INTRODUCTION

In the years following its initial conception, the hydrogen bond (HB) has become one of the most important and far-reaching phenomena for both chemistry and biology.1−4 Recent years have witnessed the growth of study of a set of parallel sorts of interactions, replacing the bridging proton of the HB by any set of other elements in the p-block of the periodic table. These electronegative elements are able to attract an electron donor by way of a region of depleted electron density on their periphery, which in turn are commonly referred to as σ- or π-holes.5−9 A good deal of work has addressed the factors that contribute to this bonding phenomenon, the strength of the interaction, and the subsidiary part played by monomer deformation, to amplify its role in biological systems, pharmacology, and technology.1,2,19−30 For example, it is now understood that these noncovalent bonds are stabilized by contributions from charge transfer, polarization, and dispersion, in addition to the electrostatic attraction.

Recent work has described a dual scheme, via either σ- or π-hole, by which a base might bind to the tetrel31,32 or pnicogen33 atom of a Lewis acid. As one relevant example, the NH3 base can interact with a substituted TF4C6H2R3 (T = C, Si, Ge, Sn, Pb; R = H, CH3, F) acid through either its axial or equatorial σ-hole, with respect to the phenyl ring.34 Likewise, a substituted pyridine base engages in a tetrel bond with the central T atom of TF4 by substituting pyridine base engages in a tetrel bond with the central T atom of TF4 by

concerning the clustering of molecules, for instance (PH2F)n, (PH2Cl)n, NH3, PH3, and PFH2,46 and HF, FCI46−49 wherein such multiple bonds are integral. It has long been recognized that the formation of a HB polarizes each participant and affects their ability to engage in a second such bond. For example, the formation of a AH···BH dimer shifts electron density from BH to AH, making the former a better electron donor. The addition of a third CH molecule to the growing chain can take advantage of this charge shift so that AH···BH···CH is bound by more than the simple sum of the AH···BH and BH···CH bond energies within these respective dimers, a phenomenon known as positive cooperativity. A second factor takes on added importance in the case of certain other noncovalent bonds. The formation of a tetrel bond, for instance, can drastically alter the internal geometry of the Lewis acid. This nuclear rearrangement in turn exerts a strong influence upon the electrostatic potential surrounding it, which in turn can enhance or inhibit its ability to engage in a second such bond.

The earlier work cited above has documented the ability of the central tetrel atom to engage in two noncovalent interactions simultaneously. Very recent calculations have noted that the hypervalent YF4 (Y = S, Se, Te, Po) can similarly engage in a pair of chalcogen bonds.53 Two NCH molecules can form a pair of tetrel bonds to a central TF4 molecule (T = Si, Ge, Sn, Pb).31,54−56

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How Many Pnicogen Bonds can be Formed to a Central Atom Simultaneously?

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These earlier findings lead to the natural question as to just how many nucleophiles can be attached to a Lewis acid at the same time. What is the maximum number of such bonds that can be present, and how does this number differ for tetrel, pnictogen, and chalcogen bonds? Surely there will be a point at which simple issues of steric strain will prevent any further bases from approaching. Just how much can the central molecule alter its structure so as to accommodate additional bonds? How might this maximum number depend on the precise nature of the Lewis acid and base molecules? Another issue relates to cooperativity. Does the presence of the first bond strengthen or weaken the second and so on? Does this cooperativity operate through simple electronic polarization or does geometric deformation play an important role?

As a vehicle to begin to answer some of these questions, the work described below considers the pnictogen bonds (ZBs) that might be formed by ZF₃ (Z = P, As, Sb, Bi). As guidance in terms of the formal definition of a pnictogen bond, we employ the IUPAC definitions that have been developed for the very similar halogen and chalcogen bonds. These bonds are characterized by the approach to a pnicogen atom, acting as a Lewis acid, of a nucleophile, which are built upon electrostatic attraction, polarization, and dispersion.

Three different bases are considered. Neutral HCN can engage in a ZB through its N atom, whereas the negative HCNO molecules, and CN⁻ but its sp³ hybridization makes it stronger than HCN. One, another base unit.

changes occurring in each system upon each addition of time, the properties of each complex are monitored to follow noncovalent forces.62 available experimental quantities, for complexes stabilized by consistent with CCSD(T) with larger basis sets and with these structures in Table S1, the Z−F bond length increases as the Z atom grows in size from 1.630 for PF₃ to 2.016 in BiF₃. The sum of the three θ(F−Z−F) angles in the last column of Table S1 decreases slightly with larger Z, indicating a less planar geometry.

The MEP of each ZF₃ molecule has a similar profile, exemplified in Figure 1 for AsF₃. Each F atom is surrounded by a blue negative region, while a red positive area termed a σ-hole lies opposite each Z−F bond. There is another positive region, but a much less intense one, that lies opposite the Z lone pair, amongst the three F atoms. For lack of a better name, and for convenience in discussion, this latter point is designated as a σ-hole here, although the reader must be aware that the ZF₃ molecule is not flat and does not contain a σ-electron system per se. The values of Vₛ,max for these σ and π-holes are listed in the upper portion of Table 1, which shows the expected trend of a more intense positive region for larger Z atoms (with a small irregularity between P and As for the π-holes). The HCN molecule contains a minimum in its MEP on its N atom along the molecular axis, with a Vₛ,min value of −31.4 kcal/mol, as seen in the lower part of Table 1. The MEP minimum of NH₃ is along its θ-s equator, its σ-region.

Figure 1. MEP on the 0.001 au isodensity surface at the MP2/cc-pVDZ level of AsF₃ (a, top view and b, bottom view) isolated monomers. Color ranges, in kcal/mol, are red greater than 35, yellow between 15 and 35, green between 0 and 15, and blue below 0 kcal/mol.

ZF₃ + 1 Base. The structures of the most stable complexes arising from the addition of a single base to ZF₃ are presented in Figure 2. The neutral HCN approaches N-atom first, toward one of the σ-holes of ZF₃ opposite the F atom labeled F1. As observed in the first column of Table 2, the intermolecular...
Table 1. MEP Maxima (kcal/mol) on the 0.001 au Isodensity Surface of ZF₃ (Z = P, As, Sb, Bi) and HCN and CN⁻ Monomers, Calculated at the MP2/aug-cc-pVDZ Level of Theory

| molecule | Vₛ,ₘₐₓ (Z–F) σ-hole | Vₛ,ₘₐₓ π-hole below Z atom |
|----------|---------------------|---------------------------|
| PF₃      | 35.6                | 9.7                       |
| AsF₃     | 43.9                | 7.1                       |
| SbF₃     | 51.6                | 10.6                      |
| BiF₃     | 61.5                | 12.7                      |

The lowest section of Table 2 lists the same properties for the complexes with the CN⁻ anion. Importantly, the structures of these complexes are rather different than those with the neutral bases. As seen in Figure 2c, the ZF₃ molecule becomes very nearly planar. This approach to planarity is evident in the last two columns of Table 2 where the sum of the three \( \theta(F–Z–F) \) angles grows by 50–60⁰ up to nearly 360⁰. The full charge on this base leads to much shorter intermolecular distances, around 2 Å. In addition, the trend in \( \theta(C···Z) \) is opposite that for the complexes with neutral HCN in that the separation increases as the Z atom grows in size. The stronger binding to the anion is also exemplified by the much longer internal \( r(Z–F) \) distances.

The binding energies of these complexes, corresponding to the reaction that forms the dimer from the pair of isolated monomers, displayed in the first two columns of Table 3, reaffirms the indications of the binding strength arising from Table 2. Whereas HCN binds with an energy between 3 and 7 kcal/mol, dimers involving NH₃ are bound by 4.5–13 kcal/mol, and the anion range is considerably larger, 23–39 kcal/mol. In all cases, the binding is enhanced for larger Z atoms. The interaction energies in the next two columns of Table 3 refer to the pure interaction between the monomers which have already been deformed into the geometries they adopt within the complex. As such \( E_{\text{int}} \) is more negative than \( E_{\text{b}} \) differing by a deformation energy \( E_{\text{def}} \) which is needed to distort each monomer appropriately. There is little deformation involved in the complexation with the neutral bases.

However, the large distortion of ZF₃ from its pyramidal structure when complexed with the anion leads to much more negative interaction energies in the bottom segment of Table 3. These deformation energies are the largest for the smaller Z atoms, with \( E_{\text{def}} \) rising from 33.9 kcal/mol for BiF₃ up to 55.0 kcal/mol.
Table 3. Binding ($E_b$) and Interaction Energies ($E_{int}$) (kcal/mol) of ZF$_3$ Complexes with HCN and CN$^-$ Calculated at the MP2/aug-cc-pVDZ (I) and CCSD(T)/aug-cc-pVDZ (II) Levels of Theory$^a$

|        | ($E_b$) | ($E_{int}$) | ($E_b$) | ($E_{int}$) |
|--------|---------|-------------|---------|-------------|
|        | (I)     | (II)        | (I)     | (II)        |
| HCN···PF$_3$ | $-2.74$  | $-2.51$     | $-2.82$  | $-2.54$     |
| HCN···AsF$_3$ | $-4.09$  | $-3.72$     | $-4.24$  | $-3.80$     |
| HCN···SbF$_3$ | $-5.88$  | $-5.35$     | $-6.15$  | $-5.53$     |
| HCN···BiF$_3$ | $-7.48$  | $-6.95$     | $-7.75$  | $-7.14$     |
| H$_2$N···PF$_3$ | $-4.45$  | $-4.40$     | $-4.87$  | $-4.75$     |
| H$_2$N···AsF$_3$ | $-7.32$  | $-7.05$     | $-8.24$  | $-7.90$     |
| H$_2$N···SbF$_3$ | $-11.70$ | $-11.35$    | $-13.09$ | $-12.71$    |
| H$_2$N···BiF$_3$ | $-13.20$ | $-12.92$    | $-14.31$ | $-13.99$    |
| NC$^-$···Z$_3$ | $-22.68$ | $-20.00$    | $-77.66$ | $-74.64$    |
| NC$^-$···AsF$_3$ | $-30.93$ | $-28.44$    | $-77.79$ | $-75.06$    |
| NC$^-$···SbF$_3$ | $-38.67$ | $-36.70$    | $-74.72$ | $-72.36$    |
| NC$^-$···BiF$_3$ | $-39.24$ | $-37.41$    | $-73.16$ | $-70.74$    |

$^a$All values corrected for BSSE.

kcal/mol for PF$_3$, as reported in Table S2. While $E_b$ and $E_{int}$ obey similar trends for the neutral bases which involve only small deformation energies, there is a reversal for the anion. The binding energies of the NC$^-$···ZF$_3$ complexes rise steadily for the P < As < Sb < Bi sequence, but there is no such increase for $E_{int}$ which in fact shows a small decrease. It should be mentioned finally that these energetics are not very sensitive to the means of incorporating electron correlation. The CCSD(T) quantities in Table 3 are rather similar to the MP2 values, and all trends are identical.

The AIM diagrams of all of these complexes contain a bond path between the Z and N/C atoms involved in the interaction. The relevant properties of the bond critical point are displayed in Table S3 and reflect the energetics fairly well. For example, the density at this critical point for the two neutral bases rises regularly as the Z atom is enlarged from P to Bi, although there is a small dip from Sb to Bi; $\nabla^2\rho$ undergoes a similar increase. Just as the interaction energies of the complexes with CN$^-$ diminish with larger Z atom, so do the values of $\rho_{HCP}$, although the Laplacian changes are less consistent.

There are also secondary minima for the dimers discussed above. In the case of HCN, this neutral molecule can approach along the C$_3$ axis, directly opposite the Z lone pair, facilitated by a shallow $\pi$-hole in this region. Such a structure is less stable than the $\sigma$-hole geometries by the following amounts: 3.6, 5.7, 7.6, and 9.0 kcal/mol for the P, As, Sb, Bi series, respectively. In fact, after correction for BSSE, these alternative structures are barely bound at all, with positive interaction and binding energies. NH$_3$ can also engage in a similar sort of complex, approaching opposite the Z lone pair, but these structures are quite a bit higher in energy and only those with SbF$_3$ and BiF$_3$ are bound after counterpoise correction.

The complexes with the anion have three alternative secondary minima. In addition to the global minimum A in Figure S1, another minimum B occurs when the anion approaches along a $\sigma$-hole of ZF$_3$, causing a lesser degree of deformation. According to Table S4, this structure lies some 1.5–4 kcal/mol higher in energy than A. In configurations C and D, it is the N atom of CN$^-$ that approaches Z rather than C. If the anion approaches a $\sigma$-hole, structure C is less stable than A by 2–6 kcal/mol, but this margin rises to the 8–12 kcal/mol level when approaching the $\pi$-hole as in D. The energetic edge of geometry A is the smallest for the largest Z atom Bi, where for example, the A conformer involving the $\sigma$-hole is more stable than the B $\pi$-hole approach by only 1.5 kcal/mol. As one would expect from the diagrams, the transformation of the ZF$_3$ geometry to a nearly planar configuration structure D leads to high deformation energies as were noted for A, with these values in the 33–53 kcal/mol range reported in Table S5. The less extensive rearrangement within structures B and C leads to much smaller deformation energies, of 11 kcal/mol or less.

Some of these trends would not be easily predictable from a purely electrostatic standpoint, referring to the MEP of each subunit. In the first place, there is little to differentiate the C and N ends of CN$^-$ in terms of $V_{s,max}$ as documented in Table 1, so the strong preference for the C end might appear surprising. However, more to the point, the $\sigma$-hole of each ZF$_3$ molecule is far more intense than its $\pi$-hole which is at odds with the dominance of the A structure. This preference for the $\pi$-hole geometry of the F$_3$Z···CN$^-$ dimers is particularly notable in that this sort of geometry must overcome a very large deformation energy involved in the rearrangement of the F$_3$Z unit, indicated above.

MEP diagrams were generated for various dimers, as pertinent to the next step involving addition of a second base. These complexes retain a $\sigma$-hole that lies opposite each F$_2$–Z bond, that is, those not occupied by a base. However, the charge transferred from the base to ZF$_3$ reduces the magnitude of the remaining $\sigma$-holes. The values of $V_{s,max}$ for each of these dimers are provided in Table S6. They remain positive for both neutral bases but are reduced in magnitude by some 11–15 kcal/mol by NCH and by 14–18 kcal/mol for NH$_3$. The much larger charge transfer from the CN$^-$ anion reverses the previous positive value of $V_{s,max}$ making it negative. The charge transferred, even the smaller amount coming from the neutral bases, causes the shallow $\pi$-holes of ZF$_3$ to all become negative. This characterization of the dimer MEPs would predict that the one involving a CN$^-$ anion ought to be incapable of forming a trimer with a second base and those with the neutral bases retain a positive $\sigma$-hole; so the formation of a trimer is a possibility.

ZF$_3$ + 2 Bases. The addition of another base molecule to each heterotrimer leads to the structures of the trimers in Figure 3. As in the case of the dimers, it is the N atom of HCN
and NH₃ that approaches the central pnicogen and the C of CN⁻ in the most stable trimers. The structure of each trimer can be thought of as a distorted octahedron. One apex is occupied by the Z lone pair, and the two ligands lie syn to one another, both directly opposite a F atom, designated F1 in Figure 3. As can be seen by the angles in Table 4, these θ(N/C−ZF1) angles are roughly linear. Note that the intermolecular R(N/C−Z) distances are a bit longer in the trimers than in the corresponding dimers. This stretch amounts to some 0.04−0.08 Å for the HCN trimers and 0.05−0.14 Å for NH₃ but is much longer for the trimers involving the CN⁻ anion, on the order of 0.4 Å. In fact, for the smaller P and As atoms, there is no trimer of the sort illustrated in Figure 3 for a pair of CN⁻ anions. This failure to form a trimer is likely due first to the negative values of V_{σ,max} for the σ-holes within the CN⁻⋯ZF₃ dimers mentioned above. As another consideration, the P and As atoms have fairly small radii, 1.90 and 1.88 Å, respectively, as compared to 2.47 Å for Sb and 2.54 Å for Bi. The short R(C−Z) distances to this anion (see Table 2) result in overcrowding to the smaller Z atoms, coupled with Coulombic repulsion between the two CN⁻ anions. For illustrative purposes, if the C atoms are each placed 2 Å from Z, roughly equivalent to these lengths in the dimer, and positioned 90° from one another, they would lie only 1.4 Å from one another, inducing obvious strong steric repulsion. It is no wonder then that this distance stretches to more than 2.5 Å for those trimers that can overcome this repulsive effect. The approach of the ZF₃ geometry toward an octahedron is evident by the Σθ(F−Z−F) sums in Table 4 which lie between 260 and 288°; this sum would be 3 × 90° = 270° for a perfect octahedron. However, these angle sums are notably smaller for the NC⁻ complexes where the F atoms are forced closer together by the short R(Z−C) contacts. The presence of the base opposite each Z−F1 bond elongates this covalent bond even more than in the dimer.

The energetics of formation of these trimers from three separate subunits are compiled in Table 5. As noted above for the dimers, the two separate levels of theory are in good agreement with one another. The addition of a second HCN or NH₃ to form the trimer leads to a significant enhancement of the complexation energies. This magnification is not quite a doubling, lying in the range between 1.6 and 1.9. The situation is quite different for CN⁻ where the trimer is much more weakly bound. Indeed, the binding energy is positive and only becomes negative when considering the interaction energy. This weak binding of the second anion can be attributed in large part to the Coulombic repulsion between the NC⁻⋯ZF₃ anionic complex and the incoming CN⁻ anion.

Some of these effects are emphasized when considering the various pairwise interaction energies within the trimers. Eᵢ and E₂ in Table 5 which reference the interaction of each base with ZF₃ are all negative. In the case of the two neutral bases, these quantities are similar to those in Table 3 for the dimers, but they are reduced for the CN⁻ trimers, consistent with the R(Z−C) bond stretches. Most important are the interaction energies computed between the two bases, within the geometric context of the trimer. These quantities are only very slightly positive, roughly 1 kcal/mol for HCN and NH₃. However, the Coulombic repulsion between the two anions raises E₃ in Table 5 up to more than +70 kcal/mol, severely reducing the total interaction energy within the full trimer. The difference between the total interaction energy and the sum of pairwise interactions represents a measure of the cooperativity within the trimer. While E_{coop} is again only slightly positive for HCN and NH₃, less than 3 kcal/mol, it rises to more than 10 kcal/mol for the anions. In other words, the trimerization...
suffers not only from the pure Coulombic repulsion between the two anions but also by an anticooperative effect.

The various AIM parameters that describe these interactions are displayed in Table S8 where these quantities are again notably larger for the complexes involving the anions than with the neutrals. The bond critical point densities, for example, are in the 0.037–0.047 au range for (NC\(^{-}\)).\(\cdots\)ZF\(_{3}\) but only 0.011–0.030 for the neutral analogues. While these AIM descriptors are smaller for the anion trimers than for the corresponding anion dimers, their larger magnitudes when compared to the neutral trimers are consistent with the idea that the anions are intrinsically bonded more strongly than the neutrals, but the overall binding energies suffer from the interanionic repulsions.

Anticipating the possibility of adding a third base, the MEP of the various L\(_{2}\).\(\cdots\)ZF\(_{3}\) trimers was examined. There is a further erosion of the σ-holes relative to the dimers, caused by the charge transfer from the second base. The values of \(V_{\text{max}}\) contained in Table S9 for the σ-holes are reduced by some 10–17 kcal/mol for the neutral bases, leaving them in the range of only 13–35 kcal/mol. The values for the (NC\(^{-}\)).\(\cdots\)ZF\(_{3}\) trimers are very negative, between −120 and −147 kcal/mol, which would of course make it exceedingly difficult for these trimers to accept a third anion.

As was the case for the dimers, there are other alternate minima for the trimers as well. For the CN\(^{-}\) trimers, the other configurations look very much like those in Figure 3, except that the approaching atom can be N rather than C (but only for Z = Sb and Bi). There is not much of a distinction between them in terms of energy. For example, flipping one of the two anions around raises the energy by less than 1 kcal/mol. Very much the same is true if both CN\(^{-}\) anions are rotated around to approach via their N atoms. In addition to the (NH\(_{3}\))\(_{2}\).\(\cdots\)ZF\(_{3}\) geometry pictured in Figure 3, there are two alternate minima on the surface (see Figure S2). Whereas the two NH\(_{3}\) molecules in global minimum A occupy two of the four legs of a tetragonal pyramid, they are located nearly opposite one another in geometry B. The latter is higher in energy than global minimum A by 5–19 kcal/mol. A third structure C is similar to A in that the framework is that of a tetragonal pyramid, except that the NH\(_{3}\) molecules are located at the vertex and on one leg. This sort of geometry only occurs for the two heavier Z atoms Sb and Bi, for which it is 4–6 kcal/mol higher in energy than A.

More than Two Bases. The situation becomes more varied and interesting upon the addition of a third base to form a tetramer with ZF\(_{3}\). Three CN\(^{-}\) anions will not engage in a stable complex with a central ZF\(_{3}\). This failure is likely due to the energetic difficulty of adding yet another anion to a ZF\(_{3}\).\(\cdots\) (CN\(^{-}\)).\(\cdots\) complex that already bears a charge of −2. The situation is a bit more nuanced for HCN. Three HCN molecules can form a stable complex with ZF\(_{3}\) with all positive vibrational frequencies. However, the AIM molecular diagrams in Figure S3 make it clear that only two of the HCN molecules engage in a pnicogen bond with the central Z. For PF\(_{3}\), the HCN rotates around so that its H participates in a bifurcated H-bond with two F atoms. For the other ZF\(_{3}\) molecules, the binding is dependent on weak C···F tetrel bonds with the central C of HCN.

It is only NH\(_{3}\) which can engage in three simultaneous pnicogen bonds with ZF\(_{3}\). Two views of the structure of these tetraters are displayed in Figure 4, with their corresponding structural parameters in Table 6. Because of the negative cooperativity, the R(N···Z) distances are all a bit longer for the tetraters than for the corresponding trimers. (There is a small amount of asymmetry for PF\(_{3}\), with three slightly different \(R(N···P)\) distances.) There is a further lengthening of the internal Z···F bond lengths, and the pyramidalization of ZF\(_{3}\) is enhanced relative to the trimers, via a via the smaller Σ(F···Z−F) sums.

The energetics of these tetraters are reported in Table 7. Comparison with the data in Table 5 shows that the total complexation energies are larger than in the trimers. There is a certain degree of negative cooperativity, as these quantities are a bit less than 3/2 as would be expected from simple addition of bond energies. The AIM diagrams of these tetraters in Figure S4 confirm that the binding is indeed due to three Z···N pnicogen bonds, although there are some secondary interactions for Z = Bi. The AIM parameters in Table S10 show an increasing ZB strength with growing Z atom, P < As < Sb < Bi, but each is slightly smaller than the corresponding quantity in the trimers, further evidence of negative cooperativity.

A last issue considered was the question as to whether a ZF\(_{3}\) molecule could engage in a fourth ZB. It was found that a pentamer of this type could only be formed between 4 NH\(_{3}\) molecules and BiF\(_{3}\), the largest Z atom considered. The structure displayed in Figure 5 is not symmetric in that there are four unequal \(R(B···N)\) distances, varying from 2.65 to 3.14 Å. Moreover, the crowded nature of the complex pushes the \(θ(F···Bi···N)\) angles away from linearity. Nevertheless, there are indeed four pnicogen bonds present according to AIM analysis, with bond critical point densities between 0.013 and 0.035 au. On the other hand, Figure S5 indicates that these four ZBs are not the only interactions holding the complex together. They are complemented by a set of a N···F pnicogen bond and NH···F HBs. The entire pentamer is held together with a binding energy of −38.7 kcal/mol. This quantity is only slightly larger than the value in the tetramer of −34.4, so one can conclude that the fourth NH\(_{3}\) is held by only 4.3 kcal/mol. Given this small amount, which depends not only on the four Bi···N ZBs but also on a number of secondary interactions, the ability of BiF\(_{3}\) to engage in more than three ZBs is in doubt. In addition, the lighter Z atoms do not show any proclivity whatsoever to form more than three ZBs.

CSD Survey. A survey of previously derived crystals within the CSD\(^{81}\) (Cambridge Structural Database) provides some experimental context for the computational data above. In order to provide a comprehensive overview, only trivalent ZR\(_{3}\) units were considered. The samples were divided into those with all three R substituents a halogen (X) atom, and all others separately. N was chosen as the atom of the approaching nucleophile. In order to rule out covalent Z···N bonds and focus on noncovalent pnicogen bonds, a minimum criterion was set for the \(R(Z···N)\) interatomic distance. This threshold was taken at three different values: 110, 120, and 130% of the sum of the covalent radii of the Z and N atoms. The maximum

![Figure 4. Two views of the optimized structure of (H\(_{3}N\)).\(\cdots\)ZF\(_{3}\).](https://doi.org/10.1021/acs.jPCA.6b00257)
Table 6. Structural Parameters (Å and Degrees) in (H₃N)₃−ZF₃ at the MP2/aug-cc-pVDZ Level of Theory

|         | r(N−Z) | R(Z−F) | Φ(N−Z−F) | Σ(F−Z−F) | ΔΣ(F−Z−F) |
|---------|--------|--------|----------|----------|-----------|
| (NH₃)₃−PF₃ | 2.959  | 1.657  | 163.5    | 282.0    | −9.2      |
| (NH₃)₃−PF₃ | 2.954  | 1.656  | 163.4    |          |           |
| (NH₃)₃−PF₃ | 2.949  | 1.656  | 163.2    |          |           |
| (NH₃)₃−AsF₃ | 2.822  | 1.786  | 159.6    | 275.1    | −13.1     |
| (NH₃)₃−AsF₃ | 2.820  | 1.786  | 159.6    |          |           |
| (NH₃)₃−AsF₃ | 2.820  | 1.785  | 159.5    |          |           |
| (NH₃)₃−SbF₃ | 2.789  | 1.970  | 150.8    | 266.5    | −18.0     |
| (NH₃)₃−SbF₃ | 2.789  | 1.970  | 150.7    |          |           |
| (NH₃)₃−SbF₃ | 2.788  | 1.970  | 150.7    |          |           |
| (NH₃)₃−BiF₃ | 2.769  | 2.081  | 150.9    | 268.3    | −18.3     |
| (NH₃)₃−BiF₃ | 2.769  | 2.081  | 150.9    |          |           |
| (NH₃)₃−BiF₃ | 2.769  | 2.081  | 150.9    |          |           |

Table 7. Binding (Eᵣ) and Interaction Energies (Eᵢnd) (kcal/mol) of ZF₃ Complexes with Three NH₃, Calculated at the MP2/aug-cc-pVDZ (I) and CCSD(T)/aug-cc-pVDZ (II) Levels of Theory

|         | Eᵣ     | Eᵢnd   |
|---------|---------|---------|
| (H₃N)₃−ZF₃ | −10.14  | −11.86  |
| (NH₃)₃−PF₃ | −10.32  | −11.90  |
| (NH₃)₃−AsF₃ | −17.39  | −20.64  |
| (NH₃)₃−SbF₃ | −26.50  | −34.68  |
| (NH₃)₃−BiF₃ | −34.43  | −40.24  |

“All values corrected for BSSE.

Figure 5. Optimized geometry of (H₃N)₄−BiF₃. Distances in Å.

distance which was taken as evidence of a ZB was the sum of the vdW radii.

The data extracted from this survey are presented in Table 8 where each row refers to the number of systems where the

Table 8. Number of Instances Observed in CSD for Complexes Containing Indicated Number of Z−N Pnicogen Bonds to Central Z Atom

|         | ZF₃  | ZR₃  |
|---------|------|------|
| number of Z−N contacts | 10% | 120% | 130% | 10% | 120% | 130% |
| 1      | 7    | 5    | 1    | 285 | 105 | 14  |
| 2      | 12   | 4    | 4    | 178 | 69  | 7   |
| 3      | 4    | 2    | 1    | 55  | 36  | 10  |
| 4      | 9    | 0    | 0    | 12  | 0   | 0   |
| 5      | 0    | 0    | 0    | 13  | 0   | 0   |

“X refers to halogen atoms, and R refers to any substituent. Percentages indicate the internuclear Z−N distance as a fraction of the sum of their covalent radii. R(Bi−N) = 2.92 Å, 134% of covalent radii sum. ¹ with Z = P, 0 with As, 7 with Sb, 2 with Bi.

Table 7. Binding (Eᵣ) and Interaction Energies (Eᵢnd) (kcal/mol) of ZF₃ Complexes with Three NH₃, Calculated at the MP2/aug-cc-pVDZ (I) and CCSD(T)/aug-cc-pVDZ (II) Levels of Theory

|         | Eᵣ     | Eᵢnd   |
|---------|---------|---------|
| (H₃N)₃−ZF₃ | −10.14  | −11.86  |
| (NH₃)₃−PF₃ | −10.32  | −11.90  |
| (NH₃)₃−AsF₃ | −17.39  | −20.64  |
| (NH₃)₃−SbF₃ | −26.50  | −34.68  |
| (NH₃)₃−BiF₃ | −34.43  | −40.24  |

“All values corrected for BSSE.

It appears, then, that the number of pnicogen bonds in which a ZF₃ molecule is capable of engaging is dependent upon the nature of the base. The sp hybridization of N in NCH makes it a powerful nucleophile, binding to ZF₃ by upwards of 20 kcal/mol, as much as 40 kcal/mol for Z = Bi. However, once
bound to the Lewis acid, the ensuing NC\textsuperscript{−}···ZF\textsubscript{3} complex acquires a negative charge which impedes the approach of a second CN\textsuperscript{−}. Consequently, the second ZB is very weak and only exists at all for the larger Sb and Bi atoms. A base like NH\textsubscript{3}, on the other hand, fits into the Goldilocks region of being just right. Its electrical neutrality prevents the acquisition of charge, so there is no Coulombic obstacle to the approach of multiple NH\textsubscript{3} units. It is a strong base, which can approach to within 2.6–2.8 Å of the central Z atom, and is bound by 4–13 kcal/mol, depending on the size of Z. It is thus to easily engage simultaneously in three ZBs with ZF\textsubscript{3}, with an overall complexation energy of 10–34 kcal/mol. A fourth such bond is marginal though. In the first place, it is only the largest Z = Bi that can engage with four NH\textsubscript{3} units. In addition, the entire complex is held together not only by four ZBs but also by a number of secondary interactions. Moreover, the complexation energy of the (NH\textsubscript{3})\textsubscript{4}···BiF\textsubscript{3} system is only slightly larger than the smaller (NH\textsubscript{3})\textsubscript{3}···BiF\textsubscript{3}.

Given the strength of the interaction between CN\textsuperscript{−} and the central Z atom, it is worth considering whether the addition of this anion to a ZF\textsubscript{3} molecule that is already engaged in a pair of ZBs with two HCN molecules might induce the system to engage in a third ZB. This idea seemed plausible as the incoming CN\textsuperscript{−} will not be repelled by a (HCN)\textsubscript{2}···ZF\textsubscript{3} complex that already contains a single or double negative charge. In order to examine this possibility, the CN\textsuperscript{−} anion was initially placed in a wide range of positions with respect to each (HCN)\textsubscript{2}···ZF\textsubscript{3} complex. Ensuing geometry optimizations led to a variety of situations. For example, in most cases, the anion replaced one of the two HCN units, leaving only two ZBs. In other cases, one or both of the two HCN molecules engaged in a HB with the CN\textsuperscript{−} anion, or with the F atoms, instead of a ZB with the central ZF\textsubscript{3}. However, most importantly, in no case did any of the myriad of initial structures considered optimize to the one containing three ZBs. This result confirms the idea that a third ZB requires a neutral strong base like NH\textsubscript{3}.

A prior paper\textsuperscript{60} yielded results that have some relevance to the calculations reported above. While the first two N\textsubscript{2} or NCH Lewis bases attach themselves to a central NH\textsubscript{4}\textsuperscript{+} cation via NH···N H-bonds, succeeding base molecules engage via a N···N pnicogen bond.

Aside from the survey of crystal structures described above, there is additional specific experimental verification of some of these ideas. The Cozzolino group\textsuperscript{53} has constructed alkoxide cages containing two Sb···O ZBs, each of which is stronger than 7 kcal/mol. The central Sb atom of SbCl\textsubscript{3} engages in three Sb···O contacts short enough to be characterized as ZBs\textsuperscript{52} or in three Sb···S bonds with trithiane;\textsuperscript{93} three Bi···S bonds with BiX\textsubscript{3} have also been observed quite recently.\textsuperscript{94} Radha et al.\textsuperscript{95} have shown that a Sb atom can engage in three Sb···S ZBs, that complement its three covalent Sb···S bonds. Their analysis also concluded that a bulky alkyl substituent can inhibit the formation of this number of noncovalent interactions. A very recent work\textsuperscript{96} offers further confirmation that with proper formulation of substituents, Bi is capable of three simultaneous ZBs.

The forgoing analysis provides a framework for consideration of multiple pnicogen bonds to a given system, a set of general rules that might be applied to a particular case. As the strength of the base increases, so too does the probability of multiple pnicogen bonds. So, a weak base like NCH might be limited to only two such bonds, whereas a stronger base like NH\textsubscript{3} can engage in three and even four in certain circumstances. In addition, a larger central pnicogen atom is more prone to a greater number of ligands. However, there are secondary issues which might affect these numbers. The overall structural restraints within a crystal, for example, might prevent the central Lewis acid molecule from properly distorting so as to receive a third or fourth ligand. Or the ligands might be large enough that steric repulsions could obstruct the approach of one or more ligands. Another factor is related to the nature of the substituents on the pnicogen atom. The work described above made use of three F substituents which are highly electron-withdrawing and thus enhance the σ-holes that attract the ligands. Less electronegative substituents might be expected to weaken the pnicogen bonds and act to reduce their number. On the other hand, stabilizing interactions between the ligands themselves can promote the ability of the central Z atom to accommodate a larger number of them. The various attractive interactions between the various NH\textsubscript{3} molecules in F\textsubscript{3}Bi(NH\textsubscript{3})\textsubscript{4} described above is a case in point. Another example of a special circumstance arises if several of the electron donor atoms are part of a single ligand. Such a situation has been observed wherein SbCl\textsubscript{3} can be induced to engage in as many as five ZBs when all five electron donor O atoms are part of a single crown ether ligand.\textsuperscript{97} While an anion represents a much stronger nucleophile, its charge works against multiple bonding of this type, as was noted above for CN\textsuperscript{−} because each such anion adds to the electrostatic repulsion between central unit and approaching ligand.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c00257.

Structural parameters of isolated monomers, deformation energies, AIM descriptors of the neutral and anionic complexes, electronic and Gibbs free energy differences, \( \chi_{\text{max}} \) of dimers, energies of cooperativity, AIM descriptors of the neutral and anionic trimers, \( \chi_{\text{max}} \) of trimers, AIM descriptors of the tetramers, crystal structures of tetra and penta-coordinated complexes (from CSD); and Structural parameters in isolated ZF\textsubscript{3} (Z = P, As, Sb, Bi) calculated at the MP2/aug-cc-pVQZ level of theory (PDF)

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between like atoms; a fallacy of atomic charges. Kennepohl, P.; et al. Computational approaches and sigma-hole Del Bene, J. E.; Edwards, A. J.; Esterhuysen, C.; Guru Row, T. N.; 2012 overview. Holes, University Press, 1997.

Comprehensive Hydrogen Bond Theory Oxford, 1976; Vol. 222 5104.

Synthesis and Organocatalysis. 14450.

Phys. Chem. Chem. Phys. 2001.

Structural Chemistry and Biology Netherlands: Berlin, 2006; Vol. 168.

Comparison Based on Halogen Bond. Discussion.

Notes

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REFERENCES

(1) Kendall, K.; Roberts, A. D. van der Waals forces influencing adhesion of cells. Philos. Trans. R. Soc. London, Ser. B 2015, 370, 20140078.

(2) Müller-Dethlefs, K.; Hobza, P. Noncovalent Interactions: A Challenge for Experiment and Theory. Chem. Rev. 2000, 100, 143–168.

(3) Grabowski, S. Hydrogen Bonding—New Insights, 1 ed.; Springer Netherlands: Berlin, 2006; Vol. 3, p 524.

(4) Desiraju, G. R.; Steiner, T. The Weak Hydrogen Bond: In Structural Chemistry and Biology; Oxford University Press; Oxford, 2001.

(5) Gilli, G.; Gilli, P. The Strength of the H-Bond: Definitions and Thermodynamics. The Nature of the Hydrogen Bond; Oxford, 2009; pp 222–244.

(6) Zundel, G.; Sandorfy, C.; Schuster, P. The Hydrogen Bond: Recent Developments in Theory and Experiments; North-Holland: Amsterdam, Oxford, 1976; Vol. 2.

(7) Gilli, G.; Gilli, P. The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory; Oxford University Press: Oxford, 2013.

(8) Scheiner, S. Hydrogen Bonding: A Theoretical Perspective; Oxford University Press, 1997.

(9) Politzer, P.; Murray, J. S.; Concha, M. C. σ-hole bonding between like atoms; a fallacy of atomic charges. J. Mol. Model. 2008, 14, 659–665.

(10) Murray, J. S.; Politzer, P. The electrostatic potential: an overview. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2011, 1, 153–163.

(11) Murray, J. S.; Lane, P.; Clark, T.; Riley, K. E.; Politzer, P. σ-Holes, π-holes and electrostatically-driven interactions. J. Mol. Model. 2012, 18, 541–548.

(12) Aakeröy, C. B.; Alavi, S.; Brammer, L.; Bryce, D. L.; Clark, T.; Del Bene, J. E.; Edwards, A. J.; Esterhuysen, C.; Guru Row, T. N.; Kennespolh, P.; et al. Computational approaches and sigma-hole interactions: general discussion. Faraday Discuss. 2017, 203, 131–163.

(13) Murray, J. S.; Politzer, P. Molecular electrostatic potentials and noncovalent interactions. Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2017, 7, No. e1326.

(14) Politzer, P.; Murray, J. S. σ-Hole Interactions: Perspectives and Misconceptions. Crystals 2017, 7, 212.

(15) Politzer, P.; Murray, J. S.; Clark, T.; Resnati, G. The σ-hole revisited. Phys. Chem. Chem. Phys. 2017, 19, 32166–32178.

(16) Politzer, P.; Murray, J. S. Analysis of Halogen and Other σ-Hole Bonds in Crystals. Crystals 2018, 8, 42.

(17) Politzer, P.; Murray, J. S. Halogen Bonding: An Interim Discussion. Chemphyschem 2013, 14, 278–294.

(18) Wang, H.; Wang, W.; Jin, W. J. σ-Hole Bond vs σ-Hole Bond: A Comparison Based on Halogen Bond. Chem. Rev. 2016, 116, 5072–5104.

(19) Bullfeld, D.; Huber, S. M. Halogen Bonding in Organic Synthesis and Organocatalysis. Chem.—Eur. J. 2016, 22, 14434–14450.

(20) Cordier, P.; Tournilhac, F.; Soulé-Zakovic, C.; Leibler, L. Self-healing and thermoreversible rubber from supramolecular assembly. Nature 2008, 451, 977–980.

(21) Hobza, P.; Müller, D. K. Non-Covalent Interactions; Royal Society of Chemistry: Cambridge, 2011.

(22) Lacour, J.; Moraleda, D. Chiral anion-mediated asymmetric ion pairing chemistry. Chem. Commun. 2009, 7073–7089.

(23) Lehn, J.-M. Toward Self-Organization and Complex Matter. Science 2002, 295, 2400.

(24) Lim, J. Y. C.; Beer, P. D. Sigma-Hole Interactions in Anion Recognition. Chem 2018, 4, 731–783.

(25) Strekowski, L.; Wilson, B. Noncovalent interactions with DNA: an overview. Mutat. Res. 2007, 623, 3–13.

(26) Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. Supramolecular Materials: Self-Organized Nanostructures. Science 1997, 276, 384.

(27) Wagner, J. P.; Schreiner, P. R. London Dispersion in Molecular Chemistry—Reconsidering Steric Effects. Angew. Chem., Int. Ed. 2015, 54, 12274–12296.

(28) Whitesides, G.; Mathias, J.; Seto, C. Molecular self-assembly and nanotechnology: a chemical strategy for the synthesis of nanostructures. Science 1991, 254, 1312.

(29) Zhao, Y.; Cotelle, Y.; Sakai, N.; Matile, S. Unorthodox Interactions at Work. J. Am. Chem. Soc. 2016, 138, 4270–4277.

(30) Zhuo, P.; Huang, J.; Tian, F. Specific Noncovalent Interactions at Protein-Ligand Interface: Implications for Rational Drug Design. Curr. Med. Chem. 2012, 19, 226–238.

(31) Michalczuk, M.; Zierkiewicz, W.; Wysokiński, R.; Scheiner, S. Hexacoordinated Tetrel-Bonded Complexes between TF4 (T = Si, Ge, Sn, Pb) and NCH: Competition between σ- and π-Holes. ChemPhysChem 2019, 20, 959–966.

(32) Zierkiewicz, W.; Michalczuk, M.; Wysokiński, R.; Scheiner, S. Dual Geometry Schemes in Tetrel Bonds: Complexes between TF4 (T = Si, Ge, Sn, Pb) and Pyridine Derivatives. Molecules 2019, 24, 376.

(33) Zierkiewicz, W.; Michalczuk, M.; Wysokiński, R.; Scheiner, S. On the ability of picogen atoms to engage in both σ and π-hole complexes. Heterodimers of FZF2COH (Z = P, As, Sb, Bi) and NH3. J. Mol. Model. 2019, 25, 152.

(34) Wysokiński, R.; Michalczuk, M.; Zierkiewicz, W.; Schell, N. Influence of monomer deformation on the competition between two types of σ-holes in tetrel bonds. Phys. Chem. Chem. Phys. 2019, 21, 10336–10346.

(35) Esrafili, M. D.; Vakili, M.; Solimannejad, M. Cooperative effects in picogen bonding: (PH2F)2−7 and (PH2Cl)2−7 clusters. Chem. Phys. Lett. 2014, 609, 37–41.

(36) Adhikari, U.; Scheiner, S. Comparison of P⋯(D = P, N) with other noncovalent bonds in molecular aggregates. J. Chem. Phys. 2011, 135, 184306.

(37) Del Bene, J. E.; Alkorta, I.; Elguero, J. Hydrogen and Halogen Bonding in Cyclic FH(4+n)-FCl Complexes, for n = 0 to 4. J. Phys. Chem. A 2018, 122, 2587–2597.

(38) Sánchez-Sanz, G.; Trujillo, C. Improvement of Anion Transport Systems by Modulation of Chalcogen Interactions: The influence of solvent. J. Phys. Chem. A 2018, 122, 1369–1377.

(39) Chakraborty, S.; Maji, S.; Ghosh, R.; Jana, R.; Datta, A.; Ghosh, P. Aryl-platform-based tetrapodal 2-iodo-imidazolium as an excellent halogen bond receptor in aqueous medium. Chem. Commun. 2019, 55, 1506–1509.

(40) Scheiner, S. Differentiable Binding of Tetrel-Bonding Bipodal Receptors to Monatomic and Polyatomic Anions. Molecules 2019, 24, 227.

(41) Lee, L. M.; Tseng, M.; Poblador-Bahamonde, A. I.; Benz, S.; Sakai, N.; Sugihara, K.; Matile, S. Anion Transport with Pnicogen Bonds in Direct Comparison with Chalcogen and Halogen Bonds. J. Am. Chem. Soc. 2019, 141, 810–814.

(42) Lim, J. Y. C.; Marques, I.; Félix, V.; Beer, P. D. Chiral halogen and chalcogen bonding receptors for discrimination of stereo- and geometric dicarboxylate isomers in aqueous media. Chem. Commun. 2018, 54, 10851–10854.
Interaction: Chalcogen-Bonded Complexes With Singlet Carbene as an Electron Donor. Int. J. Quantum Chem. 2011, 111, 3881–3887.

(65) Scheiner, S. Effects of Substituents upon the P···N Noncovalent Interaction: The Limits of Its Strength. J. Phys. Chem. A 2011, 115, 11202–11209.

(66) Peterson, K. A. Systematically convergent basis sets with relativistic pseudopotentials. I. Correlation consistent basis sets for the post-d group 13-15 elements. J. Chem. Phys. 2003, 119, 11099–11112.

(67) Purvis, G. D.; Bartlett, R. J. A full coupled-cluster singles and doubles model: The inclusion of disconnected triples. J. Chem. Phys. 1982, 76, 1910–1918.

(68) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. Quadratic configuration interaction. A general technique for determining electron correlation energies. J. Chem. Phys. 1987, 87, 5968–5975.

(69) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37, 785–789.

(70) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. A fifth-order perturbation comparison of electron correlation theories. Chem. Phys. Lett. 1989, 157, 479–483.

(71) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648–5652.

(72) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. Phys. Chem. Chem. Phys. 2005, 7, 3297–3305.

(73) Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. Phys. Chem. Chem. Phys. 2006, 8, 1057.

(74) Boys, S. F.; Bernardi, F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. Mol. Phys. 1970, 19, 553–566.

(75) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; et al. Gaussian 16, Rev. C.01: Wallingford, CT, 2016.

(76) Bulat, F. A.; Toro-Labbé, A.; Brinck, T.; Murray, J. S.; Politzer, P. Quantitative analysis of molecular surfaces: areas, volumes, electrostatic potentials and average local ionization energies. J. Mol. Model. 2010, 16, 1679–1691.

(77) Lu, T.; Chen, F. Multifit: a multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33, 580–592.

(78) Lu, T.; Chen, F. Quantitative analysis of molecular surface based on improved Marching Tetrahedra algorithm. J. Mol. Graphics Modell. 2012, 36, 314–323.

(79) Keith, A. T. AlMAll, version 14.11.23; TK Gristmill Software: Overland Park KS, USA, 2014, aim.tkgristmill.com.

(80) Glendening, E. D.; Landis, C. R.; Weinhold, F. NBO 6.0: natural bond orbital analysis program. J. Comput. Chem. 2013, 34, 1429–1437.

(81) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater. 2016, 72, 171–179.

(82) Webster, M.; Keats, S. Crystal Structure of Arsenic Trichloride-Trimethylamine, AsCl3,NMe3. J. Chem. Soc. A 1971, 6, 836–838.

(83) Müller, G.; Brand, J.; Jetter, S. E. Donor-acceptor complexes between organoamines and phosphorus tribromide. Z. Naturforsch., B: J. Chem. Soc. 2001, 56, 1163–1171.

(84) Burford, N.; Edelstein, E.; Landry, J. C.; Ferguson, M. J.; McDonald, R. Identification of new N-Sb topologies: understanding the sequential dehydrochloride coupling of primary amines and trichloromercaptanes. Chem. Commun. 2005, 5074–5076.

(85) Mourgias, G.; Nieger, M.; Förster, D.; Gudat, D. Conformationally Constrained N-Heterocyclic Phosphine-Diimine with Dual Functionality. Inorg. Chem. 2013, 52, 4104–4112.

(86) Day, B. M.; Coles, M. P.; Hitchcock, P. B. Neutral and Anionic Antimony(III) Species Supported by a Bicyclic Guanidinate. Eur. J. Inorg. Chem. 2012, 841–846.
(87) Bell, S. A.; Geib, S. J.; Meyer, T. Y. Iminophosphorane-mediated carbodiimide metathesis. Chem. Commun. 2000, 1375–1376.
(88) Davidovich, R. L.; Tkachev, V. V.; Atovmyan, L. O. Crystal-Structure of Molecular Adduct of Antimony(iii) Fluoride with Nicotinamide SbF3-Center-Dot-2L. Koord. Khim. 1995, 21, 20–22.
(89) Alić, B.; Stefančić, A.; Tavčar, G. Small molecule activation: SbF3 auto-ionization supported by transfer and mesoionic NHC rearrangement. Dalton Trans. 2017, 46, 3338–3346.
(90) Grabowski, S. J. Clusters of Ammonium Cation-Hydrogen Bond versus σ-Hole Bond. Chemphyschem 2014, 15, 876–884.
(91) Moaven, S.; Yu, J.; Yasin, J.; Unruh, D. K.; Cozzolino, A. F. Precise Steric Control over 2D versus 3D Self-Assembly of Antimony(iii) Alkoxide Cages through Strong Secondary Bonding Interactions. Inorg. Chem. 2017, 56, 8372–8380.
(92) Alcock, N. W.; Ravindran, M.; Roe, S. M.; Willey, G. R. Synthesis and Structure of Antimony(iii)Chloride-1,4,7,10,13,16-Hexaoxocyclooctadecane-(18-Crown-6)-Acetonitrile (1/1/1). Inorg. Chim. Acta 1990, 167, 115–118.
(93) Leroy, C.; Johansson, R.; Bryce, D. L. 121/123Sb Nuclear Quadrupole Resonance Spectroscopy: Characterization of Non-Covalent Pnictogen Bonds and NQR Crystallography. J. Phys. Chem. A 2019, 123, 1030–1043.
(94) Mokrai, R.; Barrett, J.; Apperley, D. C.; Batsanov, A. S.; Benkő, Z.; Hefft, D. Weak Pnictogen Bond with Bismuth: Experimental Evidence Based on Bi–P Through-Space Coupling. Chem.—Eur. J. 2019, 25, 4017–4024.
(95) Radha, A.; Kumar, S.; Sharma, D.; Jassal, A. K.; Zareba, J. K.; Franconetti, A.; Frontera, A.; Sood, P.; Pandey, S. K.—Indirect influence of alkyl substituent on sigma-hole interactions: The case study of antimony(iii) diphenyldithiophosphates with covalent Sb-S and non-covalent Sb···S pnictogen bonds. Polyhedron 2019, 173, 114126.
(96) Moaven, S.; Andrews, M. C.; Polaske, T. J.; Karl, B. M.; Unruh, D. K.; Bosch, E.; Bowling, N. P.; Cozzolino, A. F. Triple-Pnictogen Bonding as a Tool for Supramolecular Assembly. Inorg. Chem. 2019, 58, 16227–16235.
(97) Hough, E.; Nicholson, D. G.; Vasudevan, A. K. Stereoechemical role of lone pairs in main-group elements. Part 3. Structure and bonding in trichloro(1,4,7,10,13-pentaoxycyclopentadecane)-antimony(iii) studied by means of X-ray crystallography at 120 K. J. Chem. Soc., Dalton Trans. 1987, 427–430.