text{S}_{\text{N}}2$ reactions of the tetrel centres, the transition states are characterized by the α angle being equal to 90° or nearly so.



Scheme 1. Definition of the α^* and α angles for the isolated Lewis acid unit and for the complex; examples of the SiFH_3 unit and of the $\text{SiFH}_3\cdots\text{Cl}^-$ complex are presented.

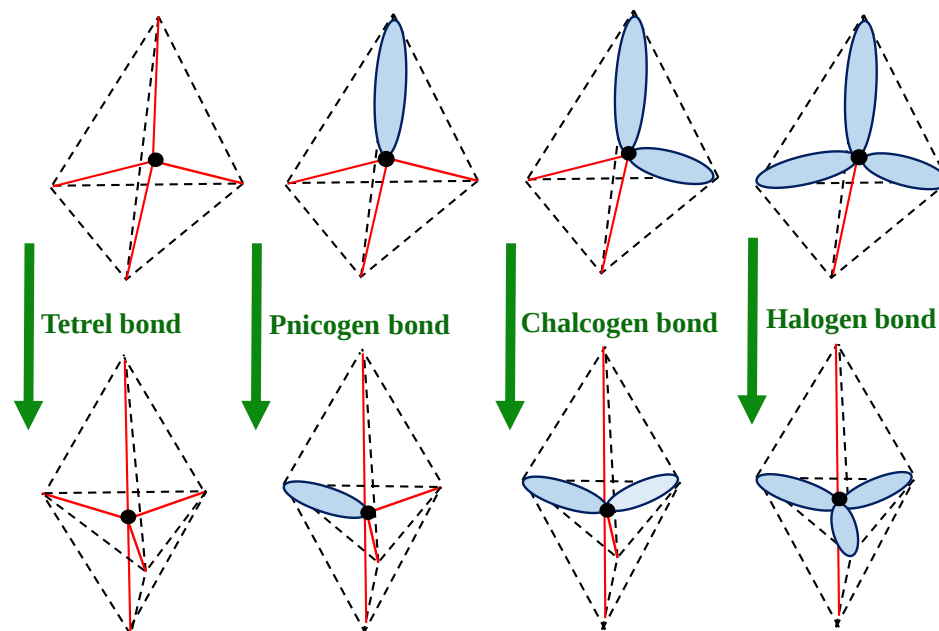
Table 1. Interaction energy (in kcal/mol) and the geometrical parameters (in Å, lengths, and degrees, angles) of the complexes analysed here. The α^* and α angles are defined in Scheme 1; the $\text{F}-\text{Z}\cdots\text{Cl}$ angle concerns the intermolecular contact. $\text{Z}\cdots\text{Cl}$ is the intermolecular distance, the difference between the sum of the corresponding van der Waals radii (the Bondi radii, ref. [53], were applied here), and this $\text{Z}\cdots\text{Cl}$ distance is given in parentheses. The $\text{F}-\text{Z}$ bond length and its corresponding length of the isolated Lewis acid unit, $\text{F}-\text{Z}^*$, are also given. $\text{Z}\cdots\text{Cl}$ distances and E_{int} energies were also presented earlier in another study (ref.17).

Complex	$\text{F}-\text{Z}^*$	$\text{F}-\text{Z}$	$\text{Z}\cdots\text{Cl}$	$\text{F}-\text{Z}\cdots\text{Cl}$	α^*	α	E_{int}
$\text{SiFH}_3\cdots\text{Cl}^-$	1.615	1.707	2.485 (1.37)	180.0	108.2	95.7	−32.6
$\text{PFH}_2\cdots\text{Cl}^-$	1.622	1.733	2.598 (0.95)	167.7	97.7	92.2	−23.6
$\text{SFH}\cdots\text{Cl}^-$	1.634	1.802	2.432 (1.12)	170.0	95.7	88.9	−31.3
$\text{FCl}\cdots\text{Cl}^-$	1.639	1.884	2.276 (1.22)	180.0	–	–	−45.0
$\text{GeFH}_3\cdots\text{Cl}^-$	1.738	1.843	2.587 (>1.26)	180.0	106.5	95.0	−32.6
$\text{AsFH}_2\cdots\text{Cl}^-$	1.751	1.877	2.614 (0.99)	167.0	95.5	89.7	−29.4
$\text{SeFH}\cdots\text{Cl}^-$	1.755	1.914	2.500 (1.15)	169.7	94.2	87.5	−36.7
$\text{FBr}\cdots\text{Cl}^-$	1.758	1.829	2.293 (1.31)	179.9	–	–	−46.3

The above mentioned changes in configurations from the tetrahedral into the trigonal bipyramid were analysed in another study for the tetrel and pnictogen centres if they interacted with the electron-donating species through the σ -hole bonds, through the tetrel bond, or the charge-assisted pnictogen bond [33]. It was found that the reduction of the α angle occurs if the Lewis acid unit interacts with the electron donor; this reduction is greater with the greater electron charge transfer from the Lewis base unit to the Lewis acid unit.

Various changes in configurations that result from interactions are observed. For example, the triel trigonal centres interact with the Lewis base units, causing a change into tetrahedral configurations in the case of strong interactions [54]. However, it is worth mentioning that the configuration in the complex is usually intermediate between that which corresponds to the isolated Lewis acid moiety and that corresponding to the very strong and covalent-in-nature link between interacting units. The aim of this study is to analyse the changes in the tetrel, pnictogen, chalcogen, and halogen centres that interact with the strong Lewis base unit, chloride anion. The following centres are considered here: tetrel ones that possess four covalent bonds, pnictogen centres possessing three bonds and one electron pair, two bonds and two electron pairs occurring in the chalcogen centres, and, for the halogen centres, one bond and three electron pairs were observed (see Scheme 2). It was assumed that all of these centres were characterized by a tetrahedral structure and sp^3 hybridization, at least approximately. However, this was not always true. For example, the water structure was characterized by two covalent O–H bonds and two lone electron pairs. However, in contrast to numerous monographs and scholarly books, these pairs are not equivalent and they do not fit into sp^3 hybridization [55]. Similarly, the latter hybridization does not occur in the case of halogen centres. However, the reaction

paths are often in agreement with this rough assumption [23]. The oxygen of the water molecule in crystal structures is often characterized by the coordination four corresponding to the sp^3 hybridization; the HF dimer possesses the structure that also corresponds to this hybridization for the fluorine centre [24].



Scheme 2. Changes in the tetrahedral configuration into the trigonal bipyramid resulting from the formation of tetrel, pnictogen, chalcogen, and halogen bonds. Red lines correspond schematically to covalent bonds (or strong interactions), while blue ellipsoids correspond to lone electron pairs.

Scheme 2 presents the changes in the configurations of the above centres if they interact strongly with the Lewis base units. The tetrel centre linked by very strong interactions with the Lewis base centre is characterized by the trigonal bipyramid configuration; one can observe three equatorial and two axial neighbours of this centre here. In the case of the remaining interactions—pnictogen, chalcogen, and halogen bonds—the lone electron pairs in complexes possessing trigonal bipyramid configuration are always situated in equatorial positions, while the axial positions are reserved for covalent bonds (Scheme 2). This may be explained by the occurrence of three-centre–four-electron (3c/4e) hypervalent bonds [9] that are observed for the linear systems and axial positions in complexes analysed here. These axial bonds are more polarized and characterized by lower orders than those occurring in the equatorial positions. The latter bond orbitals are usually characterized by high occupancy, close to two, similar to the lone electron pairs located in equatorial positions. The existence of weaker axial bonds than equatorial ones guarantees that the octet rule is obeyed, at least approximately.

3.2. Geometries and Energies

The Quantum Theory of Atoms in Molecules [56,57], QTAIM, is applied here to indicate the interactions between centres in the species analysed in this study. Figures 3 and 4 present molecular graphs of the species that act as the Lewis acid units and the molecular graphs of their corresponding complexes with the chloride anion. There are links between the Z-centre (halogen, chalcogen, pnictogen, or tetrel) and the chloride anion in these systems. The bond paths with bond critical points (BCPs), which are presented in the figures, correspond to the above-mentioned links; this is evidence of the stabilizing interactions in complexes analysed here [58,59]. The Z-centre is linked to the chlorine one through its σ -hole located in the elongation of the F–Z bond. The links through the σ -holes located in the extension of the H–Z bonds are not considered, since the EP positive values are lower here than those for the corresponding F–Z σ -holes. The aim of this study is to

discuss the very strong interactions, and the links through the σ -holes enhanced by the F-substituent guarantee them. The molecular graphs in Figures 3 and 4 correspond to Scheme 2. They also present the changes in the tetrahedral configurations of the Z-centres into trigonal bipyramidal ones. These figures do not show the localizations of lone electron pairs, however. This is why, only in the case of the tetrel bonded complexes, $\text{SiFH}_3\cdots\text{Cl}^-$ and $\text{GeFH}_3\cdots\text{Cl}^-$, the trigonal bipyramidal structures are expressed clearly by the molecular graphs; there are no lone electron pairs in tetrel centres here.

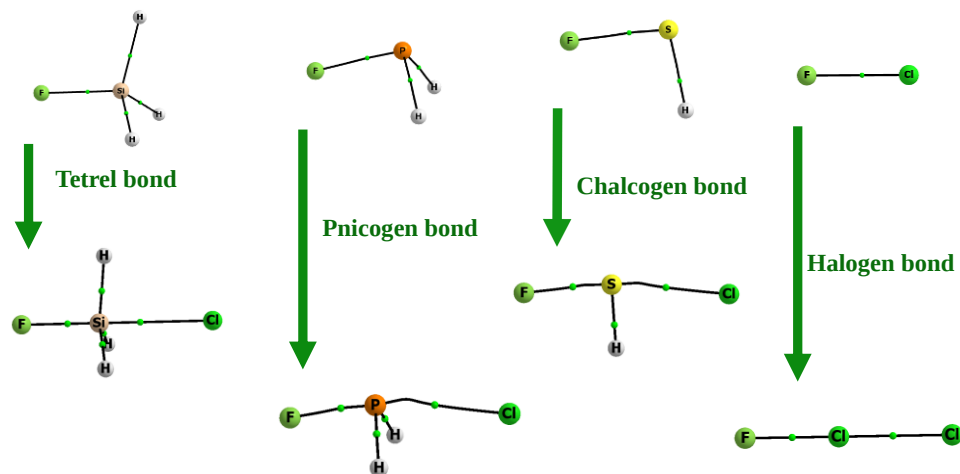


Figure 3. Molecular graphs of the Lewis acid units and the corresponding complexes (Z centre is of the third row of the periodic system). The big circles correspond to attractors (related to the atoms' positions) and the small green circles to bond critical points; attractors are connected by bond paths.

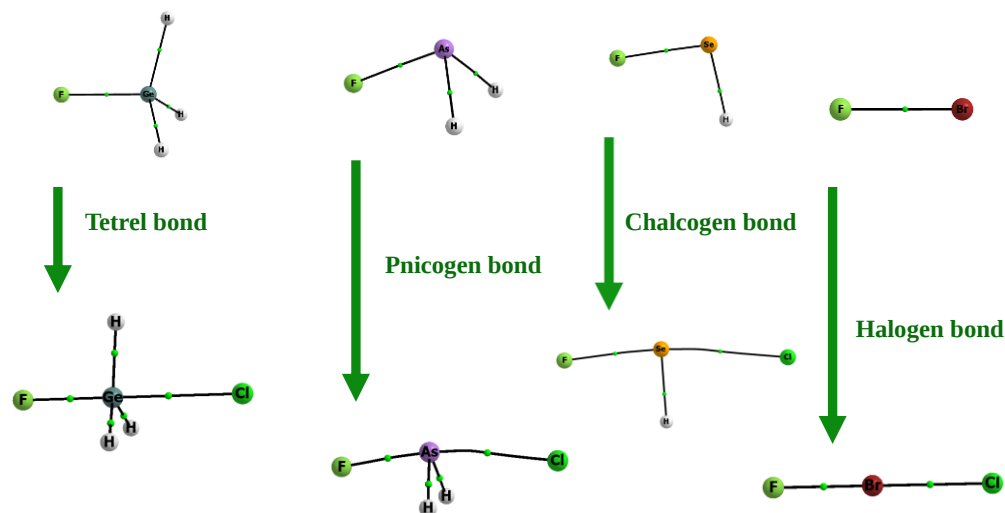


Figure 4. Molecular graphs of the Lewis acid units and the corresponding complexes (Z centre is of the fourth row of the periodic system). The big circles correspond to attractors (related to the atoms' positions) and the small green circles to bond critical points; attractors are connected by bond paths.

It is worth mentioning, however, that the chalcogen bonded systems with the chalcogen centre possessing the trigonal bipyramidal structure were analysed [34], and the ELF approach [60–63] was applied to localize lone electron pairs.

Table 1 presents selected parameters of the analysed complexes; the interaction energies, E_{int} s, are included. Large $|E_{\text{int}}|$ values, usually exceeding 30 kcal/mol, may indicate the covalent character of interactions with the chloride anion. Only for the pnictogen-bonded complexes, $\text{PFH}_2\cdots\text{Cl}^-$ and $\text{AsFH}_2\cdots\text{Cl}^-$, lower $|E_{\text{int}}|$ values, but still high, are observed, which are 23.6 kcal/mol and 29.4 kcal/mol, respectively. It was found in a former study [17] that all interactions with the chloride anion, which are analysed here, possess

numerous characteristics of covalent bonds. Several various parameters indicate the latter characteristics, such as the total electron energy density at the $Z\cdots\text{Cl}$ BCP, H_{BCP} , which is negative, the important contribution to the total interaction of the interaction related to electron charge shifts, or the Heitler–London term of the energy of interaction that is positive. Other parameters that express the covalency of interactions, being a subject of this study, are discussed further here.

Table 1 also presents a few geometrical parameters. One can see that the α angle discussed earlier (Scheme 1), which is included in this table, was greater for the isolated Lewis acid units (α^*) than for these species involved in interactions in complexes (α). In other words, this angle is closer to the tetrahedral configurations for the former species, while, for the latter ones, it is closer to the trigonal bipyramid. However, only in a few cases is the agreement with the parameters of ideal configurations observed; for the isolated tetrel centres, this angle is close to 109.5° , and for the pnictogen and chalcogen-bonded complexes, an angle close to 90° occurs. However, the above differences in the α angle between isolated units and complexes show that the σ -hole interactions lead to the change of configurations (Scheme 2), or at least one can observe the disruption of geometries towards other configurations—from tetrahedral to trigonal bipyramid for the species discussed in this study.

The $\text{F}-\text{Z}\cdots\text{Cl}$ σ -hole interactions analysed here correspond to the linear, or nearly so, arrangements. In particular, the $\text{F}-\text{Z}\cdots\text{Cl}$ angles are equal to or are very close to 180° for the systems linked by tetrel and halogen bonds. This may be explained in the following way. For the former interactions, the σ -hole characterized by the positive electrostatic potential is situated exactly in the extension of the $\text{F}-\text{Z}$ bond, since the ZFH_3 Lewis acid unit possesses the C_{3v} symmetry; in the case of FZ (Z is a halogen centre) species, the same location of the σ -hole is observed—in the extension of the $\text{F}-\text{Z}$ bond. The “belt” of the negative EP around the Z-centre resulting from the lone electron pairs was also observed for such FZ species [15] (see FBr species in Figure 1). In the case of ZFH_2 and ZFH , which are pnictogen and chalcogen species, respectively, the occurrence of lone electron pairs disturbs the location of the σ -holes from the extension of the $\text{F}-\text{Z}$ bond. This is why the $\text{F}-\text{Z}\cdots\text{Cl}$ angle was slightly different from 180° here.

The $\text{F}-\text{Z}$ bond lengths are also presented in Table 1 for the isolated Lewis acid units and for the corresponding complexes with the chloride anion. One can see that, for almost all species, the complexation leads to the elongation of the $\text{F}-\text{Z}$ bond by about 0.1–0.2 Å or even more; only for the $\text{SiFH}_3\cdots\text{Cl}^-$ complex, this elongation is slightly lower than 0.1 Å. The similar elongation of the $\text{A}-\text{H}$ bond that results from the formation of the $\text{A}-\text{H}\cdots\text{B}$ hydrogen bond is observed for the majority of the hydrogen-bonded complexes [3,4]. The shortening of the $\text{A}-\text{H}$ bond being the effect of hydrogen bond formation is not so usual [64,65].

Table 1 shows the $\text{Z}\cdots\text{Cl}$ distances corresponding to the local intermolecular atom–atom contacts. Distances between 2.28 Å and 2.61 Å are observed. They are shorter than the corresponding sums of the van der Waals radii. Referring to these radii, the following values for those were proposed by Bondi [53]: Cl—1.75 Å, Br—1.85 Å, S—1.80 Å, Se—1.90 Å, P—1.80 Å, As—1.85 Å, and Si—2.10 Å (the Bondi value for Ge is not given, but it should be greater than or close to that one of the Si centre). One can see that, for the majority of the $\text{Z}\cdots\text{Cl}$ contacts, the corresponding sum of van der Waals radii amounted to ~ 3.6 Å; this was much greater than the distances in complexes by about 0.95–1.37 Å (Table 1).

3.3. Nature of σ -Hole Bonds

Table 2 shows the NBO [9,45,46] atomic charges for the centres directly involved in the $\text{F}-\text{Z}\cdots\text{Cl}$ σ -hole bond. The Cl centre was characterized by a lower charge (less negative) in the complex than that observed for the free chloride anion (−1 au). This indicates that the complexation leads to the outflow of the electron charge from the anion into the Lewis acid species. Outflow between −0.18 au and −0.44 au is observed for the complexes analysed here. This outflow results in charge changes at the F and Z centres directly involved in

the σ -hole bond; a lower positive charge of the Z-centre and a greater negative charge of fluorine are observed. Both changes oscillate around a value of 0.1 au. However, they are the greatest for the halogen-bonded complexes. For the $\text{FCl}\cdots\text{Cl}^-$ interaction, a decrease in the positive charge of Z by 0.15 au and an increase in the negative charge of the F-centre by 0.30 au are observed; in the case of the $\text{FBr}\cdots\text{Cl}^-$ complex, these changes amount to 0.14 au and 0.24 au, respectively.

Table 2. NBO charges (in au) of the centres of the complexes analysed in this study. $q\text{Cl}_c$ is the charge of the chloride anion involved in the interaction in the complex (for a free anion, this charge is equal to -1 au). $q\text{F}_c$ and $q\text{Z}_c$ are the charges of the F and Z centres in the complex, while $q\text{F}_m$ and $q\text{Z}_m$ are these charges in the isolated Lewis acid units.

Complex	$q\text{F}_m$	$q\text{Z}_m$	$q\text{F}_c$	$q\text{Z}_c$	$q\text{Cl}_c$
$\text{SiFH}_3\cdots\text{Cl}^-$	−0.683	1.500	−0.751	1.387	−0.772
$\text{PFH}_2\cdots\text{Cl}^-$	−0.628	0.898	−0.716	0.797	−0.822
$\text{SFH}\cdots\text{Cl}^-$	−0.524	0.468	−0.684	0.352	−0.730
$\text{FCl}\cdots\text{Cl}^-$	−0.387	0.387	−0.682	0.238	−0.556
$\text{GeFH}_3\cdots\text{Cl}^-$	−0.693	1.401	−0.775	1.318	−0.800
$\text{AsFH}_2\cdots\text{Cl}^-$	−0.660	0.978	−0.761	0.880	−0.804
$\text{SeFH}\cdots\text{Cl}^-$	−0.584	0.590	−0.737	0.470	−0.727
$\text{FBr}\cdots\text{Cl}^-$	−0.482	0.482	−0.718	0.340	−0.622

One can see that the above changes differ from those that occur in hydrogen-bonded systems. For the $\text{A-H}\cdots\text{B}$ hydrogen bond, complexation led to the outflow of the electron charge from the B Lewis base unit, an increase in the negative charge of the A-centre, and an increase in the positive charge of the H-centre [9]. In the case of the σ -hole bonds analysed here, the positive charge of the Z-centre being in contact with the chloride anion decreased.

Table 3 shows the other NBO parameters—the polarizations of bonds involved in interactions in complexes. For the F–Z bonds (in complexes and in isolated species designated by a star), such polarization is understood as the percentage of the F–Z σ bond orbital electron density at the Z-centre. In complexes, these polarizations were lower than those in the isolated Lewis acid units. This means that the complexation leads to the greater outflow of the electron charge from the Z-centre to the more electronegative F-substituent than that observed for isolated Lewis acid units. However, in complexes, the transfer of the electron charge from the chloride anion to the Z-centre is also observed (Table 2); thus, the positive charge of Z decreased, as discussed earlier. It is worth mentioning that the meanings of the F–Z σ -bonds' polarizations discussed here and presented in Table 3 are not the same as those related to the polarization interaction energies resulting from the decomposition schemes [66]. For example, the hybrid variation–perturbation theory (HVPT) [67–69] was applied to perform the decomposition of the energy of the interactions for complexes linked by various σ -hole bonds [17]. It was found that the significance of the delocalization energy term and, consequently, the ratio between the delocalization and electrostatic terms increases with the increase in the strength of the interaction. For the complexes of the chloride anion, the latter ratio is situated between approximately 0.6 and 1.1. The delocalization interaction energy in the HVPT approach is related to the electron charge shift phenomena and it contains the polarization and charge transfer interaction energy terms, which are not separated here. However, they are separated in some other decomposition schemes.

Table 3. Polarizations of the F–Z and Cl–Z bonds; F–Z* is the polarization in the isolated Lewis acid unit. Polarizations express the percentage of the bond orbital electron charge density at the Z-centre. The 3c/4e hyperbonds in halogen-bonded systems are presented; the percentages of the configurations with the Cl–Cl bond and the Cl–Br bonds are given in parentheses.

Complex	Pol F–Z*	Pol F–Z	Pol Cl–Z	3c/4e Hyperbond
SiFH ₃ ...Cl [−]	12.4	8.8	9.0	-
PFH ₂ ...Cl [−]	16.5	10.5	7.1	-
SFH...Cl [−]	22.9	12.2	10.7	-
FCl...Cl [−]	30.3	-	25.6	Cl–Cl–F (62.1)
GeFH ₃ ...Cl [−]	13.1	8.0	7.4	-
AsFH ₂ ...Cl [−]	15.5	8.5	7.4	-
SeFH...Cl [−]	20.1	9.8	10.4	-
FBr...Cl [−]	25.8	-	21.5	Cl–Br–F (60.8)

One can see (Table 3) that the polarizations of Z–Cl links are also presented; this is because the NBO approach shows the Z–Cl bond orbitals for very strong interactions discussed here. In two cases of halogen-bonded complexes, the hypervalent 3c/4e (three centre—four electrons) bonds are formed. These F:–Cl(Br):–Cl hyperbonds are characterized by the following equilibrium: F–Cl(Br): Cl ↔ F:Cl(Br)–Cl. For the F:–Cl:–Cl system, the percentage of the configuration with the Cl–Cl bond amounted to 62.1%, while, for the F:–Br:–Cl system, the percentage of the configuration with the Br–Cl bond amounted to 60.8%. This is why, according to the NBO approach, complexation led to the disappearance of F–Cl(Br) bonds.

Table 4 presents the delocalization indices for the F–Z, $\delta(F,Z)$ and Z–Cl, $\delta(Z,Cl)$ contacts in the F–Z...Cl σ -hole bonds. For the former index, the values for the complex, $\delta(F,Z)$, and for the isolated Lewis acid unit, $\delta(F,Z)^*$ are given. This parameter may be treated as that which expresses the covalent characteristics of the interaction [70,71] (Equation (1)).

$$\delta(A,B) = -2 \int_A \int_B (2\Gamma(r_1, r_2) - \rho(r_1)\rho(r_2)) dr_1 dr_2 \quad (1)$$

where $\rho(r)$ and $\Gamma(r_1, r_2)$ are the one- and two-electron densities, respectively; the integrations are performed here through two atomic basins. Hence, the delocalization index $\delta(A,B)$ corresponds to the number of electrons delocalized between two atoms (A and B). Thus, it expresses the degree of covalency and indicates the number of shared electrons.

Table 4. Delocalization indices for the F–Z and Z–Cl bonds, $\delta(F,Z)$ and $\delta(Z,Cl)$, respectively. $\delta(F,Z)^*$ is the delocalization index for the F–Z bond of the isolated Lewis acid unit.

Complex	$\delta(F,Z)^*$	$\delta(F,Z)$	$\delta(Z,Cl)$
SiFH ₃ ...Cl [−]	0.322	0.256	0.169
PFH ₂ ...Cl [−]	0.572	0.506	0.336
SFH...Cl [−]	0.862	0.692	0.585
FCl...Cl [−]	0.996	0.662	0.749
GeFH ₃ ...Cl [−]	0.544	0.429	0.286
AsFH ₂ ...Cl [−]	0.664	0.543	0.403
SeFH...Cl [−]	0.825	0.639	0.588
FBr...Cl [−]	0.942	0.669	0.728

One can see that the $\delta(F,Z)$ value was lower than the corresponding $\delta(F,Z)^*$ value. This is connected to the elongation of the F–Z bond resulting from the complexation discussed earlier. Such elongation is connected to the decrease in the bond order (bond number) [72,73] and thus with the decrease in the covalent character of the interacting F–Z pair of atoms. The latter decrease is compensated by the additional Z...Cl interaction in the complex. Table 4 shows the $\delta(Z,Cl)$ values for the complexes analysed here. The greatest $\delta(Z,Cl)$ indices are observed for the FCl...Cl[−] and FBr...Cl[−] complexes, 0.749 and 0.728,

respectively. These values correspond to the greatest decreases of the $\delta(F,Z)^*$ values from the isolated species to the $\delta(F,Z)$ values in complexes. They also correspond to the strongest interactions (Table 1); the greatest $|E_{\text{int}}|$ values are observed here, which are 45.0 kcal/mol and 46.3 kcal/mol.

4. σ -Hole Bonds and VSEPR Model—Discussion and Summary

The σ -hole bonds discussed in this study, similar to numerous other interactions, are in line with the Valence-Shell Electron-Pair Repulsion, VSEPR, model. There are the following main assumptions of this model [24,74,75]:

The location of covalent bonds with the centre considered depends on the number of electron pairs in the valence shell; these pairs are attributed to bonds and to nonbonding pairs, such as lone electron pairs.

The valence electron pairs of the centre analysed are located in such a way as to maximize their distances apart.

It is assumed in the VSEPR model that the non-valence inner electrons with the nucleus (this means the core) are characterized by spherical symmetry; in particular, such symmetry is observed for the main groups' elements.

There are the following structures, according to the VSEPR approach, for the increase in the number of electron pairs from two to six: linear (L), trigonal (Tr), tetrahedral (Td), trigonal bipyramid (TBP), and octahedral (Oc); the Tr, Td, TBP, and Oc abbreviations of structures were proposed by Martin [76]. Other designations of structures may be mentioned that indicate the numbers of bonds and lone electron pairs, such as AX_nE_m , (ref. 24) where A indicates the central atom, n is the number of X atoms (not necessarily the same atoms) linked by single bonds with the A centre, and m is the number of nonbonding or lone electron pairs (marked by E). Thus, there are $n+m$ electron pairs in the valence shell of the central atom.

If one refers to the designations mentioned above here, the following changes for the σ -hole bonds analysed in this study can be observed for halogen, chalcogen, pnictogen, and tetrel bonds: $AXE_3 \rightarrow AX_2E_3$, $AX_2E_2 \rightarrow AX_3E_2$, $AX_3E \rightarrow AX_4E$ and $AX_4 \rightarrow AX_5$, respectively.

Another way to mark various interactions was proposed recently [23]. This is because marks related to changes in configurations are much more informative than those often applied in various studies so far. For example, for halogen bonds that occur in the complexes analysed here, there are the following marks: $(AXE_3 \rightarrow AX_2E_3) \text{ Cl} \cdots \text{Cl}$, $(AXE_3 \rightarrow AX_2E_3) \text{ Br} \cdots \text{Cl}$; for chalcogen bonds, $(AX_2E_2 \rightarrow AX_3E_2) \text{ S} \cdots \text{Cl}$ and $(AX_2E_2 \rightarrow AX_3E_2) \text{ Se} \cdots \text{Cl}$; for pnictogen bonds, $(AX_3E \rightarrow AX_4E) \text{ P} \cdots \text{Cl}$ and $(AX_3E \rightarrow AX_4E) \text{ As} \cdots \text{Cl}$; and for tetrel bonds, $(AX_4 \rightarrow AX_5) \text{ Si} \cdots \text{Cl}$ and $(AX_4 \rightarrow AX_5) \text{ Ge} \cdots \text{Cl}$. These designations inform of the changes in the configurations and the centres being in contact; the Lewis acid and the Lewis base centres at the left and right sites, respectively. For all interactions analysed here, a change of the tetrahedral structure towards the trigonal bipyramid occurs (see Scheme 2 as well as Figures 3 and 4).

There were interrelations between the positions of bonds and lone electron pairs for the trigonal bipyramid structure, TBP. The positions of vertices for TBP are not equivalent. The non-equivalency may be interpreted in relation to the positions of lone electron pairs and bonds [24]. However, one can refer also to the ω 3c/4e hypervalent bonds discussed by Weinhold and Landis [9] that correctly explains the locations of lone electron pairs in TBP structures. These pairs are characterized by electron occupancies equal to or very close to two. On the other hand, the bonds often have occupancies much lower than two, especially in the case of significant bonds' polarizations. Hence, for TBP structures, the lone pairs occupy the positions in the triangle and they are not directed to the axial vertices. The axial XAX arrangement may be considered as the ω 3c/4e hypervalent bond, where a shift of the electron charge to the X centres is observed. In the case of such arrangements where lone electron pairs may occupy only triangle positions, the eight-electron valence

shell of the A-centre is exceeded only slightly (if at all) and the octet rule is obeyed, at least approximately.

The details of the new designations of interactions were discussed in the previous study [23]. Only selected types of interactions (see Scheme 2) are discussed here. It is shown here that they are at least partly covalent in nature; three-centre–four-electron, 3c/4e, bonds found for the halogen-bonded systems. The most important is that, for all interactions discussed here—halogen, chalcogen, pnictogen, and tetrel bonds—if one refers to the designations often applied in various studies, they possess similar characteristics. The common feature is that they are related to the change in the tetrahedral structure towards the trigonal bipyramid. This is connected certainly to the electron charge shifts from the chloride anion to the Lewis acid unit.

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