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Hydrogen Bond vs Proton Transfer between Neutral Molecules in the Gas Phase

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The possibility of observing a spontaneous proton transfer (PT) between a proton donor AH and a proton acceptor B has been analyzed using, as suitable model systems, the hydrogen bond complexes between HF, HCl, and HBr and a set of bases which covers a large range in the gas-phase basicity scale. This analysis was based on theoretical estimates obtained by means of high-level density functional theory calculations. We propose a model which permits us to predict that, when $\Delta_{\text{acid}}H(\text{AH}) + \text{PA}(\text{B}) + 102 \geq 0$ (in kcal mol⁻¹), $\Delta_{\text{acid}}H(\text{AH})$ being the acidity of AH and PA(B) the proton affinity of B, a spontaneous PT from AH toward B should be observed. In contrast, if the value of this expression is negative, only a hydrogen-bonded cluster between the corresponding neutrals would be stable. We have also reached the conclusion that, to obtain a strong hydrogen bonded complex, a very polarized A–H bond and a sufficiently strong Lewis base, B, are necessary, whereas to observe a spontaneous PT the acidity of A–H and the basicity of B are determining factors, and to a much lesser extent the size of the interacting systems.

Introduction

From the moment that Bürgi and Dunitz pointed out the similarity between hydrogen bond (HB) and proton transfer (PT) by stating that “the HB in general can be regarded as the incipient stage of a PT process”,^{1,2} the possible relationships between these two phenomena have received a great deal of attention, but they are still not clearly understood. This analysis is particularly complicated in solution or in the solid state, because of the interference of many external factors. On the contrary, the problem is particularly well suited for a theoretical scrutiny based on the use of molecular orbital methods, which permit us to investigate the truly isolated systems. Therefore, the aim of this paper is to carry out such a theoretical study at a convenient computational level through the use of a suitable density functional theory approach.

If we considered two generic systems, A–H as the initial proton donor and B as the initial proton acceptor in a hydrogen bond, four different configurations can be defined (See Figure 1).

Although in configurations **1** and **4** there are no interactions between the two systems, because they are supposedly separated at infinite distance, in **2** and **3**, they are in close contact.

To have a spontaneous proton transfer from a neutral acid AH to a neutral base B, to form structure **4**, the acidity of AH must be equal or higher than that of the cationic form BH⁺, or alternatively, B, a neutral molecule, should be more basic than A⁻, an anion. This seems to be a limit difficult to reach. Actually, nowadays, the gap between the proton affinity of the strongest superbase and the deprotonation enthalpy of the strongest superacid is ca. 25 kcal mol⁻¹, a large enough gap as to prevent an autoionization of the system. It should be mentioned however, that some very basic lithium and sodium amines have been proposed, on theoretical grounds, as suitable systems where the spontaneous transformation from **1** to **4** is

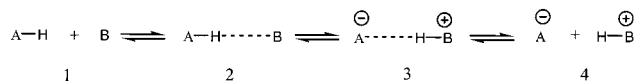


Figure 1. Four possible configurations of hydrogen bonded clusters. possible, provided they interact with strong acids.³ On the other hand, the possibility of obtaining ion-pair complexes as **3** has been shown both theoretically^{4–6} and experimentally⁷ for different sets of acids and bases.

One fundamental question remains still to be answered: when will a spontaneous^{8,9} proton transfer from AH toward B will occur; in other words, is it possible to predict when the interaction between a proton donor (AH) and a proton acceptor B will lead to an ion-pair **3** rather than to a hydrogen-bonded cluster **2**?

To answer this question, we have studied the relative stability of these four situations, namely **1–4**, using as suitable model systems all of the possible complexes formed by a series of bases with the three smallest halogen hydrides (HF, HCl, and HBr). The corresponding complexes with HI will be used as a test of the predictive capacity of the model.

Computational Details

The calculations have been carried out with the Gaussian 98 program.¹⁰ The geometries of structures **1–4** were initially optimized at the B3LYP/6-31G* computational level to obtain a starting geometry and to evaluate whether that the stationary points found are minima of the corresponding potential energy surface. These structures were then refined at the B3LYP/6-311++G** level in order to obtain more reliable geometries and more accurate energies. For several cases, a proton-transfer coordinate has been calculated in order to confirm the uniqueness of the minimum obtained.

Results and Discussion

The bases selected cover a broad range of proton affinities, as indicated in Table 1. It is important to emphasize the good agreement between our theoretically estimated proton affinities and the experimental ones, where available. Similarly, the

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TABLE 1: Proton Affinities (kcal/mol) of the Selected Neutral Bases

base	PA (B3LYP/6-311++G**) ^a	expt ¹¹
Me ₃ N-CH ₂	297.6 (287.4)	
Me ₃ N-NH	270.6 (260.7)	
Me ₂ O-NH	254.9 (245.5)	
Me ₃ N-O	241.6 (233.6)	235.0
Me ₃ N	234.4 (225.0)	226.8
Me ₃ P-O	228.8 (221.9)	217.4
H ₃ N	211.9 (202.6)	204.0
Me ₂ HN	230.0 (220.6)	222.2

^a Values within parentheses corrected with the scaled ZPE calculated at the B3LYP/6-31G* level.

TABLE 2: Acidity of the Halogen Hydrides

halogen hydride	acidity (B3LYP/6-311++G**) ^a	expt ¹¹ (ΔH°)
HF	-372.5 (-367.1)	-371.6
HCl	-332.8 (-328.7)	-333.4
HBr	-323.4 (-319.8)	-323.5
HI	-317.5 (-314.3)	-314.3

^a Values within parentheses corrected with the scaled ZPE calculated at the B3LYP/6-31G* level.

TABLE 3: Total Energy (hartrees) of Configuration 1 and Relative Energies (kcal/mol) of 2–4 Configurations Referred to 1

complexes with HF	1 (E _T)	2	3	4
Me ₃ N-CH ₂	-314.231531		-40.93	74.92
Me ₃ N-NH	-330.288253		-26.83	101.95
Me ₂ O-NH	-310.78155	-21.51		117.64
Me ₃ N-O	-350.183948	-20.44		130.93
Me ₃ N	-275.010142	-15.27		138.12
Me ₃ P-O	-636.927595	-15.50		143.72
H ₃ N	-157.065106	-14.28		160.68
complexes with HCl	1 (E _T)	2	3	4
Me ₃ N-CH ₂	-674.58317		-57.71	35.14
Me ₃ N-NH	-690.639893		-39.57	62.17
Me ₂ O-NH	-671.13319		-31.63	77.86
Me ₃ N-O	-710.535587		-21.69	91.15
Me ₃ N	-635.361782		-14.89	98.34
Me ₃ P-O	-997.279235	-11.33		103.94
H ₃ N	-517.416746	-10.18		120.90
complexes with HBr	1 (E _T)	2	3	4
Me ₃ N-CH ₂	-2788.50226		-62.28	25.75
Me ₃ N-NH	-2804.55899		-43.53	52.77
Me ₂ O-NH	-2785.05228		-35.18	68.46
Me ₃ N-O	-2824.45468		-24.48	81.75
Me ₃ N	-2749.28088		-17.84	88.95
Me ₃ P-O	-3111.19833	-10.02	-11.23	94.55
H ₃ N	-2631.33584	-9.05		111.50

experimental gas-phase acidity of the four halogen hydrides, which vary also within a reasonably large range, from 372 to 323 kcal mol⁻¹ (Table 2), are in good agreement with our theoretical estimates.

The relative energy of configurations 2–4 for the twenty one complexes considered in this work, using the corresponding configuration 1 as the reference, are summarized in Table 3. With the exception of the Me₃PO/HBr system where, both 2 and 3 are minimum, in the rest of the cases only one of the configurations 2 and 3 is a local minimum of the potential energy surface, i.e., depending on the acidity of the proton donor and the basicity of the proton acceptor, one obtains either a hydrogen-bonded complex 2 or an ion-pair 3. In general, the interaction of the weaker acids with the weaker bases favor the formation of 2, whereas the interaction of the stronger acids

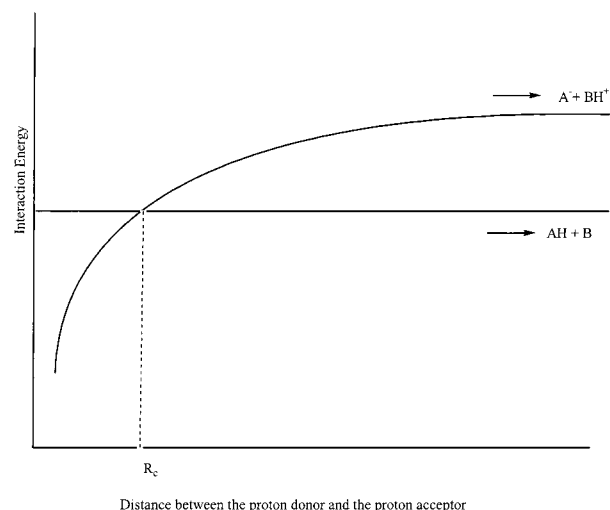


Figure 2. Variation of the interaction energy between a deprotonated species, A⁻, and a protonated one, BH⁺, as a function of the distance between both moieties considered as point charges. At R → ∞, the energy of the A⁻ + BH⁺ system is equal to the difference between the acidity of AH and the proton affinity of B. For distances smaller than R_c, the ion-pair formation becomes an exothermic process.

with the stronger bases produces 3. Indeed, the interaction of the weakest acid HF, yields configurations 2 with all bases except Me₃N-NH and Me₃N-CH₂. In contrast, the strongest acid of Table 3, HBr, yields configurations 3 with all bases except H₃N and Me₃P-O which are the weakest bases.

It is also important to note that, for a given base, the stability of complex 2 increases with the net positive charge of the hydrogen atom involved in the hydrogen bond (the atomic charge of the hydrogen atom in the isolated HF, HCl, HBr, and HI molecules calculated within the NBO¹² formalism are 0.548, 0.254, 0.187, and 0.068, respectively). Thus, the complexes with HF are stronger than complexes with HCl, and these are stronger than those involving HBr.

For configuration 3, the situation is just the opposite, with the strongest complexes being those formed by the protonated base and Br⁻, whereas the weakest ones are those involving F⁻. The interaction energy of configuration 3 can be divided in two opposite components: (i) the energy needed to form the corresponding cation and anion, which is given by the sum of the deprotonation energy of the acid and the protonation energy of the base, and (ii) the stabilization energy arising from the interaction of two systems with opposite charges. For a given protonated base, the second term should be more favorable the smaller the anion (F⁻), because the smaller the anion the closer it is the protonated base. On the contrary, the first term is more favorable the higher the acidity of the proton donor is in the gas phase (BrH). Our theoretical results clearly indicate that the second component dominates. Actually, despite the small size of F⁻, only in two cases the conformation 3 is stable. In contrast, and despite the large size of Br⁻, most of the complexes adopt a 3-type conformation reflecting the high intrinsic acidity of HBr.

This very simple model permits us to also predict when a spontaneous proton transfer (PT) will take place within the complex or not. As illustrated in Figure 2, the enthalpy of formation of a BH⁺-A⁻ ion-pair at an infinite distance will be given by the sum of the deprotonation enthalpy of AH, Δ_{acid}H(AH), and the proton affinity of B, PA(B), and which according our previous discussion will be positive, i.e., the formation of the ion pair is an endothermic process at infinite distance. When the two ions approach each other, the Coulombic

interaction energy between them, considered as point charges, will be given by

$$E_{\text{int}} = \frac{q_1 q_2}{4\pi\epsilon_0 R} = -\frac{3.322 \times 10^2}{R} \text{ kcal mol}^{-1} \quad (1)$$

where R is the distance between both ions in Å.

This implies that for distances smaller than R_c , at which the potential energy curve crosses the abscissas axis, the formation of the ion-pair will become an exothermic process, that is, energetically possible. In more quantitative terms, if the difference between the acidity of AH and the proton affinity of B is greater than 120 kcal mol⁻¹, the crossing point will take place at a distance between the two moieties ($R_c < 2.8$ Å) too short as to allow the formation of the ion pair. In agreement with this very simple model, our calculations indicate that the PT occurs when the difference between the acidity of AH and the proton affinity of B is (in absolute value) ≤ 112 kcal mol⁻¹, whereas no PT takes place when the difference (absolute value) is ≥ 100 kcal mol⁻¹. In an attempt to predict all of the calculated situations, including the 100–112 kcal mol⁻¹ range, models that gives different weights to the acidity of AH and the basicity of B (related to HSAB type models) have been used. For the nontransferred and transferred situation, eqs 2 and 3 were respectively found:

$$\Delta H_{\text{HB}} (\text{kcal mol}^{-1}) = 62.07 + 0.114\Delta_{\text{acid}}H(\text{AH}) - 0.158\text{PA}(\text{B}), \quad n = 9, \quad r^2 = 0.922 \quad (2)$$

$$\Delta H_{\text{PT}} (\text{kcal mol}^{-1}) = 17.75 - 0.382\Delta_{\text{acid}}H(\text{AH}) - 0.683\text{PA}(\text{B}), \quad n = 13, \quad r^2 = 0.987 \quad (3)$$

When these two potential surfaces intersect ($\Delta H_{\text{HB}} = \Delta H_{\text{PT}}$), the following equation is fulfilled:

$$\text{PA}(\text{B}) = -84.4 - 0.95\Delta_{\text{acid}}H(\text{AH}) \quad (4)$$

Considering that the values of $\Delta_{\text{acid}}H(\text{AH})$ range in the present study between -372 and -315 kcal mol⁻¹, the equation can be simplify as

$$\text{PA}(\text{B}) + \Delta_{\text{acid}}H(\text{AH}) \approx -102 \text{ kcal mol}^{-1} \quad (5)$$

We represented in Figure 3 the twenty-one calculated situations we have considered in our analysis. In the ordinates, we have plotted the proton affinity (PA(B)) of the different bases and, in the abscissas, the acidity ($\Delta_{\text{acid}}H(\text{AH})$) of the different proton donors in kcal mol⁻¹.

The straight line with slope near -1 corresponds to eq 4. It can be observed that this line divides the plane in two well defined regions. Above it we found those systems (black dots) where proton transfer occurred and below those systems (open circles) where no proton transfer took place. The only case that is not properly predicted corresponds to the case that presents both configurations, Me₃PO/HBr, because the lowest energy minimum is **3**, whereas our model predict it as **2**. This is not surprising, if one takes into account that the correlation coefficient for eq 2 is only 0.922 and we are very close to the region where both structures would be equally probable.

To explore in a more detail the borderline region, we have investigated the potential energy curve associated with the proton-transfer reaction coordinate for those systems which are in this borderline region. The first important finding is that these potential energy curves present a unique minimum, with the

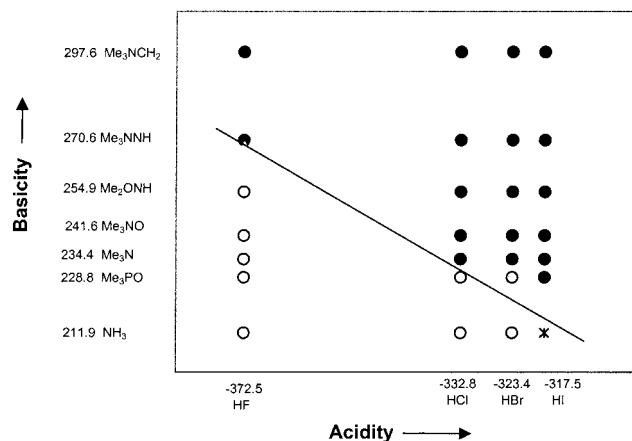


Figure 3. Minimum configuration obtained (**3**, black dots; **2**, white dots; and simultaneous **2** and **3**, gray dots) in the acidity of AH vs proton affinity of B grid. The line corresponding to 0 for eq 4 which divides the surface into two regions has been represented. The HI/NH₃ complex that, based on eqs 2 and 3, is ambiguous has been represented with a star.

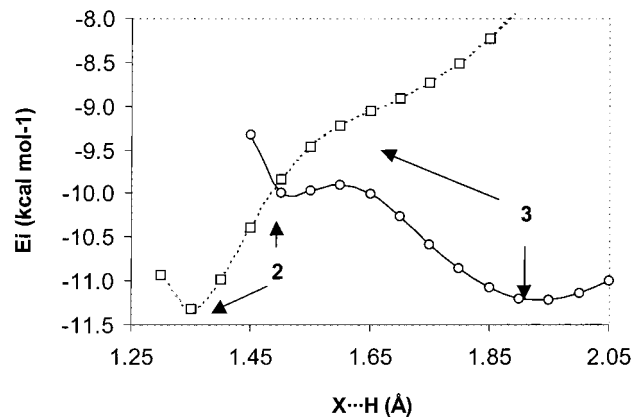


Figure 4. Interaction energy, E_i , vs $\text{H}\cdots\text{X}$ distance ($\text{X} = \text{Cl}$ and Br). Squares and the dotted line correspond to the Me₃PO/HCl system and circles and the straight line to the Me₃PO/HBr one.

exception of the complexes between Me₃PO and HBr where both **2** and **3** are minima (Figure 4). However, in many cases, the curve presents a shoulder which corresponds to the alternative configuration (as an example, the case of the Me₃PO/HCl system has been included in Figure 4). In several of these cases, the nonequilibrium structure located at the shoulder is less than 2 kcal mol⁻¹ above the true minimum. This is consistent with the idea that for those systems lying on the straight line both configurations would be equally favorable. Furthermore, for these limiting cases, the relative stabilities of the two alternative conformations depend on the level of calculation used. Thus, for the Me₃NNH \cdots HF complex, the configuration **2** is predicted at the MP2/6-311++G** level⁵, whereas **3** is found when the B3LYP/6-311++G** approach is used. In addition, Jordan and Del Bene⁹ have shown recently that for proton-shared hydrogen bonds small variations of the environment (modulated by external electric field) can induce the formation of conventional HB or ion-pair complexes.

Using the extended all-electrons basis set developed by Radom et al.¹³ for iodine, we have estimated the acidity of hydrogen iodide (-314.3 kcal mol⁻¹) which is in excellent agreement with the experimental value (see Table 2). Using this estimate and eqs 2 and 3, we have added in Figure 3 the points corresponding to the complexes between HI and the seven bases

TABLE 4: Selected Geometric Parameters (Å) of Complexes 2 and 3 Calculated at the B3LYP/6-311++G Level**

	HF			HCl			HBr		
	B...A	B...H	H...A	B...A	B...H	H...A	B...A	B...H	H...A
Complex 2									
Me ₃ N-CH ₂									
Me ₃ N-NH									
Me ₂ O-NH	2.448	1.407	1.055						
Me ₃ N-O	2.436	1.441	1.003						
Me ₃ N	2.569	1.588	0.981						
Me ₃ P-O	2.535	1.582	0.959	2.957	1.615	1.346	3.060	1.552	1.513
H ₃ N	2.635	1.674	0.961	3.074	1.724	1.350	3.196	1.687	1.509
Complex 3									
Me ₃ N-CH ₂	2.940	1.104	1.848	3.367	1.097	2.386	3.537	1.097	2.544
Me ₃ N-NH	2.462	1.126	1.366	3.082	1.055	2.065	3.264	1.050	2.250
Me ₂ O-NH				3.024	1.063	2.014	3.201	1.058	2.192
Me ₃ N-O				2.846	1.065	1.790	3.043	1.043	2.011
Me ₃ N				2.853	1.165	1.688	3.029	1.127	1.902
Me ₃ P-O							2.973	1.068	1.935
H ₃ N									

under consideration. In all cases, proton transfer should occur, although, in the case of the HI/NH₃ complex, the situation is ambiguous, as it corresponds to a point near the borderline ($\Delta H_{\text{HB}} = -7.6$; $\Delta H_{\text{PT}} = -5.7$ kcal mol⁻¹).

Using the calculated value for the proton affinity of dimethylamine (220.6 kcal mol⁻¹), four more values, not represented in Figure 3, can be predicted. They correspond to the complexes between this base and the four proton donors considered in our analysis. When the reference acid is either HI or HBr, a spontaneous proton transfer should take place ($\Delta H_{\text{PT}} = -18.1$ and -15.8 kcal mol⁻¹, respectively). In contrast, when the reference acid is HF, a conventional hydrogen bonded complex should be formed ($\Delta H_{\text{HB}} = -16.7$ kcal mol⁻¹), whereas if the proton donor is HCl, we are again in an ambiguous situation ($\Delta H_{\text{HB}} = -12.2$; $\Delta H_{\text{PT}} = -12.2$ kcal mol⁻¹).

An alternative approach to discuss the difference in stability between complexes **2** and **3** in the cases of H₃N and Me₃N as bases and the four hydrogen halides as acids has been proposed by Legon.¹⁴ This difference can be calculated as the sum of four terms: proton affinity of B, dissociation energy of HA, hydrogen bond dissociation energy of **2**, and Coulombic energy (for the dissociation of **3**). The values thus obtained cannot be compared with those of the present work, because we have found only a minimum, either **2** or **3** for the cases of H₃N and Me₃N. Nevertheless, in the case of trimethylamine/hydrogen chloride, where experimentally the PT occurs,¹⁴ Legon calculations lead to a heterodimer of type **2**, whereas we have found (Table 3) that complex **3** is more stable.¹⁴

It is also important to emphasize that the geometries of the complexes (Table 4) can be fitted in a unique equation¹⁵ derived from the bond-valence theory model (Figure 5).^{8,16} The sum of the valences for the hydrogen in a HB system is equal to one: $\exp(R^{\text{A}\cdots\text{H}}/b) + \exp(R^{\text{H}\cdots\text{B}}/b) = 1$, where b is an adjustable parameter. To unify the data for different acids and bases, we have subtracted from the A...H and B...H distances in the complex the corresponding A-H and B-H⁺ bond distances in the isolated systems ($R_1 = R_{\text{A}\cdots\text{H}}^{\text{complex}} - R_{\text{AH}}^{\text{isolated}}$ and $R_2 = R_{\text{B}\cdots\text{H}}^{\text{complex}} - R_{\text{BH}^+}^{\text{isolated}}$). The resulting modified equation is

$$(R_1 + R_2) = (R_1 - R_2) + 2b \ln\{1 + \exp[(-R_1 + R_2)/b]\} \quad (6)$$

The symmetry of the equation around the zero value of $R_1 - R_2$ allows us to duplicate the points as ($R_1 - R_2$ and $R_1 + R_2$) and ($R_2 - R_1$ and $R_1 + R_2$).

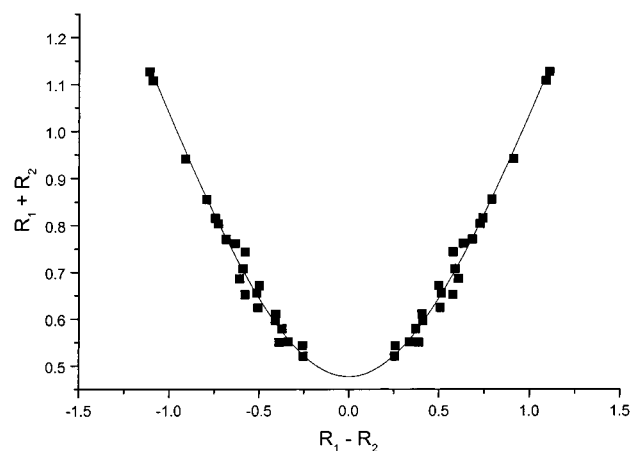


Figure 5. Plot of ($R_1 + R_2$) vs ($R_1 - R_2$), both in Å. Fitted curve: $(R_1 + R_2) = (R_1 - R_2) + 2b \ln\{1 + \exp[(-R_1 + R_2)/b]\}$, $b = 0.343 \pm 0.004$, $n = 42$, and $r^2 = 0.985$.

Conclusions

From our analysis of the interactions between HF, HCl, and HBr with different bases, it is possible to establish a model which allows to predict that when $\Delta_{\text{acid}}H(\text{AH}) + \text{PA}(\text{B}) + 102$ is ≥ 0 (in kcal mol⁻¹), $\Delta_{\text{acid}}H(\text{AH})$ being the acidity of AH and PA(B) the proton affinity of B, a spontaneous PT from AH toward B should be observed. In contrast, if the value of this expression is negative, only a hydrogen-bonded cluster between the corresponding neutrals would be stable. The same type of approach can be used to discuss the strengths of the hydrogen bonds in other A-H...B and A⁻...HB⁺ complexes. In this respect, we can also conclude that, to obtain a strong hydrogen bond complex, a very polarized A-H bond and a good Lewis base, B, are necessary, whereas to observe a spontaneous PT, the acidity of A-H and the basicity of B are determining factors and to a much lesser extent the size of the interacting systems. Also importantly, the geometries of the complexes can be fitted in a unique equation derived from the bond-valence theory model.

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