Molecular Orbital Investigation of the Protonated $H_2X_2AlNH_n(CH_3)_{3-n}^+$ (X = F, Cl, and Br; *n* = 0−3) Complexes

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Received: May 17, 2005; In Final Form: September 30, 2005

Structures of protonated alane−Lewis base donor−acceptor complexes $H_2X_2AlNH_n(CH_3)_{3-n}^+$ (X = F, Cl, and Br; $n = 0-3$) as well as their neutral parents were investigated. All the monocations $H_2X_2AlNH_n(CH_3)_{3-n}^+$ are Al−H protonated involving hypercoordinated alane with a three-center two-electron bond and adopt the C_s symmetry arrangement. The energetic results show that the protonated alane−Lewis complexes are more stable than the neutral ones. They also show that this stability decreases on descending in the corresponding periodic table column from fluorine to bromine atoms. The calculated protonation energies of $HX_2AlNH_n(CH_3)_{3-n}$ to form $H_2X_2AlNH_n(CH_3)_{3-n}^+$ were found to be highly exothermic. The possible dissociation of the cations $H_2X_2AlNH_n(CH_3)_{3-n}^+$ into $X_2AlNH_n(CH_3)_{3-n}^+$ and molecular H_2 is calculated to be endothermic.

Introduction

The binding interactions between an electron pair donor (Lewis base) and an electron pair acceptor (Lewis acid) are well-known to play an important role in many chemical processes. Donor−acceptor complexes of Lewis acid AlH_3 and AlX_3 have been the subject of many experimental and theoretical studies.[1−14] Our group has shown that the stability of these complexes does not depend on the charge transfer and the donor−acceptor interaction was notably based on a simple HOMO−LUMO mixture.[15−20] Recently, Olah et al.[21−25] reported ab initio calculated structures and energies of the B−H protonated H_3BX^+ systems (X = NH_3, PH_3, OH_2, SH_2, CO, CO_2, COS, and CS_2). They have found that the protonation of H_3BX to form H_4BX^+ was highly exothermic. They have also shown that the protonation of AlH_3 leads to the C_{2v} symmetrical structure AlH_4^+ with a three-center two-electron (3c-2e) bond.[26] On the other hand, 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).[27] We have shown that all the monocations $H_4AlXH_3(YH_2)^+$ are Al−H protonated involving hypercoordinated alane with a 3c-2e bond and adopt the C_s symmetry arrangement. The energetic results show that the protonated alane−Lewis complexes are more stable than the neutral ones. 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 is endothermic.[27] Recently, we have reported our investigation on the 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).[28] We have also shown that all the dihydrogen complexes involve a hypercoordinated aluminum atom with a 3c-2e bond. The calculated protonation energies of $AlXH_2$ and AlX_2H to form $AlXH_3^+$ and $AlX_2H_2^+$, respectively, were found to be highly exothermic.[28] In continuation of our work, we have now extended our investigation to the structures and energetics of protonated $H_2X_2AlNH_n(CH_3)_{3-n}^+$ (X = F, Cl, and Br; $n = 0-3$) as donor−acceptor complexes. The relative stabilities of these protonated complexes are examined. The possible dissociation of cations $H_2X_2AlNH_n(CH_3)_{3-n}^+$ into $X_2AlNH_n(CH_3)_{3-n}^+$ and molecular H_2 is also examined. To the best of our knowledge, no comparative study of these complexes has been carried out.

Computational Details

Calculations were performed using the Gaussian 98 program system.[29] The geometry optimization and vibrational frequency calculations were performed at the B3LYP/6-311+G(d,p) level.[30] Vibrational frequencies were used to characterize stationary points as minima and to evaluate zero-point vibrational energies (ZPEs), which were scaled by a factor of 0.98.[31] Final energies were calculated at the B3LYP/6-311+G(d,p) + ZPE level. The electronic structures were determined using the natural bond orbital (NBO)[32] partitioning analysis at the B3LYP/6-311+G(d,p) level.

Results and Discussion

Optimized geometries of the protonated complexes and the corresponding neutral ones are shown, respectively, in Figures 1 and 2. Tables 1 and 2 list the most important optimized geometrical parameters of $H_2X_2AlNH_n(CH_3)_{3-n}^+$ protonated complexes (X = F, Cl, and Br; $n = 0-3$) and $HX_2AlNH_n(CH_3)_{3-n}$ nonprotonated ones, respectively. Table 3 lists the calculated complexation energies of $H_2X_2Al^+$ with $NH_n(CH_3)_{3-n}$, charge transfer from the $NH_n(CH_3)_{3-n}$ Lewis base to the $H_2X_2Al^+$ Lewis acid, and proton affinities of $HX_2AlNH_n(CH_3)_{3-n}$ neutral complexes. For accurate comparison, we also report in Table 3 the MP2/6-311+G(d,p)//MP2/6-311G+(d,p) complexation energies of $H_2X_2Al^+$ with NH_3 (X = F, Cl, and Br). Table 4 lists the thermodynamic values for the dissociation process of $H_2X_2AlNH_n(CH_3)_{3-n}^+$ into $X_2AlNH_n(CH_3)_{3-n}^+$ and molecular H_2. In Table 5 we report the entropy and thermal corrections to the internal energy for all species studied in this work.

Al−H protonation of HX_2AlNH_3 (C_s symmetry conformation) leads to monocation $H_2X_2AlNH_3^+$, which was calculated to be a stable structure. It contains a five-coordinate aluminum atom

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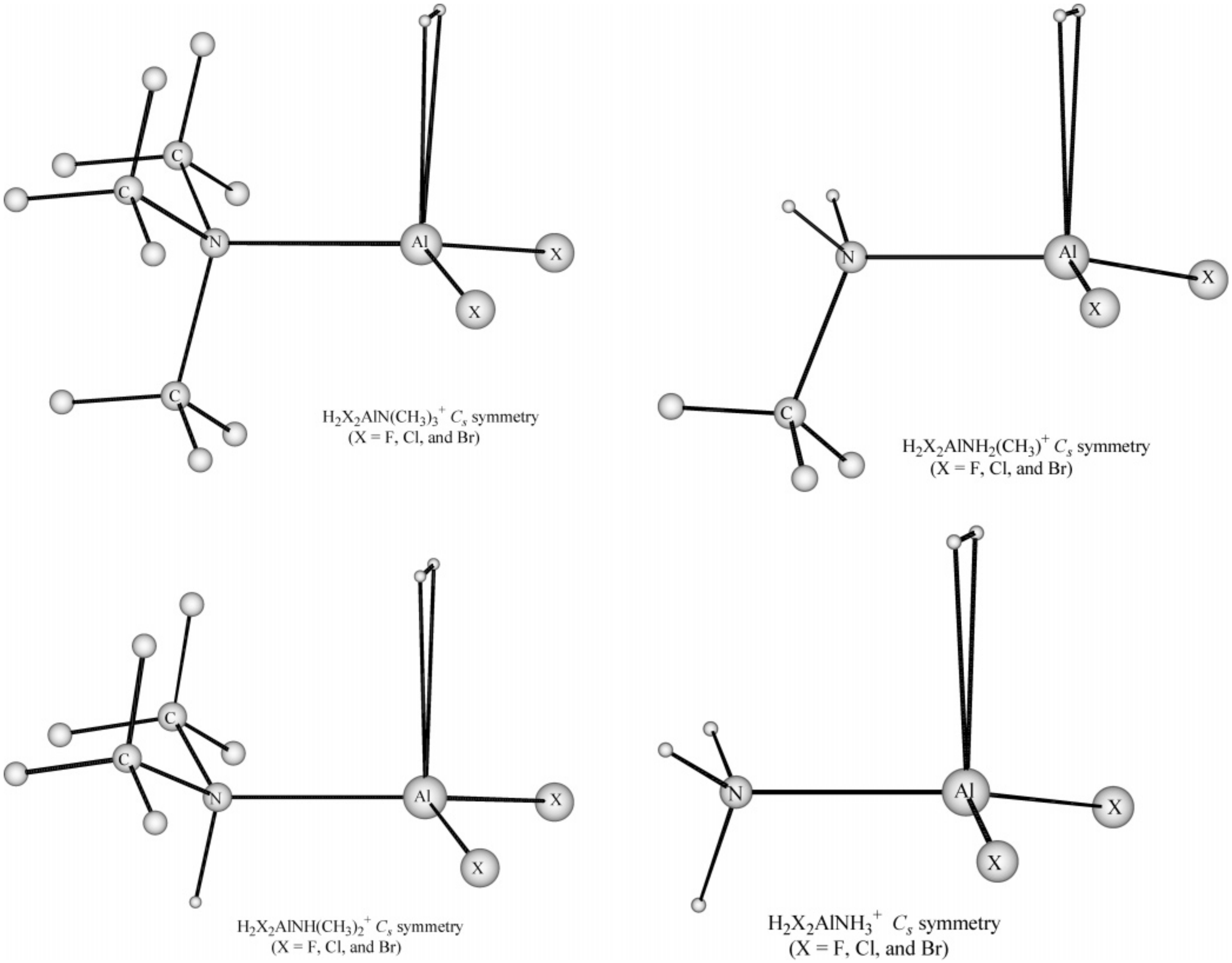


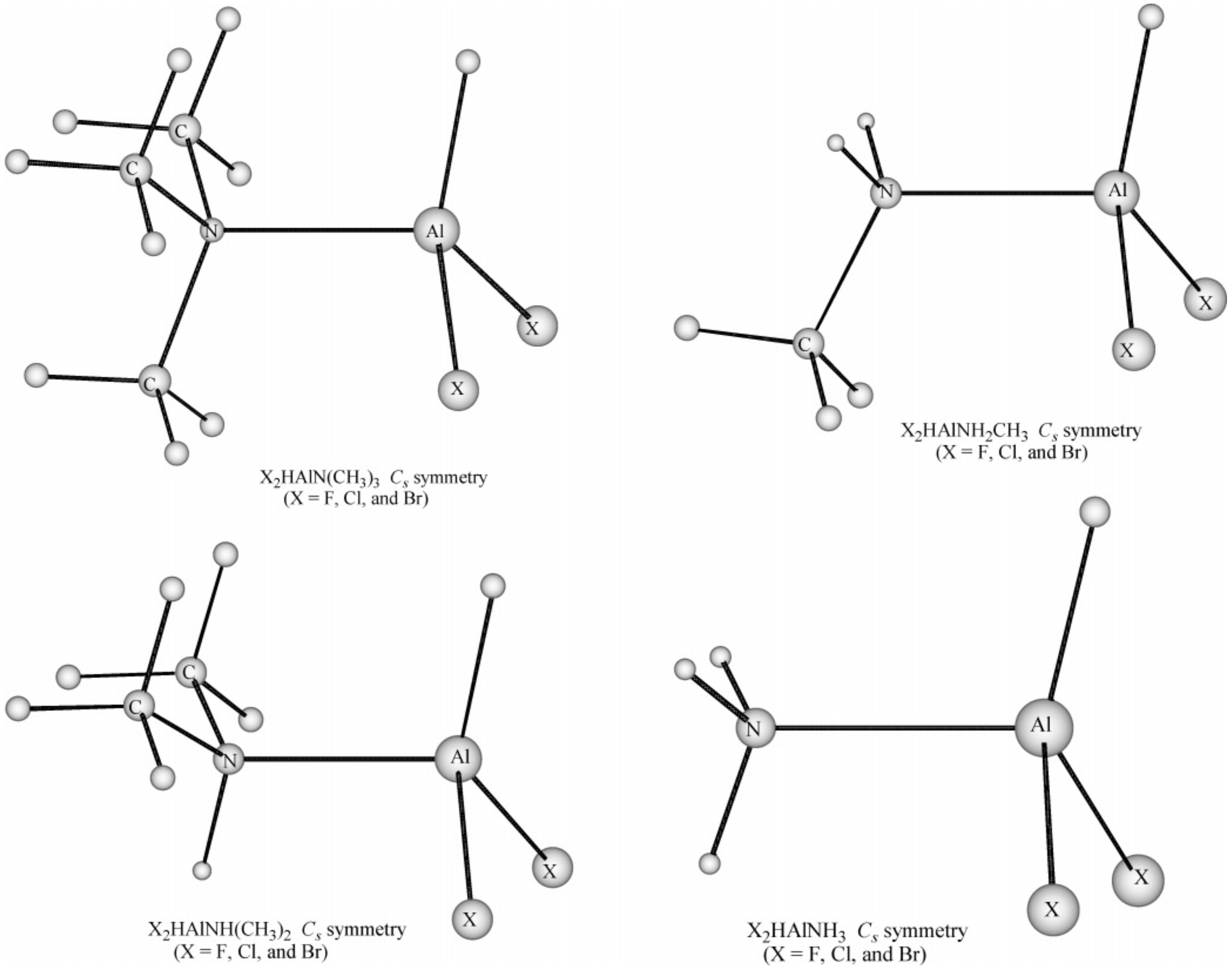
Figure 1. Definition of the geometrical parameters of protonated $H_2X_2AlNH_n(CH_3)_{3-n}^+$ (X = F, Cl, and Br; $n = 0-3$) complexes.

TABLE 1: Selected Optimized Bond Lengths (Å) and Bond Angles (deg) of $H_2X_2AlN(CH_3)_{3-n}H_n^+$ (X = F, Cl, and Br; $n = 0-3$) Protonated Complexes

complex	Al−N	Al−X	Al−H_2	N−C[a]	N−H[a]	H−H	−X−Al−N	−C(H)−N−Al[a]
$H_2F_2AlNH_3^+$	1.957	1.644	2.041		1.027 1.025	0.763	108.36	110.40 113.85
$H_2F_2AlNH_2CH_3^+$	1.941	1.646	2.050	1.525	1.024	0.762	109.32	111.68 111.65
$H_2F_2AlNH(CH_3)_2^+$	1.940	1.648	2.057	1.512	1.025	0.761	110.53	113.54 105.30
$H_2F_2AlN(CH_3)_3^+$	1.934	1.650	2.064	1.507 1.513		0.760	111.16	111.74 105.20
$H_2Cl_2AlNH_3^+$	1.982	2.055	2.135		1.026 1.024	0.760	109.92	110.27 113.81
$H_2Cl_2AlNH_2CH_3^+$	1.965	2.059	2.145	1.520	1.023	0.759	110.76	112.25 111.26
$H_2Cl_2AlNH(CH_3)_2^+$	1.972	2.063	2.141	1.511	1.025	0.759	112.58	114.56 104.07
$H_2Cl_2AlN(CH_3)_3^+$	1.968	2.066	2.154	1.506 1.511		0.758	113.12	112.37 105.10
$H_2Br_2AlNH_3^+$	1.993	2.211	2.189		1.025 1.024	0.758	110.15	110.14 113.72
$H_2Br_2AlNH_2CH_3^+$	1.976	2.215	2.211	1.518	1.023	0.757	111.01	112.80 110.92
$H_2Br_2AlNH(CH_3)_2^+$	1.985	2.220	2.196	1.510	1.025	0.757	112.95	114.82 103.62
$H_2Br_2AlN(CH_3)_3^+$	1.982	2.224	2.214	1.505 1.510		0.757	113.63	112.42 105.32

[a] The second value corresponds to equivalent atoms.

with a 3c-2e bond (Figure 1). $H_2X_2Al^+$ is of C_{2v} symmetry and also contains a 3c-2e bond.[24] The Al−N bond lengths of $H_2X_2AlNH_3^+$ (X = F, Cl, and Br) are 1.957, 1.982, and 1.993 Å, 0.089, 0.067, and 0.068 Å shorter than those found in HF_2-



$X_2HAlN(CH_3)_3$ C_s symmetry
(X = F, Cl, and Br)

$X_2HAlNH_2CH_3$ C_s symmetry
(X = F, Cl, and Br)

$X_2HAlNH(CH_3)_2$ C_s symmetry
(X = F, Cl, and Br)

X_2HAlNH_3 C_s symmetry
(X = F, Cl, and Br)

Figure 2. Definition of the geometrical parameters of neutral $HX_2AlNH_n(CH_3)_{3-n}$ (X = F, Cl, and Br; $n = 0-3$) complexes.

TABLE 2: Selected Optimized Bond Lengths (Å) and Bond Angles (deg) of $HX_2AlN(CH_3)_{3-n}H_n$ (X = F, Cl, and Br; $n = 0-3$) Nonprotonated Complexes

complex	Al−N	Al−X	Al−H	N−C[a]	N−H[a]	−H−Al−N	−X−Al−N	−C(H)−N−Al[a]
HF_2AlNH_3	2.047	1.700	1.571		1.018 1.020	107.24	96.64	112.88 108.00
$HF_2AlNH_2CH_3$	2.037	1.702	1.573	1.495	1.019	106.70	97.60	112.98 109.14
$HF_2AlNH(CH_3)_2$	2.034	1.703	1.574	1.487	1.020	107.05	97.75	112.44 103.14
$HF_2AlN(CH_3)_3$	2.045	1.703	1.575	1.487 1.490		106.20	98.86	109.11 108.68
HCl_2AlNH_3	2.049	2.148	1.572		1.019 1.020	104.58	98.72	112.13 109.66
$HCl_2AlNH_2CH_3$	2.043	2.150	1.574	1.494	1.020	102.94	100.50	117.39 107.07
$HCl_2AlNH(CH_3)_2$	2.047	2.153	1.575	1.490	1.021	103.69	100.97	112.33 104.85
$HCl_2AlN(CH_3)_3$	2.063	2.154	1.575	1.490 1.491		102.41	102.41	108.43 111.63
HBr_2AlNH_3	2.050	2.313	1.573		1.019 1.020	104.15	98.99	112.04 109.91
$HBr_2AlNH_2CH_3$	2.045	2.315	1.576	1.494	1.020	102.12	101.05	118.27 106.68
$HBr_2AlNH(CH_3)_2$	2.051	2.319	1.576	1.491	1.021	103.09	101.67	102.37 105.07
$HBr_2AlN(CH_3)_3$	2.069	2.320	1.576	1.492 1.491		102.05	103.29	108.30 109.43

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

$AlNH_3$, HCl_2AlNH_3, and HBr_2AlNH_3, respectively, at the same B3LYP/6-311+G(d,p) level of theory, which indicate stronger Al−N bonding in protonated $H_2X_2AlNH_3^+$ than that in neutral X_2HAlNH_3 complexes. The complexation energies $H_2X_2Al^+$ +

TABLE 3: Complexation Energies, E_{comp} (kcal/mol), of $H_2X_2Al^+$ with $NH_n(CH_3)_{n-3}$ (X = F, Cl, and Br; n = 0−3), and Charge Transfer, Q_c (electrons), and Proton Affinities, PAs (kcal/mol), of $HX_2AlNH_n(CH_3)_{n-3}$ Neutral Complexes

complex	$E_{comp}{}^a$	$Q_c{}^b$	PA^c
$H_2F_2AlNH_3^+$	−72.33 (−30.13) −73.42^d	0.199 (0.149)	183.35
$H_2F_2AlNH_2CH_3^+$	−78.98 (−32.72)	0.201 (0.146)	187.41
$H_2F_2AlNH(CH_3)_2^+$	−81.78 (−33.44)	0.199 (0.138)	189.49
$H_2F_2AlN(CH_3)_3^+$	−83.50 (−32.64)	0.192 (0.129)	192.01
$H_2Cl_2AlNH_3^+$	−60.18 (−29.03) −63.63^d	0.221 (0.176)	187.76
$H_2Cl_2AlNH_2CH_3^+$	−66.23 (−31.62)	0.220 (0.171)	191.22
$H_2Cl_2AlNH(CH_3)_2^+$	−67.86 (−31.98)	0.218 (0.162)	192.49
$H_2Cl_2AlN(CH_3)_3^+$	−69.07 (−30.54)	0.212 (0.153)	195.15
$H_2Br_2AlNH_3^+$	−55.49 (−28.21) −60.20^d	0.219 (0.178)	190.45
$H_2Br_2AlNH_2CH_3^+$	−61.25 (−30.67)	0.217 (0.172)	193.75
$H_2Br_2AlNH(CH_3)_2^+$	−62.45 (−30.97)	0.216 (0.163)	194.66
$H_2Br_2AlN(CH_3)_3^+$	−63.36 (−29.24)	0.212 (0.153)	197.29

[a] $E_{comp} = E[H_2X_2AlNH_n(CH_3)_{3-n}^+] - [E(H_2X_2Al^+) + E(NH_n(CH_3)_{3-n})]$. The reported values in parentheses correspond to the nonprotonated parental complexes. [b] Charge transfer from $NH_n(CH_3)_{3-n}$ to $H_2X_2Al^+$. [c] $PA = E[HF_2AlNH_n(CH_3)_{3-n}] - E[H_2F_2AlNH_n(CH_3)_{3-n}^+]$. [d] MP2/6-311+G(d,p)//MP2/6-311+G(d,p) + ZPE level.

TABLE 4: Calculated Thermodynamic Values of the Dissociation Processes of Protonated Complexes, ΔE (kcal/mol), ΔH_0 (kcal/mol), and ΔG_{298} (kcal/mol)

dissociation process	ΔE_0	ΔH_0	ΔG_{298}
$H_2F_2AlNH_3^+ \rightarrow F_2AlNH_3^+ + H_2$	5.59	6.68	−1.07
$H_2F_2AlH_2NCH_3^+ \rightarrow F_2AlNH_2CH_3^+ + H_2$	5.18	5.68	−0.06
$H_2F_2AlNH(CH_3)_2^+ \rightarrow F_2AlNH(CH_3)_2^+ + H_2$	4.42	4.95	−0.93
$H_2F_2AlN(CH_3)_3^+ \rightarrow F_2AlN(CH_3)_3^+ + H_2$	4.18	5.26	−2.92
$H_2Cl_2AlNH_3^+ \rightarrow Cl_2AlNH_3^+ + H_2$	1.78	2.81	−4.84
$H_2Cl_2AlNH_2CH_3^+ \rightarrow Cl_2AlNH_2CH_3^+ + H_2$	1.51	1.97	−3.93
$H_2Cl_2AlNH(CH_3)_2^+ \rightarrow Cl_2AlNH(CH_3)_2^+ + H_2$	1.14	1.60	−3.96
$H_2Cl_2AlN(CH_3)_3^+ \rightarrow Cl_2AlN(CH_3)_3^+ + H_2$	0.90	1.38	−4.41
$H_2Br_2AlNH_3^+ \rightarrow Br_2AlNH_3^+ + H_2$	0.55	1.49	−5.86
$H_2Br_2AlH_2NCH_3^+ \rightarrow Br_2AlNH_2CH_3^+ + H_2$	0.31	0.69	−5.09
$H_2Br_2AlNH(CH_3)_2^+ \rightarrow Br_2AlNH(CH_3)_2^+ + H_2$	0.07	0.45	−4.89
$H_2Br_2AlN(CH_3)_3^+ \rightarrow Br_2AlN(CH_3)_3^+ + H_2$	−0.18	0.72	−7.63

NH_3 (X = F, Cl, and Br) are −72.33, −60.18, and −55.99 kcal/mol (Table 3) for $H_2F_2AlNH_3^+$, $H_2Cl_2AlNH_3^+$, and $H_2Br_2AlNH_3^+$, respectively. The same trend is observed at the MP2/6-311+G(d,p)//MP2/6-311+G(d,p) + ZPE level. The complexation energies are only −30.13, −29.03, and −28.21 kcal/mol for the corresponding nonprotonated complexes HF_2AlNH_3, HCl_2AlNH_3, and HBr_2AlNH_3, respectively. However, the complexation energy decreases for each group on descending in the corresponding periodic table column from fluorine to bromine atoms. Protonation of HX_2AlNH_3 to form $H_2X_2AlNH_3^+$ (X = F, Cl, and Br) is calculated to be highly exothermic by 183.35, 187.76, and 190.46 kcal/mol, respectively (Table 3). Nevertheless, by protonation of the corresponding neutral complexes, the complexation energies increase. Indeed, the protonation stabilizes the complexes by ~42, ~31, and ~28 kcal/mol for HF_2AlNH_3, HCl_2AlNH_3, and HBr_2AlNH_3 complexes, respectively.

On the other hand, one can see, from the NBO analysis (Table 3), that there is no correlation between charge transfer and the complexation energies. For the most stable complex $H_2F_2AlNH_3^+$ the charge transferred is 0.20e, while for the less stable complex $H_2Br_2AlNH_3^+$, this transferred charge is 0.22e. We note also the same trend for the nonprotonated complexes. Nevertheless, we notice that the increase of the transferred charge contributes to the stability of protonated $H_2X_2AlNH_3^+$ (X = F, Cl, and Br) complexes according to their nonprotonated homologues HX_2AlNH_3.

Complexation of $NH_n(CH_3)_{3-n}$ (n = 0−2) with $H_2X_2Al^+$ leads to the monocation $H_2X_2AlNH_n(CH_3)_{3-n}^+$ (X = F, Cl, and Br; n = 0−2) with C_s symmetry and a 3c-2e bond. The Al−N bond lengths of $H_2F_2AlNH_n(CH_3)_{3-n}^+$ are 1.934, 1.940, and 1.941 Å, 0.111, 0.094, and 0.096 Å shorter than those found in $H_2FAlNH_n(CH_3)_{3-n}$, respectively, indicating stronger Al−N bonding in $H_2F_2AlNH_n(CH_3)_{3-n}^+$. The Al−F bond lengths of $H_2F_2AlNH_n(CH_3)_{3-n}^+$ are 1.650, 1.648, and 1.646 Å, 0.098, 0.055, and 0.059 Å shorter than those found in $H_2FAlNH_n(CH_3)_{3-n}$, respectively, indicating stronger Al−F bonding in $H_2F_2AlNH_n(CH_3)_{3-n}^+$. The same trends are observed for chlorine and bromine complexes (Tables 1 and 2).

Protonation of $HX_2AlNH_n(CH_3)_{3-n}$ complexes to form $H_2X_2AlNH_n(CH_3)_{3-n}^+$ (X = F, Cl, and Br; n = 0−2) complexes is also calculated to be highly exothermic by 192.01, 198.49, and 187.41 kcal/mol for X = F, 195.15, 192.49, and 191.22 kcal/mol for X = Cl, and 197.29, 194.65, and 193.75 kcal/mol for X = Br (Table 3). Upon protonation, the complexation energy and the charge transfer increase. Indeed, the protonation stabilizes the complex by ~50−40 kcal/mol for $HF_2AlNH_n(CH_3)_{3-n}$ complexes, by ~40−30 kcal/mol for $HCl_2AlNH_n(CH_3)_{3-n}$ complexes, and by ~35−25 kcal/mol for $HBr_2AlNH_n(CH_3)_{3-n}$ complexes. On the other hand, one can see that the methyl substitution decreases the Al−N bond length and increases the stability of the corresponding complexes. Indeed, the first methyl substitution stabilizes the complexes by ~6−7 kcal/mol for $H_2X_2AlNH_2(CH_3)^+$ complexes, the second substitution by ~8−10 kcal/mol for $H_2X_2AlNH(CH_3)_2^+$ complexes, and the third substitution by ~8−12 kcal/mol for $H_2X_2AlN(CH_3)_3^+$ complexes.

One can see, from the NBO analysis (Table 3), that there is no correlation between charge transfer and the complexation energies, as for the nonmethylated complexes $H_2X_2AlNH_3^+$.

TABLE 5: Entropies (298 K, 1 atm, Ideal Gas) (cal/(mol K)) and Thermal Corrections to the Internal Energy (kcal/mol)

molecule	entropy	thermal correction	molecule	entropy	thermal correction
$H_2F_2AlNH_3^+$	83.07	42.01	$F_2AlNH_3^+$	78.48	31.72
$H_2F_2AlNH_2CH_3^+$	90.63	60.78	$F_2AlNH_2CH_3^+$	79.13	49.91
$H_2F_2AlNH(CH_3)_2^+$	95.81	79.10	$F_2AlNH(CH_3)_2^+$	84.80	68.20
$H_2F_2AlN(CH_3)_3^+$	101.07	96.99	$F_2AlN(CH_3)_3^+$	97.93	86.72
$H_2Cl_2AlNH_3^+$	88.01	40.90	$Cl_2AlNH_3^+$	83.15	30.83
$H_2Cl_2AlNH_2CH_3^+$	95.06	59.70	$Cl_2AlNH_2CH_3^+$	84.11	49.01
$H_2Cl_2AlNH(CH_3)_2^+$	101.20	78.08	$Cl_2AlNH(CH_3)_2^+$	89.11	67.40
$H_2Cl_2AlN(CH_3)_3^+$	105.56	95.97	$Cl_2AlN(CH_3)_3^+$	94.21	85.36
$H_2Br_2AlNH_3^+$	94.34	40.47	$Br_2AlNH_3^+$	88.34	30.52
$H_2Br_2AlNH_2CH_3^+$	100.70	59.28	$Br_2AlNH_2CH_3^+$	89.34	48.96
$H_2Br_2AlNH(CH_3)_2^+$	107.19	77.68	$Br_2AlNH(CH_3)_2^+$	94.33	67.12
$H_2Br_2AlN(CH_3)_3^+$	111.73	95.57	$Br_2AlN(CH_3)_3^+$	109.16	85.68
H_2	31.14	7.80			

Indeed, the charge transferred is ~0.22e for all the complexes. Nevertheless, we notice that the increase of the transferred charge contributes to the stability of the protonated complexes.

On the other hand, the structure of $H_2X_2AlNH_n(CH_3)_{3-n}^+$ (X = F, Cl, and Br; n = 0−3) can also be viewed as a weak complex between $X_2AlNH_n(CH_3)_{3-n}^+$ and H_2. Indeed, the Al−H_2 hypercoordinated bonds are longer, and the dissociation of $H_2X_2AlNH_n(CH_3)_{3-n}^+$ complexes into $X_2AlNH_n(CH_3)_{3-n}^+$ and molecular H_2 is slightly endothermic by 1−5 kcal/mol (Table 4). At room temperature (298 K) the dissociation reactions are slightly exothermic.

Conclusion

Complexes of $H_2X_2Al^+$ with $NH_n(CH3)_{3-n}$ (X = F, Cl, and Br; n = 0−3) were found to have C_s symmetry involving hypercoordinated alane with a 3c-2e bond. The formation of the cations $H_2X_2AlNH_n(CH_3)_{3-n}^+$ (X = F, Cl, and Br; n = 0−3) was calculated to be exothermic by 55−83 kcal/mol, and the cations were found to be more stable than their nonprotonated parents. The energetic results show that the stability of the protonated alane−Lewis complexes decreases on descending in the corresponding periodic table column from fluorine to bromine atoms. The calculated protonation energies of $HX_2AlNH_n(CH_3)_{3-n}$ to form $H_2X_2AlNH_n(CH_3)_{3-n}^+$ were found to be highly exothermic. The possible dissociation of the complexes $H_2X_2AlNH_n(CH_3)_{3-n}^+$ into $X_2AlNH_n(CH_3)_{3-n}^+$ and molecular H_2 is calculated to be endothermic by 1−5 kcal/mol and exothermic at room temperature.

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