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# Radial Potential Energy Functions of Linear Halogen-bonded Complexes $YX \cdots ClF$ , ( $YX = FB, OC, SC, N_2$ ) and the Effects of Substituting X by Second-row Analogues: Mulliken Inner and Outer complexes.

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## ABSTRACT

Energies of linear, halogen-bonded complexes in the isoelectronic series  $YX \cdots ClF$  ( $YX = FB, OC$  or  $N_2$ ) are calculated at several levels of theory as a function of the intermolecular distance  $r(X \cdots Cl)$  to yield radial potential energy functions. When  $YX = OC$ , a secondary minimum was observed corresponding to lengthened and shortened distances  $r(ClF)$  and  $r(CCl)$ , respectively, relative to the primary minimum, suggesting a significant contribution from the Mulliken inner complex structure  $[O=C-Cl]^+ \cdots F^-$ . A conventional weak, halogen-bond complex  $OC \cdots ClF$  occurs at the primary minimum. For  $YX = FB$ , the primary minimum corresponds to the inner complex  $[F=B-Cl]^+ \cdots F^-$ , while the outer complex  $FB \cdots ClF$  is at the secondary minimum. The effects on the potential energy function of systematic substitution of Y and X by second row congeners and of reversing the order of X and Y are also investigated. Symmetry adapted perturbation theory and natural population analyses are applied to further understand the nature of the various halogen-bond interactions.

## 1. INTRODUCTION

In a recent publication concerned with the calculation of radial potential energy functions of known linear and other axially symmetric halogen-bonded complexes  $B \cdots ClF$  formed by chlorine monofluoride,<sup>1</sup> it was found that when the Lewis base B is CO, the function contains two minima but in the other cases only one minimum was present. The potential energy curve when the Lewis base was carbon monoxide displayed evidence of not only the expected

minimum corresponding to the conventional halogen-bonded species  $\text{OC}\cdots\text{Cl}$  as observed experimentally,<sup>2</sup> but also a secondary minimum at  $(r-r_e) \approx -1.0 \text{ \AA}$ . The C to Cl distance is therefore approximately  $1 \text{ \AA}$  shorter than in the conventional halogen-bonded isomer  $\text{OC}\cdots\text{ClF}$ . Moreover, the distance  $r(\text{Cl}-\text{F})$  was significantly increased. An explanation of this observation is that, as the Cl atom approaches the C atom along the intermolecular axis more closely than the distance in the conventional halogen-bonded species  $\text{OC}\cdots\text{ClF}$ , there is a chemical interaction of C and Cl which leads to partial C–Cl covalent bond formation. This is a particular example of Mulliken’s general classification of complexes, which is based on charge transfer between an electron donor D and an electron acceptor A.<sup>3</sup> A typical halogen-bonding interaction that is almost entirely electrostatic in nature is usually signified as  $\text{D}\cdots\text{XA}$  and corresponds to a Mulliken “outer complex”. Inner complexes are more strongly bound and may be written in the form  $[\text{D}-\text{X}]^+ \cdots \text{A}^-$ . Recent examples of Mulliken inner complexes are those involving the interaction of  $\text{PH}_3$  with  $\text{ClF}^{4,5}$  and phosphabenzene and  $\text{ClF}^{6}$ .

The purpose of the present article is to investigate the observations reported in Ref. 1 for  $\text{OC}\cdots\text{ClF}$  in some detail and to answer the following questions:

- (a) Is the presence and position of the secondary minimum in the radial potential curve of the complex  $\text{OC}\cdots\text{ClF}$  independent of the level of theory at which the curve is calculated?
- (b) What is the electronic structure of the complex at the secondary minimum?
- (c) What is the effect on the radial potential energy function when O in CO is substituted by the second row chalcogen atom S to form the analogous complex  $\text{SC}\cdots\text{ClF}$ ?
- (d) Does the secondary minimum observed for the (OC,ClF) complex occur in the related complex  $\text{OSi}\cdots\text{ClF}$  in which C is replaced by the second row, Group 14 atom Si?
- (e) How does CO differ from CS and SiO in halogen bond formation with ClF?
- (f) What happens when the isoelectronic series  $\text{FB}\cdots\text{ClF}$ ,  $\text{OC}\cdots\text{ClF}$ ,  $\text{N}_2\cdots\text{ClF}$  is similarly examined?

In what follows we attempt to answer these questions by calculating the radial potential energy functions of the various B...ClF complexes using several different levels of theory, and analyzing the electronic structure and nature of the interactions at the minima located on these potential energy functions.

## 2. THEORETICAL METHODS.

Relaxed potential energy scans were carried out, in which the B...Cl distance is fixed, all atoms were constrained to be collinear, and all other internal coordinates are optimized. The explicitly correlated coupled cluster CCSD(T)-F12c method [also known as CCSD(T)(F12\*)]<sup>7</sup> in the Molpro system of ab initio programs<sup>8,9</sup> was employed. The triple-zeta correlation consistent basis set designed specifically for use in explicitly correlated calculations, cc-pVTZ-F12,<sup>10</sup> was used for all atoms, along with the aug-cc-pVTZ/MP2Fit,<sup>11</sup> aug-cc-pVTZ/JKFit,<sup>12</sup> and cc-pVTZ-F12/OptRI auxiliary basis sets.<sup>13</sup> The geminal Slater exponent was set to  $1.0 a_0^{-1}$ . To investigate the sensitivity of the relaxed scans to basis set size, some calculations were also carried out with the double-zeta cc-pVDZ-F12 basis set, along with the equivalent auxiliary basis sets.

Density functional theory calculations were carried out with the Gaussian 16 package,<sup>14</sup> using two exchange-correlation functionals: M06-2X<sup>15</sup> and  $\omega$ B97X-D.<sup>16</sup> In both cases the correlation consistent aug-cc-pV(T+d)Z basis sets were used,<sup>17-19</sup> where the +d indicates that additional “tight” functions were included for second row atoms. An ultrafine integration grid (99 radial shells and 590 angular points per shell) was also used.

Symmetry-adapted perturbation theory (SAPT) calculations were carried out to decompose the interaction energy of a complex into electrostatic, exchange, induction and dispersion components at the SAPT2+(3)(CCD) $\delta$ MP2/aug-cc-pV(T+d)Z level.<sup>20-22</sup> A SAPT charge-transfer analysis<sup>23</sup> was also carried out at the SAPT2+(3)(CCD)/aug-cc-pV(T+d)Z level, and all SAPT calculations were performed with the Psi4 V1.3.1 program.<sup>24</sup> For brevity, SAPT2+(3)(CCD) $\delta$ MP2/aug-cc-pV(T+d)Z will be referred to as SAPT herein. Natural

population analysis (NPA) at the local minima used the NBO6 program<sup>25</sup> interfaced to Molpro, with the MP2/aug-cc-pV(T+d)Z density. Molecular electrostatic potential maps (MESPs) were obtained at the M06-2X/6-311++G\*\* level<sup>26</sup> in the SPARTAN package,<sup>27</sup> with an iso-density surface of 0.001 e bohr<sup>-3</sup>.

To ensure the SAPT results are reliable, the total SAPT interaction energy ( $E_I$ ), defined as the difference in energy between the interacting complex and its “monomers” frozen in the geometries they adopt in the interacting complex, is compared with the CCSD(T)-F12c/cc-pVTZ-F12 analogue. As SAPT is inherently free of basis set superposition error (BSSE), the coupled cluster interaction energies included the counterpoise correction.<sup>28</sup> The magnitude of the counterpoise correction is small at the CCSD(T)-F12c/cc-pVTZ-F12 level, with an average value of 0.60 kJ mol<sup>-1</sup> for the complexes under consideration.

### 3. RESULTS

#### 3.1 Evidence that the secondary minimum in the radial potential energy function of OC...CIF is independent of the method of calculation.

Figure 1 shows the energy  $V(r-r_e)$  calculated as a function of  $(r-r_e)$ , where  $r$  is the C...Cl internuclear distance and  $r_e$  is its equilibrium value for the weak, halogen-bonded complex OC...CIF.

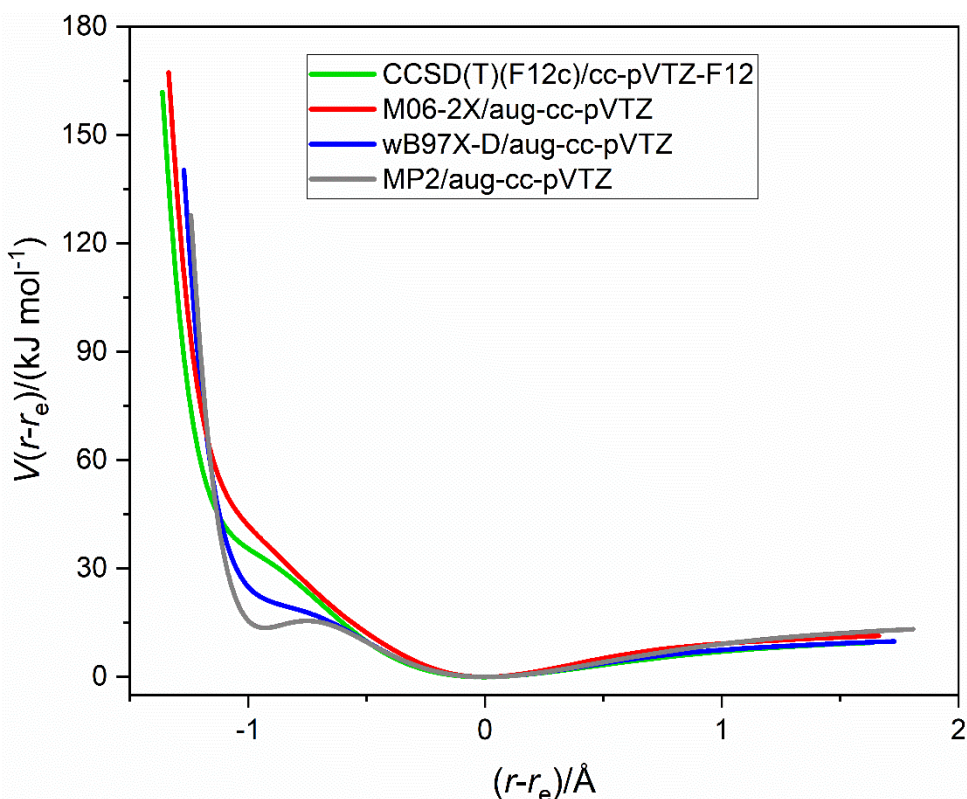


Figure 1. Radial potential energy curves  $V(r - r_e)$  versus  $(r - r_e)$  of the linear complex  $\text{OC}\cdots\text{ClF}$  calculated at the four indicated levels of theory. Each shows a secondary minimum/inflection at  $(r - r_e) \approx -1 \text{ \AA}$  interpreted to correspond to a geometry to which the valence-bond structure  $[\text{O}=\text{C}-\text{Cl}]^+\cdots\text{F}^-$  makes a significant contribution. Points were calculated at  $0.05 \text{ \AA}$  intervals and joined by a spline function.

The results of four calculations are plotted on the same axes in Figure 1 and for clarity the calculated points are not explicitly indicated. Two of the calculations use density functional theory and employ the popular functionals M06-2X and  $\omega\text{B97X-D}$ . The other two calculations were carried out at the MP2/aug-cc-pV(T+d)Z level and the explicitly correlated CCSD(T)-F12c/cc-pVTZ-F12 level. It is clear from Figure 1 that, whatever the level of theory employed, there is a secondary minimum/point of inflection at  $(r - r_e) \approx -1 \text{ \AA}$ , although this appears more pronounced at the MP2 level. The values of  $r_e$  determined by geometry optimization at the four levels of theory were  $2.7356$ ,  $2.6713$ ,  $2.6413$  and  $2.7604 \text{ \AA}$ , respectively. An investigation of  $\text{OC}\cdots\text{ClF}$  by rotational spectroscopy concluded that the molecule so observed was a weakly bound,<sup>2</sup> linear complex with the atoms in the indicated order and with the distance  $r(\text{C}\cdots\text{Cl}) = 2.770(3) \text{ \AA}$ . The experimental value of  $r(\text{C}\cdots\text{Cl})$  was determined under the assumption of unchanged monomer geometries and after correction for the contribution of the intermolecular bending modes (but not the intermolecular stretching mode). It is the best approximation to the

equilibrium value available and is in excellent agreement with that from the CCSD(T)-F12c calculation, thereby confirming that experiment and theory are referring to the same molecular species. The MP2 calculation leads to too short a C $\cdots$ Cl bond (as does  $\omega$ B97X-D to a lesser extent) and led us to prefer CCSD(T)-F12c and M06-2X calculations in Sections 3.2 to 3.4. The four calculations of the one-dimensional PE function all indicate that at the secondary minimum/point of inflection the distance  $r(\text{C}-\text{Cl})$  is in the range  $1.70 \pm 0.05 \text{ \AA}$ , which should be compared with the  $r(\text{C}-\text{Cl}) = 1.781 \text{ \AA}$  for the covalent bond in  $\text{CH}_3\text{Cl}$ .<sup>29</sup> Correspondingly, the distances  $r(\text{Cl}-\text{F})$  and  $r(\text{CO})$  are predicted to be lengthened by  $0.16(1) \text{ \AA}$  and  $0.005(1) \text{ \AA}$  at the secondary minima/points of inflections where the range of values is that resulting from the average over the calculations at the four levels of theory.

The evidence given in the preceding paragraphs can be interpreted in terms of a simple valence-bond approach. At the secondary minimum/point of inflection, the structure  $[\text{O}=\text{C}-\text{Cl}]^+\cdots\text{F}^-$  is

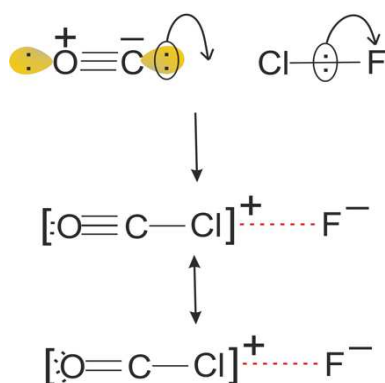


Figure 2. An  $\text{S}_{\text{N}}2$ -type mechanism for formation of the geometry found at the secondary minimum/point of inflection in the radial potential energy function of  $\text{OC}\cdots\text{ClF}$ .

assumed to make a significant contribution to the valence-bond description of the molecule. Contribution from this structure would result in a molecule with lengthened distances  $r(\text{ClF})$  and  $r(\text{CO})$ , with the latter change smaller in nature because of the higher bond order, and a significant decrease in the  $r(\text{C}-\text{Cl})$  distance because of formation of a  $\text{C}-\text{Cl}$  bond.

The formation of  $[\text{O}=\text{C}-\text{Cl}]^+\cdots\text{F}^-$  can be envisaged by means of the diagrams shown in Figure 2. According to Pauling,<sup>30</sup> the predominant valence-bond contribution to the electronic structure of carbon monoxide is that in Figure 2, with both C and O carrying a non-bonding electron pair and (formally at least) the indicated charges. Figure 2 is reminiscent of the  $\text{S}_{\text{N}}2$  mechanism proposed by Ingold.<sup>31</sup> As  $\text{OC}$  and  $\text{ClF}$  approach each other, there is, at a certain distance, the synchronous transfer of the non-bonding pair at C to form the  $\text{C}-\text{Cl}$  bond pair and

the transfer of the Cl–F bond pair to F to form F<sup>-</sup>. The double-headed arrow in Figure 2 indicates resonance between two valence-bond structures ascribed to the product. The [O=C–Cl]<sup>+</sup>...F<sup>-</sup> structure is also consistent with the Mulliken inner complex classification described in the Introduction.

### **3.2 Does the secondary minimum in the radial potential energy function of OC...ClF occur in other halogen- and hydrogen-bonded complexes?**

The one-dimensional potential energy functions  $V(r-r_e)$  versus  $(r-r_e)$  of the five axially symmetric complexes N<sub>2</sub>...ClF, OC...ClF, HCN...ClF, H<sub>3</sub>P...ClF and H<sub>3</sub>N...ClF were calculated in Ref. 1 at the CCSD(T)-F12c/cc-pVTZ-F12 level. Only the CO complex showed a secondary minimum. The hydrogen-bonded complexes B...HF formed by the same set of Lewis bases with hydrogen fluoride were similarly investigated. None showed the presence of a secondary minimum at small distances  $(r-r_e)$ , perhaps unsurprisingly given that HF has the strongest known single bond and requires much energy to extend it significantly to form [O=C–H]<sup>+</sup>...F<sup>-</sup>.

Perhaps, the molecule carbon monoxide is unique in respect of exhibiting secondary minima of the type  $[\text{O}=\text{C}-\text{Cl}]^+\cdots\text{F}^-$  in the radial potential energy function of complexes  $\text{B}\cdots\text{ClF}$ . To test this, we calculated this function for  $\text{SC}\cdots\text{ClF}$ , that is for the halogen-bonded complex in which the chalcogen atom O is replaced by its second row congener S. The result is shown in Figure 3. Again, the complex was constrained to be linear and points were calculated at 0.05 Å intervals in  $(r-r_e)$ , with optimization of  $r(\text{SC})$  and  $r(\text{ClF})$  at each point.

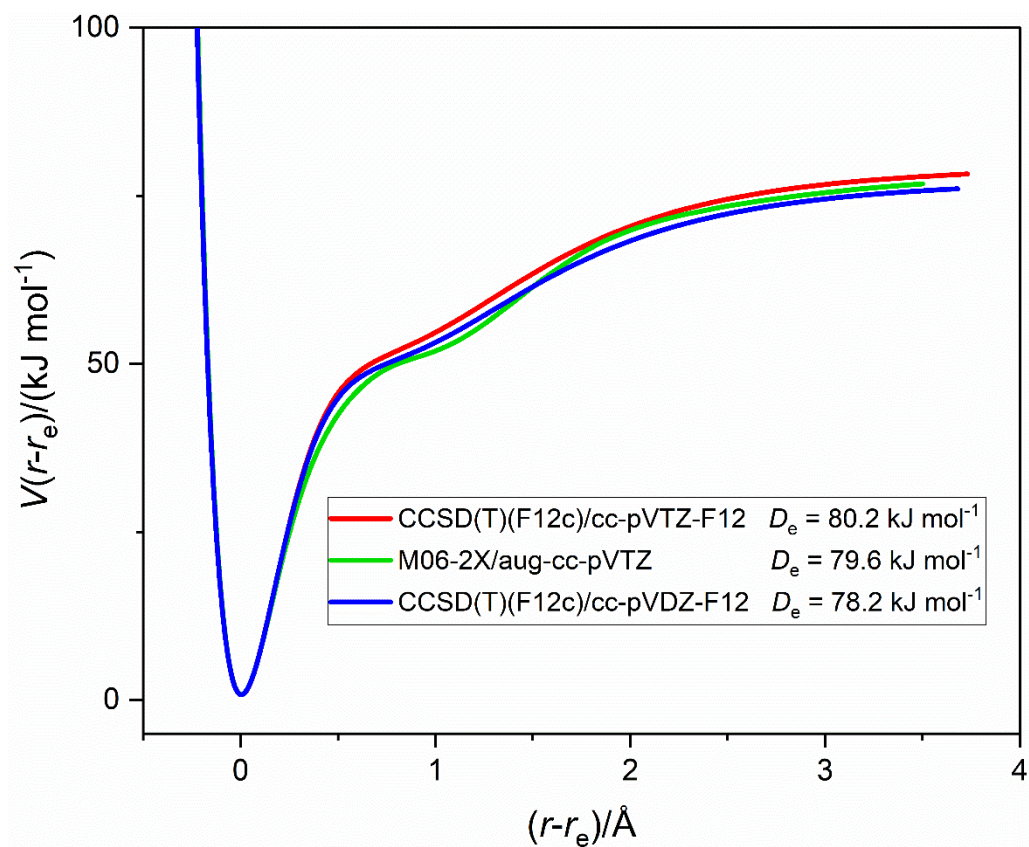


Figure 3. Radial potential energy function  $V(r-r_e)$  versus  $(r-r_e)$  of  $\text{SC}\cdots\text{ClF}$  calculated at the three indicated levels of theory. Points were calculated at 0.05 Å intervals, with optimization of other internuclear distances at each point and were joined by a spline function. Note the close agreement between the calculated dissociation energies  $D_e$ . The secondary minima now occur at  $r \approx 2.6$  Å while the primary minimum is at  $r \approx 1.61$  Å. Note that in this and following Figures energies are uncorrected for basis set superposition error.  $D_e$  in the Figures in this article is the energy required to take the complex  $\text{B}\cdots\text{ClF}$  from its hypothetical equilibrium state to infinitely separated components B and ClF, each in its hypothetical equilibrium state.

Figure 3 shows clearly that there is good agreement between the curves calculated by the DFT method and the explicitly correlated CCSD(T)-F12c method and that there is little difference in the latter case when the basis set is changed from cc-pVDZ-F12 to cc-pVTZ-F12. The values of  $r_e$  for the  $\text{SC}\cdots\text{ClF}$  complex are 1.6111, 1.6195 and 1.6189 Å at the M06-2X/aug-

cc-pVTZ and CCSD(T)-F12c/cc-pVnZ-F12 ( $n = 2$  and  $3$ ) levels, respectively. It is striking that although there is, as for  $\text{OC}\cdots\text{ClF}$ , evidence of a secondary minimum, it now occurs at ( $r_e$ )  $\approx 1$  Å or  $r \approx 2.6$  Å and clearly corresponds to the conventional, weakly bound, halogen-bonded species  $\text{SC}\cdots\text{ClF}$ . The primary minimum, on the other hand, occurs at  $r(\text{C}-\text{Cl}) = 1.6189$  Å (which is very short), the distance  $r(\text{Cl}-\text{F})$  is increased by  $0.27$  Å from the free ClF value, but the distance between S and C is changed by  $-0.01$  Å from free CS. Thus, the primary minimum now corresponds to an electronic structure, in valence bond terms, that has a significant contribution from the structure  $[\text{S}=\text{C}-\text{Cl}]^+\cdots\text{F}^-$ . The energy required to form infinitely separated CS and ClF from the primary minimum is large at  $D_e \approx 80$  kJ mol<sup>-1</sup> (uncorrected for BSSE), which is much larger than  $D_e = 13.7$  kJ mol<sup>-1</sup> (similarly calculated) for the dissociation process  $\text{OC}\cdots\text{ClF} = \text{OC} + \text{ClF}$  from its primary minimum. Both CS and CO have the sign of their electric dipole moments  $\mu$  corresponding to a positive charge on C,<sup>32</sup> but the magnitude of that of CS is much larger [ $1.958(5)$  D]<sup>33</sup> than the CO value of  $\mu = 0.1222$  D.<sup>34</sup> The greater polarity of CS is likely to lead to an increased preference for the ionic form.

The molecular electrostatic surface potentials (MESP) of CO and CS are revealing in understanding the differences in the behaviour of these molecules in complexes with Cl. The MESP is commonly defined as the potential energy of a unit charge on the isosurface at which the electron density is  $0.001$  e bohr<sup>-3</sup>. Figure 4 shows the MESPs at the  $0.001$  e bohr<sup>-3</sup> isosurface for CO and CS calculated at the M06-2X/6-311++G\*\* level. Part of the surface has been cut away to reveal the molecular model. We note for CS that the axial region of the isosurface near to C is highly negative (nucleophilic) and likely to undergo a strong interaction with the electrophilic axis region of ClF near to Cl (see Figure 4). The region on the axis near to S is highly electrophilic, however. The situation with CO is quite different. Both of the axial regions of the surface are negative and therefore nucleophilic. Thus, by examining the MESP of CO and CS, we predict that CO might form two isomeric complexes with the electrophilic region near Cl of ClF (the MESP of which is included Figure 4), namely  $\text{OC}\cdots\text{ClF}$  and  $\text{CO}\cdots\text{ClF}$ , with the second of these the more weakly bound.

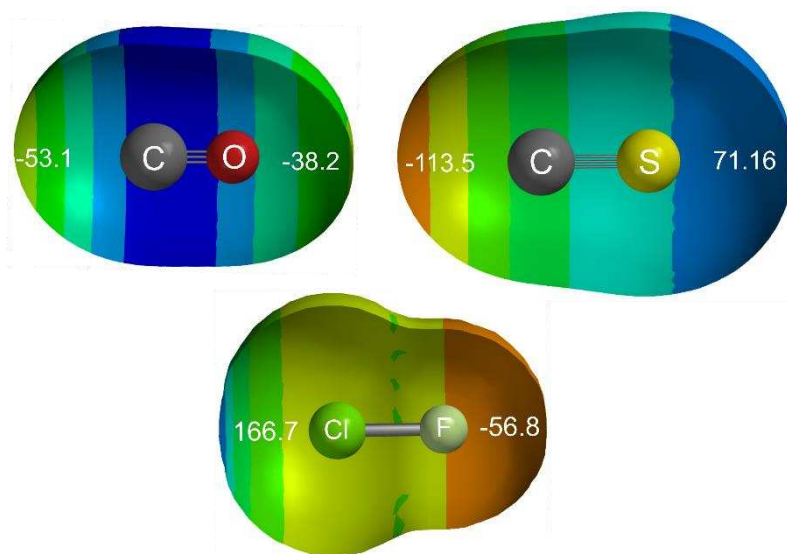


Figure 4. The MESP of carbon monoxide, carbon monosulfide and chlorine monofluoride calculated at the  $0.001 \text{ e bohr}^{-3}$  iso-surface at the M06-2X/6-311++G\*\* level. Colours at the blue end of the spectrum indicate the more positive (electrophilic) regions of the potential, while those towards the red indicate the more negative (nucleophilic) regions. The numbers in white are in  $\text{kJ mol}^{-1}$  and indicate the value of the MESP at the iso-surface on the molecular axis at each end of each molecule.

Displayed in Figure 5 are the radial potential energy functions of the complexes OC...CIF and CO...CIF [calculated at the CCSD(T)-F12c/cc-pVTZ-F12 level in 0.05 Å steps in  $r(X\cdots Cl)$ , X = C or O]. Note that the dissociation energies are consistent with the ratio of

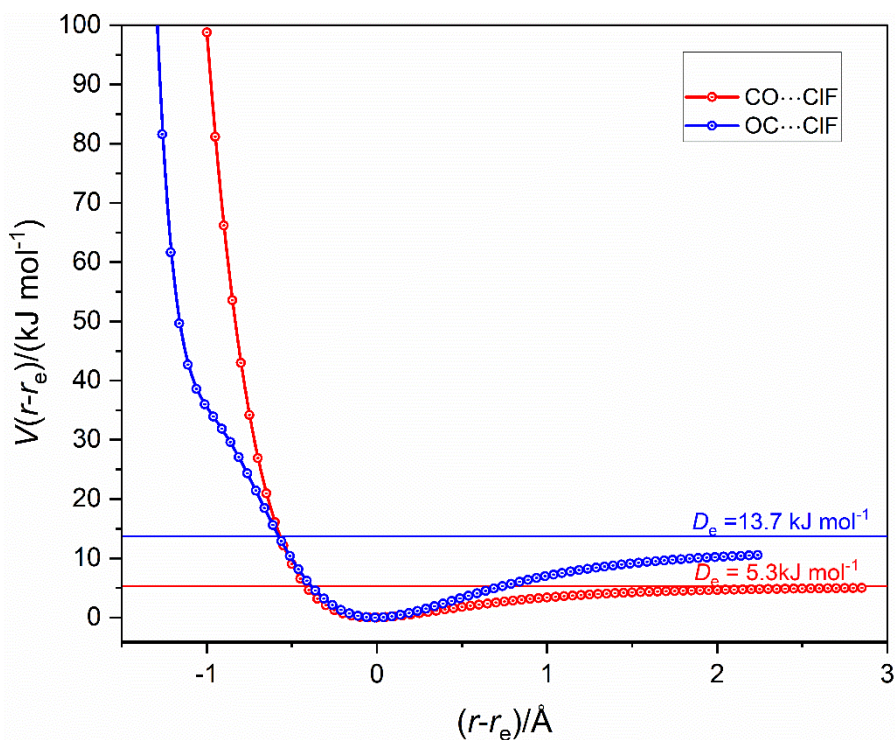


Figure 5. Radial potential energy functions  $V(r - r_e)$  versus  $(r - r_e)$  of the linear complexes OC...CIF and CO...CIF calculated at 0.05 Å intervals in  $r(X\cdots Cl)$  (X = C or O) at the CCSD(T)-F12c/cc-pVTZ-F12 level. The points are connected by a spline function.

the axial values of the MESP's near to C in OC...CIF and O in CO...CIF and that the curve for CO...CIF exhibits no secondary minimum. A similar approach to the SC...CIF and CS...CIF pair is not possible because the calculations at the CCSD(T)-F12c level reveal that CS...CIF is not even weakly bound and has  $D_e = -0.1 \text{ kJ mol}^{-1}$ , a result consistent with the highly electrophilic region of the MESP on the axis near to S.

### 3.3 What happens if C in the complexes OC...CIF and SC...CIF is replaced by its second row congener Si?

The diatomic molecules SiO and SiS (like CO and CS) are well characterised and all possess  $^1\Sigma$  ground states.<sup>35</sup> The MESP's of SiO and SiS calculated at the M06-2X/6-311++G\*\* level are given in Figure 6. The potentials on the axes near the O and S atoms are both

nucleophilic (negative, red) while on the axes near to Si both regions are electrophilic. Thus, we expect very weak complexes of the type  $\text{OSi}\cdots\text{ClF}$  and  $\text{SSi}\cdots\text{ClF}$ . The question of main interest is: will they nevertheless, like their carbon congeners, show a secondary minimum?

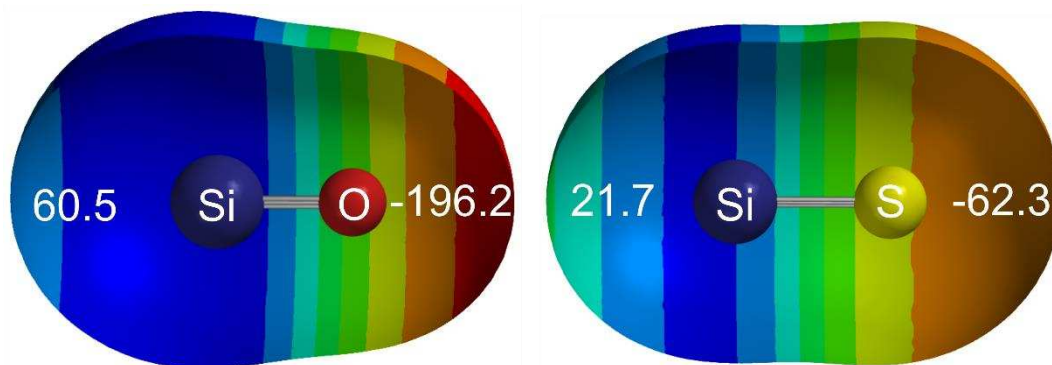


Figure 6. The MESP of silicon monosulfide and silicon monoxide calculated at the  $0.001 \text{ e bohr}^{-3}$  iso-surface at the M06-2X/6-311++G\*\* level. Colours at the blue end of the spectrum indicate the more positive (electrophilic) regions of the potential while red indicates the more negative (nucleophilic) regions. The values in white on the axes are in  $\text{kJ mol}^{-1}$  and indicate the values of the MESP on the iso-surface and on the axis at each end of each molecule. The deep red region is the most nucleophilic (most negative) while the dark blue region is the most electrophilic (most positive).

Graphs of the radial potential energy functions  $V(r-r_e)$  versus  $(r-r_e)$  for the two isomers  $\text{OSi}\cdots\text{ClF}$  and  $\text{SiO}\cdots\text{ClF}$  are in Figure 7. As previously, points were calculated at the CCSD(T)-F12c/cc-pVTZ-F12 level at  $0.05 \text{ \AA}$  intervals in the distance  $r(\text{Si}\cdots\text{Cl})$  or  $r(\text{O}\cdots\text{Cl})$ , as appropriate, and joined by a spline function. The corresponding diagram for the pair of complexes  $\text{SSi}\cdots\text{ClF}$  and  $\text{SiS}\cdots\text{ClF}$  is presented in Figure 8.

Figure 7 confirms that the behaviour of the complexes  $\text{OSi}\cdots\text{ClF}$  and  $\text{SiO}\cdots\text{ClF}$  parallels that of the pair in which Si is replaced by C. Thus, the radial PEF of  $\text{OSi}\cdots\text{ClF}$  has a secondary minimum at approximately  $(r-r_e) = -1 \text{ \AA}$ , presumably likewise arising from a complex with significant  $[\text{O}=\text{Si}-\text{Cl}]^+\cdots\text{F}^-$  character. In addition, the complex  $\text{SiO}\cdots\text{ClF}$  has, like its C atom counterpart, only a single minimum in the PE function, the only significant difference being that the dissociation energy  $D_e = 26.0 \text{ kJ mol}^{-1}$  in the case of the Si complex

is larger than that  $D_e = 4.5 \text{ kJ mol}^{-1}$  of the  $\text{OSi}\cdots\text{ClF}$  isomer, while the order is reversed for C in place of Si.

Figure 8 should be compared with Figure 3, which displays the radial PE function for the  $\text{SC}\cdots\text{ClF}$  complex. Recall that  $\text{CS}\cdots\text{ClF}$  was found to be unbound, unsurprisingly in view

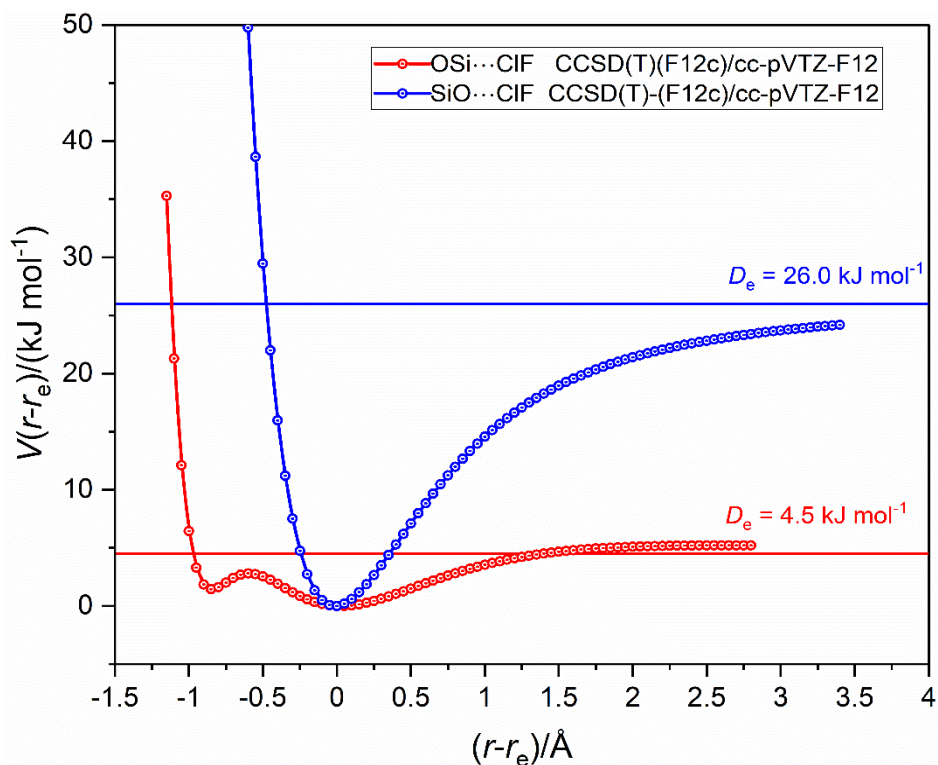


Figure 7. Radial potential energy functions of  $\text{OSi}\cdots\text{ClF}$  and  $\text{SiO}\cdots\text{ClF}$  calculated at  $0.05 \text{ \AA}$  intervals in  $r(\text{X}\cdots\text{Cl})$  ( $\text{X} = \text{Si}$  or  $\text{O}$ ) at the  $\text{CCSD(T)-F12c/cc-pVTZ-F12}$  level. The points are connected with a spline function.

of the very large positive axial value of the MESP near S. Clearly, the radial PE functions for  $\text{SC}\cdots\text{ClF}$  and  $\text{SSi}\cdots\text{ClF}$  considered here are very similar. Both show a shallow secondary minimum at  $(r-r_e) = 1$  and much deeper minima at  $r_e = 1.6189$  and  $1.9347 \text{ \AA}$ , with  $D_e$  values of

$80.2$  and  $29.6 \text{ kJ mol}^{-1}$ . Thus, in these cases the primary minimum also corresponds to a molecule in which the Mulliken inner complex structure  $[\text{S}=\text{T}-\text{Cl}]^+\cdots\text{F}^-$  ( $\text{T} = \text{a Group 14 atom C or Si}$ ) makes a substantial contribution to the overall wavefunction. The value ( $-62.3 \text{ kJ mol}^{-1}$ , see Figure 6) of the axial MESP near to the S atom of  $\text{SiS}$  is negative and therefore nucleophilic while that near S in  $\text{CS}$  is positive ( $71.2 \text{ kJ mol}^{-1}$ , electrophilic, see Figure 4).

Consequently, while  $\text{CS}\cdots\text{ClF}$  is not bound,  $\text{SiS}\cdots\text{ClF}$  is ( $D_e = 9.1 \text{ kJ mol}^{-1}$ ). We note again that the radial PE functions of both  $\text{SiO}\cdots\text{ClF}$  and  $\text{SiS}\cdots\text{ClF}$ , in which a chalcogen atom is directly involved in the halogen bond, possess only a single minimum, as is the case for  $\text{CO}\cdots\text{ClF}$ .

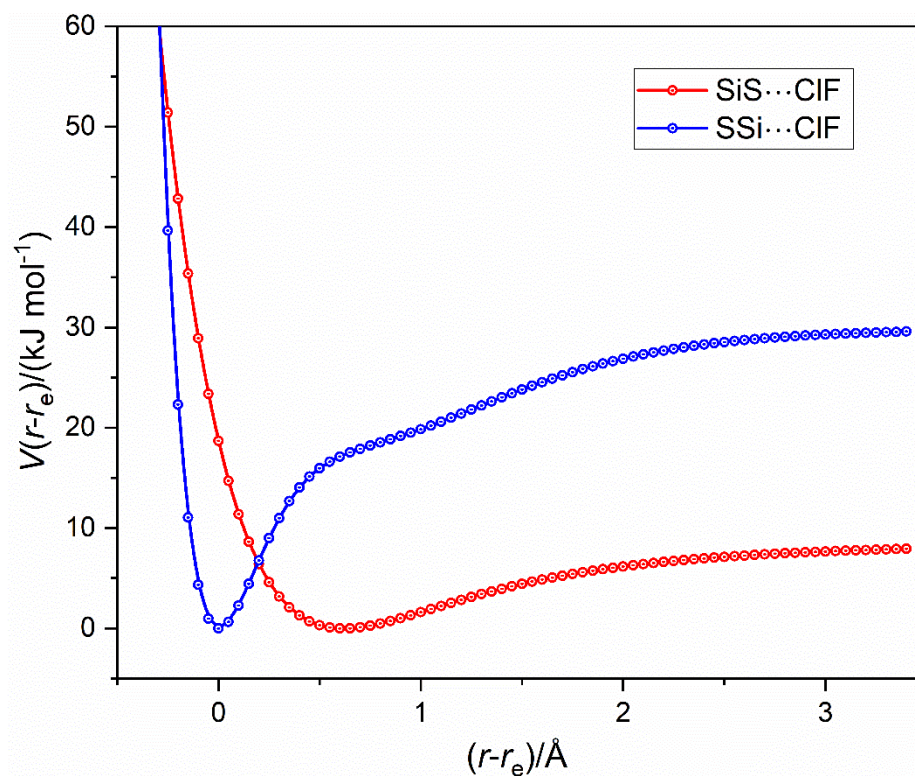


Figure 8. Radial potential energy functions of  $\text{SSi}\cdots\text{ClF}$  and  $\text{SiS}\cdots\text{ClF}$  calculated at  $0.05 \text{ \AA}$  intervals in  $r(\text{X}\cdots\text{Cl})$  ( $\text{X} = \text{Si}$  or  $\text{S}$ ) at the CCSD(T)-F12c/cc-pVTZ-F12 level. The points are connected with a spline function.

The conclusion from the present work is that the presence of secondary minima in the radial potential energy functions of halogen-bonded complexes formed with ClF as the halogen donor can be predicted from the MESP maps, and, from the complexes investigated, such secondary minima only occur when the halogen bond is formed to one of the Group 14 atoms C or Si.

Possible explanations of the observations made in Sections 3.2 and 3.3 will be advanced in Section 3.5.

### 3.4 The isoelectronic series $\text{FB}\cdots\text{ClF}$ , $\text{OC}\cdots\text{ClF}$ and $\text{N}_2\cdots\text{ClF}$

The diatomic molecules FB, CO and NN are isoelectronic, each has at least some triple bond character and a  $^1\Sigma^+$  ground state.<sup>35</sup> The radial potential energy functions of OC...CIF and N<sub>2</sub>...CIF calculated at the CCSD(T)-F12c/cc-pVTZ-F12 level have been discussed in an earlier publication.<sup>1</sup> The function for OC...CIF (as already discussed) has a secondary minimum that can be attributed to a Mulliken inner complex structure of the type [O=C-Cl]<sup>+</sup>...F<sup>-</sup>. Moreover, it was shown that on replacing C by the Group 14 second row atom Si this behaviour persists. In the present section, the effect of moving from OC...CIF along an isoelectronic series to either FB...CIF in one direction along the first row of the Periodic Table or to N<sub>2</sub>...CIF in the other direction is considered.

The radial potential energy of FB...CIF was calculated as a function of the internuclear distance  $r(\text{B}\cdots\text{Cl})$ . The energy calculations were conducted at two levels of theory, namely CCSD(T)-

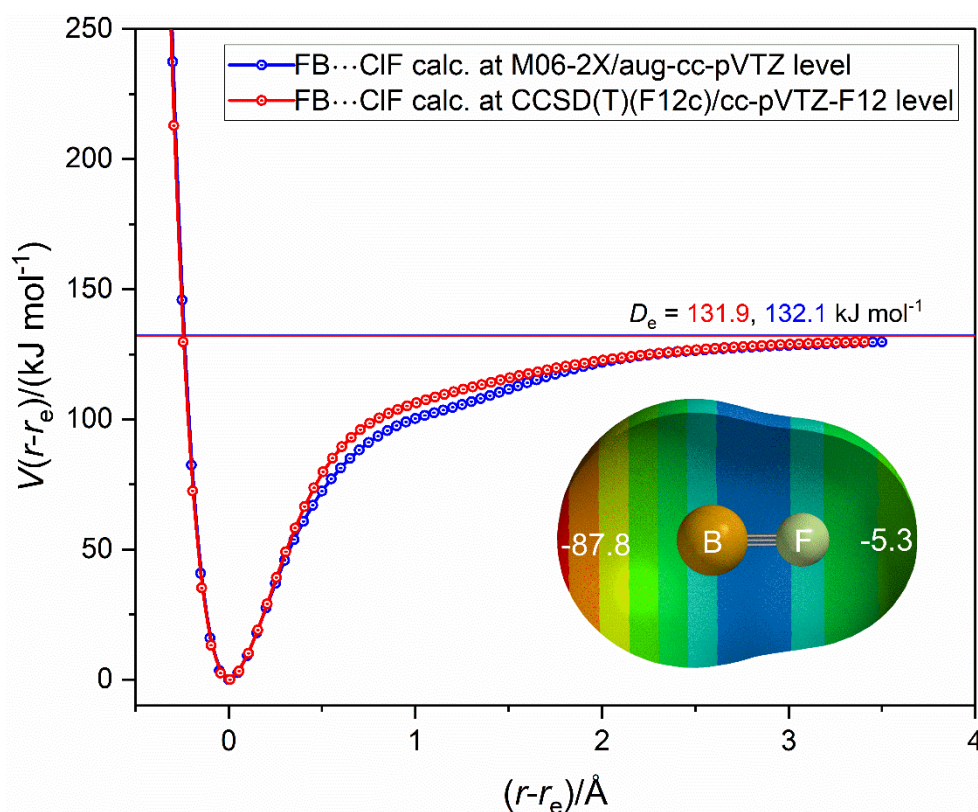


Figure 9. The radial potential energy function  $V(r-r_e)$  versus  $(r-r_e)$  of FB...CIF calculated at two different levels of theory. Points were calculated at  $0.05 \text{ \AA}$  intervals and joined by a spline function. The inset is the MESP of BF calculated at the M06-2X/6-311++G\*\* level of theory on the  $0.001 e \text{ bohr}^{-3}$  iso-surface. The numbers in white are the values (in  $\text{kJ mol}^{-1}$ ) of the MESP at the surface and on the molecular axis.

F12c/cc-pVTZ-F12 and M06-2X/aug-cc-pV(T+d)Z. For convenience of comparison, the potential energy  $V(r-r_e)$  plotted against  $(r-r_e)$  for each is displayed in Figure 9. Also shown in Figure 9 is the MESP  $0.001e \text{ bohr}^{-3}$  iso-surface for FB calculated at the M06-2X/6-311++G\*\*level. The surface potential on the molecular axis and outside the B atom is large, negative and therefore likely to be highly nucleophilic.

Both functions in Figure 9 have a very deep primary minimum at  $r_e \approx 1.64 \text{ \AA}$ , with an equilibrium dissociation energy  $D_e = 132 \text{ kJ mol}^{-1}$  and the hint of a very shallow secondary minimum at  $(r-r_e) \approx 1 \text{ \AA}$  and therefore  $r \approx 2.64 \text{ \AA}$ .

Figure 10 shows a plot of  $V(r)$  versus  $r$ , where  $r$  is the distance  $r(X \cdots \text{Cl})$  between the atom  $X$  ( $= \text{B}, \text{C}$  or  $\text{N}$ ) directly adjacent to  $\text{Cl}$  of  $\text{ClF}$  in the complexes  $\text{FB} \cdots \text{ClF}$ ,  $\text{OC} \cdots \text{ClF}$  or  $\text{N}_2 \cdots \text{ClF}$ , respectively. This method of presentation shows clearly how much shorter is the equilibrium distance  $r_e(\text{B} \cdots \text{Cl}) = 1.6439 \text{ \AA}$  than those of its counterparts  $\text{OC} \cdots \text{ClF}$  and  $\text{N}_2 \cdots \text{ClF}$ . Moreover, it illustrates that the secondary minimum occurs in the repulsive part of the  $\text{OC} \cdots \text{ClF}$  function but coincides with the primary minimum of  $\text{FB} \cdots \text{ClF}$ . This adds weight to the argument that such minima correspond to molecules in which the Mulliken inner

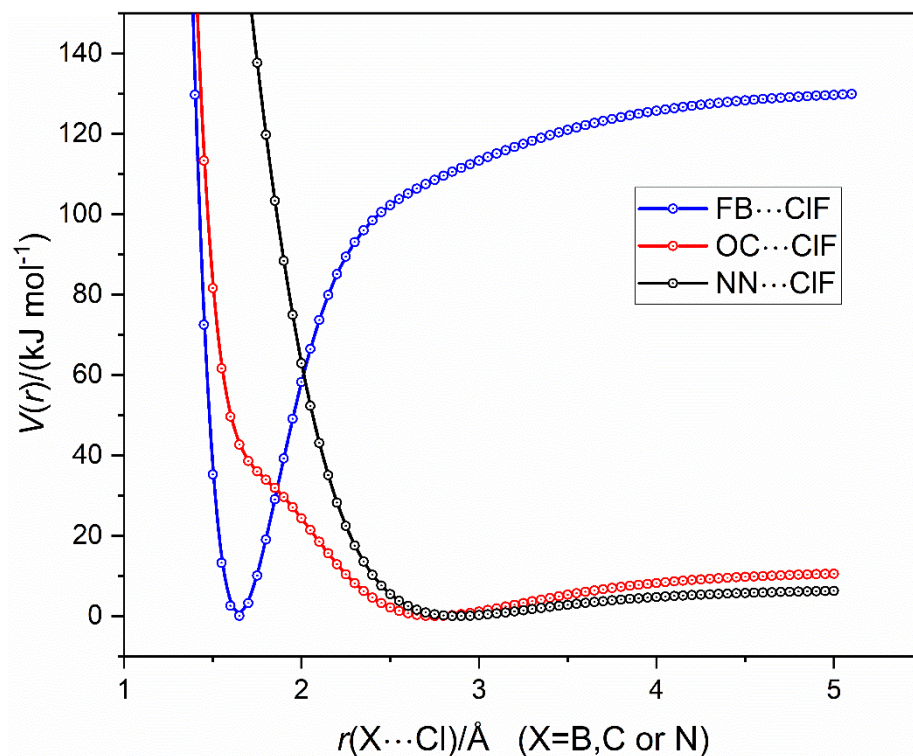


Figure 10. Radial PE curves  $V(r)$  versus  $r(X\cdots Cl)$  for  $FB\cdots ClF$ ,  $OC\cdots ClF$  and  $N_2\cdots ClF$  calculated at the CCSD(T)-F12c/cc-pVTZ-F12 level. For the MESP of BF, CO and  $N_2$  on the  $0.001 e bohr^{-3}$  iso-surface, as calculated at the M06-2X/6-311++G\*\* level, see Figures 9, 4 and 12, respectively.

complex structures  $[F=B-Cl]^+\cdots F^-$  and  $[O=C-Cl]^+\cdots F^-$  make a major contribution. The secondary minimum in the case of the  $FB\cdots ClF$  potential energy curve is just detectable and occurs at the same distance  $r$  as the primary minima of  $OC\cdots ClF$  and  $N_2\cdots ClF$ , thereby reinforcing the conclusion that this minimum corresponds to the simple halogen-bonded complex  $FB\cdots ClF$  formed first when ClF approaches FB but rapidly destroyed again as the distance  $r(B\cdots Cl)$  decreases further. On the other hand, it is noted that no secondary minimum occurs in the repulsive part of the  $N_2\cdots ClF$  potential. Evidently, no structure of the type  $[N=N-Cl]^+\cdots F^-$  is encountered in the approach of ClF to  $N_2$ . An explanation of why no minima of the Mulliken inner type of complex is observed will be offered in Section 4.

It is of interest to compare the counterpart of the  $\text{FB}\cdots\text{ClF}$ ,  $\text{OC}\cdots\text{ClF}$ ,  $\text{N}_2\cdots\text{ClF}$  series in which the atom directly involved in forming the halogen bond with ClF is replaced by the second row atom of the same group in the periodic table, that is the series  $\text{FAI}\cdots\text{ClF}$ ,  $\text{OSi}\cdots\text{ClF}$  or  $\text{NP}\cdots\text{ClF}$ . The values of the dissociation energy  $D_e$  are 69.4, 4.5 and 0.3  $\text{kJ mol}^{-1}$ , respectively, (all uncorrected for BSSE), when calculated at the CCSD(T)-F12c/cc-pVTZ-F12 level. Clearly,  $\text{NP}\cdots\text{ClF}$  must be considered unbound, but the radial potential energy functions of  $\text{FAI}\cdots\text{ClF}$  and  $\text{OSi}\cdots\text{ClF}$  calculated at this level of theory can be compared and these are set

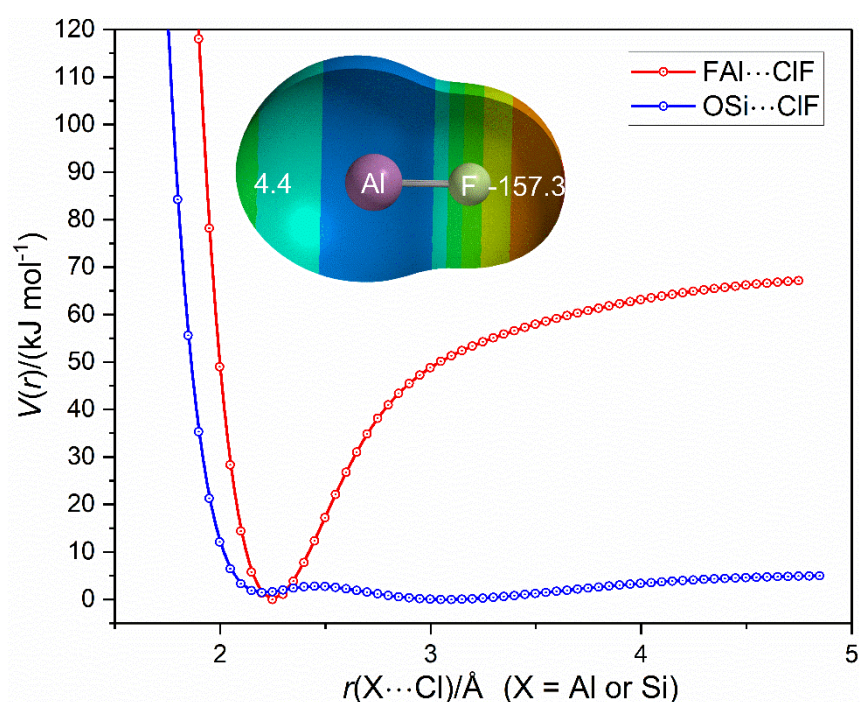


Figure 11.  $V(r)$  versus  $r(\text{X}-\text{Cl})$  for  $\text{FAI}\cdots\text{ClF}$  and  $\text{OSi}\cdots\text{ClF}$  calculated at the CCSD(T)-F12c/cc-pVTZ-F12 level. The primary minima for the two complexes are at  $r_e = 2.194$  and  $3.0480 \text{ \AA}$ , respectively. The MESP at  $0.001 \text{ e bohr}^{-3}$  iso-surface of  $\text{AlF}$ , as calculated at the M06-2X/6-311++G\*\* level, is shown inset, and can be compared with that similarly calculated for  $\text{SiO}$  in Figure 6.

out in Figure 11. The relationship of the two potential curves is similar to that observed for  $\text{FB}\cdots\text{ClF}$  and  $\text{OC}\cdots\text{ClF}$  shown in Figure 10.

It remains to examine the relationship between  $\text{N}_2$  and  $\text{NP}$  and understand why the complex of the latter with ClF is essentially unbound. Figure 12 displays the MESP of  $\text{N}_2$  and  $\text{PN}$ , at the  $0.001 \text{ e bohr}^{-3}$  iso-surface in each case, both calculated at the M06-2X/6-311++G\* level of theory. The MESP of  $\text{NP}$  has axial values of 94.4 and  $-153.1 \text{ kJ mol}^{-1}$  at the P and N ends, respectively. Thus, it is clear that the P end of  $\text{NP}$  is highly electrophilic (positive) and it is

therefore not surprising that the complex  $\text{NP}\cdots\text{ClF}$  is essentially unbound when P is interacting with the electrophilic Cl end of ClF (see Figure 4 for the MESP of ClF). On the other hand, the N end of NP is highly nucleophilic compared with the corresponding region in  $\text{N}_2$  and therefore the complex  $\text{PN}\cdots\text{ClF}$  is more strongly bound than  $\text{N}_2\cdots\text{ClF}$ .

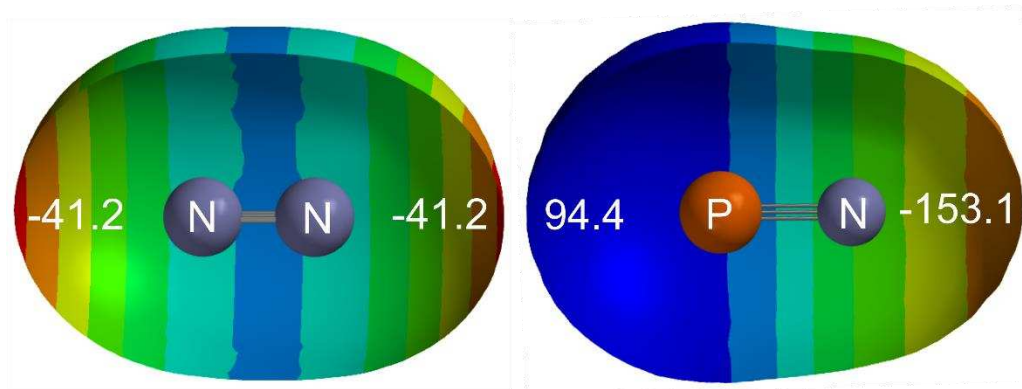


Figure 12. The MESP of  $\text{N}_2$  and  $\text{PN}$  at their  $0.001 \text{ e bohr}^{-3}$  iso-surfaces. These were calculated at the M06-2X/6-311++G\*\* level of theory using Spartan 20. The numbers in white give the MESP (in  $\text{kJ mol}^{-1}$ ) at the point where the molecular axis intersects the iso-surface.

The radial potential energy curves of  $\text{N}_2\cdots\text{ClF}$  and  $\text{PN}\cdots\text{ClF}$  calculated at the CCSD(T)-F12c/cc-pVTZ-F12 level are displayed in Figure 13. The comparisons in Figures 12 and 13 confirm the conclusion drawn earlier, namely: if the atom Y of a diatomic molecule YX consisting of a pair of first-row atoms is substituted by its second row analogue, the binding strength of  $\text{YX}\cdots\text{ClF}$  increases. We note also from Figure 13 that, like  $\text{N}_2\cdots\text{ClF}$ ,  $\text{PN}\cdots\text{ClF}$  has only a single minimum in its radial PEF.

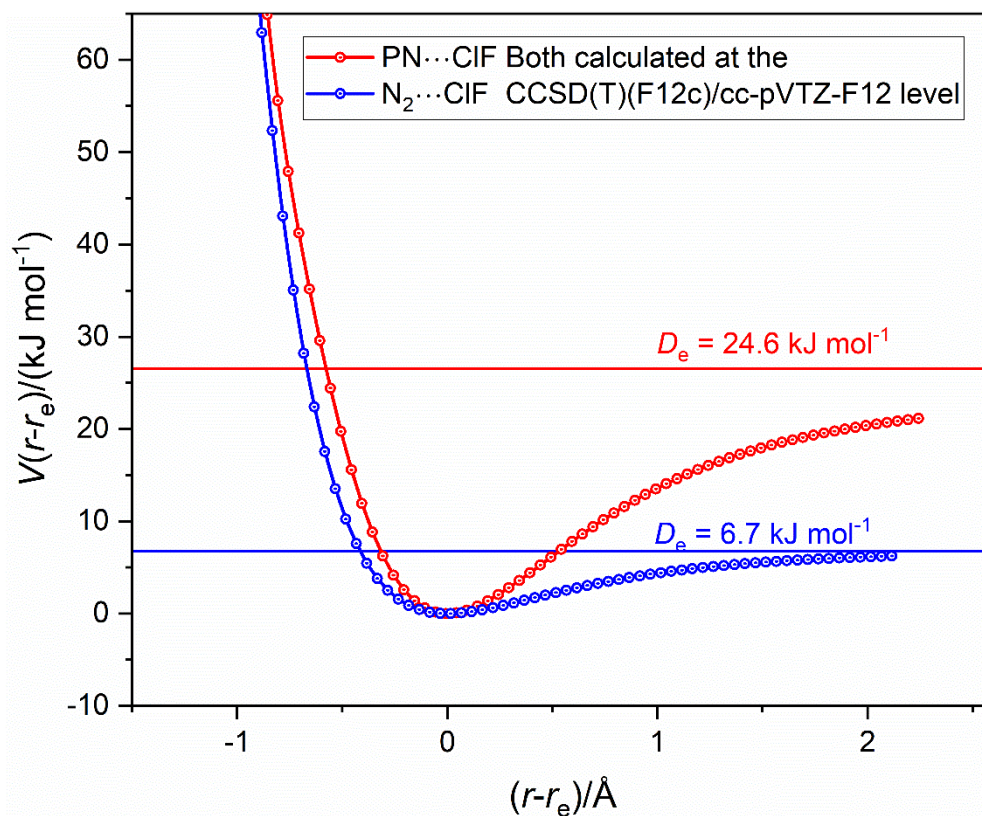


Figure 13. A comparison of the radial PE functions of  $\text{N}_2 \cdots \text{CIF}$  and  $\text{PN} \cdots \text{CIF}$  calculated at the CCSD(T)-F12c/cc-pVTZ-F12 level of theory.

### 3.5 SAPT and NBO analyses of complexes $\text{B} \cdots \text{CIF}$ .

Further insights into the underlying nature of the interaction in both the primary and secondary minima of the series  $\text{B} \cdots \text{CIF}$  are provided by using SAPT calculations to decompose the interaction energies into a “chemist’s grouping”, with the results given in Tables S1 and S2 of the Supporting Information. Comparisons of the SAPT interaction energies with those from counterpoise-corrected CCSD(T)-F12c/cc-pVTZ-F12 are shown in Tables S3 and S4. In general, there is a very good level of agreement between the two methods, although the level of SAPT chosen does appear to underestimate the strength of the interaction for the most strongly bound complexes. As an explicitly correlated coupled-cluster methodology was used, some of this difference is presumably due to basis set incompleteness errors. The basis set superposition error (BSSE) at the CCSD(T)-F12c/cc-pVTZ-F12 level is also shown in Tables S3 and S4, where the BSSE is typically between one and two orders of magnitude smaller than the interaction energy, justifying the decision not to include a counterpoise correction in the calculation of the radial potential energy functions.

Table 1. SAPT decomposition of the attractive components of the B...CIF interaction energy for the primary minima as percentages of the total of the attractive terms.

B	Electrostatic (%)	Induction (%)	Dispersion (%)	Charge-transfer (%)	$E_1$ (kJ mol <sup>-1</sup> )
OC	47.59	20.12	26.65	5.64	-11.06
CO	37.55	11.51	46.86	4.08	-5.01
SC	45.33	25.75	9.06	19.85	-133.23
SiS	34.28	22.97	37.68	5.07	-8.76
SSi	39.62	27.11	10.45	22.82	-80.76
OSi	28.84	34.71	28.48	7.98	-2.98
SiO	51.28	20.43	21.84	6.45	-26.07
FB	43.00	23.24	8.43	25.32	-211.85
N <sub>2</sub>	43.66	13.64	38.50	4.20	-6.47
PN	50.66	21.75	21.24	6.34	-22.71

The SAPT decomposition of the attractive components of the B...CIF interaction energy are presented as percentages of the total of the attractive terms in Tables 1 and 2, for the primary and secondary minima, respectively. Focusing momentarily on the primary minima, the interaction energies of the complexes SC...CIF, SSi...CIF, and FB...CIF are immediately striking due to their strength. It should be noted that these are interaction energies and hence are missing the energetic effects of distorting the “monomers” from their isolated geometries and are not directly comparable to the analogous dissociation energies presented earlier. Inspecting the contribution of the attractive components within these interaction energies it is clear that the three strongly bound complexes all have significantly increased charge-transfer and reduced dispersion when compared to the primary minima of the other complexes. This supports the designation of Mulliken inner complexes, where structures of the type [B-Cl]<sup>+</sup>...F<sup>-</sup> would make a significant contribution to an overall valence bond wavefunction. Table 1 also indicates that the dispersion contribution to the interaction energy is greater than the electrostatic contribution for the primary minimum of complexes CO...CIF and SiS...CIF, and dispersion also makes a large contribution to OSi...CIF and N<sub>2</sub>...CIF.

Table 2. SAPT decomposition of the attractive components of the B...ClF interaction energy for the secondary minima as percentages of the total of the attractive terms. No secondary minimum was located when CO, SiS, SiO, N<sub>2</sub> or PN were acting as the Lewis base B.

B	Electrostatic (%)	Induction (%)	Dispersion (%)	Charge-transfer (%)	$E_1$ (kJ mol <sup>-1</sup> )
OC	45.90	26.65	10.90	16.55	+7.86 <sup>†</sup>
SC	50.81	20.71	23.19	5.28	-22.05
SSi	35.76	33.09	23.05	8.10	-10.08
OSi	38.24	29.28	11.80	20.68	-28.66
FB	46.43	28.22	18.42	6.93	-22.73

<sup>†</sup>SAPT2+(3)(CCD) $\delta$ MP2/aug-cc-pV(T+d)Z indicates this complex to be unbound.

The SAPT decompositions of the secondary minima shown in Table 2 show a similar pattern; those complexes previously identified as having Mulliken inner complex character in their secondary minimum, namely OC...ClF and OSi...ClF, have increased charge-transfer and reduced dispersion contributions. It should be noted that the OC...ClF secondary minimum has a positive interaction energy, which is consistent with the secondary minimum being in the repulsive part of the radial potential energy curve in Figure 10. Comparing Tables 1 and 2 reveals that the secondary minimum of OSi...ClF has a stronger interaction energy than the primary minimum. While this seems initially inconsistent with Figure 7, this is again due to the neglect of relaxation energy when considering interaction energy rather than dissociation energy.

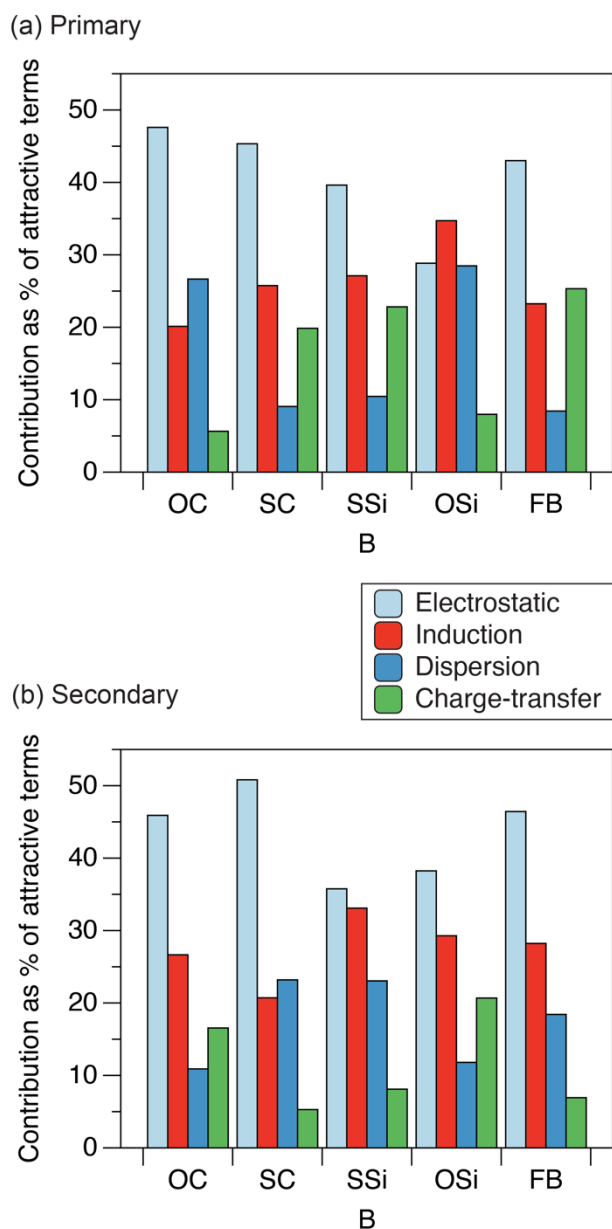


Figure 14. Individual attractive SAPT components of the B...ClF interaction energy as a percentage of the total of the attractive terms. Only the intermolecular complexes found to have both primary and secondary minima are shown.

Figure 14 compares the SAPT components of the interaction energy for those complexes where both primary and second minima have been found, showing how the underlying nature of the interaction changes between the two minima. For those complexes with a strongly bound primary minimum, SC...ClF, SSi...ClF, and FB...ClF, the decrease in charge-transfer and increase in dispersion on going from the primary to secondary minimum is clearly visible. As

expected, OC...CIF and OSi...CIF show this same trend on going from the secondary to the primary minimum. Changes to the other components of the interaction energy are present, but generally less dramatic.

Further evidence for the change in the underlying nature of the interaction in the complexes with both primary and secondary minima can be found from the NBO derived natural population analysis, summarised in Table 3. The values presented are the partial charges located on the FCI subunit of the complex, with the partial charge on the Lewis base subunit equal in magnitude, but opposite in sign (not shown). SC...CIF, SSi...CIF, and FB...CIF show relatively large partial charges for the primary minimum, which is significantly reduced in the respective secondary minimum. Meanwhile, the secondary minimum for OC...CIF and OSi...CIF has a large partial charge, which becomes almost negligible for the primary minimum. This is consistent with the trends in charge-transfer from the SAPT analysis above, and with these minima of the complexes possessing significant  $[B-Cl]^+ \cdots F^-$  character (Mulliken inner complexes). For those complexes where no secondary minimum was located, the partial charges are negligibly small in all cases.

Table 3. NBO derived natural population analysis (NPA) partial charges on FCI in the complex B...CIF. No secondary minimum was located when CO, SiS, SiO, N<sub>2</sub> or PN were acting as the Lewis base.

B	NPA partial charge on CIF (e)	
	Primary minimum	Secondary minimum
OC	-0.03	-0.25
CO	0.00	---
SC	-0.15	-0.03
SiS	-0.01	---
SSi	-0.55	-0.08
OSi	-0.06	-0.48
SiO	-0.03	---
FB	-0.53	-0.09
N <sub>2</sub>	-0.01	---
PN	-0.04	---

Inspection of the NBO second-order perturbation theory analysis indicates that, for the six minima identified as Mulliken inner complexes above, the electron density is being partitioned as  $[YX-Cl]^+ \cdots F^-$ , with significant intermolecular interactions where the lone pair on F is donated into an antibonding X-Cl orbital. All remaining minima have the  $YX \square ClF$  structure with a Cl lone pair donating into an antibonding Y-X orbital, adding further weight to the above classification of Mulliken inner or outer complexes.

## 4 CONCLUSIONS

The main conclusions concerning the radial potential energy functions of the  $YX \cdots ClF$  complexes considered in this article are conveniently summarized in Table 4. Also included in Table 4 are: the dissociation energy  $D_e$  for the process  $YX \cdots ClF \rightarrow YX + ClF$ , as calculated here at the CCSD(T)-F12c/cc-pVTZ-F12 level, the dissociation energy  $D_e$  of  $ClF$ ,<sup>36,37</sup> typical values of  $\Delta H(X-Cl)$  for the dissociation of X-Cl covalent bond,<sup>38</sup> the structure from Mulliken's classification (inner or outer complex), and some comments.

It is assumed that as  $ClF$  approaches  $YX$  from an infinite  $r(X \cdots Cl)$  distance, a halogen-bonded system of the type  $YX \cdots ClF$  is first encountered at separations of about 3 Å. This corresponds to a minimum in the radial PE curve. As  $r(X \cdots Cl)$  decreases further one of two things can happen. First, if the energy required to dissociate  $ClF$  into atoms and then to produce the ions  $Cl^+$  and  $F^-$  is smaller than the energy gain  $\Delta E(X-Cl)$  through formation of the X-Cl covalent bond in the ion  $[Y=X-Cl]^+$  then another minimum in the radial PEF corresponding to a species in which the Mulliken inner complex structure  $[Y=X-Cl]^+ \cdots F^-$  makes a significant contribution to its electronic structure will be encountered. The larger the energy gain, presumably the deeper will be this minimum. If, on the other hand, the energy  $\Delta E(X-Cl)$  returned by formation of the X-Cl bond in  $[Y=X-Cl]^+$  is insufficient, the Mulliken inner complex structure  $[Y=X-Cl]^+ \cdots F^-$  will not contribute significantly and the energy of the system will merely rise as exchange repulsion sets in. Both types of result have been encountered in the investigations reported here. Further evidence for the Mulliken inner or outer complex nature has also been provided by natural population

analysis at the minima, and from SAPT decomposition of the interaction energy, which shows clear changes in the underlying nature of the interaction.

Calculation of  $\Delta E(X-Cl)$  requires, *inter alia*, knowledge of the detailed electric charge distributions of both YX and ClF as well as that in the ion  $[Y=X-Cl]^+$ , ionisation potentials, electron affinities, polarisation effects, and van der Waals energy, and is beyond the scope of the present work. Nevertheless, it is interesting to compare the  $D_e$  values for the process  $ClF = Cl + F$  and  $\Delta H(X-Cl)$  for the formation  $X + Cl = X-Cl$  of a typical XCl bond. The former is accurately known while a useful compilation of the latter is available.<sup>38</sup> The appropriate values are included in Table 4. It is immediately obvious from Table 4 that when  $\Delta H(X-Cl)$  is significantly greater than  $D_e(ClF)$ , the primary minimum in the radial PEF corresponds to a molecule in which the Mulliken inner complex structure is important. When combined with an YX molecule in which the MESP has a large negative value at the X end of the molecule, this leads to very deep minima, as is the case when YX = SC, FB or FAI. These show weaker minima, corresponding to simple chlorine-bonded species  $YX \cdots ClF$  at larger  $r(X \cdots Cl)$ . When  $\Delta H(X-Cl)$  is closer to  $D_e(ClF)$ , there can still be two minima but the depths of the primary and secondary minima are more nearly equal, as is the case for XY = OC, OSi and SSi. We also note from Table 4 that when  $\Delta H(X-Cl) < D_e(ClF)$  only single minima corresponding to the simple halogen bonded species  $XY \cdots ClF$  are observed. This is true for  $CO \cdots ClF$ ,  $SiO \cdots ClF$ ,  $N_2 \cdots ClF$ , and  $PN \cdots ClF$ .  $CS \cdots ClF$  and  $NP \cdots ClF$  are unbound at the level of calculation employed. Thus, it appears that the formation of N-Cl, O-Cl and S-Cl bonds does not provide sufficient energy for the formation of complexes of the type  $[Y=X-Cl]^+ \cdots F^-$  (X = N, O, S or P). These are conclusions based on the simple correlation mentioned earlier and the must be treated cautiously in view of the neglect of the contributions described. Nevertheless, at that level of approximation, it is concluded that the ion-pair type minima occur when X = B, Al, C and Si because of the strength of B-Cl, Al-Cl, C-Cl, and Si-Cl bonds but not for X = N, P, O and S.

Table 4. Summary of conclusions concerning the radial potential energy functions of YX...CIF

Complex YX...CIF	$D_e(\text{XY}\cdots\text{CIF})$ /kJ mol <sup>-1a</sup>	$D_e(\text{CIF})$ / kJ mol <sup>-1. b</sup>	$\Delta H(\text{X-Cl})$ / kJ mol <sup>-1. c</sup>	Mulliken classification structure (inner or outer complex)		Comments
				Primary	Secondary	
OC...CIF	13.7	257.2	330	OC...CIF	[O=C-Cl] <sup>+</sup> ...F <sup>-</sup>	MESP shows CO is axially binucleophilic. Strong energy gain by forming C-Cl bond.
CO...CIF	5.3		205	CO...CIF	none	No gain in energy by forming O-Cl covalent bond in CO...CIF
SC...CIF	80.2	257.2	330	[SC-Cl] <sup>+</sup> ...F <sup>-</sup>	SC...CIF	MESP of CS is strongly nucleophilic at C end. There is net energy gain for breaking CIF bond and making C-Cl bond. S end of CS wholly electrophilic and no significant energy gain by breaking CIF bond and forming S-Cl bond.
CS...CIF	~0		250	unbound	none	
OSi...CIF	4.5	257.2	359	OSi...CIF	[O=Si-Cl] <sup>+</sup> ...F <sup>-</sup>	MESP of SiO is electrophilic on axis near Si, so OSi...CIF weakly bound. Net gain in energy by forming Si...Cl bond.
SiO...CIF	26.0		205	SiO...CIF	none	Strongly nucleophilic at O end but no energy gain if [SiO-Cl] <sup>+</sup> ...F <sup>-</sup> were to be formed.
SSi...CIF	29.6	257.2	359	[S=Si-Cl] <sup>+</sup> ...F <sup>-</sup>	SSi...CIF	Si end of SiS is electrophilic but strong energy gain by breaking CIF bond and forming Si-Cl bond.
SiS...CIF	9.1		250	SiS...CIF	none	S end is strongly nucleophilic but no net energy gain by forming S-Cl bond. Hence a single minimum which corresponds to SiS...CIF
FB...CIF	131.9	257.2	494(40)	[F=B-Cl] <sup>+</sup> ...F <sup>-</sup>	F≡B...CIF	Huge energy gain by breaking CIF and making B-Cl or Al-Cl bond. Deep minima for inner complex forms
FAI...CIF	69.4	257.2	487(7)	[F=Al-Cl] <sup>+</sup> ...F <sup>-</sup>	F≡Al...CIF	Large energy gain when Al-Cl bond is formed, [FAl-Cl] <sup>+</sup> ...F <sup>-</sup> at primary min. Secondary min. at FAI...CIF
N <sub>2</sub> ...CIF	6.7	257.2	200	NN...CIF	none	N ends of N <sub>2</sub> and NP are nucleophilic. No energy gain by breaking CIF and making N-Cl bond. No secondary minimum. Only minimum is halogen bond in each case. P end of NP is wholly electrophilic. No energy gain by breaking CIF and making P-Cl bond.
PN...CIF	24.6		200	PN...CIF	none	
NP...CIF	unbound		264(40)	none	none	

complexes.

<sup>a</sup> Values of  $D_e$  are those displayed in the appropriate Figures and are therefore uncorrected for BSSE.

<sup>b</sup> Data from Refs. 36,37.

<sup>c</sup> Data from Ref. 38.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/>.....

1. Grouping of SAPT terms: Tables S1 and S2
2. Comparison of Interaction energies: Tables S3 and S4

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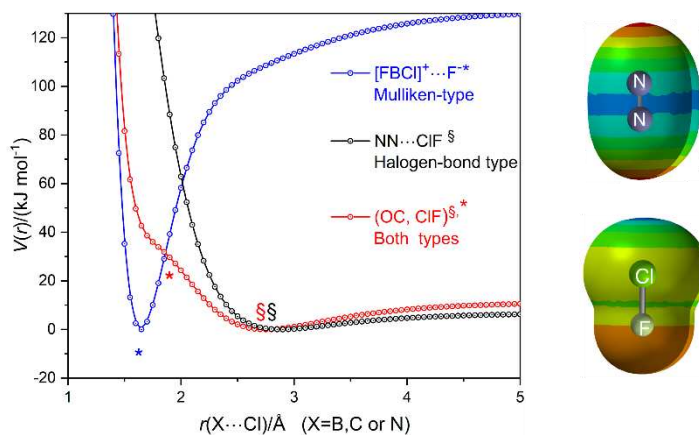
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