Coordination of Anions by Noncovalently Bonded σ -Hole Ligands

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Abstract

Research on σ -hole interactions that include halogen, chalcogen, pnictogen, and tetrel bonding has been accelerating in recent years. These cousins of the H-bond have many similar properties, including geometric preferences and energetics. Most of the work to date has focused on neutral complexes, with less known about these bonds to anions. This review summarizes the current state of knowledge about the complexes of anions with ligands that engage in these sorts of noncovalent bonds. Of particular interest are comparisons with H-bonds, and how the geometry of the fully coordinated complex varies as the number of surrounding ligands increases. A specific application of these ideas is explored in which these noncovalent bonds can be used to selectively bind certain anions in a multidentate arrangement, where a symbiotic interplay of experimental and computational methods has provided some useful insights.

keywords: halogen bond; chalcogen bond; pnictogen bond; tetrel bond; H-bond

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I. INTRODUCTION

The purpose of this review is an exploration of the current state of knowledge concerning the way in which anions are coordinated by various numbers of different ligands. The focus lies with ligands which bind to the anion with the aid of noncovalent bonds. In particular, these noncovalent bonds are close cousins of H-bonds (HBs), but the bridging proton is replaced by atoms from the right side of the periodic table. Depending upon the specific column from which this substitute bridging atom is drawn, these bonds are commonly known as halogen, chalcogen, pnictogen, and tetrel bonds. (The abbreviations that will be used for these noncovalent bonds are respectively XB, YB, ZB, and TB.)

Because of their close similarity to HBs, this review begins with a very brief summary of a vast literature of anions within a surrounding atmosphere of one or more H-bonding ligands, which will set up the background by which to understand the other, and perhaps more interesting, noncovalent bonding ligands. This outline is followed by a quick overview of the general features of these noncovalent cousins of HBs, in particular the nature and strength of their bonding, and the fundamental features that lead to certain preferred geometries. The review then turns to a discussion of what has been learned to this point about the interactions of an anion to a single ligand, on which rests an understanding of the interactions with multiple ligands. In fact, work dealing with a situation wherein an anion is surrounded by more than one ligand of this type remains in its early stages, and the next section summarizes what is presently known on this score. This section is organized into two parts: The first deals with a monatomic anion, and the second section concerns itself with various diatomic or larger anions.

Following the preceding discussion of the fundamentals of the coordination of anions by these noncovalently bonding ligands, the review turns to a specific related problem as an instructional exercise. As understanding of halogen and related bonds has developed, so too has the interest in applying this idea to a practical purpose, the design a new class of anion receptors. The goal is the development of a new set of molecules that bind an anion by a number of noncovalent bonds, in a sort of cage structure. It is hoped that the incorporation of the fundamental ideas about these bonds will enable receptors to be constructed that not only bind the anion strongly, but also selectively, picking one anion in particular out of a soup containing many. Work on this problem has been double-pronged, with computations coming together with experimental approaches, and the two guiding one another.

II. ANIONS BOUND BY H-BONDS

Because of the basic similarities between HBs and the spectrum of related noncovalent bonds, it might be helpful to begin with a very brief outline of the most important aspects of the coordination of anions by H-bonding ligands. This summary can provide a point of contact with the later discussion of XB, YB, ZB, and TB coordination. The overview focuses on work that has appeared in the literature over the last five years [1-28]. A good deal of the work has involved complexes of monoatomic anions (i.e. F^- , Cl^-) with a single ligand, stabilized by one or more HBs [2, 6, 10, 13, 15, 16, 23, 25, 26]. The binding energies for each of these anions, comprising the halides and Au^- , combined with a series of proton donating ligands, are

summarized in the upper portion of Table 1. (In some indicated cases, the quantity reported is the interaction energy, which differs from the binding energy by the internal deformation energies associated with the morphing of the geometry of each monomer from its optimized structure to that adopted within the complex. This quantity is alternately referred to as reorganization energy.) These quantities extend over a wide range from a few kcal/mol (e.g. 2.9 kcal/mol for the complex of the Au anion with methane [6]) up to 70.0 kcal/mol in the doubly H-bonded chloride with squaramide [23] or even 200 kcal/mol as for the $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}^+$ complex (where the Cl^- is bonded through three HBs to the cationic ligand [2]). In general, the binding energies are reduced as the anion grows in size, although there are certainly exceptions. There are also substantial data for H-bonding of polyatomic anions (i.e. NO_3^- , OH^- , CH_3COO^- , HPO_4^{2-}) [2, 5, 6, 11, 16, 17, 20, 22, 28]. The binding energies are typically in the range between about 10 and 30 kcal/mol, as reported in the lower section of Table 1.

The binding of an anion to more than one ligand presents interesting questions of preferred geometry, as well as energetics. The case of a pair of ligands is probably the most studied [3, 12, 14, 19, 21, 27]. One might expect that those two ligands ought to lie directly opposite one another on either side of the anion but this supposition is not borne out by calculations. For example, halide anions with two H_2 ligands [12] are slightly bent as when F^- is surrounded by two water ligands [3, 19]. Even greater deviation from linearity (about 109°) was found when Cl^- is surrounded by HF or HCl ligands [27], also the case in the $\text{F}^-\cdots(\text{HF})_2$ complex [14]. Note that three HF molecules take up positions on an equilateral triangle, and four occupy vertices of a tetrahedron. The situation becomes a bit more complicated when two ligands surround a polyatomic anion. As one example, the complex of carbonate anion plus two water molecules takes up a geometry wherein each water engages in two $\text{O}\cdots\text{H}$ HBs [3]. A set of complexes between polyatomic anions like OH^- , NH_2^- , NO_2^- , CN^- , ClO^- plus two H_2 ligands has been investigated by Della and Suresh [12]. They calculated that the total interaction energy is about twice that calculated for one ligand complex, i.e. little cooperativity, and that the binding energy follows the order $\text{OH}^- > \text{NH}_2^- > \text{ClO}^- > \text{NO}_2^- > \text{CN}^-$. The literature also contains evidence of clustering of the noble metal anion Au_2^- with two water or methanol molecules [21], for which the binding energies with water (-24.44 kcal/mol) were larger than with methanol (-19.42 kcal/mol).

Anionic complexes with more than two ligands ($n=3$ or $n=4$) have also been considered [1, 3, 9, 12, 14, 19]. For $n=3$, monoatomic anions tend to form trigonal planar or pyramidal clusters, which changes to tetrahedral upon addition of a fourth ligand [3, 12, 14, 19, 27]. Not unexpectedly, increasing the number of ligands raises the total binding energy. Negative cooperativity, decreasing the average binding energy with larger number of ligands was observed by Kuchеров et al. [14]. A larger number of ligands ($n=5$ and $n=6$) yields trigonal bipyramidal and octahedral arrangement, respectively [12, 14] (see Fig. 1). A trigonal pyramid geometry was obtained when all ligands interact with one and the same atom [1, 12] of a polyatomic anion. When the ligands are bounded to more than one atom, for instance CO_3^{2-} or NO_2^- the cluster takes on another shape [1, 3, 12]. It has been found that for four H_2 ligands the OH^- , NH_2^- , ClO^- anions form a square pyramid [12].

III. GENERAL FEATURES OF NONCOVALENT BONDS

One begins with a few fundamental issues concerning these sorts of bonds that have a great deal of impact on their clustering around anions or any other nucleophile. The angular

preferences can be largely understood on the basis of electrostatics. A nucleophile is likely to be attracted, at least to a first approximation, by a region of positive electrostatic potential on the partner molecule. The location of this region can be understood by consideration of two principles. In the first place, the atom of interest, whether halogen, chalcogen, pnictogen, or tetrel, will be engaged in a covalent bond with an electron-withdrawing substituent. The molecules in Fig. 2 take F as this substituent. The $\sigma(\text{F-A})$ orbital of this covalent bond will draw some of A's electron density toward it, leaving a depletion along the extension of the F-A axis. This reduction of density amounts to what is commonly termed a σ -hole. In this same location, there exists the antibonding $\sigma^*(\text{F-A})$ orbital which is empty of electrons. Importantly, this empty orbital can serve as a natural place into which the approaching nucleophile can transfer some of its electron density, an important component in the strength of the interaction, which imparts to it what may be called partial covalent character. This σ^* orbital is indicated by the light blue regions in Fig. 2, each directly opposite the F-A bond.

The second factor is associated with the lone pairs on each A atom. There are no such lone pairs on the T atom, as in Fig. 2a, so the most positive region of the MEP, indicated by the blue region, is coincident with the σ^* orbital. The pnictogen atom, on the other hand, contains a single lone pair, represented by the red lobe in Fig. 2b. The attendant negative potential associated with this density pushes the positive region of the MEP down away from itself, as is evident in the figure. Consequently, a nucleophile attracted to this region is located a certain angle away from the F-P axis, and a ZB would be expected to have a $\theta(\text{F-Z}\cdots\text{Nuc})$ angle less than 180° . The displacement of the nucleophile from the σ^* orbital will reduce the interorbital overlap with the nucleophile, and has a weakening effect on the ZB. The two lone pairs of a chalcogen atom, as in Fig. 2c, have a similar, and even stronger, effect of pushing the positive MEP down away from the F-Y axis. In fact, in this particular FSH molecule, the most positive MEP is associated with the H atom so a $\text{SH}\cdots\text{Nuc}$ HB can be expected, as an alternative to a potential chalcogen bond. In the case of three lone pairs on the X atom, their symmetry places the positive MEP back up along the F-X axis, collinear with the σ^* orbital, which explains the linearity of XBs. As in the case of TBs, this collinearity maximizes the interorbital overlap with the nucleophile, helping to strengthen the XB.

As for the strength of these noncovalent bonds, they are sensitive to the intensity of the σ -hole as a principal factor. Such a hole is dependent upon the ability of the substituent, F in Fig. 2, to draw density toward itself. So these bonds are strengthened as the substituent becomes more electron-withdrawing. The number of electron-withdrawing substituents is an issue as well, as more of them will further enhance the intensity of the σ -hole, even if they do not lie directly opposite this hole. Second, as one goes down a column of the periodic table, the A atom becomes more electropositive which will enhance the intensity of the positive region. A second issue is the increasing polarizability, which will allow more density to be drawn away from the σ -hole region, again making it more positive. It is for these reasons that atoms from the first row of the periodic table, i.e. F, O, N, and C, are reluctant participants in these sorts of bonds. They do form these bonds, but they are generally quite weak. And of course, the strength of the bond

will be highly dependent on the basicity of the nucleophile, which both interacts with the positive MEP of the Lewis acid and donates charge to its σ^* orbital. Charge on either subunit amplifies the interaction whether an anionic nucleophile, as discussed below, or a positive charge on the Lewis acid [29-31].

It would be a mistake to equate the strength of any of these bonds with only the intensity of the σ -hole. There are other factors which add in, most notably charge transfer and dispersion, which can make comparable contributions, and which do not necessarily obey the same trends. As for magnitudes, these bonds run a wide gamut, from only 1 or 2 kcal/mol, up to 100 kcal/mol or more. There does not seem to be any rule that has yet been elucidated that places one sort of bond, say a XB, as uniformly stronger than any of the others. But it is emphasized at the outset that these bonds are quite comparable in strength to the venerable H-bond, and can be quite a bit stronger.

IV. NONCOVALENT INTERACTIONS WITH A SINGLE LIGAND

As a prelude to considering the clustering of ligands around an anion, it would be worthwhile to first review what has been learned over the last few years concerning the interactions of anions with a single molecule. There is a great deal of evidence to support the supposition that an anion will engage in a considerably stronger noncovalent bond than will an equivalent neutral molecule. This idea is already widely accepted for HBs, so there is no reason to believe it will not be equally true for other related bonds. For example, Br^- and CN^- were the targets of binding by a series of bromocarbons [32] via a XB. In a forerunner of succeeding calculations, the binding was attributed only in part to formal Coulombic attraction, supplemented by very substantial contributions from charge transfer and other interorbital interactions. The Br-containing molecules were rather diverse, including alkanes, alkenes, and alkynes as well as aromatic systems, with and without F-substitution. Interaction energies varied from as small as 1 kcal/mol for CH_3Br up to 14 kcal/mol for its CF_3Br perfluorosubstituted analogues. Binding to the C atom of CN^- was somewhat stronger than to the Br^- . In common with H-bond donors, the binding strength varied along the $\text{sp}^3 < \text{sp}^2 < \text{sp}$ sequence.

Del Bene et al [33] diversified the sample by examination of both the halogen and tetrel bonds that the halides can form with a family of simple substituted methanes, and compared their data to HBs. They found HBs the strongest, followed by TB and then by XB as the weakest. However, most of these bonds were fairly strong in any case. The tetrel bond between H_3FC and F^- amounted to some 13 kcal/mol, and the $\text{H}_3\text{ClC}\cdots\text{Cl}^-$ analogue was only slightly weaker at 11 kcal/mol. Rotating the molecule around leads to a XB, but the binding energy of this interaction for $\text{H}_3\text{CCl}\cdots\text{Cl}^-$ is considerably weaker, and in fact slightly repulsive. In contrast the HB energy for $\text{F}_3\text{CH}\cdots\text{F}^-$ is 27 kcal/mol. Along similar lines, halides were paired with a series of dihalomethanes $\text{H}_2\text{XC-X}$ and studied by single-crystal X-ray diffraction, followed by DFT calculations [34]. The computed binding energies confirmed Br to be a stronger XB donor than Cl by a factor of roughly 2, whereas Cl^- engages in slightly stronger XBs than does Br^- . Fig. 3

confirms the ability of calculations on the right to reasonably mimic experimental geometries on the left.

The general case of anion binding, viz. Cl^- and Br^- , via halogen, chalcogen, or pnictogen bonding was evaluated in 2013 [35] with an eye toward identification of the most accurate computational method. The results pointed toward M06-2X as an excellent DFT choice, particularly for the anions involved in halogen and chalcogen bonds. The two smaller halides were placed within chalcogen bonding situations [36], and again F^- bound more strongly than its larger Cl^- cousin, reaching up to 55 kcal/mol when bound to $\text{S}(\text{CN})_2$. The strong chalcogen bonding to halides and other anions was confirmed by experimental measurements [37] which placed binding enthalpies in the 20 kcal/mol range. Also with respect to chalcogen bonds, a set of pyrylium cations and thio-, seleno- and telluro- analogues were paired [38] with Cl^- as well as the larger anions NO_3^- and BF_4^- . These ion-pair complexes, some of which with Cl^- are pictured in Fig. 4, had particularly large interaction energies, exceeding 100 kcal/mol. CN^- and YCN^- ($\text{Y}=\text{O}, \text{S}, \text{Se}, \text{Te}$) anions engaged in complexes with 1,2,5-chalcogenadiazoles [39] and were studied experimentally and computationally. Interaction energies in the 37-52 kcal/mol were obtained [40]. A wide range of anions from monatomic halides, to diatomic CN^- , OH^- , and SH^- and triatomics like N_3^- , SCN^- all interact with KrO_3 , XeO_3 , and XeOF_2 [41] with interaction energies as large as 15 kcal/mol. Anions such as the halides have also been studied when interacting with a radical such as PO_2 [42]. The interactions can occur through either a σ or π -hole on the central P atom, the former being a bit stronger.

Tetrel bonds have attracted a great deal of attention in recent years, including such bonds to anions. CF_4 interacts with F^- via a tetrel bond with a binding energy of 6.5 kcal/mol; FCH_3 is even stronger at 14 kcal/mol. These quantities are considerably larger than for the corresponding halogen bonds. Tetrel bonds can also form by H_3FT with N_3^- , OCN^- and SCN^- anions [43]. Again, these tetrel bonds can be rather strong, varying between 8 and 50 kcal/mol. This sort of tetrel bond, in this case to the carboxylate anionic group of an aspartate residue, can have important biological implications [44]. Tetrel bonds to anions were studied extensively for halides, as well as CN^- , N_3^- , and SCN^- . The interaction energies span a large range, from 1.7 to 84 kcal/mol in $(\text{CN})\text{F}_3\text{Si}\cdots\text{F}^-$ [45]. Later expansion of the system considered [46] led to a higher upper limit of 96 kcal/mol, as tetrel atoms tested included the entire Si, Ge, Sn set. Anions of various sorts were among the set of nucleophiles that engaged in tetrel bonds [47], for which the interaction energies were computed at a high level. As is typically the case, the monatomic halides tend to form the strongest such bonds. Although atoms of the first row of the periodic table are reluctant to engage in noncovalent bonds, even the C of the methyl group participates when coupled with an anion [48]. These tetrel bonding interactions, including those to anions, have recently reviewed by Frontera et al [49, 50], particularly with respect to the heavier tetrel atoms Sn and Pb.

Whereas most calculations involve in vacuo situations, interactions within solvent or biological macromolecules are of great importance. Solvent was found [51] to considerably weaken interaction energies with halides, and to elongate intermolecular distances. Although

binding strengths of the halides in the gas phase diminish with anionic size, they are much more similar in solution. In a potentially useful finding, calculated free energies of formation of the complexes correlate well with halogen-bonding association constants determined experimentally.

In terms of larger Lewis acids, with multiple atoms that might attract an anion that compete with one another, halides [51] were found able to interact at various sites on a substituted s-triazine, engaging in both XBs and HBs. The authors noted different behavior between F^- and its larger halide cousins. In this same vein, Zhang et al [52] found that an approaching halide can avoid the σ -hole of the Cl atom of a molecule like $CHCl-CHOCH_3$, approaching instead from an angle of some $124-150^\circ$ from the $C=Cl$ double bond. Another unique geometry is associated with the $-NO_2$ group which attracts a nucleophile like a halide from above the NO_2 plane [53] toward what is termed a π -hole. But an anion such as NO_3^- , Cl^- or even neutral CO approaches [54] in such a way as to form more than a single intermolecular contact, as seen in Fig. 5. Anions can be attracted not only to HB or XB groups, but to the π -systems of aromatic rings as well [55, 56], and aerogen bonds to atoms like Xe are another possibility [57, 58].

Whereas inspection of the molecular electrostatic potential (MEP) surrounding a Lewis acid usually provides strong guidance as to just where an anion is likely to attach itself, this is not always the case. When paired with tetracyanopyrazine, complexes with halide anions [59] do not bind where the MEP is most positive. The authors believe these deviations are caused by larger-than-expected donor-acceptor interactions between frontier molecular orbitals. A combined experimental/computational effort [60] noted other weaknesses in the idea of applying a simple electrostatic model to provide correlation with a more comprehensive data set in which both XB donor and acceptor abilities are varied.

Of course, pairing an anion with a cation will result in especially large interaction energies, as when quinuclidine-like cation derivatives interact with any of a set of simple anions [61]. The full range of binding energies of various anions to single ligands are compiled in Tables 2 - 6. As is the case with HBs, these noncovalent bonds also are at their strongest for the highly concentrated charge within the fluoride anion. There is also of course sensitivity to the specific Lewis acid, and in particular if this ligand carries a charge.

V. MULTIPLE LIGANDS

1. Background

Although the bulk of calculations have been concerned with an anion bound to a single Lewis acid molecule, there are results available that are relevant to the coordination of an anion by multiple binding sites.

The number of ligands was increased to 2 when Br^- and I^- were each allowed to interact with first one and then two of either CH_3X or CF_3X molecules [62]. The total interaction energy increased upon adding the second ligand, but by less than occurred upon a single ligand. The $I \cdots I \cdots I$ triad was bound slightly more strongly than $Br \cdots Br \cdots Br$, and the trifluoromethyl engaged in much stronger halogen bonds than simply CH_3 . The most strongly bound triad, with an

interaction energy of 30 kcal/mol, was $\text{CF}_3\text{I}\cdots\text{I}\cdots\text{ICF}$. In terms of geometry, the two ligands were not spaced 180° apart, but rather manifested $\theta(\text{X}\cdots\text{X}\cdots\text{X})$ angles of only 97° to 103° .

A crystal structure was the inspiration for an analysis of the interactions between a halide (Cl^- and Br^-) and a variety of arylbromines [63]. The authors found that the $\text{CBr}\cdots\text{X}^-$ XBs are of strength comparable to $\text{NH}\cdots\text{X}^-$ H-bonds. Another crystal structure shows a possible arrangement of halogen bonding I atoms around a SCN^- anion [64]. Fig. 6 displays an aspect of this geometry, with two XBs to the N atom and three more to S.

Bryce's group also pursued the idea of a halide centered between a pair of aromatic XB donors [65] as indicated in Fig. 7, focusing on certain spectroscopic aspects, from both experimental solid-state and computational perspectives. The $\theta(\text{I}\cdots\text{X}\cdots\text{I})$ angle in the crystals under study were again far from linear for the most part, spanning a wide range from 80° to 176° . The calculations indicated that the lone pair orbitals on the anion govern the magnitude and orientation of the quadrupolar tensor as the geometry about the anion is systematically altered. The authors also observed a correlation between ηQ and the $\theta(\text{I}\cdots\text{X}\cdots\text{I})$ angle. The XB distance was correlated to both ^{13}C NMR and chemical shifts.

A structural analysis of $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{NCS})_4]\cdot 3\text{CBr}_4$ crystals [66] uncovered an arrangement whereby each thiocyanate anion is tied to the Zn as well as to 3 CBr_4 molecules, as exhibited in Fig. 8a. To clarify certain aspects of the various interactions, DFT calculations were carried out on two and three-point models, shown in Figs 8b and 8c, where the central $\text{Zn}(\text{NCS})_4$ unit is attached to respectively two or three Br atoms of a neighboring CBr_4 molecule. They found that the total interaction energy did not increase by adding the third contact. Indeed, even a single XB contact was just as effective in an energetic sense. This result was attributed to the larger XB angle deviations required for the greater number of contacts.

The set of halides, including also NO_3^- and SO_4^{2-} , were surrounded by 2-4 pnictogen-bonding H_2FZ molecules [67]. The $\theta(\text{Z}\cdots\text{Cl}\cdots\text{Z})$ angle for $n=2$ is much smaller than 180° , closer to 95° . The interaction energies fell in the sequence $\text{SO}_4^{2-} > \text{F}^- > \text{Cl}^- > \text{NO}_3^- > \text{Br}^- > \text{I}^-$. The geometries for $n=3$ and 4 are roughly trigonal pyramid and tetrahedral, respectively. The structures of the larger complexes for the other anions were not provided with any precision.

2. Detailed Systematic Calculations

There have been some recent quantum calculations that address the optimal geometries and energetics of a larger number of ligands clustering around an anion in a systematic manner. This work [27] has focused first on the simple Cl^- anion. This halide was surrounded by a set of ligands, of the sort that can engage in HBs as well as XB, YB, ZB and TB interactions so as to generate a thorough data set that can foster comparisons of these types of bonds with one another. The number of ligands spanned a range from 2 to 4 so that it is possible to monitor how each new addition to the cluster modifies its geometry and other characteristics.

Beginning with the case of two solvating molecules ($n=2$), both HBs and YBs are associated with nonlinear geometries [27]. The two HCl molecules are located about 109° from one another when surrounding chloride, as illustrated in Fig. 9a. The switch of H-bonding HCl to Y-bonding

FSeMe yields a similar structure (Fig. 9b). Fig 9c shows that the change of FSeMe to a linear Se=C=Se ligand increases the angle to 132°. This angle widening is accompanied by longer R(Cl...Se) distances due to the weaker basicity of SeCSe as compared to FSeMe.

As *n* increases to 3, and a third HCl ligand is added, the angles remain tetrahedral, and the H-bond lengths are stretched a bit when compared to *n*=2, as may be seen in Fig. 9d. The symmetry is relaxed in the SeCSe YB trimer in Fig. 9e. While two of the $\theta(\text{SeClSe})$ angles are as small as 77°, the third angle widens to 126°. The sum of these three angles is 280°, characteristic of a more pyramidal geometry. That is, the three SeCSe ligands lie closer together than is the case for the three HCl molecules, where the angle sum is 329°. This distinction may be thought of in terms of the beginnings of clustering between ligands, even for *n* as small as 3.

As the number of ligands increases to 4, differences between HB and XB or YB clustering become more manifest. The four HCl molecules maintain their tetrahedral separation, as seen in 10a. The total interaction of this tetracoordinated complex is 66.0 kcal/mol. Changes begin to occur from tetrahedral geometry as HBs are replaced by XBs. Fig 10b illustrates that four BrF molecules provide a roughly tetrahedral ligand grouping, even if two of the $\theta(\text{BrClBr})$ angles are enlarged to 115°. The interaction energy of the tetracoordinated Cl(BrF)₄ complex is 92.6 kcal/mol, which would be considered as strongly bound. The energy of this system rises very little even if the structure is forced to be purely tetrahedral. Transition to XB ligands ClF leads to a bit more deviation from tetrahedral geometry, as displayed in Fig 10c. The six $\theta(\text{ClClCl})$ angles range from a minimum of 98° up to 118°. But even with this greater deviation, there is little energy required to force strict tetrahedral angles. More drastic structural changes occur for ClC≡N ligands, which Fig 10d shows to be a sort of trigonal pyramid. Those angles which include the ClCN at the apex of this pyramid are all acute. But again, the energy is relatively insensitive to distortion, as a purely tetrahedral geometry lies only 0.4 kcal/mol higher. Whereas the tetracoordinated HB systems are tetrahedral, clear deviations from this idealized geometry are noted for XB complexes, even if these structures are only slightly more stable than pure tetrahedral.

Greater deviations are associated with YB ligands. Fig. 10e with four SF₂ ligands is typical. Perhaps the best characterization of these structures are distorted trigonal pyramids. The three S atoms in the base of the pyramid are separated from the apical S atom by less than 100°. The distortion extends to the spacing of the three base S atoms which are far from evenly spaced. The various $\theta(\text{SClS})$ angles are as small as 55 and as large as 167°. The substitution of S by its heavier Se congener changes the situation by very little. The three $\theta(\text{SeClSe})$ angles involving the apical Se remain small, in the 72-102° range, and those involving only the three base Se atoms cover the 73°-161° interval. A further iteration changes one F atom of SeF₂ to CH₃, which leads to a 81°-105° range for angles including the apex, and a 87°-122° range for base atoms.

Inspection of these figures suggests that the ligands tend to cluster around the chloride in such a way as to leave one hemisphere nearly vacant. This issue was examined by consideration of linear SeCSe ligands since they do not contain substituents that might attract other such

solvent molecules. But even here, there is some clustering in evidence. Fig 10f manifests a geometry that could be described as an open umbrella. The molecule that occupies the handle of this umbrella lies some 74° from those along the three spokes. But there is a great deal of variability within the spokes themselves, with $\theta(\text{SeClSe})$ angles between 75° and 140° . The total interaction energy is only 47 kcal/mol for this complex of chloride surrounded by four SeCSe molecules, much less than the 90 kcal/mol for the SeF_2 complexes which also engage in YBs.

The next sort of bonding considered involves the pnictogen family. When four PF_3 ligands surround the anion, Fig 11a shows that the open hemisphere above the Cl^- remains in place. The larger As atom places the AsF_3 molecules into another version of the umbrella, as documented in Fig 11b. Two of the spoke molecules lie close together, with $\theta(\text{AsClAs})=90^\circ$ but the three angles involving the handle are in the 84° - 89° range. In contrast, the arrangement of the PF_3 molecules might better be described as a see-saw, with the $\theta(\text{PClP})$ angle between the two opposite P atoms equal to 169° ; all other angles are less than 96° . Fig 11c shows that the placement of AsCF molecules leaves the open hemisphere again, aided by very small $\theta(\text{AsClAs})$ handle-spoke angles less than 80° . In terms of interaction energies, the ZB systems are somewhat less strongly bound than their YB correlates.

A first glance at the open hemisphere might lead to the idea that the ligands tend to cluster together so as to maximize any stabilizing interactions between themselves. This notion was tested in the context of AIM and NBO which both indicated that absence of interligand noncovalent bonds in the HB and XB complexes. The YB and ZB structures, which differ from HB and YB in that there is clustering into a single hemisphere, do exhibit such interligand noncovalent bond. As an example, the complex containing four SF_2 molecules manifests a pair of $\text{S}\cdots\text{S}$ YBs, and another between the chloride and a F atom. The total interaction energy involving linear SeCSe molecules is reinforced by four $\text{Se}\cdots\text{Se}$ YBs. The ZB complexes exhibit similar patterns. In fact, one sees $\text{As}\cdots\text{As}$ ZBs when linear AsCF ligands are considered, supplemented by a $\text{As}\cdots\text{C}$ tetrel bond.

As a central conclusion, whether HB or XB, four ligands tend toward the vertices of a tetrahedron. On the other hand, when the molecules are capable of interacting with one another, e.g. HOH, which can engage simultaneously in HBs with each other, this geometrical preference changes. In the case of YB or ZB ligands, the four molecules tend toward a single hemisphere above the central anion, leaving the other hemisphere largely vacant. This arrangement can be traced to intersolvent attractive forces, which are present even in the case of linear solvent molecules like $\text{Se}=\text{C}=\text{Se}$ and $\text{As}\equiv\text{CF}$.

3. Clustering around Diatomic Anions

The addition of a second atom to the central anion adds a higher level of complexity. Calculations were carried out for CN^- , NO^- , and OH^- , surrounded by a set of coordinating molecules again capable of forming HB, XB, YB, or TB interactions. The first two anions place an atom adjacent to N which are similarly on either side of it in the periodic table, so are either

less or more electronegative than N. OH^- offers the possibility of acting as proton donor in a H-bond, as well as providing an electron donor atom.

n=2

The optimized geometries of each of the three anions with a pair of H-bonding ligands HCl are depicted in the upper panels of Fig. 12. These molecules situate themselves so as to form one HB with each of the two atoms of CN^- . The surprising feature is that the CN^- anion has a sufficiently strongly basic nature as to remove the H from one HCl molecule, leaving a $\text{ClH}\cdots\text{NCH}\cdots\text{Cl}^-$ configuration. The two HCl molecules both participate in HBs with the N atom of NO^- , and in this case both of the protons are extracted from the HCl molecules, leading to the $\text{Cl}^-\cdots\text{ONH}_2^+\cdots\text{Cl}^-$ system, with two anions surrounding a cation. The structures of OH^- are very much like NO^- , with both the protons dissociated from the HCl molecules.

The next panels of Fig. 12 illustrate how each anion engages in a complex with a pair of halogen bonding FBr molecules. As in the HB cases, these ligands approach the CN^- from either end, and both attack the N atom of NO^- and the O of OH^- . The Br atom lies nearly midway between the C and the F, so might be better characterized as Br-shared. Similar sharing occurs in most of the other complexes as well. In all cases, the XB complexes are more strongly bound than are their H-bonding parallels.

The most stable geometries of each anion with the YB SeF_2 are illustrated in the next panels of Fig. 12. The general geometric patterns remain in terms of positioning of the two ligands: one on either end of CN^- , and both located so as to interact with the N of NO^- and the O of OH^- . On the other hand, there are certain large-scale deformations of some of the monomers. When bound to OH^- , for example, one of the SeF_2 molecules distorts from a bent to a very nearly linear structure. This distortion comes with a cost. The particular distortion of this SF_2 molecule from its optimized structure to that adopted in this configuration requires 68.5 kcal/mol, so there is clearly some important benefit afforded by this deformation in terms of the interaction. The binding energies of these chalcogen-bonded configurations are smaller than their XB counterparts but follow the same $\text{CN}^- < \text{OH}^- < \text{NO}^-$ pattern.

The binding energies suffer another drop when chalcogen atoms are replaced by pnictogens, while changing the order to $\text{CN}^- < \text{NO}^- < \text{OH}^-$. The geometric dispositions in Fig. 12 remain largely unchanged from the other types of ligands and these ZF_3 ligands do not manifest any inter-ligand interactions. These same geometrical arrangements persist for TB ligands in the next panels of Fig. 12, but with some new wrinkles. Structures appear in which there are one or more F atoms shared between the two ligands, representing an extreme form of inter-ligand interaction. In the structure pairing OH^- with GeF_4 , the OH^- anion serves as a proton donor in a H-bond with an F atom of one of the GeF_4 ligands. The binding energies of these TB complexes deviate from the drops seen on progressing from halogen to chalcogen to pnictogen; the tetrel values grow to rough equivalence with the XB systems. One also observes a sharp increase in OH^- binding energies to the point where it is the most strongly bound of all three anions. Indeed, the tetrel bonded OH^- complexes exceed even the H-bonded systems. One factor in the latter

strength is the formation of T-F...T tetrel bonds between ligands, a phenomenon which does not occur of the other sorts of ligands.

Triel-bonded (TrB) complexes characterized by GaF₃ are even stronger. Part of their magnitude can be attributed to the electron-deficient nature of the Tr atoms. As was the case for H and T-bonding, OH⁻ and CN⁻ represent the most strongly and weakly bound anions, respectively. These triel ligands generally maintain the basic disposition of the other ligands. These TrF₃ units are far enough apart that there are no interactions between ligands.

n=3

As may be seen in the top panels of Fig. 13, one of the three HCl molecules again transfers its proton to the CN⁻ C atom, and the other two HCl molecules congregate around the N. And while both HCl molecules lost their proton to the N atom of NO⁻ for n=2, there is only one such full transfer when a third HCl is added, the other proton being roughly equally shared between the N and Cl atoms. Note also that the third HCl engages with another HCl rather than the central anion. With respect to OH⁻, one HCl molecule donates its proton to the O atom. The addition of the third ligand adds an increment to each binding energy, relative to n=2, but this increment varies with anion and HX. As in the dicoordinated systems, OH⁻ is most tightly bound and CN⁻ the least. HCl is more tightly bound than HF to NO⁻, but there is little distinction between them for CN⁻ and OH⁻.

As observed for n=2, there are again elements of halogen transfer for n=3. The overall geometries in Fig. 13, though, can be considered as a fairly simple addition of the third ligand. This ligand adds to the N atom of CN⁻ and to the O atoms of NO⁻ and OH⁻. The third chalcogen-bonding ligand adds in much the same way as was noted for the XB units. When there are three YF₂ molecules present, the deformation of one of them to a quasi-linear shape becomes standard for all three anions, whereas it only occurred for OH⁻ when n=2. With the addition of a third YF₂ molecule, a new element creeps into the factors contributing to the geometries. For example, the upper left Se atom in Fig. 13 lies 3.079 Å from the N of CN⁻, but also approaches to within 3.73 Å of another SeF₂, engaging in a Se...F chalcogen bond. In fact, one or more of these inter-ligand interactions are present for all of the structures with three YF₂ molecules, including NO⁻ and OH⁻. It is probably because of the addition of this new inter-ligand stabilizing interaction, that most of the binding energies for YF₂ are larger than their XF parallels. The same sort of inter-ligand interactions appears in the ZB systems as well. As was noted above for n=2, the pnictogen ligands bind more weakly to each of the anions than do the chalcogens for n=3 as well.

The transition from ZB to TB had dramatically raised the binding energies for n=2, and that same pattern occurs for n=3. While the crowded nature of the T atoms precludes their approach by any but the central anion, there are numerous inter-ligand interactions involving F atoms, even to the point of sharing F atoms between a pair of tetrel atoms. Despite its formal negative charge OH⁻ is able to act as proton donor in a OH...F HB. The binding energies of NO⁻ and OH⁻ rise considerably upon adding a third ligand, due in part to these augmenting effects. The addition of the third ligand increases the binding energy of CN⁻ by a smaller amount since it adds

only a weak interaction with the π -system of the anion, and several weak inter-ligand F $\cdots$ F interaction.

Quite large increments of 47-57 kcal/mol occur in the TrB systems upon adding a third ligand. These large increases are due in part to a host of inter-ligand bonds involving their F atoms, that were absent until the third molecule was added. AIM analysis suggests that these ligand-ligand interactions are of comparable strength to those involving the central anion. The binding energies now approach and exceed 200 kcal/mol, largest for OH $^-$.

n=4

HCl adds to the prior CN $^-$ complex with three HCl molecules by simply adding another HB to the N, as depicted in Fig. 14. The fourth HCl molecule results in double proton transfers to both NO $^-$ and OH $^-$, leading to a central H $_2$ NO $^+$ and H $_3$ O $^+$, respectively, along with a pair of Cl $^-$ anions. The latter are stabilized by formation of two HBs each. The fourth FBr interacts via a combination of a OH $\cdots$ Br HB and a Br $\cdots$ Br XB to another BrF. These last ligands add an increment in the range of 6-10 kcal/mol to the n=3 binding energies, but a larger increment of 13 kcal/mol for the fourth FBr which engages in the aforementioned pair of noncovalent bonds.

Rather than fitting itself in to interact with CN $^-$ directly, the fourth SeF $_2$ molecule instead presents each system with a ring configuration, with several Se $\cdots$ Se chalcogen bonds augmenting the two direct interactions with the central anion, as well as several Se $\cdots$ F chalcogen bonds. The pnictogen atoms also form an interconnected ring around the central anion, but one in which the anion occupies more of a central location, and in which the ligands are connected to one another via As $\cdots$ F pnictogen bonds. Both the C and N atoms of CN $^-$ engage in ZBs, and the N of NO $^-$ forms two ZBs. In addition to the OH $\cdots$ Z HB of OH $^-$ with one ligand, the O engages in three pnictogen bonds.

The central CN $^-$ anion engages in two tetrel bonds with GeF $_4$. The third and fourth GeF $_4$ associate via noncovalent bonds to the first two ligands; a similar arrangement occurs with NO $^-$. The H of OH $^-$ forms a OH $\cdots$ F HB with the fourth ligand, as the O atom is engaged in a pair of tetrel bonds. One sees a higher degree of F-sharing between Ge atoms. The F-sharing becomes even more predominant in the GaF $_3$ ligands, whose arrangements are surprisingly similar to the ZB ligands, except that the ligand-ligand associations become more prominent here in that there are two ligands with little connection to the central anion.

In terms of binding energies, the HB, ZB, TB, and TrB ligands follow the OH $^-$ > NO $^-$ > CN $^-$ pattern, whereas the NO $^-$ exceeds OH $^-$ for XB and YB. The strongest interactions occur for the TrB ligands with binding energies reaching 300 kcal/mol for n=4. Tetrel and chalcogen bonds are next in magnitude; the remaining types of ligands do not fit a simple and consistent pattern.

VI. MULTIPLY COORDINATED ANION RECEPTORS

A particularly fascinating offshoot concerning the coordination of anions lies in the efforts over recent years to design and construct receptors for anions. The central goal is to make these receptors strong, so that they might pull the anions out of a solution in which they might exist in

low concentration. Another objective is selectivity, in that an optimal receptor can bind one anion much more strongly than others, even those closely related to it. Whereas biological evolution has developed some very specific and selective anion binding agents, modern technology lags behind. Many receptors make use of general electrostatic interactions, and sometimes of H-bonds [68-74]. The thiourea molecule, for example, is a widely used [75-79] anion binder, taking advantage of its H-bonding capability. The guanidinium cation and its derivatives [80, 81] have also found use in this regard.

However, the anion receptors that have been developed to date still suffer from certain disadvantages. Their selectivity lags behind what is needed, or they are unable to detect the presence of a particular anion below a given concentration threshold. In fact, at this point in time, the biggest need is the development of highly selective receptors that can function in an aqueous, rather than organic or biological environment. As mentioned in a recent review [82], “examples of receptors that are neutral or of low charge and operate in organic–aqueous mixtures are uncommon, and those that function in 100% water are rarer still”.

The central idea guiding the search for such receptors relies on the formation of several binding interactions to the anion simultaneously, so as to amplify the strength of each one in the final complex. Some early modest success had been achieved by relying on HB interactions, in that the receptor contained several HB proton donor groups. But along with the emergence of XB and related noncovalent bonding, came the notion that perhaps one might use these interactions to replace the HBs. Systems were thus designed that contained bipodal and even tripodal and higher order receptors, containing C-X or N-X bonds, each of which could interact strongly with a given anion.

1. Experimental Developments

An early effort by the Taylor group [83] constructed a tripodal receptor, such that I atoms on aromatic groups formed XBs with an anion. The computed geometry of this receptor is shown in Fig. 15a, binding a chloride anion. While its binding strength was only modest when compared to synthetic receptors at the time, it was nonetheless the highest-affinity receptor of this type developed to that point by several orders of magnitude. This idea was expanded upon in the same year [84] to consider tridentate receptors involving more than just I-XBs and even $\text{CH}\cdots\text{X}^-$ HBs. A combination of both XBs and HBs proved effective as well [85]. In some preliminary calculations involving halides and iodobenzene, Sarwar et al [86] found the binding of anions decreased in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$. They then placed two substituted perfluorosubstituted phenyl groups on a single molecule and measured its binding to halides. They found the longer four-carbon spacer better accommodated the Cl^- anion, and that enlarging the system to a tridentate receptor further improved the binding.

Beer's group considered a bidentate bromimidazoliophane receptor [87] to capture Br^- anions in aqueous solution via halogen bonding. Another effort [88] attempted to improve upon the interaction by activating the C-X bond via strong XBs. This same group has used a picket-fence scaffold on which to place iodinated triazole rings that can engage with an anion [89] as well as a rotaxane framework [90, 91]. Introduction of metal atoms into the receptor (Fig. 15b)

led to strong anion recognition [92], a result that was mirrored soon thereafter [93] with Ru(II) metal atoms amidst halogen bonding iodotriazole units and α -cyclodextrin structured anion receptors to capture perrhenate [94] as illustrated in Fig. 15c.

The Beer group upped the ante in 2016 [95] by synthesizing an anion receptor with four stations within a rotaxane framework. A later work considered neutral iodotriazole foldamers which could serve as tetradentate halogen bonding anion receptors [96]. Two views of the complex with I^- are displayed in Fig. 15d. Another tetradentate receptor was tested [97] two years later which utilized an interlocked host framework, as exhibited in Fig. 16a. This class of receptors, part of a foldamer molecular film, selectively binds perrhenate, iodide and thiocyanate anions in water.

Without needing charge on the receptor to attract an anion, neutral XB rotaxanes containing 2, 3, and 4 iodotriazole groups integrated into the rotaxane macrocycle were found to be excellent anion binding agents [98]. The authors were able to adjust the strength and selectivity of binding by modifying the number and position of XB iodotriazole groups. The best halide receptors were those with the largest number of XB groups. Another sort of tetrapodal receptor [99] utilizes four 2-I-imidazolium binders, all attached to a central phenyl ring, to bind halides in both organic and aqueous media

Halogen bonding receptors have also been applied [100] to the discrimination of stereoisomers of a dicarboxylate anion. A pair of halogen-bearing triazolium entities surrounded a pyrrole spacer [101] in a receptor applied to oxoanion binding, as in Fig. 16b.

Another active group in this arena is that of Huber who used isothermal calorimetric titration to determine the strong effect of entropy [102] in the binding of halides to bidentate XB receptors. A pair of I-substituted imidazolium units engaged a halide in a bipodal fashion [103], as illustrated in Fig. 16c, for which some catalytic activity was observed. This group later verified [104] via isothermal titration calorimetry, NMR, and calculations that halogen bonding does in fact occur when 2-haloimidazolium salts are mixed with anions. They also constructed XB receptors [105] where the I atom was incorporated directly into a central ring, as depicted in Fig. 16d.

There have also been efforts to carry out the sensing and recognition of anions using XBs embedded within catenane skeletal structures [106], and modified imidazoliums within other macromolecular geometries [107], as in Fig. 17a. An interesting study [108] compared binding of larger anions like PF_6^- , $H_2PO_4^-$, and SO_4^{2-} by a set of bipodal XB receptors by use of NMR.

The influence of the specific halogen atom, the electron-withdrawing group, and the group linking together the two legs of the receptor were assessed [109] by NMR and isothermal titration calorimetry and the results suggested smaller halides are preferred over larger ones but that sulfate is bound more strongly than halides. An example of the sulfate bound to one of these receptors is illustrated in Fig. 17b.

The superiority of XB over HB anion receptors was shown again [110] in terms of stronger, water resistant halide binding. The number of XB groups participating in the binding of a halide can be raised by changing the structure. The Berryman group [111] showed an iodide anion can

be encapsulated by a triple helicate via several XBs. The receptors were expanded into supramolecular polymer type structures [112] which bind anions of several charges, SO_4^{2-} , H_2PO_4^- and $\text{HP}_2\text{O}_7^{3-}$, by a combination of XBs and HBs. Another study examined the effect of the charge on the receptor [113] and found XB molecules based on either a bis(iodotriazolium)benzene or a bis(iodotriazolyl)-pyridinium showed little effect of this charge, whether +1 or +2.

A variation on this theme was developed [114] by Riel et al in which the two binding groups of the bidentate receptor were separated by a fairly long spacer group containing both a phenyl ring and two $\text{C}\equiv\text{C}$ spacers on either side. A similar pattern of this same large spacer group was found an effective anion binder [115]. In this case the central species was a pyridinium, flanked by a pair of iodobenzene groups.

Another interesting structural motif is that of a cyclopeptide, containing halogen-substituted triazole units, as pictured in Fig. 17c where it is binding a chloride anion [116]. In addition to the three XBs, there are also three HBs involved in the cage structure.

The conversation expanded a bit in 2015 [117] when the Taylor group went beyond XBs, successfully incorporating chalcogen bonding into the receptor. The Y atom was situated on a 5-membered ring, bonded on both sides by N atoms. This same idea was expanded upon [118] a year later in the form of a bipodal Te-related YB receptor, visualized in Fig. 17d. The idea of replacing XBs by YBs in anion recognition received a boost in 2016 [119] when S-containing dithieno-thiophene molecules of the type illustrated in Fig. 18a were shown to bind halides. This YB concept was further refined soon thereafter [120] in a receptor where anions were bound to rotaxanes via YBs, as illustrated in Fig. 18b. A year later, another group bound a series of anions including CN^- and YCN^- (Y=one of several chalcogen atoms) by 1,2,5-chalcogenadiazoles [39], and the Beer group [121] measured the thermodynamics of anions bound to other chalcogen-binding receptors, and one that incorporated Te in particular. In another study, this same group [122] compared binding of both chiral XB and YB receptors and found different anion selectivities for dicarboxylate isomers. A very recent work [123] has supported the idea of using YB receptors, especially in aqueous phase. Calorimetric measurements showed these receptors to display strong and selective binding for large weakly hydrated anions such as I^- and ReO_4^- .

In addition to anion-binding receptors based on XBs and YBs, there is also evidence that tetrel bonds can be added to this arsenal. The idea that a Sn atom in particular could participate in anion binding via tetrel bonds was advanced by the Jurkschat group [124]. They linked a $\text{Ph}_2\text{FSnCH}_2\text{SnFPh-CH}_2$ moiety to 19-crown-6 and found rapid transport of KF. The structure in Fig. 18c holds the F^- via a pair of $\text{Sn}\cdots\text{F}$ tetrel bonds, and the K^+ is bound in the crown segment. This group has recently reviewed developments in using organotin complexes as anion receptors [125]. The variety of shapes in which these receptors come, and the versatility of the coordination around the anions is exhibited in a number of these structures in Fig. 19.

In addition to the XB, YB, and TB receptors, a very recent work has extended this theme to pnictogen bonds as well [126]. Lee et al find that both Te and Sb, as YB and ZB agents,

respectively, are three orders of magnitude more effective transmembrane anion transporters as the XB I atom.

The forgoing represents just an outline of some of the work that has been carried out in the last decade concerning the development of multipodal anion receptors based on these noncovalent bonds. Much more detail and a fuller development can be gleaned from several recent reviews [127-131].

2. Computational Exploration

The experimental data presents a problem bursting at the seams with possibilities. While the bulk of the prior work had concentrated on halogen bonds in a wide variety of frameworks, geometries, bonding situations, charges, and so forth, workers are shifting the focus of their attention to chalcogen, pnictogen, and tetrel bonds which may offer additional dials by which to tune the binding and selectivity in unprecedented ways. In an attempt to provide guidance in these efforts, and to develop a set of principles of rational synthesis of new receptors, a number of quantum chemical studies have been carried out.

Some examples of how quantum calculations have been able to contribute to this conversation may illustrate this point. Bis-triazole-pyridine (BTP) has been shown to be an effective halide chelator, through two or perhaps three H-bonds. The two H atoms on each of the two triazole rings can be replaced by halogen atoms, as indicated by the X atoms in Fig. 20, which would replace two of the $\text{CH}\cdots\text{Y}^-$ HBs by a pair of $\text{CX}\cdots\text{Y}^-$ XBs, where Y represents the halide that is being chelated [132]. There are several perturbations one can make to this model system. In the first place, the coordinating halide can be any of F^- , Cl^- , Br^- , or I^- . Secondly the X atoms on the receptor can represent any of the halogen bonding atoms Cl, Br, or I. And the total charge on the receptor can be any of 0, +1 or +2, by adding $-\text{CH}_3^+$ groups to the locations indicated in Fig. 20. The calculations described below were carried out in a polarizable continuum of water so as to mimic aqueous solution conditions

The coordination of the halide by this receptor is illustrated in Fig. 21; in these examples, the total charge is +1, the halide is F^- , and the X atoms that coordinate with it are both H and I. Note that the halide fits nicely into the coordination provided by the receptor. The binding energies of the entire set of systems are displayed in Table 7 where several trends are immediately clear. The F^- binds most strongly, followed in diminishing order by larger halides: $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. Replacement of the two H atoms of the receptor by Cl weaken the interaction, while Br and I strengthen it in that order, i.e. the Br and I XBs are superior to HBs. And finally, the interaction is strengthened as the positive charge of the receptor rises, not surprising in view of the simple Coulombic law.

In terms of how the energetics translate into binding, Table 8 indicates the ability of each of the halogen bonding atoms to outdo H. In other words, the equilibrium ratio of binding of the indicated halide by X vs H shows the obvious superiority of I over H, with ratios varying between 660 and 2×10^7 . Br is only slightly superior to H, whereas Cl is inferior, with ratios typically well below unity. Another way to look at this issue is via selectivity for one halide over

another. As mentioned above F^- binds most strongly of all the other halides. When placed into the perspective of the equilibrium ration of this anion over the other halides, the selectivity for F^- is quite high. As illustrated in Table 9, this selectivity is somewhat akin to the preferences expressed in Table 8. That is $X=Cl$ is only mildly selective, H more so, Br better, but I is best of all. Its equilibrium ratio of F^- over the other halides is at least 1,000 and as large as 2×10^6 . So the replacement of HBs on the receptor by XBs, particularly $X=I$ not only binds halides much more strongly, but also adds to the selectivity of one halide over another.

As another perturbation, one can consider substituents placed upon these same triazole rings. As shown in Fig. 22, the Z substituents were placed [133] adjacent to the X atoms that coordinate directly with the halides. As can be seen in Fig. 23, the binding energy rises as the Z substituent become more electron withdrawing, from NH_2 to NO_2 on either extreme. This pattern persists whether the halide is F^- (green), Cl^- (olive), Br^- (red), or I^- (purple), and whether the coordinating atoms are H (broken curves) or I (solid). Note also that the superior binding of I -bonds over HBs persists. But the calculations to suggest that one can add to the ability of I XBs to bind strongly and selectively by adding electron-withdrawing substituents to the triazole rings. While Fig. 22(I) refers to the neutral receptor, the patterns in the dicationic receptor [Fig. 22(II)] are very much the same.

Still another variation can be considered in terms of the spacer in the receptor. That is, the phenyl ring in Fig. 22 can be replaced by any of a number of other sorts of groups, each of which would induce certain geometric and inductive perturbations on the coordination of the halide. Along with the original phenyl ring shown in Fig. 24a, other spacers tested [134] include the thiophene in Fig. 24b, a carbazole as in Fig. 24c, and dimethylnaphthalene illustrated in Fig. 24d. In the same vein, the triazole groups considered earlier can be substituted by imidazole groups, which are reflected in the structures of Fig. 24. While those pictured place I atoms on the imidazolium groups, H and Br were also placed into the mix. And as before, the entire panoply of halides F^- , Cl^- , Br^- , and I^- were taken as coordinated bound anions. Regardless of the spacer chosen, the order of binding remained $F^- > Cl^- > Br^- > I^-$, and the I atom was much more effective in binding the halide, with an enhancement of binding as large as 13 orders of magnitude. Imidazolium was found to be more effective than triazolium. Benzene and dimethylnaphthalene represent the best spacers, followed by thiophene and carbazole.

The coordination around the halides does not have to be limited to halogen bonds. As an extension of this idea, YBs, ZBs, and TBs were added to the mix [135]. The receptors take as their starting point a dithieno thiophene framework in which two S atoms can engage in a pair of YBs with a nucleophile, as pictured in Fig. 25a. To that is added zero, one, or two O atoms the thiophene S which is not directly involved in the interaction with the halides, as displayed in Figs 25b and 25c, respectively. Although perhaps remote, it was thought that such additions might affect the coordination of a halide. The two S atoms which engage in chalcogen bonds with the halide, are replaced by P and As atoms to compare chalcogen with pnictogen bonding, as indicated in Figs 26b and 26c, respectively. The replacement by Ge , shown in Fig. 26d permits study of TBs with the receptor. As in the earlier cases, F^- is bound most strongly, followed by

$\text{Cl}^- > \text{Br}^- > \text{I}^-$. Replacing S by the ZBs of P enhances the binding, as does changing to the larger As. Another increment accompanies the switch to the TBs arising from Ge. Despite the distance of the thiophene S atom from the binding site, the binding energy enlarges along with each additional O atom added to it. The final binding energy can be quite large, as much as 63 kcal/mol for the $\text{Ge} \cdots \text{F}^-$ interaction. One sees again a strong selectivity for fluoride over the other halides, which can be as large as 27 orders of magnitude. The data suggest that the switch from halogen to the other noncovalent bonds, particularly tetrel, offer unique opportunities for binding strength and selectivity. There were related calculations several years later [136] that verified these ideas, and found interaction energies are much reduced in a simulated solution environment.

Given the newfound effectiveness of tetrel bonds to bind halides, some further ideas were tested [137] regarding how to construct an optimal receptor. Beginning with a monopodal imidazolium, its CH was replaced first by I and then by tetrel groups SnH_3 and SiF_3 . The three F atoms on the latter group made it the strongest halide binder. The simple addition of a phenyl ring had little effect. On the other hand, placing two such modified imidazolium rings in a bipodal arrangement enhanced the binding, but did not double it. On one hand, replacement of the H atom on the imidazolium groups with the halogen-bonding I has an inconsistent effect, the binding with either halide is significantly enhanced by tetrel-bonding SnH_3 , and SiF_3 even more so. The tetrel-bonding receptors are the most selective for F^- over Cl^- with an equilibrium ratio on the order of 10^{14} for SnH_3 and 10^{28} for SiF_3 . When combined with their strong halide binding, $\text{SiF}_3\text{-ImF}_3\text{-Bz-ImF}_3\text{-SiF}_3^{+2}$ bipodal receptors represent an optimal choice in terms of both binding strength and selectivity.

Taking this information as a starting point several more dicationic receptors were constructed [138] based on a pair of imidazolium units, connected via a benzene spacer. The CH groups on each imidazolium was replaced by Br, Se, As, and Ge so as to model XBs, YBs, ZBs and TBs, respectively. The coordination of chloride by each of these prototype receptors is illustrated in Fig. 27. Regardless of the binding group considered, F^- is bound much more strongly than are Cl^- and Br^- , but the binding energy is not very sensitive to the nature of the binding atom for Cl^- and Br^- , even if H. On the other hand, one notes a great deal of differentiation with respect to F^- , where the order varies as $\text{TB} > \text{H} \sim \text{ZB} > \text{XB} > \text{YB}$. The replacement of each of these binding atoms by their analogues in the next row of the periodic table raises the fluoride binding energy by 22-56%. The strongest F^- binding agents take advantage of the TBs of Sn, whereas it is I-halogen bonds that are preferred for the two larger halides. After incorporation of thermal and entropic effects, the XB, YB, and ZB receptors do not represent much of an improvement over HBs with regard to this selectivity for F^- , even I which binds quite strongly. In stark contrast, the Ge and Sn TB derivatives manifest by far the greatest selectivity for F^- over Cl^- and Br^- , as much as 10^{13} , an enhancement of six orders of magnitude when compared to the H-bonding receptor.

Ortolan et al [139] considered the electron-deficient cavity of heterocalixarenes and a full range of anions: Cl^- , Br^- , I^- , BF_4^- , CH_3CO_2^- , H_2PO_4^- , HSO_4^- , NCS^- , NO_3^- , PF_6^- , and SO_4^{2-} . They found the anions bound to multiple sites, and the particular form of bonding ranged among

anion- π , lone pair- π , HB, as well as σ -hole. Some of these bound complexes are displayed in Fig. 28.

VII. PROSPECTS

Past work has opened new vistas in terms of halogen, chalcogen, pnictogen, and tetrel bonds which have placed them firmly in the chemist's arsenal of important intermolecular interactions. It is now clear that they are competitive in strength with their better known H-bond cousin, and new applications of these noncovalent bonds appear in the literature on what seems like a daily basis. Although these interactions with anions are presently less thoroughly studied than their neutral analogues, that situation is changing quickly. It seems certain that new results and insights will lead to a rapidly developing understanding of the clusters that are formed by these ligands around anions of all sorts. It ought to be fairly soon when rules will be established as to the structure that can be expected when a given number of ligands surrounds monoatomic and larger anions. Principles will be forthcoming as to the competition between one sort of ligand and another, with ligands of any given charge and atomic configuration. In summary, in short order we will have as solid an understanding of the coordination of an anion by these σ -hole ligands as is currently the case for H-bonded systems.

The work reviewed here has concentrated on the geometry of the clusters, and the strength of binding, as well as its fundamental nature in terms of basic principles of noncovalent bonding. But there are a plethora of areas where the conclusions will have practical applications. One of these areas, which was explored in some depth above involves poly-coordinating anion receptors. It is hoped that the ideas discussed here will guide experimentalists in the construction of new and more effective receptors. Just as some H-bonding receptors have demonstrated selectivity for certain sizes and shapes of anions, e.g. tetrahedral oxyanions, one might expect analogous selectivity rules to emanate from receptors utilizing the noncovalent bonds discussed here. But the list of applications is far more broad. Clearly, the preferred arrangement of molecules around a given anion will have profound implications on crystal structures. Due to the preponderance of anions in biological systems, e.g. the phosphate anions that surround a DNA molecule or the carboxylate of the Asp residue, the principles involved in anion coordination are important in understanding such fundamental biological processes as DNA expression and enzyme catalysis. Indeed, in the simpler chemical reactions that involve anions at one stage or another, understanding of their coordination will inform a full exploration of the entire reaction.

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Table 1 Calculated binding energies between anion and a single ligand in H-bonded clusters.

anion	ligand	-E _b , kcal/mol	level of theory	reference
monoatomic anion				
F ⁻	HF	181.7 ^b	CCSD(T)/aug-cc-pVTZ	142
F ⁻	(CH ₃) ₂ Se	79.5 ^a	MP2/6-311++G(d,p)	47
F ⁻	(CH ₃) ₂ S	74.3 ^a	MP2/6-311++G(d,p)	47
F ⁻	(CH ₃) ₂ O	58.6 ^a	MP2/6-311++G(d,p)	47
F ⁻	CFH ₃	55.7	MP2/aug'-cc-pVTZ	141
F ⁻	CF ₄	26.8	MP2/aug'-cc-pVTZ	141
F ⁻	CF ₃ H	26.15	MP2/aug-cc-pVDZ	49
Cl ⁻	[Co(NH ₃) ₅ NO ₂] ²⁺	199.33 ^a	MP2/6-31+G(d,p)	39
Cl ⁻	HCl	125.7 ^b	CCSD(T)/aug-cc-pVTZ	142
Cl ⁻	squaramide	70 ^a	B3LYP/MidiX	44
Cl ⁻	croconamide	68 ^a	B3LYP/MidiX	44
Cl ⁻	thiourea	64 ^a	B3LYP/MidiX	44
Cl ⁻	CClH ₃	45.2	MP2/aug'-cc-pVTZ	141
Cl ⁻	HF	23.1 ^a	MP2/aug-cc-pVTZ	10
Cl ⁻	CClF ₃	17.6	MP2/aug'-cc-pVTZ	141
Cl ⁻	CF ₃ H	15.16	MP2/aug-cc-pVDZ	49
Cl ⁻	triazine	9.70	MP2/aug-cc-pVTZ	43
Br ⁻	HBr	109.9 ^b	CCSD(T)/aug-cc-pVTZ	142
Br ⁻	squaramide	59 ^a	B3LYP/MidiX	44
Br ⁻	croconamide	57 ^a	B3LYP/MidiX	44
Br ⁻	thiourea	54 ^a	B3LYP/MidiX	44
Br ⁻	HF	18.7 ^a	MP2/aug-cc-pVTZ	10
Br ⁻	CF ₃ H	13.19	MP2/aug-cc-pVDZ	49
Br ⁻	triazine	8.22	MP2/aug-cc-pVTZ	43
I ⁻	HI	92.1 ^b	CCSD(T)/aug-cc-pVTZ	142
I ⁻	squaramide	42 ^a	B3LYP/MidiX	44
I ⁻	croconamide	39 ^a	B3LYP/MidiX	44
I ⁻	thiourea	38 ^a	B3LYP/MidiX	44
I ⁻	triazine	6.55	MP2/aug-cc-pVTZ	43
Au ⁻	HF	23.4 ^a	MP2/aug-cc-pVTZ	37
Au ⁻	HCN	21.6 ^a	MP2/aug-cc-pVTZ	37

Au ⁻	H ₂ O	15.1 ^a	MP2/aug-cc-pVTZ	37
Au ⁻	HCCH	10.3 ^a	MP2/aug-cc-pVTZ	37
Au ⁻	NH ₃	8.9 ^a	MP2/aug-cc-pVTZ	37
Au ⁻	CH ₄	2.9 ^a	MP2/aug-cc-pVTZ	37
polyatomic anion				
NO ₃ ⁻	[Co(NH ₃) ₅ NO ₂] ²⁺	193.25 ^a	MP2/6-31+G(d,p)	39
NO ₃ ⁻	tetraoxacalix[2]arene[2]triazine	30.48	MP2/aug-cc-pVDZ	45
NO ₃ ⁻	CF ₃ H	14.48	MP2/aug-cc-pVDZ	49
NO ₃ ⁻	H ₂ O	13.2	MP2/aug-cc-pVTZ	138
PO ₄ ³⁻	CF ₃ H	44.55	MP2/aug-cc-pVDZ	49
HPO ₄ ²⁻	H ₂ O	28.2	MP2/aug-cc-pVTZ	138
HPO ₄ ²⁻	CF ₃ H	27.55	MP2/aug-cc-pVDZ	49
SO ₄ ²⁻	CF ₃ H	26.70	MP2/aug-cc-pVDZ	49
SO ₄ ²⁻	H ₂ O	26.3	MP2/aug-cc-pVTZ	138
CH ₃ COO ⁻	CF ₃ H	16.66	MP2/aug-cc-pVDZ	49
CH ₃ COO ⁻	H ₂ O	16.5	MP2/aug-cc-pVTZ	138
SCN ⁻	tetraoxacalix[2]triazine	25.19	MP2/aug-cc-pVDZ	45
SCN ⁻	H ₂ O	11.3	MP2/aug-cc-pVTZ	138
H ₃ C ⁻	F ₃ CH	12.46	MP2/aug-cc-pVTZ	140
H ₃ C ⁻	HNH ₂	10.50	MP2/aug-cc-pVTZ	140
H ₃ C ⁻	H ₂ NH	6.57	MP2/aug-cc-pVTZ	140
H ₃ C ⁻	H ₃ CH	1.50	MP2/aug-cc-pVTZ	140
CO ₃ ²⁻	H ₂ O	34.2	MP2/aug-cc-pVTZ	138
BF ₄ ⁻	tetraoxacalix[2]arene[2]triazine	22.31	MP2/aug-cc-pVDZ	45
OH ⁻	H ₂ O	20.45	MP2/aug-cc-pVTZ	140
HCC ⁻	H ₂ O	17.50	MP2/aug-cc-pVTZ	140
F ₃ C ⁻	H ₂ O	16.78	MP2/aug-cc-pVTZ	140
PF ₆ ⁻	tetraoxacalix[2]arene[2]triazine	16.33	MP2/aug-cc-pVDZ	45
HCOO ⁻	CF ₃ H	16.26	MP2/aug-cc-pVDZ	49
CN ⁻	CF ₃ H	14.89	MP2/aug-cc-pVDZ	49
H ₂ PO ₄ ⁻	CF ₃ H	13.76	MP2/aug-cc-pVDZ	49
HSO ₄ ⁻	CF ₃ H	12.31	MP2/aug-cc-pVDZ	49
H ₂ FC ⁻	HNH ₂	10.63	MP2/aug-cc-pVTZ	140
ClO ₄ ⁻	H ₂ O	10.2	MP2/aug-cc-pVTZ	138
HF ₂ C ⁻	HNH ₂	10.10	MP2/aug-cc-pVTZ	140
F ₃ C ⁻	HNH ₂	8.26	MP2/aug-cc-pVTZ	140

^a interaction energy

^b bond dissociation energies

Table 2 Calculated binding energies between monoatomic anion and a single ligand in tetrel bonded clusters.

anion	ligand	-E _{bin} , kcal/mol	level of theory	reference
F ⁻	SiF ₃ -ImF ₃ -Bz-ImF ₃ -SiF ₃ ²⁺	251.50	M06-2X/aug-cc-pVDZ	137
F ⁻	SiF ₃ -ImF-Bz-ImF-SiF ₃ ²⁺	242.79	M06-2X/aug-cc-pVDZ	137
F ⁻	SiF ₃ -Im-Bz-Im-SiF ₃ ²⁺	231.65	M06-2X/aug-cc-pVDZ	137
F ⁻	SnH ₃ -ImF ₃ -Bz-ImF ₃ -SnH ₃ ²⁺	223.88	M06-2X/aug-cc-pVDZ	137
F ⁻	H-ImF ₃ -Bz-ImF ₃ -H ²⁺	221.16	M06-2X/aug-cc-pVDZ	137
F ⁻	SnH ₃ -ImF-Bz-ImF-SnH ₃ ²⁺	216.83	M06-2X/aug-cc-pVDZ	137
F ⁻	H-ImF-Bz-ImF-H ²⁺	212.86	M06-2X/aug-cc-pVDZ	137
F ⁻	I-ImF ₃ -Bz-ImF ₃ -I ²⁺	209.58	M06-2X/aug-cc-pVDZ	137
F ⁻	SnH ₃ -Im-Bz-Im-SnH ₃ ²⁺	206.14	M06-2X/aug-cc-pVDZ	137
F ⁻	I-ImF-Bz-ImF-I ²⁺	202.44	M06-2X/aug-cc-pVDZ	137
F ⁻	H-Im-Bz-Im-H ²⁺	196.57	M06-2X/aug-cc-pVDZ	137
F ⁻	I-Im-Bz-Im-I ²⁺	191.17	M06-2X/aug-cc-pVDZ	137
F ⁻	Im-SiF ₃ ⁺	175.13	M06-2X/aug-cc-pVDZ	137
F ⁻	Im-SnH ₃ ⁺	142.06	M06-2X/aug-cc-pVDZ	137
F ⁻	Im-H ⁺	130.09	M06-2X/aug-cc-pVDZ	137
F ⁻	Im-I ⁺	126.01	M06-2X/aug-cc-pVDZ	137
F ⁻	SnF ₃ CN	96.30 ^b	MP2/aug-cc-pVDZ	46
F ⁻	SnF ₄	93.58 ^b	MP2/aug-cc-pVDZ	46
F ⁻	GeF ₃ CN	84.92 ^b	MP2/aug-cc-pVDZ	46
F ⁻	SiF ₃ CN	84.37 ^b	MP2/aug-cc-pVDZ	46
F ⁻	SiF ₃ CN	84.37 ^b	MP2/aug-cc-pVTZ	45
F ⁻	GeF ₄	79.17 ^b	MP2/aug-cc-pVDZ	46
F ⁻	SiF ₄	70.11 ^b	MP2/aug-cc-pVDZ	46
F ⁻	SiF ₄	70.11 ^b	MP2/aug-cc-pVTZ	45
F ⁻	Ge-receptor	63.35	M06-2X/aug-cc-pVDZ	135
F ⁻	SiH ₄	60.17	CCSD/aug-cc-pVTZ	47
F ⁻	GeH ₄	40.17	CCSD/aug-cc-pVTZ	47
F ⁻	Sn-receptor	30.11	M06-2X/aug-cc-pVDZ	138
F ⁻	Ge-receptor	24.73	M06-2X/aug-cc-pVDZ	138
F ⁻	CFH ₃	13	MP2/aug'-cc-pVTZ	10
F ⁻	CF ₃ CN	8.73 ^b	MP2/aug-cc-pVTZ	45
F ⁻	CF ₄	6	MP2/aug'-cc-pVTZ	10
F ⁻	CF ₄	5.84 ^b	MP2/aug-cc-pVTZ	45
F ⁻	CH ₄	3.42	CCSD/aug-cc-pVTZ	47
Cl ⁻	SiF ₃ -ImF ₃ -Bz-ImF ₃ -SiF ₃ ²⁺	127.57	M06-2X/aug-cc-pVDZ	137
Cl ⁻	SiF ₃ -ImF-Bz-ImF-SiF ₃ ²⁺	124.88	M06-2X/aug-cc-pVDZ	137
Cl ⁻	SnH ₃ -ImF ₃ -Bz-ImF ₃ -SnH ₃ ²⁺	116.07	M06-2X/aug-cc-pVDZ	137

Cl ⁻	I-ImF ₃ -Bz-ImF ₃ -I ²⁺	111.17	M06-2X/aug-cc-pVDZ	137
Cl ⁻	H-ImF ₃ -Bz-ImF ₃ -H ²⁺	110.77	M06-2X/aug-cc-pVDZ	137
Cl ⁻	SnH ₃ -ImF-Bz-ImF-SnH ₃ ²⁺	109.33	M06-2X/aug-cc-pVDZ	137
Cl ⁻	SiF ₃ -Im-Bz-Im-SiF ₃ ²⁺	106.62	M06-2X/aug-cc-pVDZ	137
Cl ⁻	H-ImF-Bz-ImF-H ²⁺	104.90	M06-2X/aug-cc-pVDZ	137
Cl ⁻	I-ImF-Bz-ImF-I ²⁺	104.19	M06-2X/aug-cc-pVDZ	137
Cl ⁻	SnH ₃ -Im-Bz-Im-SnH ₃ ²⁺	99.08	M06-2X/aug-cc-pVDZ	137
Cl ⁻	H-Im-Bz-Im-H ²⁺	97.89	M06-2X/aug-cc-pVDZ	137
Cl ⁻	I-Im-Bz-Im-I ²⁺	93.45	M06-2X/aug-cc-pVDZ	137
Cl ⁻	TMHYZC ^a	82.67	M06-2X/aug-cc-pVDZ	48
Cl ⁻	VAPREJ ^a	81.80	M06-2X/aug-cc-pVDZ	48
Cl ⁻	GETQIF ^a	81.07	M06-2X/aug-cc-pVDZ	48
Cl ⁻	calix[4]pyrrol	71.7	BP86-D3/def2-TZVP	144
Cl ⁻	LONGEB ^a	71.05	M06-2X/aug-cc-pVDZ	48
Cl ⁻	octamethyl calix[4]pyrrol derivative	66.7	BP86-D3/def2-TZVP	144
Cl ⁻	tetramethyl calix[4]pyrrol derivative	64.6	BP86-D3/def2-TZVP	144
Cl ⁻	SnF ₃ CN	64.11 ^b	MP2/aug-cc-pVDZ	46
Cl ⁻	SnF ₄	61.84 ^b	MP2/aug-cc-pVDZ	46
Cl ⁻	ortho	56.45	M06-2X/aug-cc-pVDZ	142
Cl ⁻	ortho di C≡C	56.41	M06-2X/aug-cc-pVDZ	142
Cl ⁻	ortho C≡C	54.46	M06-2X/aug-cc-pVDZ	142
Cl ⁻	1,3-cyclohex	52.47	M06-2X/aug-cc-pVDZ	142
Cl ⁻	ZENJAD ^a	52.28	M06-2X/aug-cc-pVDZ	48
Cl ⁻	Im-SiF ₃ ⁺	52.13	M06-2X/aug-cc-pVDZ	137
Cl ⁻	octocycle	48.14	M06-2X/aug-cc-pVDZ	142
Cl ⁻	1,4-cyclohex	48.09	M06-2X/aug-cc-pVDZ	142
Cl ⁻	GeF ₃ CN	46.32 ^b	MP2/aug-cc-pVDZ	46
Cl ⁻	meta	45.03	M06-2X/aug-cc-pVDZ	142
Cl ⁻	para	43.37	M06-2X/aug-cc-pVDZ	142
Cl ⁻	GeF ₄	41.26 ^b	MP2/aug-cc-pVDZ	46
Cl ⁻	meta-Me	40.72	M06-2X/aug-cc-pVDZ	142
Cl ⁻	meta C≡C	40.28	M06-2X/aug-cc-pVDZ	142
Cl ⁻	mono ^c	39.06	M06-2X/aug-cc-pVDZ	142
Cl ⁻	Im-SnH ₃ ⁺	38.08	M06-2X/aug-cc-pVDZ	137
Cl ⁻	SiF ₃ CN	37.29 ^b	MP2/aug-cc-pVDZ	46
Cl ⁻	SiF ₃ CN	37.29 ^b	MP2/aug-cc-pVTZ	45
Cl ⁻	Ge-receptor	35.20	M06-2X/aug-cc-pVDZ	135
Cl ⁻	PbMe ₃ CN	32.4	PBE0-D3/def2-TZVPD	50
Cl ⁻	Im-I ⁺	28.38	M06-2X/aug-cc-pVDZ	137
Cl ⁻	PbMe ₃ F	28.3	PBE0-D3/def2-TZVPD	50

Cl ⁻	SnMe ₃ F	26.9 ^b	PBE0-D3/def2-TZVPD	50
Cl ⁻	PbMe ₃ CF ₃	25.9	PBE0-D3/def2-TZVPD	50
Cl ⁻	Im-H ⁺	25.08	M06-2X/aug-cc-pVDZ	137
Cl ⁻	SiF ₄	25.00 ^b	MP2/aug-cc-pVDZ	46
Cl ⁻	SiF ₄	25.00 ^b	MP2/aug-cc-pVTZ	45
Cl ⁻	ImSnF ₃	23.47	M06-2X/aug-cc-pVDZ	143
Cl ⁻	ImPbF ₃	20.62	M06-2X/aug-cc-pVDZ	143
Cl ⁻	Sn-receptor	13.79	M06-2X/aug-cc-pVDZ	138
Cl ⁻	CClH ₃	11	MP2/aug'-cc-pVTZ	10
Cl ⁻	Ge-receptor	9.32	M06-2X/aug-cc-pVDZ	138
Cl ⁻	ImGeF ₃	8.81	M06-2X/aug-cc-pVDZ	143
Cl ⁻	PbMe ₃ CH ₃	7.7	PBE0-D3/def2-TZVPD	50
Cl ⁻	CF ₃ CN	5.51 ^b	MP2/aug-cc-pVTZ	45
Cl ⁻	CClF ₃	4	MP2/aug'-cc-pVTZ	10
Cl ⁻	ImSnH ₃	3.57	M06-2X/aug-cc-pVDZ	143
Cl ⁻	CF ₄	3.20 ^b	MP2/aug-cc-pVTZ	45
Cl ⁻	ImPbH ₃	2.78	M06-2X/aug-cc-pVDZ	143
Cl ⁻	ImSiF ₃	2.73	M06-2X/aug-cc-pVDZ	143
Cl ⁻	ImGeH ₃	1.87	M06-2X/aug-cc-pVDZ	143
Cl ⁻	ImSiH ₃	1.79	M06-2X/aug-cc-pVDZ	143
Br ⁻	FADXIR ^a	81.09	M06-2X/aug-cc-pVDZ	48
Br ⁻	POSTUM02 ^a	79.82	M06-2X/aug-cc-pVDZ	48
Br ⁻	LILLOH ^a	78.67	M06-2X/aug-cc-pVDZ	48
Br ⁻	SiO ₂	78.06	CCSD/aug-cc-pVTZ	47
Br ⁻	ZZZGVM01 ^a	77.97	M06-2X/aug-cc-pVDZ	48
Br ⁻	ZZZUQO03 ^a	76.63	M06-2X/aug-cc-pVDZ	48
Br ⁻	GeO ₂	65.37	CCSD/aug-cc-pVTZ	47
Br ⁻	calix[4]pyrrol	64.9	BP86-D3/def2-TZVP	144
Br ⁻	octamethyl calix[4]pyrrol derivative	60.2	BP86-D3/def2-TZVP	144
Br ⁻	tetramethyl calix[4]pyrrol derivative	58.2	BP86-D3/def2-TZVP	144
Br ⁻	SnF ₃ CN	56.59 ^b	MP2/aug-cc-pVDZ	46
Br ⁻	SnF ₄	54.44 ^b	MP2/aug-cc-pVDZ	46
Br ⁻	GeF ₃ CN	37.73 ^b	MP2/aug-cc-pVDZ	46
Br ⁻	GeF ₄	32.99 ^b	MP2/aug-cc-pVDZ	46
Br ⁻	Ge-receptor	29.95	M06-2X/aug-cc-pVDZ	135
Br ⁻	PbMe ₃ CN	28.0 ^b	PBE0-D3/def2-TZVPD	50
Br ⁻	SiF ₃ CN	27.60 ^b	MP2/aug-cc-pVDZ	46
Br ⁻	SiF ₃ CN	27.60 ^b	MP2/aug-cc-pVTZ	45
Br ⁻	PbMe ₃ F	23.9 ^b	PBE0-D3/def2-TZVPD	50
Br ⁻	PbMe ₃ CF ₃	21.6 ^b	PBE0-D3/def2-TZVPD	50

Br ⁻	SnMe ₃ F	21.3 ^b	PBE0-D3/def2-TZVPD	50
Br ⁻	SiF ₄	16.35 ^b	MP2/aug-cc-pVDZ	46
Br ⁻	SiF ₄	16.35 ^b	MP2/aug-cc-pVTZ	45
Br ⁻	Sn-receptor	11.87	M06-2X/aug-cc-pVDZ	138
Br ⁻	Ge-receptor	8.55	M06-2X/aug-cc-pVDZ	138
Br ⁻	CO ₂	5.60	CCSD/aug-cc-pVTZ	47
Br ⁻	CF ₃ CN	4.83 ^b	MP2/aug-cc-pVTZ	45
Br ⁻	PbMe ₃ CH ₃	3.4 ^b	PBE0-D3/def2-TZVPD	50
Br ⁻	CF ₄	2.67 ^b	MP2/aug-cc-pVTZ	45
I ⁻	calix[4]pyrrol	56.5	BP86-D3/def2-TZVP	144
I ⁻	octamethyl calix[4]pyrrol derivative	52.2	BP86-D3/def2-TZVP	144
I ⁻	tetramethyl calix[4]pyrrol derivative	51.3	BP86-D3/def2-TZVP	144
I ⁻	PbMe ₃ CN	24.6 ^b	PBE0-D3/def2-TZVPD	50
I ⁻	Ge-receptor	24.46	M06-2X/aug-cc-pVDZ	135
I ⁻	PbMe ₃ F	19.7 ^b	PBE0-D3/def2-TZVPD	50
I ⁻	PbMe ₃ CF ₃	17.6 ^b	PBE0-D3/def2-TZVPD	50
I ⁻	SnMe ₃ F	15.9 ^b	PBE0-D3/def2-TZVPD	50
I ⁻	PbMe ₃ CH ₃	2.7 ^b	PBE0-D3/def2-TZVPD	50

^a ligands with CH₃Y (Y=N, O) motifs taken from CSD

^b interaction energy

Table 3 Calculated binding energies between polyatomic anion and a single ligand in tetrel bonded clusters.

anion	ligand	-E _b , kcal/mol	level of theory	reference
NCS ⁻	SiF ₃ CN	37.38 ^b	MP2/aug-cc-pVTZ	45
NCS ⁻	SiF ₄	26.59 ^b	MP2/aug-cc-pVTZ	45
SCN ⁻	SiF ₃ CN	22.10 ^b	MP2/aug-cc-pVTZ	45
SCN ⁻	SiF ₄	12.53 ^b	MP2/aug-cc-pVTZ	45
NCS ⁻	CF ₃ CN	4.93 ^b	MP2/aug-cc-pVTZ	45
SCN ⁻	CF ₃ CN	3.48 ^b	MP2/aug-cc-pVTZ	45
NCS ⁻	CF ₄	3.08 ^b	MP2/aug-cc-pVTZ	45
SCN ⁻	CF ₄	1.74 ^b	MP2/aug-cc-pVTZ	45
CN ⁻	SnF ₃ CN	72.26 ^b	MP2/aug-cc-pVDZ	46
CN ⁻	SnF ₄	70.26 ^b	MP2/aug-cc-pVDZ	46
NC ⁻	SnF ₃ CN	64.21 ^b	MP2/aug-cc-pVDZ	46
NC ⁻	SnF ₄	62.50 ^b	MP2/aug-cc-pVDZ	46
CN ⁻	GeF ₃ CN	58.35 ^b	MP2/aug-cc-pVDZ	46
CN ⁻	GeF ₄	53.57 ^b	MP2/aug-cc-pVDZ	46
NC ⁻	GeF ₃ CN	50.96 ^b	MP2/aug-cc-pVDZ	46
CN ⁻	SiF ₃ CN	50.72 ^b	MP2/aug-cc-pVDZ	46
CN ⁻	SiF ₃ CN	50.72 ^b	MP2/aug-cc-pVTZ	45
NC ⁻	GeF ₄	46.62 ^b	MP2/aug-cc-pVDZ	46
NC ⁻	SiF ₃ CN	46.59 ^b	MP2/aug-cc-pVDZ	46
NC ⁻	SiF ₃ CN	46.59 ^b	MP2/aug-cc-pVTZ	45
CN ⁻	SiF ₄	38.86 ^b	MP2/aug-cc-pVDZ	46
CN ⁻	SiF ₄	38.86 ^b	MP2/aug-cc-pVTZ	45
NC ⁻	SiF ₄	35.03 ^b	MP2/aug-cc-pVDZ	46
NC ⁻	SiF ₄	35.03 ^b	MP2/aug-cc-pVTZ	45
NC ⁻	CO ₂	8.34	CCSD/aug-cc-pVTZ	47
CN ⁻	CO ₂	8.25	CCSD/aug-cc-pVTZ	47
NC ⁻	CF ₃ CN	5.68 ^b	MP2/aug-cc-pVTZ	45
CN ⁻	CF ₃ CN	5.00 ^b	MP2/aug-cc-pVTZ	45
NC ⁻	CF ₄	3.54 ^b	MP2/aug-cc-pVTZ	45
CN ⁻	CF ₄	2.93 ^b	MP2/aug-cc-pVTZ	45
N ₃ ⁻	calix[4]pyrrol	69.5	BP86-D3/def2-TZVP	144
N ₃ ⁻	octamethyl calix[4]pyrrol derivative	63.0	BP86-D3/def2-TZVP	144
N ₃ ⁻	SnF ₃ CN	62.09 ^b	MP2/aug-cc-pVDZ	46
N ₃ ⁻	SnF ₄	60.07 ^b	MP2/aug-cc-pVDZ	46

N ₃ ⁻	tetramethyl calix[4]pyrrol derivative	59.9	BP86-D3/def2-TZVP	144
N ₃ ⁻	GeF ₃ CN	47.94 ^b	MP2/aug-cc-pVDZ	46
N ₃ ⁻	GeF ₄	43.30 ^b	MP2/aug-cc-pVDZ	46
N ₃ ⁻	SiF ₃ CN	42.68 ^b	MP2/aug-cc-pVTZ	45
N ₃ ⁻	<i>S</i> -SnH ₃ F	42.49 ^b	MP2/aug-cc-pVTZ	43
N ₃ ⁻	SiF ₃ CN	41.87 ^b	MP2/aug-cc-pVDZ	46
N ₃ ⁻	SiH ₃ F	40.91	CCSD/aug-cc-pVTZ	47
N ₃ ⁻	<i>S</i> -SiH ₃ F	37.17 ^b	MP2/aug-cc-pVTZ	43
N ₃ ⁻	GeH ₃ F	36.72	CCSD/aug-cc-pVTZ	47
N ₃ ⁻	<i>S</i> -GeH ₃ F	34.41 ^b	MP2/aug-cc-pVTZ	43
N ₃ ⁻	SiF ₄	30.89 ^b	MP2/aug-cc-pVTZ	45
N ₃ ⁻	SiF ₄	30.08 ^b	MP2/aug-cc-pVDZ	46
N ₃ ⁻	CH ₃ F	9.21	CCSD/aug-cc-pVTZ	47
N ₃ ⁻	<i>L</i> -CH ₃ F	8.98 ^b	MP2/aug-cc-pVTZ	43
N ₃ ⁻	CO ₂	6.79	CCSD/aug-cc-pVTZ	47
N ₃ ⁻	CF ₃ CN	6.32 ^b	MP2/aug-cc-pVTZ	45
N ₃ ⁻	CF ₄	4.25 ^b	MP2/aug-cc-pVTZ	45
HCO ₂ ⁻	ortho C≡C ^c	66.38	M06-2X/aug-cc-pVDZ	142
HCO ₂ ⁻	ortho di C≡C ^c	65.74	M06-2X/aug-cc-pVDZ	142
HCO ₂ ⁻	ortho ^c	59.00	M06-2X/aug-cc-pVDZ	142
HCO ₂ ⁻	1,3-cyclohex ^c	57.23	M06-2X/aug-cc-pVDZ	142
HCO ₂ ⁻	1,4-cyclohex ^c	56.32	M06-2X/aug-cc-pVDZ	142
HCO ₂ ⁻	octocycle ^c	54.91	M06-2X/aug-cc-pVDZ	142
HCO ₂ ⁻	meta ^c	51.18	M06-2X/aug-cc-pVDZ	142
HCO ₂ ⁻	para ^c	48.74	M06-2X/aug-cc-pVDZ	142
HCO ₂ ⁻	meta C≡C ^c	45.76	M06-2X/aug-cc-pVDZ	142
HCO ₂ ⁻	meta-Me ^c	45.19	M06-2X/aug-cc-pVDZ	142
HCO ₂ ⁻	mono ^c	43.24	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	ortho di C≡C ^c	51.58	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	ortho C≡C ^c	45.37	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	1,4-cyclohex ^c	41.32	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	meta ^c	39.37	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	ortho ^c	39.12	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	1,3-cyclohex ^c	38.98	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	octocycle ^c	37.58	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	meta-Me ^c	34.17	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	para ^c	33.49	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	meta C≡C ^c	31.99	M06-2X/aug-cc-pVDZ	142
HSO ₄ ⁻	Mono ^c	29.12	M06-2X/aug-cc-pVDZ	142

H ₂ PO ₄ ⁻	ortho C≡C ^c	64.01	M06-2X/aug-cc-pVDZ	142
H ₂ PO ₄ ⁻	ortho di C≡C ^c	58.65	M06-2X/aug-cc-pVDZ	142
H ₂ PO ₄ ⁻	ortho ^c	53.18	M06-2X/aug-cc-pVDZ	142
H ₂ PO ₄ ⁻	1,4-cyclohex ^c	52.76	M06-2X/aug-cc-pVDZ	142
H ₂ PO ₄ ⁻	meta ^c	50.87	M06-2X/aug-cc-pVDZ	142
H ₂ PO ₄ ⁻	1,3-cyclohex ^c	50.83	M06-2X/aug-cc-pVDZ	142
H ₂ PO ₄ ⁻	meta-Me ^c	48.19	M06-2X/aug-cc-pVDZ	142
H ₂ PO ₄ ⁻	octocycle ^c	46.93	M06-2X/aug-cc-pVDZ	142
H ₂ PO ₄ ⁻	meta C≡C ^c	42.48	M06-2X/aug-cc-pVDZ	142
H ₂ PO ₄ ⁻	para ^c	39.26	M06-2X/aug-cc-pVDZ	142
H ₂ PO ₄ ⁻	mono ^c	35.43	M06-2X/aug-cc-pVDZ	142
NCO ⁻	calix[4]pyrrol	57.6	BP86-D3/def2-TZVP	144
NCO ⁻	octamethyl calix[4]pyrrol derivative	56.2	BP86-D3/def2-TZVP	144
NCO ⁻	tetramethyl calix[4]pyrrol derivative	53.1	BP86-D3/def2-TZVP	144
NCO ⁻	CH ₃ F	9.89	CCSD/aug-cc-pVTZ	47
OCN ⁻	CH ₃ F	8.37	CCSD/aug-cc-pVTZ	47
PhO ⁻	perfluorotoluene	76.3 ^b	MP2/def2-TZVP	44
PhO ⁻	perfluorotoluene	8.9 ^b	MP2/def2-TZVP	44
HCOO ⁻	perfluorotoluene	11.6 ^b	MP2/def2-TZVP	44
HCOO ⁻	perfluorotoluene	91.2 ^b	MP2/def2-TZVP	44
SH ⁻	CO ₂	3.99	CCSD/aug-cc-pVTZ	47

^a ligands with CH₃Y (Y=N, O) motifs taken from CSD

^b interaction energy

^c the names concern the position of SnFH₂ substitution position on phenyl ring

Table 4 Calculated binding energies between anion and a single ligand in pnictogen bonded clusters.

anion	ligand	-E _b , kcal/mol	level of theory	reference
monoatomic anion				
F ⁻	FH ₂ As	46.08	MP2/aug-cc-pVTZ	67
F ⁻	FH ₂ P	41.94	MP2/aug-cc-pVTZ	67
F ⁻	CF ₃ NO ₂	27.1 ^a	BP86-D3/def2-TZVP	53
F ⁻	CH ₃ NO ₂	11.5 ^a	BP86-D3/def2-TZVP	53
Cl ⁻	spiro-[2.2]pentane cation with As (A)	183.3	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with P (A)	165.7	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with N (A)	144.2	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with As (B)	119.4	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with P (B)	116.2	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with As (C)	112.8	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with P (C)	111.5	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with N (B)	99.8	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with N (C)	96.3	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with As (D)	91.7	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with N (D)	85.9	MP2/6-311++G(d,p)	145
Cl ⁻	spiro-[2.2]pentane cation with P (D)	85.6	MP2/6-311++G(d,p)	145
Cl ⁻	As ₃ Cl	53.5 ^a	CCSD(T)/aug-cc-pVTZ	26
Cl ⁻	PO ₂ ⁻ π -hole	47.3 ^a	RI-MP2/aug-ccpVQZ	42
Cl ⁻	PO ₂ ⁻ σ -hole	35.3 ^a	RI-MP2/aug-ccpVQZ	42
Cl ⁻	FH ₂ As	25.01	MP2/aug-cc-pVTZ	67
Cl ⁻	FH ₂ P	19.80	MP2/aug-cc-pVTZ	67
Cl ⁻	4-nitrobenzonitrile	15.0 ^a	RI-MP2/def2-TZVPD	54
Cl ⁻	CF ₃ NO ₂	12.2 ^a	BP86-D3/def2-TZVP	53
Cl ⁻	4-nitropyridine	11.5 ^a	RI-MP2/def2-TZVPD	54
Cl ⁻	CH ₃ NO ₂	6.7 ^a	BP86-D3/def2-TZVP	53
Br ⁻	PO ₂ ⁻ π -hole	41.1 ^a	RI-MP2/aug-ccpVQZ	42
Br ⁻	PO ₂ ⁻ σ -hole	33.4 ^a	RI-MP2/aug-ccpVQZ	42
Br ⁻	As ₃ Cl	33.3 ^a	CCSD(T)/aug-cc-pVTZ	26
Br ⁻	FH ₂ As	21.59	MP2/aug-cc-pVTZ	67
Br ⁻	FH ₂ P	16.79	MP2/aug-cc-pVTZ	67
Br ⁻	4-nitrobenzonitrile	13.5 ^a	RI-MP2/def2-TZVPD	54
Br ⁻	CF ₃ NO ₂	10.3 ^a	BP86-D3/def2-TZVP	53
Br ⁻	4-nitropyridine	10.2 ^a	RI-MP2/def2-TZVPD	54
Br ⁻	CH ₃ NO ₂	5.9 ^a	BP86-D3/def2-TZVP	53
I ⁻	FH ₂ As	18.17	MP2/aug-cc-pVTZ	67

I ⁻	FH ₂ P	13.85	MP2/aug-cc-pVTZ	67
I ⁻	4-nitrobenzonitrile	12.7 ^a	RI-MP2/def2-TZVPD	54
I ⁻	4-nitropyridine	9.1 ^a	RI-MP2/def2-TZVPD	54
polyatomic anion				
NO ₃ ⁻	FH ₂ As	22.60	MP2/aug-cc-pVTZ	67
NO ₃ ⁻	FH ₂ P	18.49	MP2/aug-cc-pVTZ	67
NO ₃ ⁻	4-nitrobenzonitrile	15.4 ^a	RI-MP2/def2-TZVPD	54
NO ₃ ⁻	4-nitropyridine	11.8 ^a	RI-MP2/def2-TZVPD	54
SO ₄ ²⁻	FH ₂ As	49.61	MP2/aug-cc-pVTZ	67
SO ₄ ²⁻	FH ₂ P	43.20	MP2/aug-cc-pVTZ	67
SCN ⁻	PO ₂ •– π-hole	38.0 ^a	RI-MP2/aug-ccpVQZ	42
SCN ⁻	PO ₂ •– σ-hole	33.7 ^a	RI-MP2/aug-ccpVQZ	42
(PH ₂ F) ₂ ²⁻	dimer	28.69	CCSD(T)/aug-cc-pVTZ	146
(PH ₂ F) ₂ ⁺	dimer	-30.39	CCSD(T)/aug-cc-pVTZ	146

^a interaction energy

Table 5 Calculated binding energies between anion and a single ligand in chalcogen bonded clusters.

anion	ligand	-E _b , kcal/mol	level of theory	reference
monoatomic anion				
F ⁻	3,4-dicyano-1,2,5-telluradiazole	86.2	B97-D3/def2-TZVP	37
F ⁻	3,4-dicyano-1,2,5-selenadiazole	72.1	B97-D3/def2-TZVP	37
F ⁻	3,4-dicyano-1,2,5-sulfuradiazole	61.2	B97-D3/def2-TZVP	37
F ⁻	Se(CN) ₂	54.7	MP2/aug-cc-pVTZ	36
F ⁻	S(CN) ₂	46.8	MP2/aug-cc-pVTZ	36
F ⁻	C ₆ F ₄ O ₂	32.6	MP2/6-311++G(d,p)	140
F ⁻	SeCl ₂	32.6	MP2/aug-cc-pVTZ	36
F ⁻	C ₆ F ₄ (CN) ₂	28.3	MP2/6-311++G(d,p)	140
F ⁻	C ₆ H ₄ O ₂	15.8	MP2/6-311++G(d,p)	140
F ⁻	C ₆ H ₄ (CN) ₂	14.3	MP2/6-311++G(d,p)	140
Cl ⁻	Unsubstituted pyrylium cation, X= Se	108.2 ^a	CCSD(T)/CBS	38
Cl ⁻	Unsubstituted pyrylium cation, X= S	104.6 ^a	CCSD(T)/CBS	38
Cl ⁻	Unsubstituted pyrylium cation, X= O	98.5 ^a	CCSD(T)/CBS	38
Cl ⁻	3,4-dicyano-1,2,5-telluradiazole	54.2	B97-D3/def2-TZVP	37
Cl ⁻	3,4-dicyano-1,2,5-selenadiazole	42.3	B97-D3/def2-TZVP	37
Cl ⁻	Se(CN) ₂	33.5	MP2/aug-cc-pVTZ	36
Cl ⁻	3,4-dicyano-1,2,5-sulfuradiazole	33.0	B97-D3/def2-TZVP	37
Cl ⁻	S(CN) ₂	27.7	MP2/aug-cc-pVTZ	36
Cl ⁻	SFCl	24.4	MP2/aug-cc-pVTZ	36
Cl ⁻	DTT(SO ₂)	22.3 ^a	MP2/6-311++G(d,p)	136
Cl ⁻	C ₆ F ₄ (CN) ₂	20.8	MP2/6-311++G(d,p)	140
Cl ⁻	C ₆ F ₄ O ₂	20.2	MP2/6-311++G(d,p)	140
Cl ⁻	DTT(O)	14.5 ^a	MP2/6-311++G(d,p)	136
Cl ⁻	DTT(S)	12.9 ^a	MP2/6-311++G(d,p)	136
Cl ⁻	DTT(PCH ₃)	12.1 ^a	MP2/6-311++G(d,p)	136
Cl ⁻	DTT(CH ₂)	10.9 ^a	MP2/6-311++G(d,p)	136
Cl ⁻	C ₆ H ₄ (CN) ₂	10.7	MP2/6-311++G(d,p)	140
Cl ⁻	DTT(NCH ₃)	9.9 ^a	MP2/6-311++G(d,p)	136
Cl ⁻	C ₆ H ₄ O ₂	9.3	MP2/6-311++G(d,p)	140
Br ⁻	3,4-dicyano-1,2,5-telluradiazole	46.3	B97-D3/def2-TZVP	37
Br ⁻	3,4-dicyano-1,2,5-selenadiazole	35.4	B97-D3/def2-TZVP	37
Br ⁻	3,4-dicyano-1,2,5-sulfuradiazole	29.1	B97-D3/def2-TZVP	37
I ⁻	3,4-dicyano-1,2,5-telluradiazole	39.8	B97-D3/def2-TZVP	37
I ⁻	3,4-dicyano-1,2,5-selenadiazole	29.8	B97-D3/def2-TZVP	37
I ⁻	3,4-dicyano-1,2,5-sulfuradiazole	25.0	B97-D3/def2-TZVP	37

polyatomic anion				
(o-CH ₃ -PhSe) ₂ ^{•-}	dimer	94.9	MP2/6-311++G(d,p)	40
(PhSe) ₂ ^{•-}	dimer	94.2	MP2/6-311++G(d,p)	40
(PhS) ₂ ^{•-}	dimer	69.6	MP2/6-311++G(d,p)	40
(PhCH ₂ S) ₂ ^{•-}	dimer	68.8	MP2/6-311++G(d,p)	40
(PhCH ₂ Se) ₂ ^{•-}	dimer	62.8	MP2/6-311++G(d,p)	40
(o-NO ₂ -PhSe) ₂ ^{•-}	dimer	60.7	MP2/6-311++G(d,p)	40
CN ⁻	3,4-di-cyano-1,2,5-telluradiazoles	52.3	B97-D3/def2-TZVP	39
NC ⁻	3,4-di-cyano-1,2,5-telluradiazoles	48.0	B97-D3/def2-TZVP	39
NC ⁻	3,4-di-cyano-1,2,5-telluradiazoles	47.1	B97-D3/def2-TZVP	39
SPh ⁻	3,4-dicyano-1,2,5-telluradiazole	50.1	B97-D3/def2-TZVP	37
SPh ⁻	3,4-dicyano-1,2,5-selenadiazole	39.1	B97-D3/def2-TZVP	37
SPh ⁻	3,4-dicyano-1,2,5-sulfuradiazole	31.7	B97-D3/def2-TZVP	37
SCN ⁻	3,4-di-cyano-1,2,5-telluradiazoles	40.6	B97-D3/def2-TZVP	39
NCS ⁻	3,4-di-cyano-1,2,5-telluradiazoles	40.1	B97-D3/def2-TZVP	39
SeCN ⁻	3,4-di-cyano-1,2,5-telluradiazoles	39.8	B97-D3/def2-TZVP	39
NCSe ⁻	3,4-di-cyano-1,2,5-telluradiazoles	37.1	B97-D3/def2-TZVP	39
OCN ⁻	3,4-di-cyano-1,2,5-telluradiazoles	38.7	B97-D3/def2-TZVP	39
TeCN ⁻	3,4-di-cyano-1,2,5-telluradiazoles	37.0	B97-D3/def2-TZVP	39

^a interaction energy

Table 6 Calculated binding energies between anion and a single ligand in halogen bonded clusters.

anion	ligand	-E _b , kcal/mol	level of theory	ref.
monoatomic anion				
F ⁻	CH ₃ OCFCl ⁺	119.17	M05-2X/6-311++G(d,p)	52
F ⁻	CH ₃ OCHCl ⁺	115.50	M05-2X/6-311++G(d,p)	52
F ⁻	CH ₃ OCICl ⁺	113.18	M05-2X/6-311++G(d,p)	52
F ⁻	CN-Quin_II-Br	101.77 ^a	ωB97XD/aug-cc-pVTZ	61
F ⁻	H-Quin_II-Br	93.42 ^a	ωB97XD/aug-cc-pVTZ	61
F ⁻	CN-Quin_I-Br	87.09 ^a	ωB97XD/aug-cc-pVTZ	61
F ⁻	CN-Quin_II-Cl	86.83 ^a	ωB97XD/aug-cc-pVTZ	61
F ⁻	H-Quin_I-Br	79.98 ^a	ωB97XD/aug-cc-pVTZ	61
F ⁻	H-Quin_II-Cl	79.05 ^a	ωB97XD/aug-cc-pVTZ	61
F ⁻	CN-Quin_I-Cl	73.86 ^a	ωB97XD/aug-cc-pVTZ	61
F ⁻	H-Quin_I-Cl	67.44 ^a	ωB97XD/aug-cc-pVTZ	61
F ⁻	C ₃ H ₂ N ₃ I	32.27	MP2/CBS	151
F ⁻	C ₃ H ₂ N ₃ Br	20.41	MP2/CBS	151
F ⁻	C ₃ H ₂ N ₃ Cl	13.09	MP2/CBS	151
Cl ⁻	CH ₃ OCFCl ⁺	95.66	M05-2X/6-311++G(d,p)	52
Cl ⁻	CH ₃ OCHCl ⁺	94.44	M05-2X/6-311++G(d,p)	52
Cl ⁻	CH ₃ OCICl ⁺	92.89	M05-2X/6-311++G(d,p)	52
Cl ⁻	2-halo-1H-imidazol -3-ium Br derivative	87.00 ^a	CCSD(T)/aug-cc-pVDZ	147
Cl ⁻	CN-Quin_II-Br	78.36 ^a	ωB97XD/aug-cc-pVTZ	61
Cl ⁻	H-Quin_II-Br	71.08 ^a	ωB97XD/aug-cc-pVTZ	61
Cl ⁻	CN-Quin_II-Cl	67.47 ^a	ωB97XD/aug-cc-pVTZ	61
Cl ⁻	CN-Quin_I-Br	66.49 ^a	ωB97XD/aug-cc-pVTZ	61
Cl ⁻	H-Quin_II-Cl	61.48 ^a	ωB97XD/aug-cc-pVTZ	61
Cl ⁻	H-Quin_I-Br	60.69 ^a	ωB97XD/aug-cc-pVTZ	61
Cl ⁻	CN-Quin_I-Cl	58.32 ^a	ωB97XD/aug-cc-pVTZ	61
Cl ⁻	H-Quin_I-Cl	53.40 ^a	ωB97XD/aug-cc-pVTZ	61
Cl ⁻	BrF	53.1 ^a	CCSD(T)/aug-cc-pVTZ	26
Cl ⁻	C ₃ H ₂ N ₃ I	17.75	MP2/CBS	151
Cl ⁻	I ₂	34 ^a	M06-2X/aug-cc-pVTZ	150
Cl ⁻	C ₆ F ₅ I	23.80 ^a	MP2/aug-cc-pVDZ	51
Cl ⁻	C ₂ F ₃ I	23.19 ^a	MP2/aug-cc-pVDZ	51
Cl ⁻	iodoimidazolium	10.6	B3LYP/SVP	148
Cl ⁻	C ₃ H ₂ N ₃ Br	10.52	MP2/CBS	151
Cl ⁻	imidazolium	7.4	B3LYP/SVP	148
Cl ⁻	tetracyanopyrazine	6.71 ^a	M062X/def2tzvpp	59

Cl ⁻	C ₃ H ₂ N ₃ Cl	6.44	MP2/CBS	151
Br ⁻	CH ₃ OCFCl ⁺	93.89	M05-2X/6-311++G(d,p)	52
Br ⁻	CH ₃ OCHCl ⁺	92.27	M05-2X/6-311++G(d,p)	52
Br ⁻	CH ₃ OCICl ⁺	90.96	M05-2X/6-311++G(d,p)	52
Br ⁻	CN-Quin_II-Br	74.53 ^a	ωB97XD/aug-cc-pVTZ	61
Br ⁻	I ₂	69 ^a	M06-2X/aug-cc-pVTZ	150
Br ⁻	H-Quin_II-Br	67.35 ^a	ωB97XD/aug-cc-pVTZ	61
Br ⁻	CN-Quin_II-Cl	64.20 ^a	ωB97XD/aug-cc-pVTZ	61
Br ⁻	CN-Quin_I-Br	63.05 ^a	ωB97XD/aug-cc-pVTZ	61
Br ⁻	H-Quin_II-Cl	58.50 ^a	ωB97XD/aug-cc-pVTZ	61
Br ⁻	H-Quin_I-Br	57.48 ^a	ωB97XD/aug-cc-pVTZ	61
Br ⁻	CN-Quin_I-Cl	55.71 ^a	ωB97XD/aug-cc-pVTZ	61
Br ⁻	H-Quin_I-Cl	51.05 ^a	ωB97XD/aug-cc-pVTZ	61
Br ⁻	HF	23.0 ^a	CCSD(T)/aug-cc-pVTZ	26
Br ⁻	C ₆ F ₅ I	21.00 ^a	MP2/aug-cc-pVDZ	51
Br ⁻	C ₂ F ₃ I	20.40 ^a	MP2/aug-cc-pVDZ	51
Br ⁻	CF ₃ Br	16.83 ^a	CCSD(T)/lanl2DZ*	62
Br ⁻	C ₃ H ₂ N ₃ I	15.36	MP2/CBS	151
Br ⁻	F ₃ C-Br	11.95 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	HC≡C-Br	10.47 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	C ₃ H ₂ N ₃ Br	8.91	MP2/CBS	151
Br ⁻	4-pyridyl-Br	8.11 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	3-pyridyl-Br	7.30 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	F ₂ CH-Br	6.87 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	tetracyanopyrazine	6.42 ^a	M062X/def2tzvpp	59
Br ⁻	4-F-phenyl-Br	6.35 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	C ₃ H ₂ N ₃ Cl	5.37	MP2/CBS	151
Br ⁻	Phenyl-Br	4.52 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	FCH ₂ -Br	4.45 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	2-pyridyl-Br	3.66 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	H ₂ C=CH-Br	3.51 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	4-NH ₂ -phenyl-Br	3.13 ^a	MP2/aug-cc-pVDZ	32
Br ⁻	CH ₃ Br	2.39 ^a	CCSD(T)/lanl2DZ*	62
Br ⁻	H ₃ C-Br	0.89 ^a	MP2/aug-cc-pVDZ	32
I ⁻	I ₂	38 ^a	M06-2X/aug-cc-pVTZ	150
I ⁻	CF ₃ I	19.08 ^a	CCSD(T)/lanl2DZ*	62
I ⁻	C ₆ F ₅ I	17.66 ^a	MP2/aug-cc-pVDZ	51
I ⁻	C ₂ F ₃ I	17.11 ^a	MP2/aug-cc-pVDZ	51
I ⁻	C ₃ H ₂ N ₃ I	12.91	MP2/CBS	151
I ⁻	C ₃ H ₂ N ₃ Br	7.21	MP2/CBS	151

I ⁻	tetracyanopyrazine	6.06 ^a	M062X/def2tzvpp	59
I ⁻	CH ₃ I	4.86 ^a	CCSD(T)/lanl2DZ*	62
I ⁻	C ₃ H ₂ N ₃ Cl	4.23	MP2/CBS	151
polyatomic anion				
NC ⁻	CN-Quin_II-Br	73.76 ^a	ωB97XD/aug-cc-pVTZ	61
NC ⁻	H-Quin_II-Br	67.25 ^a	ωB97XD/aug-cc-pVTZ	61
NC ⁻	CN-Quin_II-Cl	63.72 ^a	ωB97XD/aug-cc-pVTZ	61
NC ⁻	CN-Quin_I-Br	63.01 ^a	ωB97XD/aug-cc-pVTZ	61
NC ⁻	H-Quin_II-Cl	58.47 ^a	ωB97XD/aug-cc-pVTZ	61
NC ⁻	H-Quin_I-Br	57.78 ^a	ωB97XD/aug-cc-pVTZ	61
NC ⁻	CN-Quin_I-Cl	55.92 ^a	ωB97XD/aug-cc-pVTZ	61
NC ⁻	H-Quin_I-Cl	51.51 ^a	ωB97XD/aug-cc-pVTZ	61
CN ⁻	F ₃ C-Br	13.68 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	HC≡C-Br	12.36 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	4-pyridyl-Br	9.40 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	F ₂ CH-Br	9.37 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	3-pyridyl-Br	8.60 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	4-F-phenyl-Br	7.61 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	Phenyl-Br	5.78 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	FCH ₂ -Br	5.77 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	2-pyridyl-Br	4.95 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	H ₂ C=CH-Br	4.81 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	4-NH ₂ -phenyl-Br	4.40 ^a	MP2/aug-cc-pVDZ	32
CN ⁻	H ₃ C-Br	1.05 ^a	MP2/aug-cc-pVDZ	32
NCS ⁻	CBr ₄	12.2 ^a	M062X/6-311+G(d,p)	66
BF ₄ ⁻	NCN	41.7 ^a	BP86-D3/def2-TZVP	149
BF ₄ ⁻	NPy	32.6 ^a	BP86-D3/def2-TZVP	149
NO ₃ ⁻	I ₂	34 ^a	M06-2X/aug-cc-pVTZ	150
Ac ⁻	I ₂	34 ^a	M06-2X/aug-cc-pVTZ	150
ClO ₄ ⁻	I ₂	24 ^a	M06-2X/aug-cc-pVTZ	150
PF ₆ ⁻	I ₂	24 ^a	M06-2X/aug-cc-pVTZ	150
TfO ⁻	I ₂	20 ^a	M06-2X/aug-cc-pVTZ	150
NCS ⁻	sym-C ₆ F ₃ I ₃	16.97 ^a	B3LYP/6-311++G(d,p)	64
[Zn(NCS) ₄] ²⁻	CBr ₄	12.1 ^a	M062X/6-311+G(d,p)	66

^a interaction energy

Table 7 Binding energies (kcal/mol) for complexes of neutral, singly and doubly charged BTP with different halide anions.

anion Y ⁻	2H	2Cl	2Br	2I
neutral BTP				
F ⁻	9.70	4.20	10.18	16.02
Cl ⁻	5.44	3.26	6.77	10.33
Br ⁻	4.77	3.24	6.55	9.88
I ⁻	4.10	3.21	6.30	9.37
monocation BTP ⁺				
F ⁻	13.18	5.93	12.38	18.83
Cl ⁻	7.35	4.34	8.22	12.16
Br ⁻	6.42	4.23	7.88	11.59
I ⁻	5.47	4.10	7.47	10.94
dication BTP ⁺²				
F ⁻	11.12	9.11	16.87	24.13
Cl ⁻	8.57	6.11	10.81	15.49
Br ⁻	7.77	5.82	10.28	14.61
I ⁻	6.74	5.50	9.60	13.66

Table 8 Preference of halide anion for halogenated vs H-bonding agent expressed as equilibrium ratio

	2Cl	2Br	2I
	neutral BTP		
F ⁻	7.92E-05	2.70E+00	5.62E+03
Cl ⁻	1.04E-01	3.88E+01	6.60E+02
Br ⁻	9.51E-01	1.68E+02	1.76E+03
I ⁻	8.51E+00	1.88E+03	3.30E+04
	monocation BTP ⁺		
F ⁻	8.07E-07	2.47E-01	5.08E+03
Cl ⁻	1.57E-03	1.52E+00	3.91E+02
Br ⁻	6.19E-02	2.61E+02	1.18E+04
I ⁻	1.85E-01	3.62E+03	1.06E+05
	dication BTP ⁺²		
F ⁻	1.44E-05	7.31E+00	1.87E+07
Cl ⁻	5.46E-03	3.88E+01	2.41E+05
Br ⁻	2.75E-02	9.98E+01	4.82E+05
I ⁻	3.90E-03	1.76E+01	3.71E+04

Table 9 Selectivity of binding agent for F⁻ over other halogen anions, expressed as equilibrium ratio

	2H	2Cl	2Br	2I
	neutral BTP			
Cl ⁻	5.48E+02	4.16E-01	3.82E+01	4.67E+03
Br ⁻	2.26E+03	1.88E-01	3.63E+01	7.24E+03
I ⁻	3.59E+04	3.34E-01	5.17E+01	6.11E+03
	monocation BTP ⁺			
Cl ⁻	2.63E+03	1.35E+00	4.26E+02	3.41E+04
Br ⁻	1.46E+05	1.90E+00	1.38E+02	6.26E+04
I ⁻	3.19E+06	1.39E+01	2.17E+02	1.53E+05
	dication BTP ⁺²			
Cl ⁻	1.08E+04	2.87E+01	2.04E+03	8.41E+05
Br ⁻	2.74E+04	1.44E+01	2.01E+03	1.06E+06
I ⁻	4.08E+03	1.51E+01	1.70E+03	2.05E+06

Fig. 1 Structures of $\text{F}\cdots(\text{H}_2)_n$ ($n = 1 - 6$) complexes (from ref [12]). Distances given in Å.

Fig. 2 Molecular electrostatic potential of four molecules, each with a σ -hole. Positive potential is denoted by blue regions, and negative in red. The light blue oval represents the lobe of each $\sigma^*(\text{F-A})$ orbital that lies directly opposite the F-A bond. Idealized positions of A lone pairs are indicated as red ovals.

Fig. 3. Geometries derived from experiment (on the left) and DFT calculations on the right for indicated $\text{H}_2\text{XC}-\text{X}\cdots\text{Y}^-$ pairs [34].

Fig. 4. Sample structures pairing Cl^- with substituted pyrylium cations [38].

Fig. 5. Geometries of complexes of NO_3^- , Cl^- or CO paired with indicated $-\text{NO}_2$ bearing molecules [54]. Distances in Å.

Fig. 6 Halogen bond network surrounding the SCN^- anion within the crystal structure [64].

Fig. 7 Geometry of a pair of $\text{C}_6\text{F}_4\text{I}_2$ ligands surrounding a halide, containing a pair of $\text{C-I}\cdots\text{X}^-$ XBs [65]

Fig. 8. Structure of a) $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{NCS})_4] \cdot 3\text{CBr}_4$ [66] showing halogen bonds in light blue. Zn atom is in center. Two (b) and three (c) point complexes studied by DFT calculations.

Fig. 9 Optimized geometries of Cl^- surrounded by 2 and 3 ligands [27], that can engage in either HBs (a and d) or YBs (b,c,e). Distances in Å.

Fig. 10 Optimized geometries of Cl^- surrounded by 4 ligands [27], that can engage in HBs (a), XBs (b,c,d) or YBs (e,f). Distances in Å.

Fig. 11 Optimized geometries of Cl^- surrounded by 4 ZB ligands of a) PF_3 , b) AsF_3 , and c) $\text{As}\equiv\text{CF}$ [27]. Distances in Å.

	CN ⁻	NO ⁻	OH ⁻
HCl
BrF
SeF ₂
AsF ₃
GeF ₄
GaF ₃

Fig. 12 Optimized geometries of CN⁻, NO⁻, and OH⁻ surrounded by 2 ligands, as indicated in the first column. Distances in Å [28].

	CN ⁻	NO ⁻	OH ⁻
HCl
BrF
SeF ₂
AsF ₃

Fig. 13 Optimized geometries of CN⁻, NO⁻, and OH⁻ surrounded by 3 ligands. Distances in Å [28].

Fig. 14 Optimized geometries of CN⁻, NO⁻, and OH⁻ surrounded by 4 ligands. Distances in Å [28].

Fig. 15

a) Calculated structure of a) tripodal receptor bound to Cl^- by a set of $\text{C-I}\cdots\text{Cl}^-$ XBs [68]. Cl is green and I atoms are purple.

b) placement of Re atoms into the bipodal receptor [77]

c) Schematic illustration of perhenate anion bound by an α -cyclodextrin unit via either HBs or XBs [79]

d) two views of tetradentate XB receptor [81] with I^- .

Fig. 16

- a) Schematic drawing of a receptor which binds an anion with four XBs and several HBs [82]
 b) pyrrole spacer surrounded by a pair of triazole species used to bind oxoanions [86]
 c) structure of Cl^- bound to a bipodal imidazolium-based I XB receptor [88],
 d) binding of Br^- (on the left) and Cl^- (right) through I atom in the XB receptor generated by Heinen et al [90].

Fig. 17 a) A receptor [92] which binds the halide through I-substituted imidazoliums. b) the binding of sulfate to a bipodal receptor based on iodotriazolium [94], c) Cl^- anion bound to a pseudocyclopeptide containing three 5-I-triazole units [101] d) a bipodal pair of Se YBs binds to a Cl^- [103]

Fig. 18
a) S-containing bipodal halide receptors studied by Benz et al [104].
b) $\text{Se} \cdots \text{I}^-$ YBs hold the iodide anion [105].

c) Manner of binding of KF to $\text{Ph}_2\text{FSnCH}_2\text{SnFPh-CH}_2$ connected to 19-crown-6 [109],

Fig. 19 A variety of anion receptors based on Sn tetrel bonds [110].

Fig. 20 Schematic diagrams of model receptors incorporating Bis-triazole-pyridine (BTP) [117] with various charges.

Fig. 21 Structures of two BTP receptors bound to fluoride [117]

Fig. 22 Model receptors tested, of charges 0 and +2 [118], with a variety of substituents Z.

Fig. 23 Binding energy calculated [118] in terms of substituent. Halide being bound shown as F⁻ (green), Cl⁻ (olive), Br⁻ (red), or I⁻ (purple). Broken curves indicate HB receptor, and solid curves refer to XB.

Fig. 24 Receptors that differ in the spacer group connecting the two I-substituted imidazoliums [119]

Fig. 25 Chalcogen-bonding receptors based on dithieno thiophene framework with S atoms engaging in YBs with a halide [120]

Fig. 26 Selected geometries binding halides to variant of dithieno thiophene receptor [120].

Fig. 27 Receptors based on four types of noncovalent bonding, shown bound to Cl⁻ [123]

Fig. 28 Structures of calixarenes bound [124] to Cl^- , acetate, H_2PO_4^- , NCS^- , HSO_4^- and BF_4^- .