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Computational Study of the Protonation of $AlXH_2$ and AlX_2H (X = F, Cl, and Br). Structures of $AlXH_3^+$ and $AlX_2H_2^+$ and Their Dihydrogen Complexes $AlXH_5^+$ and $AlX_2H_4^+$

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Structures of protonated $AlXH_2$ and AlX_2H ($AlXH_3^+$ and $AlX_2H_2^+$) and their dihydrogen complexes $AlXH_5^+$ and $AlX_2H_4^+$ (X = F, Cl, and Br) were investigated using the ab initio method at the G2 level of theory. All the dihydrogen complexes involving hypercoordinated aluminum atom with a three-center two-electron (3c−2e) bond. The G2 calculated protonation energies of $AlXH_2$ and AlX_2H to form $AlXH_3^+$ and $AlX_2H_2^+$, respectively, were found to be highly exothermic. The possible dissociation of the cations $AlXH_5^+$ and $AlX_2H_4^+$ into $AlXH_3^+$ and $AlX_2H_2^+$ and molecular H_2, respectively, are calculated to be endothermic.

1. Introduction

There has been increasing experimental and theoretical interest in various types of donor acceptor complexes involving the Lewis acids AlH_3 and AlX_3 in recent years.[1−20] Our group has shown that the stability of these complexes does not depend on the charge transfer and the donor−acceptor interaction was not based on a simple HOMO−LUMO mixture.[15−20] Recently, Olah and Rasul[21] reported on the calculated structures and energies of the hexa-, hepta-, and octacoordinate alonium ions, AlH_6^+, AlH_7^{2+}, and AlH_8^{3+} and related AlH_4^+, AlH_5^{2+}, and AlH_6^{3+} ions. They have shown that the structure of AlH_4^+ is C_{2v} symmetrical with a three-center two-electron (3c−2e) bond. More recently, we have reported a theoretical investigation on the structures of protonated alane−Lewis base donor−acceptor complexes $H_4AlXH_3^+$ (X = N, P, and As) and $H_4AlYH_2^+$ (Y = O, S, and Se) as well as their neutral parents at the G2 level of theory.[22] We have shown that all the monocations $H_4AlXH_3(YH_2)^+$ are Al−H protonated, involving hypercoordinated alane with a three-center two-electron (3c−2e) bond and adopt the C_s symmetry arrangement. We have also shown that the protonation energies of $H_3AlXH_3(YH_2)$ to form $H_4AlXH_3(YH_2)^+$ were found to be highly exothermic and the possible dissociation of the cations $H_4AlXH_3(YH_2)^+$ into $H_2AlXH_3(YH_2)^+$ and molecular H_2 are endothermic. In continuation of our work, we have now extended our investigation to the structures and energetics of protonated $AlXH_3^+$ and $AlX_2H_2^+$ and their dihydrogen complexes $AlXH_5^+$ and $AlX_2H_4^+$ (X = F, Cl, and Br) by ab initio calculations. The relative stability of these protonated complexes are examined. The possible dissociation of the cations $AlXH_5^+$ and $AlX_2H_4^+$ into $AlXH_3^+ + H_2$ and $AlX_2H_2^+ + H_2$, respectively, are also examined. To the best of our knowledge, no comparative study of these complexes has been carried out.

2. Computational Details

Ab initio calculations were performed with the GAUSSIAN 98 program.[23] Geometry optimizations were performed at the MP2(full)/6-31G(d) level.[24] No symmetry constraints were imposed during the optimization process, and the geometry searches were carried out for a number of possible isomers to ensure the location of the global minimum. The zero-point vibrational energies (ZPE) are obtained from scaled HF/6-31G(d) calculated frequencies (scaled by the factor 0.893).[24] For improved energy, the Gaussian-2 (G2) energies[25] were computed. This level of calculation has recently been satisfactorily used to calculate similar complexes.[22]

TABLE 1: G2 Total Energies (au) and Relative Energies (kJ/mol) of $AlXH_3^+$ and $AlXH_5^+$ Complexes

complex	energy	ΔE	complex	energy	ΔE
$AlFH_3^+$ (**1a**)	−343.26589	0.0	$AlClH_5^+$ (**4a**)	−704.43203	0.0
$AlFH_3^+$ (**1b**)	−343.24934	43.43	$AlClH_5^+$ (**4b**)	−704.41150	54.81
$AlFH_5^+$ (**2a**)	−344.44336	0.0	$AlBrH_3^+$ (**5a**)	−2816.09303	0.0
$AlFH_5^+$ (**2b**)	−344.42323	52.84	$AlBrH_3^+$ (**5b**)	−2816.07344	51.42
$AlClH_3^+$ (**3a**)	−703.25746	0.0	$AlBrH_3^+$ (**6a**)	−2817.26649	0.0
$AlClH_3^+$ (**3b**)	−703.23791	51.34	$AlBrH_3^+$ (**6b**)	−2817.24671	51.92

TABLE 2: G2 Total Energies (au) and Relative Energies (kJ/mol) of $AlX_2H_2^+$ and $AlX_2H_4^+$ Complexes

complex	energy	ΔE	complex	energy	ΔE
$AlF_2H_2^+$ (**7a**)	−442.48950	0.0	$AlCl_2H_4^+$ (**10a**)	−1163.65269	0.0
$AlF_2H_2^+$ (**7b**)	−442.48687	7.70	$AlCl_2H_4^+$ (**10b**)	−1163.63334	50.79
$AlF_2H_2^+$ (**7c**)	−442.48457	12.93	$AlCl_2H_4^+$ (**10c**)	−1163.63267	52.55
$AlF_2H_4^+$ (**8a**)	−443.67328	0.0	$AlBr_2H_2^+$ (**11a**)	−5388.14855	0.0
$AlF_2H_4^+$ (**8b**)	−443.66222	29.04	$AlBr_2H_2^+$ (**11b**)	−5388.13246	42.26
$AlF_2H_4^+$ (**8c**)	−443.66016	34.43	$AlBr_2H_2^+$ (**11c**)	−5388.13240	42.38
$AlCl_2H_2^+$ (**9a**)	−1162.47722	0.0	$AlBr_2H_4^+$ (**12a**)	−5389.32121	0.0
$AlCl_2H_2^+$ (**9b**)	−1162.46293	37.40	$AlBr_2H_4^+$ (**12b**)	−5389.30469	43.39
$AlCl_2H_2^+$ (**9c**)	−1162.46248	38.70	$AlBr_2H_4^+$ (**12c**)	−5389.30455	43.72

3. Results and Discussion

Calculated G2 energies and relative energies are listed in Tables 1 and 2, respectively, for $AlXH_3^+$ and $AlXH_5^+$ and $AlX_2H_2^+$ and $AlX_2H_4^+$ complexes (X = F, Cl, and Br). G2 thermodynamics of the selected complexation and protonation processes are given in Tables 3 and 4. MP2(full)/6-31G(d)

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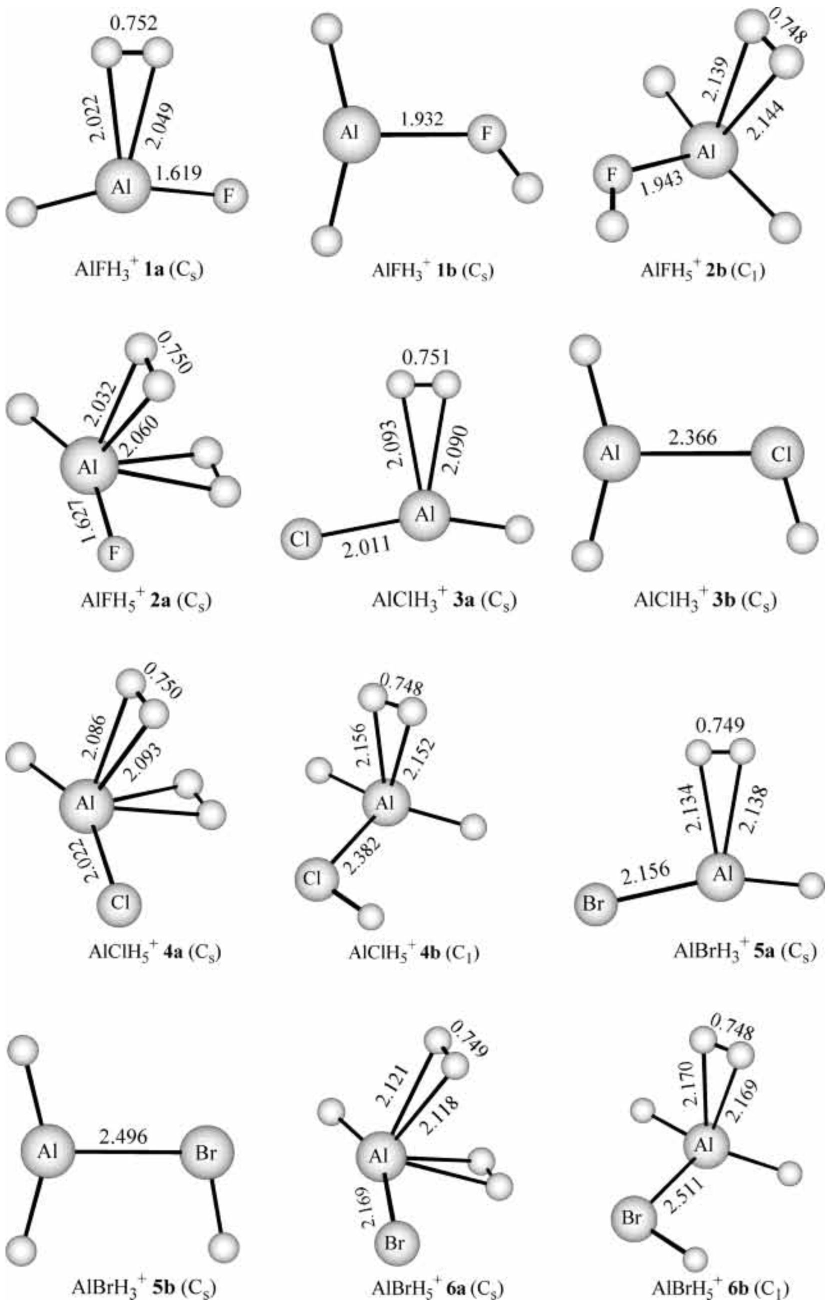


Figure 1. MP2(full)/6-31G(d) optimized structures of **1**−**6** complexes.

TABLE 3: Thermodynamics (kJ/mol) of the Selected Process

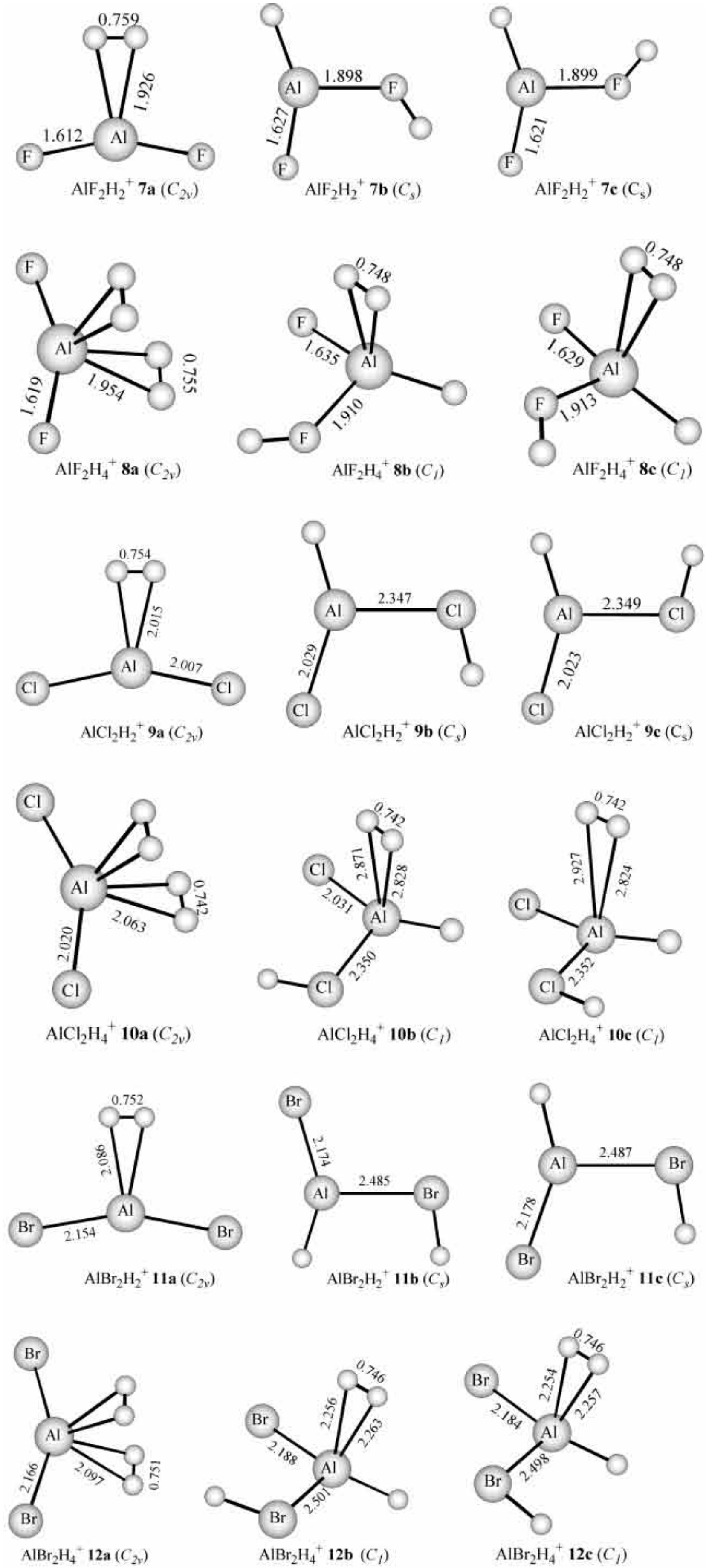
	G2		
process	ΔE_0	ΔH_0	ΔG_{298}
$AlFH^+ + H_2 \rightarrow AlFH_3^+$ (**1a**)	−33.09	−37.70	−12.22
$AlFH_2 + H^+ \rightarrow AlFH_3^+$ (**1a**)	−684.38		
$AlFH_3^+$ (**1a**) + $H_2 \rightarrow AlFH_5^+$ (**2a**)	−29.16	−33.26	−3.35
$AlClH^+ + H_2 \rightarrow AlClH_3^+$ (**3a**)	−22.51	−26.61	−2.09
$AlClH_2 + H^+ \rightarrow AlClH_3^+$ (**3a**)	−707.97		
$AlClH_3^+$ (**3a**) + $H_2 \rightarrow AlClH_5^+$ (**4a**)	−21.55	−25.06	+4.10
$AlBrH^+ + H_2 \rightarrow AlBrH_3^+$ (**5a**)	−19.79	−23.14	−0.33
$AlBrH_2 + H^+ \rightarrow AlBrH_3^+$ (**5a**)	−717.22		
$AlBrH_3^+$ (**5a**) + $H_2 \rightarrow AlBrH_5^+$ (**6a**)	−18.66	−22.38	+7.03

TABLE 4: Thermodynamics (kJ/mol) of the Selected Process

	G2		
process	ΔE_0	ΔH_0	ΔG_{298}
$AlF_2^+ + H_2 \rightarrow AlF_2H_2^+$ (**7a**)	−67.20	−71.76	−42.17
$AlF_2H + H^+ \rightarrow AlF_2H_2^+$ (**7a**)	−612.79		
$AlF_2H_2^+$ (**7a**) + $H_2 \rightarrow AlF_2H_4^+$ (**8a**)	−45.73	−50.17	−21.13
$AlCl_2^+ + H_2 \rightarrow AlCl_2H_2^+$ (**9a**)	−27.11	−31.88	−5.77
$AlCl_2H + H^+ \rightarrow AlCl_2H_2^+$ (**9a**)	−674.71		
$AlCl_2H_2^+$ (**9a**) + $H_2 \rightarrow AlCl_2H_4^+$ (**10a**)	−23.93	−28.16	+0.96
$AlBr_2^+ + H_2 \rightarrow AlBr_2H_2^+$ (**11a**)	−18.45	−22.72	+2.09
$AlBr_2H + H^+ \rightarrow AlBr_2H_2^+$ (**11a**)	−695.00		
$AlBr_2H_2^+$ (**11a**) + $H_2 \rightarrow AlBr_2H_4^+$ (**12a**)	−16.53	−20.71	+8.20

optimized geometries for all species studied in this work are given in Figures 1 and 2.

$AlXH_3^+$ and $AlXH_5^+$. Two structures (C_s symmetry conformation) of protonated $AlXH_2$, Al−H protonated **1a**, **3a**, and **5a** and X-protonated **1b**, **3b**, and **5b** (Figure 1), were found to be minima on the potential energy surface at the MP2(full)/6-31G(d) level of theory. Structures **1a**, **3a**, and **5a** are planar and contain a three-center two-electron (3c−2e) Al−H bond. Structures **1b**, **3b**, and **5b** are also planar and have a halogenonium ion with a slightly longer Al−X bond (1.932, 2.366,



$AlF_2H_2^+$ **7a** (C_{2v}) $AlF_2H_2^+$ **7b** (C_s) $AlF_2H_2^+$ **7c** (C_s)

$AlF_2H_4^+$ **8a** (C_{2v}) $AlF_2H_4^+$ **8b** (C_1) $AlF_2H_4^+$ **8c** (C_1)

$AlCl_2H_2^+$ **9a** (C_{2v}) $AlCl_2H_2^+$ **9b** (C_s) $AlCl_2H_2^+$ **9c** (C_s)

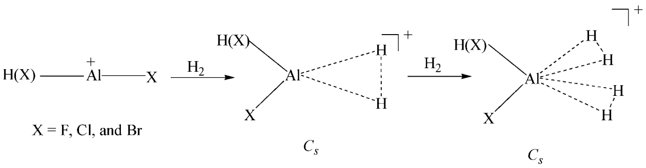
$AlCl_2H_4^+$ **10a** (C_{2v}) $AlCl_2H_4^+$ **10b** (C_1) $AlCl_2H_4^+$ **10c** (C_1)

$AlBr_2H_2^+$ **11a** (C_{2v}) $AlBr_2H_2^+$ **11b** (C_s) $AlBr_2H_2^+$ **11c** (C_s)

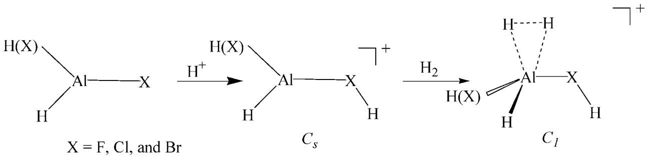
$AlBr_2H_4^+$ **12a** (C_{2v}) $AlBr_2H_4^+$ **12b** (C_1) $AlBr_2H_4^+$ **12c** (C_1)

Figure 2. MP2(full)/6-31G(d) optimized structures of **7**−**12** complexes.

SCHEME 1



SCHEME 2



and 2.496 Å, respectively for X = F, Cl, and Br). **1a**, **3a**, and **5a** are more stable than **1b**, **3b**, and **5b** by 43.43, 52.84, and 51.34 kJ/mol, respectively. This shows that the Al−H bond is a better donor than the halogen nonbonded electron pair in $AlXH_2$ system. The 3c−2e Al−H bond distances of **1a** and **3a** (2.022 and 2.049 Å for $AlFH_3^+$, 2.090 and 2.093 Å for $AlClH_3^+$) are slightly shorter than that of AlH_4^+ (2.104 Å), and the 3c−2e Al−H bond distances of **5a** ($AlBrH_3^+$) (2.134 and 2.138 Å) are slightly longer than that of AlH_4^+. Protonation of $AlXH_2$ to give respectively **1a**, **3a**, and **5a** ($AlXH_3^+$) were calculated to be exothermic by −684.38, −707.97, and −717.22 kJ/mol, respectively, for X = F, Cl, and Br, which are less exothermic than protonation of AlH_3 at the same G2 level of theory (−738.06 kJ/mol)[21]

On the other hand, **1a**, **3a**, and **5a** can be viewed as complexes between the dicoordinated $AlXH^+$ ion and molecular H_2. The complexation processes were computed to be exothermic (Scheme 1, Table 3). Similar complexation of AlH_2^+ and H_2 leading to AlH_4^+ is exothermic by −21.34 kJ/mol, at the same G2 level of theory. The same trends are observed at room temperature (298 K). These observations indicate that the complexes **1a**, **3a**, and **5a** are expected to be experimentally characterizable in the gas phase.

Further complexation of **1a**, **3a**, and **5a** with molecular H_2 leads to $AlXH_5^+$ (C_s symmetry conformations) **2a**, **4a**, and **6a**, which were found to be stable minima at the MP2(full)/6-31G(d) level of theory (Scheme 1, Figure 1). All the $AlXH_5^+$ complexes contain a six-coordinate aluminum and two 3c−2e bonds. Formation of **2a**, **4a**, and **6a** complexes from **1a**, **3a**, and **5a**, respectively, are also exothermic processes. However, the complexation energy decreases when descending in the corresponding periodic table column, from the fluorine to the bromine atom. In comparison, complexation of AlH_4^+ with H_2 leading to hexacoordinate AlH_6^+ is indicated to be exothermic by −20.50 kJ/mol, at the same G2 level of theory.[21]

Complexation of **1b**, **3b**, and **5b** (C_s symmetry conformation) structures with molecular H_2 lead to C_1 symmetry monocations **2b**, **4b**, and **6b**, respectively (Scheme 2, Figure 1), which were calculated to be stable structures on the potential energy surface at the MP2(full)/6-31G(d) level of theory. They also contain a five-coordinate aluminum atom with a three-center two-electron (3c−2e) bond (Figure 1). The calculated complexation energies of **1b**, **3b**, and **5b** with molecular H_2 are −29.16, −21.55, and −18.66 kJ/mol, respectively. Indeed, the complexation energy decreases when descending in the corresponding periodic table column, from fluorine to bromine. At room temperature (298 K) the free energy change for the complexation processes are calculated to be slighly endothermic. This indicates that the ions **2a**, **4a**, and **6a** should be unstable at room temperature. On the other hand, **2b**, **4b**, and **6b** (X = F, Cl, and Br) structures can be considered as a complex between AlH_4^+ and XH. Formation of **2b**, **4b**, and **6b** complexes were calculated to be exothermic by −100.25, −95.31, and −101.10 kJ/mol, respectively for X = F, Cl, and Br, at the G2 level of theory.

AlX_2H^+ and $AlX_2H_2^+$. Tree structures (C_s symmetry conformation) of protonated AlX_2H (X = F, Cl, and Br), Al−H protonated **7a**, **9a**, and **11a** and X-protonated 7**b**,**c**, **9b**,**c**, and **11b**,**c** (Figure 2), were found to be minima on the potential energy surface at the MP2(full)/6-31G(d) level of theory. The C_s structures **7a**, **9a**, and **11a** are planar and also contain a 3c−2e Al−H bond. The structures 7**b**,**c**, **9b**,**c**, and **11b**,**c** are also planar and have a halogenonium ion with a longer Al−X bond (Figure 2). **7a**, **9a**, and **11a** structures are, like $AlXH_3^+$ structures, more stable than 7**b**,**c**, **9b**,**c**, and **11b**,**c** structures, respectively (see Table 2). Protonation of AlX_2H to give respectively **7a**, **9a**, and **11a** ($AlX_2H_2^+$) were calculated to be exothermic by −612.79, −674.71, and −695.0 kJ/mol, respectively for X = F, Cl, and Br, which are also less exothermic than protonation of AlH_3 (−738.06 kJ/mol)[21] On the other hand, **7a**, **9a**, and **11a** can be considered as complexes of AlX_2^+ ion and H_2. The coresponding complexation processes were computed to be exothermic by −67.20, −27.11, and −18.45 kJ/mol for X = F, Cl, and Br, respectively (Scheme 1, Table 4). Similar results are obtained for the complexation of $AlXH^+$ and H_2 leading to $AlXH_3^+$ at the same G2 level of theory. The same trends are observed at room temperature (298 K). Thus, these observations indicate that the complexes **7a**, **9a**, and **11a** can be expected to be experimentally characterizables in the gas phase.

Complexation of **7a**, **9a**, and **11a** with molecular H_2 also give respectively C_{2v} symmetry stable strucrures **8a**, **10a**, and **12a**, which also contain a six-coordinate aluminum and two 3c−2e bonds (Scheme 1, Figure 2). The complexation processes are calculated to be exothermic by −45.73, −23.93, and −16.53 kJ/mol for X = F, Cl, and Br, respectively. Complexation of 7**b**,**c**, **9b**,**c**, and **11b**,**c** (C_s symmetry conformation) structures with molecular H_2 lead to C_1 symmetry monocations 8**b**,**c**, **10b**,**c**, and **12b**,**c**, respectively (Scheme 2, Figure 2), which were calculated to be stable structures on the potential energy surface at the MP2(full)/6-31G(d) level of theory. They also contain a five-coordinate aluminum atom with a three-center two-electron (3c−2e) bond. On the other hand, 8**b**,**c**, **10b**,**c**, and **12b,c** structures can be considered as a complex between $AlX_2H_2^+$ (**1a**, **3a**, and **5a**) and XH. Formation of $AlX_2H_4^+$ (8**b**, **10b**, and **12b)** from $AlX_2H_2^+$ and XH are also calculated to be be exothermic by −121.63, −93.76, and −101.0 kJ/mol, respectively, for X = F, Cl, and Br. These values are comparable to that obtained for the formation of $AlXH_5^+$ from AlH_4^+ and XH systems.

4. Conclusion

Structures of protonated $AlXH_2$ and AlX_2H ($AlXH_3^+$ and $AlX_2H_2^+$) and their dihydrogen complexes $AlXH_5^+$ and $AlX_2H_4^+$ (X = F, Cl, and Br) were investigated by the ab initio method at the G2 level of theory. All the dihydrogen complexes involved a hypercoordinated aluminum atom with a three-center two-electron (3c−2e) bond. The G2 calculated protonation energies of $AlXH_2$ and AlX_2H to form $AlXH_3^+$ and $AlX_2H_2^+$, respectively, were found to be highly exothermic. The possible dissociation of the cations $AlXH_5^+$ and $AlX_2H_4^+$ into $AlXH_3^+$ and $AlX_2H_2^+$ and molecular H_2, respectively, are calculated to be endothermic. These observations indicate that the $AlXH_3^+$,

$AlX_2H_2^+$, $AlXH_5^+$, and $AlX_2H_4^+$ complexes are expected to be experimentally observable in the gas phase.

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