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# Non-Covalent Interactions of the Lewis Acids Cu–X, Ag–X, and Au–X (X = F and Cl) with Nine Simple Lewis Bases B: A Systematic Investigation of Coinage–Metal Bonds by Ab Initio Calculations

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**Abstract:** The equilibrium geometry and two measures (the equilibrium dissociation energy in the complete basis set limit,  $D_e$ (CBS) and the intermolecular stretching force constant  $k_\sigma$ ) of the strength of the non-covalent interaction of each of six Lewis acids M–X (M = Cu, Ag, Au) with each of nine simple Lewis bases B (B = N<sub>2</sub>, CO, HCCH, CH<sub>2</sub>CH<sub>2</sub>, H<sub>2</sub>S, PH<sub>3</sub>, HCN, H<sub>2</sub>O, and NH<sub>3</sub>) have been calculated at the CCSD(T)/aug-cc-pVTZ level of theory in a systematic investigation of the coinage–metal bond. Unlike the corresponding series of hydrogen-bonded B···HX and halogen-bonded B···XY complexes (and other series involving non-covalent interactions),  $D_e$  is not directly proportional to  $k_\sigma$ . Nevertheless, as for the other series, it has been possible to express  $D_e$  in terms of the equation  $D_e = cN_B E_{MX}$ , where  $N_B$  and  $E_{MX}$  are the nucleophilicities of the Lewis bases B and the electrophilicities of the Lewis acids M–X, respectively. The order of the  $E_{MX}$  is determined to be  $E_{AuF} > E_{AuCl} > E_{CuF} > E_{CuCl} > E_{AgF} \approx E_{AgCl}$ . A reduced electrophilicity defined as  $(E_{MX}/\sigma_{\max})$  is introduced, where  $\sigma_{\max}$  is the maximum positive value of the molecular electrostatic surface potential on the 0.001 e/bohr<sup>3</sup> iso-surface. This quantity is, in good approximation, independent of whether F or Cl is attached to M.

**Keywords:** electrophilicity; nucleophilicity; ab initio calculations; coinage-metal bonds; Lewis acids; Lewis bases



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## 1. Introduction

Isolated complexes of the general type B···M–X, where B is a simple Lewis base, M is a coinage–metal atom (Cu, Ag, or Au), and X is a halogen atom, have been investigated extensively in the gas phase via rotational spectroscopy [1–15]. Properties, such as geometry, intermolecular stretching force constant  $k_\sigma$ , and the change in ionicity of M–X on complexation have thereby been determined. A perspective on such investigations is set out in reference [16]. In view of the closed-shell nature of the molecules M–X, their interaction with Lewis bases in the B···M–X complexes can be classified as of the non-covalent type and, following recent practice in the naming and definition of halogen and chalcogen bonds [17,18], can be called coinage–metal or Group 11 bonds [16,19]. This method of naming non-covalent interactions focusses on the group in the periodic table containing the element whose atom provides the electrophilic centre that interacts with the most nucleophilic region (non-bonding or  $\pi$ -bonding electron pairs) carried by B.

Complexes of the type B···M–X (M = Cu, Ag, and Au) are likely to have a large electrostatic contribution to the strength of the intermolecular binding, given that the coinage metal halides MX considered here have large electric dipole moments (5.77 D for CuF [20]) and large fractional ionic characters (0.71 can be calculated from the <sup>35</sup>Cl nuclear quadrupole coupling constant of CuCl [21]). Thus, it is of interest to compare properties

of the  $B \cdots M-X$  with those of their hydrogen-bonded analogues  $B \cdots H-X$  to examine the extent to which the greater polar character of  $M-X$  than that of the  $H-X$  affects those of the former group.

In earlier reports, it was shown [22,23] by means of ab initio calculations of the properties of a large number of simple hydrogen-bonded complexes  $B \cdots H-X$  and halogen-bond complexes  $B \cdots X-Y$  ( $X$  and  $Y$  are halogen atoms) that there is a direct proportionality between two measures of the intermolecular binding strength, namely, the equilibrium dissociation energy  $D_e$  (the energy required for the infinite separation process  $B \cdots H-X = B + HX$ ) and the intermolecular stretching force constant  $k_\sigma$  (the restoring force per unit infinitesimal extension of the weak bond). This conclusion has implications for the form of the potential energy as a function of the intermolecular distance. It was also found that  $D_e$  (and therefore  $k_\sigma$ ) can be written in terms of a nucleophilicity  $N_B$  assigned to the Lewis base  $B$  and an electrophilicity  $E_A$  of the Lewis acid  $A$  according to the simple expression  $D_e = N_B E_A$ . We have recently published reports of a similar type for tetrel (or Group 14) bonds, pnictogen (or Group 15) bonds, chalcogen (or Group 16) bonds [24], Be, Mg (or Group 2) bonds [25], and Li and Na (or Group 1) bonds [26], all of which are of the non-covalent type.

In this article, we report an ab initio investigation of the properties of the 54 coinage-metal complexes  $B \cdots Cu-F$ ,  $B \cdots Cu-Cl$ ,  $B \cdots Ag-F$ ,  $B \cdots Ag-Cl$ ,  $B \cdots Au-F$ , and  $B \cdots Au-Cl$ , where  $B$  is one of the nine simple Lewis base  $B = N_2$ , CO, HCCH,  $CH_2CH_2$ ,  $H_2S$ ,  $PH_3$ , HCN,  $H_2O$ , and  $NH_3$ . We seek thereby the answers to several questions:

1. How do the distances  $r(Z \cdots M)$ , where  $Z$  is the acceptor atom of  $B$ , and the force constants  $k_\sigma$  compare with those determined spectroscopically?
2. Is  $D_e$  directly proportional to  $k_\sigma$ ?
3. Can  $D_e$  be simply expressed as a product of a nucleophilicity  $N_B$  assigned to  $B$  and an electrophilicity  $E_{MX}$  assigned to  $M-X$ , and if so, do the  $N_B$  agree with those determined earlier for the analogous hydrogen-bonded, halogen-bonded, and other non-covalently bound complexes?
4. In view of the enhanced ionic character of a given  $M-X$  compared with that of the corresponding  $H-X$ , as alluded to earlier, are there any differences attributable to it?
5. In addition, we shall consider the effects of normalising the  $D_e$  values with respect to the maximum positive values of the molecular electrostatic surface potentials (MESP) of the  $M-X$  molecules. Does this indicate whether the electrophilicity per unit positive potential along the molecular axis near to the atom  $M$  changes from F to Cl?

## 2. Computational Methods

The equilibrium geometries, dissociation energies  $D_e$ , and intermolecular force constants  $k_\sigma$  were obtained at the CCSD(T) computational level [27] for each of the 54 complexes  $B \cdots AgX$ ,  $B \cdots CuX$ , and  $B \cdots AuX$  ( $X = F$  and  $Cl$ ) investigated. The geometry of the monomers and complexes were optimised by employing the aug-cc-pVTZ basis set [28] for all atoms except for Ag and Au, for which the aug-cc-pVTZ-PP [29] version was used, at the CCSD(T) computational level. The optimised geometries are gathered in Table S1 of the Supplementary Materials. More accurate values of  $D_e$  were sought by extrapolation to the complete basis set energy [CCSD(T)/CBS]. This was achieved via the CCSD(T)/aug-cc-pVTZ//CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVQZ//CCSD(T)/aug-cc-pVTZ energies [30,31] for all complexes and monomers, thereby allowing  $D_e$  values to be determined as the difference of the CCSD(T)/CBS energies of the complex and the two monomers. All these ab initio calculations were performed with the MOLPRO-2012 program [32]. Table 1 displays the values of  $D_e$  so calculated for all 54 complexes considered here. Molecular electrostatic surface potentials (MESP) of the various  $M-X$  monomers were calculated at the  $0.001 e/\text{bohr}^3$  electron density iso-surface using the MP2/aug-cc-pVTZ level of theory by means of the GAUSSIAN16 program [33] and represented with the Jmol program [34].

**Table 1.** Equilibrium dissociation energies  $D_e^{CBS}/(\text{kJ mol}^{-1})$  calculated at the CCSD(T)/CBS level (see text) for 54 complexes  $B \cdots M-X$ .

Lewis Base B	Lewis Acid, M-X					
	Cu-F	Cu-Cl	Ag-F	Ag-Cl	Au-F	Au-Cl
N <sub>2</sub>	107.6	90.2	58.9	51.5	138.6	106.4
CO	173.1	149.4	120.8	104.3	256.2	208.9
C <sub>2</sub> H <sub>2</sub>	154.5	136.1	107.3	97.9	209.8	174.8
CH <sub>2</sub> CH <sub>2</sub>	161.2	143.3	121.8	111.4	229.9	194.2
PH <sub>3</sub>	177.9	161.2	151.0	137.4	277.9	237.8
H <sub>2</sub> S	145.2	132.1	114.0	105.5	208.8	176.5
HCN	160.3	145.1	109.3	102.9	195.6	163.8
H <sub>2</sub> O	123.4	114.0	82.7	80.8	139.1	118.6
NH <sub>3</sub>	184.0	171.9	140.1	134.7	229.6	200.5

To evaluate the other measure of binding strength used here, namely, the intermolecular stretching quadratic force constants  $k_\sigma$ , the following procedure was employed. For each complex, geometry optimisations were conducted at the same computational level but with the intermolecular distance  $r$  fixed. This was repeated at 0.025 Å intervals over the range of  $\pm 0.1$  Å about the equilibrium length  $r_e$  to yield the variation of the energy  $E(r-r_e)$  as a function of the displacement of  $(r-r_e)$  from equilibrium. These points were then fitted with a third-order polynomial in  $(r-r_e)$ , from which the value of  $k_\sigma$ , that is, the second derivative of  $E(r-r_e)$  with respect to  $(r-r_e)$  evaluated at  $r_e$ , was obtained (Table S2). The results for each of the 54 complexes  $B \cdots M-X$  investigated are shown in Table 2.

**Table 2.** Intermolecular stretching quadratic force constants  $k_\sigma/(\text{N m}^{-1})$  of complexes  $B \cdots M-X$  calculated at the CCSD(T)/aug-cc-pVZ/aug-cc-pVTZ-PP level of theory (see text for the method).

Lewis Base B	Lewis Acid, M-X					
	Cu-F	Cu-Cl	Ag-F	Ag-Cl	Au-F	Au-Cl
N <sub>2</sub>	189.1	154.0	89.7	71.3	238.1	176.3
CO	260.3	220.8	174.4	140.0	379.3	312.6
C <sub>2</sub> H <sub>2</sub>	179.7	143.7	101.8	86.2	244.2	192.8
CH <sub>2</sub> CH <sub>2</sub>	166.9	139.7	113.7	97.6	237.5	195.0
PH <sub>3</sub>	167.8	147.1	140.6	120.7	271.4	231.0
H <sub>2</sub> S	137.0	119.4	102.1	89.4	201.0	165.0
HCN	204.9	178.2	121.8	106.7	257.0	205.6
H <sub>2</sub> O	149.3	132.3	86.1	80.0	168.4	136.6
NH <sub>3</sub>	184.0	168.0	133.5	121.7	235.3	200.4

### 3. Results

#### 3.1. Comparison of Calculated and Experimental Properties of $B \cdots M-X$

Tables 1 and 2 show immediately that the complexes  $B \cdots M-X$  are much more strongly bound than either their hydrogen-bonded  $B \cdots \text{HCl}$  or halogen-bonded  $B \cdots \text{ClF}$  analogues, which typically have  $D_e \sim 10\text{--}50 \text{ kJ mol}^{-1}$  and  $k_\sigma \sim 10\text{--}30 \text{ N m}^{-1}$ . No experimental values of  $D_e$  are available for comparison with the calculated quantities in Table 1.

In principle,  $k_\sigma$  (an alternative measure of the strength of the intermolecular bond) for a complex of the  $B \cdots M-X$  type can be obtained experimentally from its known centrifugal distortion constant  $D_J$  or  $\Delta_J$  (depending on the molecular symmetry) by using the model developed by Millen [35]. Although centrifugal distortion constants are available from the rotational spectra of some of the  $B \cdots M-X$  listed in Table 2, the application of this model leads to results that are far too low compared with those in Table 2. This is because the model was developed explicitly for hydrogen-bonded complexes and assumes unperturbed monomer geometries and rigid components. While these assumptions are very good approximations for most  $B \cdots \text{HF}$  complexes, for example, they do not apply here because the intermolecular bond is no longer weak. In particular, the intermolecular stretching

mode and the M–X stretching mode (which are of the same symmetry) are not very different in wavenumber. A two force-constant model involving these two modes has been developed to deal with such eventualities [36], but its full use requires a knowledge of the M–X stretching force constant  $k_{MX}$ . Although reasonably assumed values of  $k_{MX}$  yield  $k_\sigma$  that are (1) much larger than those given by the Millen single force constant model and are (2) similar in magnitude to those in Table 2 [15], even a relatively small range in  $k_{MX}$  implies sufficiently large errors in  $k_\sigma$  to make this approach unappealing.

A comparison of intermolecular distances  $r(Z \cdots M)$ , where Z is the atom of B directly involved in the coinage–metal bond, with those available from their rotational spectra is valid, however. The experimental values of the  $(Z \cdots M)$  distance so far available are given in Table 3 together with their ab initio counterparts. There are several varieties of the distance  $r(Z \cdots M)$  that can be determined from the rotational spectrum of a polyatomic molecule such as  $B \cdots M-X$ . These are the  $r_0$  distance (usually obtained by fitting ground-state rotational constants of a sufficient number of isotopologues), the  $r_s$  distance (available from the principal-axis coordinates of atoms Z and M determined by isotopic substitution at each [37]), and from the  $r_m$ -geometry defined by Watson et al. [38]. The  $r_m$  geometry requires the fitting of ground-state rotational constants of a large number of isotopically substituted species but has been shown to lie close to the  $r_e$  geometry. The  $r_0$  quantity differs most from the equilibrium value because the effect of zero-point motion on the rotational constants is not taken into account. In general,  $r_0 > r_s > r_e$  for diatomic molecules and this order should pertain for polyatomic molecules. The footnotes to Table 3 indicate to which of these classes a given experimental entry belongs. We note from Table 3 that experimental values of  $r(Z \cdots M)$  are, in general, in good agreement with those that were obtained ab initio, given that the latter are all equilibrium quantities.

**Table 3.** Comparison of calculated and observed intermolecular distances  $r(Z \cdots M)/\text{\AA}$  in complexes  $B \cdots M-X$ , where Z is the acceptor atom/centre in the Lewis base B.

Lewis Base B	B $\cdots$ Cu–F		B $\cdots$ Cu–Cl		B $\cdots$ Ag–F		B $\cdots$ Ag–Cl		B $\cdots$ Au–F		B $\cdots$ Au–Cl	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
N <sub>2</sub>	1.815	1.790(2) <sup>a</sup>	1.854	–	2.086	–	2.144	–	1.934	–	1.991	–
CO	1.785	1.76385(4) <sup>b</sup>	1.817	1.79447(1) <sup>b</sup>	1.970	1.96486(1) <sup>c</sup>	2.019	2.01281(9) <sup>c</sup>	1.859	1.847 <sup>d</sup>	1.897	1.88593(6) <sup>d</sup>
C <sub>2</sub> H <sub>2</sub>	1.874	1.8474(7) <sup>e</sup>	1.915	1.887(2) <sup>f</sup>	2.139	–	2.192	2.1795(4) <sup>g</sup>	2.002	–	2.043	–
CH <sub>2</sub> CH <sub>2</sub>	1.895	–	1.934	1.908(12) <sup>g</sup>	2.126	–	2.172	2.1697(4) <sup>h</sup>	2.004	–	2.045	–
PH <sub>3</sub>	2.134	–	2.168	–	2.287	–	2.331	–	2.188	–	2.224	–
H <sub>2</sub> S	2.154	–	2.190	2.1531(3) <sup>i</sup>	2.355	–	2.400	2.3838(1) <sup>i</sup>	2.239	–	2.285	–
HCN	1.819	–	1.851	–	2.061	–	2.101	–	1.940	–	1.987	–
H <sub>2</sub> O	1.918	–	1.943	1.925(5) <sup>j</sup>	2.183	2.168(11)	2.210	2.204(7) <sup>j</sup>	2.085	–	2.132	–
NH <sub>3</sub>	1.911	1.8928(6) <sup>k</sup>	1.934	1.9182(13) <sup>l</sup>	2.123	–	2.154	2.1545(8) <sup>m</sup>	2.039	–	2.077	–

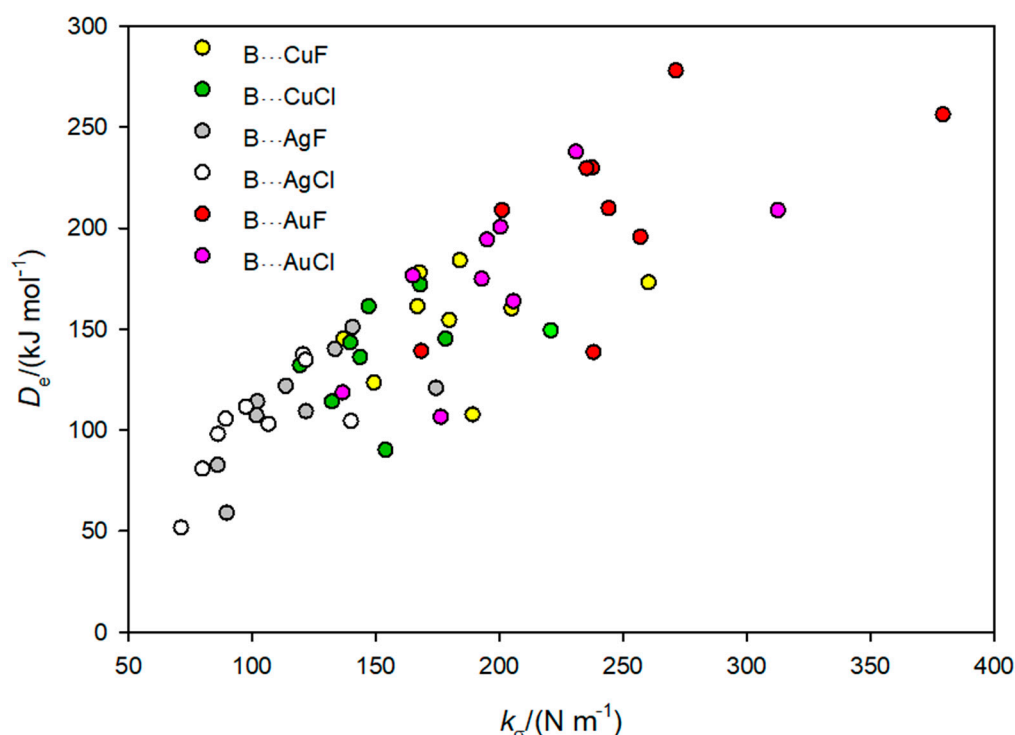
<sup>a</sup> Reference [4],  $r_0$  <sup>b</sup> Reference [2],  $r_m$  <sup>c</sup> Reference [3],  $r_m$  <sup>d</sup> Reference [1],  $r_0$  (F)  $r_s$  (Cl) <sup>e</sup> Reference [14],  $r_0$  <sup>f</sup> Reference [12],  $r_s$  <sup>g</sup> Reference [11],  $r_m$  <sup>h</sup> Reference [10],  $r_s$  <sup>i</sup> Reference [9],  $r_0$  <sup>j</sup> Reference [8],  $r_s$  <sup>k</sup> Reference [15],  $r_0$  <sup>l</sup> Reference [13],  $r_0$  <sup>m</sup> Reference [6],  $r_s$ .

The electric dipole moments  $\mu$  of the 54  $B \cdots M-X$  and their component molecules were calculated at the MP2/ aug-cc-pVTZ level and are available in Table S3 of the Supplementary Materials. Some of the moments are large. For example, the value for  $\text{HCN} \cdots \text{AgF}$  is 10.59 Debye, corresponding to an enhancement  $\Delta\mu$  of 0.7 Debye relative to the sum of the monomer values for this linear molecule. For the complexes involving non-polar bases (such as N<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, etc.) there is no significant enhancement but instead,  $\mu$  is smaller than the vector sum of the component values. There is no evidence of a significant correlation of  $\Delta\mu$  values with either  $D_e$  or  $k_\sigma$ .

### 3.2. Is There a Linear Relationship between $D_e$ and $k_\sigma$ for the $B \cdots M-X$ Complexes?

It was shown elsewhere that, to a good approximation, the two measures of binding strength  $D_e$  and  $k_\sigma$  were directly proportional to each other for a large number of hydrogen-bonded complexes  $B \cdots \text{HX}$  (X = F, Cl, Br and I) [22,23] and halogen-bonded complexes  $B \cdots \text{XY}$  and for tetrel-, pnictogen-, and chalcogen-bonded complexes [24], for alkaline-earth non-covalent interactions [25], and even for complexes containing alkali–metal bonds [26].

The last-named group involved Li and Na bonds made by lithium and sodium halides to a set of simple Lewis bases similar to that employed here. Given that the isolated diatomic molecules LiCl and NaCl, for example, have  $\geq 95\%$  ion-pair character in the gas phase [39], compared with  $\sim 70\%$  for the coinage-metal (monovalent) halides (see reference [7], for example)), it seemed likely at the outset that the  $B \cdots M-X$  ( $M = Cu, Ag, Au$ ;  $X = F, Cl$ ) complexes would behave similarly to all other non-covalent interactions in respect of the relationship between  $D_e$  and  $k_\sigma$ . Figure 1, in which  $D_e$  is plotted against  $k_\sigma$  for all  $B \cdots M-X$ , shows that this is not so and, moreover, reveals no obvious correlation between the two measures of binding strength. Does this mean that it is not possible to express  $D_e$  as the product of the nucleophilicity of B and the electrophilicity of M for the  $B \cdots M-X$ , as was found for the other non-covalent interactions mentioned earlier?



**Figure 1.**  $D_e$  versus  $k_\sigma$  for  $B \cdots CuX$ ,  $B \cdots AgX$ , and  $B \cdots AuX$ , where  $X = F$  and  $Cl$ . This diagram shows that there is no significant correlation between these two properties.

### 3.3. Electrophilicities of $M-X$ and Nucleophilicities of $B$

Dissociation energies  $D_e$  calculated at the CCSD(T)/CBS level of theory are available here for the 54 complexes of the type  $B \cdots M-X$  that can be obtained by a combination of the nine Lewis bases ( $B = N_2, OC, C_2H_2, C_2H_4, PH_3, H_2S, HCN, H_2O$ , and  $NH_3$ ) and the six Lewis acids  $CuF, CuCl, AgF, AgCl, AuF$ , and  $AuCl$ . As shown elsewhere for hydrogen-bonded, halogen-bonded [22,23] and other complexes [24–26] involving a single, non-covalent bond,  $D_e$  can be expressed as the product of a nucleophilicity  $N_B$  assigned to the Lewis base B and an electrophilicity  $E_A$  assigned to the Lewis acid A, according to Equation (1)

$$D_e = c \times N_B \times E_A, \quad (1)$$

where  $c$  is a constant defined conveniently as  $1.0 \text{ kJ mol}^{-1}$  when  $D_e$  is expressed in  $\text{kJ mol}^{-1}$  so that both  $N_B$  and  $E_A$  are dimensionless. To test whether Equation (1) holds for the coinage-metal complexes  $B \cdots M-X$  the procedure is as follows:

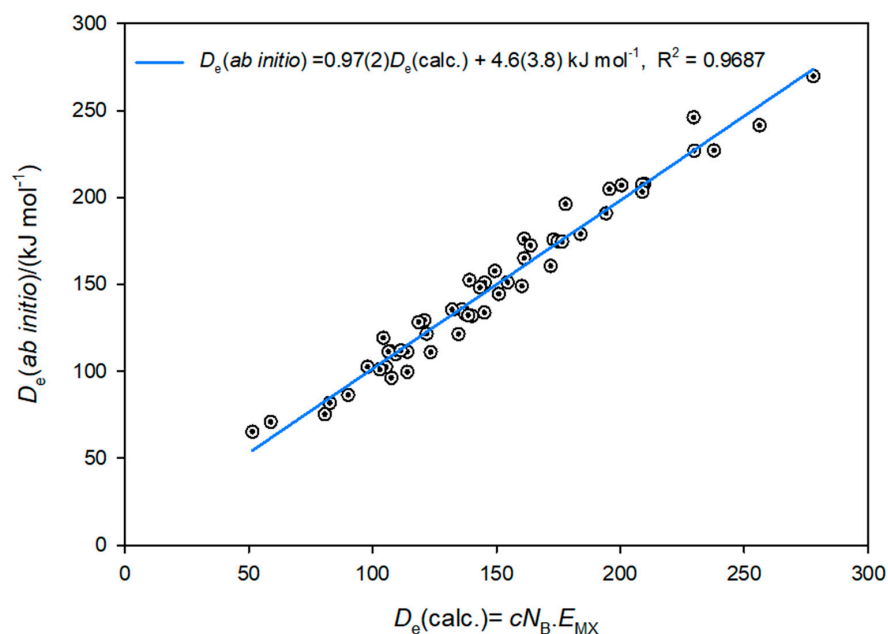
Equilibrium dissociation energies  $D_e$  of all 54 complexes were fitted simultaneously (by the least-squares method) to the nucleophilicities  $N_B$  of the nine Lewis bases and the electrophilicities  $E_A$  of the six Lewis acids by means of Equation (2)

$$D_e = \left( \sum_{i=1}^9 x_i \times N_{Bi} \right) \times \left( \sum_{j=1}^6 x_j \times E_{Aj} \right) \quad (2)$$

The  $x_i$  and  $x_j$  have the values 1.0 if the corresponding Lewis base or Lewis acid, respectively, are present in the complex and 0.0 otherwise. The  $N_B$  and  $E_A$  values so obtained are given in Table 4, while the observed and calculated  $D_e$  and the residuals of the fit are included as Table S4 of the Supplementary Materials. The  $N_B$  and  $E_A$  are well determined, as revealed by Figure 2, in which  $D_e$  re-calculated from the  $N_B$  and  $E_A$  values of Table 4 by means of Equation (2) are plotted against those from Table 1. The linear regression has the associated value  $R^2 = 0.9687$ .

**Table 4.** Values of (a) the nucleophilicity  $N_B$  of the Lewis bases and (b) the electrophilicities  $E_{MX}$  of the Lewis acids M–X determined by fitting 54  $D_e$  values to Equation (2).

Lewis Base B	$N_B$	Lewis Acid M–X	$E_{MX}$
N <sub>2</sub>	7.68	Cu–F	12.52
CO	14.03	Cu–Cl	11.24
C <sub>2</sub> H <sub>2</sub>	12.07	Ag–F	9.22
CH <sub>2</sub> CH <sub>2</sub>	13.18	Ag–Cl	8.49
PH <sub>3</sub>	15.67	Au–F	17.21
H <sub>2</sub> S	12.05	Au–Cl	14.48
HCN	11.90		
H <sub>2</sub> O	8.86		
NH <sub>3</sub>	14.29		

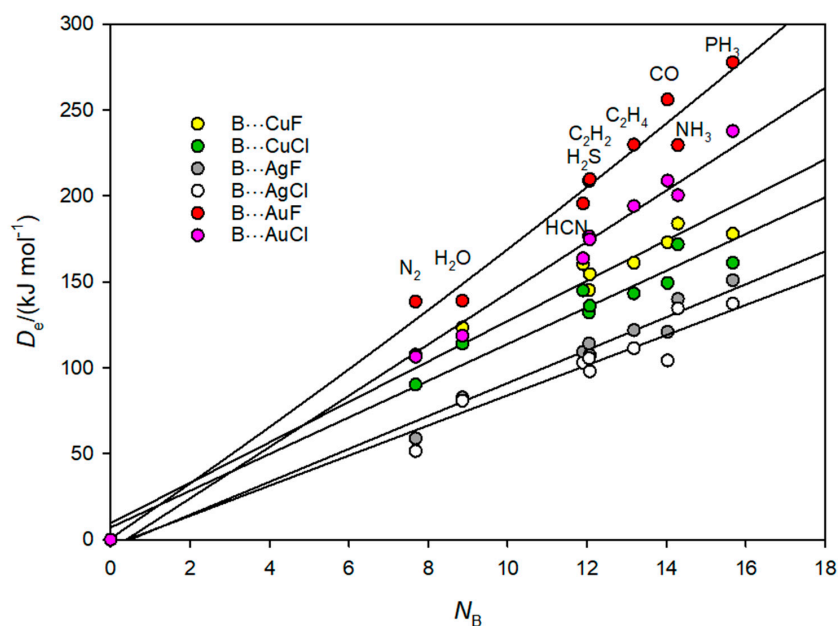


**Figure 2.**  $D_e$  as calculated ab initio versus the values calculated from the nucleophilicity  $N_B$  and electrophilicities  $E_{MX}$  by Equation (2),  $D_e = cN_B \cdot E_{MX}$ .

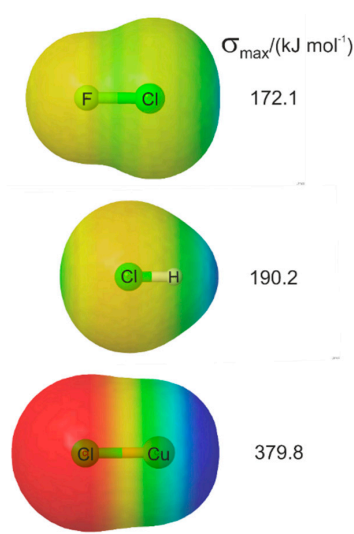
Another way to judge the quality of the fit to Equation (1) is to plot the ab initio value of  $D_e$  of each complex B ··· M–X against  $N_B$  of the corresponding Lewis acid B. This graph is shown in Figure 3. A linear regression fit was made for each series, and for each, the



origin was included as a point because, presumably, when the nucleophilicity of the Lewis base is zero, the dissociation energy of the complex will also be zero. Figure 3 indicates that there is a reasonable fit to a straight line through the origin for each series, in which B varies but M–X is fixed, according to Equation (1), and the gradient of each straight line in Figure 4 corresponds to the electrophilicity of the Lewis acid M–X involved. Clearly, Figure 3 reinforces the conclusion from Table 3, which is the order of the electrophilicities is  $E_{\text{AuF}} > E_{\text{AuCl}} > E_{\text{CuF}} > E_{\text{CuCl}} > E_{\text{AgF}} \approx E_{\text{AgCl}}$ . These results are in agreement with previous reports showing similar trends in the interaction strength with coinage metals  $\text{Au} > \text{Cu} > \text{Ag}$  [19,40–42].



**Figure 3.**  $D_e$  plotted against  $N_B$  for each series  $\text{B} \cdots \text{CuF}$ ,  $\text{B} \cdots \text{CuCl}$ ,  $\text{B} \cdots \text{AgF}$ ,  $\text{B} \cdots \text{AgCl}$ ,  $\text{B} \cdots \text{AuF}$ , and  $\text{B} \cdots \text{AuCl}$ , where  $\text{B} = \text{N}_2$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{HCN}$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ . Each straight line is a linear regression fit to the set of points for the associated  $\text{B} \cdots \text{M-X}$ .



**Figure 4.** MESPs drawn at the  $0.001 e/\text{bohr}^3$  iso-surfaces of (a)  $\text{ClF}$ , (b)  $\text{HCl}$ , and (c)  $\text{CuCl}$ , calculated at the  $\text{MP2}/\text{aug-cc-pVTZ}$  level of theory. Dark blue represents the most positive potential, and this clearly increases dramatically from  $\text{ClF}$  to  $\text{HCl}$  to  $\text{CuCl}$ . The numerical values of the maximum positive electrostatic potentials at the iso-surface, along the molecular axis, are shown.

Figure 3 also indicates that direct proportionality of  $D_e$  and  $k_\sigma$  is not a necessary condition for the existence of nucleophilicities and electrophilicities related by Equation (1), given the extensive scatter seen in Figure 1. Another matter worthy of note about the  $N_B$  values determined here (see Table 4) is that they are different, both in magnitude and numerical order, from the set obtained by fitting (using the same method) the ab initio generated  $D_e$  values of a large number of hydrogen-bonded complexes and halogen-bonded complexes [23]. In particular, we note that  $N_{H_2O}$  is very low, adjacent to that of  $N_2$ , while CO and  $PH_3$  have the highest  $N_B$  values when interacting with coinage-metal halides. For hydrogen-bonded  $B \cdots HX$  and halogen-bonded  $B \cdots XY$  complexes ( $X, Y$  are halogen atoms) [23],  $N_{H_2O}$  is near the top end of the scale while  $N_{CO}$  is the second smallest. For the  $B \cdots LiX$  and  $B \cdots NaX$  series [26], the order of the  $N_B$  values is as for the hydrogen- and halogen-bonded analogues but the magnitudes are significantly different. These observations probably indicate that the nature of the interaction and the relative contributions of electrostatics, polarisation, and exchange repulsion affect the numerical nucleophilicity (and electrophilicity) that is generated by this particular approach.

### 3.4. Molecular Electrostatic Surface Potentials and Reduced Electrophilicities of $M-X$ Lewis Acids

It is of interest to examine whether the electrophilicity of the  $M-X$  molecule can be generalised for different atoms  $X$ . One way this might be done is via the molecular electrostatic surface potential (MESP). Conventionally, this is chosen as the potential energy of a unit charge at the iso-surface for which the electron density is  $0.001 e/\text{bohr}^3$  and this can be calculated by using the GAUSSIAN16 program. Figure 4 compares the MESP for  $ClF$ ,  $HCl$ , and  $CuCl$ , as calculated at the  $0.001 e/\text{bohr}^3$  iso-surface at the MP2/aug-cc-pVTZ level of theory. The maximum positive potential  $\sigma_{\max}$  (values indicated in Figure 4) occurs on the extension of the internuclear axis near the  $Cl$ ,  $H$ , or  $Cu$  atoms of the diatomic molecules.  $\sigma_{\max}$  represents the most electrophilic site of the Lewis acid on the iso-surface and is the region involved in a chlorine bond, a hydrogen bond, or a coinage-metal bond, respectively. Figure 4 illustrates graphically why, for a given Lewis base  $B$ , the non-covalent bond strength increases greatly along the series.

One approach to a reduced electrophilicity of  $M-X$  is to divide the value of  $D_e$  by the maximum positive MESP ( $\sigma_{\max}$ ) to give  $D_e/\sigma_{\max}$ , that is the dissociation energy per unit maximum positive surface potential energy, a dimensionless quantity. Equation (1) then becomes  $(D_e/\sigma_{\max}) = (E_{MX}/\sigma_{\max})N_B$ , where  $(E_{MX}/\sigma_{\max})$  is the electrophilicity of  $M-X$  per unit maximum positive MESP and might serve as a reduced electrophilicity. The necessary values of  $\sigma_{\max}$  for the diatomic molecules  $Cu-X$ ,  $Ag-X$ , and  $Au-X$  ( $X = F$  and  $Cl$ ) are in Table 5.

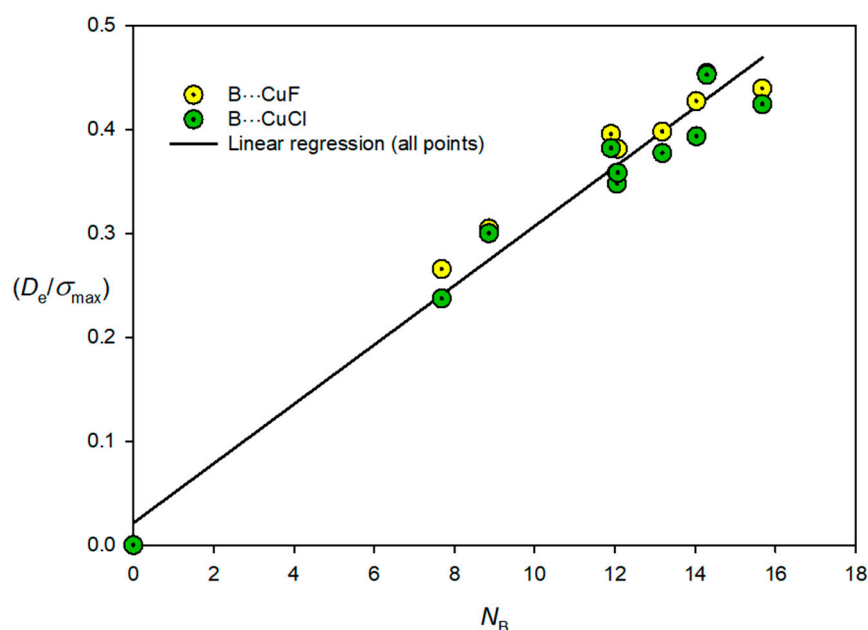
**Table 5.** The maximum positive molecular electrostatic surface potentials ( $\sigma_{\max}$ ) for the diatomic molecules  $M-X$  ( $M = Cu, Ag, Au$ ;  $X = F, Cl$ ) at the  $0.001 e/\text{bohr}^3$  iso-surface. These were calculated at the MP2/aug-cc-pVTZ level of theory and occur on the molecular axis near to the metal atom  $M$ .

Molecule	$\sigma_{\max}/(\text{kJ mol}^{-1})$
Cu-F	405.1
Cu-Cl	379.8
Ag-F	294.5
Ag-Cl	308.0
Au-F	404.8
Au-Cl	346.7

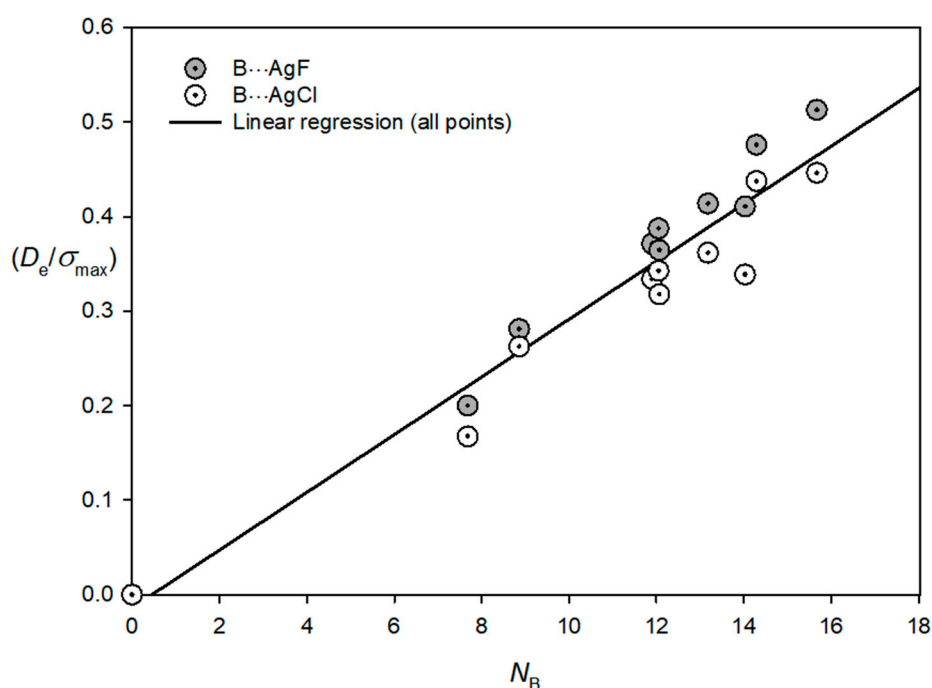
Plots of  $(D_e/\sigma_{\max})$  versus  $N_B$  should be straight lines of the same quality as those in Figure 4, with a gradient  $(E_{MX}/\sigma_{\max})$ , and are shown in Figures 5–7 for the  $Cu-X$ ,  $Ag-X$ , and  $Au-X$  ( $X = F$  and  $Cl$ ) pairs, respectively. We note that in each of these figures, to a reasonable level of approximation, the points for each  $M-F$  and  $M-Cl$  pair lie close to a straight line. This observation implies that  $(E_{MX}/\sigma_{\max})$  is the same for both  $M-F$  and  $M-Cl$  for a given  $M$ , thereby fulfilling the role of a reduced electrophilicity. Accordingly, all



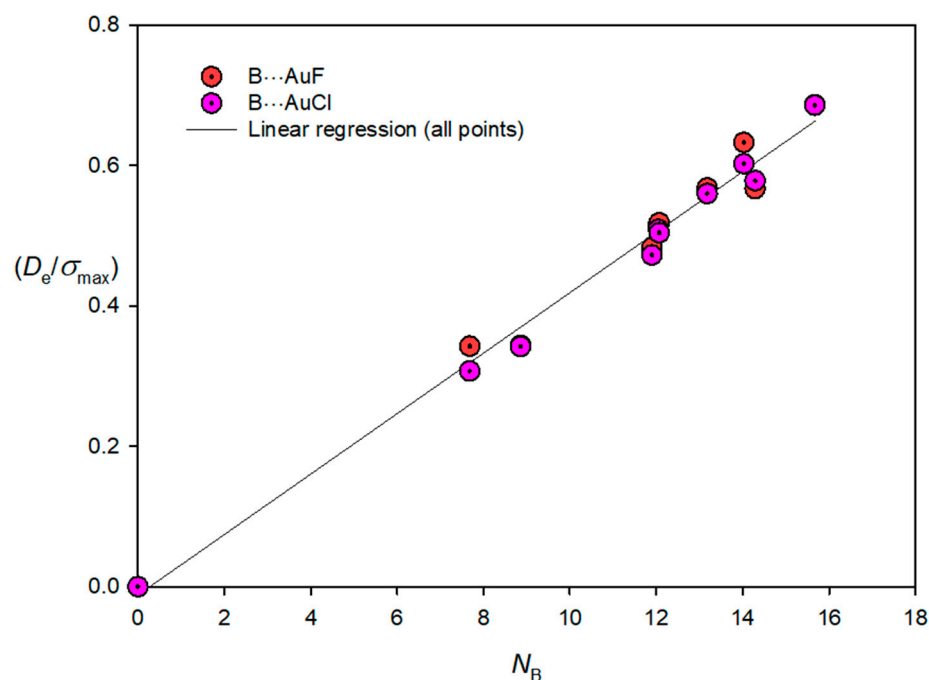
points were fitted by a single linear regression in each case. The values of the gradients are  $2.76(15) \times 10^{-2}$ ,  $3.12(22) \times 10^{-2}$ , and  $4.36(14) \times 10^{-2}$ , respectively, and correspond to reduced electrophilicities of the Cu–X, Ag–X, and Au–X (X = F and Cl) pairs, respectively. The first two are the same within their standard errors, while the third is significantly larger. Thus, the order of the reduced electrophilicities is Cu–X  $\approx$  Ag–X < Au–X.



**Figure 5.** Normalised  $D_e$  values ( $D_e/\sigma_{\max}$ ) plotted against the nucleophilicities of the Lewis bases B for 18 complexes  $B \cdots CuX$  (X = F and Cl). The straight line is the linear regression fit to all 18 points and has the equation  $(D_e/\sigma_{\max}) = [2.086(13) \times 10^{-2}]N_B + 0.021(15)$ , with  $R^2 = 0.9661$ . Some points are obscured by overlap.



**Figure 6.** Normalised  $D_e$  values ( $D_e/\sigma_{\max}$ ) plotted against the nucleophilicities of the Lewis bases B for 18 complexes  $B \cdots AgX$  (X = F and Cl). The straight line is the linear regression fit to all 18 points and has the equation  $(D_e/\sigma_{\max}) = [3.05(17) \times 10^{-2}]N_B - 0.014(21)$ , with  $R^2 = 0.9441$ .



**Figure 7.** Normalised  $D_e$  values ( $D_e/\sigma_{\max}$ ) plotted against the nucleophilicities of the Lewis bases B for 18 complexes  $B \cdots AuX$  ( $X = F$  and  $Cl$ ). The straight line is the linear regression fit to all 18 points and has the equation  $(D_e/\sigma_{\max}) = [4.31(11) \times 10^{-2}]N_B - 0.011(13)$ , with  $R^2 = 0.9876$ . Several of the AuF and AuCl points are obscured by overlap.

#### 4. Conclusions

Several properties of each of the 54 coinage-metal complexes  $B \cdots Cu-F$ ,  $B \cdots Cu-Cl$ ,  $B \cdots Ag-F$ ,  $B \cdots Ag-Cl$ ,  $B \cdots Au-F$ , and  $B \cdots Au-Cl$ , formed by the six Lewis acids  $Cu-X$ ,  $Ag-X$ ,  $Au-X$  ( $X = F$  or  $Cl$ ) with the nine simple Lewis bases  $B = N_2$ ,  $CO$ ,  $HCCH$ ,  $CH_2CH_2$ ,  $H_2S$ ,  $PH_3$ ,  $H_2O$ ,  $HCN$ , and  $NH_3$  have been calculated ab initio. The properties include the equilibrium geometry, the electric dipole moment, and two measures (the equilibrium dissociation energy  $D_e$ (CBS) and the intermolecular stretching force constant  $k_\sigma$ ) of the strength of the non-covalent interaction of  $M-X$  with the Lewis base B.

It has been shown that, unlike the corresponding series of hydrogen-bonded complexes  $B \cdots HX$  and halogen-bonded complexes  $B \cdots XY$ ,  $D_e$  is not directly proportional to  $k_\sigma$  and that there is no obvious correlation between the two quantities for the  $B \cdots M-X$ . Nevertheless, similar to the other two series of non-covalent interactions, it is possible to represent the  $D_e$  values by the simple equation  $D_e = c * N_B * E_{MX}$ , where  $c$  is a constant (chosen as  $1.00 \text{ kJ mol}^{-1}$  for convenience) and  $N_B$  and  $E_{MX}$  are nucleophilicities and electrophilicities assigned to the Lewis base B and the Lewis acid  $M-X$ , respectively. The magnitudes of  $N_B$  for the set of Lewis bases, and indeed their numerical order, differ from those obtained for the hydrogen-bonded and halogen-bonded series by a similar approach. This difference of behaviour is presumably related to the fact that the non-covalent interaction is very much stronger in the coinage-metal bond series  $B \cdots M-X$  than in the other two series (as indicated by both the  $D_e$  and  $k_\sigma$  values). Moreover, the electrostatic component of the interaction in the  $B \cdots M-X$  is likely to be stronger, as indicated by the large calculated electric dipole moments, especially for  $B = HCN$ ,  $H_2O$ , and  $NH_3$  when complexed with  $Ag-X$  and  $Au-X$ . These have significant electric dipole moment enhancements accompanying their formation. The order of the electrophilicities determined is  $E_{AuF} > E_{AuCl} > E_{CuF} > E_{CuCl} > E_{AgF} \approx E_{AgCl}$ .

The molecular electrostatic surface potentials of the  $M-X$  calculated at the  $0.001 e/\text{bohr}^3$  iso-surface have their maximum positive values  $\sigma_{\max}$  on the molecular axis near to the atom M, which is, therefore, the region of maximum electrophilicity. The order of the  $\sigma_{\max}$  values

is similar to that of the  $E_{MX}$ , except for the position of AuCl, which seems anomalous. A reduced or normalised electrophilicity ( $E_{MX}/\sigma_{max}$ ) was tested by separate plots of ( $D_e/\sigma_{max}$ ) against  $N_B$  for each of the three series  $B \cdots Cu-X$ ,  $B \cdots Ag-X$ , and  $B \cdots Au-X$ , ( $X = F$  and  $Cl$ ) (see Figures 5–7). In each graph, the points can be fitted by a single non-linear regression of good  $R^2$  value, with the gradient corresponding to the reduced electrophilicity ( $E_{MX}/\sigma_{max}$ ). The fact that, to a reasonable approximation, the points for each  $B \cdots M-F$  and  $B \cdots M-Cl$  pair lie on the same straight line suggests that the reduced electrophilicity is an intrinsic property of the atom  $M$  and independent of whether  $X = F$  or  $Cl$ . The order of the reduced electrophilicities is  $(E_{CuX}/\sigma_{max}) \approx (E_{AgX}/\sigma_{max}) < (E_{AuX}/\sigma_{max})$ .

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/2304-6740/9/2/13/s1>, Table S1: Optimised geometry (Å) and electronic energy (Hartree) at CCSD(T)/aug-cc-pVTZ/aug-cc-pVTZ-PP computational level, Table S2: Intermolecular stretching quadratic force constants  $k_\sigma$  calculations, Table S3: Dipole moment (debye) computed at MP2/aug-cc-pVTZ/aug-cc-pVTZ-PP computational level, Table S4:  $D_e$  [CCSD(T)] and fitted using Equation (2) (kJ mol<sup>−1</sup>). The residuals (kJ mol<sup>−1</sup>) of the fitting are also included.

**Author Contributions:** The conceptualization of the project, the calculations, the writing of the manuscript, the drawing of figures, checking of proofs, etc. were shared between I.A., N.R.W. and A.C.L. All authors have read and agreed to the published version of the manuscript.

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