Structures and Energetics of Clusters Surrounding Diatomic Anions Stabilized by Hydrogen, Halogen, and other Noncovalent Bonds

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Abstract

Diatomic anions CN^- , NO^- , and OH^- are surrounded by 2, 3, and 4 ligand molecules drawn from the HF, HCl, XF, YF_2 , ZF_3 , TF_4 , and TrF_3 set wherein X= Cl,Br, Y=S,Se, Z=P,As, T=Si,Ge, and Tr=Al,Ga. In the case of two ligands, both interact with the N of NO^- and the O of OH^- , but one approaches either end of CN^- . Unlike the H and halogen bonding units, as the number of ligands increases there is a tendency for chalcogen, pnictogen, tetrel, and triel-bonding ligands to form a cage around the central anion, with strong inter-ligand noncovalent bonds. There are a number of unusual features observed as well, including proton transfers from the ligands to the central anion, halogen atom sharing, linearization of normally highly bent YF_2 molecules, F-sharing between tetrel atoms, and $\text{OH}^- \cdots \text{F}$ H-bonds. Triel-bonding ligands engage in the strongest binding but the patterns of the other types of ligands depend upon the particular central anion and the number of ligands involved.

Keywords: chalcogen bond; pnictogen bond; tetrel bond; triel bond

1. INTRODUCTION

The prevalence of the hydrogen bond (HB) and its involvement in the structure and function of biomolecular systems and solvation phenomena, particularly in aqueous media, has motivated decades of research [1-4]. As a first step toward greater understanding of solvation phenomena, there have been numerous studies of small clusters of a single species surrounded by a few such molecules [5-8]. This work has yielded information concerning the preferred geometries of such clusters, details about the forces holding them together, and their flexibility in terms of the energetic cost of deviating from an optimal structure.

It has become increasingly acknowledged that there exists a set of noncovalent interactions, parallel in many ways to H-bonding wherein the bridging proton is replaced with one of several electronegative atoms. As one example, the halogen bond (XB) [9-16] represents a potentially powerful force that can, for example, stabilize the β -hairpin structure [17] of a protein system, in the same way as the more traditional HBs. Just as the elements of the halogen family (Cl, Br, I, etc) can replace H as a bridging atom in strongly bound complexes, the same is equally true for other columns of the periodic table. In particular, the S,Se, etc group can engage in chalcogen bonds (YBs) [18-24], and the same is true of the P,As family which forms pnictogen bonds (ZBs) [25-33]. Despite the congestion caused by four substituents surrounding a typical tetrel atom (Si, Ge, etc), a nucleophile is nonetheless able to approach close enough to form a tetrel bond (TB) of surprising strength [34-43]. Moving over one more column in the periodic table, the triel atoms such as Al and Ga are not to be excluded from this sort of behavior, forming [44-50] what are termed triel bonds (TrB).

Given the parallel nature of these latter noncovalent bonds and the more thoroughly studied HB, and the similarity in their strengths, it is natural to wonder in what ways the coordination of a central species by H-bonding ligands might differ if these ligands interact via any of these other related noncovalent bonds. This question is of growing importance as it is becoming increasingly apparent that chalcogen bonds are involved in solution [51] or for supramolecular capsules [52] to give two simple examples. Halogen bonds, too, play out in this arena as they are involved in biomimetic processes [53] and have unique properties in supramolecular chemistry [54].

There has been relatively little study of this question to date. Most of the earlier work concerns the clustering of molecules around each other, without a central species. For example, pnictogen bonding accounts for the structures of $(\text{PH}_2\text{F})_n$ and $(\text{PH}_2\text{Cl})_n$ clusters [55] and aggregates [56] of NH_3 , PH_3 , and PFH_2 . Similarly, halogen bonds in four-membered mixed clusters of HF and FCl [57] form ring structures that appropriately mix HBs with XBs. A theoretical study [58] examined intermolecular halogen bond properties in one-dimensional NCX clusters as large as 10 monomers ($\text{X}=\text{Cl}$ and Br) and noted cooperative

effects. With regard to placement of a central molecule within a cluster, the halogen bonds that stabilize Cl_2 and Br_2 within cages of water molecules [59] have been examined. The interactions of a halide ion with neutral molecules via HBs, XBs, or related noncovalent bonds has seen some prior scrutiny [60]. There is also a burgeoning effort [61-73] to design molecules that bind to halides and other anions via XBs, YBs, ZBs, and even TBs via a sort of clustering in that the anion is held jointly by several such bonds.

However, there is little known at present about how a small number of molecules might arrange themselves around a central species, and how their geometries might differ from analogous H-bonding molecules. Might the molecules dispose themselves as far as possible so as to minimize repulsive steric or electrostatic interactions, or might they be drawn together via intermolecular attractions? How flexible would this optimal arrangement be; how much energy would be required for deformations of various sorts? Does the optimal arrangement depend upon the strength of the noncovalent bond to the central species? Do XB molecules differ from YB, ZB, etc in these respects, as well as any comparison with HBs.

Our own group recently took a first step in this direction [74] by surrounding both a monatomic anion and cation with a number of HB ligands, and then comparing the most stable geometries with those when the ligands engage via halogen, chalcogen, and pnictogen bonds. One interesting finding to emerge from this work was the distinction that while four HB or XB ligands surround an anion uniformly in a tetrahedral arrangement, both YB and ZB ligands tend to cluster together to some extent, occupying one hemisphere around the anion while leaving the other vacant. On the other hand, no such clustering was observed when the central species is a cation.

The present work intends to expand on these preliminary findings. In the first place, the central monatomic anion is expanded to a set of heteronuclear diatomics, thus offering a wider range of interaction sites for the ligands. The ligands can bind with either of the two central atoms, and at various angles of approach, or can interact not with the atoms themselves but with the bonding region between them. As a second issue, the types of interactions include not only the HB, XB, YB, and ZB ligands, but is extended to tetrel and triel bonds as well. The characteristics of tetrel bonds are unique, for example in the high degree of steric crowding, and triel bonds involve a highly electron-deficient central Tr atom. The calculations are also able to monitor how the coordination pattern and binding energies change as the number of ligands increases from 2 to 3 and then to 4.

2. SYSTEMS AND COMPUTATIONAL METHODS

Diatomic anions considered here are CN^- , NO^- , and OH^- . As show below, the two atoms on the first of these anions displays nearly equivalent minima in the molecular electrostatic potential, but the full three-dimensional potential points to the overall neighborhood of the N atom as more negative. NO^- is unique in that there is no MEP minimum connected with the O, and it is the nominally less electronegative N atom

which is more negative. The H atom on OH⁻ is clearly less electronegative than O, so offers the possibility that OH...E HBs may be formed with incoming electrophiles E, which might augment the putatively stronger direct interactions with the O atom with its high negative charge.

In terms of ligands that ought to engage in HBs with the central ligand both HF and HCl were considered. ClF and BrF were taken as models of halogen-bonding ligands. This same protocol was used to identify other ligands: each central atom, one from the second row and one from the third, was surrounded by n F atoms. Chalcogen bonding ligands are thus SF₂ and SeF₂. PF₃ and AsF₃ were used to generate pnictogen bonds, and tetrel bonding ligands considered were SiF₄ and GeF₄. Lastly, triel bonds comprised AlF₃ and GaF₃. For purposes of compact notation, H-bonding is abbreviated as HB, with XB, YB, ZB, TB, and TrB used to refer to halogen, chalcogen, pnictogen, tetrel, and triel bonding, respectively.

Each of the three central anions was surrounded by 2, 3, and 4 ligands, and the geometries optimized by the M06-2X functional in conjunction with the aug-cc-pVDZ basis set [75,76], within the context of Gaussian-09 [77]. This DFT functional and basis set have had past success [45,47,50,63,78-91] in studying systems of these sorts. For each combination of anion and ligands, a wide array of starting geometries was considered as starting points for optimization and a number of minima were identified. In most cases, there was a gap of several kcal/mol between the global and the next most stable minimum, but in some cases, this separation was smaller. In any case, due to the very large number of minima which preclude analysis of all of them, concentration is focused here on the global minimum.

The binding energy E_b of each complex was assessed as the electronic energy difference between the complex $[AL_n]^-$ and its constituent parts, all fully optimized, i.e. the energy of reaction (1), where ligands are represented by L and the central anion as A⁻.

Interaction energies E_{int} reference the geometry of the central anion and its fully assembled ligand cage L_n in the geometries they adopt within the particular complex, reaction (2).

The difference between E_b and E_{int} thus comprises two key parts. There is first of all the energy of distortion associated with the change in internal energy of both A⁻ and the n ligands as they adjust their geometry from their fully optimized monomer structure to that within the complex. The second component arises from any interactions between the n ligands, whether attractive or repulsive, as they aggregate around the central anion to form the ligand cage. Counterpoise corrections were added to E_b and E_{int} via the standard counterpoise procedure [92] as described in the text. The energies of each structure were also computed applying MP2 to assess the correlation energy as a point of comparison.

The nature of minima were verified by the fact that all frequencies are positive, which were used to extract zero point vibrational energies. For the isolated molecules molecular electrostatic potentials (MEPs) were calculated on the 0.001 au electron density isosurface, and the extrema were computed using the MultiWfn program [93,94]. These MEPs were also presented graphically via Chemcraft [95]. QTAIM analysis was applied in order to identify bonding paths and measure the strength of each noncovalent bond [96]. NBO analysis (GenNBO 5.0 program) [97] was applied to focus on interorbital transfers.

3. RESULTS

Table 1 presents the values of the extrema of the molecular electrostatic potential of each monomer on its $\rho=0.001$ au isodensity surface. Several features are worth noting. Despite the greater electronegativity of N vs C, the $V_{s,min}$ minima in the MEP on these two atoms are very nearly equal in CN^- . There is one minimum on the N atom of NO^- along the N-O axis. The other minimum, somewhat more intense is located directly above the center of the N-O axis in what may be termed the π -region. With only one electronegative atom, the only minimum of OH^- is associated with O, directly along the HO axis. It is the most negative of any of the three anions. As another means of viewing these potentials, one can take a three-dimensional view of the potential on a surface which corresponds to 1.5 x the vdW radius of each atom, at approximately the distance where the interaction might be expected to be most intense. These surfaces are illustrated in Fig 1 where red and blue colors respectively indicate the most and least negative regions around each of these anions. Unlike the $V_{s,min}$ in Table 1, which are nearly equal for CN^- , the greater electronegativity of N manifests itself by the much redder color surrounding this atom. The dark red regions on either side of the N atom of NO^- presages placement of ligands in those regions (see below), and the disposition of the MEP around the O of OH^- hints that a nonlinear approach of a ligand might be preferred, along what might be thought of as O “rabbit-ear” lone pairs.

n=2

The optimized geometries of each of the three anions with a pair of H-bonding ligands HF and HCl are depicted in the upper two panels of Fig 2. Given the nearly identical MEP minima on the C and N atoms of CN^- , it is perhaps no surprise that a pair of H-bonding molecules like HF and HCl situate themselves so as to form one HB with each of these two atoms. It is logical as well that both of these HBs are fully linear, with both $\theta(XH\cdots C/N)=180^\circ$, and that the two HX molecules lie along the C-N axis. 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 $ClH\cdots NCH\cdots Cl^-$ configuration. The two HF molecules both participate in HBs with the N atom of NO^- , engaging with the negative region lying off of the O-N axis, consistent with the MEP pattern in Fig 1. The same sort of geometry occurs with HCl, except that both of the protons are extracted from the HCl

molecules, leading to the $\text{Cl}^{\cdot-}\text{ONH}_2^+\text{Cl}^{\cdot-}$ system, with two anions surrounding a cation. The structures of OH^- are very much like NO^- : two $\text{FH}\cdots\text{O}$ HBs are formed with HF, and the protons are dissociated from both HCl molecules.

The binding energies E_b of these complexes refer to the energy of the reaction for the formation of the complex from the n fully optimized isolated ligands. It is clear first that OH^- forms the strongest complexes with the H-bonding ligands and CN^- the weakest. This pattern fits the AIM values of ρ_{BCP} that are displayed in Fig S1 for the cases where a proton is not physically transferred. As a second trend, a pair of HCl molecules engage in a more strongly bound complex than HF. This is perhaps surprising as HF is normally a stronger proton donor than is HCl. However, it is the ability of the anions to extract one or more protons from HCl, but not HF, that undergirds this extra stability. Any energetic cost needed to pull these protons from the HCl molecule is more than repaid in terms of the interaction energy in the resulting anion--cation--anion complex. Taking the OH^- system as an example, the interaction energy between the central H_3O^+ and the pair of surrounding Cl^- anions is -274.6 kcal/mol, far exceeding the -106.0 for OH^- surrounded by the pair of neutral HF molecules. In most cases the M06-2X energetics are closely matched by MP2 data, although there is a larger deviation for the OH^- values.

The next two panels of Fig 2 illustrate how each anion engages in a complex with a pair of halogen bonding molecules, either FCl or FBr. 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^- . There are some interesting differences as well. Whereas HCl was quick to release its proton, and HF was not, FX is prone to transfer its halogen atom to the anion, partially if not completely. The Cl atom of FCl is transferred over to the C of CN^- anion, whereas the X transfers are less complete in the other cases. 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, whether Br or Cl. With respect to binding energies, NO^- and OH^- reverse their order from the H-bonding cases, with the former engaging in the strongest complexes with XF; CN^- remains the weakest. 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 chalcogen-bonding SF_2 and SeF_2 are illustrated in the next two panels of Fig 2. The general geometric patterns remain in terms of positioning of the two ligands: one on either end of CN^- , and both positioned to interact with the N of NO^- and the O of OH^- . The earlier issues of full or partial transfer are less profound here, although the $R(\text{C}\cdots\text{S})$ distances are only about 0.1 Å longer than $R(\text{S}-\text{F})$ for several. On the other hand, there are certain large-scale deformations of some of the monomers. When bound to OH^- , for example, one of the SF_2 or 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. Indeed, the AIM bond critical point density is 2-3 times larger for the $O\cdots Y$ chalcogen bond to this linearized FYF than for the other $O\cdots Y$ bond, as may be seen in Fig S1. As further evidence, another minimum on the surface of $OH^- + 2 SF_2$ does not have to pay the steep price of such a linearization, yet still lies 4.7 kcal/mol higher in energy. With regard to CN^- , there is both geometric and AIM evidence that the chalcogen bonds to C are stronger than that to N. The binding energies of these chalcogen-bonded configurations are smaller than their XB counterparts but follow the same $CN^- < OH^- < NO^-$ pattern. One also sees a repeat of the trend that the heavier bridging atom, i.e. Br vs Cl, and Se vs S, corresponds to the stronger interaction. AIM analysis indicates the presence of a secondary, and weaker, interaction between ligand molecules, in the form a $Y\cdots F$ chalcogen bond for the OH^- configurations, as well as for $ON^- + 2 SeF_2$.

The binding energies suffer another drop when chalcogen atoms are replaced by pnictogens, while changing the order to $CN^- < NO^- < OH^-$. As in the other cases, enlarging the pnictogen atom from P to As induces a notable increase in the binding energies for all anions. The geometric dispositions in Fig 2 remain largely unchanged from the other types of ligands. Unlike the chalcogen bonds, the pnictogen ligands do not show much differentiation between the bonds to C or N of CN^- , either through intermolecular distances or AIM quantities. Nor do these ZF_3 ligands manifest any inter-ligand interactions.

These same geometrical arrangements persist for tetrel-bonding ligands in the next two panels of Fig 2, 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. There is AIM evidence of weak $F\cdots F$ halogen bonding between SiF_4 units when paired with NO^- . While seemingly unusual, such interactions have been observed from time to time in the literature [98]. 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 $T-F\cdots T$ tetrel bonds between ligands, a phenomenon which does not occur of the other sorts of ligands. Consistent with the other complexes, the heavier Ge atom engages in stronger complexes than does its Si counterpart.

Triel-bonded complexes characterized by AlF_3 and GaF_3 are even stronger. Part of their magnitude can be attributed to the electron-deficient nature of the Tr atoms which are manifested by the very intense $V_{s,max}$ in Table 1. On the other hand, the AIM bond critical point densities are not appreciably larger for the TrBs than for their cousins in Fig 2, nor are they shorter. As was the case for H and T-bonding, OH^- and CN^-

represent the most strongly and weakly bound anions, respectively. As shown in the last two panels of Fig 2, these triel ligands generally maintain the basic disposition of the other ligands. An anomaly occurs here in that the heavier Ga atom is not appreciably more strongly bound than Al. These TrF_3 units are far enough apart that there are no interactions between ligands. For these TrB systems, as well as all of the others MP2 data are fairly close to M06-2X, and even when there are significant differences, the trends are identical.

n=3

The addition of a third ligand leads to some meaningful modifications of the geometries of the $n=2$ complexes. As may be seen in the top panels of Fig 3, a third HF adds to the N end of CN^- , forcing the other HF bound to N to move over to make room. This displacement is aided by the diffuse nature of the negative MEP around this N atom, as seen in Fig 1, which can more easily accommodate this off-line arrangement than can the C atom. One of the HCl molecules again transfers its proton to this C atom, and the other two HCl molecules congregate around the N. Whereas both HF molecules engaged in HBs with the N atom of NO^- for $n=2$, it is the O atom that attracts both of these HBs for $n=3$. 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^- , the third HF results in a very different configuration. After donating its proton to OH^- , the remaining F^- then engages in a centrosymmetric $(\text{F}\cdots\text{H}\cdots\text{F})^-$ anion, which in turn forms a pair of $\text{OH}\cdots\text{F}$ HBs with the water. Precisely the same process occurs for 3 HCl, but with one interesting difference. Instead of the third HX molecule forming a $\text{XH}\cdots\text{O}$ HB as is the case for HF, the HCl molecule rotates around so that this third interaction is instead a $\text{Cl}\cdots\text{O}$ halogen bond. 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 3, 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^- . With the addition of an increment to the binding energy that arises with this third ligand, the patterns remain intact: $\text{NO}^- > \text{OH}^- > \text{CN}^-$ and $\text{Br} > \text{Cl}$.

The third chalcogen-bonding ligand adds in much the same way as was noted for the XB units. Interestingly, when there are three YF_2 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 YF_2 molecule, a new element creeps into the factors contributing to the geometries. For example,

the upper left S atom in Fig 3 lies 3.053 Å from the N of CN⁻, but is only 2.702 Å from the S atom of another SF₂. This geometric suggestion of a S...S YB is confirmed by an AIM ρ_{BCP} of 0.041 au in Fig S2, as well as the absence of a bond path between this S and the central CN⁻. This interaction is modified to a Se...F chalcogen bond in the SeF₂ analogue. 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 in Table 4 are larger than their XF parallels.

The same sort of inter-ligand interactions appear in the ZB systems as well, except that it is a F atom that acts as electron donor in the pnictogen bond, rather than a pair of chalcogen atoms, or in the form of F...F bonds, as is evident in the AIM diagrams in Fig S2. 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 pnictogen to tetrel had dramatically raised the binding energies for n=2, and that same pattern occurs for n=3. While the crowded nature of the tetrel atoms precludes their approach by any but the central anion, Fig S2 documents 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...F interactions (see Fig S2).

Quite large increments of 47-57 kcal/mol occur in the triel-bonded 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

The fourth HF molecule adds to the n=3 cluster of CN⁻ in a straightforward fashion, binding to the N atom, as may be seen in Fig 4. The same is true when HF is added to NO⁻, such that each of the O and N atoms are involved in a pair of HBs. Placement of all four HF molecules around the O atom of OH⁻ in a square pyramidal arrangement is most stable, although there is a structure, akin to that in Fig 3 for 3 HF molecules surrounding OH⁻, which is very nearly equally stable. HCl adds to the prior CN⁻ complex with three HCl molecules by simply adding another HB to the N. The fourth HCl molecule results in double proton transfers to both NO⁻ and OH⁻, leading to a central H₂NO⁺ and H₃O⁺, respectively, along with a pair

of Cl^- anions. The latter are stabilized by formation of two HBs each. The $n=4$ binding energies are of course larger than those for $n=3$, especially for the NO^- and OH^- anions.

The Cl or Br partial transfers that occurred for the smaller complexes continue for $n=4$. One X atom is partially transferred to the C end of CN^- , but the fourth FX simply adds to the O end of NO^- , with no such transfers. The fourth FCl adds to OH^- in a standard way via four $\text{O}\cdots\text{Cl}$ XBs but the fourth HBr interacts instead via a combination of a $\text{OH}\cdots\text{Br}$ HB and a $\text{Br}\cdots\text{Br}$ 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 YF_2 molecule instead presents each system with a ring configuration, with several $\text{Y}\cdots\text{Y}$ chalcogen bonds augmenting the two direct interactions with the central anion, as well as several $\text{Y}\cdots\text{F}$ 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 $\text{Z}\cdots\text{F}$ 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 $\text{OH}\cdots\text{Z}$ HB of OH^- with one ligand, the O engages in three pnictogen bonds.

The central CN^- anion engages in two tetrel bonds with TF_4 . The third and fourth TF_4 associate via noncovalent bonds to the first two ligands; a similar arrangement occurs with NO^- . The H of OH^- forms a $\text{OH}\cdots\text{F}$ HB with the fourth ligand, as the O atom is engaged in a pair of tetrel bonds. In the GeF_4 cases, one sees a higher degree of F-sharing between Ge atoms. The F-sharing becomes even more predominant in the TrF_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 $\text{OH}^- > \text{NO}^- > \text{CN}^-$ 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.

4. DISCUSSION

There are several terms which can be added to the binding energies. While the quantities reported above refer to the strict energetics of reaction 1, there is a certain amount of basis set superposition which occurs as the various species aggregate. Following the removal of the BSSE between the central anion and the set of n surrounding ligands by the counterpoise procedure the resulting quantities are reported in Tables S1-S3. While these additions generally reduce the exothermicity of the binding, the trends remain intact. A second quantity that can be added is the zero point vibrational energy (ZPVE) difference between

the complex and its constituent parts. Inclusion of this term yields the data listed in Tables S4-S6. These ZPVE corrections add a further small decrement to the binding energies, but again all trends are unchanged.

The binding energies E_b of each anion A^- with n ligands L reported in Tables 2-4 refer to the energy of reaction (1) above where all species are fully optimized. This quantity captures not only the interaction between the central anion and the ligands, but also includes any geometrical deformations of each species in order to conform to the complex geometry, as well as any direct interactions that may be present between the ligands. It would also be of interest to consider the pure interaction energy between the central ligand and the ligands. E_{int} is evaluated here according to Eq (2) where L_n refers to the energy of the entire cage of n ligands, in the structure they adopt within the fully formed complex. Since the energetically costly geometric deformations of the ligands (and the central anion) are already accounted for, E_{int} ought to be considerably more negative than E_b , as is typically the case in calculation of these quantities. However, there is another factor that must be reckoned with. Since E_{int} considers the preformed L_n cage as one subunit, it does not benefit from any inter-ligand attractions which are included in E_b , nor does E_{int} reap the rewards of any cooperative three-body effects. It is this second factor which counters and competes with the first. As a further complication are the partial and full atom transfers which occur in several of these complexes. As a bottom line, there is no clear rule as to whether E_b or E_{int} should be the more negative.

Tables S7-S9 display the interaction energies defined by Eq (2) which can be quite different than E_b . In most cases, particularly for small n , E_{int} is more negative, which would be expected for substantial monomer deformations, and/or in the absence of sizable inter-ligand interactions. Prime examples include those cases where the YF_2 molecule deformed into a nearly linear structure, where the $E_b - E_{int}$ difference reaches up to 60 or 70 kcal/mol. Large advantages of E_b over E_{int} occurs when there are multiple strong attractions between ligands, as for example the $n=3$ and $n=4$ cases of pnictogen or triel-bonded ligands. Tables 10-12 add the ZPVE corrections to E_{int} , which again cause a small diminution in its magnitude.

The differences between E_b and E_{int} are defined as the deformation energy, displayed in Tables S13-S15. As pointed out earlier, E_{def} is positive when monomer geometric distortions predominate as is true for most cases considered here. This quantity is particularly large for the tetrel-bonded ligands which undergo a good deal of angular rearrangement to accommodate interactions with the anion. Negative values of E_{def} arise chiefly for the triel-bonded systems, with $n=3$ and 4, where there are strong interactions between these ligands, which include sharing of F atoms. Another aspect of the triel-bonded systems is the puckering of each ligand. The isolated AlF_3 and GaF_3 molecules are planar as the sum of their three bond angles equals 360° . One consequence of their strong bonding to the central anion is their short intermolecular distances. The $Tr \cdots C$ or $Tr \cdots N$ distances in $[(AlF_3)_2CN]^-$ and $[(GaF_3)_2CN]^-$, for example, are about 2 Å, only about

half of the sum of van der Waals radii. This close contact deforms the planar shape of the TrF_3 ligands. For illustrative purposes, $\text{Tr}\cdots\text{C}$ and $\text{Tr}\cdots\text{N}$ distances in these two complexes were elongated to 4.0 Å and the rest of the geometry was fully optimized. This stretching allowed relaxation to a more planar ligand, as the sum of bond angles rose from about 340° in the fully optimized complex to 356° for the stretched variant.

And continuing on that line, there were a number of cases presented here wherein F atoms were not only involved in strong interactions, but were shared nearly equally between central atoms. Such a situation is not unprecedented, but has been noted in a number of crystal structures in the past. Several such examples are displayed in Fig S4.

There are surprising phenomena observed here that go above and beyond simple coordination. One or more HCl molecules transfer their proton to the central anion in a number of cases. The halogen atom is involved in at least partial transfer in some situations. In order to optimize its interaction with other units, one YF_2 molecule can deform from its most stable highly bent structure to a nearly linear geometry, even though this straightening is costly in terms of intramolecular energy. There are also a number of cases where F atoms of a TF_4 molecule act as bridges between a pair of T atoms in two different ligands. Although part of an anion, the H atom of OH^- is still capable of engaging in a $\text{OH}\cdots\text{F}$ HB which supplements the binding energy. Another unusual structure involving this anion occurs when one HF ligand dissociates, donating its proton to OH^- and its F^- to a second HF ligand. The final complex includes a pair of $\text{OH}\cdots\text{F}$ HBs between HOH and a centrosymmetric FHF^- . Inter-ligand interactions begin to play a prominent role for complexes with three or more YF_2 , ZF_3 , TF_4 , and TrF_3 molecules.

As a final issue, the nature and strength of the various interactions can be considered through the lens of AIM analysis of the electron density. The values of the density at each pertinent bond critical point are listed in Tables S16-S18. NBO measures energetic consequences of charge transfer from one orbital to another. The relevant NBO quantities are displayed in Tables S19-S21 for tetracoordinated complexes of CN^- , NO^- , and OH^- , respectively.

5. CONCLUSIONS

When there are two ligands present, they tend to align one on each end of the CN^- anion. In contrast, both ligands orient toward the N of NO^- and the O of OH^- . Exceptions occur for the tetrel bonding GeF_4 ligands, whose primary interaction is with one another. A third HB, XB, or YB ligand attaches itself to the N end of CN^- , adding to the first that is already there. Pnictogen, tetrel, and triel bonding ligands situate the third ligand above the $\text{C}\equiv\text{N}$ axis, where it can interact with the other two ligands. Introduction of a third ligand to NO^- changes the clustering geometry in different ways for each sort of ligand. While the XB ligands simply add to the O atom, most of the others place themselves closer to the N, but their primary interactions are with one another. The third ligand gravitates toward the O of OH^- , but the TB and TrB

ligands eschew the O in favor of inter-ligand attractions and a $\text{OH}\cdots\text{F}$ HB to the central anion. Four HB or XB ligands place three near the N of CN^- , and the other close to the C. The other ligands form a sort of cage around the anion, emphasizing interactions with one another. Four HB and XB ligands are similar with respect to NO^- as well: two ligands attached to each atom, but the cage model applies to other ligands, and similar observations apply to OH^- . In sum, the HB and XB ligands behave similar to one another, due in large measure to their linear diatomic geometry, which minimizes inter-ligand interactions.

In terms of energetics, the addition of each new ligand of course increases the total binding energy. TrB ligands consistently engage in the strongest binding, but the patterns of the other types of ligands depend upon the particular central anion as well as the number of ligands involved. For example, TB ligands are second only to TrB in their binding to OH^- , but are comparable to YB and XB for CN^- and NO^- . With respect to ligands, CN^- is typically more weakly bound than OH^- and NO^- , but the comparison between the latter two depends upon the particular value of n and the type of ligand.

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Table 1. MEP extrema on the 0.001 au isodensity surface for central anions and ligands obtained at the M06-2X/aug-cc-pVDZ level.

	$V_{s,max}$	$V_{s,min}$
CN ⁻	-133.4(C), -138.7(N)	-136.0(C), -139.1(N)
NO ⁻	-132.3(O), -138.1(N)	-157.4(π), -147.5(N)
OH ⁻	-107.8(H)	-172.9(O)
HF	68.2 (H) -20.1 (F)	-21.2
HCl	45.5 (H) +7.3 (Cl)	-10.0
ClF	38.2 (Cl) -2.7 (F)	-8.5
BrF	47.1 (Br) -7.6 (F)	-11.9
SF ₂	38.3	-9.7
SeF ₂	48.5	-14.5
PF ₃	34.9	-10.6
AsF ₃	45.0	-16.6
SiF ₄	49.1	-5.6
GeF ₄	59.5	-6.9
AlF ₃	108.6	-16.7
GaF ₃	95.9	-16.7

Table 2. E_b (kcal/mol) of complexes with two ligands at two levels of calculation for M06-2X geometries

	CN ⁻		NO ⁻		OH ⁻	
	M06-2X	MP2	M06-2X	MP2	M06-2X	MP2
HF	-52.04	-50.30	-69.92	-70.13	-82.53	-76.15
HCl	-55.94	-55.87	-91.41	-91.82	-103.55	-93.02
ClF	-69.59	-77.91	-111.04	-122.39	-86.25	-87.82
BrF	-78.82	-85.19	-120.48	-128.83	-101.03	-101.20
SF ₂	-52.09	-54.02	-104.46	-107.93	-91.53	-87.90
SeF ₂	-66.24	-68.34	-115.98	-120.39	-106.01	-103.35
PF ₃	-38.25	-35.50	-74.50	-73.05	-82.71	-74.44
AsF ₃	-52.30	-50.93	-86.66	-87.89	-98.45	-92.69
SiF ₄	-73.11	-68.56	-106.92	-102.78	-125.18	-110.99
GeF ₄	-88.17	-87.48	-124.67	-123.43	-138.38	-129.07
AlF ₃	-137.14	-130.26	-155.66	-149.86	-189.40	-175.81
GaF ₃	-136.40	-132.76	-155.93	-153.94	-181.32	-171.79

Table 3. E_b (kcal/mol) of complexes with three ligands at two levels of calculation for M06-2X geometries

	CN ⁻		NO ⁻		OH ⁻	
	M06-2X	MP2	M06-2X	MP2	M06-2X	MP2
HF	-65.62	-63.79	-79.53	-77.94	-110.67	-103.70
HCl	-61.93	-63.19	-106.11	-106.51	-110.96	-103.93
ClF	-77.36	-85.89	-118.18	-128.81	-102.35	-105.62
BrF	-87.94	-95.14	-130.92	-139.27	-121.49	-124.17
SF ₂	-80.82	-86.05	-130.66	-136.61	-112.28	-106.12
SeF ₂	-89.80	-96.18	-143.77	-152.31	-129.73	-126.61
PF ₃	-47.91	-45.65	-84.15	-83.36	-95.93	-87.69
AsF ₃	-65.73	-65.29	-101.24	-101.56	-118.93	-113.52
SiF ₄	-78.54	-72.59	-120.14	-111.57	-141.38	-124.65
GeF ₄	-94.52	-92.52	-143.54	-144.32	-165.52	-155.10
AlF ₃	-182.63	-164.37	-210.70	-193.38	-248.11	-228.50
GaF ₃	-183.36	-173.52	-212.89	-204.89	-236.73	-224.32

Table 4. E_b (kcal/mol) of complexes with four ligands at two levels of calculation for M06-2X geometries

	CN ⁻		NO ⁻		OH ⁻	
	M06-2X	MP2	M06-2X	MP2	M06-2X	MP2
HF	-76.74	-74.94	-99.30	-97.99	-121.07	-115.01
HCl	-66.40	-67.70	-116.76	-118.06	-133.80	-122.31
ClF	-84.84	-93.48	-124.47	-134.71	-107.96	-109.39
BrF	-97.46	-104.95	-139.78	-148.14	-134.32	-137.76
SF ₂	-94.82	-100.36	-143.51	-149.08	-123.59	-116.87
SeF ₂	-97.49	-100.80	-160.33	-170.20	-146.10	-143.72
PF ₃	-58.16	-55.77	-92.82	-92.58	-103.89	-96.15
AsF ₃	-81.02	-80.45	-118.77	-121.30	-130.66	-126.67
SiF ₄	-88.05	-80.16	-124.01	-115.94	-145.15	-126.55
GeF ₄	-107.65	-104.27	-155.81	-156.12	-174.27	-160.98
AlF ₃	-238.55	-214.24	-266.18	-244.92	-301.34	-273.10
GaF ₃	-233.06	-221.71	-261.87	-252.05	-288.70	-272.47

Fig 1. Molecular electrostatic potentials of anions, values are in au.

	CN ⁻	NO ⁻	OH ⁻
HF
HCl
ClF
BrF
SF ₂

SeF ₂
PF ₃
AsF ₃
SiF ₄

Fig 2. Geometries of structures containing a central anion surrounded by two ligands. Selected distances in Å.

	CN ⁻	NO ⁻	OH ⁻
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HF
HCl
ClF

BrF
SF ₂
SeF ₂

PF ₃
AsF ₃

SiF ₄
GeF ₄
AlF ₃

Fig 3. Geometries of structures containing a central anion surrounded by three ligands. Selected distances in Å.

HCl
ClF

BrF	<p>Diagram of a bromine trifluoride (BrF₃) molecule. The central bromine atom (red) is bonded to three fluorine atoms (cyan) in a T-shaped geometry. The bond lengths are labeled: 1.953 Å (top), 2.673 Å (bottom-left), and 2.554 Å (bottom-right). A lone pair is represented by a grey sphere on the left.</p>	<p>Diagram of a bromine pentafluoride (BrF₅) molecule. The central bromine atom (red) is bonded to five fluorine atoms (cyan) in an octahedral geometry with one lone pair. The bond lengths are labeled: 2.627 Å (top-left), 2.604 Å (top-right), 2.101 Å (bottom-left), and 2.104 Å (bottom-right).</p>	<p>Diagram of a bromine heptafluoride (BrF₇) molecule. The central bromine atom (red) is bonded to seven fluorine atoms (cyan) in a pentagonal bipyramidal geometry. The bond lengths are labeled: 2.273 Å (top), 2.254 Å (middle-left), 2.132 Å (middle-right), 2.830 Å (bottom-right), and 2.865 Å (bottom-left).</p>
SF ₂	<p>Diagram of a sulfur hexafluoride (SF₆) molecule. The central sulfur atom (yellow) is bonded to six fluorine atoms (cyan) in an octahedral geometry. The bond lengths are labeled: 3.019 Å (top-left), 1.704 Å (top-right), 2.826 Å (middle-left), 2.511 Å (middle-right), 2.895 Å (bottom-left), and 2.396 Å (bottom-right).</p>	<p>Diagram of a sulfur octafluoride (SF₈) molecule. The central sulfur atom (yellow) is bonded to eight fluorine atoms (cyan) in a square antiprismatic geometry. The bond lengths are labeled: 2.792 Å (top-left), 2.927 Å (top-right), 1.780 Å (middle-left), 2.357 Å (middle-right), 2.715 Å (bottom-left), and 2.715 Å (bottom-right).</p>	<p>Diagram of a sulfur decafluoride (SF₁₀) molecule. The central sulfur atom (yellow) is bonded to ten fluorine atoms (cyan) in a dodecahedral geometry. The bond lengths are labeled: 1.700 Å (top), 2.941 Å (middle-left), 2.854 Å (middle-right), 3.969 Å (bottom-left), and 2.467 Å (bottom-right).</p>

SeF ₂
PF ₃

AsF ₃	<p>Molecular structure of AsF₃ showing bond lengths (Å): 2.994, 2.490, 3.062, 3.035, 3.051, 2.491, 3.299, 3.105.</p>	<p>Molecular structure of AsF₃ showing bond lengths (Å): 2.719, 2.279, 2.281, 2.960, 2.734.</p>	<p>Molecular structure of AsF₃ showing bond lengths (Å): 2.786, 1.980, 2.269, 2.253, 2.303.</p>

SiF ₄	<p>3D ball-and-stick model of SiF₄ showing Si-Si distances: 2.747, 2.765, 1.976, 2.046, 3.175.</p>	<p>3D ball-and-stick model of SiF₄ showing Si-Si distances: 2.609, 2.881, 2.007, 2.565, 2.032.</p>	<p>3D ball-and-stick model of SiF₄ showing Si-Si distances: 2.936, 2.598, 2.146, 2.333, 1.863, 1.834.</p>
GeF ₄	<p>3D ball-and-stick model of GeF₄ showing Ge-Ge distances: 2.664, 2.587, 2.071, 2.101, 3.087.</p>	<p>3D ball-and-stick model of GeF₄ showing Ge-Ge distances: 2.335, 3.353, 2.086, 2.126.</p>	<p>3D ball-and-stick model of GeF₄ showing Ge-Ge distances: 1.789, 2.582, 1.831, 2.018.</p>

Fig 4. Geometries of structures containing a central anion surrounded by four ligands. Selected distances in Å.