Cooperative Effects in Weak Interactions: Enhancement of Tetrel Bonds by Intramolecular Hydrogen Bonds

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Abstract: A series of silyl and germanium complexes containing halogen atoms (fluorine and chlorine atoms) and exhibiting tetrel bonds with Lewis bases were analyzed by means of Møller-Plesset computational theory. Binding energies of germanium derivatives were more negative than silicon ones. Amongst the different Lewis bases utilized, ammonia produced the strongest tetrel bonded complexes in both Ge and Si cases, and substitution of the F atom by Cl led to stronger complexes with an ethylene backbone. However, with phenyl backbones, the fluorosilyl complexes were shown to be less stable than the chlorosilyl ones, but the opposite occurred for halogermanium complexes. In all the cases studied, the presence of a hydroxyl group enhanced the tetrel bond. That effect becomes more remarkable when an intramolecular hydrogen bond between the halogen and the hydrogen atom of the hydroxyl group takes places.

Keywords: non-covalent interactions; MP2; binding energy; intramolecular hydrogen bonds; tetrel bonds

1. Introduction

One of the major achievements in contemporary chemistry was the introduction by Jean-Marie Lehn of supramolecular chemistry [1]. According to Vögtle “In contrast to molecular chemistry, which is predominantly based upon the covalent bonding of atoms, supramolecular chemistry is based upon intermolecular interactions, i.e., on the association of two or more building blocks, which are held together by intermolecular bonds”. Today, these intermolecular bonds are called weak interactions regardless of whether they are intra or intermolecular. There are numerous weak interactions, also known as non-covalent interactions, and they have been shown to be of the utmost importance across different domains including biology, chemistry and material science [2]. These non-covalent interactions have been categorised based on the interacting atoms involved: hydrogen bonds [3,4], halogen bonds [5], hydride bonds [6,7], pnictogen bonds [8–13], chalcogen interactions [14–18] and tetrel bonds [19–22]. The latter, tetrel bonds, are defined, analogous to halogen bonds, as interactions between electron donors and tetrel atoms (C, Si and Ge), in which the tetrel atom acts as an electron acceptor, usually through an electron-deficient outer lobe of a p orbital, called a σ-hole [23] by Politzer and Murray [24–26], which is formed in the tetrel atom, especially when the atom bonded to the tetrel is highly electronegative. It has also been shown that interactions through σ-holes are mainly driven by the electrostatic interaction term [27–38].
Related to this topic is cooperativity, usually intermolecular (allosteric), but also, although much less studied, intramolecular [39]. There are two relevant papers. Berryman et al. reported the synthesis and anion-binding properties of receptor 1 (2,6-bis-(4-ethynylpyridinyl)-4-fluoroaniline) which can act as a halogen donor, trapping a wide variety of anions (Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), SCN\(^{-}\), NO\(_3\)^\(^{-}\), HSO\(_4\)^\(^{-}\), H\(_2\)PO\(_4\)^\(^{-}\) and ReO\(_4\)^\(^{-}\)) [40] (Scheme 1). The presence of intramolecular N-H···I hydrogen bonds (HBs) increases the strength of the I···anion halogen bonds (XBs).

![Scheme 1. Schematic description of 2,6-bis(4-ethynylpyridinyl)-4-fluoroaniline interacting with anions.](image)

For each X, they calculated the electrostatic potential map as a function of the torsion angle \(\phi\). They found that the positive zone increases considerably when the torsion angle approaches 0\(^{\circ}\), i.e., when there is an IMHB.

In the present article, the effect of the intramolecular hydrogen bond in fluoroaryl and fluorogermainium derivatives and their abilities as tetrel bond donors is studied (Scheme 3). The following notation will be used to label the complexes studied throughout the manuscript: \(nTX_{aZ}:LB\), where “\(n\)” stands for the two types of carbon backbone (1=allyl, 2=phenyl), “T” stands for the tetrel atom (Si or Ge), “Z” indicates whether the complex exhibits, or does not exhibit, an intramolecular hydrogen bond (IMHB or none), “a” indicates the presence of an OH group in the molecule (hydroxyl=H) or not (allyl=A). Finally, LB stands for the Lewis Base involved (NH\(_3\), H\(_2\)O or HCN). For example, 1GeCl\(_{A}^{\text{IMHB}}\)N\(_{3}\) corresponds to an allylchlorogermainium derivative interacting with ammonia in which the OH group is present and forming an intramolecular hydrogen bond. The short notation 1TX:LB will be used to refer the whole complex family.
2. Results

In order to evaluate the appropriate computational level for the present study, a benchmark across different basis sets has been carried out. For such purpose, 1SiF:NH₃ complexes (1SiF₆:NH₃, 1SiF₇:NH₃, and 1SiF₈(IMHB):NH₃) were optimized by means of Møller-Plesset (MP2) using different basis sets, i.e., aug-cc-pVDZ (avdz), aug-cc-pVTZ (avtz), aug-cc-pVQZ (avqz), and using Helgaker’s method to extrapolate to the complete basis set (CBS) with two pairs of basis: aug-cc-pVDZ and aug-cc-pVTZ (CBSDT) and aug-cc-pVTZ and aug-cc-pVQZ (CBSTQ). Using those levels, the binding energies (Eb), obtained as a difference of the energy of the complex minus the energies of the isolated monomers in their optimized structure, for these three complexes, were calculated and are summarized in Table 1. As observed, for the evolution of the energy values, avdz < avtz < avqz, it seems that there is a strong dependency of the binding energy with respect to the basis set size. When extrapolation to the complete basis set (CBS) is taken into account, it was also observed that extrapolations using two different pairs of basis set, CBSDT and CBSTQ, also provide different results, with the latter, in our opinion, more accurate than the former. Taken into account the outcome of the current benchmark and the computational feasibility of the calculations, the MP2/CBSTQ computational method was chosen to evaluate the rest of the complexes, and from hence forth, named MP2/CBS for simplicity.

Table 1. Binding energies (E_b), in kJ·mol⁻¹, of 1SiF:NH₃ complexes at the MP2 computational level with different basis sets including extrapolation to the complete basis set limit (CBS) with two different basis set pairs.

|         | avdz | avtz | avqz | CBSDT | CBSTQ |
|---------|------|------|------|-------|-------|
| 1SiF₆:NH₃ | −29.3 | −25.4 | −23.8 | −24.5 | −21.8 |
| 1SiF₇:NH₃ | −32.3 | −28.2 | −25.9 | −27.4 | −22.9 |
| 1SiF₈(IMHB):NH₃ | −40.5 | −36.3 | −34.4 | −35.4 | −31.7 |

*a avdz, avtz and avqz stand for aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ respectively. **CBS stands for extrapolation to the complete basis set limit, and DT and TQ refer to the pair of basis set used to extrapolate: avdz-avtz and avtz-avqz, respectively.

2.1. Allylfluorotetrel Derivatives: Effect of the Lewis Bases (1TF:LB)

The effect of the Lewis bases upon complexation within 1TF:LB complexes (Figure 1) was evaluated using three different Lewis bases, i.e., NH₃, H₂O and HCN. The intermolecular T···Y (Y = N or O) distances at the MP2/aug-cc-pVTZ computational level are gathered in Table 2. Molecular graphs and Cartesian coordinates can be found in the electronic supplementary information (Table S1). The intermolecular Si···N distances found in 1SiF:NH₃ range from 2.276 (1SiF₈(IMHB):NH₃) to 2.518 Å.
(1SiF₃:NH₃), while in 1GeF:NH₃, the Ge···Y distance ranges from 2.450 (1GeF₃ IMHB: NH₃) to 2.661 Å (1GeF₃: NH₃). As observed, 1TF₃ IMHB: NH₃ complexes present the shortest intermolecular T···Y distances (Table 2). Looking at the 1SiF₃: NH₃ complex, the intermolecular Si···N distance is 2.518 Å. When the 1SiF₃: NH₃ complex is taken into account, there is a shortening of 0.183 Å on the Si···N distance. This shortening can point to a decrease in the electron density on the Si atom due to the OH group and therefore an increase in the σ-hole depth, which eventually will enhance the tetrel bond. This shortening is even more visible in 1SiF₃ IMHB: NH₃ complex (0.242 Å), which may indicate that the intramolecular hydrogen bond (IMHB) enhances the tetrel bond. In the case of 1GeF: LB germanium complexes, similar but more pronounced trends in the intermolecular Ge···N distances were found due to the IMHB and hydroxyl groups. Furthermore, the T-F distance was also analyzed to evaluate the polarity of the T-F bonds with the IMHB. T-F distance for the 1SiF₃: NH₃ complex is 1.643 Å, while in 1SiF₃: NH₃ and 1SiF₃ IMHB: NH₃ complexes, they are 1.654 and 1.685 Å, respectively, indicating an increase in the charge transfer to the T-F σ* orbital, particularly in the complexes exhibiting IMHB. The same is true for 1GeF: NH₃ complexes (1.768, 1.776 and 1.815 Å for 1GeF₃:NH₃ complex, 1GeF₃:NH₃ and 1GeF₃ IMHB: NH₃ complexes, respectively).

![Figure 1. Molecular graphs for 1SiF:LB complexes at the MP2/aug-cc-pVTZ computational level. Green dots correspond to bond critical points.](image)

When different Lewis bases are considered (Table 2), it can be seen that complexes with ammonia have the shortest intermolecular T···Y distances. However, similar trends were observed for 1TF: H₂O complexes compared with 1TF: NH₃ complexes, where the T···Y distance evolves as follows: 1TF₃: H₂O > 1TF₃: H₂O > 1TF₃ IMHB: H₂O. In the case of 1TF: HCN complexes, the 1TF₃: HCN complex seems to deviate from this trend, exhibiting a lengthening in the intermolecular T···Y distance. The reason

| Comp.       | NH₃   | H₂O   | HCN  |
|-------------|-------|-------|------|
| 1SiF₃:LB    | 2.518 | 2.885 | 2.991|
| 1SiF₃:LB    | 2.335 | 2.883 | 4.033|
| 1SiF₃ IMHB:LB | 2.276 | 2.765 | 2.873|
| 1GeF₃:LB    | 2.661 | 2.829 | 2.898|
| 1GeF₃:LB    | 2.570 | 2.782 | 2.891|
| 1GeF₃ IMHB:LB | 2.450 | 2.720 | 2.789|
behind is that in those complexes (both for 1SiF\textsubscript{4}:HCN and 1GeF\textsubscript{4}:HCN), the O atom from the OH group acts as an electron donor and performs an intermolecular hydrogen bond with the Lewis base. In other words, the Lewis base acts as a hydrogen donor. That provokes a re-orientation of the Lewis base which lengthens the T···N distance. If the molecule is constrained to Cs symmetry, forcing those abovementioned to be co-planar, an imaginary frequency is found which, if followed, reverts into the actual rotated structure with \textit{C\textsubscript{1}} symmetry.

In order to evaluate the interaction energies between 1TF compounds and the Lewis base, binding energies (\(E_b\)), interaction energies (\(E_{\text{int}}\)) and deformation energies (\(E_{\text{def}}\)) were calculated at the MP2/CBS computational level and are summarized in Table 3 and with a histogram plotted in Figure 1. Binding energies (\(E_b\)) and interaction energies (\(E_{\text{int}}\)) were calculated as described in the “Materials and Methods” section. The deformation energy (\(E_{\text{def}}\)), also called re-organization energy, was calculated as the difference between \(E_b\) and \(E_{\text{int}}\). \(E_b\) ranges from \(-21.8\) to \(-41.0\) kJ·mol\(^{-1}\) for 1TF:HCN complexes. In 1TF:H\textsubscript{2}O, it ranges from \(-15.9\) to \(-26.9\) kJ·mol\(^{-1}\), and \(-14.5\) to \(-25.1\) kJ·mol\(^{-1}\) for 1TF:HCN ones. In all cases, 1TF:NH\textsubscript{3} complexes show stronger interactions than 1TF:H\textsubscript{2}O or 1TF:HCN ones as per the \(E_b\) values. Focusing on the 1SiF:NH\textsubscript{3} complexes, it was observed that the \(E_b\) value calculated for 1SiF\textsubscript{4}:NH\textsubscript{3} is \(-21.8\) kJ·mol\(^{-1}\), and when the hydroxyl groups are present, \(E_b\) becomes slightly more negative (\(-22.9\) kJ·mol\(^{-1}\)), which indicates a strengthening of the interaction. This strengthening is even larger in 1SiF:IMHB:NH\textsubscript{3} (\(E_b = -31.7\) kJ·mol\(^{-1}\)), which shows that when the IMHB takes place, the interactions between the complex and the Lewis base are stronger. The same occurs for the 1GeF:NH\textsubscript{3} complexes. In the case of water complexes, the \(E_b\) follows the same trend as in ammonia complexes. However, the 1TF\textsubscript{4}:H\textsubscript{2}O complex presents slightly more negative values of \(E_b\) than the 1TF\textsubscript{4}:IMHB:H\textsubscript{2}O complex, which is likely due to a secondary intermolecular hydrogen bond in which water is acting as a hydrogen bond donor (Figure 1). This could be the reason behind the extra stabilization in the \(E_b\). The opposite happens for the 1TF:HCN complexes in which 1TF\textsubscript{4}:HCN is less stable than its parental complex, 1TF\textsubscript{4}:HCN. As explained above, this is provoked by a re-orientation of the Lewis base in the 1TF\textsubscript{4}:HCN due to the presence of the hydroxyl group, which acts as an electron donor and forms an intermolecular hydrogen bond with the HCN (Figure 1). Poor correlations between the binding energy and the intermolecular distances were found, which may be due to the secondary hydrogen bonds in the 1TF\textsubscript{4}:LB complexes and electronic repulsions between atoms due to the electron lone pairs [42].

| Complex          | \(E_b\)  | \(E_{\text{int}}\) | \(E_{\text{def}}\) |
|------------------|----------|---------------------|---------------------|
|                  | NH\textsubscript{3} | H\textsubscript{2}O | HCN | NH\textsubscript{3} | H\textsubscript{2}O | HCN | NH\textsubscript{3} | H\textsubscript{2}O | HCN |
| 1SiF\textsubscript{4}:NH\textsubscript{3} | -21.8   | -15.9 | -14.6 | -35.2 | -17.7 | -16.1 | 13.6 | 1.8 | 1.4 |
| 1SiF\textsubscript{4}:NH\textsubscript{3} | -22.9   | -19.2 | -14.5 | -51.3 | -24.1 | -16.7 | 28.4 | 4.9 | 2.2 |
| 1SiF\textsubscript{4}:IMHB:NH\textsubscript{3} | -31.7   | -18.2 | -16.9 | -60.6 | -21.2 | -19.2 | 28.8 | 3.0 | 2.4 |
| 1GeF\textsubscript{4}:NH\textsubscript{3} | -31.2   | -21.6 | -21.6 | -38.0 | -23.1 | -22.9 | 6.8 | 1.5 | 1.3 |
| 1GeF\textsubscript{4}:NH\textsubscript{3} | -31.9   | -26.9 | -14.7 | -43.9 | -31.1 | -16.6 | 12.0 | 4.2 | 1.9 |
| 1GeF\textsubscript{4}:IMHB:NH\textsubscript{3} | -41.0   | -25.1 | -25.6 | -56.1 | -27.6 | -27.9 | 15.1 | 2.4 | 2.3 |

To evaluate the re-organization energy, i.e., the relaxation energy of the monomers and the energy penalty upon complexation, the interaction energies were evaluated. As observed (Figure 2), \(E_{\text{int}}\) values for all the complexes studied are more negative than the corresponding \(E_b\) values; this is particularly dramatic for the 1SiF:NH\textsubscript{3} complexes in which the \(E_{\text{int}}\) values are the most negative of all complexes. When the difference of both quantities (\(E_b - E_{\text{int}}\)) is taken into account, the deformation energy, \(E_{\text{def}}\), values (Table 3) indicate that 1TF:NH\textsubscript{3} complexes suffer a larger penalty in binding energy due to re-organization than 1TF:H\textsubscript{2}O and 1TF:HCN complexes.
Table 4. Binding energies (\(E_b\)), interaction energies (\(E_{int}\)) and deformation energies (\(E_{def}\)), at the MP2/CBS computational level, in kJ mol\(^{-1}\), intermolecular T···N distances and T-X bond distances (T=Si, Ge and X=F, Cl), in Å for 1TX:NH\(_3\) complexes at the MP2/aug-cc-pVTZ computational level.

| Complex         | \(E_b\)   | \(E_{int}\) | \(E_{def}\) | \(T\cdots N\) | \(T-X\) |
|-----------------|-----------|-------------|-------------|--------------|---------|
| 1SiX\(_3\):NH\(_3\) | -21.8     | -33.4       | 14.2        | 3.6          | -2.8    |
| 1SiX\(_4\):IMHB:NH\(_3\) | -22.9     | -36.9       | 18.5        | 3.8          | -3.1    |
| 1GeX\(_4\):NH\(_3\) | -31.2     | -43.9       | 19.7        | 4.3          | -3.5    |
| 1GeX\(_4\):IMHB:NH\(_3\) | -41.0     | -56.1       | 22.9        | 4.9          | -4.4    |

In terms of binding energies, 1TF:NH\(_3\) complexes show slightly more negative \(E_b\) values than 1TCl:NH\(_3\) complexes, which may be caused by an increase in the depth of the \(\sigma\)-hole on the tetrel atom.
(Table S2). Fluorine atoms withdraw more electron density, therefore the σ-hole on the tetrel atom is deeper, so 1TF:NH₃ complexes will have more negative Eₚ values than 1TCl:NH₃ complexes. Once again, the only exception corresponds to 1SiCl:NH₃ with an Eₚ value of −24.5 kJmol⁻¹, while the 1SiF₃:NH₃ Eₚ value is −22.9 kJmol⁻¹. In both cases, the halogen atom does not form any IMHBs, which reinforces the idea that IMHBs are stabilizing the complex. Regarding the interaction energy, Eₚ is shown to be more negative than Eₚ, which is as expected because the Eₚ suffers from the re-organization penalty. In fact, Eₚ values indicate that this penalty is larger for silyl complexes than germanium ones, and within the same tetrel family (1TX:NH₃), the deformation energy is much larger, up to three times larger in some cases, for complexes with hydroxyl groups (1Tₜₐ:H₃ and 1TXₜIMHB:NH₃) than in their parental complexes (1SiX₃:NH₃).

2.3. Phenyl Halogen Tetrel Derivatives: Effect of the Backbone (2TX:NH₃)

Finally, different carbon backbones have been evaluated by means of replacing the allyl backbone with a phenyl ring focusing only on complexes with ammonia. The intermolecular T···N distances, Eₚ, Eₚ, Eₚ, and T-X bond distances are summarized in Table 5. Intermolecular T···N distances in 2TX:NH₃ complexes present similar values to those in 1TX:NH₃ complexes, but with slight variations. 2TFₚₙ:NH₃ complexes (both for Si and Ge) exhibit longer T···N distances (2.596 and 2.703 Å, respectively) than 1TFₚₙ:NH₃ complexes (2.518 and 2.661 Å), and the same occurs for 2TXₜIMHB:NH₃ complexes, while the opposite is true for 2Tₜₐ:H₃ (Si = 2.330 and Ge = 2.553 Å) compared with 1Tₜₐ:H₃ (Si = 2.335 and Ge = 2.570 Å). As in 1TX:NH₃ complexes, the ones with hydroxyl groups present, both 2Tₜₐ:H₃ and 2TXₜIMHB:NH₃ exhibit a shortening of the T···N distances. However, looking at the T-X bond distances, both for X=F and Cl, a lengthening is observed in 2TXₚₙ:H₃ and 2TXₜIMHB:NH₃ consistent with the results mentioned above and the increase in polarity of the T-X bond with the presence of hydroxyl groups and IMHBs.

| Complex               | Eₚ      | Eₚ      | Eₚ      | T···N | T-X     |
|-----------------------|---------|---------|---------|-------|---------|
| 2SiX₃:Fₙ:NH₃          | X=F     | X=Cl    | X=F     | X=Cl  | X=F     | X=Cl  |
| 2SiX₃:Cl:NH₃          | −23.7   | −28.7   | −59.13  | −61.07| 33.9    | 33.2  |
| 2SiX₃:Cl:NH₃          | −25.2   | −27.9   | −55.27  | −59.79| 31.6    | 31.1  |
| 2SiX₃Cl:IMHB:NH₃      | −29.0   | −27.8   | −34.45  | −31.73| 5.4     | 3.9   |
| 2SiX₃Cl:IMHB:NH₃      | −32.1   | −31.3   | −55.44  | −48.18| 15.3    | 13.3  |
| 2GeX₃Cl:IMHB:NH₃      | −40.1   | −34.9   | −47.60  | −44.99| 15.5    | 13.7  |

Binding energies for 2TX:NH₃ complexes are found to be within the same range as 1TX:NH₃ complexes, with 2TXₚₙ:NH₃ and 2TXₜIMHB:NH₃ complexes exhibiting larger Eₚ values than their corresponding allyl counterparts, while 2Tₜₐ:H₃:NH₃ complexes present slightly smaller Eₚ values than 1Tₜₐ:H₃:NH₃ complexes, both for T=Si, Ge and X=F, Cl. Eₚ values show that in all cases, 2SiCl:NH₃ complexes have a stronger interaction with NH₃ than 2SiF: NH₃ complexes, while the opposite is true for the germanium derivatives. In terms of interaction energies, Eₚ values in Table 5 reveal similar features to those found for the allyl complexes, i.e., large negative values of Eₚ, twice as much in some cases (for example: 2SiX₃Cl:NH₃). This indicates a substantial re-organization energy, which was also confirmed when the Eₚ values were analyzed. Eₚ values are very large, in fact, silyl complexes with hydroxyl groups (2SiX₃Cl:NH₃) present the largest deformation energies, as occurred in 1SiCl:NH₃ complexes. This can be explained in terms of electronic repulsion between groups, as explained above [42].

If we compare the evolution of the binding energy across the 2TX:NH₃ complexes, it is seen that the presence of hydroxyl (2TXₜIMHB:NH₃) enhances the interaction with the Lewis base in about 10.2%
(2SiF₃:NH₃) and 10.7% (2GeF₃:NH₃). This enhancement is even larger within 2TCl:NH₃ complexes (33.4% and 12.4% in 2SiCl₃:NH₃ and 2GeCl₃:NH₃, respectively). Besides, the enhancement of the binding energy reaches the maximum value when the IMHB takes place in the complex, reaching up to 38.2% of enhancement on the E_b with respect to the 2TXₐ:NH₃ complex.

2.4. Electron Density Properties

The electron density properties of the intermolecular tetrel interactions were studied by means of atoms in molecules (AIM) theory. In most of the cases, the tetrel bond is characterized by the existence of a bond critical point (BCP) between the tetrel atom and the electron donor on the Lewis base moiety (N or O) (Table S1). As it is denoted in the literature, this should be taken carefully, since the opposite is not true, i.e., the absence of a BCP between two interacting atoms does not necessarily imply the absence of interactions [43]. It has been found that in some cases dominant weak interactions exhibit neither BCP nor bond paths [44]. However, while the BCPs should be taken cautiously and there is a huge debate about the interpretation of the bond paths and their relationship to the chemical bond, the existence of BCPs and their associated properties has been proven to be a useful tool to identify non-covalent interactions across the different varieties: hydrogen [45,46], halogen [47], pnictogen [48], chalcogen [14] and tetrel bonds [49].

The electron density parameters obtained are summarized in Table S3. Values of the electron density at the bond critical (ρ_{BCP}) for 1SiF:NH₃ and 1GeF:NH₃ complexes range from 0.0270 to 0.045 a.u. and 0.0241 to 0.0366 a.u., respectively. Values for 1SiF:HCN and 1GeF:HCN complexes, which show similar T⋯N interactions, are smaller at 0.0101–0.0129 a.u. and 0.0132–0.0158 a.u., respectively. This is aligned with the interaction and binding energy values found and the intermolecular T⋯N distance evolution. Similar comparison trends are found for the Laplacian (∇²ρ_{BCP}) values and total electron energy density (H_{BCP}) values between those complexes.

1TCl:NH₃ complexes show very similar ρ_{BCP} values to 1TF:NH₃, concomitantly with similar Laplacian and H_{BCP} values, with slight differences. Cremer et al. demonstrated that the sign of the total electron energy density (H_{BCP}), defined as the sum of G_{BCP} + V_{BCP}, could be used to indicate the degree of covalency for chemical interactions [50–52]. H_{BCP} values have been found to be negative for interactions that significantly share electrons. In fact, in other interactions, such as pnictogen bonds, the electron density increment within intermonomeric regions has been postulated as a stabilizing factor [53]. As observed for 1TX:NH₃ complexes (Table S3), negative H_{BCP} values are found and they may indicate a certain covalent character of the tetrel interaction. Furthermore, 1TXₐ^{IMHB}:NH₃ complexes present the most negative H_{BCP} values, which reinforces the idea that hydroxyl groups performing IMHB enhance tetrel bonds.

Exponential relationships have been found between the electron density at the BCP and the intermolecular T⋯N distance; Si⋯N distances show better correlations (ρ = 3.8959 e⁻¹.9863 d(T⋯N), R² = 0.991) than Ge⋯N (ρ = 5.7894 e⁻².0706 d(T⋯N), R² = 0.943) interactions as observed in Figure 3a. Similar relationships have also been found between the Laplacian and T⋯N distance (∇²ρ = 0.76454 e⁻¹.0514 d(T⋯N), R² = 0.947 and ∇²ρ = 3.6611 e⁻¹.5177 d(T⋯N), R² = 0.982 for T = Si and Ge complexes, respectively) as depicted in Figure 3b.

In order to provide further insight into the electron density changes upon complexation, electron density shift maps (EDS) at the ±0.002 a.u. isosurfaces are plotted in Figure 4. Blue areas correspond to those regions with a decrease in the electron density upon complexation, while yellow areas indicate those regions in which an increase in the electron density occurs. As observed, the 1SiFₑ:NH₃ complex shows an increase (positive yellow area) in electron density between the N and Si atoms, corresponding to the donation of electron density from the Lewis base into the Si σ-hole. This pattern of depletion–increase in electron density has been observed for a wide range of inter/intramolecular interactions [14,54–58]. When 1SiF₃:NH₃ and 1SiF₃^{IMHB}:NH₃ complexes are considered, the changes in electron density upon complexation become even more evident: blue (negative) and yellow (positive) areas are larger for 1SiF₃:NH₃ and 1SiF₃^{IMHB}:NH₃ complexes than for 1SiF₃:NH₃ complexes,
particularly in the areas surrounding the ammonia in which a drastic decrease in electron density is observed. This decrease is due to the larger electron density donation from the Lewis base in complexes with hydroxyl groups (1SiF_H:NH_3 and 1SiF_HIMHB:NH_3) than in the 1SiF_A:NH_3 one. When the phenyl backboned complexes are taken into account, the electron density shift maps show very similar increase/decrease patterns compared to the allyl one. Furthermore, there are no appreciable changes in the shape or size of the blue and yellow areas in comparison with the 1SiF:NH_3 complexes, which is in consonance with the binding/interaction energies and the evolution of intermolecular T···N distances.

Figure 3. Exponential relationships between (a) electron density at the bond critical point and (b) Laplacian at the bond critical point with the intermolecular T···N distance at the MP2/aug-cc-pVTZ computational level.

Figure 4. Electron density shift maps for the nSiF:NH_3 (n = 1, 2) complexes on the ±0.002 a.u. electron density isosurfaces at the MP2/aug-cc-pVTZ computational level. Blue and yellow areas correspond to regions with a decrease and increase in electron density, respectively.
3. Materials and Methods

The structures of the complexes were optimized at the Møller-Plesset (MP2) [59]/aug-cc-pVTZ [60,61] computational level. Harmonic vibrational frequencies were computed at the same level used for the geometry optimizations in order to confirm that the stationary points are local minima. Calculations were performed using the Gaussian09 program [62]. Binding energies ($E_b$) were calculated as a difference in the energy of the complex minus the energy of each monomer in their optimized geometry. Interaction energies ($E_{int}$) were calculated as a difference in the energy of the complex minus the energy of each monomer, keeping the monomer geometry fixed in the complex optimized geometry. Finally, the deformation energy ($E_{def}$), also called the re-organization energy, was calculated as the difference between $E_b$ and $E_{int}$. In order to provide more accurate energies the interaction energies were also estimated at the MP2/CBS (complete basis set) limit using the method of Helgaker et al. [63,64] from the calculated interaction energies with the aug-cc-pVTZ and aug-cc-pVQZ basis sets:

$$E_X^{HF} = E_{CBS}^{HF} + Ae^{-\alpha X}$$

$$E_X^{MP2} = E_{CBS}^{MP2} + BX^{-3}$$

where $E_X$ and $E_{CBS}$ are the energies for the basis set with the largest angular momentum $X$ and for the complete basis set, respectively.

The atoms in molecules (AIM) methodology [65,66] was used to analyze the electron density of the systems with the AIMAll program [67].

The intermolecular electron density shift (EDS) [58] was calculated using Equation (3):

$$EDS = \rho(nTX:NH_3) - \rho(nTX) - \rho(NH_3)$$

where $\rho(nTX:NH_3)$, $\rho(nTX)$ and $\rho(NH_3)$ stand for the electron density of the complex and both fragments in the geometry of the complex, respectively.

4. Conclusions

The complexation of a series of silyl (nSiX:LB) and germanium (nGeX:LB) complexes, with two different halogen atoms (X=F and Cl) was studied. Three different Lewis bases (NH$_3$, H$_2$O and HCN) were considered to form the complexes and the effect of the existence or absence of intramolecular hydrogen bonds on the intermolecular tetrel bond were analyzed.

Calculated geometrical parameters and binding and interaction energies suggested that the presence of hydroxyl groups enhances the intermolecular tetrel bond. In general, $n$TX$_3$:LB and $n$TX$_2$IMHB:LB complexes presented shorter intermolecular T···Y distances than their parental $n$TX$_3$:LB complexes. This fact, concomitantly with the $E_b$ values found: $E_b(n$TX$_3$:LB) < $E_b(n$TX$_2$:LB), indicates a strengthening of the tetrel bond with the presence of hydroxyl groups, whether it is forming an IMHB or not. However, the data analyzed reveal that when the IMHB takes place, the enhancement is even larger than without it.

Regarding the Lewis base, complexes with NH$_3$ showed the most negative binding energies, followed by H$_2$O and HCN.

The substitution of the fluorine atom (X=F) by a chlorine atom, in general, weakens the tetrel bond in allyl complexes (1TCl:NH$_3$), which show $E_b$ and $E_{int}$ values larger than its fluorine counterparts.

Finally, the effect of the carbon backbone was evaluated using two different backbones, allyl and phenyl. In spite of some differences, the intermolecular T···N distances and binding energies remain within the same range values.

Supplementary Materials: The supplementary materials are available online.

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