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Strong Tetrel Bonds: Theoretical Aspects and Experimental Evidence

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Abstract: In recent years, noncovalent interactions involving group-14 elements of the periodic table acting as a Lewis acid center (or tetrel-bonding interactions) have attracted considerable attention due to their potential applications in supramolecular chemistry, material science and so on. The aim of the present study is to characterize the geometry, strength and bonding properties of strong tetrel-bond interactions in some charge-assisted tetrel-bonded complexes. Ab initio calculations are performed, and the results are supported by the quantum theory of atoms in molecules (QTAIM) and natural bond orbital (NBO) approaches. The interaction energies of the anionic tetrel-bonded complexes formed between XF$_3$M molecule (X=F, CN; M=Si, Ge and Sn) and A$^-$ anions (A$^-$=F$^-$, Cl$^-$, Br$^-$, CN$^-$, NC$^-$ and N$_3^-$) vary between −16.35 and −96.30 kcal/mol. The M atom in these complexes is generally characterized by pentavalency, i.e., is hypervalent. Moreover, the QTAIM analysis confirms that the anionic tetrel-bonding interaction in these systems could be classified as a strong interaction with some covalent character. On the other hand, it is found that the tetrel-bond interactions in cationic tetrel-bonded [p-NH$_3$(C$_6$H$_4$)MH$_3$]$^+$···Z and [p-NH$_3$(C$_6$F$_4$)MH$_3$]$^+$···Z complexes (M=Si, Ge, Sn and Z=NH$_3$, NH$_2$CH$_3$, NH$_2$OH and NH$_2$NH$_2$) are characterized by a strong orbital interaction between the filled lone-pair orbital of the Lewis base and empty BD*$_{M-C}$ orbital of the Lewis base. The substitution of the F atoms in the benzene ring provides a strong orbital interaction, and hence improved tetrel-bond interaction. For all charge-assisted tetrel-bonded complexes, it is seen that the formation of tetrel-bond interaction is accompanied by significant electron density redistribution over the interacting subunits. Finally, we provide some experimental evidence for the existence of such charge-assisted tetrel-bond interactions in crystalline phase.

Keywords: noncovalent interaction; tetrel-bond; σ-hole; electrostatic potential; ab initio

1. Introduction

Over the past decades, there has been an increasing awareness of the importance of noncovalent interactions owing to their critical roles in various fields of chemistry and biochemistry, such as protein folding, molecular recognition, drug design and crystal packing [1–3]. Of the various noncovalent interactions, hydrogen-bonding (H-bonding) has emerged as the most extensively studied case [4–8]. It is typically formulated as an attractive Lewis acid-Lewis base interaction, D-H···A, between the electron-deficient hydrogen atom of one molecule (D-H), acting as a bridge to an electron-rich site on the other molecule (A). However, much attention has been recently devoted to other types of noncovalent interactions like σ-hole bonding due to their useful applications in supramolecular chemistry, crystal engineering, and biochemistry [9–17]. A σ-hole bond [18–24] is a noncovalent interaction analogous to the H-bonding, in which a covalently bonded atom of groups 14–18 of the periodic table, rather than an H atom, serves a similar function as a bridge between two molecules. For example, the possibility of noncovalent interaction between some halocarbons and potential...
Lewis bases has been known for some time [25,26] and has continued to be studied at a rapidly increasing rate in recent years [27–30]. It has been found that the halogen atom in these molecules is able to develop a positive $\sigma$-hole region on the outermost portion of the halogen atom, along the C–X atoms (X=F, Cl, Br, I). The emergence of such a positive area, which may seem surprising due to the high electronegativity of halogen atoms, is responsible for the high directionality and formation of an electrostatically driven interaction with a negative region on the Lewis base. Note also that besides these electrostatic effects, there are also polarization effects and a substantial charge-transfer from the Lewis base into the BD*$\sigma$C-X antibonding orbital [31–33], precisely analogous to the case of a H-bond. The $\sigma$-hole interaction involving the halogen atoms is also known as halogen-bonding in view of the concept of H-bonding. Furthermore, it is not only the halogen atoms which can act as a Lewis acid center, but the elements of groups 14, 15, 16 and 18 of the periodic table as well, in which the resulting $\sigma$-hole interaction is called a tetrel-bonding [34–39], pnicogen-bonding [40–44], chalcogen-bonding [45–49] and aerogen-bonding [50–53], respectively.

Generally, $\sigma$-hole interactions share many common physical and chemical properties with the more traditional H-bonding. They offer a rich array of possibilities to design and fabricate new materials with desired properties, in areas ranging from pharmaceuticals to crystal growth [54–57].

Such diverse applications of $\sigma$-hole interactions mainly originate from their directional tunability. For example, the strength and properties of tetrel-bonds can be tuned not only by changing the tetrel atom (group 14 elements) itself, but also by changing the electron withdrawing/accepting ability of the reminder of the molecule [37,58–61]. As a result, a broad range of interaction energies may be spanned by changing the C atom in the tetrel-bond donor into a Si, Ge or Sn atom. Meanwhile, the Lewis base moiety in the tetrel-bond interaction could vary from anions like $\text{F}^-$ or $\text{Cl}^-$ [34,62,63], through lone-pair electrons on nitrogen or oxygen [64–66], to $\pi$ electrons in unsaturated bonds [67,68]. The latter may offer a further opportunity to tune the strength of tetrel-bonds and therefore expand their application scope [69,70].

A series of systematic experimental and theoretical studies have produced detailed descriptions of tetrel-bonds in either crystalline state or gas phase. However, these studies have mostly focused on the neutral complexes. For example, Mitzel et al. [71] have found short Si...N contacts in the crystalline structure of Si(ONMe$_2$)$_4$ and related compounds. Thomas and coworkers have provided an experimental evidence for the tetrel-bonding in crystalline structures based on charge density analysis. Alkorta and coworkers have investigated tetrel-bonding interactions between SiXY$_3$ (X and Y=H, F, and Cl) and some electron-rich groups (NH$_3$, NCH, CNH, OH$_2$, and FH) [72]. A detailed computational study by Mani and Arunan [73,74] has also found unusual tetrel-bond interactions called “carbon bonding” in the complexes of methanol as the tetrelbond donor with different Lewis bases. The formation of the latter interactions has also been proposed as a preliminary stage of the SN2 reaction by Grabowski [75]. These studies clearly showed that tetrel-bonding is moderately strong and could act as a possible molecular linker in crystal engineering and supramolecular chemistry, similar to H-bonding.

Recently, Scheiner has reported [76] a detailed study on the ability of hydrogen, halogen, chalcogen, pnicogen, and tetrel-bonds as a potential halide ($\text{F}^-$, $\text{Cl}^-$, $\text{Br}^-$) receptor. It was found that the tetrel-bonding exhibits a quite larger tendency to bind to halides than other $\sigma$-hole interactions.

In another study [77], the author has also shown that the addition of a -SnF$_3$ group to either an imidazolium or triazolium ion provides a strong halide receptor. Interestingly, the tetrel-bonding receptors bind far more strongly to each anion than an equivalent number of K$^+$ counterions. In the present study, we perform a systematic study on the strength and characteristic of charge-assisted tetrel-bond interactions in some model complexes (Schemes 1 and 2). The nature of anionic as well as cationic tetrel-bonds is analyzed by means of molecular electrostatic potential (MEP), quantum theory of atoms in molecules (QTAIM), natural bond orbital (NBO) and electron density difference (EDD) methods. The influence of different substituents on either Lewis acid or Lewis base is also studied in detail. Moreover, the characteristics of these charge-assisted complexes are compared with those
of available neutral ones. Finally, we provide some experimental evidence for the existence of such charge-assisted tetrel-bonds in crystalline structures and supramolecular assemblies.

Scheme 1. Representative geometrical structure of anionic tetrel-bonded complexes.

Scheme 2. Structure of monomers 1–6 and cationic tetrel-bonded complexes 7–30.
2. Systems and Methods

In this work, we report the results of ab initio calculations to study charge-assisted tetrel-bond interactions for two different sets of model systems. In the first model, XF₃M molecule (X=F, CN; M=Si, Ge and Sn) interacts with A⁻ anions (A⁻=F⁻, Cl⁻, Br⁻, CN⁻, NC⁻ and N₃⁻). This allows us to check the possibility of anionic tetrel-bonding interaction in the mentioned complexes. The second model studied here includes the cationic tetrel-bonded [p-NH₃{(C₆H₄)}MH₃]⁺···Z complexes, in which M=Si, Ge, Sn and Z=NH₃, NH₂CH₃, NH₂OH and N₂H₄. The H atoms of the benzene ring are additionally substituted by F atoms in order to study substituent effects.

All ab initio calculations were performed using the Gaussian 09 package [78]. The MP2 method was used, along with the aug-cc-pVTZ basis set to optimize geometries of the anionic XF₃M:A⁻ tetrel-bonded complexes. Frequency calculations were performed at the same computational level to ensure that the optimized structures correspond to a true minimum on the potential energy surface. In the case of the cationic tetrel-bonded systems, the geometry optimizations and the corresponding frequency calculations were performed at the MP2/aug-cc-pVDZ level. Single-point calculations with a larger aug-cc-pVTZ basis set were then performed using the aug-cc-pVDZ optimized geometries. The interaction energies for both sets of the complexes were computed at the MP2/aug-cc-pVTZ level, as the difference between the energy of the complex and the energy sum of the isolated monomers, and corrected for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise method [79].

To evaluate the possible orbital interactions between the interacting monomers, the NBO analysis was performed with the NBO 5.0 program (Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin, United States) [80]. The most positive (Vₘₙₙₛₚₐₓ) and most negative (Vₘₙₙₛₚₐₜₜ) electrostatic potentials of the isolated monomers were obtained using the Wave Function Analysis-Surface Analysis Suite (WFA-SAS) [81]. The QTAIM analysis was performed by means of the AIM2000 program [82] with the MP2/aug-cc-pVTZ generated wave functions. To see the amount of electron density shift due to the complex formation, the EDD isosurfaces were computed with the help of MultiWFN [83]. These were obtained by subtracting the electron density of the complex with the sum of the electron densities of the interacting monomers with the geometries in the optimized complex.

3. Results and Discussion

3.1. Anionic Tetrel-Bonds

Scheme 1 indicates the general structure of anionic tetrel-bonded complexes XF₃M:A⁻, in which the M atom of XF₃M acts as the Lewis acid site to interact with the excess electron density over the anions A⁻. It should be mentioned that although there might be many minima on the potential energy surface of these complexes, we are interested here in the interaction involving the linear X-M···A⁻ arrangement. The corresponding optimized geometries at the MP2/aug-cc-pVTZ level are summarized in Figure S1 of Supporting Information. All these complexes are found to have a favorable X−M···A⁻ linear arrangement. The binding distances and interaction energies of these complexes are listed in Table 1. According to the previous studies [37,62,65,67,84,85], the formation of such anionic tetrel-bonding interactions can be largely attributed to the localization of a positive electrostatic potential over the M atom in the extension of the M-X bond. Indeed, the MEP analysis of XF₃M monomers in Figure 1 reveals that the maximum positive electrostatic (Vₘₙₙₛₚₐₓ) of the Sn atom (96.5 kcal/mol) in SnF₄ is greater than that of Ge (70.2 kcal/mol) and Si (57.3 kcal/mol) in GeF₄ and SiF₄, respectively. In the case of MF₃CN monomers, it is seen that the σ-hole potential associated with the M atom becomes more positive as the size of the M atom increases. Consequently, it is expected that XF₃M molecules can participate in a σ-hole interaction with the σ-hole acting as a Lewis acid center, and the strongest acidic properties are predicted for the Sn atom of SnF₄ and SnF₃CN based on the MEP analysis.
Table 1. Binding distances (R_{int}, Å), X-M-F angles (\( \theta \), °), M-X bond lengths (R_{M-X}, Å) and their changes with respect to those of isolated MF_{3}X monomers (\( \Delta R_{M-X} \), Å), interaction energies (E_{int}, kcal/mol) of the anionic tetrel-bonded complexes, and the calculated local MEP minimum values (V_{S,min}, kcal/mol) of the anions.

| Lewis Acid | Anion | \( \text{R}_{\text{int}} \) | \( \theta \) | \( \text{R}_{M-X} \) | \( \Delta \text{R}_{M-X} \) | \( \text{E}_{\text{int}} \) | \( V_{S,min} \) |
|-----------|-------|----------------|-------|----------------|----------------|----------------|----------------|
| SiF_{4}   | F^-   | 1.679          | 90.0  | 1.679          | 0.105          | -70.11         | -175.0         |
|           | Cl^-  | 2.102          | 91.7  | 1.665          | 0.091          | -25.00         | -141.2         |
|           | Br^-  | 2.226          | 92.8  | 1.657          | 0.083          | -16.35         | -132.9         |
|           | NC^-  | 1.888          | 92.0  | 1.661          | 0.087          | -35.03         | -141.9         |
|           | CN^-  | 1.969          | 91.4  | 1.663          | 0.089          | -38.86         | -135.9         |
|           | N_3^- | 1.904          | 91.7  | 1.661          | 0.087          | -30.08         | -133.5         |
| SiF_{3}CN | F^-   | 1.662          | 91.4  | 1.970          | 0.145          | -84.37         | -175.0         |
|           | Cl^-  | 2.112          | 89.9  | 1.951          | 0.126          | -37.29         | -141.2         |
|           | Br^-  | 2.166          | 90.6  | 1.942          | 0.117          | -27.60         | -132.9         |
|           | NC^-  | 1.860          | 90.5  | 1.943          | 0.118          | -46.59         | -141.9         |
|           | CN^-  | 1.946          | 90.0  | 1.946          | 0.121          | -50.72         | -135.9         |
|           | N_3^- | 1.868          | 89.9  | 1.945          | 0.12           | -41.87         | -133.5         |
| GeF_{4}   | F^-   | 1.773          | 90.0  | 1.773          | 0.085          | -79.17         | -175.0         |
|           | Cl^-  | 2.263          | 90.3  | 1.764          | 0.076          | -41.26         | -141.2         |
|           | Br^-  | 2.436          | 90.7  | 1.760          | 0.072          | -32.99         | -132.9         |
|           | NC^-  | 1.932          | 91.3  | 1.762          | 0.074          | -46.62         | -141.9         |
|           | CN^-  | 1.994          | 90.5  | 1.762          | 0.074          | -53.57         | -135.9         |
|           | N_3^- | 1.940          | 90.7  | 1.762          | 0.074          | -43.30         | -133.5         |
| GeF_{3}CN | F^-   | 1.762          | 90.5  | 1.994          | 0.118          | -84.92         | -175.0         |
|           | Cl^-  | 2.239          | 89.7  | 1.983          | 0.107          | -46.32         | -141.2         |
|           | Br^-  | 2.407          | 90.0  | 1.977          | 0.101          | -37.73         | -132.9         |
|           | NC^-  | 1.915          | 90.8  | 1.981          | 0.105          | -50.96         | -141.9         |
|           | CN^-  | 1.979          | 90.5  | 1.979          | 0.103          | -58.35         | -135.9         |
|           | N_3^- | 1.921          | 90.0  | 1.981          | 0.105          | -47.94         | -133.5         |
| SnF_{4}   | F^-   | 1.930          | 90.0  | 1.930          | 0.048          | -93.58         | -175.0         |
|           | Cl^-  | 2.371          | 89.5  | 1.936          | 0.054          | -61.84         | -141.2         |
|           | Br^-  | 2.523          | 90.4  | 1.934          | 0.052          | -54.44         | -132.9         |
|           | NC^-  | 2.078          | 90.1  | 1.933          | 0.051          | -62.50         | -141.9         |
|           | CN^-  | 2.144          | 90.1  | 1.932          | 0.05           | -70.26         | -135.9         |
|           | N_3^- | 2.083          | 90.3  | 1.932          | 0.05           | -60.07         | -133.5         |
| SnF_{3}CN | F^-   | 2.144          | 90.1  | 2.144          | 0.091          | -96.30         | -175.0         |
|           | Cl^-  | 2.357          | 90.8  | 2.141          | 0.088          | -61.11         | -141.2         |
|           | Br^-  | 2.508          | 89.2  | 2.139          | 0.086          | -56.59         | -132.9         |
|           | NC^-  | 2.067          | 90.9  | 2.134          | 0.081          | -64.21         | -141.9         |
|           | CN^-  | 2.132          | 90.0  | 2.132          | 0.079          | -72.26         | -135.9         |
|           | N_3^- | 2.073          | 90.1  | 2.133          | 0.080          | -62.09         | -133.5         |
1.662–2.523 Å, which are much shorter than the sum of the van der Waals (vdW) radii of the interacting atoms. This has been found for other tetrel-bonds, such as SnF$_4$.

Interaction energies in the corresponding complexes. This has been found for other tetrel-bonds, indicating a strong interaction between the XF$_3$M and A$^-$ moieties. In many cases, the M atom is characterized by pentavalency, i.e., is hypervalent. This is similar to the one described for the transition state structure of SN2 reaction between a tetrel atom center and Lewis Acid Anion R int.

As Table 1 indicates, the M···A$^-$ binding distances of XF$_3$M:A$^-$ complexes are in the range of 1.662–2.523 Å, which are much shorter than the sum of the van der Waals (vdW) radii of the interacting atoms [86]. This clearly shows the existence of a strong interaction between the XF$_3$M and A$^-$ moieties. In many cases, the M atom is characterized by pentavalency, i.e., is hypervalent. This is similar to the one described for the transition state structure of SN2 reaction between a tetrel atom center and anion species [75,87]. In fact, most of the M···A$^-$ binding distances are short enough to be considered covalent bonds which have lost some degree of covalency. The binding distances for a given anion increase in the order SiF$_3$CN < SiF$_4$ < GeF$_3$CN < GeF$_4$ < SnF$_3$CN < SnF$_4$. Note also that M···A$^-$ distances become longer in the order of Si < Ge < Sn when the anion is the same, which is similar to the order of vdw or the covalent radius of these atoms (Si < Ge < Sn). The interaction between the anion and M atom is also able to induce a large distortion in the XF$_3$M molecule, as evidenced by the calculated X-M-F angles (Table 1). For each set of the complexes, one can see that the X-M-F angles are close to 90°, which may provide further evidence for the strong interaction between the XF$_3$M and A$^-$ moieties.

From Table 1, one can see that the interaction energies of XF$_3$M:A$^-$ are very large and negative, indicating a strong interaction between XF$_3$M and A$^-$ subunits. These results are in agreement with recent reports that indicate that tetrel-bonding can be used as a vehicle for strong and selective anion binding [77,88]. Moreover, the interaction energies obtained here are in good agreement with those of other related studies [62,63,76,77,88]. Comparing interaction energies clearly indicates that for a given XF$_3$M, the value of interaction energy for F$^-$ is systematically larger than other anions. In fact, such large negative interaction energies together with the corresponding very short binding distances indicate that the M···F$^-$ interactions are mainly covalent in nature. Interacting with the same anion, SnF$_4$ tends to form stronger tetrel-bond interaction than other molecules, as characterized by a larger interaction energies in the corresponding complexes. This has been found for other tetrel-bonds.

| Anion  | Molecule  | X-M-F Angle (°) | M-X Bond Length (Å) | Interaction Energy (kcal/mol) |
|--------|-----------|----------------|---------------------|-------------------------------|
| Cl$^-$ | SiF$_3$CN | 79.17          | 1.762               | 1.994                         |
| Br$^-$ | SiF$_3$CN | 70.11          | 1.773               | 1.951                         |
| I$^-$  | GeF$_3$CN | 90.0           | 1.665               | 0.091                         |
| CN$^-$ | SnF$_3$CN | 84.92          | 1.940               | 0.074                         |

Figure 1. MEPs of isolated monomers. The color code, in kcal/mol, is: red > 40; 40 > yellow > 20; 20 > green > 0 and blue < 0. The small black and blue circles indicate surface maxima and minima, respectively.
previously [37, 58, 75, 84, 89]; the increase of the interaction energy for the analogue complexes if the atomic number of the tetrel atom increases. This is connected with the electrostatic nature of these interactions due to the presence of a large positive electrostatic potential on the central atom of XF3M molecules (Figure 1). Moreover, it is natural that the more negative electrostatic potential (V\text{S,min}) associated with the anion forms a more stable M···A− interaction. However, as Figure 2 indicates, we found almost a poor linear correlation between the interaction energies of these complexes and V\text{S,min} values associated with the anions. Note that such a poor linear relationship between the E\text{int} and V\text{S,min} values has already been described in the literature [90–92]. This is mainly related to the different nature of the A− moiety in these complexes, which provides a distinct contribution of other energy terms such as polarization or charge-transfer in these systems.

![Figure 2. Correlation between the interaction energies and V\text{S,min} values associated with the A− anions in the binary XF3M:A− complexes.](image)

The results of Table 1 also indicate that due to the formation of XF3M:A− complexes, the M-X bonds are elongated. The magnitude of this bond elongation is in the range of 0.083–0.118 Å, 0.048–0.145 Å and 0.072–0.091 Å in the Si, Ge and Sn complexes, respectively. Note that the strongest M···F− interaction in these systems is characterized by a large elongation of M-X bond, which is much larger than the corresponding values in the Cl− or Br− complexes. Also, paired with the same anion, MF4 complexes show a relatively smaller variation in the M–X bond distances than MF3X analogues, which is based on the fact that the F is a poor leaving group than the CN. This result is consistent with the variation of interaction energy of these complexes, and suggests that Sn-X bond displays a larger red shift in the corresponding M-X stretching frequency than the Ge-X and Si-X ones. We will come back to this conclusion further on in our discussion when NBO analysis is illustrated.

To have a deeper understanding of the nature of anionic tetrel-bond interactions, we have performed the topological analysis of the electron density of XF3M:A− complexes (Table 2). It is found that for each system considered, there exists a bond critical point (BCP) associated with the M···A− interaction. As seen, the strong tetrel-bond interactions in XF3M:A− complexes are characterized by a large electron density value at the corresponding bond critical points (BCPs), which are much larger than those of at the neutral tetrel-bonded systems [38, 59, 87, 93, 94]. For a given M or X, the F− complexes exhibit the largest \( \rho_{\text{BCP}} \) value, while the smallest one corresponds to the Br− complexes.
Note also that, as predicted by the $\rho_{\text{BCP}}$ values, the tetrel-bond interactions of the Sn complexes are stronger than those of Ge or Si ones. This is in line with the other related studies [65,72,75,95], where it was found that the $\rho_{\text{BCP}}$ value is a good descriptor of the strength of interaction. Besides, almost a good exponential correlation was found between the binding distances and electron density values at the corresponding BCPs of XF$_3$M:A$^-$ complexes (Figure 3). Moreover, the Laplacian values of $\rho_{\text{BCP}}$ are found to be positive and in the range of 0.053–0.936 au, which is indicative of closed-shell nature of these interactions [96]. Meanwhile, the negative values of total electron energy density at M⋯A$^-$ BCPs, $H_{\text{BCP}}$, for all these complexes clearly confirm that the anionic tetrel-bond interactions could be classified as the strong interactions with some covalent character [97].

Table 2. Electron density ($\rho_{\text{BCP}}$, au), its Laplacian ($\nabla^2 \rho_{\text{BCP}}$, au) and total electron energy density ($H_{\text{BCP}}$, au) at the M⋯A$^-$ BCPs, and NBO stabilization energy ($E^{(2)}$, kcal/mol), atomic charge on the M atom ($q_{\text{M}}$, e), net charge-transfer ($q_{\text{CT}}$, e) and Wiberg bond index (WBI) values of the anionic tetrel-bonded complexes.

| Lewis Acid | Anion | $\rho_{\text{BCP}}$ | $\nabla^2 \rho_{\text{BCP}}$ | $H_{\text{BCP}}$ | $E^{(2)}$ | $q_{\text{M}}$ | $q_{\text{CT}}$ | WBI |
|-----------|-------|----------------|----------------|--------------|----------|------------|----------|------|
| SiF$_4$   | F$^-$ | 0.112 | 0.879 | −0.025 | 53.63 | 2.64 | 0.26 | 0.48 |
|           | Cl$^-$ | 0.065 | 0.152 | −0.030 | 38.72 | 2.54 | 0.33 | 0.51 |
|           | Br$^-$ | 0.054 | 0.060 | −0.028 | 32.06 | 2.55 | 0.31 | 0.49 |
|           | NC$^-$ | 0.085 | 0.421 | −0.029 | 69.31 | 2.63 | 0.21 | 0.37 |
|           | CN$^-$ | 0.081 | 0.280 | −0.045 | 47.92 | 2.50 | 0.34 | 0.56 |
|           | N$_3^-$ | 0.086 | 0.368 | −0.034 | 45.64 | 2.42 | 0.59 | 0.41 |
| SiF$_3$CN | F$^-$ | 0.117 | 0.936 | −0.028 | 65.86 | 2.50 | 0.27 | 0.56 |
|           | Cl$^-$ | 0.070 | 0.183 | −0.035 | 56.59 | 2.34 | 0.39 | 0.60 |
|           | Br$^-$ | 0.064 | 0.080 | −0.034 | 49.40 | 2.32 | 0.40 | 0.60 |
|           | NC$^-$ | 0.093 | 0.301 | −0.049 | 89.12 | 2.45 | 0.25 | 0.60 |
|           | CN$^-$ | 0.086 | 0.299 | −0.049 | 61.17 | 2.30 | 0.39 | 0.60 |
|           | N$_3^-$ | 0.094 | 0.415 | −0.040 | 60.75 | 2.42 | 0.58 | 0.46 |
| GeF$_4$   | F$^-$ | 0.130 | 0.774 | −0.050 | 54.69 | 2.68 | 0.27 | 0.42 |
|           | Cl$^-$ | 0.084 | 0.130 | −0.038 | 51.64 | 2.52 | 0.38 | 0.57 |
|           | Br$^-$ | 0.073 | 0.055 | −0.032 | 46.01 | 2.50 | 0.40 | 0.58 |
|           | NC$^-$ | 0.107 | 0.364 | −0.048 | 78.64 | 2.66 | 0.22 | 0.38 |
|           | CN$^-$ | 0.112 | 0.191 | −0.058 | 55.20 | 2.51 | 0.38 | 0.58 |
|           | N$_3^-$ | 0.109 | 0.308 | −0.053 | 53.60 | 2.60 | 0.58 | 0.44 |
| GeF$_3$CN | F$^-$ | 0.134 | 0.800 | −0.053 | 58.67 | 2.51 | 0.27 | 0.44 |
|           | Cl$^-$ | 0.089 | 0.135 | −0.042 | 60.69 | 2.31 | 0.42 | 0.63 |
|           | Br$^-$ | 0.078 | 0.053 | −0.036 | 55.20 | 2.28 | 0.46 | 0.65 |
|           | NC$^-$ | 0.112 | 0.381 | −0.052 | 91.00 | 2.45 | 0.25 | 0.42 |
|           | CN$^-$ | 0.116 | 0.194 | −0.062 | 61.82 | 2.29 | 0.42 | 0.63 |
|           | N$_3^-$ | 0.115 | 0.323 | −0.058 | 59.72 | 2.40 | 0.58 | 0.48 |
| SnF$_4$   | F$^-$ | 0.113 | 0.687 | −0.029 | 34.37 | 2.93 | 0.21 | 0.36 |
|           | Cl$^-$ | 0.081 | 0.195 | −0.027 | 42.18 | 2.75 | 0.36 | 0.37 |
|           | Br$^-$ | 0.072 | 0.117 | −0.024 | 40.60 | 2.71 | 0.40 | 0.60 |
|           | NC$^-$ | 0.098 | 0.378 | −0.031 | 53.92 | 2.90 | 0.19 | 0.34 |
|           | CN$^-$ | 0.094 | 0.229 | −0.038 | 37.04 | 2.77 | 0.33 | 0.53 |
|           | N$_3^-$ | 0.099 | 0.384 | −0.066 | 34.80 | 2.84 | 0.27 | 0.40 |
| SnF$_3$CN | F$^-$ | 0.101 | 0.702 | −0.031 | 33.81 | 2.77 | 0.22 | 0.38 |
|           | Cl$^-$ | 0.084 | 0.199 | −0.029 | 44.15 | 2.55 | 0.40 | 0.61 |
|           | Br$^-$ | 0.075 | 0.118 | −0.026 | 42.58 | 2.50 | 0.45 | 0.66 |
|           | NC$^-$ | 0.101 | 0.385 | −0.034 | 53.18 | 2.71 | 0.22 | 0.37 |
|           | CN$^-$ | 0.098 | 0.230 | −0.040 | 34.38 | 2.55 | 0.37 | 0.58 |
|           | N$_3^-$ | 0.098 | 0.341 | −0.037 | 31.10 | 2.65 | 0.54 | 0.44 |
As noted earlier, charge-transfer from the electron donor into the empty orbital of the electron acceptor also plays an important role in the formation and stabilization of tetrel-bonded complexes [61–63,85,87,98]. For the anionic tetrel-bonded complexes studied here, it is expected that there exists a stabilizing orbital-orbital interaction between the lone-pair orbital of the anion, LP (A\(^{-}\)), and empty anti-bonding M-X orbital of XF\(_3\)M molecule (BD\(^{*}\)M-X). The latter orbital interaction should be responsible for the elongation of M-X bonds and their red-shift upon the complexation. To confirm this, we performed NBO analysis on the XF\(_3\)M:A\(^{-}\) complexes. Table 2 summarizes the calculated stabilization energy E\(^{(2)}\) values due to the LP (A\(^{-}\))→BD\(^{*}\)M-X orbital interaction. As is evident, these E\(^{(2)}\) values are quite large, especially for the A\(^{-}\)=CN\(^{-}\) and F\(^{-}\) complexes, which demonstrates the significant role of the mentioned orbital interaction in these systems. It is also found that for all complexes analyzed here, the formation of tetrel bonds results in an increase in the positive charge of the M atom due to its polarization in the presence of the negative charge of the anion (Table 2). For each set of the complexes, such polarization is largest in the F\(^{-}\) complexes, which is consistent with the stronger tetrel-bond interaction in these systems. However, due to the variety of Lewis bases, it is not possible to find any regularity in the changes of the atomic charges here. The data in Table 2 also reveal that the net charge-transfer values (q\(_{CT}\)) for the XF\(_3\)M:A\(^{-}\) complexes are very large, with values ranging from 0.21 to 0.58 e. Moreover, for a given M or X, the N\(_3\)\(^{-}\) and Br\(^{-}\) complexes are identified by a larger q\(_{CT}\) values compared to other ones, which is most likely due to the large polarizability of these moieties. Hence, the larger elongation of the M-X bond in the latter complexes can be attributed to the more favorable charge-transfer, which results in the partial population of the antibonding BD\(^{*}\)M-X orbital of XF\(_3\)M and its redshift. As also shown in Table 2, the Wiberg bond index (WBI) of the anionic tetrel-bonds is large, which verifies the formation of covalent M···A\(^{-}\) interactions in these systems.

![Figure 3](image-url)

**Figure 3.** Exponential relationship between the M···A\(^{-}\) binding distances and electron density at the corresponding BCPs of the XF\(_3\)M:A\(^{-}\) complexes.

When the XF\(_3\)M molecule is paired with the A\(^{-}\) anion, there is a mutual polarization between the two moieties, which can be verified using the EDD analysis. Figure 4 shows the EDD isosurfaces for some representative complexes of XF\(_3\)M:A\(^{-}\), which were obtained by subtracting the electron density of the complex with the sum of the electron densities of the interacting monomers with the geometries...
in the optimized complex. Here, violet regions show a decreased electron density, while green areas refer to an increased electron density. As can be seen, the formation of these complexes leads to the appearance of a large electron density loss region over the M atom, facing the anion. The size of this electron density loss region becomes larger as the size of the M atom increases. Meanwhile, a large electron density accumulation is found between the M and A$^-$, which confirms the formation of a covalent M···A$^-$ interaction in these systems. Moreover, the formation of anionic tetrel-bond interaction in these complexes tends to induce an accumulation of electron density on the F atom of XF$_3$M. One can also see the localization of a large electron density loss region over the anion, which is related to the polarization of these moieties in the presence of positive σ-hole on the M atom. Clearly, such electron density shift is larger for the Sn complexes than Ge and Si ones, due to more positive σ-hole potential associated with the former systems.

Figure 4. EDD isosurfaces (±0.005 au) of some representative XF$_3$M:A$^-$ complexes. The violet and green regions indicate regions of decreased and increased electron densities, respectively.

3.2. Cationic Tetrel-Bonds

Scheme 2 depicts the general representation of cationic tetrel-bonded complexes 7–30 studied here. The corresponding optimized geometries are summarized in Figure S2 of the Supporting Information. Their intermolecular M···N distances and interaction energies are reported in Table 3. From Figure S2, one can see that all these complexes are characterized by a linear C-M···N interaction, in which nitrogen atom of the Lewis base is pointed towards the M atom of the Lewis acid. The binding distances are in the range of 2.175–2.567, 2.352–2.790 and 2.479–2.735 for the M=Si, Ge and Sn, respectively. All these binding distances are smaller than the sum of vdW radii of the respective atoms [86], which implies that there is an attractive interaction between the interacting molecules. For a given M, NH$_2$NH$_2$ forms always the shortest tetrel-bond distance, while the longest corresponds to NH$_3$. Moreover, the substitution of F atoms in the benzene ring tends to decrease the binding distances, which can be attributed to the increase of positive electrostatic potential on the M atom due to presence of the F atoms. This indicates that the formation of cationic tetrel-bond in these systems is, at least partly, a consequence of the electrostatic attraction between the nitrogen atom of Lewis bases and the M atom. As also expected, the M···N binding distances for a fixed nitrogen base increase in the order of Ge > Sn > Si can be related to the combination result of the interaction energy and the atomic radius of
these atoms. The results of Table 3 also show that the formation of cationic tetrel-bonds in the binary complexes 7–30 leads to a significant increase in the C-M-H angles (θ), as evidenced by θ values close to 90°. This is in line with previous studies, where it was found for the strong tetrel-bonded complexes that the intermolecular interaction should be a preliminary stage of the SN2 reaction [75,87].

Table 3. Binding distances (R_{int}, Å), C-M-H angles (θ, °) and interaction energies (E_{int}, kcal/mol) of the cationic tetrel-bonded complexes.

| Complex | R_{int} | θ     | E_{int} |
|---------|---------|-------|---------|
| 7       | 1+NH₃   | 2.567 | 101.1   | −7.69   |
| 8       | 1+NH₂OH | 2.459 | 101.4   | −9.25   |
| 9       | 1+NH₂CH₃| 2.291 | 98.2    | −13.58  |
| 10      | 1+NH₂NH₂| 2.245 | 97.5    | −15.05  |
| 11      | 2+NH₃   | 2.790 | 102.6   | −9.82   |
| 12      | 2+NH₂OH | 2.724 | 103.0   | −11.86  |
| 13      | 2+NH₂CH₃| 2.538 | 100.2   | −17.44  |
| 14      | 2+NH₂NH₂| 2.486 | 99.9    | −20.8   |
| 15      | 3+NH₃   | 2.735 | 100.5   | −13.36  |
| 16      | 3+NH₂OH | 2.671 | 100.2   | −16.65  |
| 17      | 3+NH₂CH₃| 2.568 | 97.7    | −19.11  |
| 18      | 3+NH₂NH₂| 2.548 | 98.1    | −22.46  |
| 19      | 4+NH₃   | 2.330 | 99.4    | −10.89  |
| 20      | 4+NH₂OH | 2.277 | 99.0    | −13.47  |
| 21      | 4+NH₂CH₃| 2.195 | 96.7    | −17.42  |
| 22      | 4+NH₂NH₂| 2.175 | 97.0    | −20.86  |
| 23      | 5+NH₃   | 2.527 | 100.3   | −14.25  |
| 24      | 5+NH₂OH | 2.498 | 101.1   | −18.48  |
| 25      | 5+NH₂CH₃| 2.370 | 98.4    | −22.55  |
| 26      | 5+NH₂NH₂| 2.352 | 98.6    | −25.5   |
| 27      | 6+NH₃   | 2.586 | 99.0    | −17.02  |
| 28      | 6+NH₂OH | 2.574 | 100.3   | −20.08  |
| 29      | 6+NH₂CH₃| 2.487 | 98.1    | −23.66  |
| 30      | 6+NH₂NH₂| 2.479 | 98.7    | −26.98  |

Considering the interaction energies in Table 3, it is found that the most strongly bound complex 30 has an interaction energy of −26.98 kcal/mol, while the most weakly bound complex 7 has an interaction energy of only −7.69 kcal/mol. These interaction energies are larger than the reported values for similar tetrel-bond interactions in the related neutral complexes [65,93]. Meanwhile, the calculated interaction energies for the Si and Ge complexes are close to those of tetrel-bonding interactions in the prorogated complexes of pyridine-MF₃ or furan-MF₃ with NH₃ [66]. Note that, for the same electron acceptor moiety, NH₂NH₂ tends to form more stable tetrel-bond interaction than others, which is not consistent with the V_{S,min} value (in kcal/mol) associated with the nitrogen atom in these bases: NH₃ (−42.7) > NH₂CH₃ (−38.6) > NH₂NH₂ (−36.5) > NH₂OH (−28.8). This may be attributed in part to secondary interactions between these Lewis bases and the H atoms of -MH₃ moiety in the Lewis acid. Moreover, this can be explained in the manner of the negative hyperconjugation effect on the side of Lewis bases as suggested by Zierkiewicz and Michalczyzk [92]. This finding clearly reveals that the V_{S,min} value, a property in a single special point of the Lewis base, cannot be regarded as a good indicator of the cationic tetrel-bond interactions, and in addition to electrostatic effects other factors such as the polarization should play an important role in the stability and formation of these interactions.

The topological analysis of the electron density of the complexes 7–30 exhibits the presence of a BCP between the M atom of Lewis acid and N atom of the nitrogen bases. The electron densities at the M···N BCPs are between 0.024 au in 7 and 0.060 au in 30 (Table 4). It is interesting to note that, like weak tetrel-bond interactions in neutral complexes [38,59,87,93,94], we found an exponential correlation between the electron density at the BCP and the interatomic distances of these systems (Figure 5).
Importantly, the calculated squared correlation confection values ($R^2$) for these cationic tetrel-bonded complexes are larger than those of anionic ones (Figure 3). Moreover, the positive $\nabla^2 \rho_{BCP}$ values associated with these complexes demonstrate that the cationic tetrel-bond interactions are within the closed-shell interaction regime. Meanwhile, negative total energy densities ($H_{BCP}$) are obtained for all complexes studied here, which confirm that the cationic tetrel-bonds have some covalent character. Note that the for each set of the complexes, most negative values of $H_{BCP}$ correspond to the stronger interactions and to the greater values of $\rho_{BCP}$ (Table 4).

![Exponential relationship between the M···N binding distances and electron density at the corresponding BCPs of the cationic tetrel-bonded complexes.](image)

**Table 4.** Electron density ($\rho_{BCP}$, au), its Laplacian ($\nabla^2 \rho_{BCP}$, au) and total electron energy density ($H_{BCP}$, au) at the M···Z BCPs, and NBO stabilization energies due to the LP(N)→BD*M-C orbital interaction ($E^{(2)}$, kcal/mol), net charge-transfer ($q_{CT}$, e) and Wiberg bond index (WBI) values of the cationic tetrel-bonded complexes.

| Complex | $\rho_{BCP}$ | $\nabla^2 \rho_{BCP}$ | $H_{BCP}$ | $E^{(2)}$ | $q_{CT}$ | WBI |
|---------|--------------|----------------|----------|-----------|----------|-----|
| 7       | 1+NH$_3$     | 0.024          | 0.049    | -0.003    | 10.42    | 0.072 | 0.114 |
| 8       | 1+NH$_2$OH   | 0.028          | 0.066    | -0.017    | 11.20    | 0.075 | 0.129 |
| 9       | 1+NH$_2$CH$_3$ | 0.039          | 0.084    | -0.021    | 13.45    | 0.078 | 0.135 |
| 10      | 1+NH$_2$NH$_2$ | 0.043          | 0.111    | -0.024    | 14.52    | 0.080 | 0.144 |
| 11      | 2+NH$_3$     | 0.029          | 0.055    | -0.005    | 12.28    | 0.076 | 0.134 |
| 12      | 2+NH$_2$OH   | 0.034          | 0.062    | -0.019    | 14.55    | 0.079 | 0.155 |
| 13      | 2+NH$_2$CH$_3$ | 0.044          | 0.088    | -0.026    | 17.70    | 0.082 | 0.167 |
| 14      | 2+NH$_2$NH$_2$ | 0.048          | 0.099    | -0.030    | 19.14    | 0.084 | 0.176 |
| 15      | 3+NH$_3$     | 0.035          | 0.090    | -0.007    | 15.25    | 0.079 | 0.155 |
| 16      | 3+NH$_2$OH   | 0.039          | 0.072    | -0.008    | 17.10    | 0.081 | 0.168 |
| 17      | 3+NH$_2$CH$_3$ | 0.048          | 0.083    | -0.022    | 18.75    | 0.084 | 0.182 |
| 18      | 3+NH$_2$NH$_2$ | 0.052          | 0.111    | -0.026    | 20.40    | 0.086 | 0.193 |
| 19      | 4+NH$_3$     | 0.035          | 0.053    | -0.008    | 13.28    | 0.079 | 0.149 |
| 20      | 4+NH$_2$OH   | 0.039          | 0.090    | -0.023    | 14.48    | 0.084 | 0.189 |
| 21      | 4+NH$_2$CH$_3$ | 0.047          | 0.136    | -0.030    | 16.05    | 0.087 | 0.201 |
| 22      | 4+NH$_2$NH$_2$ | 0.050          | 0.141    | -0.033    | 18.60    | 0.090 | 0.228 |
| 23      | 5+NH$_3$     | 0.043          | 0.113    | -0.030    | 15.08    | 0.082 | 0.165 |
| 24      | 5+NH$_2$OH   | 0.046          | 0.097    | -0.021    | 16.69    | 0.085 | 0.172 |
| 25      | 5+NH$_2$CH$_3$ | 0.054          | 0.121    | -0.028    | 18.82    | 0.089 | 0.191 |
| 26      | 5+NH$_2$NH$_2$ | 0.059          | 0.123    | -0.032    | 20.80    | 0.094 | 0.206 |
| 27      | 6+NH$_3$     | 0.046          | 0.089    | -0.010    | 17.04    | 0.092 | 0.180 |
| 28      | 6+NH$_2$OH   | 0.049          | 0.093    | -0.026    | 18.92    | 0.095 | 0.196 |
| 29      | 6+NH$_2$CH$_3$ | 0.056          | 0.131    | -0.033    | 19.77    | 0.096 | 0.212 |
| 30      | 6+NH$_2$NH$_2$ | 0.060          | 0.141    | -0.036    | 22.50    | 0.098 | 0.225 |
According to the NBO analysis, there is a noticeable charge-transfer interaction between the lone-pair bonding orbital LP(N) of nitrogen atom of the Lewis bases and the BD\(^{\ast}\)\(_{M-C}\) antibonding orbital of the Lewis acid. A similar interaction between the lone-pair of nitrogen and the BD\(^{\ast}\)\(_{M-C}\) anti-bonding orbital (M=C, Si, Ge) was analyzed recently for the prorogated complexes of pyridine-MF\(_3\) with NH\(_3\) [66]. This orbital interaction is responsible for a negligible elongation of the M-C bond in these complexes. The stabilization energies \(E^{(2)}\) associated with the latter orbital interaction are in the range of 9.22–18.60, 12.28–20.20 and 15.25–22.50 kcal/mol for the Si, Ge and Sn complexes, respectively. There is an almost linear correlation between these \(E^{(2)}\) values and interaction energies of these complexes (see Figure S3, Supporting Information), which demonstrates that the charge-transfer interaction also plays an important role in the stability of these systems. Note also that the F-substituted complexes may also be confirmed experimentally. To this end, the Cambridge Structure Database (CSD) [99] was examined to analyze whether anionic or cationic tetrel-bonding could be a generally occurring order of 15 > 11 > 7 and 27 > 23 > 19. In contrast, the lone-pair orbital of the nitrogen atom induces an electron density loss area on the nitrogen atom of the Lewis base. The degree of the accumulation depends on the strength of the tetrel-bond, and increases in the order of 15 > 11 > 7 and 27 > 23 > 19. In contrast, the lone-pair orbital of the nitrogen atom induces an electron density loss area on the M atom. Note that such mutual polarization between the interacting monomers is almost similar as that in other studied tetrel-bonded systems [38,90,93].

Finally, we would like to highlight the electron density redistribution within and between the monomers upon the formation of the cationic tetrel-bonded complexes. Figure 6 shows the EDD plots of some selected complexes. As is evident, the formation of tetrel-bond interaction in these complexes makes a large electron density accumulation region over the nitrogen atom of the Lewis base. The degree of the accumulation depends on the strength of the tetrel-bond, and increases in the order of 15 > 11 > 7 and 27 > 23 > 19. In contrast, the lone-pair orbital of the nitrogen atom induces an electron density loss area on the M atom. Note that such mutual polarization between the interacting monomers is almost similar as that in other studied tetrel-bonded systems [38,90,93].

![Figure 6. EDD isosurfaces (±0.001 au) of some representative cationic tetrel-bonded complexes. The violet and green regions indicate regions of decreased and increased electron densities, respectively.](image-url)
3.3. Experimental Evidence for Charge-Assisted Tetrel-Bonds

It is noteworthy that the existence of charge-assisted tetrel-bonds described theoretically here may also be confirmed experimentally. To this end, the Cambridge Structure Database (CSD) [99] was examined to analyze whether anionic or cationic tetrel-bonding could be a generally occurring interaction within crystal structures (CSD, version 5.34, November 2012, including three updates). In Figure 7, we show some selected examples and the CSD reference codes of crystal structures in which the anionic tetrel-bonding interaction is observed. In all these complexes, the tetrel-bonding is highly directional, as evidenced by R-M⋯A− bonding angles close to 180° (R is the electron-withdrawing atom or group attached to the M atom). A quite interesting experimental finding that reports the existence of anionic tetrel-bonding interactions is the formation of crystalline spherosilicate structures, where a fluoride ion is perfectly centered within the octasilsesquioxane cage [100,101]. The X-ray structures are indicated in Figure 7 (WAVYEZ and WAVYAV), where tetrel-bond interactions are confirmed by relatively short contacts between the Si atom and F− anion, which are significantly shorter than the sum of the corresponding vdW radii. Likewise, there also exist attractive anionic tetrel-bonding interactions between the Si atoms and encapsulated Cl− anion in FOSDUO. In Figure 7, we also show the crystalline structures of three binuclear pentacoordinate silicon complexes of diketopiperazine, which gives evidence for the covalent-bonding between the Si atom and the F−, Cl− and OSO2BF3− anions [102]. Note that the shorter Si⋯F− bond distances compared to the Si⋯Cl− confirm our earlier finding that the F− has a larger tendency to interact with the tetrel atom than the Cl−.

Figure 7. Crystalline structure of some selected anionic tetrel-bonded complexes.

The existence of short tetrel-bond interaction between the cationic tetrel atom and a potential nitrogen base has been already suggested for the complex [Sn(Me)3(NH3)2][Ni(SO2Me)2] [103] (Figure 8). Here, the positively charged Sn(Me)3NH3 moiety forms a strong Sn⋯N interaction with the NH3 molecule. Meanwhile, there is a short H-bonding interaction between the latter NH3 molecule and the negatively charged N(SO2Me)2 moiety in this complex. The formation of this H-bonding interaction is able to greatly modulate the strength and properties of the tetrel-bonding, as evidenced by the previous theoretical study about the cooperativity effects between the tetrel-bonding and H-bonding interactions [59].
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Supplementary Materials: The following are available online. Figure S1: Optimized structure of the anionic tetrel-bonded complexes, Figure S2: Optimized structure of the cationic tetrel-bonded complexes 7–30, Figure S3: Correlation between the stabilization energy, due to the LP(N) → BD*M:C orbital interaction, and interaction energies of cationic tetrel-bonded complexes 7–30, Figure S4: Correlation between the net charge-transfer and interaction energies of cationic tetrel-bonded complexes 7–30.

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