G2 Molecular Orbital Study of $[H_3AlXH]^-$ (X = NH, PH, AsH, O, S, and Se) and H_3AlYH (Y = OH, SH, SeH, F, Cl, and Br) Donor−Acceptor Complexes

Abdellah Jarid*,† and **Abderrahim Boutalib*,‡**

Département de Chimie, Faculté des Sciences Semlalia, Université Cadi Ayyad,
B.P. 2390 Marrakech, Morocco

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$[H_3AlXH]^-$ (X = NH, PH, AsH, O, S, and Se) and H_3AlYH (Y = OH, SH, SeH, F, Cl, and Br) have been investigated as donor−acceptor complex type at the G2 level of theory. Both staggered and eclipsed conformations have been examined. The G2 energetic results show that the anionic complexes are more stable than the neutral ones. They also show that this stability decreases when descending in the corresponding periodic table column, from nitrogen (or oxygen and fluorine) to arsenic (or selenium and bromine) atoms. The interaction diagrams prove that the evolution of complexation energy depends on the coordination mode. In fact, this is a simple "HOMO−LUMO" interaction for $[H_3AlXH]^-$ anionic complexes while for the H_3AlYH neutral ones it is a result of two interaction types: interaction between a′ symmetry fragment molecular orbital (stabilizing) and interaction between a″ symmetry fragment molecular orbitals (destabilizing). The NBO analysis shows that there is no correlation between the G2 complexation energy and the transferred charge from donor fragment to acceptor one.

1. Introduction

The chemistry of aluminum hydride (AlH_3) has been the subject of numerous experimental and theoretical studies. This compound and others as aluminum halides play an important role in a wide range of chemical processes. Aluminum hydride, AlH_3, is used in photography and photoimaging.[1] It has recently been implicated in desorption of hydrogen from aluminum crystals.[2] Because their adducts have a volatile behavior, alane (AlH_3) and gallane (GaH_3) are used in chemical vapor deposition (CVD) technology and other areas of material science and applications in synthesis.[3,4] It has been shown that alane and borane (BH_3) derivatives can be used in a new approach toward AlN/BN materials.[5] Both these areas require a detailed understanding of the structure and properties of such adducts.

Previous high-quality ab initio computational studies of the Lewis acid chemistry of AlX_3 complexes have generally dealt with the chemistry of the aluminum trihydride.[6−12] Nevertheless, a lot of points are still obscure such as the coordination mode nature, the charge transfer, and the relative stability in a column or row of periodic table.

For the past few years, our group carried its interest to the donor−acceptor complexes of group 13 and reported works on a series of adducts of borane.[13−17] More recently,[18] we reported a detailed theoretical study on adducts of alane, $[H_3AlXH_3]^-$ (X = C, Si, and Ge) and H_3AlYH_3 (Y = N, P, and As). We showed that the stability of these complexes does not depend on the charge transfer, whereas a correlation between the complexation energy and proton affinity has been observed. We have shown that in the borane and alane neutral complexes, the donor−acceptor interaction was not based on a simple HOMO−LUMO mixture , but it was developed between three or four fragment orbitals.[13,18] In continuation of our work, we now report our investigation on the anionic alane donor−acceptor complexes $[H_3AlYH]^-$ (Y = NH, PH, AsH, O, S, and Se) compared to the neutral isoelectronic H_3AlXH (X = OH, SH, SeH, F, Cl, and Br) ones. The relative stabilities of these complexes are examined with respect to the qualitative molecular orbital analysis (QMOA).[19,20] The choice of the complexes investigated was made with the aim to include different types of strongly bound molecules (anionic ones) and coordination compounds (neutral ones). To the best of our knowledge, no comparative study of these complexes has been carried out. A computer search of *Chemical Abstracts* did not offer any help in this matter.

2. Computational Details

Ab initio calculations were performed using the GAUSSIAN92 program.[21] The calculations were performed in the Windows environment on a 266 MHz Pentium II PC having 64 MB of RAM and about 4 GB of available disk storage space. Geometry optimizations were performed at the MP2(full)/6-31G(d) level; the zero-point vibrational energies (ZPE) were obtained from scaled HF/6-31G(d) frequencies (scaled by the factor 0.893).[22] For improved energy, the Gaussian-2 (G2) energies[23] were computed. The electronic structures were done using the natural bond orbital (NBO)[24] partitioning analysis at the MP2(full)/6-31G(d) level. NBO's are the localized set of easily recognizable Lewis-like (σ and π bond, lone pair, and core) and non-Lewis (σ^* and π^* antibond and Rhydberg) orbitals, which are optimal in the sense of orthonormality and maximum occupancy of the Lewis set. An important feature of the NBO method is that unlike other charge partitioning schemes, the presence of diffuse functions in the basis sets does not affect the result.[24] On the other hand, we did not correct for the basis set superposition errors (BSSE), which should be relatively small with a large basis set such as 6-311+G(3df,2p). Moreover, a study by Mikhali et al.,[33] using the G2(+)

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* Corresponding authors.
† E-mail: jarid@ucam.ac.ma.
‡ E-mail: boutalib@ucam.ac.ma.

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TABLE 1: Selected MP2(full)/6-31G(d) Bond Lengths (Å) and Bond Angles (deg) of Anionic Complexes

compound	Al−X	Al−H[a]	X−H[a]	∠H−Al−X[a]	∠H−Al−H[a]	∠H−X−Al	∠H−X−H
AlH_3		1.589		90.00	120.00		
$[NH_2]^-$			1.043				98.39
$[PH_2]^-$			1.437				91.85
$[AsH_2]^-$			1.554				90.69
$[H_3AlNH_2]^-$	1.895	1.666	1.020	114.41	107.67	113.44	105.56
		1.651		107.89	111.38		
$[H_3AlPH_2]^-$	2.427	1.640	1.424	111.50	110.65	99.16	93.67
		1.638		106.20	111.50		
$[H_3AlAsH_2]^-$	2.503	1.636	1.542	111.53	111.08	97.33	91.28
		1.637		105.85	111.23		
$[OH]^-$			0.980				
$[SH]^-$			1.353				
$[SeH]^-$			1.491				
$[H_3AlOH]^-$	1.807	1.645	0.968	107.68	110.08	109.15	
		1.661		110.89	107.24		
$[H_3AlSH]^-$	2.317	1.633	1.345	104.46	111.87	96.96	
		1.634		109.53	109.44		
$[H_3AlSeH]^-$	2.439	1.632	1.483	102.74	112.08	97.36	
		1.634		109.71	110.26		

[a] The second value corresponds to equivalent hydrogen atoms.

TABLE 2: Selected MP2(full)/6-31G(d) Bond Lengths (Å) and Bond Angles (deg) of Neutral Complexes

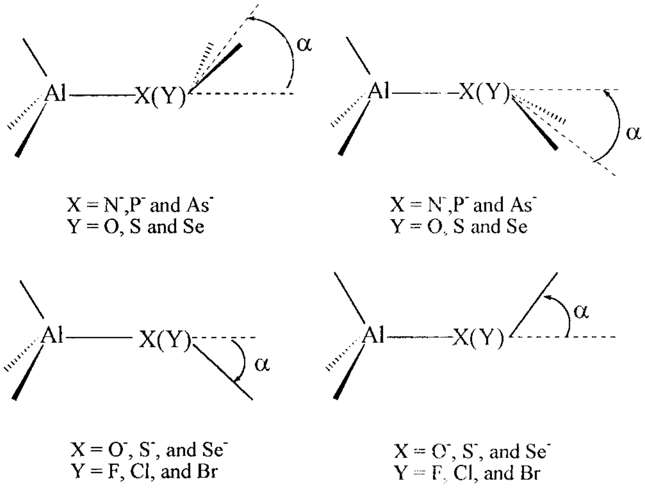
compound	Al−Y	Al−H[a]	Y−H[a]	∠H−Al−Y[a]	∠H−Al−H[a]	∠H−Y−Al	∠H−Y−H
AlH_3		1.589		90.00	120.00		
OH_2			0.969				103.96
SH_2			1.340				093.33
SeH_2			1.481				091.20
H_3AlOH_2	2.051	1.607	0.974	98.89	116.86	113.40	106.70
		1.599		97.72	120.42		
H_3AlSH_2	2.555	1.599	1.340	98.70	118.27	101.23	94.28
		1.597		95.69	119.46		
H_3AlSeH_2	2.642	1.600	1.479	99.75	118.41	98.36	91.32
		1.699		95.87	118.59		
FH			0.934				
ClH			1.280				
BrH			1.436				
H_3AlFH	2.075	1.610	0.950	87.08		101.0	
		1.591		100.55			
H_3AlClH	2.699	1.596	1.283	90.03		97.158	
		1.590		96.44			
H_3AlBrH	2.783	1.594	1.439	91.82		98.575	
		1.595		96.13			

[a] The second value corresponds to equivalent hydrogen atoms.

method, shows that the BSSE has a little effect on the calculated complexation energies.

3. Results and Discussion

3.1. Geometries. First, we have investigated the two possible structures (staggered and eclipsed conformations, Figure 1) for $[H_3AlXH]^-$ (X = NH, PH, AsH, O, S, and Se) and H_3AlYH (Y = OH, SH, SeH, F, Cl, and Br) complexes at the RHF/6-31G(d) level of theory. From calculated frequencies on the optimized geometries, the staggered optimized conformations were characterized as minima (NIMAG [number of imaginary frequencies] = 0) except H_3AlOH_2, H_3AlFH, and H_3AlClH complexes which seem as transition structures (NIMAG = 1). The same results have been reported by Ball for the AlX_3−OH_2 complexes.[11] All the minima structures, staggered ones for $[H_3AlXH]^-$ (X = NH, PH, AsH, O, S, and Se) and H_3-AlYH (Y = SH, SeH, and Br) complexes and eclipsed ones for H_3AlOH_2, H_3AlFH and H_3AlClH complexes, were reinvestigated at the MP2(full)/6-31G(d) level. Table 1 lists d_{Al-X}, d_{Al-H}, and d_{X-H} bond lengths and ∠H−Al−X, ∠H−Al−H, ∠H−X−Al, and ∠H−X−H bond angles for the anionic complexes and Table 2 lists the analogous neutral complexes parameters. The G2 total energies of all complexes and their corresponding fragments are presented in Table 3.



(a) Staggered conformation (b) Eclipsed conformation

Figure 1. Definition of the geometrical parameters of $[H_3AlXH]^-$ (X = NH, PH, AsH, O, S, and Se) and H_3AlYH (Y = OH, SH, SeH, F, Cl, and Br) complexes in (a) Staggered and (b) eclipsed conformations.

For the anionic adducts, $[H_3AlXH]^-$ (X = NH, PH, AsH, O, S, and Se), the d_{Al-X} bond length has a covalent nature. The

TABLE 3: G2 Total Energies (E_{tot}, au) of Complexes and Corresponding Free Ligands

anionic compounds			neutral compounds		
	complex	ligand		complex	ligand
$[H_3AlNH_2]^-$	−299.709 46	−55.817 40	H_3AlOH_2	−320.112 64	−76.332 05
$[H_3AlPH_2]^-$	−585.937 79	−342.094 94	H_3AlSH_2	−642.701 66	−398.930 71
$[H_3AlAsH_2]^-$	−2479.343 31	−2235.508 95	H_3AlSeH_2	−2644.939 66	−2401.170 18
$[H_3AlOH]^-$	−319.607 41	−75.712 78	H_3AlFH	−344.114 47	−100.350 01
$[H_3AlSH]^-$	−642.212 31	−398.371 59	H_3AlClH	−704.102 24	−460.340 18
$[H_3AlSeH]^-$	−2644.456 89	−2400.627 45	H_3AlBrH	−2816.934 21	−2573.173 20

[a] The G2 AlH_3 energy is −243.753 96 au.

corresponding values of $[H_3AlNH_2]^-$, $[H_3AlPH_2]^-$, $[H_3AlAsH_2]^-$, $[H_3AlOH]^-$, $[H_3AlSH]^-$, and $[H_3AlSeH]^-$ are 1.895, 2.427, 2.503, 1.807, 2.317, and 2.439 Å, respectively, close to the sum of the two covalent radii's of the Al and X atoms (1.988, 2.348, 2.458, 1.988, 2.288, and 2.418 Å, respectively).[25]

For the neutral adducts, H_3AlYH (Y = OH, SH, SeH, F, Cl, and Br), the d_{Al-Y} bond lengths are longer than the corresponding anionic ones. These distances increase as the Y atom electronegativity increases and vary from pseudo-covalent bonds to van der Waals ones. The optimized values at the MP2(full)/6-31G(d) are 2.051 and 2.075 Å for H_3AlOH_2 and H_3AlFH, respectively, to be compared with the MP2(full)/6-31G(d) d_{Al-Ne} (2.538 Å), corresponding to the hypothetical H_3Al-Ne van der Waals complex (second row of periodic table). For d_{Al-S} and d_{Al-Cl}, the optimized values are 2.555 and 2.699 Å, respectively, and the corresponding van der Waals $d_{Al-Ar} = 3.497$ Å. The optimized d_{Al-Se} and d_{Al-Br} bond lengths are 2.642 and 2.783 Å, respectively, and the corresponding van der Waals $d_{Al-Kr} = 3.120$ Å.

Upon complexation, the anionic adduct's bond length d_{X-H} becomes slightly shorter than the isolated fragments (Table 1), while the d_{Y-H} bond length corresponding to the neutral adducts becomes slightly longer (Table 2). On the other hand, the d_{Al-H} bond length becomes longer in all complexes. Concerning the bond angles, the $\angle H-Al-Y(X)$ (Figure 1, Y and X central atom of donor ligand) bond angle pass from 90° in free acceptor AlH_3 to values ranging between 104.5° and 114.5° in the anionic complexes but in the neutral ones its values are contained between 90° and 100°. The acceptor fragment AlH_3 structure passes thus from D_{3h} symmetry to a C_s symmetry upon complexation with the anionic donor ligands where the Al−H bond is more tilted. In the neutral adducts, the Al−H bond is slightly tilted. $\angle H-Al-X$ increases only by about 10°.

These geometrical considerations allow us to advance that the donor−acceptor coordination mode differs on going from anionic complexes to neutral ones and the interaction of the acceptor is thus stronger with the anionic ligand donor while it should be weaker with the neutral ones as we shall see in the complexation energy section.

Let us now examine the evolution of the $\angle H-X(Y)-Al$ (Figure 1) angle along the series where the donor fragment is bihydrogenated ($H_3AlX(Y)$ (X = $[NH_2]^-$, $[PH_2]^-$, and $[AsH_2]^-$, and Y = OH_2, SH_2, and SeH_2) complexes) and the other series where the donor fragment is monohydrogenated ($H_3AlX(Y)$ (X = $[OH]^-$, $[SH]^-$, and $[SeH]^-$, and Y = FH, ClH, and BrH) complexes). For the first series, this angle decreases on going from $[H_3AlNH_2]^-$ to $[H_3AlAsH_2]^-$ (Table 1) and from H_3AlOH_2 to H_3AlSeH_2 (Table 2), respectively. Nakano and Hirano[26] have observed this sequence in $H_3BX(CH_3)_2$ (X = O, S, and Se) compounds. As we will see below, this evolution can be explained by examining the donor fragment orbitals energetic placement in going from $[NH_2]^-$ (or OH_2) ligand to $[AsH_2]^-$ (or SeH_2) one. The same evolution is observed in the second series where the donor fragment is monohydrogenated, from $[H_3AlOH]^-$ to $[H_3AlSeH]^-$ complexes (Table 1) and from H_3AlFH to H_3AlBrH ones (Table 2). We will discuss this point in the coordination mode analysis section.

TABLE 4: G2 Complexation Energies (E_{comp} in kcal/mol) of Anionic and Neutral Complexes and NBO-MP2(full)/6-31G(d) Transferred Charge Q_c(electron)

anionic compounds			neutral compounds		
	E_{comp}[a]	Q_c		E_{comp}[a]	Q_c
$[H_3AlNH_2]^-$	−86.66	0.32	H_3AlOH_2	−16.71	0.12
$[H_3AlPH_2]^-$	−55.78	0.48	H_3AlSH_2	−10.66	0.19
$[H_3AlAsH_2]^-$	−50.45	0.49	H_3AlSeH_2	−9.74	0.22
$[H_3AlOH]^-$	−88.27	0.36	H_3AlFH	−6.59	0.10
$[H_3AlSH]^-$	−54.45	0.44	H_3AlClH	−5.16	0.11
$[H_3AlSeH]^-$	−47.36	0.41	H_3AlBrH	−4.36	0.14

[a] $E_{comp} = E(H_3Al-L) - [E(AlH_3) + E(L)]$.

3.2. Complexation Energy. In Table 4, we present the G2 computed complexation energy of all systems investigated in this work. This energy is taken as the difference between the complex energy and the sum of the AlH_3 and the free ligand ones. Ball[11] has reported an ab initio (MP2/6-31G(d,p) level) study of X_3AlOH_2 (X = H, F, and Cl) complexes, he found that the complexation energy of H_3AlOH_2 complex is about −19 kcal/mol. Furthermore, Wilson et al.[12] have calculated the complexation energies of H_3AlXH (X = F and Cl) complex at the MP4(SDTQ)/6-31G(d) level of theory. They found that the H_3AlFH and H_3AlClH complexation energies are −10.45 and −1.56 kcal/mol, respectively. More recently, Kulkarni[27] has reported that the complexation energies of H_3AlOH_2 and H_3AlFH are −16.89 and −6.58 kcal/mol, respectively, at the CCSDT//MP2/6-31++G(d,p) level. As we notice (Table 4), our G2-computed complexation energies are close to those previously obtained at higher level of calculation. In each series, we notice that the complexation energy decreases along the corresponding periodic table column. The complexation energies are −86.66, −57.78, and −50.45 kcal/mol for $[H_3AlNH_2]^-$, $[H_3AlPH_2]^-$, and $[H_3AlAsH_2]^-$ anionic complexes, respectively, while they are only −16.71, −10.66, and −9.74 kcal/mol for H_3AlOH_2, H_3AlSH_2, and H_3AlSeH_2 corresponding neutral ones, respectively. For the two other series, the complexation energies are −88.27, −54.45, and −47.36 for $[H_3AlOH]^-$, $[H_3AlSH]^-$, and $[H_3AlSeH]^-$, respectively, and −6.59, −5.16, and −4.36 kcal/mol for H_3AlFH, H_3AlClH, and H_3AlBrH, respectively. Comparing this evolution in the mono- and dihydrogenated ligand series, we can conclude that the anionic donor is strongly bound to the AlH_3 Lewis acid, the complex can be classified as a covalent compound. Nevertheless, the neutral donor ligand is weakly bound to the acceptor and the corresponding compound would be classified between a semicovalent and a van der Vaals compound type. These values can be explained since $[H_3AlNH_2]^-$, $[H_3AlPH_2]^-$, $[H_3AlAsH_2]^-$, $[H_3AlOH]^-$, $[H_3AlSH]^-$, and $[H_3AlSeH]^-$ are isoelectronic to the corresponding stable organic compounds H_3CNH_2, H_3CPH_2, H_3-

$CAsH_2$, H_3COH, H_3CSH, and H_3CSeH, respectively, and the HOMO orbital of the anionic ligands is energetically close to the AlH_3 LUMO one. Furthermore, in the anionic complexes, the central atom X of the donor is in its preferred coordination.

In Table 4, we have also reported the NBO-MP2(full)/6-31G-(d) analysis results. The most salient point is the inverted evolution of the transferred charge as compared to complexation energy. We notice that for each series, the ligand donor coordinates badly when descending in the corresponding column of the periodic table from O (or F) to Se (or Br) while the transferred charge increases in the even feel. The same trend has been observed for the anionic adduct series. One can conclude, therefore, that there is no correlation between the charge transfer and the G2 complexation energy for the two series of complexes. This point has been evoked in our previous works[13−18] and in other ones by Frenking et al.[28−30] and the same conclusion has been formulated.

3.3. Coordination Mode Analysis. In order to analyze the coordination mode in the alane complexes, we apply the QMOA to examine the factors behind the stabilization upon complexation and to show which fragment orbitals are implicated in the construction of the bond between aluminum and the central atom of the donor. We will also explain the relative stability of complexes investigated in this work. We will show why the H_3AlOH_2 (or H_3AlFH) complex is more stable than the H_3AlSH_2 (or H_3AlClH) and H_3AlSeH_2 (or H_3AlBrH) ones although all ligands have the same number of valence electrons and the same hybridization for the base center.

As is well-known, the AlH_3 vacant molecular orbital (LUMO) 7a′ which confers it the Lewis acid properties is constituted solely of p atomic orbital of aluminum atom whose the orientation is perpendicular to the molecular plan. Thanks to this MO, AlH_3 can receive from any donor fragment whose frontier occupied orbital possesses the appropriate orientation. The interaction is as good as the donor and the acceptor orbital energy levels are energetically close. In this section we shall omit in our reasoning the occupied 6a′ MO participation as we have reported it in previous work.[13,18] For the sake of simplicity, we shall describe all our systems (complexes and free fragments) in C_s symmetry.

In Figures 1, 2, and 3, we have depicted the interacting molecular orbitals of the two fragments (donor and acceptor). Figure 2 shows parallel and perpendicular preference interactions and their coordinated consequent MO. Figures 2 and 3 show the stabilizing and destabilizing interactions of both mono- and dihydrogenated donor adducts.

Concerning the neutral adducts, the YH_2 donor fragment has two a′ MO, HOMO and HOMO-1 (na′ and $(n-1)$a′ with n = 5, 8, and 14 for OH_2, SH_2, and SeH_2, respectively), which can interact with the 7a′ LUMO acceptor. Nevertheless, each one of these two a′ donor fragment MO favors a different orientation relative to the acceptor AlH_3 plane. The HOMO favors the parallel orientation (part a of Figure 2) while the HOMO-1 favors the perpendicular orientation (part b of Figure 2). The YH_2 disposition is thus a mixture of these two preferences. As we have mentioned in section 3.1 (Geometries), the leading factor controlling the donor disposition after coordination should be the rate of participation of each donor fragment MO (na′ and $(n-1)$a′) in the consequent orbital which would ensure the coordination with the fragment acceptor (part c of Figure 2). This can rationalize the tilt angle α[31] of the YH_2 plane with Al−Y axis. On the other hand, although the na′ and $(n-1)$a′ MO energies of the donor fragment become close to 7a′ of the alane ($E_{7a'}(AlH_3) - E_{na'}(YH_2)$ = 0.529 01, 0.404 12, and 0.379 13 au and $E_{7a'}(AlH_3) - E_{(n-1)a'}(YH_2)$ = 0.603 59, 0.500 14, and 0.496 52 au for Y = O, S, and Se, respectively, at MP2/6-311+G(3df,2p)//MP2(full)/6-31G(d) level) that should favor the coordination (part a of Figure 3), but the complexation energy decreases in the even feel (Table 3). To put light on this paradox, it would be necessary to take into account of the energetic levels evolution of the donor fragment molecular orbital ma″ (m = 1, 2, and 4 for O, S, and Se, respectively) that would have a π destabilizing interaction with the AlH_3 2a″ fragment MO (part b of Figure 3). The destabilizing character is due to the fact that four electrons occupy the two interacting MO's (2MO-4e$^-$). Indeed, the corresponding energetic gaps are $E_{2a''}(AlH_3) - E_{ma''}(YH_2)$ = 0.280 20, 0.160 66, and 0.119 31 au for Y = O, S, and Se, respectively, at MP2/6-311+G(3df,2p)//MP2(full)/6-31G(d) level. The ma″ MO becomes thus energetically close to the 2a″(AlH_3) one on going from OH_2 to SeH_2 fragment (part b of Figure 3). The destabilizing interaction would be stronger for SH_2 and SeH_2 adducts than the OH_2 one. These two interaction types are irregularly mixed; this gives an irregular decreasing evolution of the complexation energy.

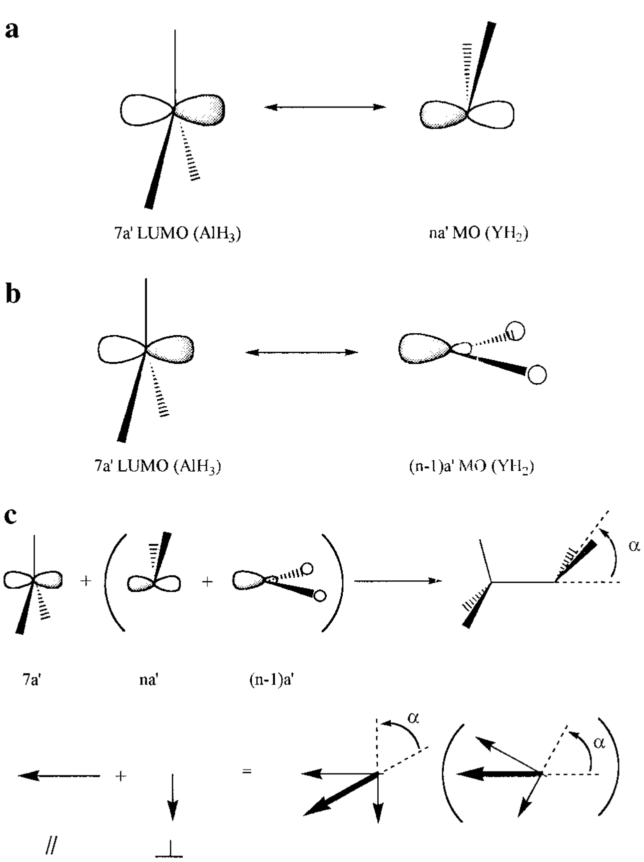


Figure 2. a′ symmetry interacting molecular orbitals (a) favoring the parallel coordination, (b) favoring the perpendicular coordination, and (c) consequence of both parallel and perpendicular interactions.

Concerning the H_3AlYH (Y = F, Cl, and Br) complexes, a similar situation is observed: a stabilizing interaction is developed between AlH_3 7a′ LUMO and a combination of na′ and $(n-1)$a′ (n = 5, 7, and 9 for Y = F, Cl, and Br atoms, respectively) MO of the hydrogen halide. The first one corresponds to one free pair localized on the halide atom and the second one is that participating to the Y−H bond (Y = halide) formation but localized on the halid atom.[32] The energetic levels of these MO increase in going from FH to BrH ($E_{na'}$ = −0.649 53, −0.477 46, and −0.435 88 au; $E_{(n-1)a'}$ = −0.763 11, −0.625 82, and −0.589 14 au for F, Cl, and Br, respectively, at the MP2/6-311+G(3df,2p)//MP2(full)/6-31G(d) level). The

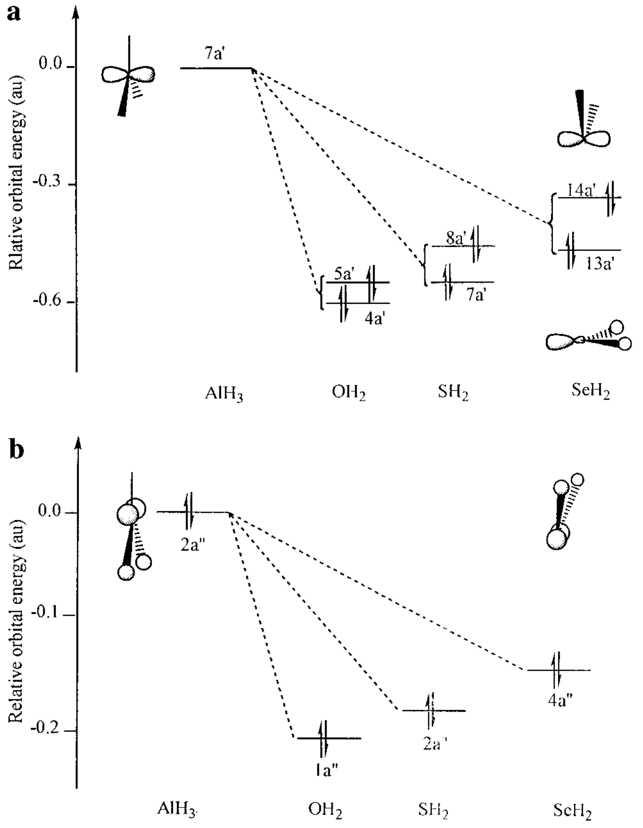


Figure 3. Relative orbital energy level diagram for AlH_3 and YH_2, (Y = O, S, and Se) of (a) a′ symmetry MO and (b) a″ symmetry MO.

7a′ AlH_3 LUMO is located at −0.431 55 au. As we notice, the Al−Y σ bond formation is favored in going from H_3AlFH to H_3AlBrH given that the interacting orbitals become energetically close (part a of Figure 4). Taking into account these gaps, we can advance that this interaction remains globally insufficient for constructing a true σ bond based on an axial overlap between donor and acceptor fragments molecular orbitals. To this handicap is added the 2MO-4e$^-$ destabilizing π interaction which is developed between the AlH_3 2a″ MO and the hydrogen halide *m*a″ (m = 1, 2, and 4 for F, Cl, and Br, respectively) one (part b of Figure 4). These interacting MO become energetically close in going from FH to BrH donor fragments, the corresponding gaps are $E_{2a''}(AlH_3) - E_{ma''}(YH) = 0.217\,98$, 0.045 91, and 0.004 33 au, respectively, and the π destabilizing interaction increases thus on descending in group 17. This has a consequence on the complexation energy which (i) decreases on going from H_3AlFH to H_3AlBrH complexes, and (ii) is so much weak that we could classify these compounds as van der Waals complexes.

In the anionic complexes, the coordination mode is based on a typical HOMO (donor)−LUMO (acceptor) interaction. These latter are *n*a′ (n = 4, 7, and 14 for $[NH_2]^-$ (or $[OH]^-$), $[PH_2]^-$ (or $[SH]^-$), and $[AsH_2]^-$ (or $[SeH]^-$) of the donor fragment and 7a′ of the acceptor one. The *n*a′ MO (or $[SeH]^-$, respectively) is energetically higher than that corresponding to neutral adducts. As is well-known, this leads to an excessively stabilizing interaction. However, by throwing a quick look on the relative energetic disposition of acceptor 7a′ and donor *n*a′ MO, we will understand why the corresponding complexation energies are globally so high (Table 4) in reference to the neutral compounds ones. The corresponding gap $E_{LUMO}(AlH_3) - E_{HOMO}([XH_2]^-)$ is about 0.06 au, and for the other series of anionic complexes, $E_{LUMO}(AlH_3) - E_{HOMO}([XH]^-)$ is about 0.11 au at the MP2/6-311+G(3df,2p)//MP2(full)/6-31G(d) level.

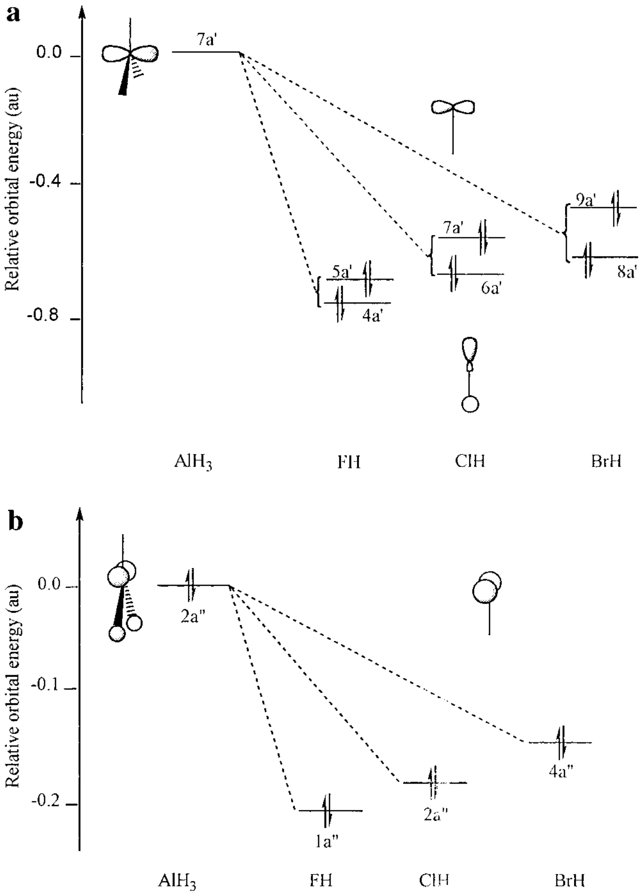


Figure 4. Relative orbital energy level diagram for AlH_3 and YH (Y = F, Cl, and Br) of (a) a′ symmetry MO and (b) a″ symmetry MO.

4. Conclusion

The stability of the H_3Al-L complex, where L is a mono- or dihydrogenated and anionic or neutral donor ligand with a central atom belonging to groups 15 ($[NH_2]^-$, $[PH_2]^-$, and $[AsH_2]^-$), 16 (OH_2, SH_2, SeH_2, $[OH]^-$, $[SH]^-$, and $[SeH]^-$), and 17 (FH, ClH, and BrH) of the periodic table, has been investigated at the G2 level of theory. For the neutral adducts the stability decreases irregularly while descending in the corresponding column. It is a consequence of two interactions that takes place between the two fragments (donor and acceptor). The first one is stabilizing and is developed between a′ symmetry molecular orbitals whereas the second one has a destabilizing character and is developed between molecular orbitals having a″ symmetry. In the anionic complexes, the mode of coordination is controlled mainly by the well-known HOMO−LUMO interaction. From NBO analysis, it was found that there is no correlation between the charge transfer and the G2 complexation energy.

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(31) The α tilt angle is that which separates the plane of XH_2 fragment and the Al−X axis; it is slightly different from the bond angle between the X−H bond and the Al−X bond axis or of its complement for the dihydrogenated ligands but is equal to $\angle$H−Y−Al bond angle for the monohydrogenated ones.

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