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Beryllium Bonds, Do They Exist?

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Abstract: The complexes between BeX_2 (X = H, F, Cl, OH) with different Lewis bases have been investigated through the use of B3LYP, MP2, and CCSD(T) approaches. This theoretical survey showed that these complexes are stabilized through the interaction between the Be atom and the basic center of the base, which are characterized by electron densities at the corresponding bond critical points larger than those found in conventional hydrogen bonds (HBs). Actually, all bonding indices indicate that, although these interactions that we named "beryllium bonds" are in general significantly stronger than HBs, they share many common features. Both interactions have a dominant electrostatic character but also some covalent contributions associated with a non-negligible electron transfer between the interacting subunits. This electron transfer, which in HBs takes place from the HB acceptor lone-pairs toward the $\sigma_{YH}{}^*$ antibonding orbital of the HB donor, in beryllium bonds goes from the lone pairs of the Lewis base toward the empty p orbital of Be and the $\sigma_{BeX}{}^*$ antibonding orbital. Accordingly, a significant distortion of the BeX_2 subunit, which in the complex becomes nonlinear, takes place. Concomitantly, a significant red-shifting of the X−Be−X antisymmetric stretching frequencies and a significant lengthening of the X−Be bonds occur. The presence of the beryllium bond results in a significant blue-shifting of the X−Be−X symmetric stretch.

Introduction

Noncovalent interactions play a very important role in chemistry, in particular as far as intermolecular interactions[1−3] and supramolecular chemistry[4−7] are concerned, where the molecular assemblies are usually held together through noncovalent and, quite often, weak interactions. Some of these interactions have special characteristics and, as a consequence, they constitute a subclass among the different kinds of intermolecular forces. This is the case of the conventional[8−11] and the nonconventional[12] hydrogen bonds as well as the so-called halogen bonds.[13−18] In these cases, the leading role of the interaction is played by a hydrogen or a halogen atom, which interacts with two moieties. For the particular case of the hydrogen bonds, these two moieties act as a Lewis base, the so-called HB acceptor, and as a

Lewis acid, which is the moiety usually called HB donor, respectively.

The nature of these interactions was not free of controversy, but it is generally accepted that the electrostatic component is dominant,[19−23] although it is not the only one responsible for the characteristics of these interactions. Actually, one of the necessary conditions to have an inter- or an intramolecular hydrogen bond is to have a hydrogen atom bonded to an electronegative element (X), so that the net positive charge on this hydrogen is usually rather high, favoring its electrostatic interaction with the basic site of the hydrogen bond acceptor, normally a heteroatom (Y) with a negative net charge.[9] Besides the electrostatic interaction between the hydrogen atom attached to X and Y, there are, unavoidably, the polarization effects and a non-negligible charge transfer from the lone-pairs of electrons of the HB acceptor toward the $\sigma_{XH}{}^*$ antibonding orbital of the HB donor.[24] Recently, different analysis has clearly shown the role of this covalent contribution, which is reflected in the

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value of delocalization indexes.[25] A very interesting analysis on the covalent/electrostatic nature of the hydrogen bond in terms of the interacting quantum atoms approach has been recently reported by Martín Pendás et al.[26] The aforementioned charge transfer process from the lone pairs of the HB acceptor toward the σ_{XH}* antibonding orbital of the HB donor is necessarily reflected in a weakening of the X−H covalent bond, which accordingly lengthens, whereas its stretching frequency is red-shifted. This red shifting is precisely one of the experimental signatures of these interactions.[9,27−29]

These characteristics are not necessarily exclusive of hydrogen bonds, and they could be found whenever an element, not very electronegative, is covalently bonded to a more electronegative one and, at the same time, has low-lying empty orbitals which allow it to behave as a good electron acceptor. One of the elements which initially fulfill these conditions is beryllium. Due to its low electronegativity, it has been shown,[30] for instance, that BeH_2 may act as a proton-accepting molecule for dihydrogen-bonded systems. It is also well established, both from the experimental and theoretical viewpoints, that BeX_2 derivatives are good Lewis acids,[31,32] in particular, the $BeCl_2$ for which different complexes with nitrogen bases have been synthesized.[33] Also very recently, new complexes between $BeCl_2$ and dimethylsulfoxide have been isolated and characterized.[34] Actually $BeCl_2$ is a very strong Lewis acid, and somewhat unexpected, the $[BeCl_3]^-$ formed by the interaction of $BeCl_2$ with Cl^- is still capable of acting as a Lewis acid forming $[BeCl_3(L)]^-$ complexes, which have been recently reported to be stable.[35−39] The bonding in complexes involving $BeCl_2$ and $[BeCl_3]^-$ has been analyzed in detail by Frenking and co-workers[40] at different levels of theory, showing that the bond dissociation energy of $Cl_2Be−NH_3$ is larger than that of $Cl_3B−NH_3$, even though Be is less electronegative than B, and that the main difference in bonding comes from a larger electrostatic contribution in Be complexes than in boron ones.

The aim of this paper is to analyze the complexes between BeH_2 and other beryllium derivatives and different Lewis basis under a different perspective. Beryllium is a electropositive element, which in the limit could be regarded as a proton, which has a core of electrons; hence, the question we would like to answer is whether the aforementioned interactions involving Be derivatives can be considered a special kind of weak interactions, sharing some common characteristics with the conventional hydrogen and halogen bonds. In other words, we want to answer the question, is it possible to define "beryllium bonds" in a similar way as we define hydrogen bonds?

For this purpose, we have considered initially the interactions between BeX_2 (X = H, F, Cl, OH) derivatives with a set of small compounds, which are able to behave as Lewis bases and contain as basic sites first-, second- and third-row atoms, namely NH_3, H_2O, FH, PH_3, SH_2, ClH and BrH, (set A).

This initial set will be enlarged to a total of 13 reference bases (set B) by including, besides the bases of set A, some additional bases such as CO, HCN, LiCN, HN=CH_2, OCH_2, and CH_3NH_2. For this set B, we will use as a suitable

example of the larger set of Be compounds investigated, the Cl_2Be derivative.

The possible existence of beryllium bonds may have some important implications in different fields. It is well established for instance that the association of beryllium fluoride to ADP inhibits protein action.[41−47] Be is also able to form half-sandwich complexes with interesting reactivity patterns.[48,49] Probably the most relevant aspect of our study concerns beryliosis or CBD (chronic beryllium disease) a very serious illness, often fatal, caused by Be metal and Be^{2+}. The mechanism is not clearly understood yet, but it involves the interaction of Be^{2+} with up to four water molecules.[50,51] In relation with CBD, beryllium water clusters have been studied theoretically[52] as well as the possibility that Be^{2+} could displace H^+ from strong hydrogen bonds.[53] Hence, the possible existence of beryllium bonds might offer alternative mechanisms to beryllium toxicity.

Computational Details

Standard MP2, CCSD(T), and density functional theory (DFT) calculations have been carried out by means of the Gaussian-03 suite of programs.[54] Among the different functionals nowadays available, we have chosen the B3LYP hybrid method,[55,56] which is likely the most frequently used because it yields quite reliable geometries and harmonic vibrational frequencies, so it would be interesting to assess its behavior as far as the description of "beryllium bonds" is concerned. For this purpose, the geometries of the complexes formed between Cl_2Be, taken as a benchmark case, and the Lewis basis included in set A were initially optimized at the B3LYP/6-311+G(d,p) and compared with those obtained when the MP2/6-311+G(d,p) approach was used. As shown in the Supporting Information, Table S1, the agreement between both set of values, as far as the length of the beryllium bond and the value of the ClBeCl angle, is very good, and only for second- and third-row basic atoms, the deviations between both sets of values are slightly larger. Hence, in what follows, we will use systematically B3LYP optimized geometries but refining the previous ones by using a larger 6-311+G(3df,2p) basis set expansion. The corresponding harmonic vibrational frequencies, which allowed us to characterize the stationary points as local minima of the potential energy surface and to estimate the thermal corrections to the enthalpy, and the Gibbs free energy were also obtained at the B3LYP/6-311+G(3df,2p) level of theory. The same level was used to evaluate the interaction energy for each complex. This interaction energy was defined as the dissociation energy of the "beryllium bond", i.e., as the negative of the enthalpy obtained by subtracting from the enthalpy of the complex the enthalpies of the two isolated monomers. The energies for the particular set of complexes formed by Cl_2Be, were also evaluated using the MP2 and CCSD(T) methods with an aug-cc-pVTZ basis set, for the sake of assessing the reliability of the DFT values. The CCSD(T) and DFT interaction energies were corrected with the basis set superposition error (BSSE) evaluated by means of the counterpoise method.[57]

The bonding of the systems under scrutiny was analyzed by means of three different approaches, namely the atoms

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in molecules (AIM) theory,[58] the electron localization function (ELF) theory,[59,60] and the natural bond orbital (NBO) method.[24] In the framework of the AIM theory, we have evaluated the electron density at the different bond critical points (BCP), since the existence of a BCP in the region between the Be atom and the basic site of the Lewis base will permit not only to establish the existence of a "beryllium bond" but also to quantitatively estimate its strength. Besides, the energy density at the BCP provides useful clues about the covalent nature of the interaction.

By means of the ELF theory,[59,60] it is possible to partition the molecular space in basins of two types, polysynaptic basins (generally disynaptic), with the participation of two (or more) atomic valence shells, and monosynaptic ones, which correspond to electron lone-pairs,[61] because the ELF function becomes large in regions of space where electron pairs, either bonding or lone pairs, are localized. ELF grids and basin integrations have been evaluated with the TopMod package.[62] For the three-dimensional plots, an ELF value of 0.8 has been used.

The NBO approach[24] describes the bonding in terms of localized hybrids and lone pairs obtained as local block eigenvectors of the one-particle density matrix. Besides, a second-order perturbation analysis of the Fock matrix permits to quantify the interactions between occupied MOs of the Lewis base and unoccupied MOs of the Lewis acid, in a typical electron transfer process from the former toward the latter. The Wiberg bond orders (BO)[63] were also evaluated as defined in the NBO-5G program package.[64]

Results and Discussion

Full optimized geometries of the complexes formed by the association of BeX_2 (X = H, F, Cl, OH) derivatives and the compounds of set A are collected in the Supporting Information, Table S2. The interaction enthalpies obtained at the B3LYP/6-311+G(3df,2p) level are summarized in Table 1.

The first conspicuous fact is that the length of the "beryllium bond", considered as the internuclear distance between Be and the basic site (Y = C, N, O, F, P, S, Cl, Br) of the Lewis base, is significantly smaller than the sum of the van der Waals radii of the two atoms (See Table 1), which clearly indicates the existence of a significant interaction between the two monomers forming the complex. The deformation undergone by the BeX_2 compound, which in the complex is not linear anymore, is a further indication of the strength of these interactions (See Table 1). The second important feature is that the interaction enthalpies are very large for most of the bases, and they are only small when the basic site is Cl or Br. More importantly, these interaction enthalpies are in some cases four or five times larger than the energies involved in typical hydrogen bonds. It must be reminded here, for instance, that the interaction energy in the water dimer is about 20 kJ mol^{-1},[65-67] whereas the enthalpy of some of the beryllium bonds investigated here are greater than 100 kJ mol^{-1}.

Statistically, it is possible to analyze the ΔH_{int} values of Table 1 with regard to NH_3 as reference base (R2 = 0.991), in terms of the presence/absence Free-Wilson matrix[68,69] which is given in the Supporting Information. The values of

Table 1. B3LYP/6-311+G(3df,2p) Optimized Be−Y Distances (R_{Be-Y} in Å), XBeX Angles (in degrees), and Dissociation Enthalpies (ΔH_{int}, kJ mol^{-1}) of Different Complexes Involving BeX_2 (X = H, F, Cl, OH) Derivatives with Lewis bases of the Set A

complex	R_{Be-Y}	XBeX angle	ΔH_{int}
H_2Be-NH_3	1.771	138.6	86
H_2Be-OH_2	1.666	143.6	69
H_2Be-FH	1.798	152.1	25
H_2Be-PH_3	2.285	145.6	24
H_2Be-SH_2	2.251	147.6	24
$H_2Be-ClH$	2.378	157.0	6
$H_2Be-BrH$	2.611	160.0	4
F_2Be-NH_3	1.776	137.6	103
F_2Be-OH_2	1.690	142.1	81
F_2Be-FH	1.802	150.2	35
F_2Be-PH_3	2.342	144.9	30
F_2Be-SH_2	2.306	146.3	31
$F_2Be-ClH$	2.377	154.3	15
$F_2Be-BrH$	2.603	156.8	11
Cl_2Be-NH_3	1.745	134.7	106
Cl_2Be-OH_2	1.653	139.2	81
Cl_2Be-FH	1.748	145.7	28
Cl_2Be-PH_3	2.264	139.3	29
Cl_2Be-SH_2	2.244	140.8	27
$Cl_2Be-ClH$	2.338	148.2	4
$Cl_2Be-BrH$	2.602	151.4	1
$(OH)_2Be-NH_3$	1.770	143.4	84
$(OH)_2Be-OH_2$	1.700	148.3	64
$(OH)_2Be-FH$	1.797	155.8	32
$(OH)_2Be-PH_3$	2.336	151.4	14
$(OH)_2Be-SH_2$	2.306	152.8	16
$(OH)_2Be-ClH$	2.470	162.6	5
$(OH)_2Be-BrH$	2.802	168.0	14

this statistical analysis (H_2Be 91.3, F_2Be 101.0, Cl_2Be 96.7, $(OH)_2Be$ 90.0, OH_2 −21.0, FH −64.8, PH_3 −70.5, SH_2 −70.3, ClH −87.3 and BrH −87.3 kJ mol^{-1}) are very close to those in Table 1, which is an indication of the goodness of this analysis. All the bases have negative coefficients because NH_3 is giving the strong interaction enthalpies; then, the order, as far as interaction energies are concerned, is NH_3 > OH_2 > FH > SH_2 > PH_3 > ClH = BrH. Concerning the beryllium derivatives, the order is F_2Be > Cl_2Be > H_2Be > $(OH)_2Be$.

In this respect, it is worth to compare the stability of the beryllium bonds with respect to the hydrogen bonds, in which the latter can be also formed between the two interacting systems. To analyze this question, the subset of complexes formed by $Be(OH)_2$ is very appropriate since this compound can act as either a HB donor or acceptor. In Figure 1, we present the structures of the two kind of possible complexes, those stabilized through beryllium and hydrogen bonds as well as the calculated interaction energies. It can be noted that $(OH)_2Be$ behaves as a HB donor with respect to NH_3, OH_2, PH_3 and SH_2, which are stronger HB acceptors, whereas it behaves as a HB acceptor when interacting with FH, ClH and BrH, which are stronger HB donors. Only for the case of water, both complexes were found to be almost equally stable. The important finding to be underlined here is that beryllium bonds are predicted to be, by far, more stabilizing than the HBs, and only for FH, ClH and BrH, both interactions are energetically similar. Nevertheless, as we shall show in forthcoming sections, even in these three cases,
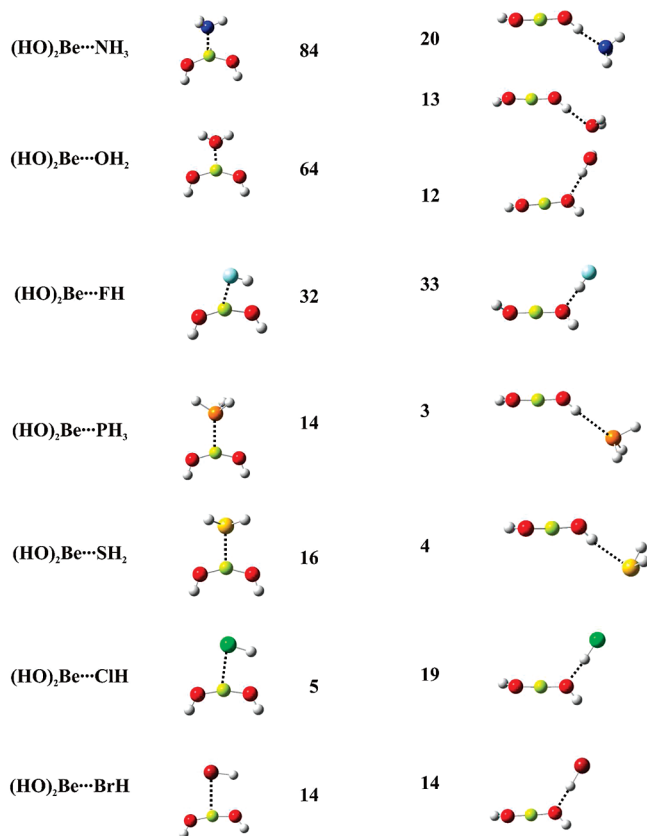
Figure 1. Optimized structures of the two kind of complexes formed by the interaction of Be(OH)$_2$ with the Lewis bases included in set A. The left-hand side column corresponds to the complexes stabilized through a beryllium bond, while those in the right-hand side column are hydrogen bonded complexes. The interaction enthalpies between both subunits are given by each structure in kJ mol^{-1}.

the beryllium bond is predicted to be stronger than the hydrogen bond, when evaluated at the CCSD(T) level.

Bonding

The origin of the strength of these intermolecular interactions, that we have named beryllium bonds, requires an analysis of their intimate nature. For this purpose, we will examine, as a suitable benchmark case, the complexes formed between BeCl$_2$ and the bases included in set B. The B3LYP/6-311+G(3df,2p) optimized geometries are shown in Figure 2. The interaction enthalpies, obtained at different levels of theory, have been summarized in Table 2.

The first important point to be emphasized is that all Be complexes investigated share the same bonding characteristics, although only those the BeCl$_2$ complexes will be discussed in detail. To better illustrate this similarity we have included in the Supporting Information, Figure S1, a comparison between the molecular graphs and the ELFs of BeCl$_2$ and BeH$_2$ complexes.

A topological analysis of the electron density of the systems under scrutiny shows the existence of a BCP associated with the beryllium bond. The electron density associated to these BCPs is typical of the interactions between closed shell systems but larger than those found for conventional HBs. It is also worth noting that the energy
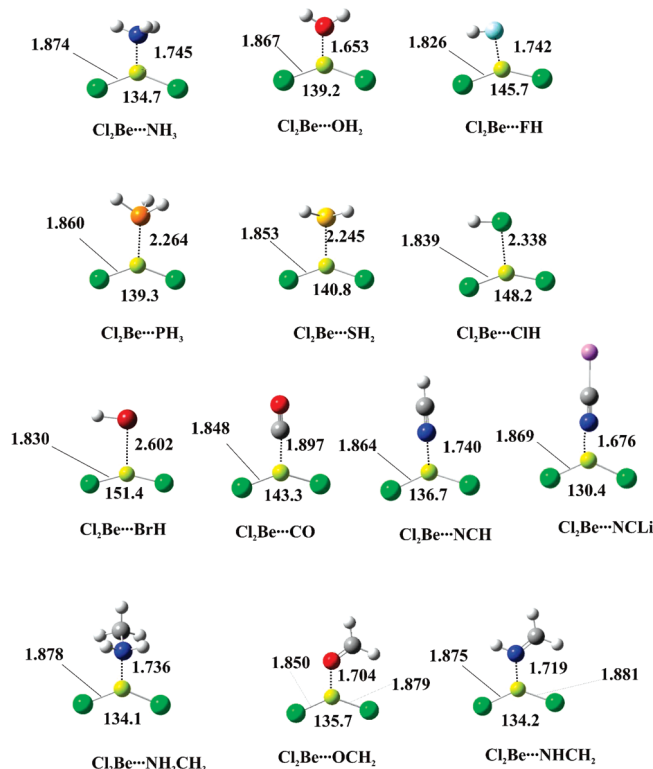

Figure 2. Optimized geometries for the complexes between BeCl$_2$ and the Lewis bases included in set B. Bond lengths are in Å and bond angles in degrees.

density, although small in absolute value, is negative in most cases (See Table 3), pointing out a non-negligible covalent contribution to these interactions. Note that only for very strong HBs, the energy density is slightly negative.

This AIM description is in harmony with the NBO picture. As shown in Table 3, the Wiberg BO of the beryllium bonds is quite significant in some cases (close or greater than 0.3). It must be recalled here, that Wiberg BOs of polar covalent bonds are generally small. Actually, the Wiberg BO for the Cl—Be polar covalent bond in the isolated BeCl$_2$ molecule is 0.44, not much greater than some of the values calculated for the beryllium bonds. No doubt, one important energetic contributor to the beryllium bonds is of electrostatic origin. As a matter of fact, the net natural charge of Be in the complexes investigated is systematically around +0.5, whereas the basic site of the different bases bear a negative net natural charge, which varies from −0.87 in CH$_3$NH$_2$ to −0.16 in HBr. However, there is not a direct correlation between the net charge of the basic site and the interaction energy, and, even in the case of CO complexes where the carbon atom bears a positive net charge (+0.39), still the interaction energy is of the order of 30 kJ mol^{-1}. Hence, other factors besides the electrostatic interactions should contribute to the stability of the beryllium bond. A NBO second-order perturbation analysis actually shows the existence of a quite large electron transfer from the lone-pairs of the Lewis base toward the empty p orbital in Be, and the σ_{ClBe}^* antibonding molecular orbital (see Table 3). As it is clearly reflected in Table 3, these second-order orbital interactions decrease as the electron donor ability of the base decrease, and therefore, they are smaller in FH complexes

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Table 2. Energetics of Complexes Between Cl_2Be and Different Lewis Bases[a]

complex	ΔH_0(adi.) B3LYP	ΔH_0(adi.) MP2	ΔH_0(adi.) CCSD(T)	ΔH_{relax} CCSD(T)	ΔH_0 (vert.) CCSD(T)
Cl_2Be-NH_3	106 (104)	126	125 (118)	54	179
Cl_2Be-OH_2	81 (78)	97	96 (90)	47	143
Cl_2Be-FH	28 (24)	39	39 (32)	32	71
Cl_2Be-PH_3	29 (27)	49	44 (39)	48	92
Cl_2Be-SH_2	27 (25)	47	43 (38)	38	81
$Cl_2Be-ClH$	4 (1)	20	17 (13)	24	41
$Cl_2Be-BrH$	1 (0)	22	19 (11)	19	38
$Cl_2Be-HCN$	57 (55)	75	71 (64)	48	119
$Cl_2Be-OCH_2$	62 (59)	82	82 (75)	53	135
$Cl_2Be-CO-a$	0	0	0		
$Cl_2Be-CO-b$	18 (16)	32	26 (20)	33	59
$Cl_2Be-LiCN$	130 (127)	149	147 (139)	67	214
$Cl_2Be-NHCH_2$	115 (113)	139	136 (128)	58	194
$Cl_2Be-MeNH_2$	117 (115)	147	145 (137)	58	203

[a] ΔH_0 (adi.), ΔH_{relax}, ΔH_0 (vert.) stand for the adiabatic dissociation energy, the relaxation energy of the products and the vertical dissociation energy. The values within parentheses correspond to the dissociation energies after the BSSE correction is included. All values are in kJ mol^{-1}.

Table 3. Electron Density (ρ_{BCP}, au) and Energy Density (au) at the Be···Y BCP, Electron Population at the V(Be,Y) and V(Cl,Be) Disynaptic Basins, Wiberg BO Associated with the Be···Y Interaction, and the Second-Order Interaction Energies (kJ mol^{-1}) between the Lone-Pairs of the Bases and the Empty p Orbital of Be and the $\sigma_{ClBe}*$ Antibonding Orbital for the Complexes Formed between $BeCl_2$ and the Lewis Bases Included in Set B

complex	ρ_{BCP} (energy density)	V(Be,Y) (V(Cl,Be)) basin populations	BO	$LP_{base}\rightarrow p_{Be}$	$LP_{base}\rightarrow\sigma_{ClBe}*$
Cl_2Be-NH_3	0.069 (−0.009)	2.08 (1.81)	0.23	87	58
Cl_2Be-OH_2	0.064 (+0.004)	2.38 (1.81)	0.10	60	56
Cl_2Be-FH	0.042 (+0.003)	1.15 (1.86)	0.08	34	38
Cl_2Be-PH_3	0.042 (−0.011)	2.06 (1.84)	0.24	Be−P bond[b]	
Cl_2Be-SH_2	0.038 (−0.008)	2.01 (1.85)	0.20	Be−S bond[c]	
$Cl_2Be-ClH$	0.025 (−0.004)	$-^a$ (1.90)	0.12	32	33
$Cl_2Be-BrH$	0.020 (−0.004)	$-^a$ (1.92)	0.11	21	24
$Cl_2Be-HCN$	0.057 (0.000)	3.08 (1.84)	0.12	71	56
$Cl_2Be-OCH_2$	0.056 (+0.003)	2.48 (1.84)	0.11	85	80
Cl_2Be-CO	0.046 (−0.005)	2.59 (1.87)	0.19	Be−C bond[d]	
$Cl_2Be-NCLi$	0.071 (−0.006)	3.08 (1.82)	0.14	105	58
$Cl_2Be-NHCH_2$	0.069 (−0.008)	2.59 (1.83)	0.13	75	75
$Cl_2Be-MeNH_2$	0.069 (−0.010)	2.15 (1.81)	0.33	Be−N bond[e]	

[a] No V(Be,Cl) disynaptic basin has been located. [b] 6% Be (31% s + 69% p) + 94% P (32% s + 68% p). [c] 5% Be (29% s + 71% p) + 95% S (15% s + 85% p). [d] 4% Be (35% s + 65% p) + 96% C (67% s + 33% p). [e] 9% Be (28% s + 72% p) + 91% N (35% s + 65% p).

than in NH_3 ones and they are very large for very basic compounds, such as LiCN, $NH=CH_2$ and $MeNH_2$. In some cases, the NBO approach actually detects the formation of a covalent bond between the Be and the basic site of the base, but this is likely a consequence of the localization scheme used by this method. In these cases, as indicated in Table 3, the situation is not essentially difference for the other ones, in the sense that the bond located implies a rather small contribution from the hybrid on Be, which is compatible with the description above in terms of an electron transfer from the lone-pairs of the base toward the empty orbitals of Be. This bonding similarity is also mirrored in the analogy of the ELF for the ammonia and the phosphine complexes (see Figure 3). This electron transfer is obviously reflected in the electron population of the initially empty p orbital of Be, which in the complexes investigated is typically around 0.06 *e*. This participation of the p orbital in the complex is actually responsible for the deformation undergone by the $BeCl_2$ subunit, which accordingly is not linear any more. Similarly the electron transfer toward the $\sigma_{ClBe}*$ antibonding molecular orbital is reflected in a significant lengthening of

the Cl−Be with respect to the isolated molecule (see Figure 2) as well as in a decrease of the electron density at the Be−Cl BCP (see Table 4) and of the population of the V(Be,Cl) disynaptic basin (See Figure 3).

The formation of the complex also has a strong effect in the frequencies of the $BeCl_2$ subunit. Both in the isolated molecule and the complexes, the Be−Cl stretching modes appear as symmetric and antisymmetric combinations. Consistently, with the weakening of the Be−Cl bonds upon complexation, the antisymmetric combination appears significantly shifted to the red (See Table 4). The larger the shifting, the stronger the interaction is between the lone pair of the base and the $\sigma_{ClBe}*$ orbital. However, the symmetric combination is significantly blue-shifted. This is so because in the complex the $BeCl_2$ subunit is bent, and therefore the symmetric stretch of the Be−Cl bonds is unavoidably coupled with the stretching of the Be−Y bond. In other words, the symmetric elongation of the two Be−Cl bonds leads to a compression of the Be−Y and vice versa. Hence, the stronger the beryllium bond, the larger the blue shifting of the BeCl symmetric stretch
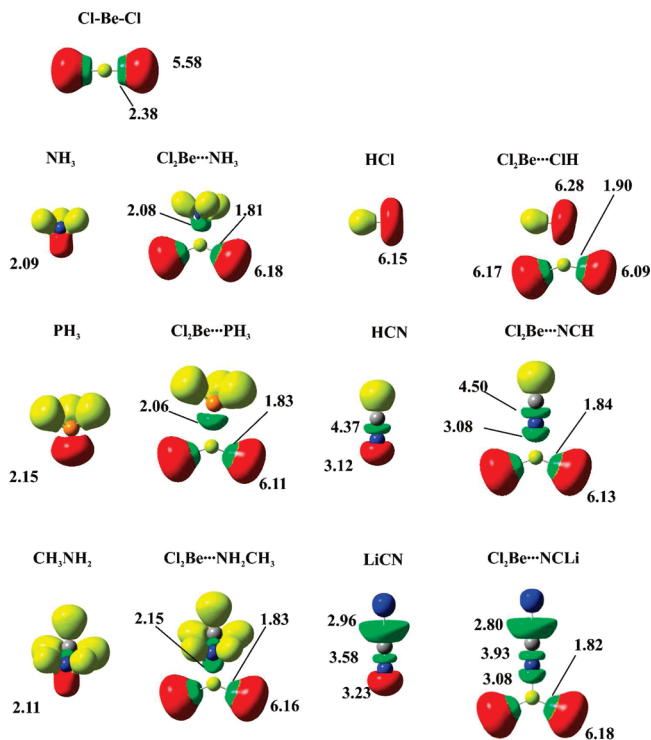
Figure 3. Three-dimensional representations of ELF isosurfaces with ELF = 0.80 for Cl_2Be-containing complexes. Yellow lobes correspond to disynaptic basins involving H atoms, red lobes correspond to monosynaptic lone-pair basins, green lobes correspond to disynaptic basins between two bonded atoms, and blue lobes correspond to monosynaptic atomic cores. The population of the different basins is given in e^-.

Table 4. Be$-$Cl Stretching Frequencies (cm^{-1}) and Electron Density at the Be$-$Cl BCP (ρ_{BCP}, au)

	ν_{Cl-Be} (sym. stret.)	ν_{Cl-Be} (asym. stret.)	ρ_{BCP}
isolated $BeCl_2$	339	1 131	0.095
complex			
NH_3	719	928	0.078
H_2O	630	954	0.080
FH	507	1 008	0.089
PH_3	539	923	0.082
SH_2	523	945	0.083
ClH	461	1 003	0.086
BrH	440	1 025	0.088
HCN	635	913	0.080
CH_2O	623	920	0.080
CO	547	954	0.083
LiCN	752	850	0.075
$NH=CH_2$	726	885	0.076
$MeNH_2$	726	897	0.077

becomes; as it is nicely illustrated by the rather good exponential correlation between the blue shifting and the electron density at the beryllium bond BCP (see Figure 4).

The existence of a beryllium bond is also ratified by the ELF analysis, which shows the existence of a disynaptic V(Be,Y) basin in most of the complexes investigated. As a matter of fact, only in those cases where the compound interacting with the $BeCl_2$ molecule is a poor Lewis base, like HCl, these disynaptic basins are not found, and only a polarization of the basic site lone-pairs is observed (See
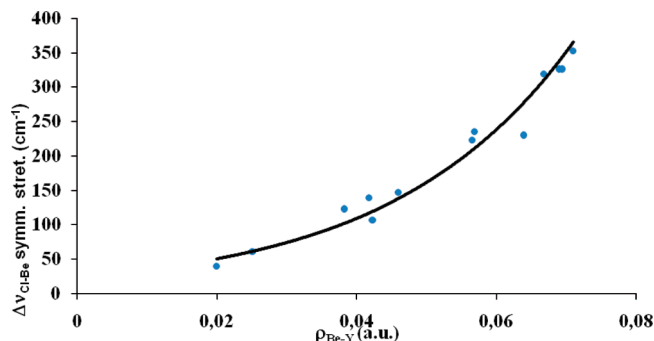

Figure 4. Exponential correlation between the blue shifting of the Cl$-$Be$-$Cl symmetric stretch and the electron density at the beryllium bond BCP. This correlation fulfils the equation: $\Delta\nu_{Cl-Be}$ 2.82 exp (39.04 ρ_{Be-Y}) ($R^2 = 0.966$).

Figure 3). It is also evident from Figure 3 that lone pairs of the basic site undergo a dramatic volume contraction on going from the isolated base to the complex. For example, upon the interaction between Cl_2Be and NH_3, the volume of the N lone pair decreases from 92 to 34 au, even though its population hardly changes. This is a direct consequence of the strong interaction between the lone pair and the empty beryllium orbitals (actually in the complex the lone pair becomes a V(N,Be) disynaptic basin), which leads to very short distances between the basic site of the Lewis base and the Be atom and, therefore, to a dramatic volume contraction of the base lone pair.

The significant geometry distortions triggered by the complexation process must have a large effect on the calculated enthalpy[40] of the beryllium bond because this is defined with respect to the isolated and, therefore, unperturbed monomers. A more realistic measure of the strength of the beryllium bonds would be obtained by calculating the vertical dissociation energy of the complex, i.e., the energy required to separate the interacting subunits at infinite distance, but keeping frozen the structure they have in the complex. This will be equivalent to adding to the adiabatic dissociation enthalpy the enthalpy involved in the relaxation of the two subunits from their structure within the complex to their equilibrium structure. As shown in Table 2, this relaxation enthalpy (ΔH_{relax}) is quite large and, for the weaker complexes, almost equal or even slightly larger than the adiabatic dissociation energy itself. It is important to note that the larger the relaxation or deformation energy the greater the stability of the complex, a fact which is nicely reflected in the good correlation between the adiabatic and the vertical dissociation energies (See Figure 5). It is also worth noting the very good agreement of our calculated values for the Cl_2Be-NH_3 complex and those reported previously in the literature.[40]

Finally, it is important to notice that the B3LYP adiabatic dissociation energies, ΔH_0(adi.), underestimate the values obtained at the CCSD(T) level. A similar result was reported by Frenking and co-workers for the particular case of the Cl_2Be-NH_3 complex when the BP86 functional was used.[40] It is worth noting that the agreement between B3LYP and CCSD(T) results improve slightly when including the BSSE correction because, at the CCSD(T) level this error is 6.7 kJ
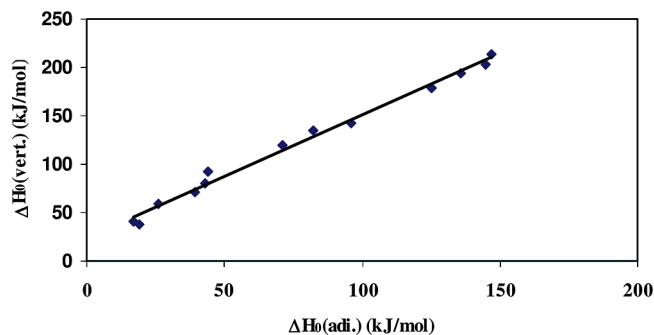
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Figure 5. Linear correlation between the vertical and the adiabatic dissociation energies of the complexes formed by $BeCl_2$ with the Lewis bases of set B. This correlation fulfils the equation ΔH_0 (vert.) = 1.265 ΔH_0 (adi.) + 24.32 kJ mol^{-1} (R^2 = 0.991).

mol^{-1}, in average, whereas for the B3LYP calculations is about three times smaller (2.4 kJ mol^{-1}, in average).

In order to establish whether a high level of electron correlation is required to adequately describe these bonds, we have also compared the CCSD(T) and B3LYP values with those obtained at the MP2 level. In general, the agreement between CCSD(T) and MP2 values is very good, and hence, one may rely on the lower level of theory to get reasonably good estimates for the energies of beryllium bonds. As a matter of fact, as shown in the Supporting Information, Figure S2, the correlation between both sets of values is very good. The correlation between B3LYP and CCSD(T) estimates is slightly poorer (see Supporting Information, Figure S3) but still very good, which means that the B3LYP method correctly reproduces the stability trends obtained with the much more expensive CCSD(T) approach. Finally, it should be mentioned that, in spite of the differences in the energetics obtained with B3LYP and MP2 (or CCSD(T)) methods, the bonding picture obtained from B3LYP and MP2 (or CCSD) densities is essentially the same. The Wiberg BOs and the electron densities at the BCP vary by less than 0.01 and 0.001 au, respectively. Similarly the populations of the ELF basins change inappreciably as illustrated in the Supporting Information, Figure S4, where the ELFs obtained at the MP2 level for four different complexes, taken as suitable examples, are compared with the B3LYP ones.

Conclusions

The complexes between BeX_2 (X = H, F, Cl, OH) with different Lewis bases are stabilized through the interaction between the Be atom and the basic center of the base. These interactions, which we have called beryllium bonds, are characterized by the existence of a BCP with electron densities similar to other typical closed-shell interactions but with energy densities, which in some cases are slightly negative, indicating the presence of non-negligible covalent contributions. All bonding indices actually indicate that, although beryllium bonds are in general significantly stronger than HBs, they share many common features.

Although both interactions have a dominant electrostatic character they have also some covalent character associated with a non-negligible electron transfer between the interacting subunits. In HBs, this electron transfer takes place from the HB acceptor lone-pairs toward the $\sigma_{YH}*$ antibonding orbital of the HB donor, whereas in beryllium bonds they go from the lone pairs of the Lewis base toward the empty p orbital of the Be and the $\sigma_{BeX}*$ antibonding orbital. This electron transfer is reflected in a significant distortion of the BeX_2 subunit, which in the complex becomes nonlinear and in a significant red-shifting of the X-Be-X antisymmetric stretching frequencies. The presence of the beryllium bond results in a significant blue-shifting of the X−Be−X symmetric stretch. Hence, also similarly to HBs whose experimental signature is the red-shifting of the XH stretching frequency of the HB donor,[27−29] in beryllium bonds, this signature should be the red-shifting of the X−Be−X antisymmetric stretch and the blue-shifting of the symmetric one.

Supporting Information Available: Comparison between B3LYP and MP2 optimized geometries, B3LYP/6-311+G(3df,2p) optimized geometries of $X_2Be\cdots YH_n$ (X = H, F, OH, Cl; Y = N, O, F, P, S, Cl, Br) complexes, presence−absence matrix corresponding to Table 1 data, molecular graphs and ELFs of H_2Be and Cl_2Be complexes, correlations between dissociation enthalpies calculated at the CCSD(T), MP2, and B3LYP levels, and comparison between the ELFs obtained using B3LYP and MP2 electron densities. This material is available free of charge via the Internet at http://pubs.acs.org.

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