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Using Beryllium Bonds to Change Halogen Bonds
From Traditional to Chlorine-shared to Ion-pair

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ABSTRACT

Ab initio MP2/aug'-cc-pVTZ calculations have been carried out to investigate the structures, binding energies, and bonding characteristics of binary complexes HFBe:FCl, R₂Be:FCl, and FCl:N-base, and of ternary complexes HFBe:FCl:N-base and R₂Be:FCl:N-base for R = H, F, Cl; N-base = NH₃, NHCH₂, NCH. Dramatic synergistic cooperative effects have been found between the Be...F beryllium bonds and the Cl...N halogen bonds in ternary complexes. The Cl...N traditional halogen bonds and the Be...F beryllium bonds in binary complexes become significantly stronger in ternary complexes, while the F-Cl bond weakens. Charge-transfer from F to the empty p(σ) orbital of Be leads to a bending of the XYBe molecule and a change in the hybridization of Be which in the limit becomes sp². As a function of the intrinsic basicity of the nitrogen base and the intrinsic acidity of the Be derivative, halogen-bond type evolves from traditional to chlorine-shared to ion-pair. The mechanism by which an ion-pair complex is formed is similar to that involved in the dissociative proton attachment process. EOM-CCSD spin-spin coupling constants ^{1X}J(Cl-N) across the halogen bond in these complexes also provide evidence of the same evolution of halogen-bond type.

Keywords: Halogen-bond type; structures and binding energies; bonding properties, cooperativity; spin-spin coupling constants

INTRODUCTION

Noncovalent interactions play a fundamental role in supramolecular chemistry, molecular biology, and materials science. The earliest research in this field focused on the most common noncovalent interaction, the hydrogen bond. However, in the past few decades, interest has increase in other intermolecular interactions, including the halogen bond, the pnictogen bond, and the beryllium bond.

The halogen bond arises when a halogen atom (F, Cl, Br or I) acts as the acid in a Lewis acid-Lewis base interaction. The molecules involved in the formation of halogen bonds usually have molecular electrostatic potentials (MEPs) at the interacting halogen atoms that exhibit positive regions, known as σ -holes.^{1,2,3} Recently, both traditional and chlorine-shared halogen bonds have been described in complexes $(\text{Ph})_3\text{P}:\text{Cl}_2$, $\text{YCl}:\text{CNX}$, $\text{YCl}:\text{SiNX}$, $\text{H}_2\text{FP}:\text{ClY}$, and $\text{H}_2\text{XP}:\text{ClY}$, with $\text{Y} = \text{F}, \text{Cl}$, and X a variety of substituents,^{4,5,6,7,8,9,10,11} as well as in complexes of nitrogen-heterocyclic carbenes with halogen bond donors.¹²

In contrast, only a few studies of intermolecular beryllium bonds have appeared in the literature. Studies of beryllium bonds in complexes between BeH_2 and HArF ¹³ have been reported, and the results analyzed using the QTAIM methodology.¹⁴ Previously, we investigated the beryllium bonds formed between the acids BeX_2 , for $\text{X} = \text{H}, \text{F}, \text{Cl}$, and OH , and a variety of Lewis bases.¹⁵ These bonds have bond critical points, and in some cases slightly negative energy densities, indicating partial covalent character. In addition, bonding indices also suggest that intermolecular bonds involving beryllium share some common features with hydrogen bonds.¹⁵ We have also investigated cooperativity in beryllium-bonded clusters of the (iminomethyl)beryllium hydride and (iminomethyl)beryllium fluoride, and concluded that there is a positive cooperativity, or synergy, as found for hydrogen-bonded chains.¹⁶ In addition, the acidity of the N-H group of an imidazole hydrogen-bonded dimer is greatly enhanced by complexation with BeX_2 , for $\text{X} = \text{H}, \text{F}$, giving evidence of cooperativity between hydrogen bonds and beryllium bonds.¹⁷ Cooperativity between beryllium bonds and other non-covalent interactions has been also reported.^{18,19}

Our previous study of uncharged binary complexes of FCl with a variety of sp , sp^2 , and sp^3 hybridized nitrogen bases indicated that only complexes with traditional $\text{F}\cdots\text{Cl}\cdots\text{N}$ halogen bonds are formed.²⁰ In the present study, we ask the question of whether or not the presence of a strong acid such as BeH_2 and its derivatives bonded to FCl can alter the type of $\text{F}\cdots\text{Cl}\cdots\text{N}$ halogen bond formed with a neutral nitrogen base. The

complexes included in this study are the binary complexes HFBe:FCl, R₂Be:FCl, and FCl:N-base, and the ternary complexes represented as HFBe:FCl:N-base and R₂Be:FCl:N-base, with R = H, F and Cl; and N-base the sp, sp², and sp³ hybridized bases NCH, NHCH₂, and NH₃, respectively. We have computed the structures, binding energies, various bonding properties, and spin-spin coupling constants for binary and ternary complexes which are stabilized by beryllium bonds and halogen bonds. The results of these calculations and their interpretation are reported in this paper.

METHODS

The structures of the isolated monomers and binary and ternary complexes were optimized at second-order Møller-Plesset perturbation theory (MP2)^{21,22,23,24} with the aug'-cc-pVTZ basis set.²⁵ This basis set is derived from the Dunning aug-cc-pVTZ basis set^{26,27} by removing diffuse functions from H atoms. In addition, the structures of the ions (XYBeF)⁻ and ⁺(Cl-N-base) have also been determined. Frequencies were computed to establish that the optimized structures correspond to equilibrium structures on their potential surfaces. Optimization and frequency calculations were performed using the Gaussian 09 program.²⁸

The binding energy (ΔE) of a binary or ternary complex is the difference between the energy of the complex and the sum of the energies of the corresponding isolated monomers at their equilibrium geometries. The cooperativity of binding energies ($\delta\Delta E$) is the difference between the binding energy of a ternary complex and the sum of the binding energies of the corresponding binary complexes. It is also possible to analyze the binding energies of binary and ternary complexes using the many-body interaction-energy formalism (MBIE).^{29,30} For a ternary complex, ΔE can be decomposed into one-, two-, and three-body interactions.

$$\Delta E = E(ABC) - \sum_{i=A}^C E_m(i) = \sum_{i=A}^C [E(i) - E_m(i)] + \sum_{i=A}^B \sum_{j>i}^C \Delta^2 E(ij) + \Delta^3 E(ABC)$$

$$E_R(i) = E(i) - E_m(i)$$

$$\Delta^2 E(ij) = E(ij) - [E(i) + E(j)]$$

$$\Delta^3 E(ABC) = E(ABC) - [E(A) + E(B) + E(C)] - [\Delta^2 E(AB) + \Delta^2 E(AC) + \Delta^2 E(BC)]$$

$E_m(i)$ is the energy of an isolated, optimized monomer, while $E(i)$ is the monomer energy at its geometry in the complex. $E_R(i)$ is the monomer distortion energy. $\Delta^2 E(ij)$ and $\Delta^3 E(ABC)$ are the two- and three-body interaction energies computed at the corresponding geometries in the complex.

The electron densities of complexes have been analyzed using the Atoms in Molecules (AIM) methodology^{31,32,33,34} employing the AIMAll³⁵ program. The topological analysis of the electron density produces the molecular graph of each complex. This graph identifies the location of electron density features of interest, including the electron density (ρ) maxima associated with the various nuclei, and saddle points which corresponds to bond critical points (BCPs). The zero gradient line which connects a BCP with two nuclei is the bond path. The electron density at the BCP (ρ_{BCP}), the Laplacian of the electron density at the BCP ($\nabla^2 \rho_{\text{BCP}}$), and the total energy density (H_{BCP}) are additional useful quantities for characterizing interactions.³⁶

Molecular electrostatic potentials (MEPs) have been computed with the Multiwfn software.³⁷ The NBO method³⁸ has been used to compute MP2/aug'-cc-pVTZ atomic populations and charge-transfer interaction energies, using the NBO-3.1 program.³⁹ Since MP2 orbitals do not exist, charge-transfer energies were obtained using the B3LYP functional^{40,41} with the aug'-cc-pVTZ basis set at the MP2/aug'-cc-pVTZ geometries, so that at least some electron correlation effects could be included.

Spin-spin coupling constants were evaluated using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI(configuration interaction)-like approximation,^{42,43} with all electrons correlated. For these calculations, the Ahlrichs⁴⁴ qzp basis set was placed on ¹³C, ¹⁵N, and ¹⁹F, and the qz2p basis set on ³⁵Cl. A basis set for ⁹Be was developed using the same approach as used previously for ⁷Li and ¹¹B.⁴⁵ The Dunning cc-pVDZ basis set was placed on all ¹H atoms. All terms, namely, the paramagnetic spin-orbit (PSO), diamagnetic spin orbit (DSO), Fermi contact (FC), and spin dipole (SD), have been evaluated for all but four complexes for which the calculation of all terms is not feasible. The EOM-CCSD calculations were performed using ACES II⁴⁶ on the IBM Cluster 1350 (Glenn) at the Ohio Supercomputer Center.

RESULTS AND DISCUSSION

Monomers and binary complexes

The molecular electrostatic potential of FCl has a σ -hole with a value of 0.065 au along the symmetry axis of the molecule close to Cl and on the side opposite to the F atom. At the F atom there is a toroid of negative MEP values. The maximum and minimum values of the MEPs for all monomers are reported in Table S1. These values change when FCl forms complexes with BeH₂ and its derivatives, and when FCl forms halogen bonds with the nitrogen bases, as can be seen from the data of Table 1. Complexation with BeH₂ and its derivatives leads to an increase in the positive values of the σ -holes in the order



In addition, the MEP minima associated with fluorine become more negative in the binary complexes with nitrogen bases, and increase in absolute value in the order



Thus, complexation of FCl with BeH₂ and its derivatives makes FCl a stronger electron-pair acceptor for the formation of halogen bonds with the nitrogen bases, while complexation with the nitrogen bases makes FCl a better electron-pair donor to the beryllium acids. Hence, when FCl interacts simultaneously with the beryllium derivatives and the nitrogen bases, synergistic cooperativity between the beryllium bond and the halogen bond should be expected, as has been observed for other weak interactions.^{47,48}

Table 1. MEP maxima of sigma-holes at Cl and MEP minima (au) at F on the 0.001 electron density isosurfaces of XYBe:FCl and FCl:N-base binary complexes.

Moiety	MEP maxima at Cl	Moiety	MEP minima at F
FCl	0.065	FCl	-0.012
H ₂ Be:FCl	0.083	FCl:NCH	-0.032
HFBe:FCl (<i>E</i>)	0.080	FCl:NH ₃	-0.052
HFBe:FCl (<i>Z</i>)	0.085	FCl:NHCH ₂	-0.056
F ₂ Be:FCl	0.091		
Cl ₂ Be:FCl	0.096		

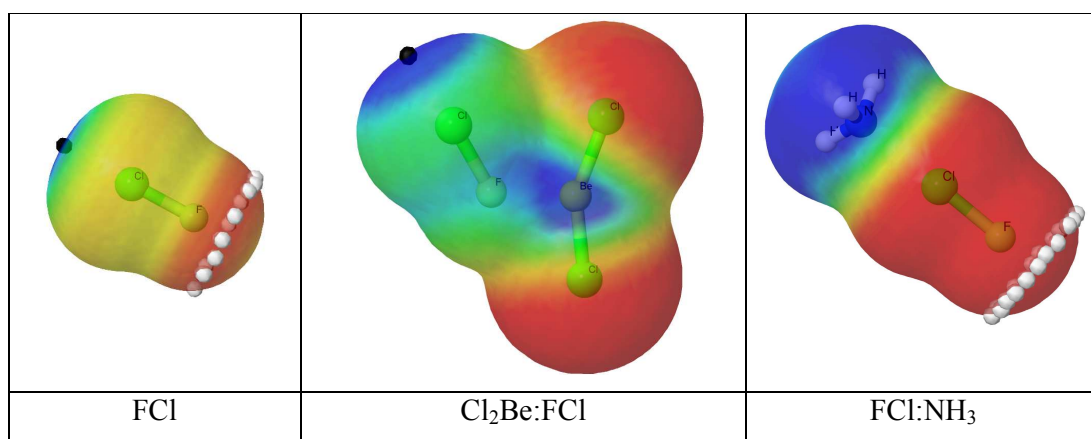


Figure 1. MEPs on the 0.001 electron density isosurfaces. Color coding corresponds to -0.015 au = red < yellow < green < blue = 0.05 au. The Cl σ -holes and the MEP minima at F are indicated with black and white dots, respectively.

The structures, total energies, and molecular graphs of the binary complexes are reported in Table S2 of the Supporting Information, and their binding energies in Table 2. In complexes of FCl with the beryllium derivatives, binding energies range from -8.5 to -16.0 $\text{kJ}\cdot\text{mol}^{-1}$, and increase in the order



Binding energies are much greater in the binary complexes between FCl and the nitrogen bases, varying from -24.5 to -51.2 $\text{kJ}\cdot\text{mol}^{-1}$, and increasing in the order $\text{FCl:NCH} \ll \text{FCl:NH}_3 \approx \text{FCl:NHCH}_2$.

Table 2. Binding energies (ΔE , $\text{kJ}\cdot\text{mol}^{-1}$), X-Be-Y angles (\angle , deg), and Be \cdots F, F-Cl, and Cl \cdots N distances (R, Å) in binary complexes XYBe:FCl and FCl:N-base

	ΔE	$\angle\text{X-Be-Y}^a$	(Be \cdots F)	R(F-Cl)	R(Cl \cdots N)
FCl monomer				1.638	
Complexes					
H ₂ Be:FCl	-9.5	164	2.061	1.656	
HFBe:FCl (E)	-8.5	168	2.286	1.645	
HFBe:FCl (Z)	-9.8	163	2.096	1.656	
F ₂ Be:FCl	-16.0	158	1.979	1.665	
Cl ₂ Be:FCl	-14.9	152	1.900	1.665	
FCl:NCH	-24.5			1.656	2.542
FCl:NH ₃	-49.1			1.714	2.235
FCl:NHCH ₂	-51.2			1.721	2.161

a) The bond angle in BeH₂ and its derivatives. The isolated molecules are linear.

What are the structural and bonding characteristics that correlate with these binding energies? From Table 2 it can be seen that complexation of BeH_2 and its derivatives with the electron-donor FCl leads to a bending of the XYBe molecule as the intramolecular X-Be-Y angle decreases from 180° in the monomers to between 168° in HFBe:FCl (E) and 152° in $\text{Cl}_2\text{Be:FCl}$. The bending of these molecules is a result of charge transfer from the F lone pairs primarily to the empty $p(\sigma)$ orbital of XYBe , and signals a change in the Be hybridization. Fig. 2 illustrates the good second-order correlation between the X-Be-Y angle and the NBO second-order stabilization energy arising from charge transfer from the F lone pairs to the empty $p(\sigma)$ orbital of beryllium, with a correlation coefficient R^2 of 0.976. The F-Cl distance tends to increase and the $\text{Be}\cdots\text{F}$ distance decrease as the interaction between the Be derivative and FCl becomes stronger. Tables S3 and S4, respectively, of the Supporting Information indicate that the electron densities at $\text{Be}\cdots\text{F}$ BCPs are largest and NBO bond orders are greatest in the two most strongly bound complexes, $\text{Cl}_2\text{Be:FCl}$ and $\text{F}_2\text{Be:FCl}$, while the electron densities at the F-Cl BCPs are depleted and the NBO bond orders reduced in the binary complexes relative to isolated FCl. The lengthening of the F-Cl bond is even greater in the binary complexes of FCl with the nitrogen bases, with the weakest and longest F-Cl bonds occurring in the complexes of FCl with NH_3 and NHCH_2 . However, the halogen bonds in these binary complexes are still characterized as traditional halogen bonds.⁶

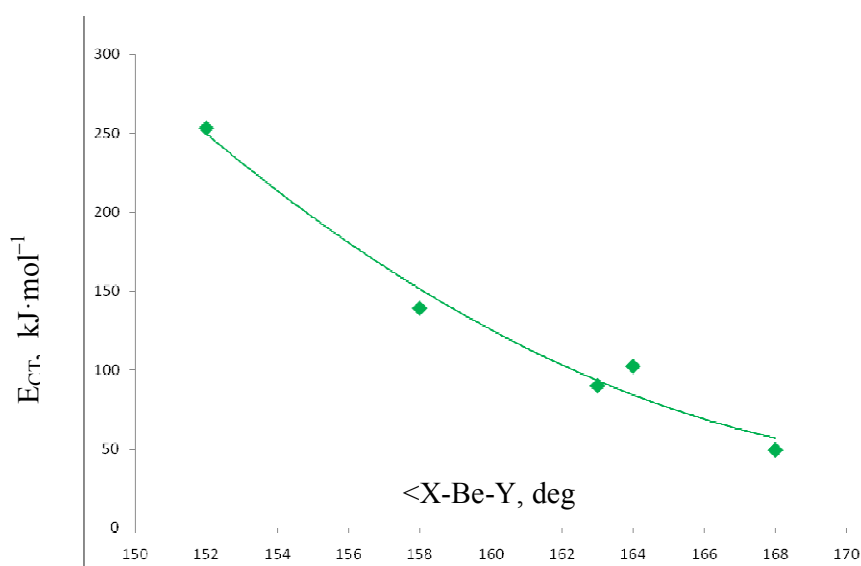
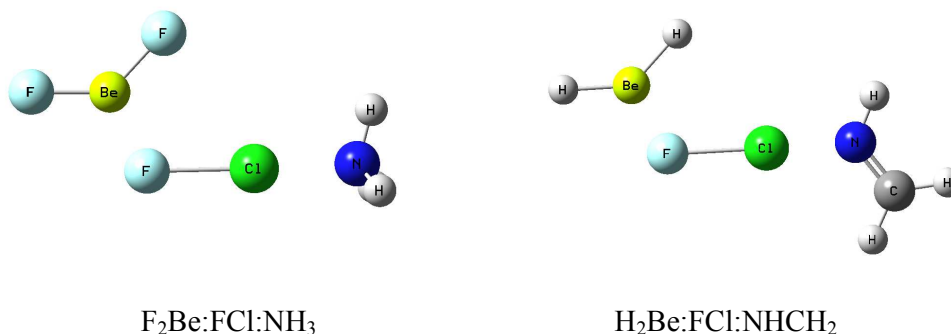


Figure 2. NBO second-order charge-transfer stabilization energy $[\text{F}(lp)\rightarrow p(\sigma)\text{Be}]$ versus the X-Be-Y angle for complexes XYBe:FCl

The binding energies of Table 2 indicate that HFBe:FCl (*Z*) is more stable than HFBe:FCl (*E*). This ordering is consistent with the shorter Be-F distance and the greater bending of the HFBe molecule in the *Z* isomer compared to *E*. In addition, even though the MBIE analyses of Table S5 indicate that the stabilizing second-order interaction energy of Cl₂Be:FCl is greater than that of F₂Be:FCl, the destabilizing distortion energies of the monomers are even greater in the former, with the result that the binding energy of F₂Be:FCl is greater than that of Cl₂Be:FCl. In contrast, in complexes between FCl and the nitrogen bases, the distortion energies of FCl are greater than those of the nitrogen bases. The largest distortion energies are found for the complex FCl:NHCH₂. As a result, although the NBO second-order energy of this complex is 5 kJ·mol⁻¹ greater than that of FCl:NH₃, its binding energy is only 2 kJ·mol⁻¹ greater.

Ternary complexes

Fifteen equilibrium ternary complexes with intermolecular Be···F and Cl···N bonds can be formed from the three bases NCH, NH₃, and NHCH₂ and the four acids BeH₂, BeHF, BeF₂, and BeCl₂, since there are two different conformers for complexes of BeHF with each base. Table S2 of the Supporting Information provides the structures, total energies, and molecular graphs of these complexes, Fig. 3 illustrates the structures of four representative ternary complexes, and Table 3 reports intra- and intermolecular distances and X-Be-Y angles. The structures of these complexes are consistent with anticipated interactions between complementary MEP regions of the corresponding isolated monomers.



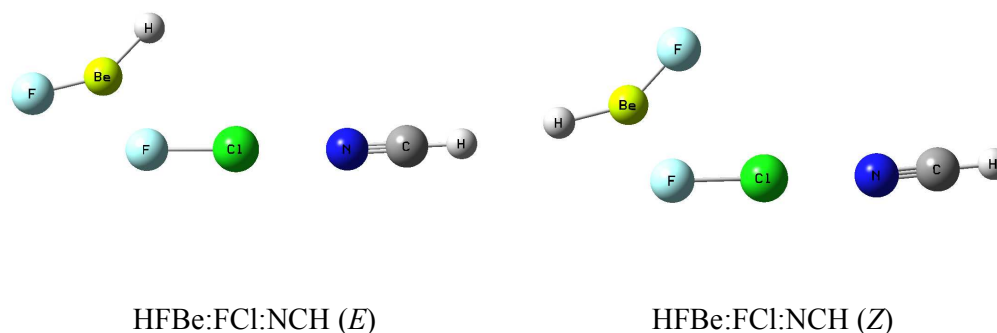


Figure 3. Ternary complexes $\text{H}_2\text{Be:FCl:NH}_3$, $\text{F}_2\text{Be:FCl:NHCH}_2$, and HFBe:FCl:NCH with *E* and *Z* conformations

Table 3. MP2/aug'-cc-pVTZ distances (Å) and X-Be-Y bond angles ($\angle\text{XBeY}$, degrees) for ternary complexes and changes in these variables (δ) relative to the corresponding binary complexes.

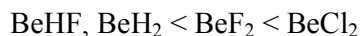
Complexes	Be \cdots F	$\delta\text{Be}\cdots\text{F}$	F-Cl ^a	Cl \cdots N	$\delta\text{Cl}\cdots\text{N}$	$\angle\text{XBeY}$	$\delta\angle\text{XBeY}$
$\text{H}_2\text{Be:FCl:NH}_3$	1.607	-0.455	1.918	1.914	-0.321	137	-27
$\text{HFBe:FCl:NH}_3(\textit{E})$	1.609	-0.677	1.927	1.905	-0.330	134	-34
$\text{HFBe:FCl:NH}_3(\textit{Z})$	1.602	-0.494	1.938	1.902	-0.333	134	-29
$\text{F}_2\text{Be:FCl:NH}_3$	1.591	-0.388	1.958	1.882	-0.353	132	-26
$\text{Cl}_2\text{Be:FCl:NH}_3$	1.530	-0.370	2.043	1.832	-0.403	126	-26
$\text{H}_2\text{Be:FCl:NHCH}_2$	1.580	-0.482	1.991	1.789	-0.372	134	-30
$\text{HFBe:FCl:NHCH}_2(\textit{E})$	1.580	-0.707	2.004	1.782	-0.379	132	-36
$\text{HFBe:FCl:NHCH}_2(\textit{Z})$	1.575	-0.521	2.020	1.776	-0.385	132	-31
$\text{F}_2\text{Be:FCl:NHCH}_2$	1.566	-0.413	2.043	1.762	-0.399	130	-28
$\text{Cl}_2\text{Be:FCl:NHCH}_2$	1.511	-0.389	2.135	1.727	-0.434	126	-26
$\text{H}_2\text{Be:FCl:NCH}$	1.738	-0.324	1.735	2.173	-0.368	147	-17
$\text{HFBe:FCl:NCH}(\textit{E})$	1.763	-0.523	1.733	2.166	-0.375	146	-22
$\text{HFBe:FCl:NCH}(\textit{Z})$	1.734	-0.362	1.745	2.142	-0.399	145	-18
$\text{F}_2\text{Be:FCl:NCH}$	1.696	-0.283	1.771	2.047	-0.494	141	-17
$\text{Cl}_2\text{Be:FCl:NCH}$	1.553	-0.347	1.962	1.742	-0.799	130	-22

^a Isolated FCl has a bond length of 1.638 Å.

The data of Table 3 illustrate that Be \cdots F and Cl \cdots N intermolecular distances dramatically decrease in the ternary complexes relative to the corresponding binary complexes. The decrease in the Be \cdots F distance ranges from 0.28 to 0.71 Å, while the decrease in the Cl \cdots N distance ranges from 0.32 to 0.80 Å. In the same complexes, the F-Cl distance increases and is longer than it is in any binary complex, and therefore significantly longer than in the isolated FCl molecule. These distance changes are reflected in increased NBO bond orders reported in Table S4 for the Be \cdots F and Cl \cdots N

bonds, and the decreased NBO bond orders for F-Cl bonds. In addition, electron densities at $\text{Be}\cdots\text{F}$ and $\text{Cl}\cdots\text{F}$ BCPs are more than three times greater in the ternary complexes than in the corresponding binary complexes. An exponential relationship exists between these densities and the corresponding distances, as is usually the case for intermolecular interactions.^{49,50,51,52,53,54,55,56,57} These relationships have correlation coefficients greater than 0.99. Changes in the $\text{Be}\cdots\text{F}$ distances are accompanied by a further decrease in the X-Be-Y bond angles to between 147° in $\text{H}_2\text{Be}:\text{FCl}:\text{NCH}$ and 126° in the two most strongly bound complexes, $\text{Cl}_2\text{Be}:\text{FCl}:\text{NH}_3$ and $\text{Cl}_2\text{Be}:\text{FCl}:\text{NHCH}_2$. Thus, it is apparent that the hybridization of Be is approaching sp^2 in these complexes. The data of Table S4 indicate that there is a dramatic increase in the $\text{Be}\cdots\text{F}$ and $\text{Cl}\cdots\text{F}$ bond orders along with a decrease in the F-Cl bond order in ternary complexes. For a given base, the $\text{Be}\cdots\text{F}$ and $\text{Cl}\cdots\text{F}$ bond orders increase in the order $\text{H}_2\text{Be} \approx \text{HFBe} < \text{F}_2\text{Be}:\text{FCl} < \text{Cl}_2\text{Be}:\text{FCl}$, while the F-Cl bond orders decrease in the same order.

These huge structural changes are associated with very strong cooperative effects between the beryllium and halogen bonds, which were anticipated from the increased positive values of the σ -holes at Cl in $\text{XYBe}:\text{FCl}$ complexes, and the increased negative values of the MEPs at F in $\text{FCl}:\text{N-base}$ complexes. The binding energies reported in Table 4 range from -50 to $-200 \text{ kJ}\cdot\text{mol}^{-1}$, while the nonadditivity of binding energies varies from about $-20 \text{ kJ}\cdot\text{mol}^{-1}$ for the more weakly-bound complexes with NCH, to $-135 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{Cl}_2\text{Be}:\text{FCl}:\text{NHCH}_2$. As expected, the variation in the three-body energies is much greater, from $-30 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{H}_2\text{Be}:\text{FCl}:\text{NCH}$ to $-219 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{Cl}_2\text{Be}:\text{FCl}:\text{NHCH}_2$. The order of increasing binding energies and nonadditivities with respect to the beryllium derivatives is



while the order with respect to the bases is



Figure 4 illustrates the excellent linear correlation between cooperative effects as measured by $\delta\Delta E$ and the binding energies of the ternary complexes, with a correlation coefficient of 0.992. It should also be noted that Table S5 indicates that although the total destabilizing monomer distortion energies of the BeCl_2 ternary complexes are greater than those of the corresponding BeF_2 ternary complexes, the sum of the stabilizing two- and three-body interaction energies in the BeCl_2 complexes are even

greater, with the result that the ternary complexes containing BeCl_2 are now much more stable than the corresponding BeF_2 complexes.

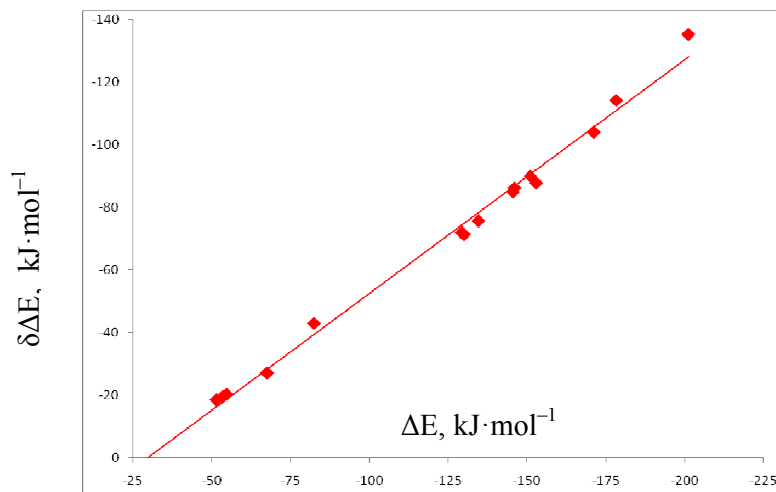


Figure 4. Cooperativity ($\delta\Delta E$) versus the binding energy (ΔE) of ternary complexes XYBe:FCI:N-base .

Table 4. Binding energies (ΔE), cooperativity ($\delta\Delta E$), and three-body interaction energies ($\Delta^3 E$, $\text{kJ}\cdot\text{mol}^{-1}$) of ternary complexes XYBe:FCI:N-base

Complex	ΔE	$\delta\Delta E^a$	$\Delta^3 E(\text{ABC})^b$
$\text{H}_2\text{Be:FCI:NH}_3$	-129.9	-71.3	-100.7
$\text{HFBe:FCI:NH}_3 (E)$	-129.4	-71.8	-116.0
$\text{HFBe:FCI:NH}_3 (Z)$	-134.5	-75.6	-107.8
$\text{F}_2\text{Be:FCI:NH}_3$	-152.8	-87.7	-136.0
$\text{Cl}_2\text{Be:FCI:NH}_3$	-178.2	-114.2	-178.8
$\text{H}_2\text{Be:FCI:NHCH}_2$	-145.5	-84.8	-127.4
$\text{HFBe:FCI:NHCH}_2 (E)$	-146.0	-86.3	-148.9
$\text{HFBe:FCI:NHCH}_2 (Z)$	-151.0	-90.0	-136.2
$\text{F}_2\text{Be:FCI:NHCH}_2$	-171.2	-104.0	-172.2
$\text{Cl}_2\text{Be:FCI:NHCH}_2$	-201.3	-135.2	-219.0
$\text{H}_2\text{Be:FCI:NCH}$	-53.5	-19.5	-30.1
HFBe:FCI:NCH (E)	-51.5	-18.5	-32.5
HFBe:FCI:NCH (Z)	-54.6	-20.3	-33.7
$\text{F}_2\text{Be:FCI:NCH}$	-67.8	-27.0	-51.8
$\text{Cl}_2\text{Be:FCI:NCH}$	-82.4	-43.0	-145.7

^aThe cooperativity computed as the binding energy of the ternary complex minus the binding energies of the two corresponding binary complexes (XYBe:FCI and FCI:N-base).

^bThe MBIE three-body interaction energy.

Given the large binding energies and cooperative effects in these complexes, it would be expected that the charge-transfer energies would also increase. Unfortunately,

it is not possible to compute these energies since the NBO program does not describe the ternary complexes as containing three identifiable monomers. However, based on the relationship between the X-Be-Y angles in the binary complexes and their charge-transfer energies, it may be anticipated that further decreases in this angle in the ternary complexes indicate a further hybridization change at Be due to increased charge-transfer from F to the Be $p(\sigma)$ orbital. This charge transfer strengthens the Be \cdots F and Cl \cdots N bonds while weakening the F-Cl bond by depopulating its F-Cl density. In complexes with the stronger bases, depopulation effects are so large that the F-Cl bond dissociates and the complex becomes an ion-pair $[\text{XBeY-F}]^- \cdots [\text{Cl-N-Base}]^+$. The X-Be-Y angles in $[\text{XBeY-F}]^-$ are between 119 and 123°, indicating sp^2 hybridization of Be. The mechanism for the formation of this ion-pair is the same as that for the well-known phenomenon of dissociative proton attachment⁵⁸ in which gas-phase protonation of compounds like fluoro- or chloro-adamantane result in the spontaneous loss of FH or ClH and the formation of adamantyl cation.

The NBO description of $\text{Cl}_2\text{Be:FCl:NHCH}_2$ has natural charges close to -1 and +1 on Cl_2BeF and Cl:NHCH_2 , respectively (± 0.84). The Be-F distance of 1.511 Å and the Cl-N distance of 1.727 Å in this complex approach the Be-F distance of 1.446 Å in the anion $[\text{Cl}_2\text{Be-F}]^-$ and the Cl-N distance of 1.686 Å in the cation $[\text{ClNHCH}_2]^+$. Dissociation of $\text{Cl}_2\text{Be:FCl:NHCH}_2$ to the two ions requires only $338 \text{ kJ}\cdot\text{mol}^{-1}$, whereas the heterolytic dissociation of FCl into F^- and Cl^+ requires $1311 \text{ kJ}\cdot\text{mol}^{-1}$. The structures and bonding properties of the complexes XYBe:FCl:N-base indicate that interaction of Be \cdots F beryllium bonds with Cl \cdots N halogen bonds leads to an evolution of halogen-bond type, from traditional to chlorine-shared to ion-pair bonds. This evolution occurs smoothly as a function of the intrinsic basicity of the nitrogen base and the intrinsic acidity of the beryllium derivative.

Spin-Spin Coupling Constants

The components of spin-spin coupling constants for the FCl monomer, the binary and ternary complexes, and the corresponding ions are reported in Table S6 of the Supporting Information. Since the calculation of EOM-CCSD coupling constants for $\text{F}_2\text{Be:FCl:NHCH}_2$ and ternary complexes with BeCl_2 as the beryllium acid are not feasible, the first question is whether or not the FC terms are good approximations to total J. Table S6 indicates that the FC term does provide a good approximation to the total coupling constant $^{1\text{be}}J(\text{Be-F})$ in the binary complexes and the ternary complexes

with NCH as the base. However, it is usually not a good approximation for ternary complexes with NH_3 and NHCH_2 in which the $\text{Be}\cdots\text{F}$ distance is shorter, and in all of the cations, even though the FC term is the dominant term in all but two of these. The FC term is a poor approximation to total $^1\text{J}(\text{F}-\text{Cl})$ due to non-negligible contributions from both PSO and DSO terms. Indeed, for all of the binary complexes and the ternary complexes with NCH as the base, the FC term is not even the dominant term. The FC term is a reasonable approximation to $^{1\text{X}}\text{J}(\text{Cl}-\text{N})$ for the binary complexes, the ternary complexes with NCH as the base, and the cation $^+\text{Cl}-\text{NCH}$. However, it is not a good approximation for ternary complexes with the stronger nitrogen bases and the corresponding cations. Therefore, the following discussion of coupling constants is based only on total J values and trends. The $\text{Be}\cdots\text{F}$ coupling constant across the beryllium bond is denoted as $^{1\text{be}}\text{J}(\text{Be}-\text{F})$, while that across the halogen bond is $^{1\text{X}}\text{J}(\text{Cl}-\text{N})$. These designations will be used throughout the following discussion, even when these bonds lose their intermolecular character and are better described as ^1J values.

$^{1\text{be}}\text{J}(\text{Be}-\text{F})$. Table 5 reports Be-F distances and values of the Be-F coupling constants for binary complexes with all acids, ternary complexes with the acids H_2Be , HFBe , and BeF_2 , and the anions XYBeF^- . Since the FC terms were computed for all ternary complexes, they are also given for comparison. The data in Table 5 are reported for a fixed acid, first for the binary $\text{XYBe}:\text{FCl}$ complex, then for the ternary complexes in the order NCH, NH_3 , NHCH_2 , and finally for the corresponding anion XYBeF^- . While the Be-F distance decreases in going from the binary complexes with H_2Be and HFBe to the corresponding ternary complexes with the weak base NCH, coupling constants $^{1\text{be}}\text{J}(\text{Be}-\text{F})$ initially increase, but subsequently decrease and change sign as the base strength increases. $^{1\text{be}}\text{J}(\text{Be}-\text{F})$ is negative for all ternary complexes with BeF_2 .

Fig. 5 provides $^{1\text{be}}\text{J}(\text{Be}-\text{F})$ versus the Be-F distance for ternary complexes with BeH_2 , BeHF , and BeF_2 . For each acid, the point at the longest distance corresponds to the ternary complex with HCN, and that at the shortest distance to the corresponding anion XYBeF^- . The correlation coefficients R^2 are 0.999, 0.966, and 1.000, the latter with only three points. Thus, $^{1\text{be}}\text{J}(\text{Be}-\text{F})$ values for these ternary complexes decrease with decreasing Cl-N distance, and approach $^{1\text{be}}\text{J}(\text{Be}-\text{F})$ for the corresponding anions as the Be-F distance decreases.

Table 5. Be-F distances (Å), and FC terms and $^{1\text{be}}J(\text{Be-F})$ (Hz) for binary complexes XYBe:FCl , ternary complexes XYBe:FCl:N-base , and ions $[\text{XYBeF}]^-$

Complex	FC	$^{1\text{be}}J(\text{Be-F})$	R(Be-F)
$\text{H}_2\text{Be:FCl}$	22.2	22.9	2.061
$\text{H}_2\text{Be:FCl:NCH}$	36.7	39.0	1.738
$\text{H}_2\text{Be:FCl:NH}_3$	12.6	16.5	1.607
$\text{H}_2\text{Be:FCl:NHCH}_2$	4.6	8.9	1.580
H_2BeF^-	-28.3	-21.4	1.485
HFBe:FCl (E)	12.5	12.6	2.286
HFBe:FCl:NCH	23.6	24.9	1.764
HFBe:FCl:NH_3	-1.8	1.0	1.609
HFBe:FCl:NHCH_2	-9.2	-5.9	1.579
HBeF_2^-	-37.4	-32.0	1.484
HFBe:FCl (Z)	25.7	26.1	2.096
HFBe:FCl:NCH	33.4	34.9	1.734
HFBe:FCl:NH_3	4.4	7.3	1.603
HFBe:FCl:NHCH_2	-4.8	-1.5	1.575
HBeF_2^-	-37.4	-32.0	1.484
$\text{F}_2\text{Be:FCl}$	8.7	9.0	1.979
$\text{F}_2\text{Be:FCl:NCH}$	-9.9	-8.8	1.696
$\text{F}_2\text{Be:FCl:NH}_3$	-29.8	-27.7	1.591
$\text{F}_2\text{Be:FCl:NHCH}_2$	-35.8		1.566
F_2BeF^-	-57.3	-53.1	1.485
$\text{Cl}_2\text{Be:FCl}$	23.3	23.9	1.900
$\text{Cl}_2\text{Be:FCl:NCH}$	-23.8		1.553
$\text{Cl}_2\text{Be:FCl:NH}_3$	-30.6		1.530
$\text{Cl}_2\text{Be:FCl:NHCH}_2$	-36.4		1.511
Cl_2BeF^-	-55.6	-49.5	1.446

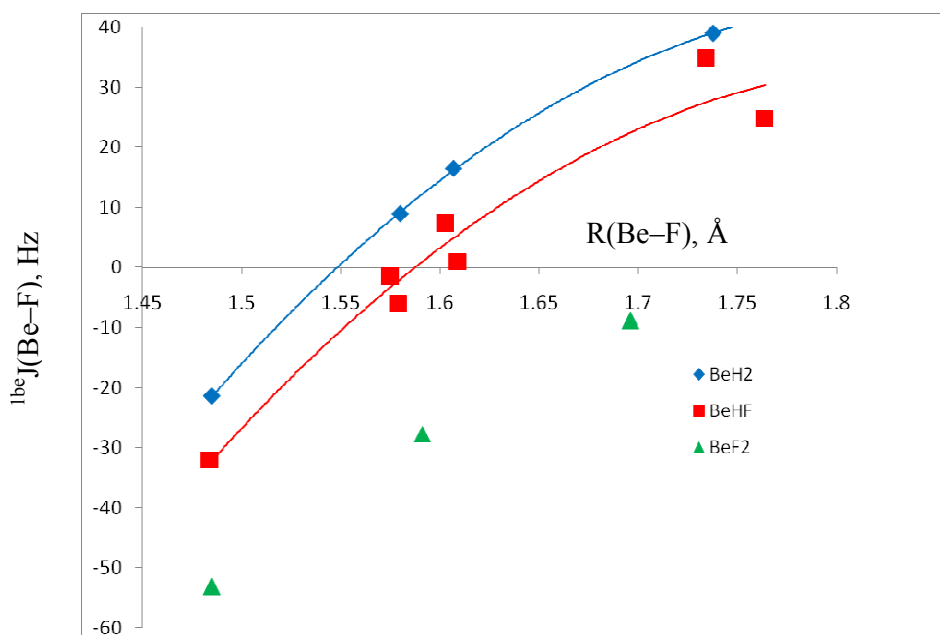


Figure 5. $^{1\text{be}}J(\text{Be-F})$ versus the Be-F distance for ternary complexes with BeH₂, BeHF and BeF₂ as the acids, and the corresponding anions BeH₂F⁻, BeHF₂⁻ and BeF₃⁻.

$^1J(\text{F-Cl})$. Table 6 reports the FC terms and $^1J(\text{F-Cl})$ for the binary complexes XYBe:FCl and FCl:N-base, and the ternary complexes XYBe:FCl:N-base. Upon formation of a Be^{...}F bond in the binary complexes with BeXY, this coupling constant decreases from its monomer value of 798 Hz to 768 Hz in Cl₂Be:FCl. The decrease is much greater in the binary complexes with the nitrogen bases, with values of 753, 694, and 680 Hz for FCl:NCH, FCl:NH₃, and FCl:NHCH₂, respectively. These decreases reflect the lengthening of the F-Cl bonds in the binary complexes.

In the ternary complexes, the decrease in $^1J(\text{F-Cl})$ is even greater, with $^1J(\text{F-Cl})$ values ranging from 663 Hz in H₂Be:FCl:NCH to 473 Hz in HFBe:FCl:NHCH₂ (Z). The range of $^1J(\text{F-Cl})$ values would probably be even greater if data for ternary complexes with Cl₂Be were available. For a fixed base, $^1J(\text{F-Cl})$ in ternary complexes decreases in the order



although the values for HFBe:FCl:NH₃ and F₂Be:FCl:NH₃ are essentially the same.

For fixed acid, the order of decreasing $^1J(\text{F-Cl})$ with respect to the base is



The changes in $^1J(\text{F-Cl})$ upon formation of binary and ternary complexes are illustrated in Fig. 6.

Table 6. FC terms and $^1J(\text{F-Cl})$ and $^{1X}J(\text{Cl-N})$ (Hz) for binary complexes FCl:N-base, ternary complexes XYBe:FCl:N-base, and ions $^+\text{Cl-N-base}$

Moiety	FC	$^1J(\text{F-Cl})$	FC	$^{1X}J(\text{Cl-N})$
FCl	-99.4	798.0		
H ₂ Be:FCl	-94.4	784.4		
HFBe:FCl (<i>E</i>)	-97.0	788.1		
HFBe:FCl (<i>Z</i>)	-96.3	785.8		
F ₂ Be:FCl	-101.5	776.8		
Cl ₂ Be:FCl	-96.5	767.9		
FCl:NCH	-57.5	753.0	-32.3	-32.7
H ₂ Be:FCl:NCH	54.3	662.5	-57.2	-58.0
HFBe:FCl:NCH (<i>E</i>)	49.3	654.5	-58.3	-59.1
HFBe:FCl:NCH (<i>Z</i>)	71.3	659.5	-57.9	-58.7
F ₂ Be:FCl:NCH	134.5	644.8	-54.2	-54.9
Cl ₂ Be:FCl:NCH	380.0		18.0	
$^+\text{Cl-NCH}$			48.6	48.8
FCl:NH ₃	36.9	693.6	-48.2	-51.1
H ₂ Be:FCl:NH ₃	294.2	562.8	-17.3	-25.9
HFBe:FCl:NH ₃ (<i>E</i>)	293.9	550.2	-16.1	-24.9
HFBe:FCl:NH ₃ (<i>Z</i>)	299.3	550.5	-14.7	-23.7
F ₂ Be:FCl:NH ₃	322.7	549.8	-10.5	-19.9
Cl ₂ Be:FCl:NH ₃	326.2		1.4	
$^+\text{Cl-NH}_3$			21.7	8.5
FCl:NHCH ₂	60.0	679.6	-54.0	-55.4
H ₂ Be:FCl:NHCH ₂	336.8	497.4	6.5	3.7
HFBe:FCl:NHCH ₂ (<i>E</i>)	330.3	480.7	7.8	5.0
HFBe:FCl:NHCH ₂ (<i>Z</i>)	329.2	473.1	9.6	6.8
F ₂ Be:FCl:NHCH ₂	338.2		12.6	
Cl ₂ Be:FCl:NHCH ₂	300.7		20.4	
$^+\text{Cl-NHCH}_2$			27.9	21.6

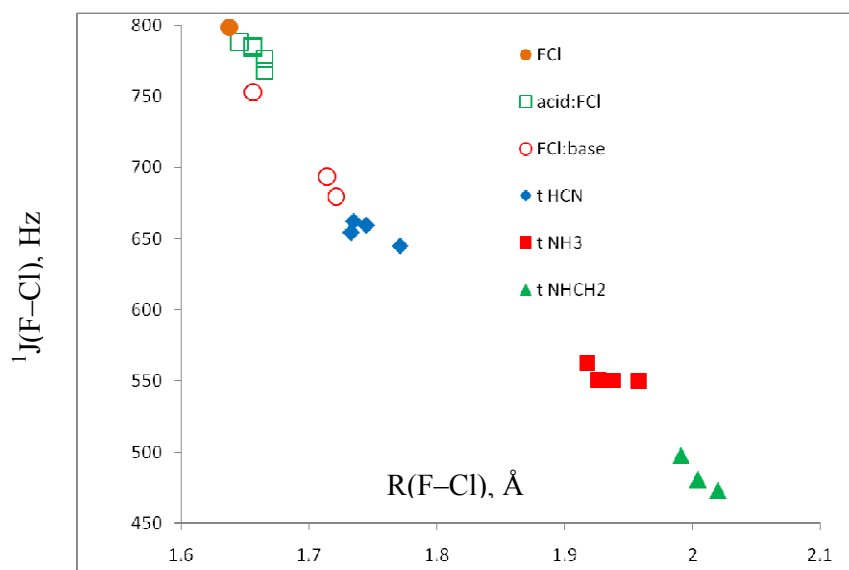


Figure 6. $^1J(\text{F-Cl})$ versus the F-Cl distance in FCl, binary complexes FCl:N-base and XYBe:FCl, and ternary complexes XYBe:FCl:N-base

$^{1X}J(\text{Cl-N})$. Table 6 also provides the FC terms and total J for the third coupling constant of interest, $^{1X}J(\text{Cl-N})$. This coupling constant is large and negative in the binary complexes, and in the ternary complexes with NCH and NH_3 . It eventually decreases as the strength of the beryllium acid increases, changes sign, and is positive in the cations $^+\text{Cl-NCH}$ and $^+\text{Cl-NH}_3$. All ternary complexes with NHCH_2 as the base have positive values of $^{1X}J(\text{Cl-N})$, with the largest value occurring in the cation $^+\text{Cl-NHCH}_2$. For fixed acid, $^{1X}J(\text{Cl-N})$ in the ternary complexes increases in the order

$$\text{NCH} < \text{NH}_3 < \text{NHCH}_2,$$

while $^1J(\text{Cl-N})$ for the cations increases in the order

$$^+\text{Cl-NH}_3 < ^+\text{Cl-NHCH}_2 < ^+\text{Cl-NCH}.$$

Figure 7 provides a plot of $^{1X}J(\text{Cl-N})$ versus the Cl-N distance. The points for each base at the longest distance are the values in the binary complex, while the point at the shortest distance corresponds to the cation. The ternary complexes with a given base are grouped together between these endpoints. The values of $^{1X}J(\text{Cl-N})$ can be fitted by a second-order trendline which has a correlation coefficient R^2 of 0.983. Of course, it should be recognized that at longer Cl-N distances, the curvature of the trendline will change as $^{1X}J(\text{Cl-N})$ asymptotically approaches 0 Hz. For comparison, the value of $^{1X}J(\text{Cl-N})$ for the binary complex of FCl with the very weak base N_2 is -13.9 Hz at a Cl-N distance of 2.802 Å.

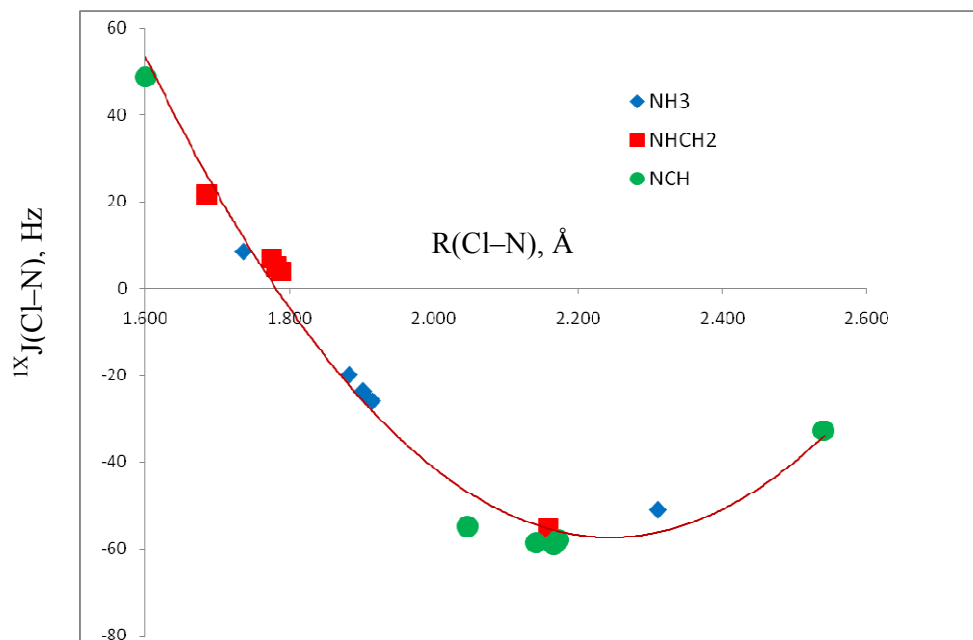


Figure 7. $^{1X}J(\text{Cl-N})$ versus the Cl-N distance in binary complexes FCI:N-base , ternary complexes XYBe:FCI:N-base , and cations $^+\text{Cl-N-base}$. The points for each base at the longest Cl-N distance are for the binary complexes.

Just as the structures, binding energies, and bonding properties of the binary and ternary complexes illustrate an evolution of halogen-bond type from traditional to chlorine-shared to ion-pair, so do the coupling constants $^{1X}J(\text{Cl-N})$ which are plotted against the Cl-N distance in Fig. 7. The plot suggests that all of the complexes XYBe:FCI:NCH are stabilized by traditional halogen bonds, except for $\text{Cl}_2\text{Be:FCI:NCH}$. Since the FC terms for the ternary complexes with NCH are excellent approximations to $^{1X}J(\text{Cl-N})$, its value of 18 Hz at a Cl-N distance of 1.742 Å suggests that $\text{Cl}_2\text{Be:FCI:NCH}$ is stabilized by an ion-pair halogen bond. Fig. 7 suggests that chlorine-shared halogen bonds are found in all complexes XYBe:FCI:NH_3 except for $\text{Cl}_2\text{Be:FCI:NH}_3$ which has an ion-pair bond. Finally, $^{1X}J(\text{Cl-N})$ values indicate that all complexes XYBe:FCI:NHCH_2 are stabilized by ion-pair halogen bonds.

CONCLUSIONS

Ab initio MP2/aug'-cc-pVTZ calculations have been carried out in this study to investigate the binary complexes HFBe:FCI , $\text{R}_2\text{Be:FCI}$, and FCI:N-base , and the ternary complexes HFBe:FCI:N-base and $\text{R}_2\text{Be:FCI:N-base}$, for $\text{R} = \text{H, F, Cl}$; and $\text{N-base} = \text{NH}_3, \text{NHCH}_2, \text{NCH}$. The presence of $\text{Be}\cdots\text{F}$ beryllium bonds and $\text{Cl}\cdots\text{N}$ halogen bonds

leads to dramatic, synergistic cooperative effects on the structures, binding energies, and bonding characteristics of ternary complexes. Charge transfer from F to Be across the beryllium bond and from N to Cl across the halogen bond strengthens both Be \cdots F and Cl \cdots N bonds, and weakens the F-Cl bond. Charge transfer to the empty p(σ) orbital of Be increases the electron density of Be and leads to a change in hybridization. In the limit, XYBe approaches sp² hybridization, and in the more strongly bound complexes, the interaction is sufficient to generate an ion-pair, such as [Cl₂Be:F]⁻ \cdots [Cl:NHCH₂]⁺, as heterolytic cleavage of the F-Cl bond occurs. The mechanism for cleavage is similar to that involved in the dissociative proton attachment process. As a function of the intrinsic basicity of the nitrogen base and the intrinsic acidity of the Be derivative, halogen-bond type evolves smoothly from traditional to chlorine-shared to ion-pair. EOM-CCSD spin-spin coupling constants ¹XJ(Cl-N) across the halogen bond also provide evidence of the evolution of halogen-bond type in these complexes.

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SUPPORTING INFORMATION

MEP minima and maxima on monomer surfaces; Total energies, structures, and molecular graphs of binary and ternary complexes; Electron density properties at BCPs; NBO bond orders; MBIE energies; PSO, DSO, FC, and SD components of coupling constants.

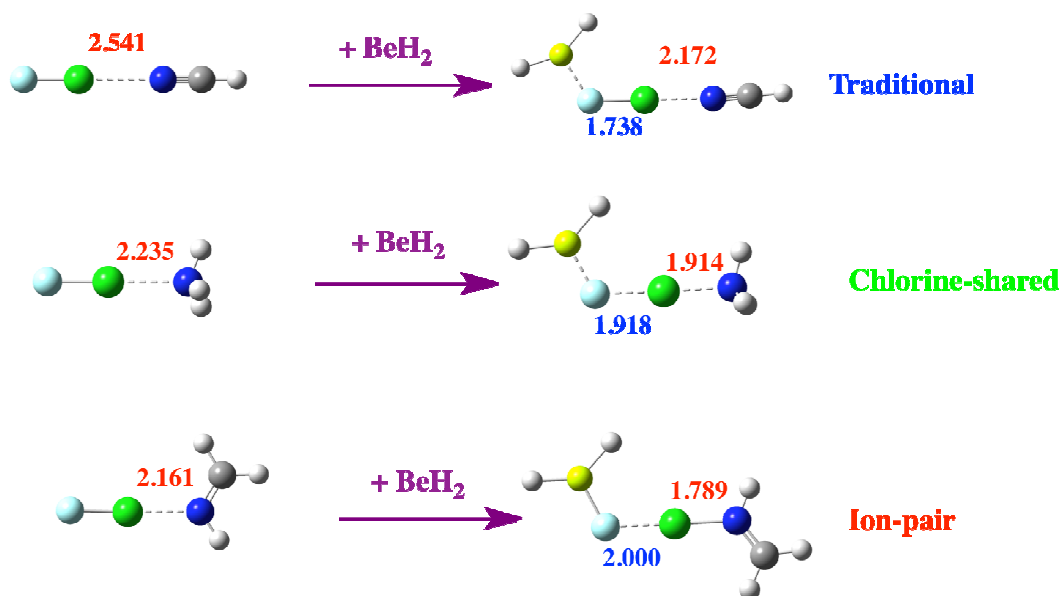
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Dramatic synergistic cooperative effects between $\text{Be}\cdots\text{F}$ beryllium bonds and $\text{Cl}\cdots\text{N}$ halogen bonds in XYBe:FCl:N -base ternary complexes lead to changes in halogen-bond type from traditional to chlorine-shared to ion-pair.